The Effect of Structure on the Mass Transport of Acetaldehyde in Virgin and Recycled Poly(ethylene terephthalate)

By

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A thesis submitted to the degree of Doctor of Philosophy

2006

Declaration

I hereby declare that all the work carried out in this project was performed while I was enrolled as a Ph.D. student in the Packaging and Polymer Research Unit, School of Molecular Sciences, Faculty of Science, Engineering and Technology, Victoria University, Werribee Campus. To the best of my knowledge, this work has not been submitted in the whole or part for any other degree or diploma in any University and no material contained in this thesis has been previously written or published by another person, except where due reference is made in the text.

January 2006

[redacted]

Endang Warsiki

Conference and Seminar Papers Arising from this Thesis

1. Warsiki, E., Miltz, J., Sonneveld, K. and Bigger, S. W., '*Overall migration of poly(ethylene terephthalate) in food simulants*', Research Review 2003 on Polymer and Recycling, Visy Recycling, Melbourne, Australia, August 7th, 2003.

2. Warsiki, E., Miltz, J., Sonneveld, K. and Bigger, S. W., '*The Effect of heating on the crystallinity of virgin and recycled poly(ethylene terephthalate)*', The National Seminar of Chemical Engineering in Indonesia, Yogyakarta, Indonesia, September 16th-17th, 2003.

3. Warsiki, E., Miltz, J., Sonneveld, K. and Bigger, S. W., '*Kinetic and thermodynamic study on the sorption of acetaldehyde by recycled poly(ethylene terephthalate)*', The National Seminar of Chemical Engineering in Indonesia, Yogyakarta, Indonesia, September 16th-17th, 2003.

4. Warsiki, E., Miltz, J., Sonneveld, K. and Bigger, S. W., '*Predictive modeling on the sorption and migration of acetaldehyde in recycled poly(ethylene terephthalate)*', Post Graduate Seminar Series, Victoria University, Melbourne, Australia, December 3rd, 2003.

5. Warsiki, E., Miltz, J., Sonneveld, K. and Bigger, S. W., '*The effect of different parameters on the migration of acetaldehyde from recycled poly(ethylene terphthalate) into food simulants*', The 14th IAPRI World Conference on Packaging, Lidingo, Sweden, June, 13th – 16th, 2004.

ABSTRACT

PET is a thermoplastic polyester prepared from terephthalic acid and ethylene glycol. It is used for the production of bottles, sheets, films, strapping and injection moulded products. PET bottles are extensively used for various food-packaging applications, particularly in developed countries, which is leading to disposal problems. Presently, there is an increasing emphasis throughout the world to recycle PET. The use of recycled PET for food packaging applications however, has raised questions regarding its safety. Recycled PET presents a source of a wide range of potential migrants such as residues from the polymerisation process and degradation compounds. These substances can then transfer to the packaged food and pose health risks, in addition to off-flavours.

Acetaldehyde is the major degradation product of recycled PET, which is formed during high temperature processing. Acetaldehyde can affect the sensory properties of the product, especially if the product has a low or no odour by itself such as mineral water. Acetaldehyde is suspected to be a carcinogenic substance.

One purpose of the present study was to learn how the overall migration from recycled PET compares to that from the virgin material in particular at elevated temperatures. Another purpose was to investigate the specific migration of acetaldehyde from recycled PET into food simulants.

The recycled PET studied in the present work exhibited no major differences in the mechanical properties compared to the virgin material except in elongation at break. The degree of crystallinity of the original virgin and the recycled PET sheets were 18.5 and 21.2% respectively. Exposing the PET samples to 120°C for 3, 6 and 10 min resulted in an increase in the degree of crystallinity to 19.8, 24.7 and 29.7% for the virgin PET and 24.8, 28.9 and 33.8% for the recycled PET respectively. Virgin PET bottles of varying volumes of 390, 600, 1200 and 2000 mL had degrees of crystallinity of 25.1, 27.3, 27.9 and 29.1% respectively.

It was found that virgin PET absorbed more acetaldehyde and required a shorter time to achieve equilibrium than the recycled material. The results also suggested that the sorption process of acetaldehyde in both samples were exothermic. Increasing the temperature increased the amount of acetaldehyde sorbed as well as the rate of sorption. In the temperature range of 5 – 20°C, the activation energy of sorption was not significantly different between the non-heated recycled PET and the non-heated virgin PET. The rate constant, sorption constant and diffusion coefficient decreased with the increase in the degree of the crystalinity of the samples. The mechanism of transports was found to be as Pseudo Fickian to Super Case II.

It was found by the conventional immersion method, the values of overall migration for all materials tested were significantly below the limit allowed by European Directive 90/128/EEC (10 mg constituent per dm^2 of packaging materials). Applying a higher temperature of exposure in the reflux method resulted in high overall migration values. By this method, the recycled PET showed values of 10.2 and 13.3 mg dm^{-2} for overall migration into 95% (v/v) aqueous ethanol and iso-octane respectively.

Migration of acetaldehyde from recycled and virgin PET sheets at different initial acetaldehyde concentrations, temperatures and degrees of polymer crystallinity were investigated using water and iso-octane as food simulants. The results showed that the diffusion coefficients calculated from the migration studies for the recycled PET were higher than those for the virgin material and depended strongly on the initial acetaldehyde concentration and degree of crystallinity. Increasing the temperature of exposure caused an increase in the acetaldehyde migration level.

ACKNWOLEDGMENTS

I would like to express my sincere gratitude to all people that helped me to realize this dream. First and foremost, I would like to thank my supervisor, Professor Joseph Miltz for his constant supervision and moral support. He helped me, challenged and inspired me during all the time of the research and in writing of this thesis. He is not only a great scientist with deep vision but also and most importantly a supportive person. His trust and scientific excitement inspired me in the most important moments of making right decisions and I was very happy to work under his supervision.

I extend my deepest gratitude and appreciation to Associate Professor Stephen W. Bigger, and Associate Professor Kees Sonneveld for their supervision, guidance and encouragement.

I am grateful to QUE Project Batch III, Agroindustrial Technology Study Program, Faculty of Agricultural Technology, Bogor Agricultural University for awarding me a scholarship.

I would like also to acknowledge

- Adjunct Professor Edward Kosior from Visy Recycling for supplying virgin and post consumer recycled PET bottles as well as recycled PET sheet samples. My appreciation is extended to Mr. Chau Bui from Visy Recycling for carrying out the intrinsic viscosity measurements;

- Mr. Robin Tuckerman from Signum Company for supplying virgin PET sheet samples;
- Mr. Dale Tomlinson, Mr. Vince Murone, Mr. Joseph Pelle, Mrs. Ira Prasatya, Mrs. Min Nguyen, laboratory staffs of School of Molecular Sciences, Victoria University, Werribee campus for assistance and guidance;
- Mrs. Alison Caruana-Smith, Polymer and Packaging Research Unit, Victoria University for looking after the administrative matters;
- Mr. Tonny Setiawan for the continuous encouragement and generous support. Without that, completion of this project would not have been possible;
- Dion Addzori, Pannuwat Suppakul, Indris Muhammad, Chanun Rardniyom, Liyana Arachchige Rupika and Yogesh Keshavlal Mistry for advice and invaluable friendship;
- My beloved husband, Ma'ruf Nur, my son, Afif Hanidar Ma'ruf, and my parents, Djaiman and Sutikni, for their support, patience and encouragement;
- All my colleagues and friends whose friendship and support at difficult times made this an enjoyable experience.

ABBREVIATIONS

ADI	Acceptable daily intake
ASTM	American Society for Testing and Materials
ATBC	Acetyltributyl citrate
BHET	Bis-(hydroxyethyl) terephthalate
BOPP	Bi-axially oriented polypropylene
CPET	Crystallized poly(ethylene terephthalate)
DEHA	Di-(2-ethyl-hexyl adipate)
DFM	Dimethylformamide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
EC	European Community
EEC	European Economic Community
EG	Ethylene glycol
EN	European standard
ENV	European pre-standard
EU	European Union
EVA	Ethyl vinyl acetate
EVOH	Ethylene vinyl alcohol
FAIR	Food Agri-Industry Research
FDA	Food and Drug Administration
FID	Flame ionization detector
GC	Gas chromatography
GC/MS	Gas chromatography coupled with mass spectrometry
GMLs	Global migration limits
h	Hour
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
HRPET	Heat set refillable polyethylene terephthalate

IR	Infra red
MeOH	Methanol
$MeCl_2$	Methylene chloride
OPET	Oriented polyethylene terephthalate
PA	Polyamide
PACIA	Plastic and Chemical Industry Association
PC	Polycarbonate
PC-PETb	Post consumer polyethylene terephthalate bottle
PCR-PETs	Post consumer recycled polyethylene terephthalate sheet
PE	Polyethylene
PEN	Polyethylene naphthalene
PET	Polyethylene terephthalate
PETvb	Polyethylene terephthalate virgin bottle
PETvs	Polyethylene terephthalate virgin sheet
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVCD	Polyvinylidene chloride
SMLs	Specific migration limits
SPME	Solid-phase micro-extraction
TDI	Total daily intake
TPA	Terephthalic acid
TFE	Tetrafluoroethylene
US-EPA	USA Environmental Protection Agency

SYMBOLS

a	Constant
A	Frequency factor
aLi,	Activities of liquid
aLiPo	Activities of liquid in polymer
aPo,	Activities of polymer
C	Concentration
C_D	Dietary level
C_f	Contaminant concentration in foodstuffs
$C_{f,\infty}$	Contaminant concentration in foodstuffs at equilibrium
CF	Consumption factor
C_i	Initial concentration of migrant in polymer
C_p	Contaminant concentration in packaging material
$C_{p,\infty}$	Contaminant concentration in packaging material at equilibrium
C_s	Concentration of migrant at surface of polymer
C_t	Concentration at time t
C_∞	Concentration at equilibrium
d	Density
D	Diffusion coefficient
D_0	Constant
E	Young's modulus
E_a	Activation energy
E_D	Activation energy of diffusion
k	Rate constant
K	Constant
K_1	Constant
K_{pf}	Partition coefficient between polymer and food simulant,
K_s	Sorption constant
L	Thickness
Li	Liquid

LiPo	Dissolved liquid in polymer
m_a	Mass of residue from test sample after evaporation of food simulant
m_b	Mass of residue from blank simulant
M	Overall migration value
$M_{p,t}$	Mass of the polymer at time t
$M_{p,0}$	Initial mass of the polymer at time t = 0
M_w	Molecular weight
M_t	Amount of compound diffused at time t
$M_{t,\infty}$	Amount of compound diffused at t equilibrium
$\overline{M}_v$	Viscosity average molecular weight
n	Type of diffusion
Po	Polymer
R	Ideal gas constant
R_{MS}	Mass to surface area ratio
S	Surface area
SMLs	Specific migration limit
t	Time
t_{∞}	Time equilibrium
T	Absolute temperature
T_g	Glass transition temperature
T_m	Melting temperature
v_i	Initial volume of food simulant
v_t	Volume of food simulant at time t
X_c	Fraction of crystallinities
ΔH_s	Enthalpy of sorption
ΔH_{cold} (T_{cold})	Enthalpy of fusion of cold crystallization of polymer measured at T_{cold}
$\Delta H^{o}_{fusion}(T^{o}_{m})$	Enthalpy of fusion of totally crystalline polymer measured at equilibrium melting point T^{o}_{m}
$\Delta H_{fusion}(T_m)$	Enthalpy of fusion measured at melting point T_m

α	Constant
ξ	Non-dimensional variable of concentration
δ	Solubility parameter
ε_Y	Yield strain
$[\eta]$	Intrinsic viscosity
τ	Non-dimensional variable of time
τ_B	Breaking strength
ΔG	Gibbs free energy
ΔH_s	Enthalpy of sorption
ΔS	Entropy
ε_Y	Yield strain
χ	Non-dimensional variable of distance

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CHAPTER 1 – INTRODUCTION

1.1 Background

Polymers (plastics) are extensively used today in various applications, packaging being one of the major areas. Three factors affecting the trend of development of plastics for food packaging are: (i) food industries; (ii) environmental issues and (iii) food safety regulations (Crosby, 1981). Packaging materials that provide good protection from contamination and extend product shelf life are needed and desired by food industries (Lupien, 1997). On the other hand, environmentalists advocate the reuse and recycling of packaging material as much as possible to save resources and protect the environment from contamination (Castle, 1994; Mariani, 1999). Food law authorities require that plastic materials should be suitable for safe contact with foodstuff and must be free from harmful additives and contaminants (Council Directive 89/109/EEC, 1989).

There has been a large growth in plastics recycling in the last decade. The Australian Plastics and Chemical Industry Association (PACIA) recorded a rise of about 53% in the volume of reprocessed plastics in Australia between 1997 and 2002. Two thirds of this increase is attributed to the use of reprocessed food packaging materials and polyethylene terephthalate (PET) bottles comprise one of the major categories of reprocessed plastics (PACIA, 2003).

The reuse of PET as returnable and refillable bottles has been in practice for over a decade. However, using a recycled plastic material to produce new packages for foodstuffs is very limited, except in some cases where the recycled plastic is used in a sandwich structure between virgin polymer layers. The proportion of recycled plastics is, however, low (Franz, 1999). For product safety reasons, the application of recycled plastics for the packaging of foodstuffs is restricted (Castle, 1994). The Food and Drug Administration (FDA) in the USA and the European Union do not prohibit, however, specifically the use of recycled materials as long as a document on the chemical composition and acceptable migration levels is provided.

Most published work regarding plastic reuse and recycling for food packaging applications has focused on the risk to food and consumers posed by absorbed hazardous contaminants that may be present in recycled plastics. Little attention has been given to the possible presence of degradation products that are formed during heat treatments such as pasteurization and sterilization and during reprocessing at high temperatures like extrusion and blow moulding. These degradation products may migrate into the food during storage and cause off-flavours and even more problematic - pose safety risks.

Acetaldehyde seems to be a major degradation product in PET (Bryk, 1991; Villain *et al.*, 1995; Franck *et al.*, 1994; Nijssen *et al.*, 1996; Eberhartinger *et al.*, 1990; Linssen *et al.*, 1995; Dong *et al.*, 1980; Wyatt, 1983; Samperi *et al.*, 2003). It represents about 80% of the total degradation products formed in this polymer

(Franck *et al.*, 1995). A minute amount of acetaldehyde can impart an off-taste to packaged food. Acetaldehyde possesses a distinct odor, a sweet plastic-like smell, with a low sensory detection threshold (Nijssen *et al.*, 1996). It also presents a potential health hazard including genetoxicity and carcinogenicity (Ashby, 1988; Benfenati *et al.*, 1991; Lo Russo *et al.*, 1985; Monarca *et al.*, 1994). Inhalation studies using experimental animals have shown that acetaldehyde is capable of inducing nasal carcinomas (Feron *et al.*, 1982). However, inhalation studies are usually not relevant for assessment of chemicals that are ingested by oral route. Concentrations higher than 125 mg acetaldehyde per kg body weight per day showed adverse hyperkeratosis effects (Till *et al.*, 1988).

There are reports in the scientific/technical literature, dealing with migration of acetaldehyde from PET bottles into water. Monarca *et al.* (1994), Sugaya *et al.* (2001), Nijjssen *et al.* (1996), Nawrocki *et al.* (2002) and Dábrowska *et al.* (2003) detected a significant level of acetaldehyde in mineral water after the water had been stored in PET bottles. Others, Fazzalari (1973), Poretta and Minuti (1995) and Linssen *et al.* (1995) found a range of acetaldehyde levels in the water. The effect of temperature and storage on the level of acetaldehyde that had migrated from PET bottles into soft drinks, has been published by Eberhartinger *et al.* (1990). However, comparative studies between virgin and recycled PET that describe the effect of structure, migrant concentration, degree of crystallinity and high temperatures on the kinetics of acetaldehyde migration have not been found. It was therefore decided to investigate the migration of acetaldehyde from recycled and virgin PET into aqueous and fatty food simulants. It is believed that this study will enhance the understanding of parameters affecting food/packaging interactions and will increase our knowledge of the effect of different variables on acetaldehyde transfer from PET into food simulants.

The sorption of acetaldehyde in virgin PET has been well documented but there has been hitherto little work conducted on the sorption of acetaldehyde into recycled PET. Hence, the present studies were conducted to complement our understanding of the effects of recycling of PET on this phenomenon. It is difficult to obtain commercial samples with a defined acetaldehyde concentration. Thus, the sorption experiments were aimed at achieving this purpose and although the concentration is relatively high, it was anticipated that from these experiments an indication of the sorption/desorption behaviour could be obtained. It is assumed that the migration of acetaldehyde within the PET matrix is independent of the means by which the acetaldehyde is introduced into the matrix.

1.2 Aims of the Research

The general aim of this research was to investigate the overall and specific migration of acetaldehyde from recycled PET into food simulants. The specific aims are:

(i) To compare physical properties of virgin and recycled PET;

(ii) To investigate the effect of thermal treatment on the crystallinity of virgin and recycled PET sheet;

(iii) To evaluate the overall migration of particular compounds in PET samples from different sources (post consumer PET bottle, virgin PET bottle, virgin PET sheet and post consumer recycled PET sheet) into food simulants;

(iv) To characterize the sorption behaviour of acetaldehyde into PET polymer;

(v) To obtain concentration profiles of acetaldehyde sorbed into PET;

(vi) To study the migration of acetaldehyde from PET samples into aqueous and fatty food simulants under different conditions including temperature, initial acetaldehyde concentration in the polymer and degree of polymer crystallinity

1.3 Scope of this Work

The European Directive on Packaging and Packaging Waste sets ambitious targets for recovery of waste and states that recycling of plastics must constitute an important part of waste recovery (Commission of the European Communities, 1994). To meet these targets, there is a pressure to recycle plastics back into food contact applications particularly in the case of post-consumer PET. The problem of possible food contamination that originates from recycled food packaging polymers attracts great attention. The present work is aimed at measuring the total residual contaminants in food simulants resulting from post-consumer recycled PET samples and to determine which and whether these samples comply with the European Economic Community (EEC) directive limits of 10 mg of contaminants per dm^2 packaging material or 60 mg of contaminant per kg of food or food simulant. The results for the recycled materials will be compared to results obtained from samples based on virgin material.

It is clear that volatile and semi-volatile compounds, including degradation products, could be released from polymers used in food packaging and could migrate into the contained food. Among the volatile compounds released from PET, acetaldehyde is most abundant and greatest concern in many migration studies. The present study concentrates on the prediction of the diffusion coefficients of acetaldehyde in PET under various experimental conditions. To achieve this purpose, the data from the experimental work were analyzed using a mathematical model suggested by Miltz *et al.* (1997).

1.4 Outline of the Thesis

This thesis is structured from five chapters, bibliography and appendixes. It starts with a background, aims, scope and outline of this research. Chapter 2 examines the recycling of PET and studies related to its food contact applications. Within this chapter seven sections describe the polymer, recycling of PET, recycled plastic for food applications, thermal oxidation and thermal degradation of PET products, properties of recycled plastics, food-package interactions, and sorption and migration.

Chapter 3 deals with the materials and methods of this project. There are five parts of the experimental work: (i) physical properties of the studied PET; (ii) iso-thermal crystallization of PET sheets; (iii) sorption of acetaldehyde into PET; (iv) overall migration and (v) migration of acetaldehyde into food simulants.

The results of the study along with their interpretation and discussion are presented in Chapter 4. This chapter comprises five sections. In the first section, the physical properties of virgin and recycled PET are described including intrinsic viscosity, elongation at break, Young's modulus and tensile stress at break.

The second section deals with the effect of time of heat treatment on the crystallinity of virgin and recycled PET sheets. Four types of PET bottles, different in capacity, are also discussed for variation in the degree of crystallinity. Percent transmittance of the polymer after it had been subjected to the heat treatment is also studied in order to obtain a quantitative estimate of the opacity caused by differences in crystallinity.

The next section describes the kinetic and thermodynamic sorption of acetaldehyde into PET, with different degrees of crystallinity. The mechanism of solvent transport was investigated by immersing strips of the polymer of known weight and dimension into neat acetaldehyde and solutions of acetaldehyde in water, and measuring the weight gain as a function of time. The laboratory findings on the sorption of acetaldehyde into virgin and recycled PET are presented at three different temperatures. From the temperature dependence of sorption, the diffusion coefficients, Arrhenius parameters, enthalpy and entropy of sorption were estimated in terms of the nature of the polymer-solvent interaction. From the sorption data, the concentration of acetaldehyde inside the PET was predicted by solving the Fick's diffusion equation (Crank, 1975) under the appropriate initial boundary conditions. For drawing the profile of the concentration of acetaldehyde sorbed in PET, a numerical solution of Fick's second law equation was used.

Overall migration results from a total of four different PET samples: (i) post-consumer PET bottle (PC-PETb); (ii) virgin PET bottle (PETvb); (iii) virgin PET sheet (PETvs) and (iv) post-consumer recycled PET sheet (PCR-PETs) intended to come in direct contact with food simulants are described in the fourth section of Chapter 4. The investigation of the overall migration at elevated temperature is also highlighted in this section.

The last section of this chapter discusses the migration of presorbed acetaldehyde in PET into food simulants under different conditions. The initial concentration of acetaldehyde in the original PET sheet is the first parameter studied. The effects of other parameters such as the temperature and the crystallinity of PET sample on the migration behaviuor are also discussed. The results are discussed in terms of diffusion coefficients derived from the migration studies.

Chapter 5 lists the conclusions of this study and recommendations for future work. A bibliographic list of the references used in the present study and the appendixes conclude this thesis.

CHAPTER 2 – LITERATURE REVIEW

2.1 Poly(ethylene terephthalate)

Poly(ethylene terphthalate) or PET is a polyester resin produced by a condensation reaction between ethylene glycol and terephthalic acid or dimethyl terephtalate (Brody and Marsh, 1997). The molecular structure of PET is given in Figure 2.1.

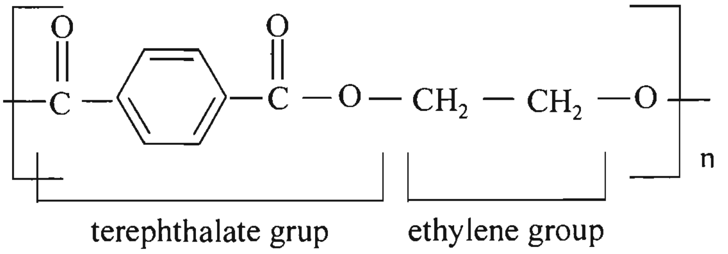


Figure 2. 1. Chemical structure of poly(ethylene terephthalate) (PET) (Feldman and Barbalata, 1996)

PET films and sheets offer good mechanical strength, dimensional stability, chemical resistance, stiffness and quite good gas barrier properties (Briston, 1994). They are also easy to handle and can be printed on or laminated to other materials (Newton, 1997). Its considerable gas barrier and decreasing cost, make this polymer particularly suitable food packaging applications such as films, laminates, bottles for carbonated beverages, mineral water and other drinks, and jars of different sizes for various foods (Poretta and Minuti, 1995). One disadvantage linked to PET is the possible release of acetaldehyde from the container into the product (Poretta and Minuti, 1995). Table 2.1 summarizes reported mechanical, thermal and chemical properties of the PET.

Table 2. 1. The reported mechanical, thermal and chemical properties of the PET

Properties	Method	Value	Unit
Breaking strength (σ_B)	Tensile	50	MPa
Tensile (Young's) modulus (E)	Tensile	1,700	MPa
Yield strain (ε_Y)	Tensile	4	%
Impact strength	ASTM D253-86	90	J m^{-1}
Glass transition temperature (T_g)	DSC	51 - 115	°C
Melting temperature (T_m)	DSC	265	°C
Enthalpy of fusion at T_m ($\Delta H_{fusion}, T_m$)	DSC	24.1	kJ mol^{-1}
Water sorption	After 24 h	0.5	%

Source: Jaquiss *et al.* (1982); Rubin (1990)

2.2 Recycling of PET

Plastics have been the most controversial component of the solid waste stream globally (Hadjilambrinos, 1996) and are considered to be a major pollutant of the environment. The increasing public awareness to the environment as well as the tightening of governmental regulations has resulted in there being considerable pressure to recycle many plastic materials (Cornell, 1995). In some countries in Europe, as well as in the USA and Australia, commercial recycling processes for plastics have been introduced (Castle, 1994). These have strived to transform recycled plastics into new products in order to reduce environmental impacts (Cornell, 1995), save on disposal costs (Selke, 1990) and reduce the use of virgin materials (Anon, 1998).

Generally, there are three classes of plastics recycling processes that the USA Environmental Protection Agency (US-EPA) has defined (Thorsheim and Amstrong, 1993; Ram, 1997; Selke, 1990; Bayer, 1997). They are:

(i) Primary recycling, which refers to the use of off-grade, pre-consumer industrial scrap and salvage to form new products. During processing, there is a certain percentage (20 – 30%) of scrap from thermoforming, injection moulding, trimmings in blow moulding and extrusion products that have not passed quality control. This material is slightly contaminated but in most cases, it can be reground and added as a blend to the virgin raw materials;

(ii) Secondary recycling, which refers to the use of post-consumer collected bottles, jars and containers, and involves cleaning, grinding or flaking of the used containers followed by melting and reforming into other products, primarily for non-food contact applications;

(iii) Tertiary recycling, which refers to the use of plastic scrap and some useful products for chemical recycling by the breakdown of the polymer into monomers (by hydrolysis, glycolysis, or methanolysis) and polymerizing the monomers to produce a virgin polymer.

Figure 2.2 summarizes the main mechanism of chemolysis reactions used in the tertiary recycling of PET. The chemical agents that can be used to depolymerize PET are water (hydrolysis), methanol (methanolysis) and ethylene glycol or diethylene glycol (glycolysis). Glycolysis and methanolysis are the main depolymerization processes that are already commercially developed

(Scheirs, 1998). However, chemically recycled PET is somewhat more expensive than virgin PET.

Richard *et al.* (1992) evaluated the tertiary recycling of PET *via* glycolysis, followed by a purification step and repolymerization into a commercial grade of PET for bottles. In this study, they mixed the recycled PET resin with virgin PET. The resulting PET bottles, which had 20% recycled content, showed comparable properties to bottles made from 100% virgin PET resin.

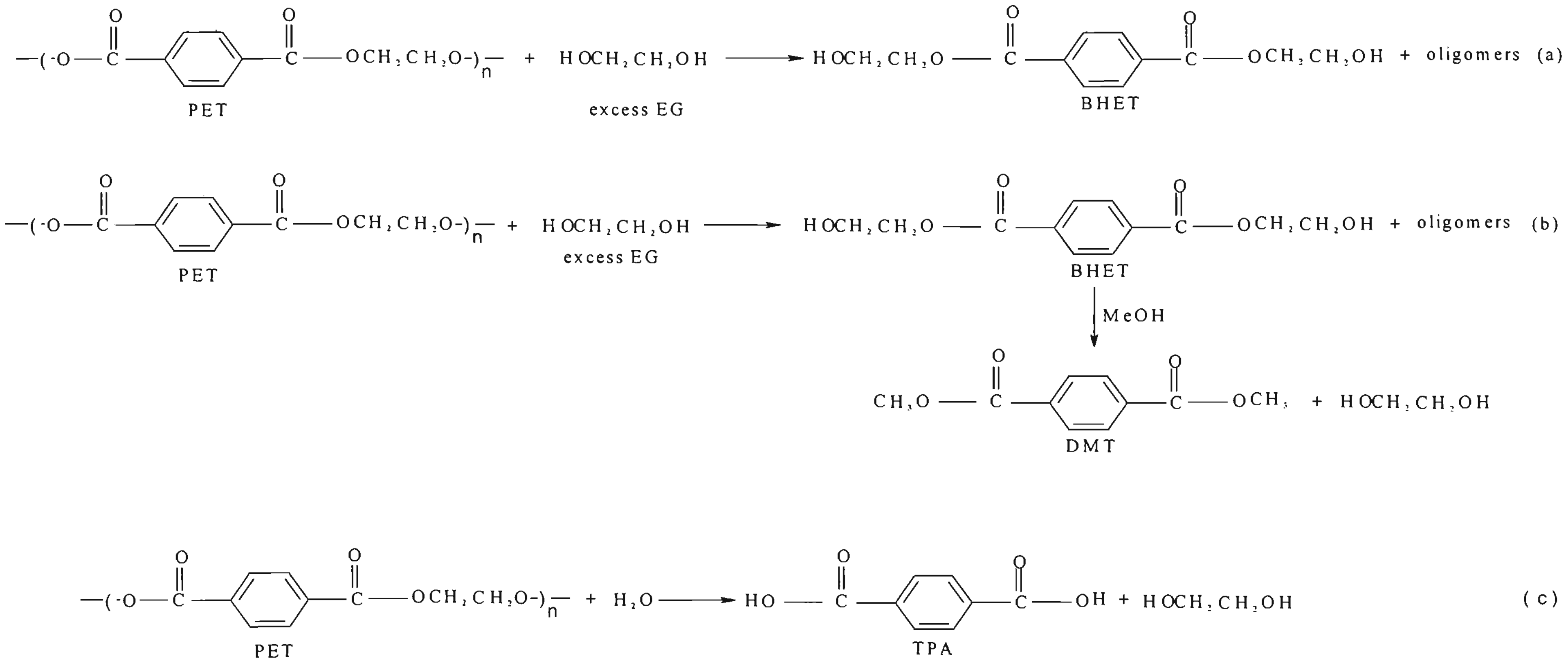


Figure 2. 2. Mechanism of chemolysis of PET during recycling: (a) glycolysis, (b) methanolysis (c) hydrolysis. Note: PET = poly(ethylene terephthalate); EG = ethylene glycol; BHET = bis-(hydroxyethyl) terephthalate; MeOH = methanol; DMT = dimethyl terephthalate; and TPA = terephthalic acid (Scheirs, 1998)

The three most widely recycled post-consumer plastics are poly(ethylene terephthalate) (PET), high-density polyethylene (HDPE) and polypropylene (PP) (Selke, 1990; Hadjilambrinos, 1996). However, among these polymers, PET is the success story of plastic recycling (Selke, 1990; Slatter, 1999; Scheirs, 1998). The main driving forces responsible for the increased recycling of post-consumer PET are its abundant supply (Slatter, 1999; Scheirs, 1998), its high value and good selling price (Selke, 1990) and its good chemical and mechanical properties, even after its first use (Selke, 1990; Miltz *et al.*, 1997).

2.3 Recycled Plastics for Food Applications

The use of recycled plastics for food packaging is still under investigation and in debate amongst researchers, legislators and manufacturers (Castle, 1994; Overton, 1994; Begley, 1997; Begley *et al.*, 2002). There is a concern that post-consumer material may contain undesirable contaminants such as residual low molecular weight compounds originating from the first use or misuse (Castle, 1994; Thorsheim and Armstrong, 1993; Begley and Hollifield, 1993; Bayer *et al.*, 1995), degradation products (Castle, 1994; Pierce *et al.*, 1995; Nerin *et al.*, 1998; Incarnato *et al.*, 1998), polymer additives (Ner *et al.*, 2000; Fordham *et al.*, 1995) or microbes (Jetten, 1999).

The different compounds and degradation products from the second generation container may ultimately be leached into the food (Sadler *et al.*, 1996) and affect the organoleptic properties to such an extent, that the polymer could be classified as being unsuitable for food contact purposes (Lox *et al.*,1992). It was found that residual monomers such as ethylene glycol (Kashtock and Breder, 1980), formaldehyde and acetaldehyde (Dábrowska *et al.*, 2003; Nawrocki *et al.*, 2002; Nijssen *et al.*, 1995) as well as oligomers (Castle *et al.*, 1989; Begley and Hollifield, 1990a) migrate from PET into food products and cause off-flavours. Hence, additional studies in this area are required in order to obtain valuable quantitative data on the migration rates and levels, and to determine the safety of recycled PET as a food contact material (Ner *et al.*, 2000).

Some researchers propose three fundamental factors that must be optimized in the recycling process, if the material is to be used for food packaging: (i) control of the raw material source (Selke, 1990; Castle, 1994); (ii) effective purification (Thorsheim and Armstrong, 1993; Franz, 1999) and (iii) evaluate the suitability of the material for its application (Franz, 1999).

Post-consumer recycled (PCR) PET in food contact applications was first introduced into the US market in 1991. Since that time, numerous studies have taken place to better understand the various issues involved in using PCR-PET for food contact applications.

2.3.1 Misuse of post-consumer plastics

Plastics are quite permeable and absorb various levels of contaminants (Thorsheim and Armstrong, 1993; Franz, 1999; Sadler *et al.*, 1996), including toxic substances such as gasoline, petrol and pesticides. Occasionally, consumers use plastic bottles and containers inappropriately to store such substances and then return the empty containers into the recycle stream (Castle, 1994; Laoubi *et al.*, 1995; Jetten *et al.*, 1999).

Absorbed toxic substances may be difficult to remove from the polymer during a recycling process (Miltz *et al.*, 1997) and may migrate into foodstuffs during the second use (Thorsheim and Armstrong, 1993; Laoubi *et al.*, 1995; Sadler *et al.*, 1996). Concerns about potential consumer misuse of PET bottles, resulting in possible contamination, has led to the addition of safeguards such as in-line detection systems to inspect the quality of the bottles before the refilling process. With a rapid computerized electronic screening system, each bottle is "sniffed" for the presence of volatile materials and rejected when those are detected (Demertzis *et al.*, 1997). However, this system does not detect non-volatile compounds that may be contained in the polymer matrix (Castle, 1994). Other non-universal detectors do not detect some of the volatile compounds either.

Currently, there is no specific national or European Union regulation or a standard test procedure, which could be applied by industry or by enforcement laboratories, to test the presence of misused post-consumer plastics. In some studies, relatively simple inertness tests of the polymer with a selection model of contaminants have been investigated. These studies usually focused on: (i) interaction between the PET and the contaminating compounds; (ii) determination of the type of compound that had been absorbed into PET; (iii) determination of contaminants quantity remained after a commercial washing processes and (iv) valuation of the migration levels of the compounds from PET into food simulants.

Feron *et al.* (1994) exposed the walls of PET bottles to 62 chemicals and found that most polar, non-polar, volatile and non-volatile organic compounds are absorbed. For these compounds the diffusion coefficients in PET were found to be in the range of $10^{-16} - 10^{-9}$ cm^2 s^{-1} at ambient temperature (Sadler *et al.*, 1996). Methylene chlorine, chloroform and o-cresol seem to be the fastest absorbed compounds into PET. Tetracosane, gasoline and malathion are the compounds absorbed at the lowest level into the same material (Sadler *et al.,* 1996). Patton *et al.* (1984) measured diffusion coefficients for benzene in PET and found values of 6.7×10^{-14} and 3×10^{-14} cm^{2}s^{-1} at 40 and 20°C respectively. In another study, Nir *et al.* (1996) measured the sorption and migration of organic liquids into and out of PET. They used neat organic liquids in direct contact with PET and calculated a diffusion coefficient, during migration, of 3.7×10^{-9} cm^{2}s^{-1} for toluene at 34°C.

The level of contaminant migration from pre-contaminated PET with neat toluene was found to be generally greater than 380 mg of organic compound (toluene) per kg of food simulant (distilled water) after 10 days at a temperature of 40°C of exposure (Miltz *et al.*, 1997). Elevated temperatures of exposure (higher than 40°C) resulted in a higher migration level of chlordane, endosulfan, ethylene glycol, methanol, gasoline and lindane, but for other compounds such as malathion, alachor, iso-octane and parathion, temperature had little or no apparent effect on the level of migration (Feron *et al.,* 1994). From the benzene sorption/contamination and migration experiment, Komolpraset and Lawson (1995) determined that essentially all the benzene migrated from PET samples into a fatty food simulant (heptane) after a storage period of 14 days at 40°C and only less than 0.01% out of a total 310 mg of benzene per kg PET material, originally sorbed, remained in the polymer.

Van Lune *et al.* (1997) found that more than 1,500 $\mu g\ g^{-1}$ of toluene and approximately 3,000 $\mu g\ g^{-1}$ of methanol were sorbed into PET wall after 16 weeks exposure at 40°C. They concluded that PET more easily absorbed the polar compound than the non-polar one.

Demertzis *et al.* (1997) discussed the sorption kinetic behavior of 20 different chemicals into PET at 10, 20 and 40°C for up to 40 days. The chemicals used in this study ranged in polarity from non-polar to polar with the solubility parameter (cal $cm^{-3})^{1/2}$ fell between $\delta = 7.4$ and $\delta = 16.9$. The solubility parameter of PET was reported to be about $\delta = 10.7$. They defined their studies as an extreme situation of sorption of the chemicals into PET because the polymer was placed in solutions made by combining six pure or undiluted liquids. Their results showed that generally, the smaller and more volatile chemicals were absorbed into the PET to a higher level than the larger, non-volatile compounds. For example, 1.4 and 5.1 mg dm^{-2} of toluene were absorbed into the polymer after 30 days at 20 and 40°C respectively compared to 0.29 and 0.62 mg dm^{-2} of phenyldecane during the same time and temperature of exposure. In this case, toluene represents a small and volatile compound whereas phenyldecane represents a large and non-volatile compound. They also reported that the chlorinated compounds, including chlorobenzene and 1,1,1-trichorobenzene, were absorbed in relatively large amounts and interacted strongly with the PET causing swelling of the polymer. The aromatic compounds were also absorbed in larger amounts than the non-aromatic compounds.

In summary, it is not obvious that the diffusion coefficient depends on: (i) the concentration of the permeating substances; (ii) the method used such as film/film, vapour/film, liquid/film; (iii) the molecular properties of the substance (especially molecular weight) and (iv) the morphology of the polymer (crystallinity and orientation).

Based on Demertzis's results, Begley *et al.* (2002) estimated the amount of organic compounds that would be sorbed after one year of storage at room temperature. In their predictions, they assumed that the transport was Fickian (linear with the square root of time) with a typical bottle having a wall thickness of 0.03 cm, 14.4 cm^2 in area and 0.25 g in mass. The researchers (Begley *et al.*, 2002) concluded that the value is not likely to exceed the amount sorbed at a temperature of 40°C for 30 days. It was also reported that the amount of lindane from shampoo sorbed into PET after 231 days was 28 mg kg^{-1} (0.1 mg dm^{-2}) and 745 mg kg^{-1} (3.7 mg dm^{-2}) at 20 and 40°C respectively (Begley *et al.*, 2002).

From their studies on contaminated PET, their general conclusion was that returnable PET bottles could be safety re-used, as long as food manufacturers use appropriate procedures, including visual and electronic inspection system, to eliminate abused bottles (Demertzis *et al.*, 1997; Begley *et al.*, 2002).

2.3.2 Effectiveness of washing and drying to remove contaminants

Washing is an important step in the recycling process, not only with regard to bottles for reuse, but also for the physical and chemical recycling process where it is used to remove impurities (Scheirs, 1998). Studies on the effect of washing and drying of recycled PET, after intentionally contaminating it with volatile and non-volatile compounds, showed that non-volatile compounds are not removed as efficiently as volatile ones. Franz *et al.* (1996) studied the effectiveness of the combination of washing and rinsing in removing contaminants from recycled PET flakes. This study showed that 80 – 90% of model volatile contaminants (trichloroethane, toluene and chlorobenzene) were removed after a washing and rinsing process at a temperature of 90°C but only a small quantity of non-volatile compounds were removed by this method.

Komolpraset and Lawson (1997) studied the migration of several chemicals from recycled PET into 8% v/v aqueous ethanol used as a food stimulant. In this study, the PET was immersed in a mixture of surrogate compounds, including polar and non-polar as well as volatile and non-volatile contaminants. The contaminated material was washed with de-ionized water at 73°C for 15 min and dried using an IR lamp. The results suggested that this method is able to remove 27 – 49% of the contaminants only. Furthermore, it was found that a simple washing, drying and extrusion procedure is insufficient to produce a recycled material that is suitable for direct food contact applications due to the relatively high levels of contaminants compared to the acceptable levels (Komolpraset *et al.*, 1997; Komolpraset and Lawson, 1997).

Devliegher *et al.* (1998) compared various washing methods of recycled HDPE milk bottles. They found that washing HDPE flakes with caustic solution, followed by steam stripping and air drying, produced a material that exhibited levels of contaminants migrating into food simulants (distilled water and 15% v/v aqueous ethanol) that were not significantly different from those exhibited by a virgin material.

Although a washing process is likely to be effective in removing contaminants from the walls of bottles, this process is unable to remove all residues such as Chlorodizone™, Triadimefon™ and Prochloraz™ and even some chemical discolourants (Feron *et al.*, 1994). It is also rather difficult to remove substances such as some of the terpene flavonoids that have a high solubility in the plastic materials (Scheirs, 1998). Increasing the temperature could provide a solution to this problem, however crystallization is favoured above 80°C, which may hinder the removal of contaminants.

Finally, based on the reviews of numerous studies on the recycling processes of PET, the US Food and Drug Administration (FDA) has found that the level of surrogate contaminants remaining in PET after washing and drying only, exceeded the concentration of 0.5 ppb after the migration test, required for there to be no regulatory concern (Begley *et al.*, 2002). Therefore an additional process to washing and drying of recycled polymers is required to render the material as being suitable for direct food contact applications.

Although many studies indicate that washing and drying is not effective for the complete removal of contaminants from PET, there is a lack of information on the actual contaminants present in commercial PET. According to Bayer (2002), the surrogate-testing studies by Demertzis *et al.* (1997), Franz *et al.* (1996), Komolpraset *et al.* (1997) and Komolpraset and Lawson (1997) demonstrate only the worst-case scenario.

2.3.3 Functional barrier layers

Another option for reusing recycled plastics, which is very attractive from the point of view of food safety, is the use of a functional barrier between the food and the recycled material. Begley and Hollifield (1993), Franz *et al.* (1994, 1996) and Laoubi *et al.* (1995) proposed the use of a layer of virgin material as a functional barrier between the recycled plastic and the foodstuff. Such systems are known as "multiple layer" structures. A functional barrier can reduce or delay the migration of adventitious contaminants into the food to levels of "no concern" from a toxicological point of view.

The diffusion coefficient of the migrant in the polymer plays an important role in controlling the process of contaminant migration in multiple-layer packaging systems. With a monolayer material, migration increases linearity with the square root of the time of contact (Crank, 1979). The situation is different for multiple layer materials. No migration, into the food, occurs during a lag time (Laoubi *et al.*, 1995). Therefore, the migration test of 10 days (commonly applied in conventional migration testing) may not be adequate (Franz, 2002) and a new method is necessary to be developed.

Laoubi *et al.* (1995) proposed the first mathematical model dedicated to functional barriers and multilayer structures using the Vergnaud approach. An advantage of this model is the use of dimensionless numbers (Dt/L^2). Begley and Hollifield (1993) and Franz *et al.* (1997) proposed a mathematical model to describe the effect of a functional barrier that is based on a 1.0 $\mu g\ kg^{-1}$ level of the contaminant in a daily diet (assumed to be 3,000 gram of food per person per day in the solid and liquid states). Begley and Hollifield (1993) calculated the maximum concentration of contaminant allowable in a recycled polymer, assuming that 100% of the chemical would migrate into the food. They used a contact factor of 1.55 g of food per cm^2 surface area of packaging material. They estimated that a 50.8 μm thick virgin layer used as a functional barrier could increase the allowed contaminant concentration in recycled PET from 9 to 138 $\mu g\ g^{-1}$.

There has been considerable activity related to mathematical modeling of functional barriers (Feigenbaum *et al.*, 1997; Franz *et al.,* 1997; Laoubi *et al.*, 1995; Laoubi and Vergnaud, 1995). Laoubi *et al.* (1995) developed a mathematical model describing both the diffusion of hazardous materials from recycled plastic into food and the diffusion of compounds from the food into the recycled plastic, through a functional barrier. In this model, the efficiency of the functional barrier was defined by the lag time for migration. The results suggested that the concentration of contaminants in the functional barrier varied exponentially with time. The barrier could efficiently protect the food from the contaminant contained in the polymer if $Dt/L^2 < 1$, where D is diffusion coefficient; t is time and L is polymer thickness (Laoubi *et al.*, 1995)

A computer simulation model program that accounts for the diffusion process inside the polymer and also for the partitioning of the contaminant between the polymer and the contacting phase was developed by Han *et al.* (2003). They have concluded that a thicker functional barrier provides better protection of the food from contamination by substances in the recycled layer and that the efficiency of the functional barrier can be increased dramatically by using higher barrier materials.

Franz *et al.* (1994) studied global migration of contaminants from a multiple layer system that contained a recycled material. They concluded that the multiple layer material was not significantly different from the corresponding virgin material. PET bottles that were made from a three-layer system were found to produce no detectable levels of migration of highly mobile contaminants such as trichloroethane, toluene, chlorobenzene, benzophenone and phenyldecane using 100% ethanol as the food simulant under standard conditions (10 days at 40°C), or even after 6 months storage at room temperature (Franz *et al.*, 1996).

2.4 Thermal Oxidation and Thermal Degradation of PET Products

The main problem in recycling of used plastics is in the recovery of the polymer namely, collection, separation and reprocessing (Selke, 1988; 1990; Hadjilambrinos, 1996). The reprocessing commonly uses high temperatures and pressures. PET is rather sensitive to heat and/or oxidation. PET thermal degradation studies have been performed mainly by Zimmerman (1984). Based on these results, some researchers (Pierce *et al.*, 1995; Nerin *et al.*, 1998; Khemani, 2000) conducted further studies. During repeated recycling in the manufacturing process, the polymer may undergo degradation (Castle *et al.*, 1994; Pierce *et al.*, 1995; Nerin *et al.*, 1998; Khemani, 2000) by thermal decomposition (Incarnato *et al.*, 1998; Jetten *et al.*, 1999) or thermo-mechanical stress (Pierce *et al.*, 1995). This degradation may generate significant amounts of by-products such as monomers and oligomers that may be leached out into liquid contents after packing, either by evaporation, if they are volatile, or by diffusion.

Monomers and oligomers are reactive substances, with respect to living organisms (Leber, 2001). Direct or indirect migration of trace amounts of monomers onto human skin or other body surfaces may pose a health risk (Leber, 2001). Therefore, regulations usually restrict the level of residual monomers in the plastic materials and articles made thereof.

The mechanism of PET degradation was studied by various researchers (Bednas *et al.*, 1981; Zimmermann, 1984; Dzięcioł and Trzeszczyński, 1998).

They agree that thermal degradation is initiated by random scission of the chain at the ester linkage, leading to carboxyl and vinyl ester end group (Zimmermann, 1984; Dzięcioł and Trzeszczyński, 1998) as shown in Figure 2.3.

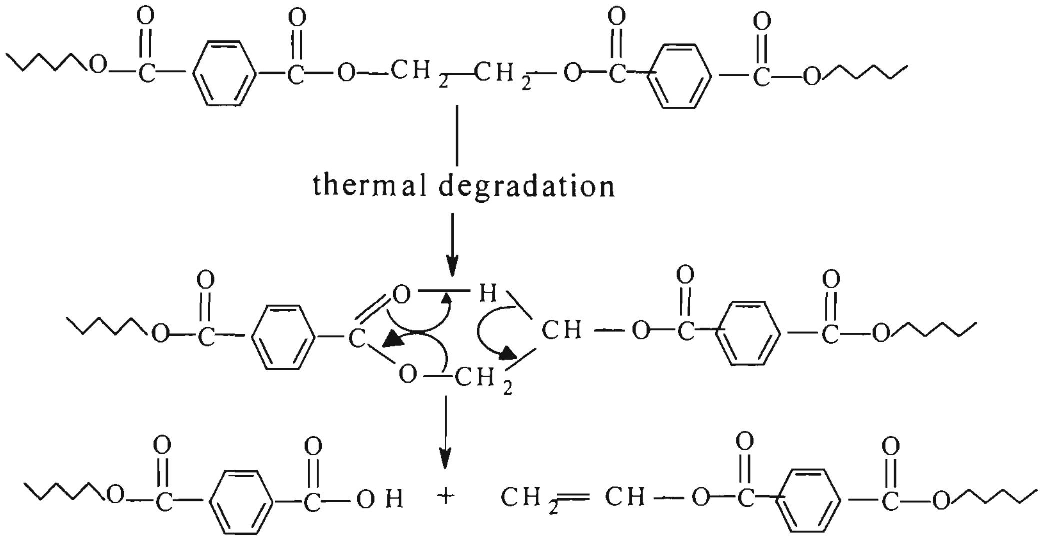


Figure 2. 3. Thermal cleavage of the ester bond in PET to give carboxylic acid and vinyl ester end groups (Zimmermann, 1984; Dzięcioł and Trzeszczyński, 1998)

Primary hydrolysis reactions are also responsible for the reduction in molecular weight during reprocessing of PET (Scheirs, 1998). Contaminants such as polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), glue, ethylene vinyl acetate (EVA) and paper, generate acidic compounds that catalyze the hydrolysis of the ester linkages in PET (Scheirs, 1998). A general overall mechanism for the generation and depletion of end products was proposed by Zimmermann (1984) and is shown in Figure 2.4.

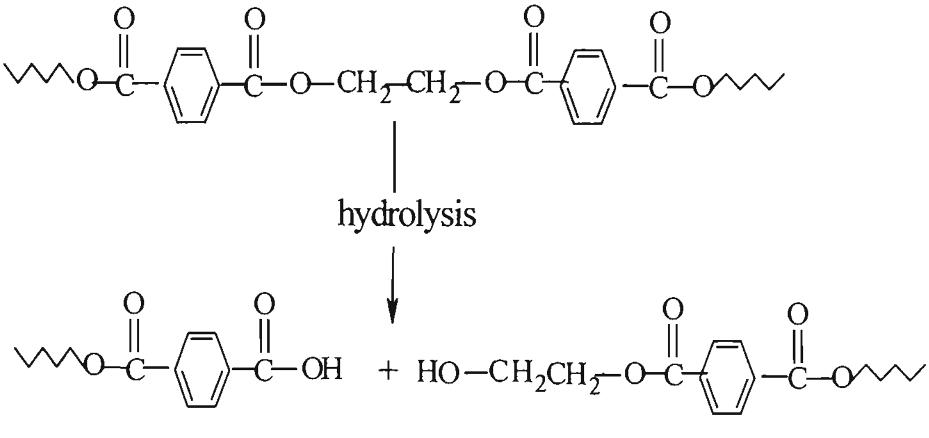


Figure 2. 4. Hydrolytic cleavage of the ester bond in PET to yield carboxylic acid and hydroxyl ester end groups (Zimmermann, 1984)

Numerous data were published in the literature concerning the contaminants released from PET as degradation products. Most of the findings have pointed to acetaldehyde and oligomer as being the major degradation products.

2.4.1 Acetaldehyde

Understanding the thermal degradation of PET with particular regard to the emission of toxic substances is very important for many commercial applications of this polymer, although the thermal stability of PET is relatively high. The toxic volatile substances (e.g. acetaldehyde, formaldehyde, benzaldehyde), aromatic hydrocarbons (e.g. benzene, toluene, ethyl benzene, styrene) are emitted within the temperature range of 200 – 300°C (Dzięcioł and Trzeszczyński, 1998). Studies by Bryk (1991); Villain *et al.* (1995); Franck *et al.* (1994); Nijssen *et al.* (1996); Eberhartinger *et al.* (1990); Linssen *et al.* (1995); Dong *et al.* (1980);

Wyatt (1983); Nawrocki *et al.* (2002) showed that acetaldehyde and formaldehyde are the main degradation products of PET.

At low temperatures, acetaldehyde and formaldehyde as well as carbon monoxide are produced from PET (Dzięcioł and Trzeszczyński, 1998). Khemani (2000) has estimated the rate of acetaldehyde generation by a mid-polymer chain-scission route to be approximately 1.1 – 1.5 ppm per min at 280°C. The rate of formation of acetaldehyde at 280°C depends on various factors and experimental conditions such as oxygen concentration, moisture content and number of acid chain ends. Dzięcioł and Trzeszczyński (2000) found that a concentration of acetaldehyde in the range of 0.2 – 352.2 mg m^{-3} is emitted from PET under isothermal conditions at temperatures of 200 – 700°C for 20 min in a nitrogen atmosphere. The maximum yield of acetaldehyde was observed at 400°C.

Acetaldehyde is formed very quickly by tautomerization of vinyl alcohol that is produced by the recombination of vinyl ester and hydroxyl end groups (Figure 2.5) during melt processing and polycondensation (Dong *et al.*, 1980; Franck *et al.*, 1995; Nijssen *et al.*, 1996; Scheirs, 1998).

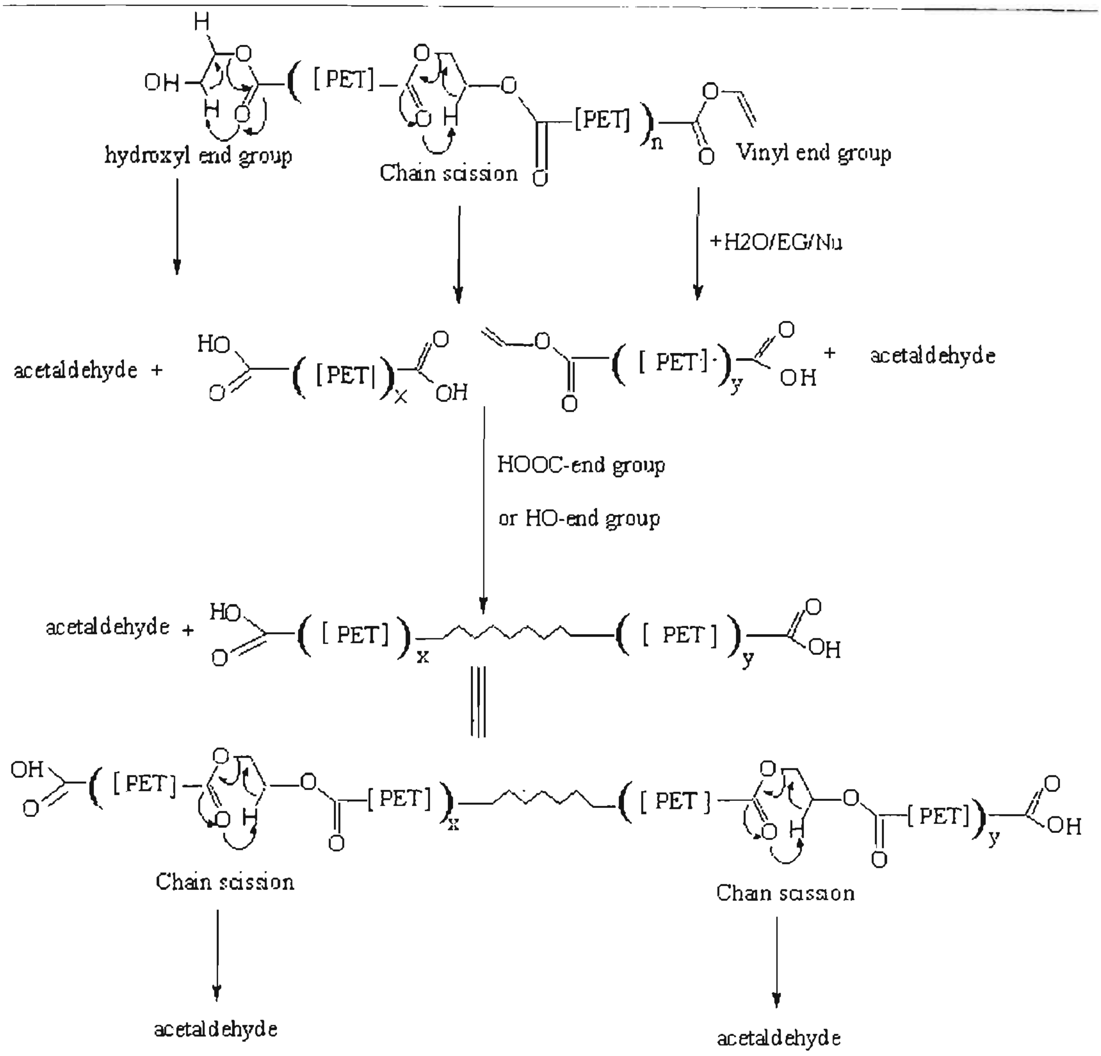


Figure 2. 5. The generation of acetaldehyde from hydroxy and vinyl end-groups, and the mid polymer chain scission in PET (Scheirs, 1998; Khemani, 2000)

According to this mechanism, acetaldehyde is generated in three different routes involving firstly hydroxyl-end groups, secondly vinyl-end groups and finally mid-polymer chain scission (Khemani, 2000).

Dong *et al.* (1980) reported a value of 35.5 ppm of acetaldehyde in virgin PET resin. Acetaldehyde has also been found in PET after being irradiated at a dose of 25 kGy at room temperature by using a caesium-137 source. An analysis using GC/MS (gas chromatography coupled with mass spectrometry) performed at 200°C showed that 10 – 12 mg of acetaldehyde per kg PET material was produced at room temperature (Komolpraset *et al.*, 2001).

Dábrowska *et al.* (2003) observed that at the beginning of the machine moulding of PET bottles, the first PET preforms had a high concentration of acetaldehyde (> 50 mg kg^{-1}) and then reached a constant value of approximately 4.5 – 5.5 mg kg^{-1}, when the production process of the bottles became stable and continuous.

2.4.1.1 Acetaldehyde in food and beverages

Acetaldehyde seems to be the major undesirable contaminant from PET because it causes a distinctive odour and taste in packaged foods (Franck *et al.*, 1995). Acetaldehyde has a high solubility in water and is readily dissolved in foods of high water content. A trace amount of acetaldehyde can adversely affect the organoleptic properties of beverages (Dong *et al.*, 1980; Wyatt, 1983; Scheirs, 1998; Nijssen *et al.*, 1996).

Maarse (1991) determined that pasteurized fresh milk packaged in polyethylene contains 10 ppb of acetaldehyde. Bills *et al.* (1972) found that the flavour threshold for acetaldehyde in milk, milk with 8% sucrose and milk with 0.4% strawberry flavour was 800, 1,000 and 1,700 ppb respectively. Adding some flavour to milk has masked the acetaldehyde, thus a high level of threshold was obtained. The threshold of acetaldehyde in skim milk is expected to be higher than that in whole milk (Miyake and Shibamoto, 1993; Yasuhata and Shibamoto, 1991).

Monarca *et al.* (1994) were able to detect acetaldehyde in water stored for 2 weeks in PET bottles using GC/MS analysis. Sugaya *et al.* (2001) detected a significant level of 260 $\mu g\ L^{-1}$ of acetaldehyde in mineral water after being stored in PET bottles. Ashby (1998) used water as a food simulant in an experiment to determine the migration of acetaldehyde from PET into foodstuff and found that the acetaldehyde concentration was < 50 ppb after 8 days exposure at 55°C. However, for a proper comparison, the concentration of acetaldehyde in PET in all the experiments cited would be useful.

Nijssen *et al.* (1996) also studied acetaldehyde migration into water during storage. They monitored the change in acetaldehyde content in uncarbonated and carbonated water stored in 1 L glass bottles, 1.5 L PET bottles (OPET) and unused refillable 1.5 L heat set PET (HRPET) bottles. In non-carbonated water, no acetaldehyde was detected, whereas the concentration of acetaldehyde in carbonated mineral water increased steadily with storage time up to a level of 100 ppb in OPET bottles. Increasing the storage temperature resulted in an increase in the amount of acetaldehyde that had migrated into the water in all PET containers.

The fact that no acetaldehyde was found in the uncarbonated water stored in the PET bottles can be partly explained by the fact that acetaldehyde can be readily oxidized by oxygen to acetic acid, acetic anhydride and paracetic acid or reduced to ethanol by catalysts such as nickel and copper oxide, and can also be easily transformed by acids into the paraldehyde trimer (Hagameyer, 1987). The other reaction products mentioned were not investigated. In this case, the permeability of the bottle to oxygen plays an important role in triggering the oxidation processes (Hagameyer, 1987).

Nawrocki *et al.* (2002) also found a higher amount of acetaldehyde in carbonated rather than non-carbonated water. They found values in the range of 2.2 – 107.2 $\mu g\ L^{-1}$ and 0.9 – 39.1 $\mu g\ L^{-1}$ for carbonated and non-carbonated bottled water respectively. Dábrowska *et al.* (2003) monitored a production line for carbonated mineral water packed in PET bottles. They detected a concentration higher than 200 $\mu g\ L^{-1}$of acetaldehyde in the carbonated mineral water.

In the mineral water industry, it is generally assumed that the odour threshold for acetaldehyde detection in water is in the range of 20 - 40 μg/L (Nawrocki *et al.*, 2002). A threshold value of 15 ppb has been suggested by Fazzalari, (1973) as well as Poretta and Minuti (1995). While an acetaldehyde flavour threshold for carbonated water was reported to be 36 ppb (Poretta and Minuti, 1995). Linssen *et al.* (1995) reported a threshold of acetaldehyde in the range of 10 μg/L to 1000 μg/L for carbonated beverages, wines and ciders.

2.4.1.2 Acetaldehyde determination

It is quite difficult to detect acetaldehyde due to its high volatility. The boiling point of this compound is 20.8°C (Weast, 1969). Different methods of analysis have been used for the determination of acetaldehyde from PET. These include simultaneous distillation extraction (Takami *et al.*, 1985), reaction with chemicals (Miyake and Shibamoto, 1998), dynamic headspace sampling (Gramshaw *et al.*, 1995), a static headspace method (Luong *et al.,* 1996; Dumas, 1980; Nijssen *et al.,* 1996; Linssen *et al.*, 1995), membrane dialysis, conventional solid phase extraction (Chin *et al.*, 1972), purge-and-trap sampling (Nerin *et al.*, 2002; Nouri *et al.*, 1996) and high performance liquid chromatography (HPLC) with fluorescent detection (Passanzini and Di Palo, 1997). In principle, there is no different between the two methods of dynamic head-space and purge-trap techniques. Among these methods, the static headspace gas chromatography appears to be the simplest and least costly. The other methods are generally very time consuming and require special solvents and/or equipment. The detection limits, however, depend on the type of detectors being used in the various chromatographic techniques.

Luong *et al.* (1996), Dumas (1980), Nijssen *et al.* (1996) and Linssen *et al.* (1995) have described the determination of acetaldehyde in an aqueous matrix by headspace gas chromatography. Wyatt (1983) described a rapid method for the determination of acetaldehyde in capped PET bottles by using a semi-automated, headspace GC analysis. Dong *et al.* (1990) described an automated gas chromatographic method for the determination of residual acetaldehyde in bottles, preforms and resin of PET at a detection limit of 50 ng L^{-1} in a standard solution. Linssen *et al.* (1995) described a headspace GC method, which uses the static equilibrium technique for the determination of low levels of acetaldehyde in aqueous food products with a detection limit of 6 ng L^{-1}. Eberhartinger *et al.* (1990) studied the migration of acetaldehyde from PET bottles into soft drinks under various conditions using a headspace GC method. The detection limit was not reported. Nijssen *et al.* (1996) reported a repeatable detection limit of 1 μg L^{-1} for acetaldehyde using a headspace sample of water.

The presence of acetaldehyde in PET was also confirmed by gas-liquid chromatography that utilized a technique of gas entrainment on column trapping and sampling at 5°C (Maarse, 1991). Improta *et al.* (1984) determined acetaldehyde as a cyanohydrin derivative by GC with a nitrogen phosphorous detector. They reported a detection limit of 100 ppb. Edlund (1987) used liquid chromatography for determining acetaldehyde as its 2,4-dinitrophenylhydrazone derivative with a detection limit of ~ 1 ppb. Takami *et al.* (1985) combined an extraction and a derivatization method to detect acetaldehyde in water. With a high performance liquid chromatography and UV detector, 0.3 ppb acetaldehyde could be determined.

Arthur and Pawliszyn (1990) and Arthur *et al.* (1992) have developed the method called solid-phase micro-extraction (SPME), which is a variation of the adsorption technique for the extraction of volatile and semi-volatile compounds from solid, liquid or gaseous samples. This method uses a fused silica optical fiber coated with a thin layer of a polymer to adsorb a targeted compound from the test samples. The adsorption process is performed either by immersing the fiber into liquid samples (SPME liquid sampling) or by exposing it to the headspace above a liquid, solid or gas phase. A partitioning between the sample matrix and the fiber surface occurs and equilibrium is reached. The adsorbed compound is then introduced into a gas chromatograph and is thermally desorbed in a hot injection port of the instrument and subsequently analyzed (Arthur and Pawliszyn, 1990; Pan *et al.*, 1995*)*. However, the method is very expensive.

Although SPME was originally developed for the analysis of pollutants in water, it has been recently applied for the analysis of volatile compounds in food and beverages. The SPME method has been successfully applied to the determination of acetaldehyde in milk of various fat contents, chocolate milk and spring water with a threshold of 3,900, 10,000 and 170 ppb respectively (Van Aardt *et al.*, 2001). The technique of SPME was shown to be an effective method for recovery of acetaldehyde in all media with detection levels as low as 200 and 20 ppb in milk and water respectively, using a polydimethyl siloxane/carboxen SPME fiber in a static headspace at 45°C for 15 min (Van Aardt *et al.*, 2001).

2.4.2 Oligomers

At high temperatures, in the range of 260 – 700°C, low molecular weight compounds such as terephthalic acid and oligomers (dimer, trimer, cyclic tetramer and cyclic pentamer) are found among the low volatility products from PET decomposition (Dulio *et al.*, 1995; Vermylen *et al.*, 1999). Samperi *et al.* (2003)

indicated that PET decomposes to cyclic oligomers at 300°C and decomposed further at about 400°C to generate acetaldehyde and anhydride-containing oligomers. However, at a lower temperature such as 260°C, Freire *et al.* (1998) found cyclic oligomers such as cyclic trimer, tetramer, pentamer and hexamer after 5 min of heating at that temperature. Furthermore, it was found that increasing the time of heating to 30 and 60 min, increases the concentration of the oligomers in PET by 9 fold and 16 fold respectively compared to the original sample (non heated).

A low percentage (1 - 3% w/w) of cyclic oligomers can be found in most commercial PET (Dulio *et al.*, 1995). The mechanism of their formation has not yet been fully elucidated. Three formation mechanisms have been proposed (Vermylen *et al.*, 1999): (i) the cyclization of linear oligomers; (ii) a backbiting process of a hydroxyl end-group on a carboxyl group of the chain and (iii) an intra-or inter-molecular trans-esterification. The reactions (i) and (ii) are both trans-esterification processes.

The major low molecular weight moieties produced from PET are cyclic oligomers (Shiono, 1979; Komolpraset *et al.*, 2001; Ashby, 1988). In most cases four oligomers (i.e.: cyclic dimer, cyclic trimer, cyclic tetramer and cyclic pentamer) were found in commercial PET (Shiono, 1979; Begley and Hollifield, 1990a, 1990c). The cyclic trimer was found at the highest concentration (Begley and Hollifield, 1990a, 1990b, 1990c; Freire *et al.*, 1999). About 83.6% of the total oligomers extracted from PET were found to be the cyclic trimer (Shiono, 1979). Komolpraset *et al.* (2001) found that 0.41 – 0.50% w/w of cyclic trimer is extracted from PET after being irradiated by a caesium-137 source. Dried PET was found to have 1.8 – 3.0% w/w of oligomers (Dulio *et al.*, 1995) or 15 – 25 mg oligomers per kg PET resin (Freire *et al.*, 1999). Begley and Hollifield (1990a, 1990b) found that 0.238 mg of cyclic trimer migrated into corn oil from PET susceptor film. In another study, migration levels ranging from 0.02 to 2.73 mg of oligomers per kg of food were found in roasting bags and susceptors (Castle *et al.*, 1989).

An HPLC method has been employed to determine the migration levels of oligomers from PET into food and food simulants (Begley and Hollifield, 1990a; Castle *et al.*, 1989). Adsorption and gel permeation chromatography were also used with a view of separating and monitoring the individual oligomers (Shiono, 1979). Castle *et al.* (1988) proposed another method involving the conversion of all the oligomers present in the food by extracting them into terephthalic acid monomer followed by GC/MS analysis using single ion monitoring. Figure 2.6 shows the structure of the most common oligomers in recycled PET.

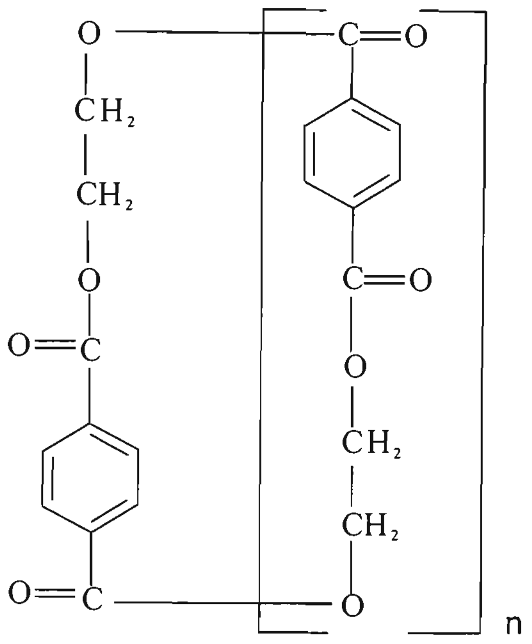


Figure 2. 6. Typical cyclic oligomeric degradation product formed during the thermal reprocessing of PET. The parameter n is the degree of polymerization and can vary from 1 to 5 (Dulio *et al.*, 1995; Shiono, 1979)

2.5 Properties of Recycled Plastics

Generally, recycled plastics without thermal and mechanical treatment have inferior in their properties compared to virgin ones. Plastic materials that have been recycled by physical processing tend to be sometimes incompatible with their virgin counterparts (Selke, 1988) due to their decreased molecular weight (Incarnato *et al.*, 1998). The intrinsic viscosity of recycled PET was found to be in the range of 0.46 - 0.76 compared to 0.72 - 0.84 for the virgin material (Scheirs, 1998). A study of thermal and mechanical properties of virgin and recycled PET before and after injection moulding showed that the presence of contaminants in the recycled PET has lead to a reduction in the intrinsic viscosity and average molecular weight. The recycled PET was also more sensitive to hydrolytic degradation (Torress *et al.*, 2000). A higher degree of crystallinity was obtained in the recycled material compared to virgin PET (Torress *et al.*, 2000). The crystallinity was found to be 31% for recycled PET sheets compared to 5 - 15% in commercial PET bottles (Komolpraset *et al.*, 1997). The degree of crystallinity, however, depends largely on the thermal history.

During the repeated cleaning and washing processes used in refillable bottle lines, the process may adulterate plastic materials and influence the absorption and desorption properties of the product (Feron *et al.*, 1994). However, Jetten *et al.* (1999) reported that in spite of the fact that the surface of PET and polycarbonate (PC) bottles were altered by repeated washing, the mechanical properties of the materials were not affected significantly.

2.5.1 Importance of crystallinity

Among all the properties of polymeric packaging materials, mechanical properties are the ones that are most important because they affect the service life and the end-use applications. The mechanical properties of semi-crystalline polymers are primarily a function of crystalline texture, crystalline percentage and molecular orientation and extension (Chaari *et al.*, 2003; Kitano *et al.*, 1995).

The degree of crystallinity is an important characteristic of a semi-crystalline polymer, determining its mechanical properties. Increasing polymer crystallinity results in a decrease in impact strength and an increase in the probability of brittle failure, whereas the amorphous region contributes to the flexibility and toughness of the polymer (Torres *et al.*, 2000; Ram, 1997). Polymers with at least some degree of crystallinity are, however, denser, stiffer and stronger than their completely amorphous counterparts. On the other hand, semi-crystalline polymers have high melting points, high densities, and high moduli of rigidity, resist dissolution and swelling, and are virtually impenetrable to the diffusion of small molecules (Mark and Atlas, 1977; Ram, 1997).

The crystalline regions of a polymer are considered as impenetrable obstacles in the path of a diffusion process and are sources of heterogeneous properties for the penetrant-polymer system. The effect of crystallinity on the mechanism of material transport and diffusion in a semi-crystalline polymer such as PET has often been analyzed from the point of view of barrier property enhancement in polymer films (Mercea, 1999).

The factors, which influence the crystallization rates of PET from the melt, can be divided into three classes:

(i) Factors that affect the molecular structure of the polymer, including molecular weight, and additives such as nucleating agents and catalyst system (Jabarin, 1987b; Gümther and Zachman, 1982; Dekoninck, 1989; Vilanova *et al.*, 1985). Molecular weight affects the melt viscosity of the crystallizing polymer and the rate of transporting the crystallizing segments across the liquid-crystal interface (Jabarin, 1987a);

(ii) Physical factors such as temperature, pressure and moisture during the crystallization process (Jabarin, 1987a, 1987c; Hatakeyama and Quinn, 1999);

(iii) Physical conditions of the polymer during crystallization such as strain, molecular structure and orientation (Lu and Hay, 2001; Jayakannan and Ramakrishnan, 1999; Myung *et al.*, 2001; Dargent *et al.*, 1997) and previous melt history of the polymer (Wang *et al.*, 1998; Verhoyen *et al.*, 1998; Zhang and Shen, 1998).

2.5.2 Effect of temperature on polymer crystallinity

Thermal treatment causes the physico-mechanical properties of packaging materials to change due to the modification of polymer structure at the molecular and morphological levels. Reheating polymeric materials to temperatures close to the melting temperature and cold quenching will increase the crystallinity of the polymer, which may affect its performance. The observed increase in the crystallinity of the polymer is a result of the melting and recrystallization processes (Selikhova, 1989; Gümther and Zachman, 1982; Donnelly *et al.*, 1997).

At low temperatures, molecular motions in the amorphous region are restricted to molecular vibration, but the chains are restricted in their ability to rotate. When the material is heated, the motion of the molecules is increased. At a certain temperature, the molecular chains can move more freely and the material transforms from a hard and brittle one to a softer one, and the polymer becomes more flexible (Mark and Atlas, 1977). The process of cold quenching crystallizes the amorphous domains thus increasing the degree of crystallinity of the polymer (Mark and Atlas, 1977). Figure 2.7 illustrates the changes in the material that occur along with heating and cold quenching treatment, which leads to the increase in overall crystallinity of the polymer.

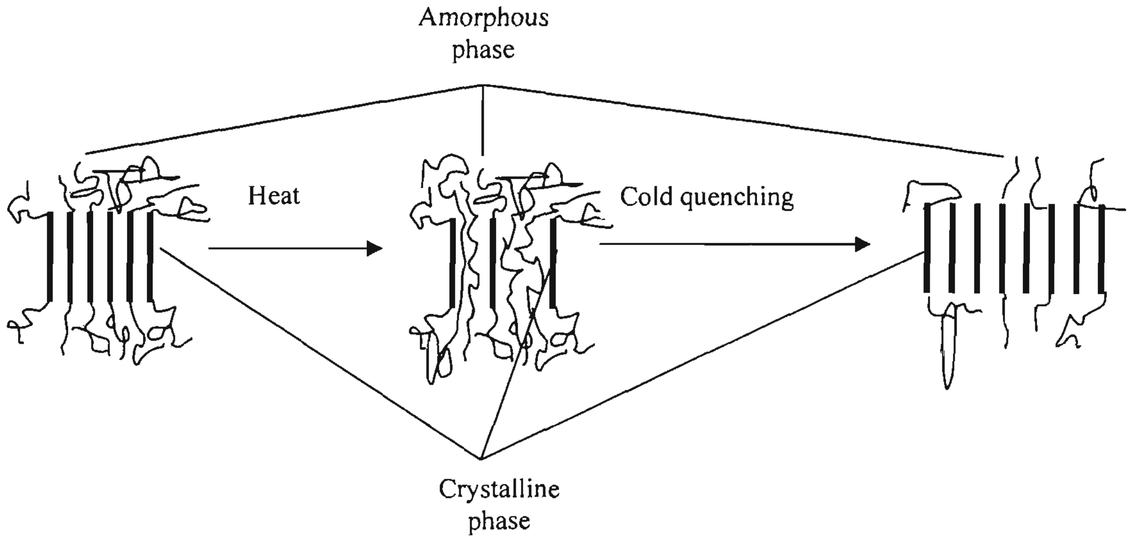


Figure 2. 7. Processes that affect the overall crystallinity during heat-treatment of PET samples

The main problem with PET is that the heating in the first run already allows an increase of crystallization through relaxation. Heating also affects the size of the crystallites as well as the extent of the amorphous region. The crystals grow from individual nuclei and radiate in three dimensions forming spherulites (Geil, 1997). Furthermore, the extent of crystallization of the polymer is also affected by the regularity of the molecular structure; a regular structure is more capable of undergoing crystallization than an irregular structure (Jayakannan and Ramakrishnan, 1999).

2.5.3 Differential scanning calorimetry

In a commercial polymer, a complete crystalline structure is never reached, and non-crystalline (amorphous) regions always exist (Kong and Hay, 2002). Therefore, it is common to use the term "semi-crystalline" and to characterize it by the degree of crystallinity, as the fraction (percentage) of the crystalline phase of the total mass (Ram, 1997). Several techniques are widely employed, such as dilatometry (Ram, 1997), calorimetry (Torres *et al.*, 2000; Kong and Hay, 2002), microscopy (Kitano *et al.*, 1995; O'Malley, 1975), light depolarization and scattering (Blundell and Osborn, 1983; Murthy *et al.*, 1994; Kitano *et al.*, 1995; Shirataki *et al.*, 1997), density (O'Malley, 1975; Murthy *et al.*, 1994; Kitano *et al.*, 1995; Bashir *et al.*, 2000), etc., to measure the degree of crystallinity in a polymer. In particular, differential scanning calorimetry (DSC) has proved to be a convenient technique because of the small sample size required, speed of operation and the possibility of quickly reaching thermal equilibrium (O'Malley, 1975; Groeninckx *et al.*, 1980; Murthy *et al.*, 1994; Dawson *et al.*, 1991; Li *et al.*, 1999). However, in many cases the results depend on the operator's estimate of the correct baseline position (Gray, 1970).

Commonly, the mass fraction crystallinity is estimated from DSC using equation (2.1) (Bashir *et al.*, 2000; Vilanova *et al.*, 1985; Torres *et al.*, 2000; Kong and Hay, 2001):

$$X_c = [\Delta H_{fusion}(T_m)/\Delta H^o_{fusion}(T^o_m)] \qquad (2.\ 1)$$

where X_c is the fraction of the crystallites; $\Delta H_{fusion}(T_m)$ is the enthalpy of fusion measured at the melting point T_m; and $\Delta H^o_{fusion}(T^o_m)$ is the enthalpy of fusion of the totally crystalline polymer measured at the equilibrium melting point, (T^o_m).

For polymers having a low degree of crystallinity with slow crystallization kinetics, cold crystallization can occur during an experiment. In these cases, a separate integration of the exothermic peak of cold crystallization and that of the endothermic peak of melting in different temperature regions is made and thus crystallinity is calculated using a modification to equation (2.1) as given in equation (2.2) (Bashir *et al.*, 2000; Torres *et al.*, 2000; Kong and Hay, 2002).

$$X_c = (\Delta H_{fusion}(T_m) - \Delta H_{cold}(T_{cold}))/\Delta H^o_{fusion}(T^o_m) \qquad (2.2)$$

In this modification, the heat due to crystallization during scanning at T_{cold} (ΔH_{cold}) is subtracted from the heat of fusion of the sample. The estimated value of ΔH^o_{fusion} for 100% crystalline PET is in the range 120 - 155 J g^{-1} (Table 2.2). $\Delta H^o_{fusion}(T^o_m) = 120$ J g^{-1} seems to be the most common value quoted in the literature.

Table 2. 2. Estimated heat of fusion ($\Delta H^{o}_{fusion}(T^{o}_{m})$) from samples of nearly 100% crystalline PET

$\Delta H^{o}_{fusion}(T^{o}_{m})$/J g^{-1}	References
120	Robert (1969); Vilanova *et al.* (1985); Jayakannan and Ramakrishnan (1999)
133	Kitano *et al.* (1995)
135	Metha *et al.* (1978); Bundell and Osborne (1983) Starkweather *et al.* (1983)
136	Dröscher and Wegner (1978)
155	Springer *et al.* (1981)

2.6 Food-Package Interactions

The composition and purity of food has been a matter of concern throughout the world for many years, leading to a highly complex system of legislation and enforcement. The basic guiding principle in most of these regulations consist of two parts (Crosby, 1981; Griffin *et al.*, 1996): (i) packaging shall not endanger the consumer through adulteration by migration of materials from the package and (ii) the package should not detract from the organoleptic properties (taste, smell) of the food.

2.6.1 Legislative approval

Various regulations are applied in different countries regarding interactions between the food and the packaging material, but it appears that only the European Union (EU) and the US Food and Drug Administration (FDA) regulations will be adopted in the future as the world standards (Borodinsky, 1991; Kay, 1991).

In 1982, the EU published a Council Directive 82/711/EEC (Council Directive, 1982) that lays down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs. Neither the EU nor the US FDA has published specific directives in relation to the use of recycled packaging materials for food applications (Bayer *et al.*, 1995; Huber and Franz, 1997, Begley *et al.*, 2002). However, the FDA has stated that various assessments must be made to ensure that the levels of potentially hazardous compounds are acceptable (Bayer *et al.*, 1995) and that all the requirements of the appropriate directive for the virgin material should also be met by the recycled ones (Huber and Franz, 1997).

The EU has supported studies to be carried out for the development of legislation in the area of recycling/reuse of plastics for food contact applications and involved nearly 30 project partners from European research institutes, laboratories, industries and universities (project conducted by Food Agri-Industry Research (FAIR)) (Jetten *et al.*, 1999). The two main themes of the project were physical recycling of thermoplastics and refillable plastic packaging (Gilbert and Rossi, 2000). One of the important conclusions of the project so far, was that PET seems likely to be the most promising polymer for reuse as a food packaging material (Gilbert and Rossi, 2000).

The most effective way to achieve the necessary control of using adequate materials is by setting migration limits. This is demonstrated in the EU Directive for plastic materials and articles intended to come into contact with foodstuffs (Commission Directive 90/128/EEC, 1990).

The EU approach was to assign global migration limits (GMLs) and specific migration limits (SMLs) to those substances with adverse toxicological properties. The SMLs assign a limit on the quantity of a specific substance allowed to migrate into a food or food simulant. The GMLs is the maximum permitted level of migration of all substances from the materials or articles into food or food simulants.

The EU has established a Corrigendum to Commission Directive 90/128/EEC amended by Commission Directive 92/39/EEC, 93/9/EEC, 95/3/EEC, 96/11/EEC, 99/91/EC, 2001/62/EC, 2002/17/EC, that mandates a positive "A-list" of approved monomers and other additives with SMLs and GMLs (Commission Directive, 1990; 1992; 1993; 1995; 1996; 1999; 2001; 2002). There are several hundred substances that are permitted for use in the manufacturing of food contact packages. More additives, with appropriate restrictions, will be added in future amendments (O'Brien and Cooper, 2002). Unfortunately, plastic packages that contain a recycled material may contain substances that are not listed in the positive "A-list" document (Franz *et al.*, 1994).

The migration limits set in the European Directive are derived from toxicological data using an assumption that the average person weight 60 kg and eats 1 kg food (solids and liquids) a day. It is further assumed that the food is wrapped in plastics containing the ingredient to be controlled and the surface to volume ratio of contact is 6 dm^2 per 1 L or kg of food. The migration limit, expressed as mg contaminant per kg food (or food simulants), is therefore calculated by multiplying the acceptable daily intake (ADI), expressed as mg contaminants per kg body weight per day, or total daily intake (TDI), expressed as mg contaminants per kg food per day by a value of 60. The EU has set the maximum quantity of migrating substances to be 10 mg constituent per dm^2 of packaging material or 60 mg constituent per kg of food (or food simulant), which is equivalent to a dietary intake of 1 mg per day for a person weighing 60 kg (Article 2, Commission Directive 90/128/EEC, 1990).

In the USA, the structure of regulations for food packaging materials is much more complex. The regulations encompass both the basic polymer resins used in food packaging and the adjuvants, which are added to the polymer during manufacturing of the final food package (Lau and Wong, 2000). The regulations frequently contain specifications for the resin, such as residual monomer content. Sometimes, the limits are placed on specific migration. The time/temperature/solvent conditions for the short-term extraction test used to test compliance are also spelled out in the regulation (US FDA, 1995). Based on these regulations, pre-market approval by FDA is currently required for food packaging materials to be used in the USA (Lau and Wong, 2000; Begley, 1997).

The US FDA developed a concept called "The Threshold of Regulation" which became part of the US Code of the Federal Register on 17 July 1995 (Thorsheim and Armstrong, 1993; Bayer *et al.*, 1995; Bayer, 1997; Begley, 1997). This regulation, which is entitled "Points to Consider for the Use of Recycled Plastics in Food Packaging", was proposed for determining when the extent of migration into food from recycled polymer has a negligible risk (Begley, 1997; Lau and Wong, 2000). The threshold is based on a review of 343 carcinogenic compounds and relates more to a specific human dietary exposure than to the level of migration of the substance (Begley, 1997). This final ruling specified a maximum concentration in the daily diet level of 0.5 $\mu g\ kg^{-1}$ of non-food substances from plastic packaging (Thorsheim and Armstrong, 1993; Begley and Hollifield, 1993; Bayer, 1997; Begley, 1997). The dietary concentration may be determined based on an assumption that 100% of contaminant migrates into the food, either as the result of an actual migration test or from migration modeling. Many scientists agree, however, that 1.0 $\mu g\ kg^{-1}$ is a level that provides an adequate degree of safety to protect public health (Thorsheim and Amstrong, 1993; Bayer, 1997).

Kroes *et al.* (2000) reviewed recently the available studies on neurotoxic, immunotoxic, endocrinologic and carcinogenic compounds and concluded that carcinogenic compounds are the most sensitive ones to be considered. In this study, they defined a "threshold of toxicological concern" and proposed 1.5 $\mu g\ kg^{-1}$ per person per day which corresponds to the "threshold of concern" assuming a diet of 3 kg of food (solids and liquids) per person per day. Using a tiered approach, under certain conditions, Cheeseman *et al.* (1999) proposed a "Threshold of Regulation" value of 1.0 μg kg^{-1}.

Based on "the threshold of regulation" concept, Begley and Hollifield (1993) and Begley (1997) calculated a maximum threshold concentration of 0.5 μg kg^{-1} of additives and/or residual contaminant originating from recycled containers for a number of commodity polymers (see Table 2.3). In these calculations it was assumed that: (i) the container has a wall thickness of 20 mil (50.8 μm) and was made from 100% recycled resin; (ii) 10 g of food contact per one square inch of container wall surface and (iii) 100% of the contaminants migrate into the foodstuffs.

The calculation of maximum contaminant in the packaging material and in the foodstuffs, related to the dietary concentration is estimated from equations (2.3 – 2.5) (US FDA, 1995):

$$R_{MS} = L \times d \tag{2. 3}$$

$$C_D = C_f \times CF \tag{2. 4}$$

$$C_p = 10C_f/R_{MS} \tag{2. 5}$$

where R_{MS} is mass-to-surface area ratio; L and d are the thickness and density of the packaging material respectively; C_D is the dietary level (0.5 μg kg^{-1}); C_f is the contaminant concentration in the foodstuffs; CF is consumption factor and C_p is the contaminant concentration in the packaging material.

Table 2.3. Threshold value for maximum residual additives/contamination and migration amounts that result in 0.5 μg kg^{-1} dietary exposure to a contaminant

Polymer	Density/g cm^{-3}	CF[1]	$R_{MS} \times 10^1$/g in^{-2}[3]	Contaminant in food/μg kg^{-1}[4]	Contaminant in polymer/μg kg^{-1}[5]
Polyethylene terephthalate (PET)	1.40[1]	0.05	4.59	10	215
Polystyrene (PS)	1.05[1]	0.08	3.44	6	180
Polyvinyl chloride (PVC)	1.58[1]	0.11	5.18	5	90
High density polyethylene (HDPE)	0.96[2]	0.13	3.15	4	123
Polypropylene (PP)	0.98[2]	0.02	3.21	25	778
Low density polyethylene (LDPE)	0.92[2]	0.18	3.02	3	92
Polycarbonate (PC)	1.20[2]	0.05	3.93	10	256

Source: [1]US FDA (1995)

[1] Mark (1999)

[3]Calculated from equation (2.3)

[4]Calculated from equation (2.4) (Begley, 1997)

[5]Calculated from equation (2.5) (Bayer, 1997)

Finally, there have been many attempts to achieve an agreement between the European and the US FDA regulatory systems. Some projects have been carried out b the European Commission on an informal and partial experimental basis, which involved the US FDA's laboratory for the purpose of safety evaluation of indirect food additives (Franz, 2002).

2.6.2 Migration testing

In food packaging terminology, migration is used to describe the transfer of substances from the packaging material (often a polymeric material) into foodstuffs. There are two kinds of migration tests, referred to as: "global" (also known as "total" or "overall") migration and "specific" migration. Global migration is understood as the total mass of substances migrating from the packaging material or article under strictly defined conditions into the food or a food simulant, whereas specific migration relates to the migration of a specific and identifiable compound (Czerniawski and Pogorzelska, 1997; Crosby, 1981; Katan, 1996). In the global migration test, no attempt is made to identify the nature of the substances and consequently the result has no significance with respect to the possible hazardous contamination of the foodstuff (Tice and Cooper, 1996).

The purpose of migration testing is to ensure food safety and to protect the consumer by controlling the level of undesirable constituents from the package entering the foodstuff. It is known that many factors play a part in the migration process of compounds into packaged foods. The most obvious parameter is the nature of the foodstuff itself, namely, its fat or alcohol content, water activity, acidity, etc. The time and temperature of exposure is also important. Other factors depend on the kind and structure of the polymer (e.g. molecular weight and its distribution), degree of crystallinity, orientation and the geometry of the package such as thickness and surface-to-volume ratio (Ashby, 1988; Sutless and Marshal, 1993).

2.6.2.1 Food simulants

It is technically difficult to measure the direct migration of a given substance into food because most foodstuffs comprise of a complex mixture of substances such as water, carbohydrates, fats, lipids, proteins, vitamins, fibers and minerals (Crosby, 1981). For this reason, the assessment of migration is usually performed using a food simulant, which has extraction ability comparable to that of the foodstuff. The packaging material is assumed to be homogenous and the environmental conditions are assumed to be constant (Ashby *et al.*, 1992). In many cases, assay conditions with higher temperature are used to accelerate migration to reduce the test time (Gnanasekharan and Floros, 1997).

In various current European food-packaging regulations, food simulants to be used for migration testing have been specified (European Standard EN 1186-1, 1999). Water (simulant A), 3% (v/v) acetic acid in water (simulant B), 15% (v/v) ethanol in water (simulant C), as well as olive oil, sunflower oil or a synthetic fat simulant HB 307 (simulant D) are generally accepted as food simulants, with each one representing a particular type of foodstuff. In addition, various food packaging regulations define standard test times and temperatures that simulate the storage conditions and temperature treatment to which packaged foods are exposed in practice (European Standard EN 1186-1, 1999; US FDA, 1995).

Oil is probably a good substitute for fatty foodstuffs. However, measurements to determine the overall and specific migration into oil are usually difficult to carry out and require skilled analytical work (De Kruijf and Rijk, 1988; Hamdani and Feigenbaum, 1996). Oil is a non-volatile compound. For overall migration, the weight lost by polymeric materials must be corrected for the amount of fat absorbed by the polymer (European Standard EN 1186-2, 1999; EN 1186-10, 1999). This method requires tedious procedures and, in many cases, exact quantification is only possible using a radiotracer technique (De Kruijf and Rijk, 1988; Philo, 1994). In the case of specific migration experiments, triglycerides often mask migrants in chromatographic determinations. Replacement of fat by a solvent, which can be distilled or evaporated, would greatly simplify the analytical work (Baner *et al.*, 1992). Therefore, in migration studies performed nowadays, attempts have been made to use simple volatile media ranging from the non-polar, n-heptane or iso-octane, to polar compounds like iso-propanol or ethanol, and are commonly called "alternative fatty food simulants" (Baner *et al.*, 1996). These solvents exhibit similar interactions with the polymer to those of fat-containing foods but are easily evaporated. Thus, the global and specific migration can be obtained directly and in a very concentrated form. In some studies, the use of iso-octane and 95% (v/v) or aqueous ethanol as volatile fatty simulants are preferred (European Standard EN 1186-1, 1999;

European Prestandard ENV 1186-15, 1999, Baner *et al.*, 1996; De Kruijf *et al.*, 1983a, 1993b; Hamdani and Feigenbaum, 1996).

2.6.2.2 Potential migration release from PET used at high temperatures

Rapid changes have been taking place in food processing technology and consumer practices. These include the widespread use of microwave ovens in addition to conventional ones for cooking and reheating of food prepackaged in plastics. The high temperatures that are used during cooking and reheating, strongly affects the total quantity of undesirable substances migrating from the packaging material into the food (Katan, 1996).

A considerable extent of migration of such compounds, mostly low molecular weight compounds, from some plastic packages has been found to occur during microwave cooking (Castle *et al.*, 1988). The levels were even higher than those found in a conventional oven (Castle *et al.*, 1990). Castle *et al.* (1989) reported that for certain types of food (such as French fries), the total level of migration of oligomer from PET tray materials was 10 times higher when the packages were heated in a microwave oven instead of a conventional oven. In addition, they observed the total amount of migrated compounds depends on the temperature attained during the cooking, time of exposure, fat content of the food and nature of the food surface (Castle *et al.*, 1990).

For some plastic materials, elevated temperatures may also affect the kind of migrating substances as a result of thermal decomposition (Castle, 1994; Nerin *et* *al.*, 1998; Incarnato *et al.,* 1998; Jetten *et al.*, 1999). Some decomposition compounds may have a notable toxic character (Svensson *et al.*, 1993). Cyclic trimer and oligomers are the most common compounds observed to migrate into food or food simulants from PET packages that are intended for use in a conventional or microwave oven (Lau and Wong, 1996; Begley and Hollifield, 1990a, 1990b; Castle *et al.,* 1989, 1990).

Migration of plasticizers from polyvinylidene chloride/polyvinyl chloride (PVDC/PVC) films, to determine the effect of microwave cooking, has also been investigated (Castle *et al.*, 1989; Begley and Hollifield, 1990c; Begley *et al.,* 1991). The result showed that 51% of acetyltributyl citrate (ATBC) and 58% of di-(2-ethyl-hexyl)-adipate (DEHA) was lost from a PVDC/PVC film during microwave cooking. Schwartz (1994) reported that the migration of antioxidants from high-density polyethylene (HDPE) and polypropylene (PP) films into corn oil and 95% aqueous ethanol, was diffusion controlled, while migration of these compound into water and 8% aqueous ethanol was controlled by the external phase at temperatures ranging from 77 to 135°C.

Volatiles, including numerous aldehydes (acetaldehyde, formaldehyde), ketones, alcohol and carboxylic acid, were also found to be released from susceptors during microwave oven cooking/heating (Hollifield and Begley, 1991). It was reported that the amount of volatiles released ranged from 35 to 105 ppm, and that it increased with the increase in the amount of paper in the susceptor construction (Hollifield and Begley, 1991).

Galotto and Guarda (1999) evaluated the overall migration of non-volatile compounds from polyamide (PA), polyethylene (PE), bi-axially oriented polypropylene (BOPP), polyvinyl chloride (PVC) and polypropylene (PP) into aqueous food simulants during microwave cooking. They found high levels of total migration from PVC film into all tested food simulants after heating in a microwave oven. These values were significantly higher than those obtained in conventional migration tests (40°C for 10 days). A thermal treatment of these polymer samples at 80 and 121°C for 30 min increased the total migration levels by a factor of 1.5 and 2 respectively compared to the values obtained in conventional migration methods.

2.6.2.3 Test conditions

The European legislation has established a positive list of monomers, additives and substances that can be used in contact with food. It also outlines the conditions at which the migration tests should be carried out. However, very little information was found in the currently available literature about the methods of materials testing for high-temperature applications.

The Council Directive 82/711/EEC provides the testing conditions (time and temperature) for different situations depending on the intended temperature of use and time of the contact with the food as shown in Table 2.4.

Table 2. 4. Test condition for migration at high temperatures

	Actual use	Test condition
Contact time/h	$t \leq 0.5$	0.5
	$0.5 < t \leq 1$	1
	$1 < t \leq 2$	2
	$2 < t \leq 24$	24
	$t < 24$	240
Temperature/°C		
	$20 < T \leq 40$	40
	$40 < T \leq 70$	70
	$70 < T \leq 100$	100 or reflux
	$70 < T \leq 121$	121
	$121 < T \leq 130$	130
	$130 < T \leq 150$	150
	$T > 150$	175

Source: Council Directive 82/711/EEC (1982); European Standard EN 1186-1 (1999)

De Kruijf and Rijk (1994) investigated the suitability of iso-octane as a volatile fatty food simulant for determination of overall migration under high temperature test conditions. According to the authors, a good correlation was obtained for most investigated samples when applying times and temperatures listed in Table 2.5. For example, the migration result of a 2 hr exposure at 175°C in olive oil is comparable to a 2.5 hr exposure at 60°C in iso-octane. However, there is no real and precise relationship between the two test media.

Table 2. 5. Test conditions selected for the determination of the overall migration into olive oil and iso-octane

Test condition in olive oil		Test condition in isooctane	
Time/h	Temperature/°C	Time/h	Temperature/°C
1	100	0.5	60
0.5	100	0.5	60
0.5	120	1	60
2	150	2	60
2	175	2.5	60

2.7 Sorption and Migration

It is known that PET has good barrier properties and limits the passage of liquids, gases and vapors. However, the polymer contains interstitial spaces (voids) between its segments through which small molecules can diffuse. The process is known as sorption (into the polymer) and or desorption (out of the polymer) (MacElroy, 1996).

Liquid transfer through a polymer occurs by a dissolution-diffusion and a desorption mechanism. The penetrant dissolves in the polymer at the upstream surface, diffuses through the polymer matrix and desorbs from the opposite surface (Mogri and Paul, 2001). Historically most of the "microscopic" diffusion models were formulated for an amorphous polymer structure and are based on concepts derived from diffusion in simple liquids (Vrentas and Duda, 1994).

From the microscopic point of view, sorption into a polymer may be described as a sequence of two processes (Ten Hulscher and Cornelissen, 1996): (i) the creation of a hole in the polymer matrix and (ii) the accommodation of a solute molecule in that hole.

Swelling of most polymers upon solute penetration indicates that holes were created during the process of diffusion (Hayashi *et al.*, 1994; Sun *et al.*, 1997; Aminabhavi *et al.*, 1999). Hole creation is an endothermic process due to the dissociation of weak interactions between the polymer segments (Van der Waals forces and/or hydrogen-bridge bonds), whereas hole occupation is an exothermic process because of the hydrophobic Van der Waals interaction and/or hydrogen-bridge formation between solute and polymer segments (Ten Hulscher and Cornelissen, 1996).

2.7.1 Factors affecting sorption and migration

An understanding of sorption and migration of organic compounds in polymeric materials requires knowledge of the chemical and physical structure of both the compound and the polymer. The factors affecting the transport of such molecules in and/or out the polymer are discussed below.

2.7.1.1 Polymer structure and properties

The properties of the polymeric material such as the glass transition temperature (T_g), crystallinity and total and/or distribution of free volume are the most important parameters controlling the sorption and migration processes (Aminabhavi and Shivaputrappa, 1991; Mercea, 1999). The free volume in polymers is the molecular "void" volume that is trapped in the solid material. Generally, a polymer with poor symetrical structure, or bulky side chains, will have a high free volume and a high permeability to gases and vapors (Salame, 1989). The diffusion coefficient of many compounds in the polymer can be predicted from the free volume present in the polymer (Boersma *et al.*, 2003; Lützow *et al.*, 1999).

Two different regimes to the diffusion mechanism have been established, notably, diffusion above and below the glass transition temperature, T_g, of the polymer (Mercea, 1999). At temperatures of $T > T_g$, where the polymer exhibits "rubbery" behaviour, the diffusion of penetrants is generally Fickian. In contrast, in the "glassy" state of the polymer, where $T < T_g$, the diffusion of penetrants is much more complex and can be classified into three categories (Vergnaud, 1991; Shieh and Peppas, 1991; Lucht and Peppas, 1987; Aminabhavi *et al.*, 1996a; Liu *et al.*, 1999; Mercea, 1999): (i) Case I (or Fickian) diffusion; where the rate of diffusion is much lower than that of the segmental relaxation rate of the polymer; (ii) Case II and Super Case II (or non-Fickian) diffusion, where the rate of diffusion is much higher than that of the relaxation rate and (iii) anomalous diffusion, where the rate of diffusion and relaxation processes are comparable.

The importance of crystallinity in sorption and migration has been recognized for many years. Most polymers are at least partly amorphous. In the amorphous regions, the polymer chains show little order whereas in the crystalline parts, the polymer chains are more aligned (Van Krevelen, 1990). The crystalline areas are denser than the amorphous parts. The diffusion process occurs mainly in the amorphous region of the polymer where small vibrational movements occur in the polymer chains (Crank and Park, 1978; Duda and Zielinski, 1996). Therefore, the higher the degree of crystallinity of the polymer, the lower its diffusion coefficient and sorption capacity (Chalykh *et al.*, 1979; Billovits and Durning, 1988; Neway *et al.*, 2004, D'Aniello *et al.*, 2000).

2.7.1.2 Liquid/solvent properties

Mohney *et al.* (1988) reported that low concentration of penetrants (solvents) will affect the polymer to a very limited extent and the absorbed compound will be directly proportional to the concentration of the solvent. At higher concentration however, the sorption of such compounds into the polymer may alter the polymer matrix structure due to swelling (Woodward *et al.*, 1960, Shieh and Peppas, 1991; Aminabhavi and Naik, 1999).

The polarities of the solvent and polymer are other important factors in the absorption process. The absorption behavior of different classes of compounds depends, to a great extent, on their polarity (Nir *et al.*, 1996; Van Lune *et al.*, 1997). Different polymers have different polarities; hence their affinities towards different liquids may differ (Billovits and Durning, 1988).

The size of penetrant is another factor. Small molecules are absorbed more rapidly and in higher quantities than large molecules (Aminabhavi and Munnolli, 1994; Aminabhavi *et al.*, 1996b; Khinnavar *et al.*, 1991; Demertzis *et al.* 1997). If the permeating chemicals differ significantly in their solubility (but similar size) in a given polymer, then the more soluble chemical will cause the polymer to swell more, thus increasing its transmissibility (Demertzis *et al.* 1997).

On the other hand, very large molecules plasticize the polymer, causing increased absorption into newly-formed holes. Shimoda *et al.* (1987) reported that the sorption of aldehydes, alcohol, and methyl esters increased with increasing molecular weight up to about 10 carbon atoms. Linssen *et al.* (1991) reported that compounds with eight or more carbon atoms were absorbed from yogurt by HDPE, while shorter molecules remained in the product. They also observed that highly branched molecules were absorbed to a greater extent than linear ones.

2.7.1.3 External conditions

Temperature is probably the most important environmental variable affecting transport processes. The permeability of gases and liquids in polymers increases with an increase in temperature according to the Arrhenius relationship. Possible reasons for the increased transport are (Ten Hulscher and Cornelissen, 1996; Neogi, 1996; Rogers, 1985): (i) increased mobility and solubility of the gas or liquid and (ii) changes in the polymer configuration, such as swelling or decrease in degree of crystallinity.

For some polymers, exposure to moisture has a strong effect on their barrier properties. The presence of water vapor often accelerates the diffusion of gases and vapors in those polymers (Galić and Ciković, 2001). Water molecules diffuse into the polymer and act like a plasticizer. Generally, the plasticizing effect of water in hydrophilic polymers, such as ethylene vinyl alcohol (EVOH) and most polyamides, would increase the permeability by increasing the diffusivity as a result of the higher mobility acquired by the polymer network (Yoon *et al.*, 2000).

2.7.2 Theoretical aspects

2.7.2.1 Rate constant and activation energy

Sorption of a solvent in a polymer is controlled by the rate of polymer expansion and follows a first-order kinetic equation (Coe, 1971; Smith, 1993; Ritchie, 1996; Aminabhavi and Shivaputrappa, 1991):

$$-\partial C/\partial t = k(C_\infty - C_t) \qquad (2.\ 6)$$

where C is the concentration of the solvent; k is a first-order rate constant; C_∞ and C_t represent the concentration at time of equilibrium, t_∞ and time t respectively.

Integration of equation (2.6) with the boundary condition $C_t = 0$ at $t = 0$ results in:

$$kt = \ln\,[C_\infty/(C_\infty - C_t)] \qquad (2.\ 7)$$

Thus the rate constant, k, is estimated from the slope of a plot of $\ln\,(C_\infty - C_t)$ versus time, t.

The concentration of solvent sorbed in the polymer at time t, C_t, is calculated from equation (2.8):

$$C_t = (M_{p,t} - M_{p,0})/(M_w \times M_{p,0}) \qquad (2.\ 8)$$

where $M_{p,t}$ is polymer mass at time t; $M_{p,0}$ is the initial mass of the polymer at time t = 0 and M_w is the molecular weight of the solvent under investigation.

The rate constant is strongly temperature dependant. In most cases, the relationship between the logarithm of the rate constant and the reciprocal of the absolute temperature over a certain range of temperatures is linear and is quantitatively described by the Arrhenius equation (Smith, 1993; Coe, 1971):

$$k = A \times e^{-Ea/RT} \qquad (2.\ 9)$$

where A is the frequency factor; E_a is the activation energy; R is the ideal gas constant and T is the absolute temperature. Thus, the activation energy, E_a, and the frequency factor, A, can be estimated from the slope and intercept of a plot of ln k versus 1/T respectively (equation 2.10).

$$\ln k = -E_a/RT + \ln A \qquad (2.\ 10)$$

*2.7.2.2 **Sorption constant, enthalpy of sorption and entropy***

Another quantity of interest in the study of liquid sorption by polymers is the sorption constant, K_S. This can be calculated by considering the equilibrium process occurring in the liquid phase at constant temperature and pressure (Smith, 1993).

Consider the sorption of liquid, Li, in a polymer, Po, to produce the dissolved liquid, LiPo. This process can be represented by equation (2.11):

$$\mathrm{Li} + \mathrm{Po} = \mathrm{LiPo} \qquad (2.\ 11)$$

The thermodynamic equilibrium constant, K_s for this process is given in equation (2.12):

$$K_s = a_{LiPo}/(a_{Li}a_{Po}) \qquad (2.\ 12)$$

where a_{Li}, a_{Po}, and a_{LiPo} are the activities of the liquid, the solid polymer and the sorbed liquid in the solid polymer film respectively. As the liquid and polymer are in a pure state, a_{Li} and a_{Po} are equal to unity and equation (2.12) can be reduced to:

$$K_s(a_{Li}a_{Po}) = K_s = a_{LiPo} \qquad (2.\ 13)$$

If there is no chemical reaction that takes place between the polymer and the liquid, and if there is negligible migration from the polymer to the liquid, K_s can be obtained from the mass uptake of the polymer and it is possible to calculate the equilibrium sorption constant for the polymer-solvent system from equation (2.14):

$$K_s = a_{LiPo} = \text{mol of solvent sorbed/mass of polymer} \qquad (2.\ 14)$$

The variation of K_s with temperature provides information about the thermodynamic quantities of equilibrium partitioning, namely the Gibbs free energy (ΔG), enthalpy of sorption (ΔH_s) and entropy (ΔS). These quantities are related through equation (2.15):

$$\Delta G = \Delta H_s - T\Delta S \tag{2. 15}$$

where ΔG is the change in Gibbs free energy; ΔH_s is the change in enthalpy of sorption and ΔS is the change in entropy.

At equilibrium, K_s is related to the free energy change by:

$$\Delta G = -RT\ln(K_s) \tag{2. 16}$$

and thus the enthalpy and entropy changes can be obtained from the variation of K_s with temperature in accordance with the Van't Hoff isochore relationship (combination of equation (2.15) and (2.16))(Smith, 1993):

$$\ln K_s = -\Delta H_s/RT + \Delta S/R \tag{2. 17}$$

2.7.2.3 Mechanism of transport

The mechanism of solvent transport in a sheet of polymer is described by equation (2.18) (Vergnaud, 1991):

$$M_t/M_\infty = 4(Dt/\pi L^2)^n \tag{2. 18}$$

where M_∞ and M_t represent the amount of compound diffused at the time taken to reach equilibrium t_∞ and time t respectively; D is diffusion coefficient and L is thickness of the polymer sheet.

When D and L are constant, equation (2.18) reduces to:

$$M_t/M_\infty = K_1 t^n \qquad (2.\ 19)$$

where K_1 is a constant that depends on the structure of the polymer and on the solvent-polymer interaction. The exponent, n, indicates the type of diffusion or the mechanism of liquid transport in the polymer. A value of $n < ½$ indicates Pseudo-Fickian transport, $n = ½$ implies Fickian transport or Case I, $½ < n < 1$ implies anomalous transport, $n = 1$ implies non-Fickian transport or Case II and for values of $n > 1$ Super Case II transport is observed (Vergnaud, 1991; Shieh and Peppas, 1991; Lucht and Peppas, 1987; Aminabhavi *et al.*, 1996a; 1996b; 1996c; Liu *et al.*, 1999; Mercea, 1999; Neogi, 1996). It is usually assumed that equation (2.19) is valid only for short times, where $M_t/M_\infty < 0.6$ (Vergnaud, 1991).

2.7.2.4 Fick's second law

According to Fick's law of diffusion, mass transport occurs in the direction of the concentration gradient thereby generating a history of concentration profiles inside the polymer (Bird *et al.,* 1975; Brodkey and Hershey, 1988). In order to calculate diffusion coefficients, Fick's equation was solved under suitable initial and boundary conditions using the following assumptions (Vergnaud, 1991; Aminabhavi *et al.*, 1997; Liu *et al.*, 1999):

(i) Transport occurs under transient conditions with a constant diffusion coefficient;

(ii) The solvent transport in the polymer is considered unidirectional;

(iii) The concentration on the polymer surface reaches equilibrium immediately upon exposure of the polymer to the liquid;

(iv) The dimensional changes of the polymer are negligibly small during transport process;

(v) The time required for the polymer to reach thermal equilibrium is negligible compared to the time of transport;

(vi) The plane sheet of material is so thin that all diffusing solvent enters or leaves through the parallel faces with a negligible amount diffusing through the edges.

For a constant diffusion coefficient, the one-dimensional diffusion process in a planar-sheet is generally expressed by Fick's second law (Bird *et al.*, 1975; Brodkey and Hershey, 1988):

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right) = D\frac{\partial^2 C}{\partial x^2} \tag{2. 20}$$

where C is the concentration of liquid within the polymer at time t and x is the distance in the x-direction. Under the boundary conditions for $t = 0$, $0 < x < L$, $C = C_i$, and for $t > 0$, $x = 0$, $x = L$, $C = C_s$, non-dimensional variables of distance, time and concentration, can be defined as $\chi = x/L$, $\tau = Dt/L^2$ and $\xi = C/C_s$, where L is the thickness of the polymer, C_i is initial concentration that is kept constant along the thickness of the polymer at $t = 0$, C_s is the concentration at the surface of the polymer sheet and remains constant during the whole process. Thus equation (2.20) can be written in a dimensionless form as follows:

$$\partial\xi/\partial\tau = \partial^2\xi/\partial\chi^2 \tag{2. 21}$$

with the dimensionless boundary condition being: $\tau = 0$, $0 < \chi < 1$, $\xi = \xi_i$ and $\tau > 0$, $\chi = 0$, $\chi = 1$, $\xi = 1$ respectively.

2.7.2.5 Computation of concentration profiles using a numerical method

The concentration profile can be calculated numerically (Crank, 1975) by taking the non-dimensional equation (2.21) and dividing the thickness χ into equal intervals $\Delta\chi$ and the time τ into equal intervals $\Delta\tau$. Let the coordinates of a representative grid point (χ, τ) be $(i\Delta\chi, j\Delta\tau)$, where i and j are integers. The value C at the point $(i\Delta\chi, j\Delta\tau)$ is denoted by $\xi_{i,j}$. By using a Taylor's series in the τ direction but keeping χ constant and neglecting the error term, one can write:

$$(\partial\xi/\partial\tau)_{i,j} = (\xi_{i,j+1} - \xi_{i,j})/\Delta\tau \tag{2. 22}$$

Similarly, by applying Taylor's series in the χ direction and keeping τ constant:

$$(\partial^2\xi/\partial\chi^2)_{i,j} = (\xi_{i+1,j} - 2\xi_{i,j} + \xi_{i-1,j})/\Delta\chi^2 \tag{2. 23}$$

Substituting equations (2.22) and (2.23) into equation (2.21) gives:

$$\xi_{i,j+1} = \xi_{i,j} + (\xi_{i+1,j} - 2\xi_{i,j} + \xi_{i-1,j})/(\Delta\tau/\Delta\chi^2) \tag{2. 24}$$

for $i = 0, 1, 2, \ldots., n$; $j = 0, 1, 2, 3, \ldots, m$

Equation (2.24) was solved using a numerical method with a pre-defined distribution concentration that is assumed to follow a parabolic equation at $\tau = 0$,

$$\xi_{i,0} = a\chi^2_{i,0} + b\chi_{i,0} + c \qquad (2.25)$$

where $\chi = 0$, $\xi_i = 1$; $\chi = L$, $\xi_i = 1$ and $\chi = 0.5$, $\xi_i = 0$, and a, b, c are constants. The substitution of these values into equation (2.25) enables the constants a = 4, b = -4 and c = 1 to be obtained and so equation (2.25) can be replaced by:

$$\xi_{i,0} = 4\chi_{i,0}^2 - 4\chi_{i,0} + 1 \qquad (2.26)$$

or

$$\xi_{i,0} = 4(\chi_{i,0} - 0.25)^2 \qquad (2.27)$$

Thus the concentration profile of the solvent along the thickness of the polymer at $\tau = \tau + \Delta\tau$ is generated from equation (2.24). Such iterations can be continued until the numerical approximation to equilibrium or steady state is achieved.

2.7.2.6 Determination of the diffusion coefficient

In migration studies into food or food simulants, assuming that the food is infinite in volume and the packaging material is finite in its dimensions, the total amount of the diffusing compound, M_t, that has entered or left a planar sample at time t relative to the amount transferred after an infinite time, M_∞, can be calculated using equation (2.28) proposed by Vergnaud (1991) and Miltz *et al.* (1997):

$$\frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2 Dt}{L^2}\right] \qquad (2.\ 28)$$

The value of M_t, the total amount of diffusing substance transported at time t, can be calculated from equation (2.29):

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{L^2}\right)^{1/2}\left(\frac{1}{\pi^{1/2}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\left(\frac{nL}{2(Dt)^{1/2}}\right)\right) \qquad (2.\ 29)$$

For short time intervals, when $M_t/M_\infty < 0.6$, equation (2.29) is reduced to the relation (Miltz *et al.*, 1997):

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi L^2}\right)^{1/2} \qquad (2.\ 30)$$

Equation 2.30 is not applicable when n = 0.5.

For long time intervals, when $M_t/M_\infty > 0.6$, equation (2.28) is reduced to include the first term only namely, n = 0 (Miltz *et al.*, 1997):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left[\frac{-\pi^2 Dt}{L^2}\right] \qquad (2.\ 31)$$

Thus, the diffusion coefficient, D, can be calculated from the slope of a plot of M_t/M_∞ versus $(t/L^2)^{1/2}$ for short times and from the slope of a plot of

ln $(1 - M_t/M_\infty)$ versus t/L^2 for long times.

In the case of Fickian diffusion, it is possible to determine D from a time $t_{1/2}$, defined as the time at which half of the final amount at equilibrium has migrated. If the value of $M_t/M_\infty = 0.5$ is substituted into equation (2.30), the following equation is obtained which enables to calculate the value of D:

$$D = 0.04909L^2/t_{1/2} \tag{2. 32}$$

2.7.2.7 Partition coefficient

The partition coefficient is also a fundamental parameter describing the transport process of migrants from a polymer into a liquid. The liquid is normally a food simulant. The migrant molecules diffuse through the amorphous portion in the polymer matrix toward the polymer/liquid interface (Chang *et al.*, 1988) where they are partitioned between the two media until their chemical potential in the polymer and fluid phases reach equilibrium (Baner, 2000). The partition coefficient is defined as the ratio between the concentration of the migrating compound in the polymer and that in the liquid or food simulant (Hamdani *et al.*, 1997):

$$K_{pf} = C_{p,\infty}/C_{f,\infty} \tag{2. 33}$$

where K_{pf} is the partition coefficient between polymer and food simulant, $C_{p,\infty}$ is the concentration of migrant in polymer at equilibrium and $C_{f,\infty}$ is the concentration of migrant in the food simulant at equilibrium.

Ideally, the ratio is constant. Under these conditions, the migrant is only moderately soluble in the polymer, thus any structural change in the polymer such as swelling can be ignored. In this case, the transport follows Henry's law (Piringer, 1999). However, in some cases, swelling affects the transport and then the process follows either a Langmuir or dual-mode sorption (Robertson, 1993). Furthermore, the value of the partition coefficient depends on the polarities of the migrant and the polymer.

There are two extreme types of behavior for K_{pf}, in practice: (i) the transport process advances until extraction of the migrant from the plastic phase is almost complete ($K_{pf} \cong 0$) (Goydan *et al.*, 1990) and (ii) the amount of mass migrated is negligible because the migrant prefers very much the polymer over the contacting phase ($K_{pf} >> 1$) (Chang *et al.*, 1988).

CHAPTER 3 – MATERIALS AND METHODS

3.1 Materials

3.1.1 Polymer

The polymers samples used in this part of the work were post-consumer PET bottles, virgin PET sheet, virgin PET bottles and post consumer recycled PET sheet. The following respective abbreviations are used throughout this thesis: PC-PETb, PETvs, PETvb and PCR-PETs. The virgin PET sheet was supplied from a local manufacturer of plastic thermoformed products. Virgin PET bottles and post-consumer recycled PET sheet were obtained from a local PET processing and recycling company. Post-consumer recycled PET was processed by secondary recycling. Post-consumer collected bottles were sorted, cleaned, grinded and then melted and reformed into a sheet form. Post-consumer PET bottles used in the current work were obtained from a post-consumer kerb-side collection. The history of the bottles is not known.

Bottles made from virgin PET resin used in the present studies were of four different capacities, 390, 600, 1250 and 2000 mL (Figure 3.1). PET bottles collected from kerb-side were of 2000 mL capacity only.

Sheets of four different crystallinities made from virgin and recycled PET were produced by thermal annealing at a certain temperature for predetermined times. The detailed method is given in Section 3.2.2.

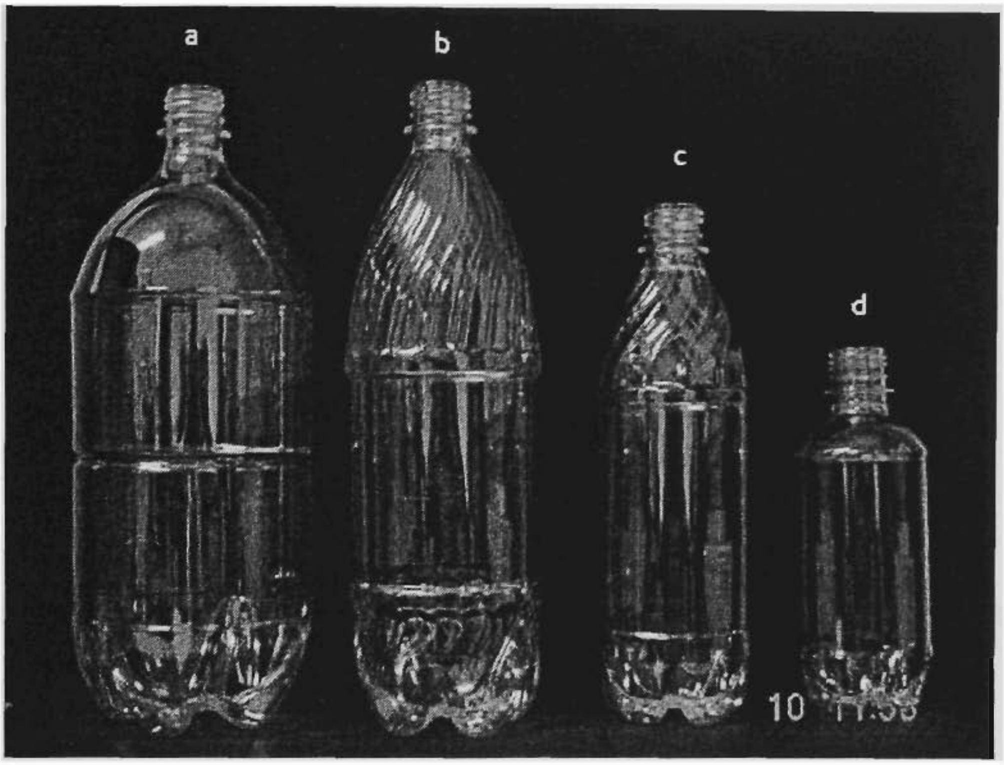


Figure 3. 1. Virgin PET bottles: (a) 2000 mL, (b) 1250 mL, (c) 600 mL and (d) 390 mL

3.1.2 Chemicals

Ethanol (AR grade, 99.8% purity), acetic acid (AR grade, 99.8% purity) and isooctane (2,2,4-trimetylpentane, AR grade, 99% purity) were purchased from Sigma Aldrich Chemical (Melbourne, Australia). Water was purified by a Milli-Q water purification system (Millipore Corp., Bedford, USA).

3.2 Methods

3.2.1 Physical properties of the studied PET

3.2.1.1 Thickness measurement

In order to determine the average thickness of each of the respective samples, four pieces of 10 × 10 cm were cut from each type of PET. The thickness was measured on five locations, the four corners and the centre of each sample, using a hand-held micrometer with a resolution of ± 0.005 mm (Miyoto Corp., Kanagawa, Japan). The quoted sample thickness represents an average of the 5 × 5 measurements.

3.2.1.2 Solution viscosity

The intrinsic viscosities of the PET samples were measured according to ASTM D 1601 - 86 method with some modification. In these experiments, a solvent of 60% (w/w) phenol and 40% (w/w) tetrachloroethane was used. The PET sample (0.1 g) was dissolved in 25 mL of the solvent, placed in 105°C oil bath with constant stirring for 30 min. The test solution then was equilibrated at 30°C and the intrinsic viscosity was measured using an Ubbelohde viscometer.

3.2.1.3 Tensile testing

Tensile tests, according to standard methods ASTM D 638 - 93, were conducted at room temperature to determine the Young's modulus (MPa), elongation at break (%) and tensile stress at break (MPa) of the virgin and recycled PET samples. A tensometer (model W 737, Tensometer Limited, England) and an Instron Extensometer (2620-602, Instron Limited, High Wycombe, England) at a constant cross-head speed of 5 cm min^{-1} were used in this experiment. The samples were cut from the sheet into ASTM dumbbell-shape using a Wallace cutting press and conditioned at 25°C and 50 ± 5% relative humidity for 48 h before testing. The gauge length of the tested samples was 140 mm and narrow width was 10 mm. The force-deformation data were transferred directly to a personal computer and were converted to stress-strain curves. Ten samples were used in each experiment.

3.2.2 Iso-thermal crystallization of PET sheets

PET samples of different crystallinities were obtained by heating the polymer sheets for a predetermined period. Sheets (10 × 10 cm) of recycled or virgin PET were dried in a vacuum oven at 80 ± 1°C and 700 mBar for 16 h prior to the crystallization in order to evaporate any moisture trapped in the sheets. To avoid warping during thermal treatment the sheet samples were then placed between stainless steel plates (300 × 18 × 0.175 cm) preheated to 120°C. The oven was thermostatically controlled at 120 ± 1°C. Samples were held at a temperature of 120°C for 3, 6 or 10 min. All samples were then quenched immediately in iced water to arrest further crystallization.

3.2.2.1 Ultraviolet visible spectrophotometer

The opacity of the PET samples after the various heat treatments was determined by measuring the visible light transmitted through the polymer samples (ASTM D 1746 - 92). A Novaspec 4049 (Biochrom Ltd., UK) UV-visible spectrophotometer set at a wavelength of 550 nm was used in these experiments. A specimen of 30 × 13 mm was cut from each sample, placed in the spectrophotometer and readings of the percent transmittance were taken. The spectrophotometer was calibrated to 100% transmittance for the blank (without a sample). This experiment was performed five times for each of the samples.

3.2.2.2 Differential scanning calorimetry (DSC)

Samples were taken from a sheet of PETvs and PCR-PETs and from the middle section of the wall of PETvb. A Perkin-Elmer differential scanning calorimeter, model DSC 7, interfaced to a personal computer was used to measure the degree of crystallinity of the PET samples. Three small pieces of the PET sample, weighing 11 to 15 mg were cut from each of the materials. The samples were weighed and placed in aluminum pans with covers. The samples were then sealed and placed in the DSC. An empty aluminum pan was used as the reference. The calorimeter was operated with a stream of dry nitrogen (flow rate of 15 mL min^{-1}) over the sample and the reference. The samples were heated at a rate of 10°C min^{-1} up to 300°C and held for 15 min at that temperature.

The temperature of the instrument was calibrated prior to each crystallinity measurement from the observed melting points of high purity indium (99.99%) and lead. Initially, the empty pans were scanned to determine the calorimeter baseline and this was repeated with a sapphire standard sample for the calibration of the thermal response of the calorimeter.

Results were recorded and analyzed with the Perkin-Elmer Analysis software. A plot was constructed of heat flow (mW) versus temperature (°C). The heat of fusion was calculated from the area under the melting peak. The area was taken from the limits of 208°C to 260°C. The percent crystallinity was determined by comparing the endotherm peak of heat absorbed during the melting of a 100% crystalline PET using the value of 120 J g^{-1} (Robert, 1969; Vilanova *et al.*, 1985; Jayakannan and Ramakrishnan, 1999). Equation (2.1) was used for calculation of the degree of crystallinity.

3.2.3 Sorption of acetaldehyde into PET

Sorption experiments were performed on virgin and recycled PET sheet samples with different degrees of crystallinity obtained by the crystallization process described above (Section 3.2.2). The samples (30 × 30 mm), were weighed to obtain their initial mass. Each sample was then placed in a screw-tight test bottle containing approximately 50 mL of acetaldehyde that covered the whole sample and was maintained at the desired constant temperature. Three different temperatures, 5, 15 and 20°C (controlled within ± 1°C), were used during the experimental work.

At specified times, the samples were removed from the test bottles and wiped with adsorbent paper. They were then weighed on a digital balance (Sartorious, Australian Instrument Services (AIS) Pty. Ltd.) to within ± 0.1 mg and immediately returned to their test bottles for the next period of soaking. The weighing of the samples was performed at 5, 15, 30, 60, 120, 240, 360, 480 min and 1, 2 days after immersion. The experiments were continued until equilibrium was attained, namely no further mass gain was observed during a period of one to two days.

3.2.4 Concentration profile calculation by a numerical method

A software package, MATLAB® Version 6.5.1, was used to compute the concentration profile of acetaldehyde in the polymer samples (equation 2.24, page 70) during the sorption process. The flow diagram of the computer program is shown in Figure 3.2.

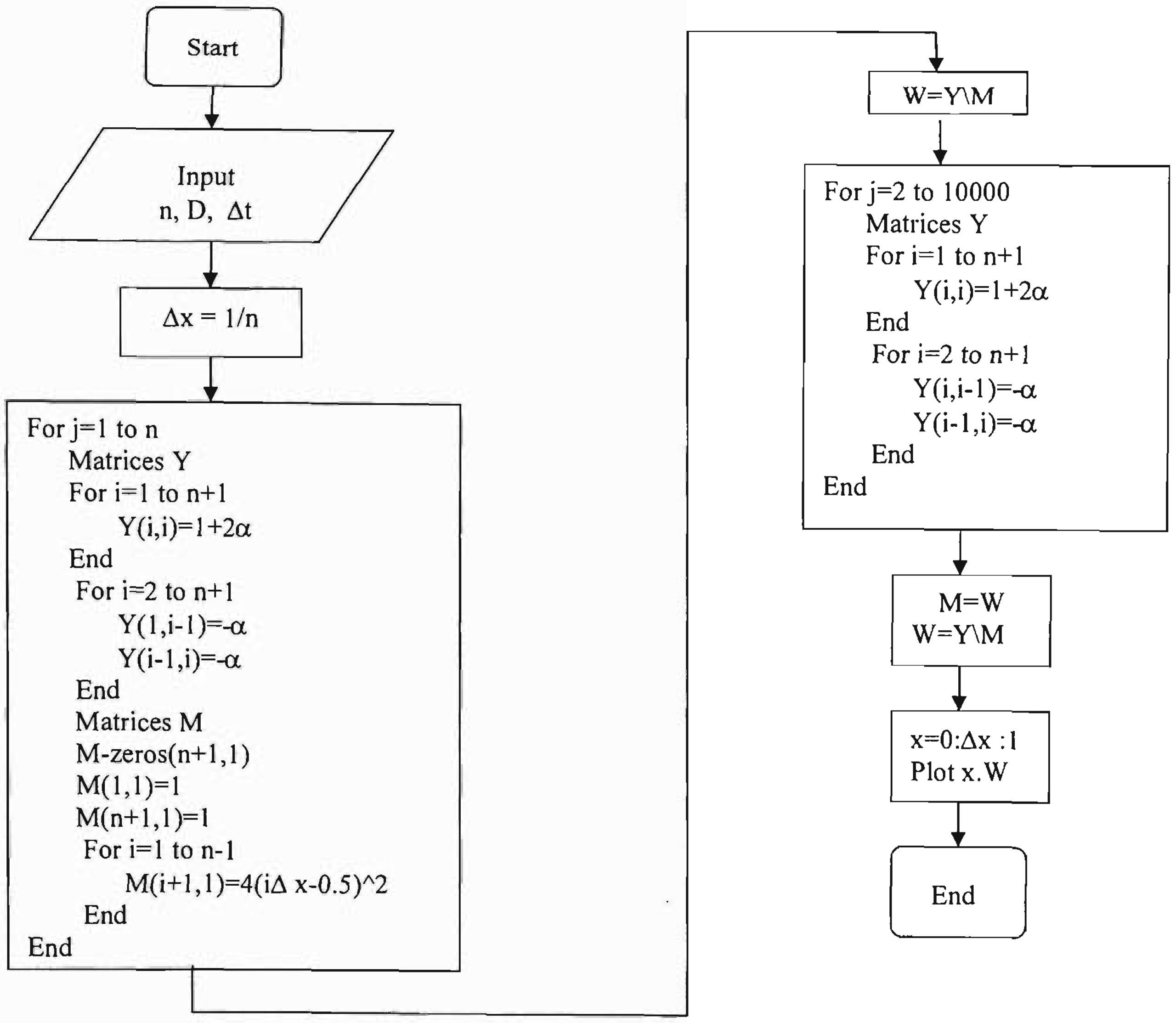


Figure 3. 2. Flow diagram of the computer program for calculation of the acetaldehyde profile in PET sheet.

3.2.5 Overall migration

3.2.5.1 Label removal

The labels of the collected post-consumer bottles were removed and the bottles were washed in warm water and then gently brushed using a soft brush to remove any further contaminants from the surface. Finally, the bottles were dried at room temperature before the migration studies.

3.2.5.2 Migration studies

Samples of virgin and recycled material were taken from PET sheet. Samples of post-consumer and virgin PET bottles were taken from the body sections of the respective bottles (see Figure 3.3). The samples were cut into pieces of 10 × 10 ± 0.05 cm using guillotine paper trimmers (Dahle, Germany) and gently wiped using a lint-free-cloth before weighing. The mass of the individual samples was in the range of 3.6865 – 5.5210 ± 0.0001 g.

Each test specimen was cut into strips approximately 2.5 × 5 cm. The overall migration experiments were performed using the following two kinds of testing methods: (i) the conventional total-immersion method (European Standard EN 1186-3, 1998; European Pre-Standard ENV1186-15, 1999); and (ii) a reflux method.

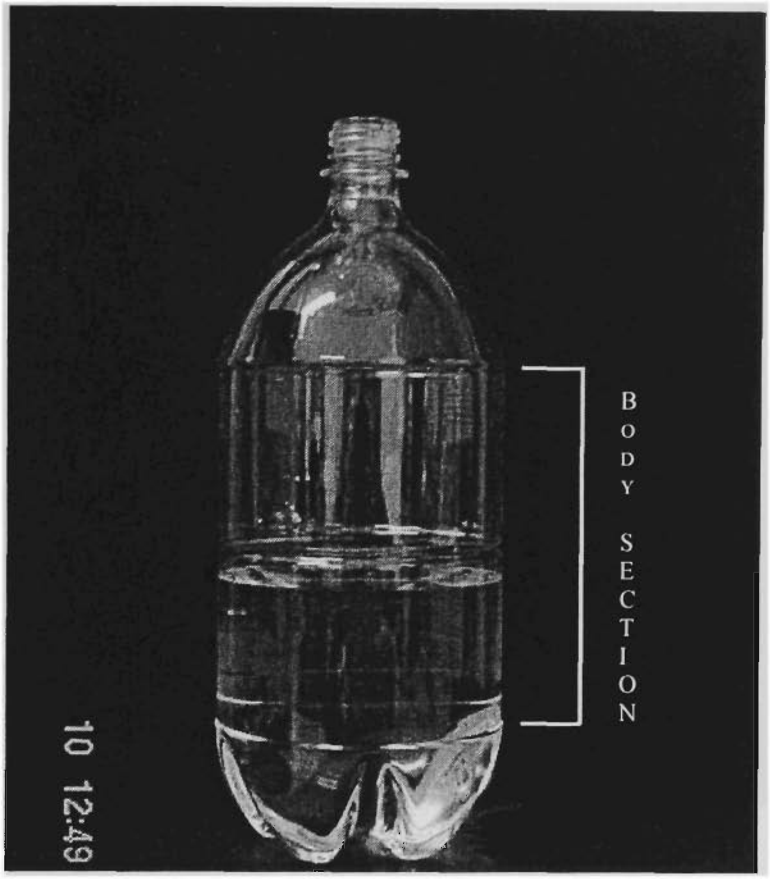


Figure 3. 3. Sample section of PET bottle

Conventional total-immersion method

The strips of PET samples were placed in a glass beaker containing 100 mL of food simulant. Food simulants used in this experiments were water, 3% (v/v) aqueous acetic acid, 15% (v/v) aqueous ethanol, 95% (v/v) aqueous ethanol and iso-octane. A stainless steel wire support (0.9 mm dia.) was used to keep the test pieces apart whilst ensuring complete contact with the simulant. The stainless steel support was thoroughly cleaned before use in the experiment. Figure 3.4 shows the stainless steel support used in this experiment.

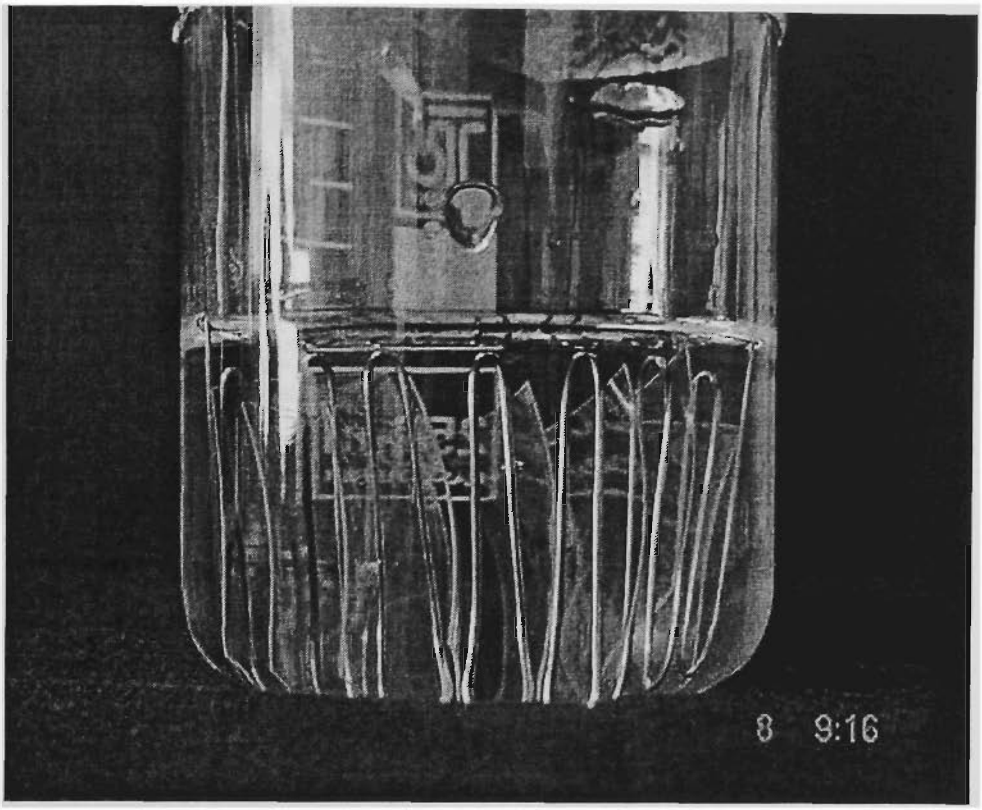


Figure 3. 4. A glass beaker containing PET samples immersed in a food simulant during conventional overall migration studies

The beakers containing the polymer samples and the food simulant were stored in a thermostatically controlled oven. The food simulants and test conditions are presented in Table 3.1. To avoid any loss of the food simulant by evaporation, the beakers were covered with an aluminum foil and sealed using Parafilm®. The liquid level of food simulant was marked on the outside of the beaker for verification. The experiments were conducted in triplicate for each simulant and in duplicate for each simulant with the wire support but without PET samples (i.e. blank tests).

Table 3. 1. Test conditions for the overall migration from PET by the conventional total-immersion method

Simulant	Description	Time of exposure / h	Temperature / °C	Test standard
A	Water	240	40	EN[1] 1186-3, 1998
B	3% (v/v) aqueous acetic acid	240	40	EN[1] 1186-3, 1998
C	15 % (v/v) aqueous ethanol	240	40	EN[1] 1186-3, 1998
D	95% (v/v) aqueous ethanol	24	50	ENV[2] 1186-15, 1999
	iso-octane	24	40	ENV[2] 1186-15, 1999

Source: [1] European Standard

[2] European Pre-Standard

Reflux method (Morrison and Freiser, 1957)

In this method, eight strips of the PET samples were placed into a refluxing flask containing 100 mL of food simulant. The total non-volatile residue was extracted in a Soxhlet apparatus during 2 h for the three aqueous food simulants (water, 3% (v/v) aqueous acetic acid and 15% (v/v) aqueous ethanol) and during 30 min for the two alternative fatty food simulants (iso-octane and 95% (v/v) aqueous ethanol). After the extraction process, the test flasks were covered with aluminium foil, sealed with Parafilm® and stored in a thermostatically controlled oven at 40°C for a total of 240 h (10 days). The experiments were conducted in triplicate and the results presented are the averages of the values obtained in each experiment. The blank tests (without the polymer sample) were conducted in duplicate under the same conditions used for the tests with the polymer.

3.2.5.3 Total non-volatile compound calculation

At the end of the contact exposure, all of the food simulant was transferred to a pre-weighed quartz dish and placed on a hot plate. The containers were washed with two portions (10 mL each) of fresh food simulant that were added to the respective dishes. The simulant was carefully evaporated on a hot plate to leave behind the solid residue. During the evaporation, the temperature was maintained at 80°C for the aqueous simulants and at 60°C for the fatty food simulants, in order to avoid simulant losses by splashing (boiling). When most of the simulant had evaporated, the dishes were placed in a thermostatically controlled oven maintained at 105 ± 5°C for a period of 30 ± 5 min in order to complete the evaporation and to dry the residue, and then cooled to room temperature in a desiccator containing silica gel. The dishes were placed again in the oven for a repeated heating, cooling and weighing process until consecutive masses differed by not more than 0.1 mg. The overall migration value was calculated using the following equation (3.1):

$$M = 1000\,(m_a - m_b)/S \qquad (3.\,1)$$

where M is the overall migration value into the food simulant (mg dm^{-2}); m_a is the mass (g) of the residue from the test sample after evaporation of the simulant; m_b is the mass (g) of residue from the blank simulant; and S is the surface area (dm^2) of the specimen.

3.2.6 Migration of acetaldehyde into food simulants

3.2.6.1 Stability of acetaldehyde in water

Stability studies of acetaldehyde in water were carried out at temperatures of 40, 60 and 80°C. A predetermined mass of pure acetaldehyde was added to vials containing 100 mL of water. The vials were hermetically capped and stored in a thermostatically controlled oven. The acetaldehyde concentration in the headspace was determined after 0, 6 h and 1, 2, 3 until 11 days by headspace gas chromatography using a flame ionization detector (FID) (see Section 3.2.6.5).

3.2.6.2 Doping of PET in acetaldehyde

In order to obtain significant quantities of acetaldehyde in the PET, the samples were soaked in 100%, 50% or 25% (v/v) solution of acetaldehyde in water, before the migration tests. Due to the low boiling point of acetaldehyde (20.8°C), the soaking was at a temperature of 5°C to avoid evaporation of the acetaldehyde. The amount of acetaldehyde absorbed in the polymer was measured by headspace gas chromatography (see Section 3.2.6.5).

3.2.6.3 Ultraviolet-visible spectrophotometry

Ultraviolet-visible spectrophotometry was used to measure the transparency of the PET samples after immersion in 100% acetaldehyde. Details of the method are presented in Section 3.2.2.1.

3.2.6.4 Migration studies

Acetaldehyde-doped PET samples were placed in vials containing 115 mL of food simulant and stored at 40, 60, 80 and 100°C (in the case of water being used as the food simulant) and at 30, 40 and 50°C (for iso-octane) in an oven that was thermostatically controlled to within ± 1°C, except for the temperature of 100°C. The acetaldehyde that had migrated from the PET into the food simulant was measured after 5, 15, 30, 60, 120, 180, 240, 360, 480 min and after 1, 2, 3, 4 days until no further migration was detected.

The migration study at 100°C was performed using a pressure vessel to avoid loss of the food simulant due to boiling (see Figure 3.5). After different periods of exposure (0.5, 1, 2, 4, 6, 8, 24 and 48 h), the vials were removed from the pressure vessel and 1 mL of the simulant was removed and stored for acetaldehyde analysis.

The acetaldehyde that had migrated into the food simulants was measured by headspace gas chromatography as described in section 3.2.6.5. The experiments were carried out in triplicate. The data presented are the average of these values.

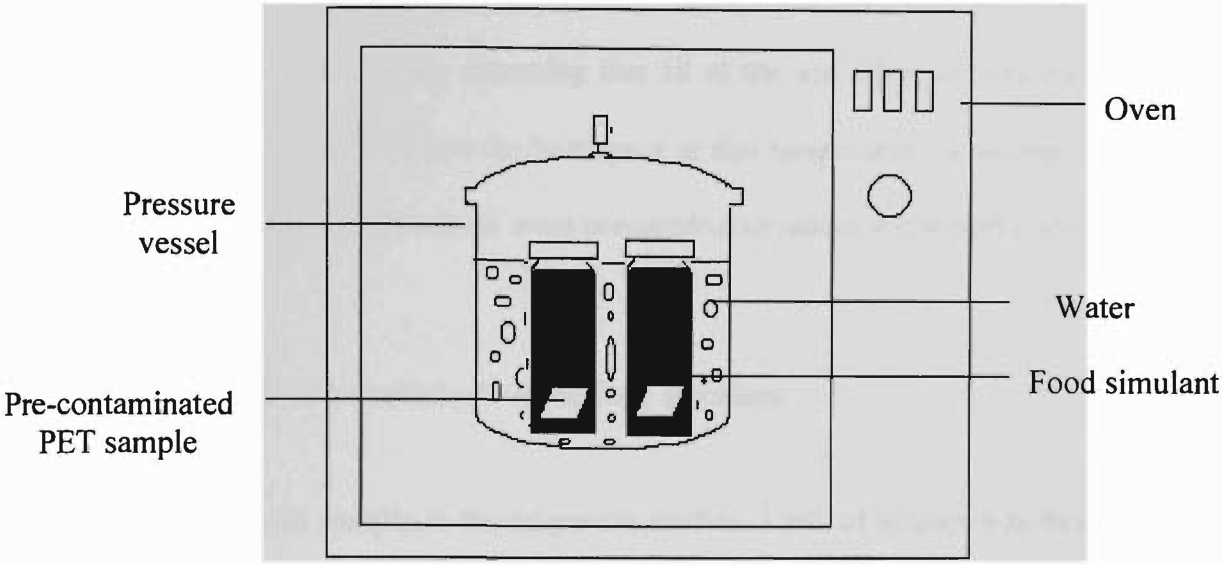


Figure 3. 5. Pressure vessel containing a vial and pre-acetaldehyde contaminated PET during migration studies at 100°C

3.2.6.5 Acetaldehyde determination

A Varian Star gas chromatograph with a flame ionization detector (FID) attached to a personal computer with Star Chromatography Workstation Version 5.3 software was used in the experiments.

Determination of acetaldehyde in PET samples

Samples (less than 5 mg) were cut from the doped PET samples, weighed and then placed into 20 mL vials. The vials were immediately sealed using poly(tetrafluoroethylene) (PTFE)-lined septa with aluminum caps and were heated at a temperature of 90°C for 3 hours to evaporate the acetaldehyde from the PET samples. A headspace sample of 1 mL was injected into the GC using a gas-tight syringe. Prior to the injection, the syringe was heated at 40°C and flushed with the headspace gas. Three samples were tested from each type of PET and the mean value was used. By assuming that all of the acetaldehyde absorbed in the polymer had evaporated into the headspace at that temperature, a number of serial dilutions of acetaldehyde in air were prepared to construct a standard curve.

Determination of acetaldehyde in the food stimulant

For each sample in the migration studies, 1 mL of aliquot was transferred to a 20 mL vial and then sealed with a PTFE-lined aluminum cap. The vials were maintained at 70°C for 2 h. Headspace samples of 1 mL were injected into the gas chromatograph. To account for the volume change, the measured GC peak areas were adjusted by the factor v_t/v_i, where v_t is the food simulant volume in the jar prior to each transfer of 1 mL of aliquot and v_i is the initial volume of the food simulant. A series of dilutions of acetaldehyde in water or iso-octane (ranging from 1 – 200 ppm) were made and a calibration curve was prepared for each series of migration experiments.

Column and gas chromatography method

Two kinds of capillary columns, a polar one (SGE Australia Pty. Ltd.) and non-polar one (J & W Scientific, Alltech Australia) were used in the experiments. The specifications and operating conditions used for the studies are summarized in Table 3.2.

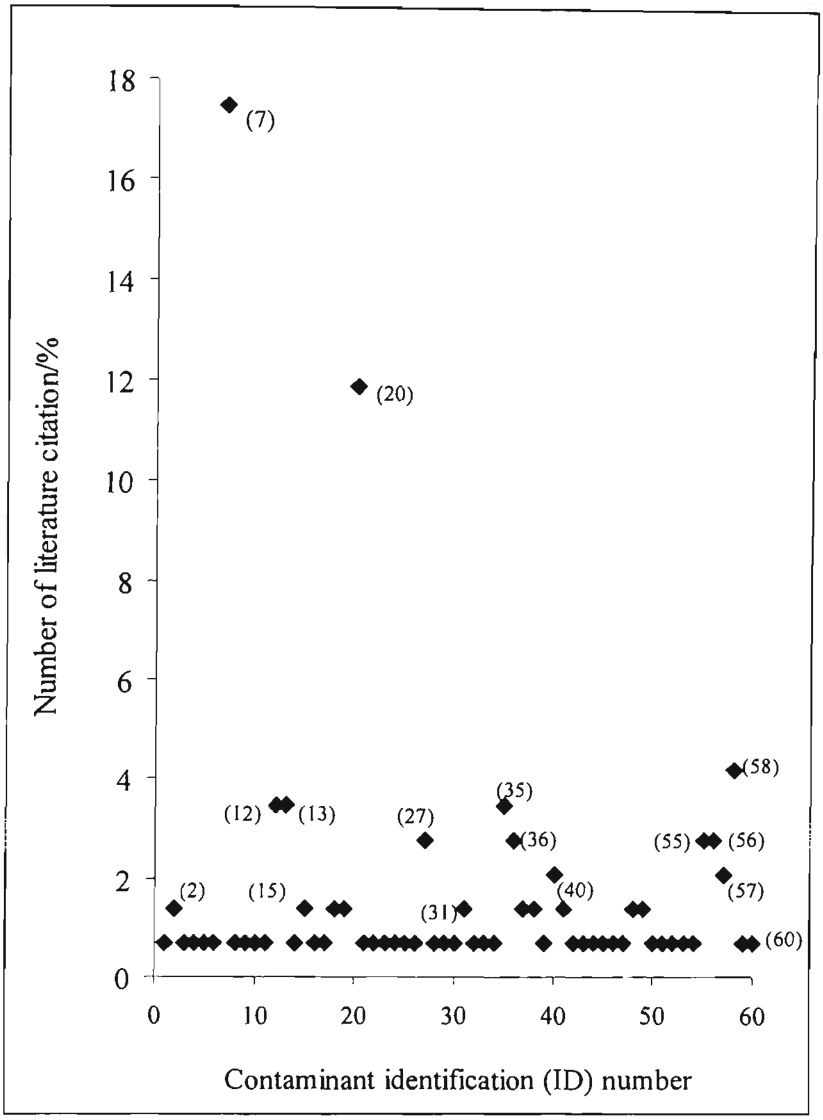
Table 3. 2. Gas chromatography operation conditions

GC Conditions	Food simulant	
	Water	Iso-octane
Column	30 m × 0.53 mm i.d. fused silica BP 20 (polar) with film thickness of 0.1 μm	30 m × 0.251 mm i.d. DB-5 (non polar) with film thickness of 0.22 μm
Carrier gas	Helium	Helium
T_{column}	40°C (Isothermal)	Temperature program of 40°C for 1.5 min and arising at 20°C/min to 80°C, hold for 1 min and finally rising at 20°C/min to 120°C for 2 min to clean
$T_{detector}$	110°C	110°C
$T_{injector}$	280°C	280°C
Injection mode	Splitless mode with splitless time on 75 s	Split mode with ratio 100:1

CHAPTER 4 – RESULTS AND DISCUSSIONS

Acetaldehyde is the major degradation product of PET and has attracted the largest attention in the literature. Figure 4.1 shows the percent of references that describe the different compounds resulting from degradation of PET. The plot represents 143 papers and journal articles. The compilation was produced from the literature collection associated with the thesis. However, it must be emphasized that any conclusion reached upon the analysis of these data may depend on what the authors were investigating: organoleptic deviations or PET chemistry and whether they used GC or HPLC. From this figure, it can be seen that in 17.5% of the references it was pointed out that acetaldehyde was the major decomposition product followed by cylic trimer/oligomer (11.9%) and toluene (4.2%). Based on these findings, acetaldehyde was chosen as the component to be studied in the present work in terms of its migration from PET into food simulant.

This chapter presents the important experimental results of the current study. It begins with the physical properties of the PET materials used in this project followed by the kinetics of sorption of acetaldehyde into virgin and recycled PET. The next section deals with the overall migration from PET. The data were obtained from two different methods namely, the conventional total-immersion and the reflux methods. The results of the specific migration of acetaldehyde from virgin and recycled PET into aqueous and alternative fatty food simulants at different initial acetaldehyde concentrations, degree of crystallinity and temperatures are also summarized in this chapter.



ID no	Contaminat	ID no	Contaminan	ID no	Contaminant
1	1,2,3-trimetyl benzene	22	Diethyl terephthalate	41	Hexanol
2	1,3-dioxolne	23	Diethylene glycol	42	Iso-propyl toluene
3	1,7-dimethylphthalene	24	Diiso-butyl terephthalate	43	Methyl acetate
4	1-4-diethylene dioxide	25	Dimethyl cyclohexane	44	Methyl alchohol
5	2 mehtyl-1-3-dioxolane	26	Dimethyl phthalate	45	Methyl salicylate
6	2,4-dimethylpropyllbenzoate	27	Dimethyl terephtalate	46	Methyl vynil terephthalate
7	Acetaldehyde	28	Di-n-butyl-phthalate	47	Methylglyoxal
8	Acetic acid	29	Dioctile phthalate	48	Naphthalene
9	Acetone	30	Dioctyl adipate	49	Nonanal
10	Acetophenon	31	d-limonene	50	Octamethyl-cyclotetrasiloxane
11	Aliphatic hydrocarbon	32	Dodecamethyl-e Cyclohexasiloxan	51	p-benzoquinone
12	Benzaldehyde			52	Propanal
13	Benzene	33	Ester	53	p-xylene
14	Benzohenone	34	Ethylbenzene	54	Squalene
15	Benzoic acid	35	Ethylene glycol	55	Styrene
16	Bis-(hydroxyethyl)-terephthalate	36	Formaldehyde	56	Terepthalic acid
17	Butoxybenzene	37	Formic acid	57	Tinuvin/nicotine
18	Carbon dioxide	38	Glyoxal	58	Toulene
19	Carbon monoxide	39	Hexamethyl- Cyclotrisiloxane	59	Tritetracontane
20	Cyclic trimer/oligomer			60	Vynil benzoate
21	Decamethyl- Cyclopentasiloxane	40	Hexanoic acid		

Figure 4. 1. Compounds identified as PET degradation products

4.1 Physical Properties of the Studied PET

4.1.1 Thickness

The following table summarizes the thickness of the PET samples used in the present study. Among these, the post consumer recycled (PCR) PET sheet was the thickest (see Table 4.1).

Table 4. 1. The Thickness of PET samples

Sample	Description	Thickness/mm
PC-PETb	Post-consumer bottle	0.300 ± 0.005
PETvb	Virgin PET bottle	0.280 ± 0.001
PETvs	Virgin PET sheet	0.250 ± 0.003
PCR-PETs	Post-consumer recycled PET sheet	0.390 ± 0.003

4.1.2 Intrinsic viscosity

Intrinsic viscosity is related to the molecular weight of the polymer. Table 4.2 gives intrinsic viscosity measured by the dilute solution method. The data indicate that the virgin PET had an intrinsic viscosity approximately 1.2 times higher than the recycled counterpart. Torres *et al.* (2000) found similar results. It has been reported in the literature that during reprocessing of PET, due to the high temperature and pressure, degradation and breaking up of polymer chains might occur and lead to a reduction in the intrinsic viscosity and average molecular weight of the recycled product (Villain *et al.*, 1995; Scheirs, 1998). The presence of some impurities and contaminants could accelerate this degradation process (Scheirs, 1998).

Table 4. 2. Intrinsic viscosity of PETvs and PCR-PETs

Sample	Intrinsic viscosity/$dm^3\ g^{-1}$
PETvs	0.75
PCR-PETs	0.63

Virgin PET used in this study had an intrinsic viscosity in the range of PET used by manufacturers of commercial bottles, which is between 0.73 – 0.80 $dm^3\ g^{-1}$ (Scheirs, 1998). However, based on the result obtained in the current study, the intrinsic viscosity of PCR-PETs was outside this range and therefore seems unsuitable for commercial bottle application.

As mentioned in Section 3.2.1.2, the intrinsic viscosity was measured using a mixture of solvents of 60% (w/w) phenol and 40% (w/w) tetrachloroethane. This measurement was made by staff at the Visy Technical Centre, Melbourne, Australia. Due to the unavailability of the K and a constants for the Mark - Houwink relation (Equation 4.1), the viscosity average molecular weight, $\overline{M}_v$, could not be calculated. However, it is clear that the viscosity average molecular weight of the recycled PET is lower than that of the virgin PET.

$$[\eta] = K\overline{M}_v{}^a \qquad 4.1$$

where $[\eta]$ is intrinsic viscosity, K and a are the Mark - Houwink constants, and $\overline{M}_v$ is viscosity average molecular weight.

4.1.3 Elongation at break, Young's modulus and tensile stress at break

The mechanical properties of the virgin and recycled PET were evaluated in tension. The samples were not subjected to experimentation as detailed in Section 3.2.2. An example of the tensile stress-strain curves of PETvs and PCR-PETs is presented in Figure 4.2. Table 4.3 summarizes the mechanical properties obtained for the virgin and recycled PET sheet.

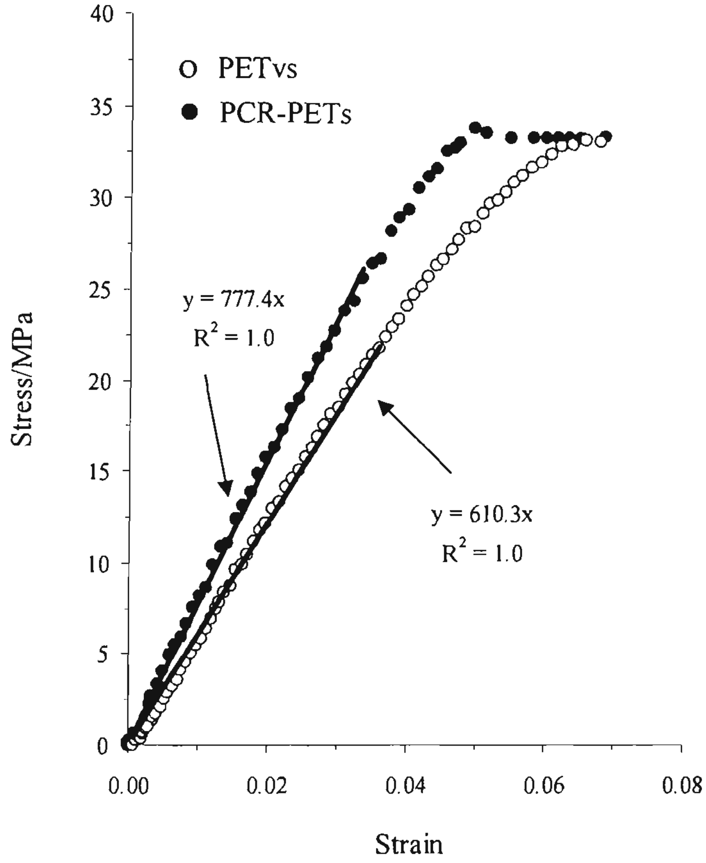


Figure 4. 2. Tensile stress-strain curves of PET taken at room temperature

Table 4. 3. Mechanical properties of PETvs and PCR-PETs

Sample	Elongation at break/%	Young's modulus/ MPa	Tensile stress at break/MPa
PETvs	7.1 ± 0.4	690 ± 30	33.2 ± 2.2
PCR-PETs	6.6 ± 0.5	750 ± 32	34.8 ± 1.3

The most sensitive mechanical property of a polymer is elongation at break (Ram *et al.*, 1980). A decrease in the elongation at break of about 7% for the PCR-PETs compared to the PETvs was found. Unfortunately, there is a lack of information on the thermal history of the materials. However, if it is assumed that both materials had the same thermal history, this decrease is believed to be due to an increase in the crystallinity on the PCR-PETs in comparison with PETvs. The more crystalline a polymer is, the more brittle is the polymer, thus lower elongations are expected as the crystallinity increases. A lower viscosity average molecular weight of PCR-PETs compared to PETvs, as indicated in the previous section, is also responsible for this elongation at break reduction.

Torres *et al.* (2000), Mancini and Zanin (1999, 2000) have found that amorphous PET had a higher elongation at break than crystalline PET. Ramakrishna *et al.* (1997) also observed a decrease in the elongation at break for PET samples after heat treatment (that caused an increase in crystallinity), compared to the samples before the heat treatment. The results of the present study are therefore consistent with the findings of the other investigators.

In contrast to the reduction in elongation at break, an increase in Young's modulus was noted for the recycled compared to the virgin material. The modulus represents the ratio of stress and strain within the elastic region at low strains where the stress is proportional to the strain. The modulus represents the stiffness of the polymer. The higher crystalliniy of the recycled PET causes a mobility restriction of molecules in the polymer matrix and thus renders the recycled material to be stiffer compared to the virgin one.

From these results the recycled PET was not found to be significantly different in its tensile stress compared to the virgin material. These findings are in a good agreement with those of Devliegher *et al.* (1998) and Jetten *et al.* (1999).

4.2 Re-Crystallization of Virgin and Recycled PET

When PET is heated to relatively high temperatures like in oven-able and microwave-able applications, changes in physico-mechanical properties of the material may occur due to changes in the morphological structure of the polymer (Gogolewski and Mainil-Varlet, 1996). Recrystallization or crystal destruction may occur during thermal treatment and these morphological changes might affect the properties of the polymer.

In the present study, virgin and recycled PET sheets have been subjected to isothermal annealing at a temperature of 120°C during periods of 3 – 10 min and immediately cooled in ice water. The transmittance and thermal properties before and after the heat treatment were investigated. Changes in the sample properties occurred as a result of the thermal treatment and the crystallinity of the samples was increased. To ensure the availability of samples with different levels of controlled crystallinity (morphology), thermally annealed samples were used to study the sorption and migration of acetaldehyde in PET as described in Sections 4.3 and 4.5 of this chapter.

4.2.1 Differences in crystallinity between virgin and recycled PET

During the DSC heating experiments, endothermic peaks associated with fusion of the crystalline fraction appeared in the thermograms at about 247 - 248°C for the virgin PET bottle sample (PETvb), 246 – 248°C for the virgin PET sheet (PETvs) and 249 – 250°C for the recycled PET sheet (PCR-PETs) (see Table 4.4). The comparison of sheets and bottles cannot be made readily as these are very different materials due to orientation effects.

Table 4. 4. Results from the analysis of the DSC thermograms for virgin PET bottle, virgin PET sheet and recycled PET sheet

Sample	$T_{\text{glass transition}}$/°C	T_{onset}/°C	T_{melting}/°C	$\Delta H_{\text{fusion}}/Jg^{-1}$
Virgin PET bottle/mL				
390	67.4 ± 0.1	241.5 ± 0.3	247.2 ± 0.8	30.1 ± 1.3
600	67.7 ± 2.6	241.1 ± 0.2	248.0 ± 0.9	32.8 ± 1.5
1250	68.4 ± 3.3	241.7 ± 0.2	248.1 ± 1.1	33.5 ± 1.3
2000	68.9 ± 1.7	241.6 ± 0.1	247.9 ± 1.1	34.9 ± 1.5
Virgin PET sheet/min				
0	60.2 ± 2.2	242.2 ± 0.3	246.0 ± 1.2	22.2 ± 1.3
3	62.0 ± 2.4	242.2 ± 0.7	247.3 ± 2.4	23.8 ± 0.7
6	61.0 ± 1.6	242.1 ± 0.2	247.9 ± 0.9	29.7 ± 1.3
10	62.6 ± 0.2	242.2 ± 0.2	247.5 ± 0.7	35.6 ±0.6
Recycled PET sheet/min				
0	62.0 ± 2.8	242.5 ± 0.3	249.6 ± 1.3	25.4 ± 1.1
3	63.5 ± 0.4	242.4 ± 0.1	250.6 ± 0.4	29.8 ± 0.4
6	66.4 ± 2.1	242.4 ± 0.3	250.9 ± 2.7	34.7 ± 0.6
10	66.8 ± 2.0	242.5 ± 1.3	249.8 ± 0.8	40.5 ± 1.0

The enthalpy of melting, for the samples before and after the heat treatment, was found to be 30 – 35 J g^{-1}, 22 – 36 J g^{-1} and 25 – 41 J g^{-1} for PETvb, PETvs and PCR-PETs respectively. As mention in Section 3.2.2.2 the samples were taken from sheets of PETvs and PCR-PETs and from the middle section of the wall of PETvb. It was found that the melting temperature of the PCR-PETs samples was the highest, as shown in Table 4.4. These results suggest that the number of crystalline entities in the recycled PET samples is higher than that in the PETvb and PETvs. Torres *et al.* (2000) found similar results.

In general, it may be noted that the glass transition (T_g) and melting (T_m) temperature increased with increasing crystallinity of the samples. According to Mark and Atlas (1977), T_g increases with the stiffness and T_m increases with the intermolecular forces and the degree of perfection of the crystallites. It should be pointed out, however, that the melting temperature of the virgin PETvb, PETvs samples is not much lower than that of the recycled PCR-PETs one (see Table 4.4).

The heat of fusion of both, the PETvs and the PCR-PETs samples, increased as a result of the thermal treatment. The increase in the heat of fusion is attributed to an increase in the crystalline regions and spherulite dimensions, thus resulting in an overall increase in the degree of crystallinity of the samples. This is in agreement with Gogolewski and Mainil Varlet (1996) who claim that the heat of fusion is directly proportional to the overall degree of crystallinity.

Figure 4.3 shows the DSC thermograms for virgin PET material taken from bottles of four different capacities.

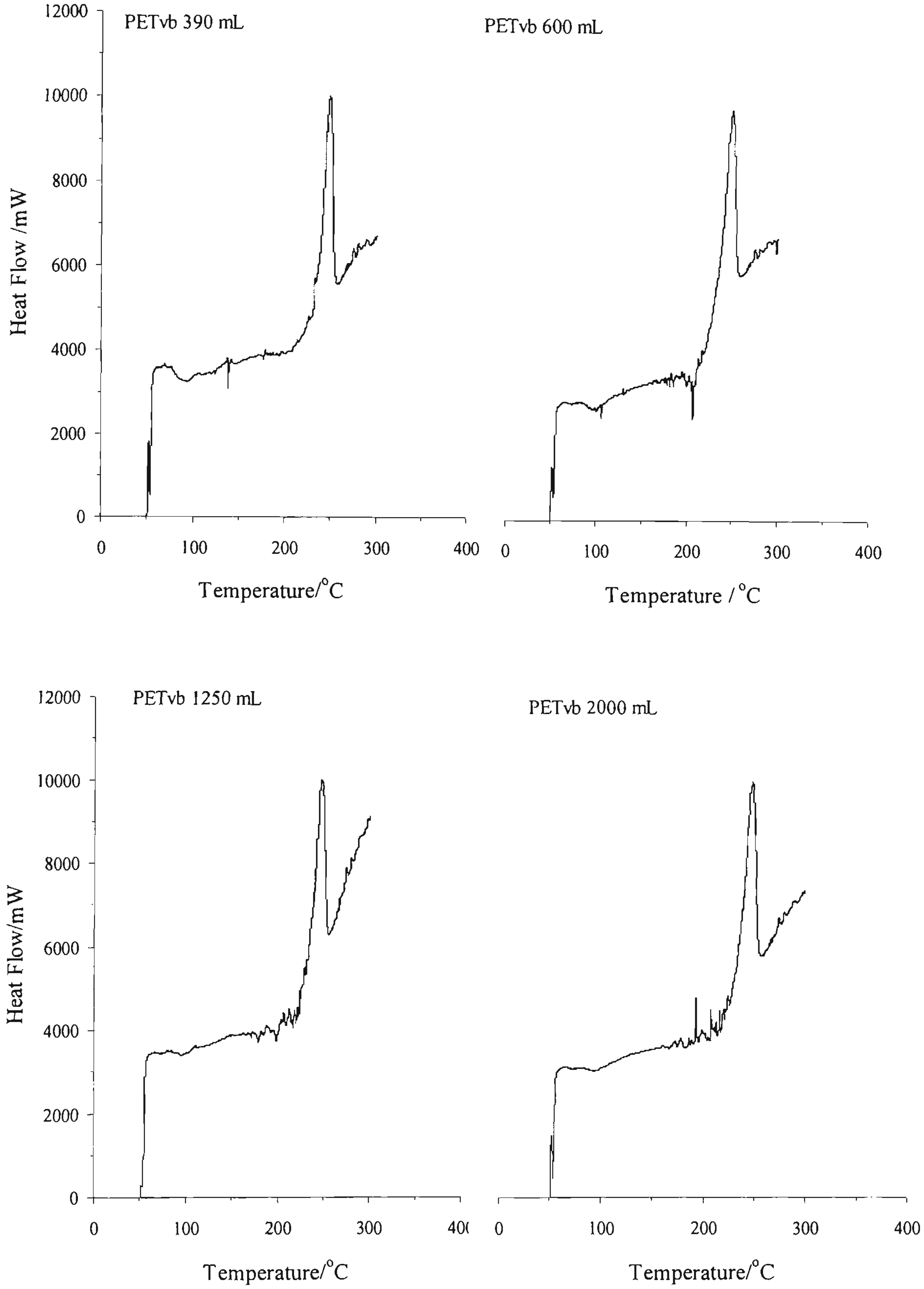


Figure 4. 3. DSC thermograms of virgin PET material taken from bottles of different capacity.

It can be seen that from about 180°C, the thermograms are not smooth and the polymers undergo some changes in the endothermic peaks. These endothermic peaks are associated with the fusion of the crystalline fraction of the material. The crystallinity of each of the samples can be calculated by dividing the melting peak areas by 120 J g^{-1}, which is the most common value cited in the literature for the heat fusion of 100% crystalline PET. The degree of crystallinity, as derived from this calculation, for the virgin PET bottles of different volumes is presented in Figure 4.4. There was no statistically significant difference in the crystallinity degree of the different bottles.

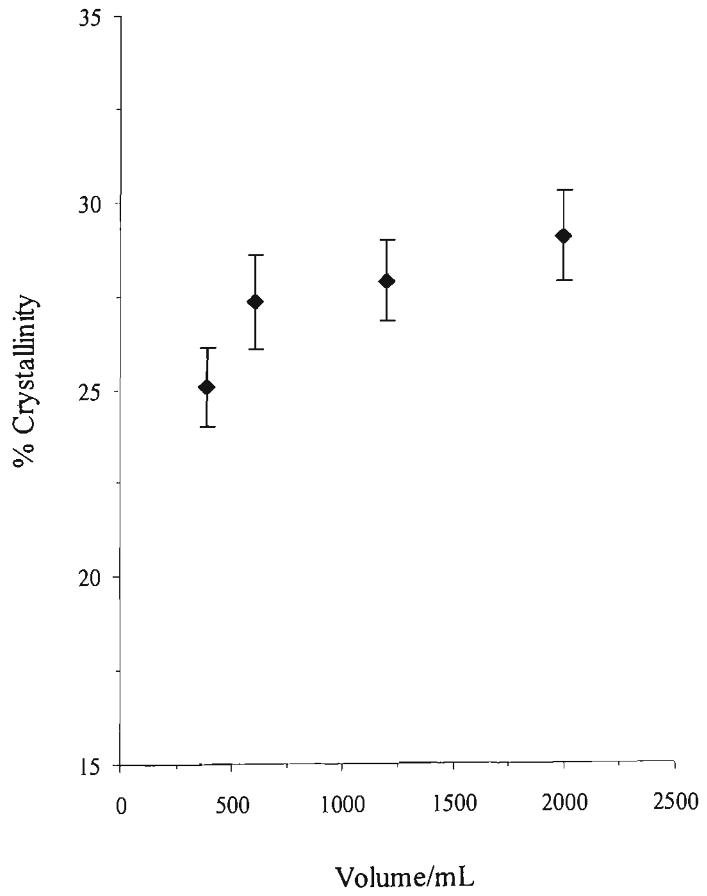


Figure 4. 4. Degree of crystallinity of PETvb material taken from bottles of 390, 600, 1250 and 2000 mL in volume. The data points represent the mean of three measurements

From Table 4.4 and Figure 4.4 an increase in the degree of crystallinity of the virgin PET bottles with the increase in their size can be observed. The reason for this increase stems from the polymer chains being oriented during the stretch blow moulding process, as a result of which they crystallize more easily, a phenomenon that is often termed "strain-induced crytallization" (Zaroulis and Boyce, 1996; Chaari *et al*, 2003). The bigger the size, the more oriented the PET becomes and consequently the bottle is more crystalline. However, none of the virgin PET bottles showed a crystallinity exceeding 30%.

Figure 4.5 and 4.6 show a series of DSC thermograms obtained from virgin PET sheet (PETvs) and recycled PET sheet (PCR-PETs) samples after treating the original samples (without heating) at 120°C for 3, 6 and 10 min.

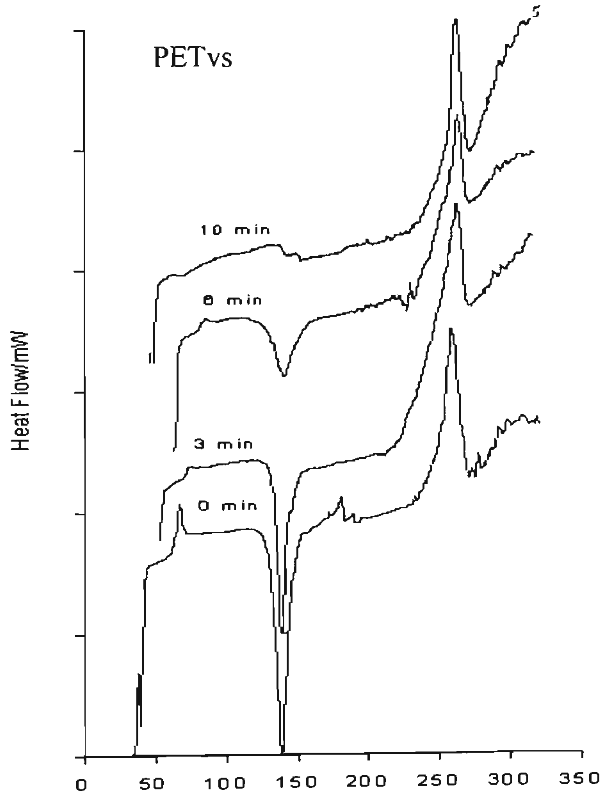


Figure 4. 5. Representative DSC scans for virgin PET sheets subjected to various treatments (120°C for 0, 3, 6 and 10 min)

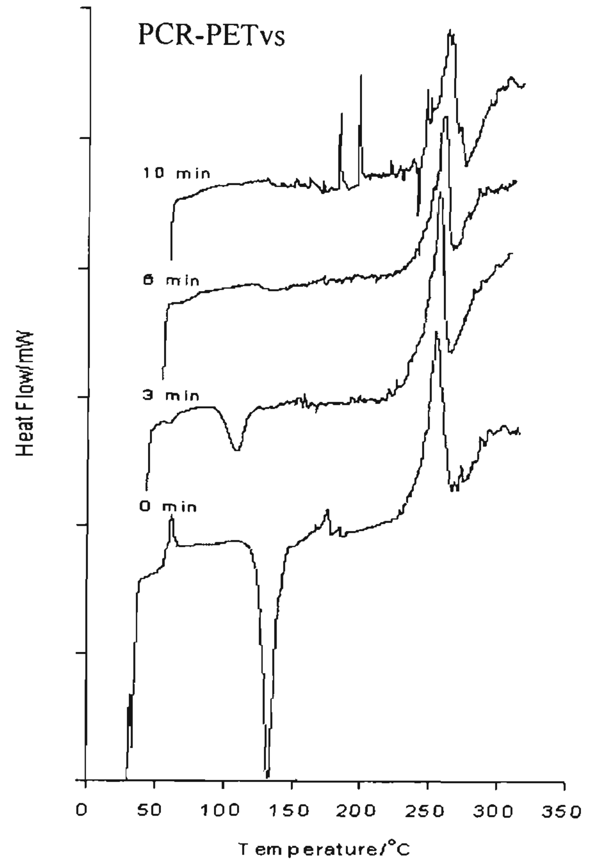


Figure 4. 6. Representative DSC scans for recycled PET sheets subjected to various treatments (120°C for 0, 3, 6 and 10 min)

The original samples for both PETvs and PCR-PETs clearly provide three major phase transitions; the glass transition at about 60°C, the exothermic peak at around 140°C (characteristic for the crystallization of poorly ordered/amorphous material) and the crystalline melting endothermic peak at about 246 - 250°C. The glass transition temperature does not exhibit enthalpic transitions indicating that the material has undergone physical ageing. Furthermore, as the temperature was increased beyond T_g, the material began to crystallize in the DSC pan, with an observed onset temperature of about 242°C. As the temperature was increased further, the crystal started to melt. The melting temperatures found in the present study are lower than that of PET reported in literature (T_g = 265°C) (Mark, 1999).

However, Torres *et al.* (2000) also found melting temperatures of 245 – 248°C for PET. The lower melting temperature than the normal range could be due to the presence of isophthalate moieties that originate from degradation during processing.

The thermograms after heating at 120°C for 3, 6 and 10 min show progressive changes with the duration of the heat treatment. The exothermic peaks occur over the same temperature range, but there is one important feature to be noted. The DSC thermograms (Figure 4.5 and 4.6) show that the exothermic area decreases with the prolongation of the heating period and disappears afterwards: in the case of the PETvs sample, after heating for 10 min and in the case of the PCR-PETs, after heating for 6 min. This result shows that the lower the degree of crystallinity of the PET sample the higher the observed exotherm peak. This is consistent with the result found by Begley *et al.* (2002) who found that APET (less crystalline) had a higher exotherm peak area than CPET (more crystalline).

The disappearance of the exothermic peak for PETvs requires a longer time of heating than that for PCR-PETs. However, further analysis found that the exotherm peaks disappeared when the PET sample reached the degree of crystallinity at about 25%. This confirms that a degree of crystallinity of 25% is about the maximum crystalline content that could be obtained from the amorphous regions in the PET to be further recrystallized during the DSC measurement.

It can also be seen from Figure 4.6 that in the PCR-PET samples the exothermic peak shifts to a lower temperature when heated for periods longer than 3 min; from 140°C for the original samples to 120°C when heated for 3 min, and then disappears. The PCR-PETs sample heated at 120°C for 10 min showed three melting peaks. According to Gogolewski and Mainil-Varlet (1996), the low temperature range of the endothermic peak can be assigned to the partial melting of the fraction originating from the recrystallization of the amorphous material or of the material with a low degree of crystal perfection. It may also reflect the formation of two types of crystals, one type that is formed during the outward growth of the sperulites and the second type that is formed during the "filling-in" of the sperulites (Nichols and Robertson, 1992).

Figure 4.7 shows the change in the degree of crystallinity of the samples as a function of the heating period. The percent crystallinity of the PET samples is in the range of 18 – 29% for PETvs and 21 – 33% for the PCR-PETs. These values are close to those that have been found by other researchers. Billovits and Durning (1988) found a crystallinity of PET in the range of 23 – 43% when samples were annealed under vacuum at temperatures of 120 – 230°C for 48 h. Komolpraset *et al.* (1997) found a degree of crystallinity of 31% for recycled PET and 5 – 15% for virgin PET. Annealing under vacuum was done to minimize oxidative degradation of the material. In the current work, the annealing was performed at 120 ± 1° C for 3 - 10 min.

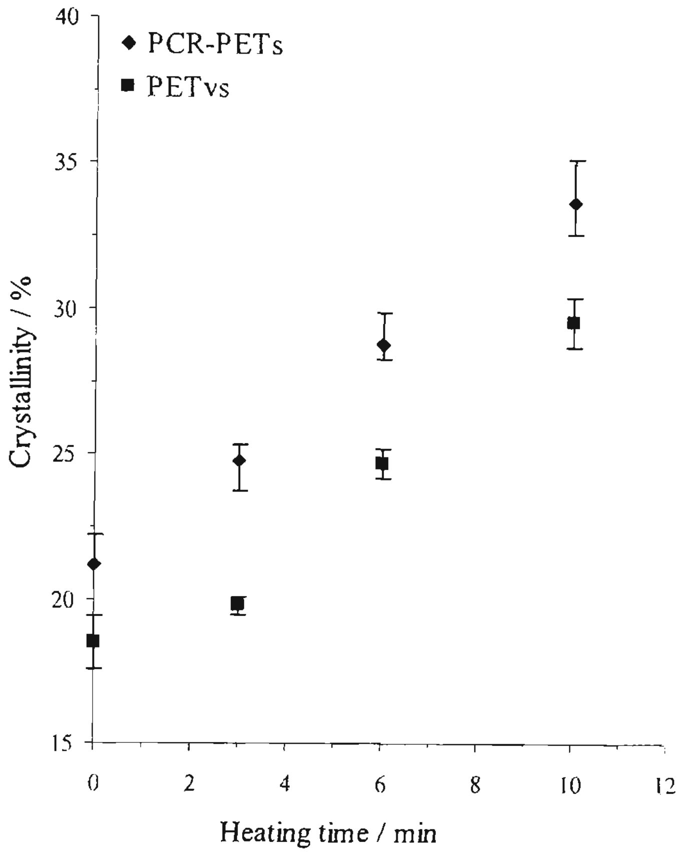


Figure 4. 7. Changes in the degree of crystallinity of PETvs and PCR-PETs samples after heating for 0, 3, 6 and 10 min at the temperature of 120°C. The data points represent the mean of three measurements

According to Figure 4.7, there is a linear increase in the heat of fusion, associated with melting (the degree of crystallinity), with heating time. However, the result for PETvs that has not been subjected to heating is a marked exception to this linear trend. This result is in accordance with the findings of Gogolewski and Mainil-Varlet (1996) who studied the increase in crystallinity of the Poly(L-lactide) after sterilizing at 135°C for 2, 10 and 50 h. Thus, it can be noted that the degree of crystallinity depends on the heating time. The highest observed value of ΔH_{fusion} of melting for 10 min heating was 35.6 J g^{-1} for PETvs as compared with

40.4 J g^{-1} obtained for the heat of melting of the crystalline region of the PCR-PETs sample.

This study shows that the crystallization of PCR-PETs is higher than that of PETvs at all heating periods. The results from these measurements are confirmed by visual observations showing that the PETvs samples were less opaque than those of PCR-PETs at the same heating time.

From Figure 4.7 is can be seen that the extent of crystallinity of PCR-PET is significantly higher than that of the PETvs, particularly after heating for 3 min. This result correlates well with the photographs shown in Figure 4.8 (a, b) and 4.9 (a, b). This observation is also confirmed by the intensities of the exothermic peaks shown in Figures 4.5 and 4.6. Whereas a slight decrease in the intensity of this peak can be seen for the PETvs sample, a significant decrease in the same peak is seen for the PCR-PETs sample during the heating range of 0 – 3 min. The reason for this difference stems from the difference between the original (not heated) PCR-PETs and PETvs samples. The PCR-PETs had a higher degree of crystallinity as expressed by the heat of fusion of 25.4 ± 1.1 J g^{-1} as compared to 22.2 ± 1.3 J g^{-1} for PETvs (see Table 4.4). The initial crystallites in PCR-PETs sample, as well as impurities, may have acted as nucleating agents to accelerate the recrystallization processes.

4.2.2 Differences in light transmittance between virgin and recycled PET

It was observed that the original virgin sheet sample was transparent whereas the recycled PET sheet was slightly yellow. During the heat treatment, the samples became opaque. The opacity was attributed to the formation of polymer crystals. Mancini and Zanin (1999) reported an increase in the opacity of PET containers, after subjecting them to a successive heating process. A strong effect of heating on the opacity of semi-crystalline polymers has also been reported by Siripatrawan *et al.* (2000). They found a discoloration in plastic containers made of polypropylene after repeated heating in a conventional oven at a temperature of 100°C.

Figures 4.8 and 4.9 show photographs of the samples (exposed against a black background) of virgin and recycled PET sheets before and after being subjected to the heating process. The different times of exposure (0, 3, 6 and 10 min) at 120°C produced significant differences in the opacity of the samples. It was found that the longer the time of exposure, the greater the decrease in transparency. Increasing the time of heating allows the molecules to possess a higher mobility for a longer period, enabling them to become more organized and produce a more opaque sample. The non-heated virgin PET samples were highly transparent and became translucent after heating for 3 min, and opaque after heating for 6 and 10 min.

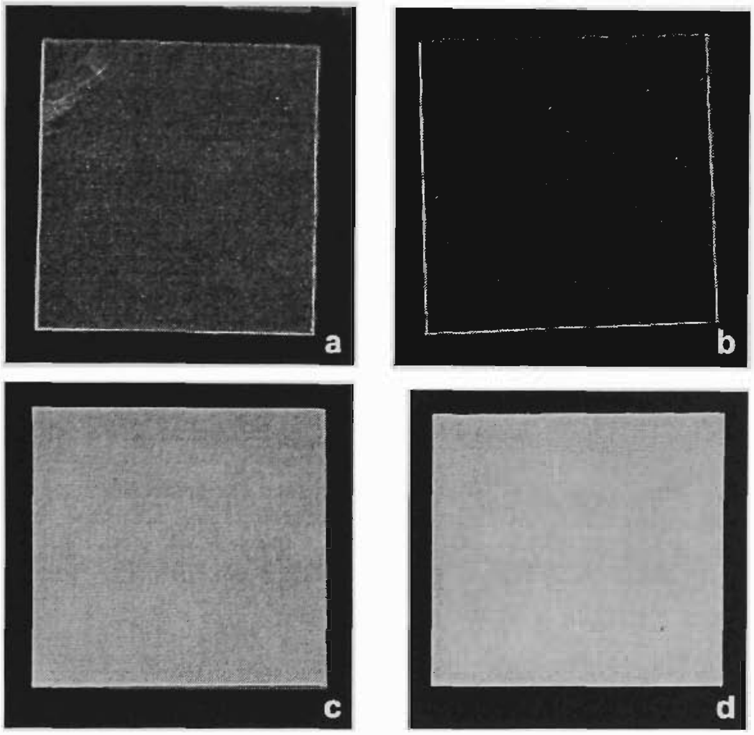


Figure 4. 8. Virgin PET sheet after heating at 120°C for: (a) 0 min, (b) 3 min, (c) 6 min and (d) 10 min

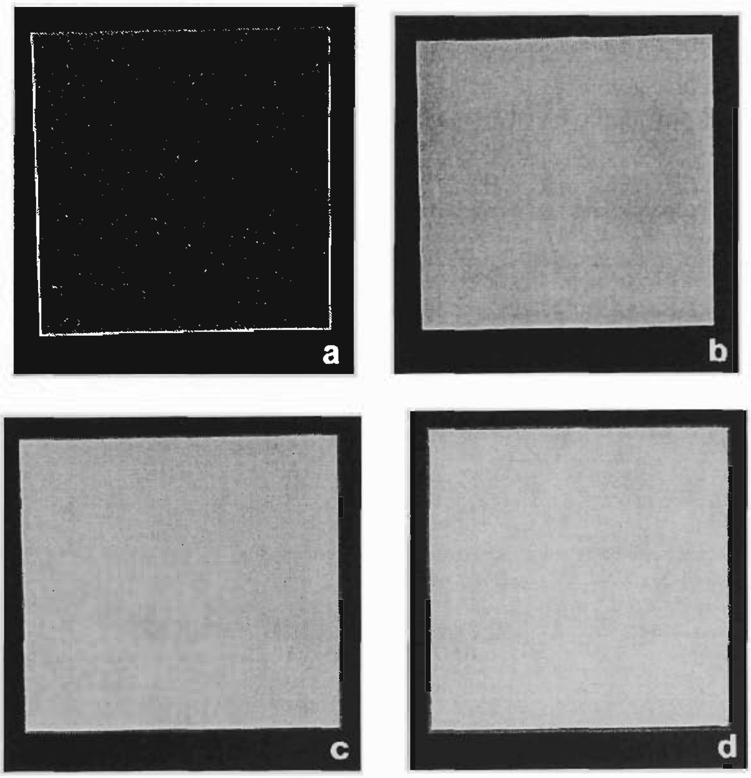


Figure 4. 9. Recycled PET sheet after heating at 120°C for: (a) 0 min, (b) 3 min, (c) 6 min and (d) 10 min

The recycled PET samples (Figure 4.9) exhibited a higher opacity than the virgin counterparts (Figure 4.8) at each identical level of the heat treatment. This result is probably because the recycled PET is more sensitive to thermal treatment and hydrolytic degradation than the virgin PET material, resulting in an enhanced crystallization process in the recycled PET.

The heat-induced changes in the opacity of the polymer are shown for virgin and recycled PET sheet as a function of percent transmittance at 550 nm versus the time of heating (Figure 4.10).

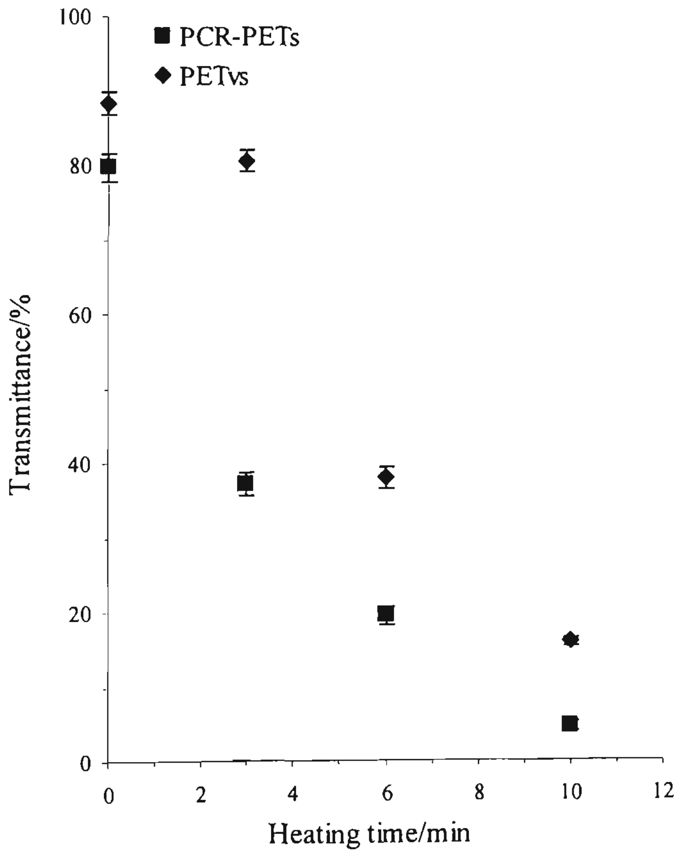


Figure 4. 10. Heating-induced changes in transmittance at 550 nm for virgin and recycled PET

It is apparent that the thermal treatment causes a reduction in the amount of transmitted light. The longer the period of heating, the lower the amount of transmitted light through the samples. This result is in agreement with the observation of Ramakrishna *et al.* (1997). A significant decrease in the transmission was reported also for other polymers (28, 8 and 7% for PP, PP/nylon/PP and CPET+PP respectively) after they were subjected to a heat treatment at 120°C in a vacuum oven (Ramakrishna *et al.*, 1997).

The change in the transmittance is generally considered to be attributable to the change in the degree of crystallinity and size of crystallites in the material resulting from the heat treatment (Ram, 1997). In addition, during the heating process, the polymer may undergo degradation and oxidation that may reduce its light transmission (Ram, 1997).

It can be observed that when the virgin PET sample was heated for 3 min, a relatively small reduction in the transmittance (about 7%) occurred compared to the recycled PET (about 16%). These results are complemented with the photographs shown in Figure 4.8 (a, b) and Figure 4.9 (a, b). The rapid increase in opacity of the PCR-PETs after the short heating treatment (3 min) is also supported by the rapid increase in the degree of crystallinity, which will be discussed in the next section.

4.3 Sorption of Acetaldehyde into Virgin and Recycled PET

The sorption of acetaldehyde into PET was studied as a function of temperature and degree of crystallinity. In order to obtain parameters for acetaldehyde diffusion in PET and to compare the behaviour of virgin and recycled PET, samples were immersed in acetaldehyde and the sorption was monitored by weight increase.

4.3.1 Effect of temperature on acetaldehyde transport in virgin and recycled PET

It is expected that the rate of acetaldehyde transport in PET increases with increasing temperature. This is partly due to an increase in molecular motion of the solvent and of the polymer chains. Consequently, the equilibrium acetaldehyde sorbed into the PET is expected to be reached faster at higher temperatures. Figure 4.11 and 4.12 show the effect of acetaldehyde mass uptake into the non-heated samples of the virgin and recycled PET respectively. No changes in the character of transport were found at the different temperatures. The main difference is due to the increased rate of sorption as the temperature increases. Temperature also affects the amount of acetaldehyde sorbed into the polymer at equilibrium (see Section 4.3.3).

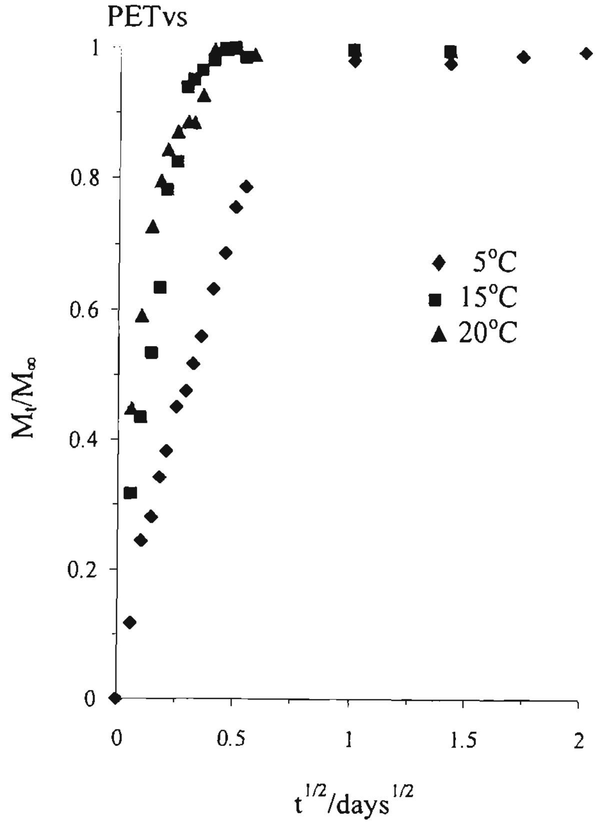


Figure 4. 11. Relative mass uptake, M_t/M_∞ versus $t^{1/2}$ during acetaldehyde sorption in non-heated virgin PET at different temperatures

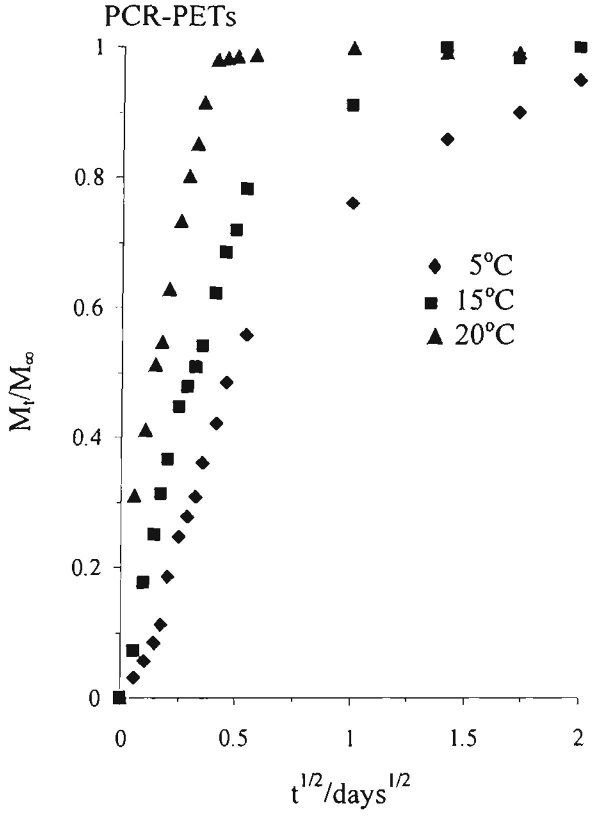


Figure 4. 12. Relative mass uptake, M_t/M_∞ versus $t^{1/2}$ during acetaldehyde sorption in non-heated recycled PET samples at different temperatures

4.3.2 Differences in rate constant between virgin and recycled PET

Figures 4.13 and 4.14 show linear relationship in the plots of ln $(C_\infty - C_t)$ versus time up to 1.5 h for virgin PET and up to 2 h for the recycled polymer at a soaking temperature of 5°C. The linear regression coefficient, r^2, values were in the range of 0.96 to 0.99. The rate constant (Equation 2.7, page 64) for sorption was found to increase with temperature for both PET samples. The same trend was also found at soaking temperatures of 15 and 20°C (see Appendix A).

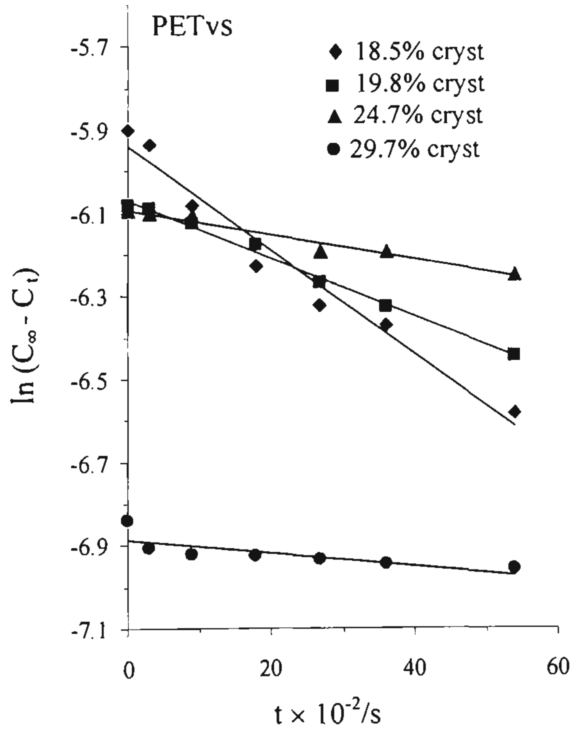


Figure 4. 13. Plot of ln $(C_\infty - C_t)$ versus t for virgin PET sheet at 5°C

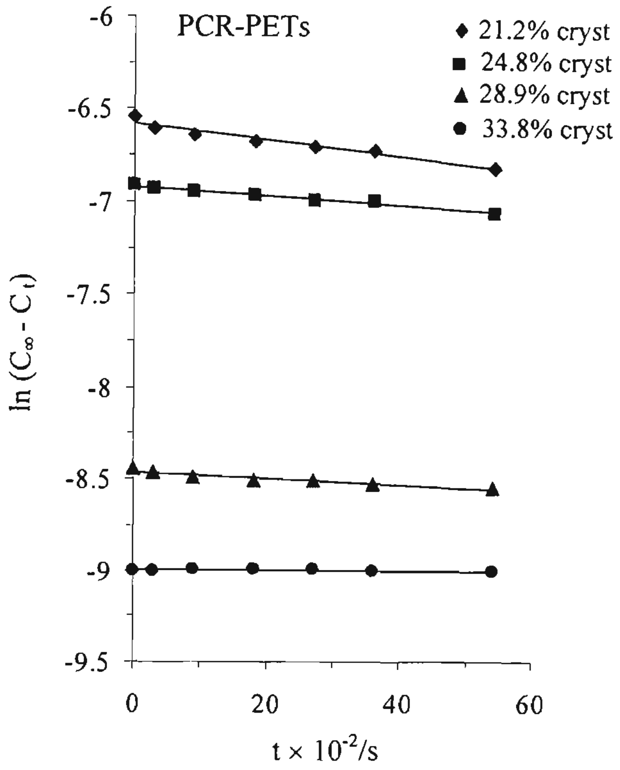


Figure 4. 14. Plot of ln (C_∞ - C_t) versus t for recycled PET sheet at 5°C

According to the literature, sorption of organic solvents in polymers has been shown to occur in at least two steps that have different rates: a fast process that occurs within a time scale of minutes to hours, and a slow process that may take days to weeks (Ten Hulscher and Cornelissen, 1996; Aminabhavi and Shivaputrappa, 1991). Furthermore, the fast sorption is commonly described by a first-order kinetic equation (Equation 2.6, page 64) (Ten Hulscher and Cornelissen, 1996) and the slow sorption is modeled by a more complex kinetic mechanism. However, only one step, i.e. the fast process, with a single rate constant was apparent in the present study. The fast process of sorption takes approximately 0.5 h longer in the recycled PET than in the virgin PET material. This may be attributable to the differences in the crystallinities of the two types of samples; the PCR-PETs have higher degrees of crystallinity than the PETvs. Crystallites embedded in a polymer matrix generally preclude transport of a penetrant (McDowell *et al.*, 1999). Therefore molecules of penetrant need some extra time to diffuse in a polymer of higher crystallinity. The values of C_∞ for recycled and virgin PET are listed in Table 4.6.

From the slope of the regression lines shown in Figures 4.13, 4.14 and Appendix A, the rate constants were calculated and are listed in Table 4.5.

Table 4. 5. Kinetic data for virgin and recycled PET-acetaldehyde systems

Material	Crystallinity	$k \times 10^5 / s^{-1}$		
		5°C	15°C	20°C
PETvs	18.5 ± 1.0	12.5 ($r^2 = 0.97$)	29.4 ($r^2 = 0.97$)	42.4 ($r^2 = 0.97$)
	19.8 ± 0.6	7.0 ($r^2 = 0.99$)	18.3 ($r^2 = 0.96$)	35.9 ($r^2 = 0.94$)
	24.7 ± 1.0	2.6 ($r^2 = 0.96$)	9.0 ($r^2 = 0.94$)	15.3 ($r^2 = 0.98$)
	29.7 ± 1.5	1.6 ($r^2 = 0.96$)	5.8 ($r^2 = 0.97$)	12.0 ($r^2 = 0.99$)
PCR-PETs	21.2 ± 0.9	4.6 ($r^2 = 0.96$)	8.8 ($r^2 = 0.95$)	16.6 ($r^2 = 0.97$)
	24.8 ± 0.3	2.6 ($r^2 = 0.98$)	7.3 ($r^2 = 0.97$)	10.3 ($r^2 = 0.99$)
	28.9 ± 0.5	1.6 ($r^2 = 0.97$)	6.4 ($r^2 = 0.96$)	9.4 ($r^2 = 0.98$)
	33.8 ± 0.9	0.6 ($r^2 = 0.94$)	3.4 ($r^2 = 0.97$)	5.2 ($r^2 = 0.95$)

The data in Table 4.5 reveal that, as expected, the rate constant increases with increasing temperature. A similar trend to this was also observed by Aminabhavi and Shivaputrappa (1991) in their studies of sorption of organic liquids such as toluene, *p*-xylene and trimethylbenzene into commercial polymers. It is understood that increasing the temperature will increase the solvent mobility as well as increase the formation of free volume in the polymer system by facilitating the breaking of Van der Waals bonds between the polymer chains and creating "cylindrical" voids (Manabe, 1996). Under these conditions, a small organic molecule such as acetaldehyde can move easily from one cavity to another in the polymer matrix.

A decrease in the kinetic rate constant has been found when the polymer crystallinity increases. This is attributable to the crystallites in the polymer making it more difficult for the solvent to permeate due to a more tortuous path for the solvent molecule to pass (McDowell *et al.*, 1998; Lützow *et al.*, 1999). Since the recycled PET samples were found to have higher crystallinity degree than their virgin counterparts, lower kinetic rate constants were obtained for the latter.

4.3.3 Differences in sorption constant between virgin and recycled PET

Table 4.6 shows the value of the sorption constant of acetaldehyde in both virgin and recycled PET as a function of crystallinity at temperatures of 5, 15 and 20°C. These values were calculated using Equation 2.14 (page 66).

It can be seen, as expected, that the sorption constant decreases with the increase in crystallinity. This finding is in agreement with the literature, as sorption and transport events of small penetrant molecules in polymers are commonly understood to occur in the non-crystalline region of the polymer only (McDowell *et al.*, 1998; Duda and Zielinski, 1996) and the transport properties are sensitive to the fraction of the free volume in the polymer matrix (D'Aniello *et al.*, 2000; Mogri and Paul, 2001; Lützow *et al.*, 1999).

The increased sorption of acetaldehyde into PET is influenced, however, not only by the degree of crystallinity. By using the value of sorption at infinite time in Figures 4.13 and 4.14, one can calculate the extent of sorption of acetaldehyde in the amorphous domain, assuming that all the sorbed acetaldehyde is located only in the amorphous regions. Upon increasing the crystallinity from 18.5 to 29.7 for virgin PET, the sorption was reduced by a factor of 2.5. On the other hand, an increase in the crystallinity from 21.2 to 33.8% for the recycled PET, reduced the sorption by almost a factor of 20 (see also Table 4.6).

Table 4. 6. Values of the sorption constant of acetaldehyde in virgin and recycled PET, for different crystallinities at temperatures of 5, 15 and 20°C

Material	Crystallinity	$K_s \times 10^3$/mol g polymer^{-1}		
		5°C	15°C	20°C
PETvs	18.5 ± 1.0	2.4 ± 0.5	2.6 ± 0.4	2.7 ± 0.4
	19.8 ± 0.6	2.4 ± 0.3	2.4 ± 0.2	2.5 ± 0.2
	24.7 ± 1.0	1.9 ± 0.1	2.0 ± 0.5	2.1 ± 0.5
	29.7 ± 1.5	0.8 ± 0.1	1.1 ± 0.2	1.2 ± 0.5
PCR-PETs	21.2 ± 0.9	2.0 ± 0.5	2.2 ± 0.1	2.3 ± 0.1
	24.8 ± 0.3	1.0 ± 0.2	1.6 ± 0.1	2.1 ± 0.3
	28.9 ± 0.5	0.3 ± 0.0	1.1 ± 0.5	1.3 ± 0.2
	33.8 ± 0.9	0.2 ± 0.0	0.6 ± 0.0	0.73 ± 0.1

The data listed in Table 4.6 show a small increase in the sorption coefficient with the increase in temperature. Similarly, Aminabhavi *et al.* (1996b) found that the sorption of an aliphatic ester into tetrafluoroethylene (TFE) increases with temperature. Hedenqvist *et al.* (1993) also stated that the sorption equilibrium increases at higher temperatures. An increase in K_s with temperature confirms that there is an increased molecular mobility of polymer chain segments (Aminabhavi *et al.*, 1996b; 1996c). The increase in mobility can also be attributed to the swelling effect.

4.3.4 Differences in activation energy, enthalpy of sorption and entropy between virgin and recycled PET

The variation of the rate constant with temperature for the process of acetaldehyde sorption in virgin and recycled PET sheets is presented in Figures 4.15 and 4.16 as the plot of ln k versus the reciprocal of the absolute temperature.

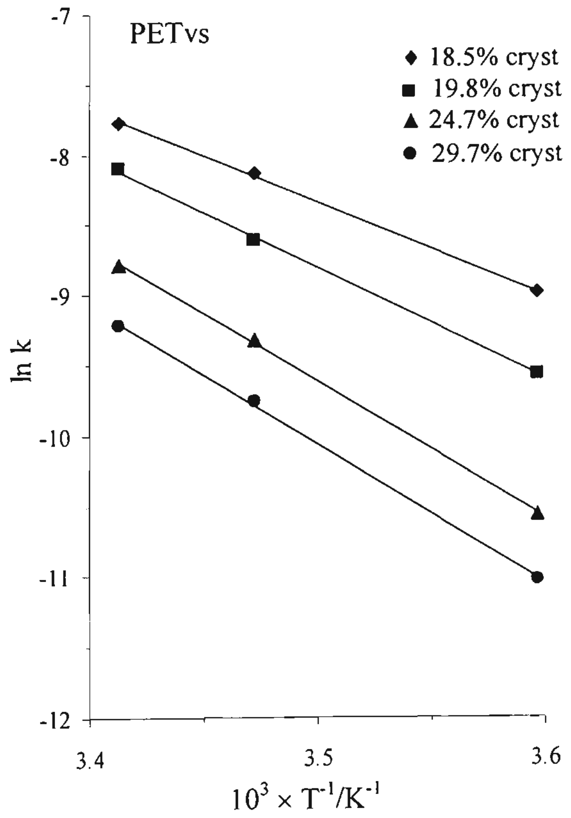


Figure 4. 15. Arrhenius plots of ln k versus 1/T for acetaldehyde absorption in virgin PET

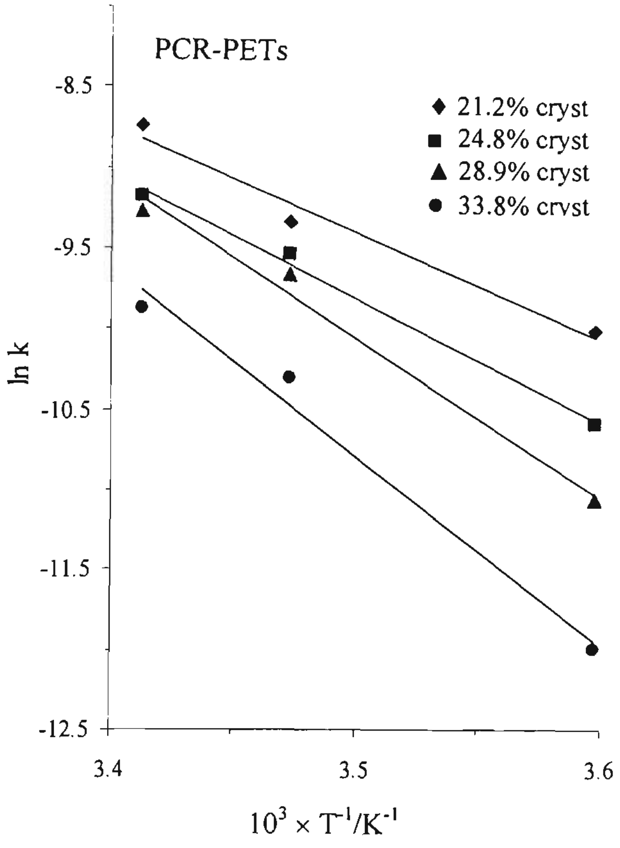


Figure 4. 16. Arrhenius plots of ln k versus 1/T for acetaldehyde absorption in recycled PET

The straight lines obtained suggest that an Arrhenius relationship (Equation 2.9, p. 65) might be applicable for this case and the activation energy can be derived from these plots.

From the Van't Hoff relation (Equation 2.17, page 67), the enthalpy of sorption, ΔH_S, and the entropy, ΔS, have been calculated from the slope and intercept, respectively (see Figures 4.17 and 4.18). Figure 4.17 shows a huge difference between PETvs, 24.7% crystallinity and PETvs, 29.7% crystallinity due to a dramatic decrease of the sorption values. However, the estimated activation energy derived from these plots shows little difference, as can be seen from Table 4.7 (about 80.7 kJ mol^{-1} for PETvs and 82.0 for PETvs).

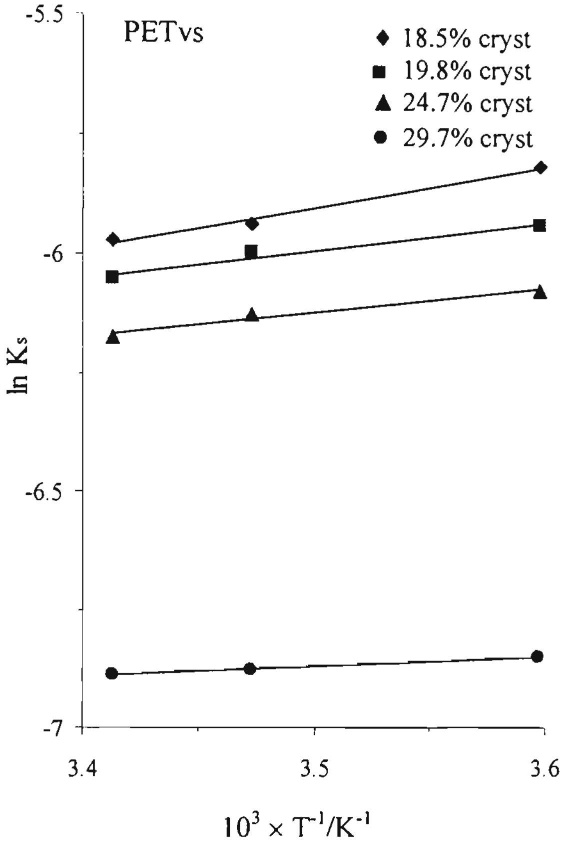


Figure 4. 17. Van't Hoff plot of ln K_S versus 1/T for acetaldehyde sorption in virgin PET sheet

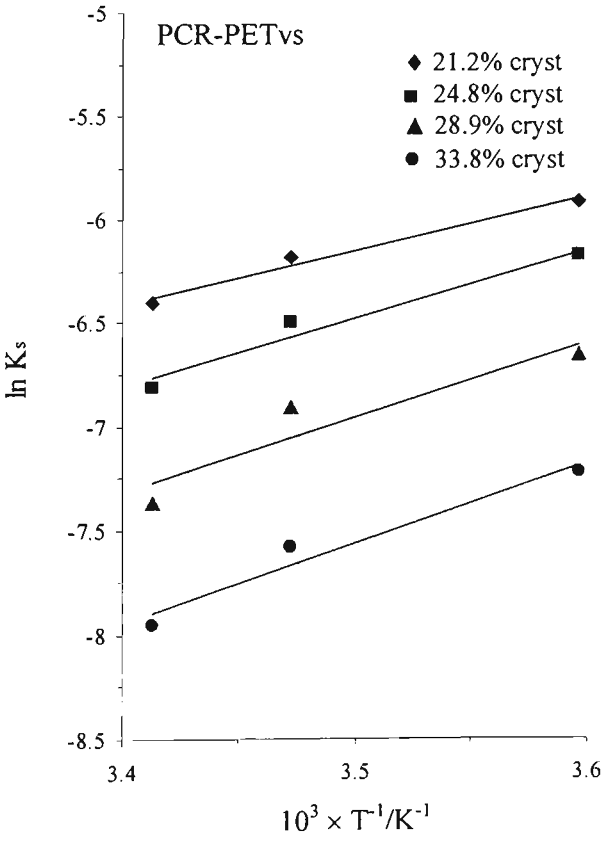


Figure 4. 18. Van't Hoff plot of ln K_S vs 1/T for acetaldehyde sorption in recycled PET

The estimated activation energy, as well as the enthalpy and entropy for sorption of acetaldehyde in the PET sheets are summarized in Table 4.7.

Table 4. 7. Values of E_a, ΔH_s and ΔS for sorption of acetaldehyde in virgin and recycled PET

Material	Crystallinity/%	E_a/kJ mol^{-1}	ΔH_s/kJ mol^{-1}	ΔS/kJ mol^{-1} K^{-1}
PETvs	18.5 ± 1.0	55.5	-7.2	74.3
	19.8 ± 0.6	65.8	-5.0	67.5
	24.7 ± 1.0	80.7	-4.4	66.2
	29.7 ± 1.5	82.0	-1.8	63.3
PCR-PETs	21.2 ± 0.9	54.7	-21.7	126.9
	24.8 ± 0.3	64.0	-27.6	150.5
	28.9 ± 0.5	82.4	-30.0	162.8
	33.8 ± 0.9	98.3	-31.7	174.0

From Table 4.7, it can be observed that the activation energy increases as the crystallinity of the virgin PET and the recycled PET samples increases. This suggests that the higher the crystallinity of the PET, the more sensitive the acetaldehyde sorption process to changes in temperature. Increasing temperature brings about changes in the structure and morphology of the polymer. Aminabhavi and Shivaputrappa (1991) presented activation energy data for the effect of temperature and solvent type on the sorption process and reported that the activation energy increases with an increase in the degree of crystallinity.

However, the activation energy values resulting from the current study are much higher than those reported for other systems: 16.74 and 41.89 kJ mol^{-1} for sorption of methylene chloride ($MeCl_2$) and dimethyl formamide (DFM) respectively in unoriented PET film (Durning *et al.*, 1996). The high activation energy in the present study suggests that the crystallinity of the PET controls the movement of penetrant trough intra and inter chain cavities in the polymer matrix (Billovits and Durning, 1988). However, the present results are consistent with the value of 91 kJ mol^{-1} found by Billovits and Durning (1988) for the sorption of methanol in thermally annealed PET. The degree of crystallinity of the PETs samples reported by Durning *et al.* (1986) was 0.5 – 4.3% and 43% by Billovits and Durning (1988) while in the current study values ranging from 18 – 33% were found.

A wide variation in ΔH_s data of about 1.8 - 7.2 kJ mol^{-1} for PETvs and 21.7 – 31.7 kJ mol^{-1} for PCR-PETs was found in the current study as presented in Table 4.7. These values are consistent with published data for similar systems of some hazardous organic liquids absorbed into high-density polyethylene (Aminabhavi and Naik, 1999).

The negative values obtained for ΔH_s confirm that the interaction between acetaldehyde and PET is an exothermic process, as was also found by Aminabhavi and Naik (1999). Enthalpy of sorption, $\Delta H_{S,}$ is a composite parameter involving both Henry's law and Langmuir's sorption mechanism. It was assumed that Henry's law mode requires both formation of a site and the dissolution of species in that site. Formation of a site generally involves an endothermic contribution to this process. In the case of the Langmuir mode, the site already exists within the polymer matrix, and hence sorption by a hole filling mechanism produces more exothermic heats of sorption (Robertson, 1993; Aminabhavi *et al.*, 1996b). Therefore, the results in this present work suggest that the sorption is mainly dominated by a Langmuir sorption mode rather than a Henry's law mode. Exothermic reaction is generally spontaneous or, in other words, the sorption of acetaldehyde in PET occurs by itself if there is sufficient energy to achieve the activated complex (Smith, 1993).

It can be pointed out that increasing crystallinity results in a decrease of the enthalpy of sorption in the case of PETvs but, in contrast to this, the enthalpy of sorption increases in the recycled PET as the crystallinity of the polymer is increased. Similar observations can be made regarding the entropy values. The reason for this may be due to differences in the extent of disorder within the two types of samples. These results are consistent with the notion that the increased degree of crystallinity in the virgin PET is achieved by an increase in the original crystalline size without increasing on the number of crystallites. On other hand, the increased degree of crystallinity in the recycled PET may have been achieved by increasing the number of crystallites with the crystalline size remaining small. Some low molecular weight compounds (like impurities) contained in the recycled PET might play a role as an active site for the formation of such small crystallites. The bigger the size of the crystallites, the more ordered the crystalline structure within the polymer is, thus, a lower entropy value is observed. In contrast, the greater the number of crystallites, the more general disorder within the ensemble which, in turn, is responsible for the higher entropy that is exhibited by the recycled samples. This is a major conclusion of the work.

4.3.5 Differences in mechanism of transport between virgin and recycled PET

To investigate the mechanism of solvent transport within the PET materials, the sorption results have been fitted using Equation 2.19 (page 68) for the short-term sorption process (i.e. before the attainment of 50 – 55% of the equilibrium sorption values). The values of n and K_1 are given in Table 4.8.

As the exposure temperatures of sorption applied in the present study were below the glass temperature of PET ($T < T_g$), the characteristics of the transport should be between pseudo Fickian and Case II as indicated in a review of major equations (Mercea, 1999)..

Table 4. 8. Estimated values of n and K_1 from Equation 2.19 (page 68)

Material	Crystallinity/ %	n			$K_1 \times 10^3$		
		5°C	15°C	20°C	5°C	15°C	20°C
PETvs	18.5 ± 1.0	0.3	0.2	0.3	43.2	80.8	119.9
	19.8 ± 0.6	0.6	0.3	0.3	2.2	47.8	86.1
	24.7 ± 1.0	0.7	0.6	0.4	1.0	6.2	61.0
	29.7 ± 1.5	0.7	0.7	0.7	0.2	0.6	2.4
PCR-PETs	21.2 ± 0.9	0.6	0.4	0.3	1.0	12.3	67.6
	24.8 ± 0.3	0.7	0.5	0.4	0.4	4.5	7.7
	28.9 ± 0.5	0.9	0.5	0.6	0.1	2.4	3.3
	33.8 ± 0.9	1.5	0.6	0.6	0.1	1.2	2.4

In this study, Equation 2.19 (page 68), assumes a constant K or no swelling effect. This is probably not the actual case in reality. As acetaldehyde penetrates into the PET, swelling increases. Further acetaldehyde molecules can thus penetrate more easily and faster. If the swelling effect is taken into account, a more appropriate relationship in which K is concentration dependent and hence time dependent, should be used.

The values of n and K_1 vary between 0.2 - 0.7 and 0.2 – 119.9 for virgin PET and in the range of 0.3 – 1.5 and 0.1 – 67.6 for the recycled PET sheet respectively. The n value shows a systematic trend with the degree of crystallinity and temperature except in a few cases. For instance, n decreases with an increase in temperature suggesting that the transport mechanism of acetaldehyde in PET is temperature dependant. The value of n increases with increasing crystallinity. This suggests that the mechanism of transport changes from a Pseudo-Fickian mechanism ($n < 0.5$) for samples that exhibit low crystallinity to an anomalous behavior ($0.5 < n < 1$) or even to the "Super Case II" ($n > 1$) for the samples that possess a high degree of crystallinity as suggested by Urdahl and Peppas (1987).

A value of $n = 1.5$, indicating a "Super Case II" mechanism, has been found for the sample with the highest degree of crystallinity, i.e PCR-PETs that was annealed for 10 min at 120°C and the absorption was carried out at the temperature of 5°C (see Table 4.8). This suggests that the diffusion process is very rapid in comparison with the relaxation processes of the penetrant-polymer system (Mercea, 1999). Similar findings of Super Case II transport was reported by Urdahl and Peppas (1987) for cyclohexane in a highly crosslinked polystyrene sample at 20°C.

From Table 4.8 it can be seen that the values of K_1 increase systematically with increasing temperature. Such behaviour has also been observed elsewhere (Aminabhavi *et al.*, 1997; Aminabhavi *et al.*, 1996a; Aminabhavi and Naik, 1999). An increase in the K_1 values was expected with a decrease in the degree of crystallinity of the PET samples since the K_1 value directly corresponds to the diffusion coefficient (see Equation 2.18 and 2.19). It will be demonstrated later that the crystallinity of the polymer samples affects the diffusion coefficient (see Section 4.3.6).

The effect of the crystallinity on the mechanism of transport of acetaldehyde sorption is also apparent in the plot of the fractional mass uptake, M_t/M_∞ versus the square root of time, $t^{1/2}$ (Figure 4.19 and 4.20).

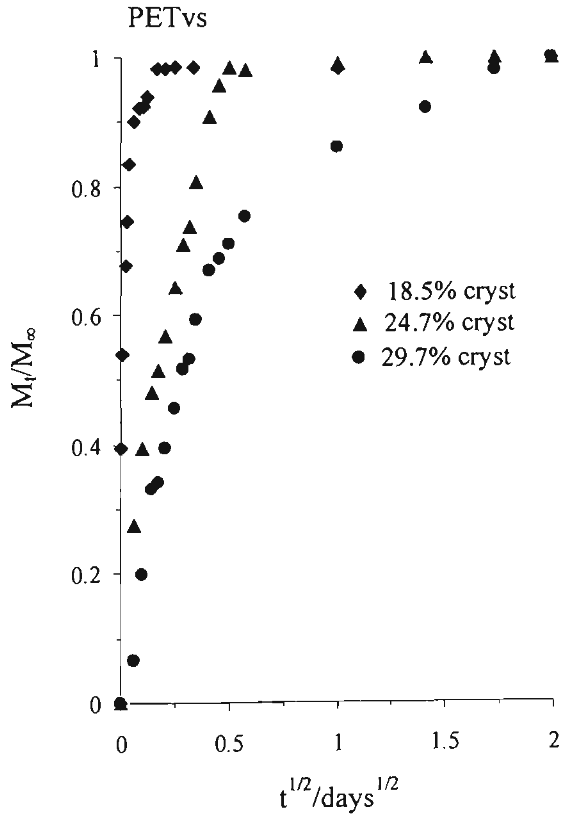


Figure 4. 19. Fractional mass uptake of acetaldehyde, M_t/M_∞, versus $t^{1/2}$, at 15°C for virgin PET

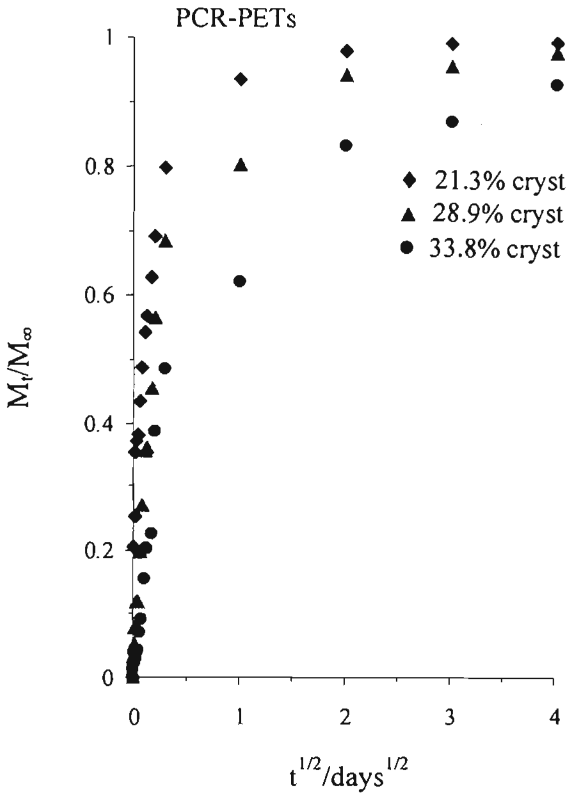


Figure 4. 20. Fractional mass uptake of acetaldehyde, M_t/M_∞, versus $t^{1/2}$, at 15°C for recycled PET

The initial linear portions of the plots of M_t/M_∞ vs $t^{1/2}$, are in particular indicative of a Fickian mechanism of transport and have been found for PET samples with the lowest crystallinity (PETvs, 18.5% crystallinity). Similar Fickian behaviour was observed for semi-crystalline PET in the presence of methylene chloride vapour (Aminabhavi and Munnolli, 1994).

A sigmoidal curve, indicating a slight deviation from the Fickian mechanism, is observed for the PET sample with the highest crystallinity (PCR-PETs, 33.8% crystallinity). As described by Billovits and Durning (1988), sorption of an organic compound into a high crystallinity polymer usually shows an induction period and is accompanied by non-Fickian transport between the two limits of classical and "Case II" sorption.

Figures 4.21 and 4.22 show the percentage of mass gain of the virgin and recycled PET sheet upon the uptake of acetaldehyde as a function of time for samples with the same thickness but having different crystallinities at 5°C. This plot reveals a linear curve at the beginning followed by a plateau.

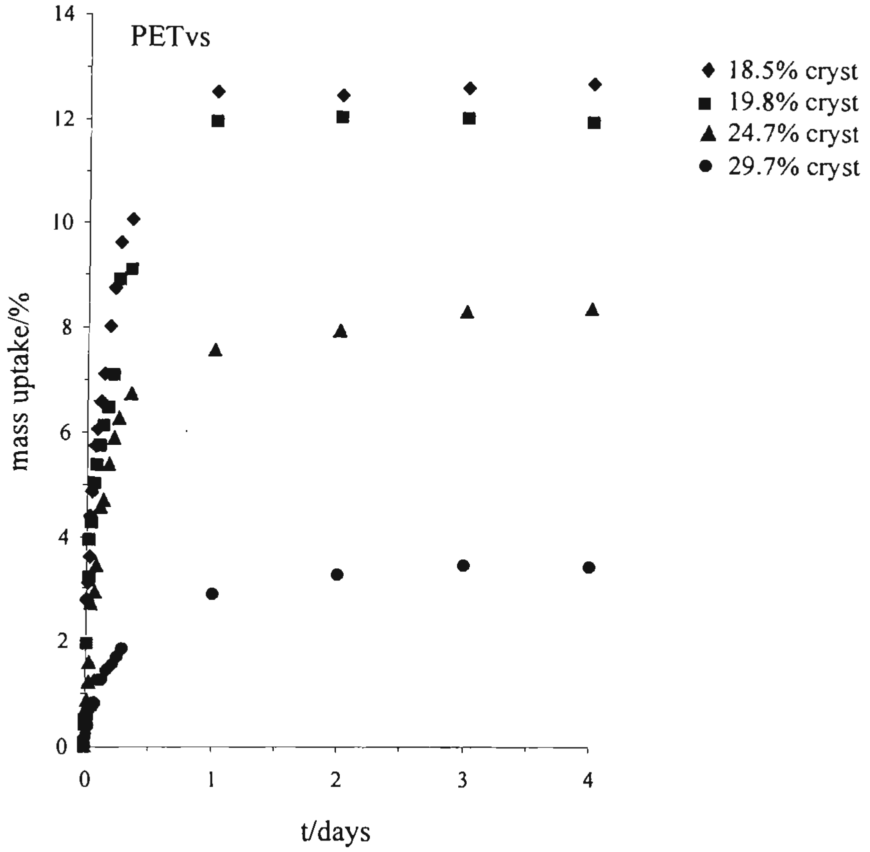


Figure 4. 21. Plot of % mass gain versus t at 5°C for acetaldehyde in virgin PET of different degrees of crystallinity

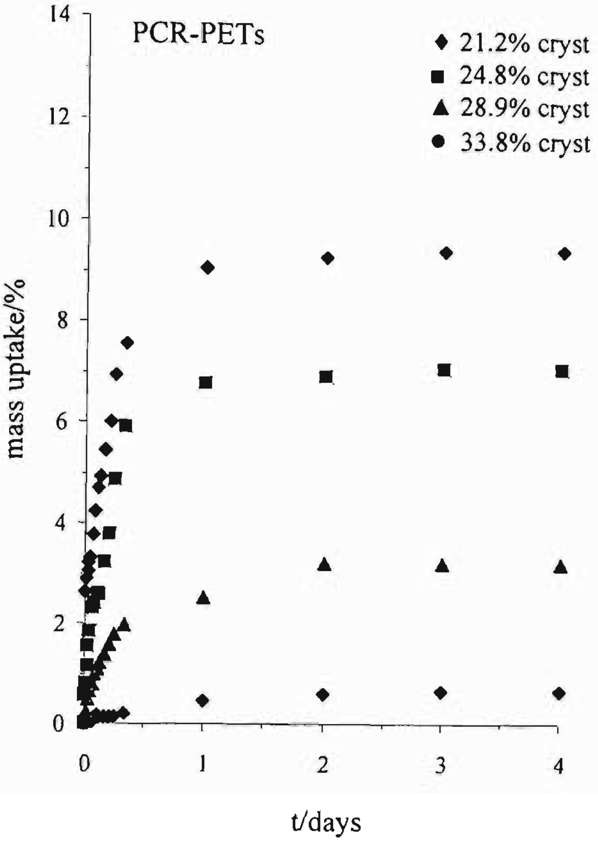


Figure 4. 22. Plot of % mass gain versus t at 5°C for acetaldehyde in recycled PET of different degrees of crystallinity

These data demonstrate that the extent of mass uptake depends on the polymer structure. A comparison of the initial portion of these curves reveals there is a difference in the time required for the samples to reach equilibrium. In general, the lower the crystallinity of the polymer, the faster the initial solvent uptake rate and the shorter the time required to reach equilibrium. For example, the most crystalline sample (PCR-PETs, 33.8% crystallinity), required the longest time to reach equilibrium, approximately 4 days, whereas the PCR-PETs (21.2% crystallinity) and PCR-PETs (24.8% crystallinity) samples reached equilibrium after approximately 1 day and 2 days respectively (see Figure 4.22). In addition, the uptake data suggest that the higher the crystallinity, the lower is the solvent uptake by the polymer.

Similar results to these were reported by Begley *et al.* (2002) with regard to lindane sorption into PET. They found that oriented PET sorbed lindane nine times less effectively (on the mass/mass basis) than amorphous PET. Markarewicz and Wilkes (1978) and Nir *et al.* (1996) also reported a similar effect of lower sorption of organic liquids (ethanol and toluene) in PET at a higher crystallinity and/or chain orientation.

Another interesting phenomenon is the apparent change in the slope of the initial solvent uptake versus time plots as was observed for the samples of higher crystallinity at a low temperature (recycled PET, 33.8% crystallinity, 5°C). This change is often indicative of Case II (non-Fickian) transport or Super Case II transport (Urdahl and Peppas, 1987) as is evident from the n values in Table 4.8.

4.3.6 Differences in diffusion coefficient between virgin and recycled PET

The diffusion coefficients were calculated from the initial rate of sorption using Equation 2.30, page 72. As expected, the diffusion coefficient value, D, decreased with increasing degree of crystallinity of the samples and increased with increasing soaking temperature. The calculated values of D for the sorption process are presented in Table 4.9. Appendix B presents an example for the calculation of D.

Table 4. 9. Diffusion coefficients at temperatures of 5, 15 and 20°C for acetaldehyde in PET for different crystallinities

Sample	Crystallinity	$D \times 10^9$ /cm ^{2}s^{-1} 5°C	15°C	20°C
PETvs	18.5 ± 1.0	4.4	27.2	32.3
	19.8 ± 0.6	4.1	11.1	25.2
	24.7 ± 1.0	2.1	7.5	13.5
	29.7 ± 1.5	0.9	4.6	3.1
PCR-PETs	21.2 ± 0.9	1.4	9.5	19.2
	24.8 ± 0.3	1.9	7.2	8.7
	28.9 ± 0.5	0.9	2.1	3.1
	33.8 ± 0.9	0.7	1.7	2.0

A decrease in the diffusion coefficient of sorption with an increase in the degree of crystallinity of the polymers was also found by other investigators (Lützow *et al.*, 1999; Neway *et al.*, 2004; D'Aniello *et al.*, 2000). The general concept is that an increase in crystallinity will result in a decrease in solvent mobility (Crank and Park, 1978). Qureshi *et al.* (2000) found that crystallization by heat treatment of PET samples above its glass transition temperature caused a dramatic decrease in the diffusion coefficient. However, the functional relationship between the degree of crystallinity and the diffusion coefficient does not necessarily follow the simple linear relationships found in this study.

The diffusion coefficient values for the recycled PET were found to be much lower than those for the virgin polymer. This is believed to be due to the higher degree of crystallinity of the recycled material. A number of investigators (Lützow *et al.*, 1999; D'Aniello *et al.*, 2000) have reported similar findings. Nir *et al.*, (1996) found that the diffusion coefficient of toluene in amorphous PET was six times higher than that in blow moulded PET possessing a higher degree of crystallinity. In the present study, PCR-PETs (33.8% crystallinity) at the soaking temperature of 5°C exhibited the lowest D value of 0.7×10^{-9} cm^2 s^{-1}, while the highest value, 32.3×10^{-9} cm^2 s^{-1}, was observed for PETvs (18.5% crystallinity) at the soaking temperature of 20°C.

Diffusion values calculated from the current sorption studies of acetaldehyde in PET are significantly higher than the values found by some other researchers who diluted a solvent prior to the sorption experiment or used a solvent in the vapour rather then the liquid phase. Sadler *et al.* (1996) reported D values derived from sorption studies in PET ranging from 10^{-9} to 10^{-16} cm^2 s^{-1} for 10 – 60% (v/v) benzene in hexadecane at 25°C. Whereas Patton *et al.* (1984) reported the value of 6.7×10^{-14} cm^2 s^{-1} for benzene vapour at 60°C. The high values of the diffusion coefficient found in the present work are probably due to the direct contact of PET with neat acetaldehyde resulting in swelling of the polymer. However, diffusion coefficients that were derived from sorption studies and that are similar in magnitude to the values found in the current work, were reported by Nir *et al.* (1996) and Miltz *et al.* (1997). These values were about 2.9×10^{-9} cm^2 s^{-1} and 15×10^{-9} cm^2 s^{-1} for toluene and benzyl alcohol in PET respectively at a temperature of 34°C. Diffusion coefficients for other organic liquids in PET as reported by Aminabhavi *et al.* (1996b) are also similar in order of magnitude to those obtained in the present study.

A clear dependence of the diffusion coefficient on the temperature of soaking was observed for both the virgin and the recycled PET samples. The equilibrium acetaldehyde concentrations sorbed into the PET are 342, 480 and 517 mg dm^{-2} for PETvs and 304, 374 and 419 mg dm^{-2} for PCR-PETs at the temperatures of 5, 15 and 20°C respectively. These values are much higher than the value of about 9.3 mg dm^{2} reported by Demertzis *et al.* (1997) for sorption of ethylene glycol into PET. Acetaldehyde used in the present study is apparently more aggressive compared to the ethylene glycol as represented by the solubility parameter (δ) value. It was reported that the solubility parameter of acetaldehyde is 9.7 $cal^{1/2}$ $cm^{-2/3}$ whereas ethylene glycol is 16.9 $cal^{1/2}$ $cm^{-2/3}$ (Yaws, 1999) and that of PET is 10.7 $cal^{1/2}$ $cm^{-2/3}$ (Brandrup *et al.*, 1998). However, in some cases (Nir *et al.*, 1996), toluene caused a large mass gain of 11% in PET, comparable to, the highest mass gain of 12% found in the present study.

During the current sorption studies, a reduced clarity of the PET samples was noticed. This result may stem from swelling, crystallization, crazing or cracking. According to McDowell *et al.* (1999), solvents that are sorbed into PET may induce crystallization that creates opaque areas in the polymer. Furthermore, they also suggested that in such situations the polymer might lose some of its desirable physical properties.

The logarithm of the diffusion coefficient versus the reciprocal of the absolute temperature is plotted in Figures 4.23 and 4.24 for the virgin and recycled PET respectively.

As can be seen, such an Arrhenius plot does not result in straight lines, especially not for the PETvs. Therefore, the activation energies for diffusion, E_{aD}, could not be determined reliably from the slopes of these plots. The conclusion reached from these data may not be totally reliable as one cannot strictly assume $n = 0.5$ in this case.

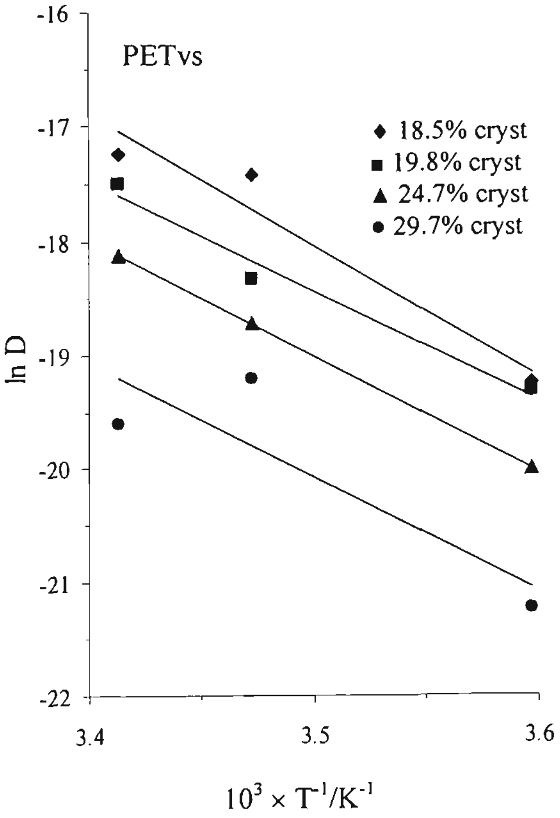


Figure 4. 23. Plot of ln D versus 1/T for acetaldehyde in virgin PET.

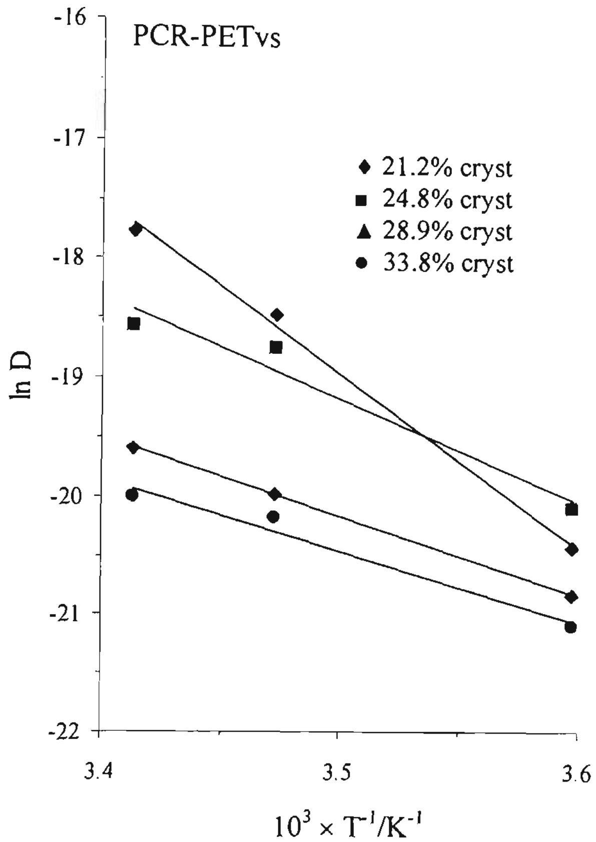


Figure 4. 24. Plot of ln D versus 1/T for acetaldehyde in recycled PET

4.3.7 Concentration profiles using a numerical method

In many cases, numerical schemes using the finite difference method are used to calculate the liquid concentration profile in a polymeric material (Crank, 1968; Vergnaud, 1991; Neogi, 1996).

Concentration profiles, $C_{(t,x)}/C_s$, of acetaldehyde along the depth (thickness) of a PET slab were calculated using Equation 2.24 (page 70) with the following assumptions: (i) a constant D and (ii) no mass transfer coefficient is applicable at the interface. A consequence of this approximation is that all calculated profiles intersect at the same concentration on the axis corresponding to the material surface. However, in practice, this may be very different. A software package MATLAB® version 6.5.1 was used to produce a numerical output. The D values used for the calculations are given in Table 4.9. The computer program and display of the output of the program are provided in Appendixes C.1-C.2.

The simulated concentration profiles of acetaldehyde at 5°C for sorption cycles after a lapse of 5 h for both PETvs (18.5% crystallinity) and PCR-PETs (21.2% crystallinity) samples are displayed in Figure 4.25 (a and b respectively).

The concentration profiles suggest a dependence on the degree of crystallinity i.e. the morphology of the polymer. For PETvs, the profiles at different times are widely spaced, suggesting a quick transport (i.e. high diffusivity) of acetaldehyde into the polymer. On the other hand, for the PCR-PETs (higher crystallinity), the concentration profiles are narrowly spaced, suggesting a slow transport (i.e. low diffusivity).

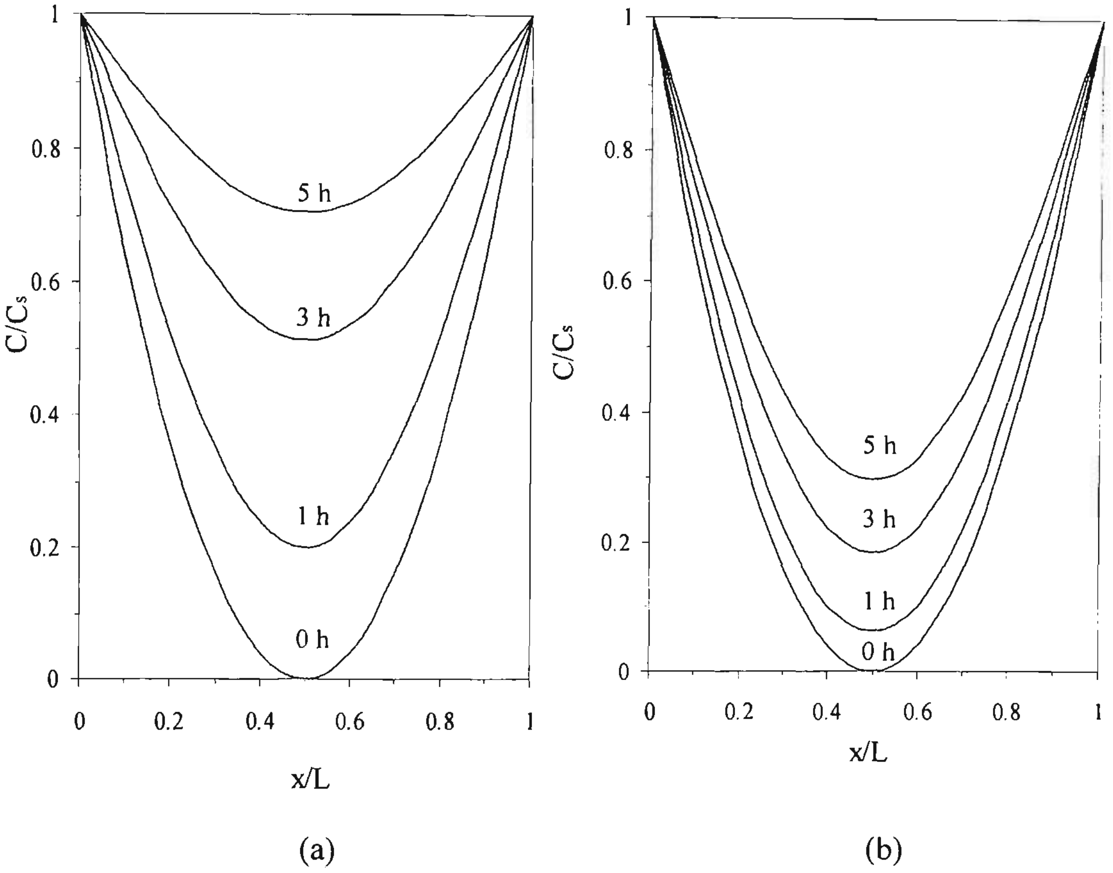


Figure 4. 25. Simulated concentration profiles of acetaldehyde from numerical calculations (Equation 2.24) for (a) PETvs (18.5% crystallinity), D = 4.4 × 10^{-9} cm^2 s^{-1} and (b) PCR-PETs (21.2% crystallinity), D = 1.4 × 10^{-9} cm^2 s^{-1}

Figure 4.26 shows more clearly the effect of the degree of crystallinity on the concentration profiles both for virgin and recycled PET after 1 h soaking at a temperature of 15°C.

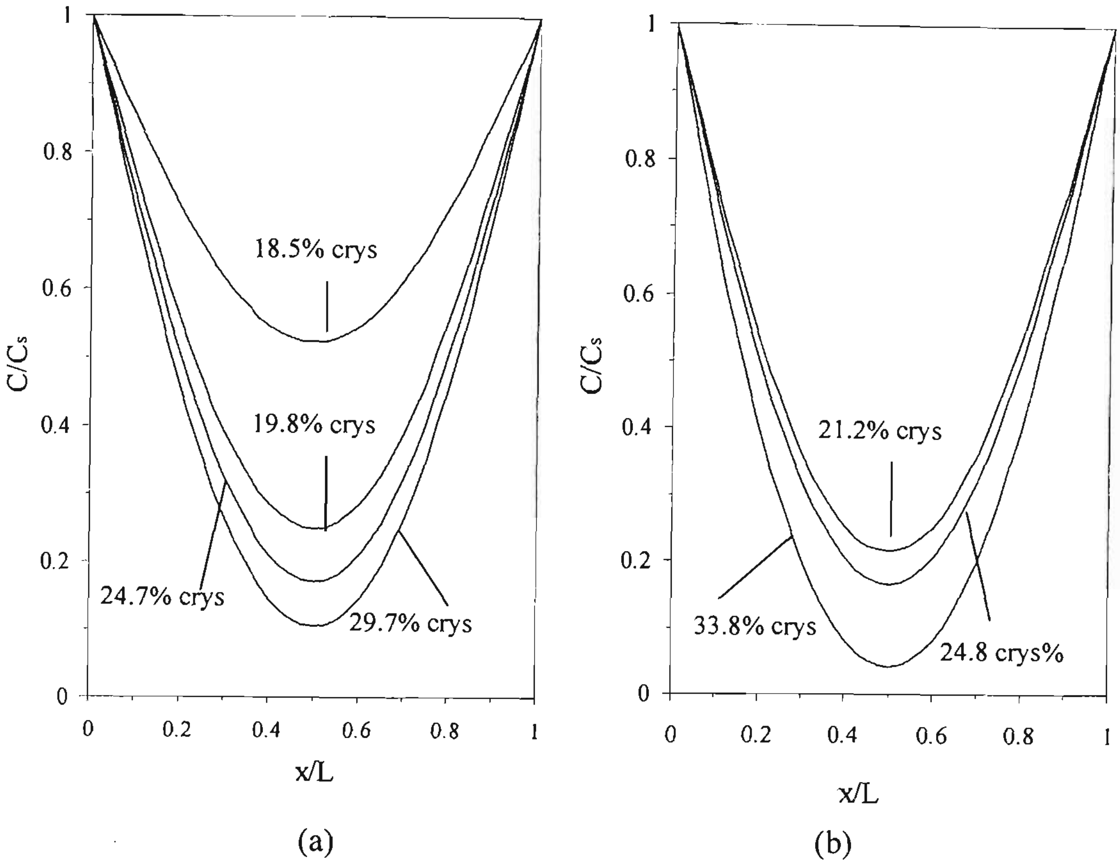


Figure 4. 26. Simulated concentration profiles of acetaldehyde from numerical calculations (Equation 2.24) for (a) PETvs and (b) PCR-PETs of different crystallinities after 1 h of soaking at a temperature of 15°C

Clearly, an increase in the crystallinity of a polymer inhibits the motion of the polymeric chains and of acetaldehyde. The next figures show the dependence of the concentration profile on temperature. Figure 4.27 shows that at 20°C the concentration profiles are at higher values than those observed at 5°C due to the higher diffusivity. Furthermore, the concentration profiles of acetaldehyde at 5°C are more narrowly spaced than those at 20°C, indicating the increased diffusivity at the higher temperature attributable to the free movement of the liquid molecules into the polymer as well as the movement of the polymer chains in the matrix.

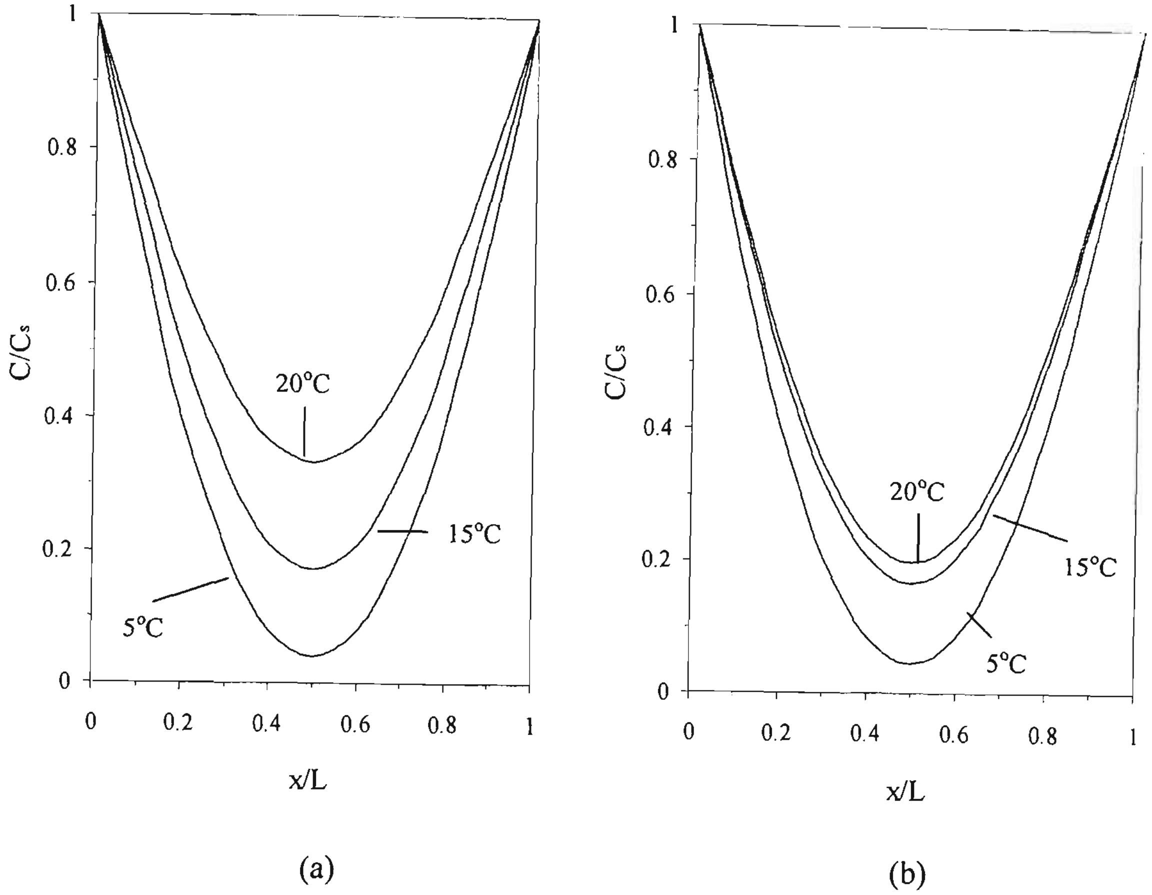


Figure 4. 27. Simulated concentration profiles of acetaldehyde from numerical calculations (Equation 2.24) for (a) PETvs (24.7% crystallinity) and (b) PCR-PETs (28.9% crystallinity) at different temperatures after 1 h of soaking

4.4 Overall Migration

One objective of the present work was to identify the total residue that could be released from the polymer sample into food simulants and to learn about the compliance of the samples with the level enforced by legislation (EU and the US FDA), especially for high-temperature applications. Study has been performed using two different testing methods namely: (i) conventional total-immersion method and (ii) reflux method. The first method was carried out by following a standard (European Standard EN 1186-3, 1999; European Pre-Standard ENV

1186-15, 1999), while the second method is a modification of the first method by extracting the polymer, for certain period of time, using a Soxhlet apparatus and then continuing the exposure in an oven as in the conventional method (see Section 3.2.5.2).

4.4.1 Conventional total-immersion method

The overall or global migration results obtained by the conventional total-immersion method with various PET samples are presented in Figure 4.28.

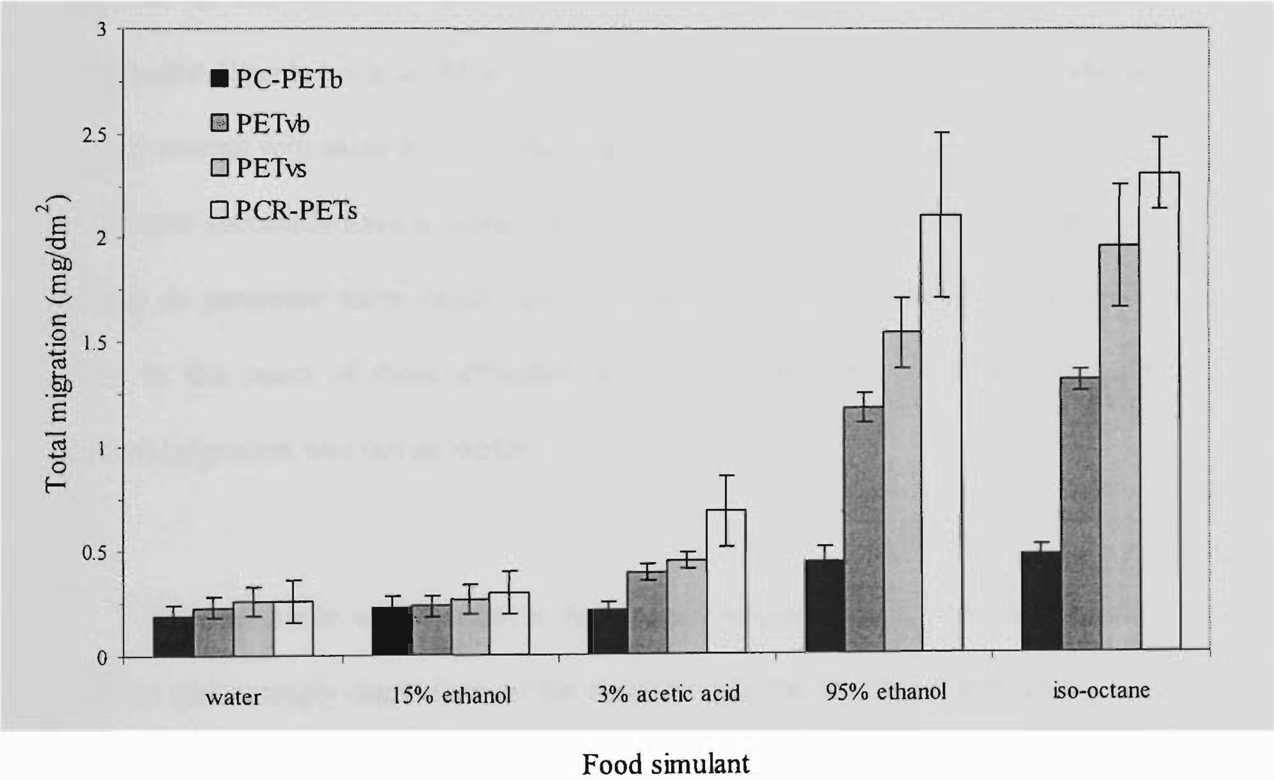


Figure 4. 28. Overall migration from PET in different food simulants obtained in the conventional total-immersion method (see Table 3.1 for test conditions). Migration values are means ± standard deviation of three determinations

A comparatively large global migration was found with iso-octane and PET. There is generally little interaction between PET (a polar polymer) with iso-octane (an apolar solvent) and so the increased global migration found in the recycled PET, is interesting. This may be due to the increased amorphous content of the recycled PET and that the iso-octane can penetrate these regions more effectively.

The total amount of migrating species was in the range of 0.2 – 2.3 mg dm^{-2}. These results indicate that when using the standard simulants, the overall migration of all four PET samples was below the upper limit (10 mg dm^{-2}) allowed by Directive 90/128/EEC (Commission Directive, 1990). The more aggressive liquids such as 95% (v/v) aqueous ethanol and iso-octane produced higher overall migration levels compared to the aqueous simulants. It is believed that these simulants have a higher solubility in the polymer and, hence, have the ability to penetrate more easily and to extract the small molecules. However, even in the cases of these efficient extraction agents, the permitted limit for overall migration was not exceeded.

The behaviour with respect to the overall migration was found to be quite diverse and strongly dependent on the structure and nature of the simulants. The results indicate an increasing overall migration trend in the order: water < 15% (v/v) aqueous ethanol < 3% (v/v) aqueous acetic acid < 95% (v/v) aqueous ethanol < iso-octane. This is probably also an indication of the relative "strength" of the different food simulants as extracting agents. The results obtained in the present study are in agreement with migration results reported by Galotto and Guarda (1999) and O'Brien *et al.* (2000) who found that 3% (v/v) aqueous acetic acid showed a greater extraction capability of the migrants from the polymeric samples than 15% (v/v) aqueous ethanol and water, with fatty food simulant being the most efficient for extraction. It is also consistent with the general recognition that fatty food simulants represent the worst-case scenario expected for migration.

Several parameters affect the level of migration. It has been reported that the migration into the food-contact phase is controlled by: (i) diffusion of the migrant through the polymer (Katan, 1996); (ii) nature of the foodstuff in regards to its fat, water, acid content, etc. (Lau and Wong, 1996); (iii) concentration and the chemical affinity of the migrant in the polymer (Galotto and Guarda, 1999); (iv) time, temperature and relative humidity of exposure (Goydan *et al.*, 1990; Lau and Wong, 1996; De Kruijf and Rijk, 1994) and (v) residual mechanical stresses (Choudhry *et al.*, 1994; 1998)

The results of the current study show that iso-octane testing at 40°C for 1 day is very aggressive and results in comparable values to 95% (v/v) ethanol at 50°C for 1 day, although iso-octane and ethanol interact differently with PET. In many cases the two solvents cause polymer swelling (Garde *et al.*, 2001). However, iso-octane does not plasticize PET, whereas ethanol does. The masses of material extracted from the samples by the 95% (v/v) aqueous ethanol and iso-octane are not significantly different as indicated by the standard deviation data. Thus, the results suggest 95% (v/v) ethanol can be used as an alternative fatty food simulant even though ethanol is different in molecular weight, chemical structure and polarity than most fats and oils. According to De Kruijf *et al.*

(1983b), the tests with 95% (v/v) ethanol for 1 day at 50°C gives comparable results to those obtained with olive oil at 40°C for 10 days so that this medium can be used as a fatty food simulant in a rapid and simple test to determine global migration from packaging materials.

It should be pointed out that the lowest migration value in water shows that water is the least aggressive food simulant. Similar results were reported by Galotto and Guarda (1999) and O'Brien *et al.* (2000). In general, the migration levels obtained from all samples into water and 15% (v/v) aqueous ethanol at 40°C for 10 days were not significantly different as indicated by the standard deviation data.

As is apparent from Figure 4.28, there was no statistically difference in the overall migration values into aqueous food simulants between PETvs and PETvb where the values became statistically different in the fatty simulants. The statistically analysis comprised of an analysis of variance. The level of total migration from PETvs was higher than that for the PETvb. The crystallinity of the two samples might affect the mass extraction process. The higher the crystallinity of the sample, the more difficult it is for the food simulant to penetrate the polymer and the less mass can be extracted from the sample. This result is confirmed from the heat of fusion of the two samples as shown in Table 4.10. By dividing the heat of fusion in the second column in Table 4.10 by the heat of fusion of 100% crystalline PET (≅ 120 J/gram) (Robert, 1969; Vilanova *et al.*, 1985; Jayakannan and Ramakrishnan, 1999), the degree of the crystallinity of the polymer is obtained as presented in the third column of Table 4.10. From this table it is evident that the bottle material had a higher degree of crystallinity than the sheet type PET.

Table 4. 10. Heat of fusion and crystallinity of PETvb and PETvs

Sample	Melting temperature (T_m)/ °C	Heat of fusion/J g^{-1}	Crytallinity/%
PETvb	247.9 ± 1.1	34.9 ± 1.5	29.1 ± 1.2
PETvs	246.0 ± 1.2	22.2 ± 1.3	18.5 ± 1.0

It was also observed that the PETvb presented a higher value of overall migration compared to PC-PETb. This may be attributed to some of the adjuvants having migrated into the product that was originally contained in the bottle.

The results obtained in the present study show that the PCR-PETs exhibited the highest level of overall migration compared to the other types of PET samples. The migration values for the recycled material can probably be attributed to higher levels of oligomers and other low-molecular weight degradation products. Bryk (1991) has pointed out that during recycling, the polymer may undergo degradation by thermal decomposition or by thermo-mechanical stresses that may produce significant amounts of oligomers. Incarnato *et al.* (1998) also reported an increase in the level of total migration, particularly into fatty simulants, after every recycling operation. However, the values found in the current study were still within the legal limits. Based on the overall migration results, the PCR-PET material evaluated in the present study is suitable for food packaging applications at temperatures of up to 40°C. The overall migration from the different PET samples (PC-PETb, PETvb, PETvs and PCR-PETs) at elevated temperatures will be dealt with in a following section.

4.4.2 Reflux method

Until recently, the largest application of PET was in blow moulded carbonated and non-carbonated beverage bottles. Another application of PET is microwave-able and oven-able containers (especially the crystallized PET (CPET)) for reheating, cooking and crisping of foods in a microwave or conventional oven. With regards to such applications, it is important to review the total migration from PET at elevated temperatures.

The study was conducted using the appropriate temperatures suggested by the Council Directives 82/711/EEC (1982) and EN 1186-1 (1999). Regarding Table 2.4, the reflux temperature of the food simulant was used with the contact time of 2 h for aqueous simulants (water, 15% (v/v) ethanol in water, and 3% (v/v) acetic acid in water) and 30 min for the alternative fatty food simulants (iso-octane and 95% (v/v) ethanol in water). The exposure time was then continued for a total of 10 days at 40°C for aqueous food simulants, 1 day at 40°C for iso-octane and 1 day at 50°C for 95% (v/v) ethanol in water. The 2 h period of exposure in the reflux was chosen based on the assumption that this is the maximum period occurring in practice for oven cooking of such foods (long time baking/roasting) as given in recipes or cook books. Due to the extreme aggressiveness of the 95% aqueous ethanol and iso-octane, the minimum period of exposure suggested by EC Directive (30 min) was applied. Therefore, this method can be considered as a relatively short-term exposures at high temperatures.

The maximum temperature applied in this study was 100°C (boiling point of water), although in some applications a considerably higher temperature may be reached during food preparation as was demonstrated by Nerin *et al.* (2001). They measured the temperature profiles of some plastic containers that had been in microwave oven (without a product) and found that most of the plastic including PP and PC reached temperatures higher than 180°C after heating for 5 min. Some commercially available containers such as CPET are also recommended for preparing caramel, which implies temperatures of well above 100°C (Nerin *et al.*, 2002).

Figure 4.29 shows the results obtained by the reflux method. The migration behaviour is similar, in behaviour, to the conventional method. However, the migration levels obtained by the reflux method are significantly higher, as could have been expected, than those obtained by the conventional method. The high temperatures accelerate the migration. The higher temperatures may also lead to the formation of degradation products that may not occur at the lower temperatures.

From figure 4.29, it can be seen that iso-octane and 95% ethanol are the most aggressive food simulants followed by 3% aqueous acetic acid, 15%

aqueous ethanol, and water. Based on the polymer samples, the total migration values decrease in the following order: PCR-PETs > PETvs> PETvb > PC-PETb.

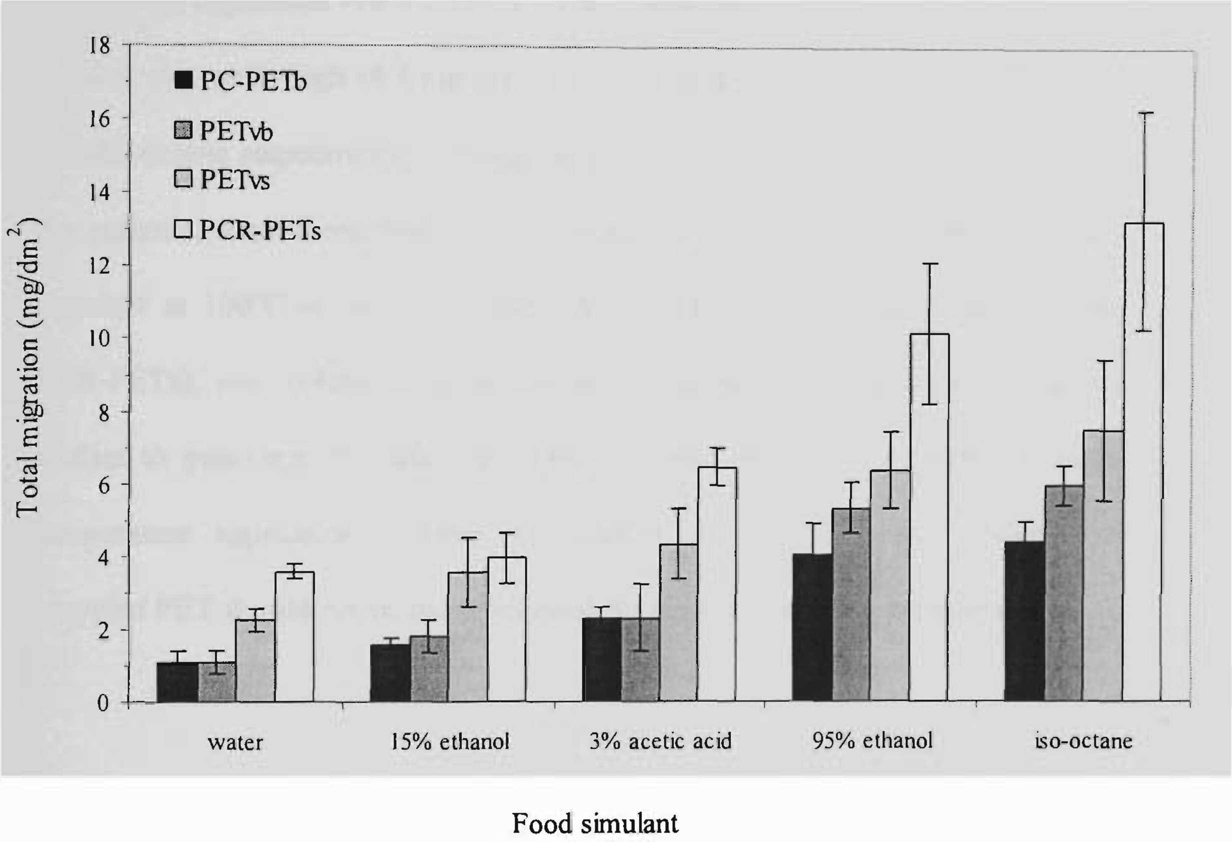


Figure 4. 29. Overall migration from different PET samples for different food simulants obtained in the reflux method. Migration values are means ± standard deviation of three determinations

The levels of overall migration in the present study are in the range of 1.1 – 6.5 mg dm^{-2} for aqueous food simulants and 4.1 – 13.3 mg dm^{-2} for the fatty food simulants. These values are about 10 times higher than the values obtained by the conventional method: 0.2 – 0.7 mg dm^{-2} for the aqueous food simulants and 0.5 – 2.3 mg dm^{-2} for the fatty food simulants.

An overall migration of 13.3 and 10.2 mg dm^{-2} was found for the recycled PET sheet in contact with iso-octane and 95% ethanol in water respectively. It should be pointed out that the values obtained for these fatty food simulants are higher (for the former simulant, and limiting for the latter one) than the values allowed by regulation (10 mg dm^{-2}). The overall migration from the virgin PET sheet is also quite high (6.4 mg dm^{-2} and 7.5 mg dm^{-2} into 95% aqueous ethanol and iso-octane respectively) although still below the allowed limit. Even though the potential overall residual compounds released from PET into the fatty food simulant at 100°C is lower than the GMLs included in EU legislation (except PCR-PETs), non volatile compounds should be taken into account in further studies to guarantee the safe use of those containers when proposed for high-temperature applications. From the present results it becomes evident that recycled PET should not be recommended for high-temperature applications.

4.5 Migration Studies of Acetaldehyde from PET into Food Simulants

4.5.1 Stability of acetaldehyde in water

The experiment was aimed at evaluating the stability of acetaldehyde in water prior to undertaking the migration studies. The experiment was carried out at room temperature and 40, 60 and 80°C. The results are presented in Figure 4.30.

The results obtained suggest that the acetaldehyde is stable at temperatures up to 40°C. A small variation in the measurement is observed, however it is still within the 98% range of confidence. At the higher temperatures of exposure of

60°C and 80°C, a decrease of about 6% and 20% in the acetaldehyde content respectively was observed during 11 days storage. The loses stem probably from acetaldehyde evaporation during the periods when the vials were opened in order to take out 1 mL aliquot for analysis. Therefore, precautions were taken in all experiments to ensure minimum losses during sample taking.

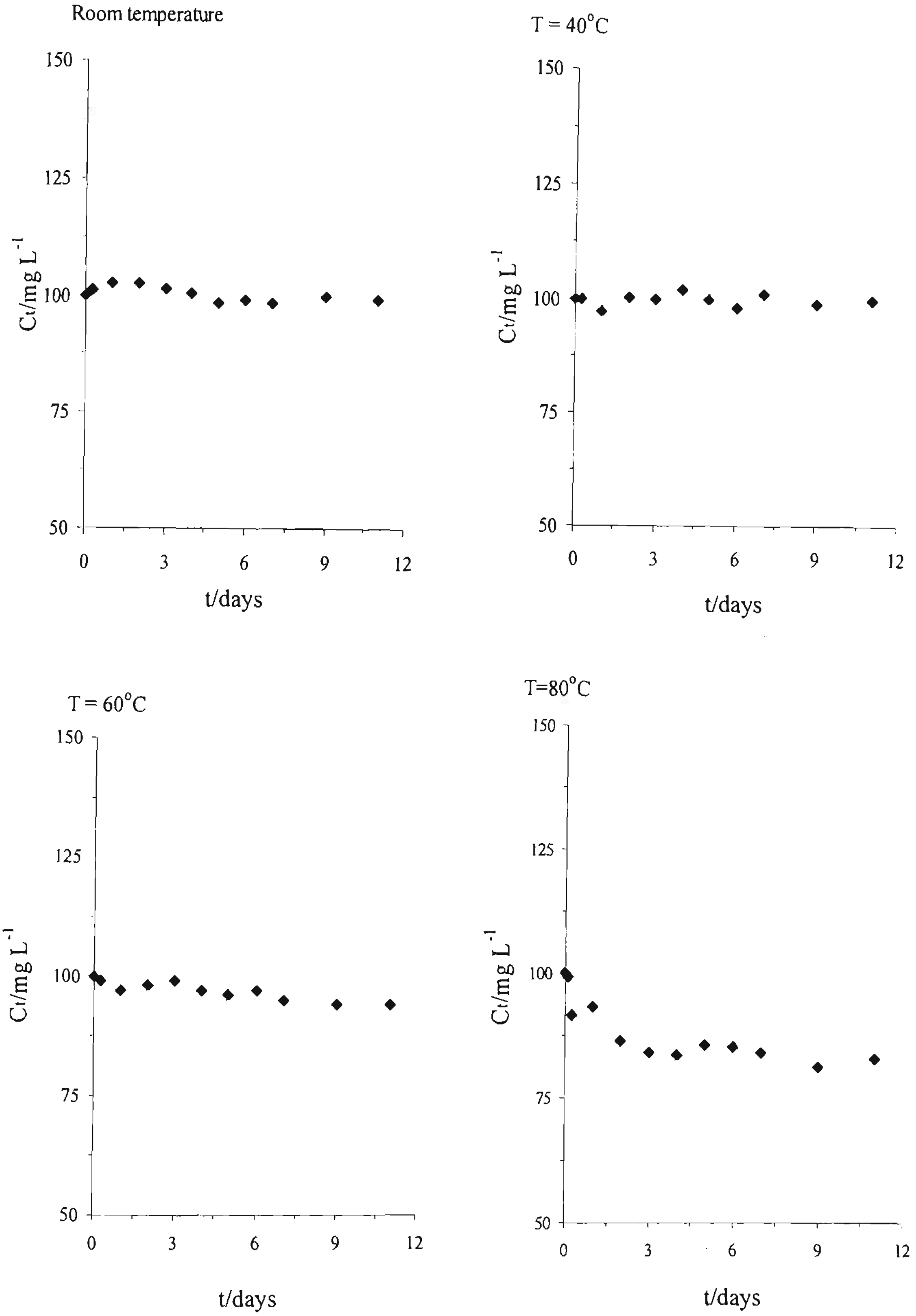


Figure 4. 30. Stability of acetaldehyde in water at different temperatures

4.5.2 Doping of PET in acetaldehyde

In order to obtain a significant quantity of acetaldehyde in the PET, the samples were contaminated by soaking them in solutions of acetaldehyde in water. Due to the low boiling point of acetaldehyde (20.8°C), the soaking was done at a temperature of 5°C to limit evaporation loss.

PET is strongly affected when in contact with acetaldehyde. When PET was exposed to absolute acetaldehyde, it became opaque after 30 min. The clarity of the PET samples, after soaking, expressed as the percentage of light transmittance, was measured using a Novaspec 4049 (Biochrom Ltd, UK) UV-visible spectrophotometer at a wavelength of 550 nm. The results are shown in Figure 4.31.

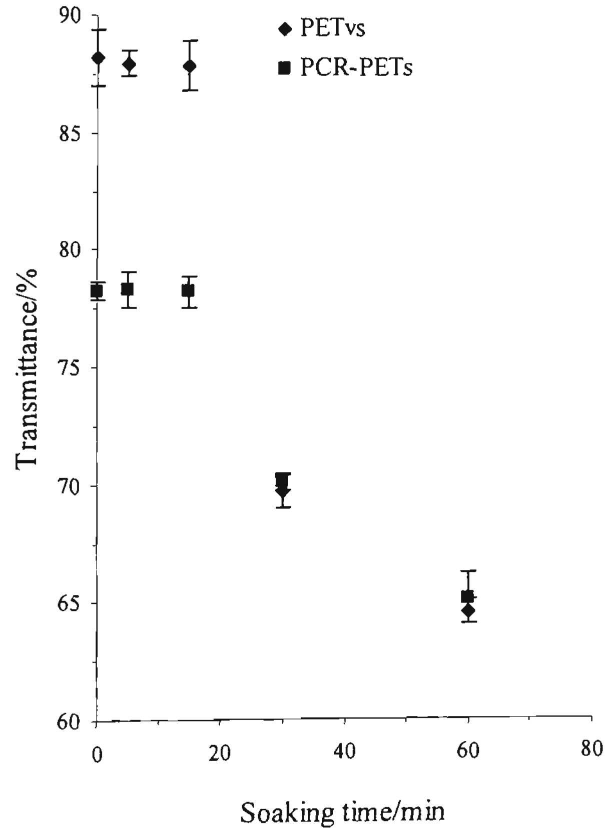


Figure 4. 31. Effect soaking time on the clarity of PET

According to the literature (Woodward *et al.*, 1960), under the action of excessive acetaldehyde, a semicrystalline polymer such as PET swells, crazes and changes its structure. The swelling gives rise to stresses, resulting in the onset of creep of the polymer molecules. De Leiris (1986) found that swelling takes place when the concentration of a highly soluble solvent increases in the polymer resulting in an enhancement of the migration rate of small molecules in the polymer matrix. If swelling occurs, it leads to plasticization of the polymer (Gavara and Hernandex, 1994) and a reduction in the gas and liquid barrier properties of the polymer (Kinnavar *et al.*, 1991). For this reason, the studies were designed by soaking the polymer in 25% and 50% (v/v) acetaldehyde solutions in water for predetermined time intervals. The latter technique allowed enough time for the polymer to relax and release internal stresses so that crazing and cracking could be prevented.

In general, it was found that recycled PET absorbed less acetaldehyde than virgin PET during all soaking periods. This is believed to be due to the higher crystallinity of PCR-PETs when compared with PETvs. A similar result was found by Van Lune *et al.* (1997) for the absorption of methanol and toluene by polyester-based bottles. Polyethylenenaphthalate (PEN) that had a high crystallinity absorbed approximately 50% less methanol and toluene compared to PET that had a low crystallinity. Actually, PEN cannot be compared directly to PET due to the higher barrier properties of the former material. The mechanism of acetaldehyde transport in the polymer has been discussed in detail in Section 4.3.

4.5.3 Head-space gas chromatography

4.5.3.1 Acetaldehyde determination in water

The headspace gas chromatography method with a flame ionization detector was used to quantify the acetaldehyde that had migrated into water. Linearity and reproducibility of the calibration curves was excellent (see Figure 4.32), which indicates the validity and efficacy of the method.

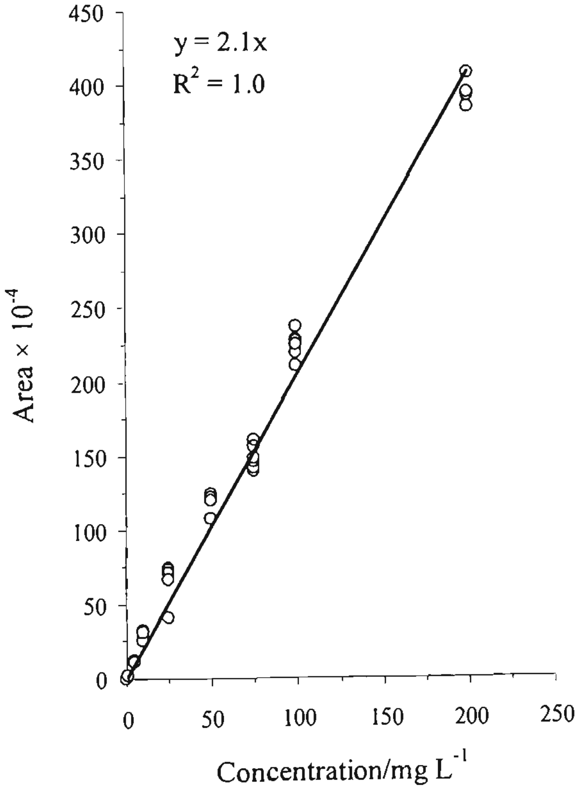


Figure 4. 32. Calibration plot of acetaldehyde in distilled water

4.5.3.2 Acetaldehyde determination in iso-octane

In this study, the determination of acetaldehyde in iso-octane was carried out originally by using gas chromatography with a polar column BP-20. However, acetaldehyde and iso-octane were found to have overlapping retention times. Acetaldehyde has a low boiling point and therefore the peaks came out quickly (at about 1.2 min). On the other hand, iso-octane is a non-polar solvent and came out as a very broad peak at almost the same retention time, when using this column. To increase the retention time of acetaldehyde, the temperature of the oven was reduced to 5°C by a cryogenic system with LCO_2 as a coolant. However, the separation between the acetaldehyde and iso-octane was still not good. Therefore it was decided to try a non-polar column. The separation between acetaldehyde and iso-octane was improved by employing the non-polar column DB-5. In this case, the acetaldehyde and iso-octane could be separated well since acetaldehyde eluted at about 1.1 min while iso-octane at about 2.2 min. Figure 4.33 shows typical gas chromatograms of blank (iso-octane) and acetaldehyde solutions in iso-octane at concentrations of 1, 10 and 100 mg L^{-1} respectively. It can be seen that the peaks resolution is satisfactory in all cases.

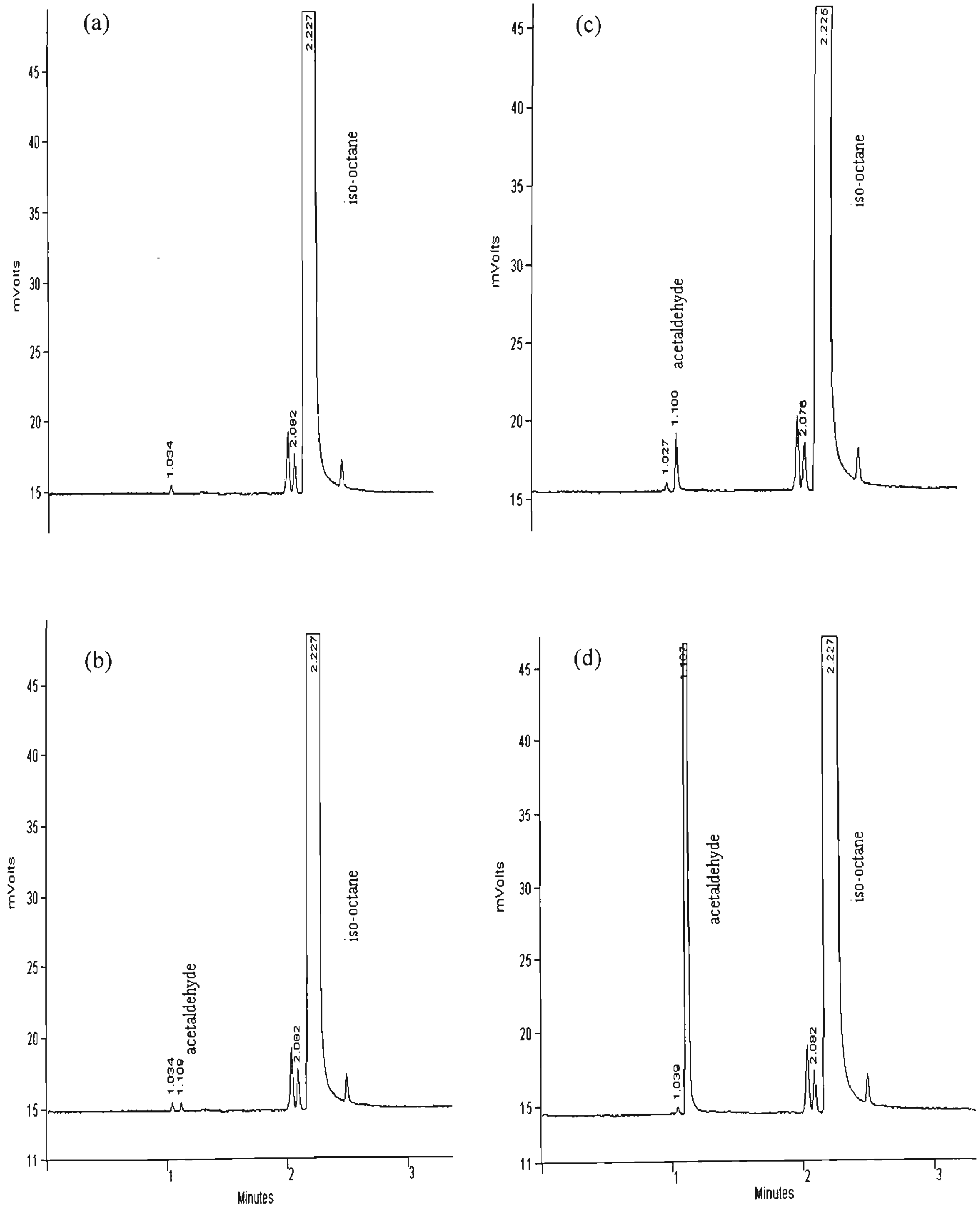


Figure 4. 33. Typical gas chromatograms obtained from the headspace gas chromatography method of acetaldehyde in iso-octane: (a) blank, (b) 1 mg L^{-1}, (c) 10 mg L^{-1} and (d) 100 mg L^{-1}

Figure 4.34 shows the calibration curve of 6 replicate measurements from 8 standard solutions of acetaldehyde in iso-octane ranging from 1 to 200 mg L^{-1}. The calibration curve was constructed by plotting the peak area versus the concentration of acetaldehyde and was found to be linear with a standard deviation of about 5%.

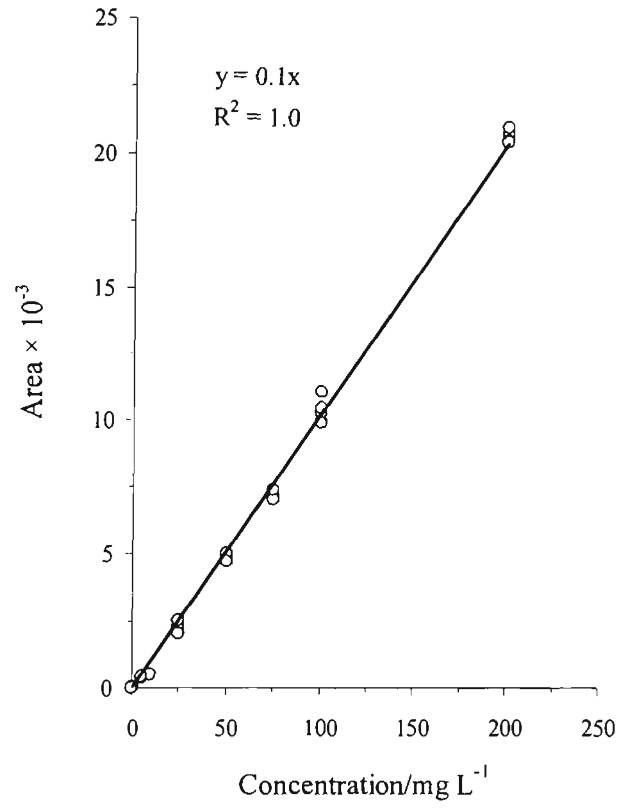


Figure 4. 34. Calibration curve for acetaldehyde in iso-octane

The calculated regression line obtained was $y = 0.1 \times 10^3x$ where x is amount of acetaldehyde in the iso-octane (mg L^{-1}) and y is the peak area, with $r^2 = 1.0$, indicating an excellent linear relationship between the acetaldehyde concentration and the FID detector response. The detection limit was defined as twice the noise level and found to be 0.1 mg L^{-1}. The regression line was used for determination of the amount of acetaldehyde migrated from contaminated PET into iso-octane.

4.5.4 Migration studies

Demertzis *et al.* (1997), Komolprasert and Lawson (1995), Markarewicz and Wilkes (1978) showed that the diffusion of non-reactive liquids and vapours in PET obeys Fick's law. Patton *et al.* (1984) also described the transport of benzene in PET as Fickian. Because the migration of acetaldehyde from PET into food simulants is expected to follow Fick's second law, Equations 2.30 and 2.31 (page 72) were used to calculate the diffusion coefficient of acetaldehyde from PET sheet samples into the food simulants for short and long time migration as a function of the initial concentration, temperature and crystallinity. These equations are only valid as long as there is no change in D brought about by the presence of the solvent or acetaldehyde.

4.5.4.1 The effect of initial acetaldehyde concentration

In Figure 4.35, the diffusion coefficients of acetaldehyde in recycled and virgin PET sheets, calculated from the migration studies into water, are presented for different initial acetaldehyde levels in the polymer. From the analysis of this figure, it is evident that the transport does not follow the Fickian Case I model. It is well known that the Fickian model for transport is limited to low migrant or any other liquid (like simulant or solvent) concentration in the polymer. At higher migrant concentrations, the contribution of the migrant to the transport may become significant and hence a strong dependence of the diffusion coefficient on the concentration could be observed, as is the case in the current study. Similar results were found by Miltz *et al.* (1997).

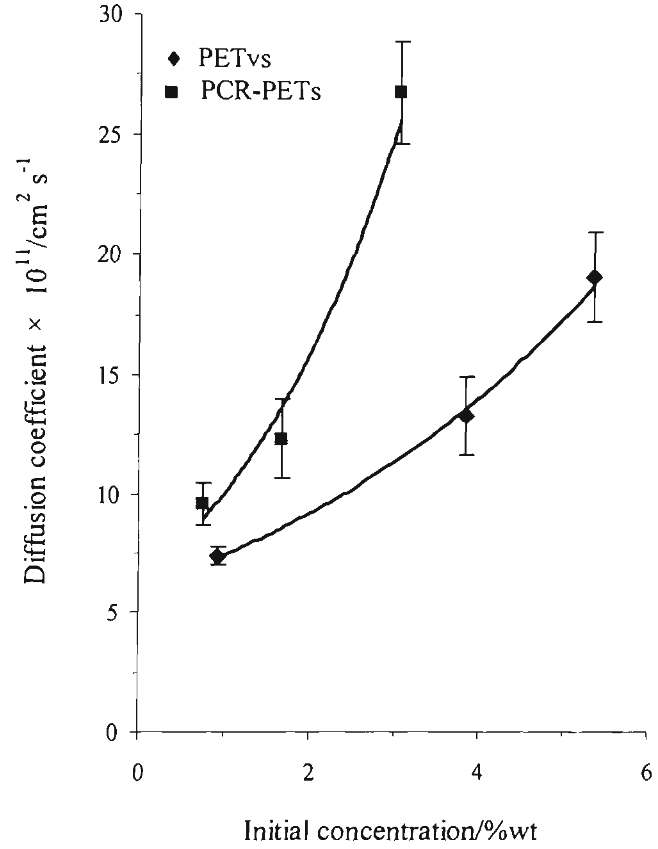


Figure 4. 35. The effect of initial acetaldehyde concentration on the diffusion coefficient in PET for short-term migration ($M_t/M_\infty < 0.6$)

Neogi (1996) proposed an exponential relationship between the diffusion coefficient and the concentration ($D = D_0e^{\alpha c}$; where D is the diffusion coefficient, D_0 and α are constants; and C is the concentration). The present results seem to fit well to Neogi's model in the range of the concentration investigated (Figure 4.35). A significant difference is also observed in the diffusion coefficient value between PETvs and PCR-PETs. The reason for the higher diffusion coefficients obtained for PCR-PETs as compared to PETvs will be explained later.

The initial acetaldehyde concentration in PET investigated in the present study is in the range of 0.9 – 5.3% (w/w) and 0.7 – 3.1% (w/w) for the virgin and recycled PET respectively. It is worthwhile to note that the acetaldehyde concentration used in the present work is high and very unlikely to occur in actual situations but needed to be set as such in order to obtain measurable effects.

The ratio of C_p/C_f (see Equation 2.33, page 73), if considered at equilibrium, reflects the affinity of acetaldehyde to the polymer. The solubility and the partition coefficient may depend on the crystallinity, and the value of these parameters changes with the percentage of acetaldehyde used in the soaking procedure. For given experimental conditions, the partition coefficients were found to have a linear dependence on the initial migrant concentration in the polymer (see Figure 4.36).

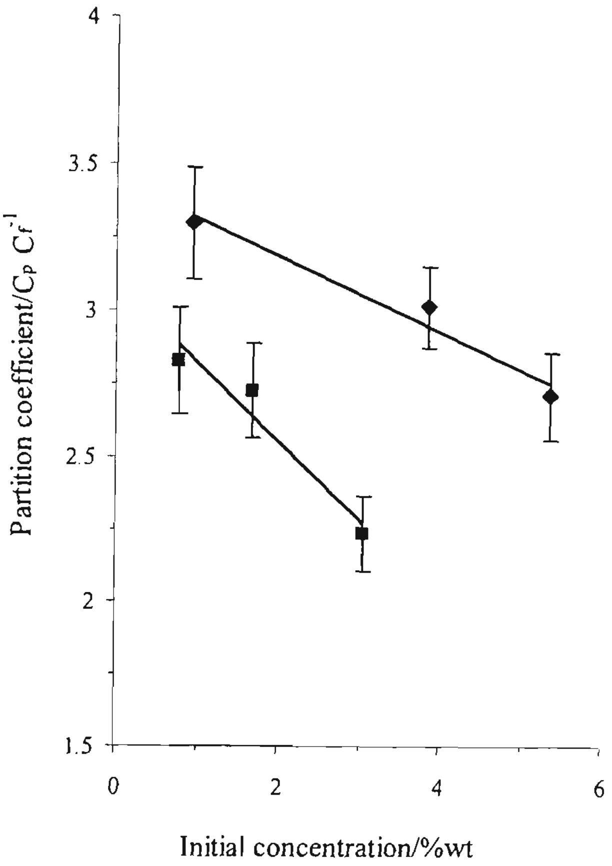


Figure 4. 36. The effect of initial acetaldehyde concentration in the polymer on the partition coefficient

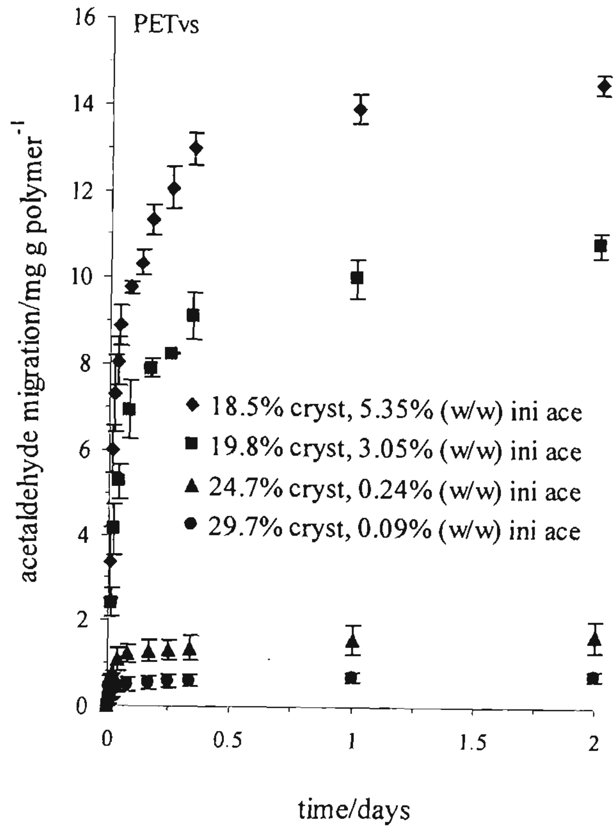
The decrease in the partition coefficient with the increase in concentration observed in this work is in good agreement with previous findings by Miltz (1992). In all cases, the values of the partition coefficient are greater than unity. The meaning of this result is that the affinity of acetaldehyde to the polymer is higher than that to the food simulant. It can also be seen from Figure 4.36 that the dependence of the partition coefficient on the initial migrant concentration is larger in the case of the recycled compared to the virgin PET. The reason for this may stem from the difference in crystallinity and morphology of the materials. Piringer (1999) has shown that the partition coefficients are strongly dependent on the degree of crystallinity of polymers.

In light of the above, it seems that the kinetics of the migration of acetaldehyde into food simulants should be studied using a model that takes into account the concentration dependence of the diffusivity. However, the use of such a model is very complicated and is beyond of the scope of the present study.

4.5.4.2 The effect of degree of crystallinity

Another parameter that affects the transport process of a migrant in a polymer is the molecular structure of the polymer or more specifically, the degree of crystallinity of the polymer. To investigate the effect of crystallinity on the migration of acetaldehyde from PET into food simulants, studies were carried out with four samples of different degrees of crystallinity. These samples were obtained by annealing the polymer at a constant temperature of 120°C for different time periods (see Section 3.2.2.). The studies were conducted using virgin and recycled PET sheets and water was used as the food simulant.

The amount of acetaldehyde that migrated from the PET samples immersed into water, as measured by the headspace gas chromatography method, as a function of the time of exposure is shown in Figure 4.37.



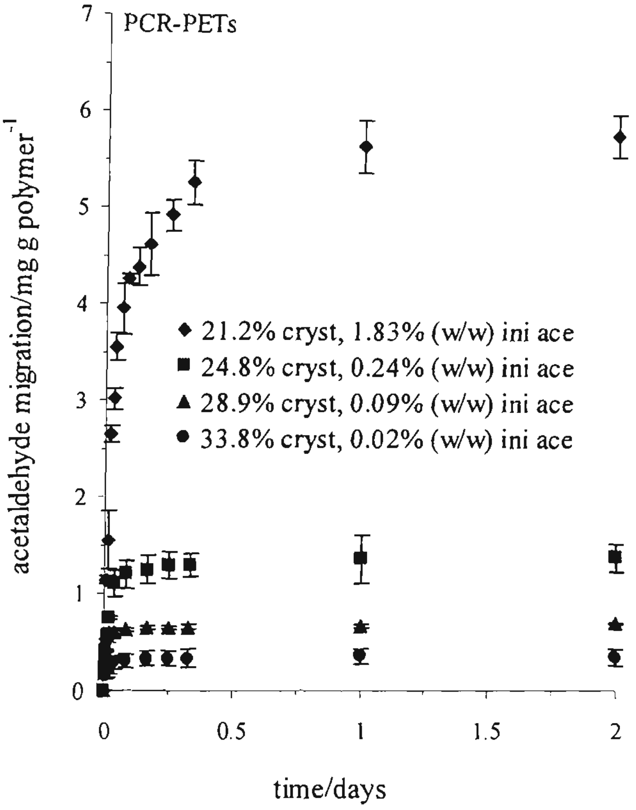


Figure 4. 37. Migration of acetaldehyde from virgin and recycled PET samples of different degrees of crystallinity, into water. The first percentage in the figures refers to the degree of crystallinity and the second refers to the initial acetaldehyde concentration on a w/w basis

As the PCR-PETs samples had a lower initial acetaldehyde concentration than the PETvs counterparts, a lower acetaldehyde level was obtained, at equilibrium, in the food simulants for the former samples compared to the latter ones. However, when comparing the recycled and the virgin PET samples at the same level of crystallinity (for instance at 24.7% crystallinity for PETvs and 24.8% crystallinity for PCT-PETs) comparable levels of acetaldehyde were observed, at equilibrium, in the food simulant.

The diffusion coefficients were calculated from the slope of a plot of M_t/M_∞ versus $t^{1/2}$, for short-term migration, and from a plot of $\ln(1 - M_t/M_\infty)$ versus t, for long-term migration and are listed in Table 4.11.

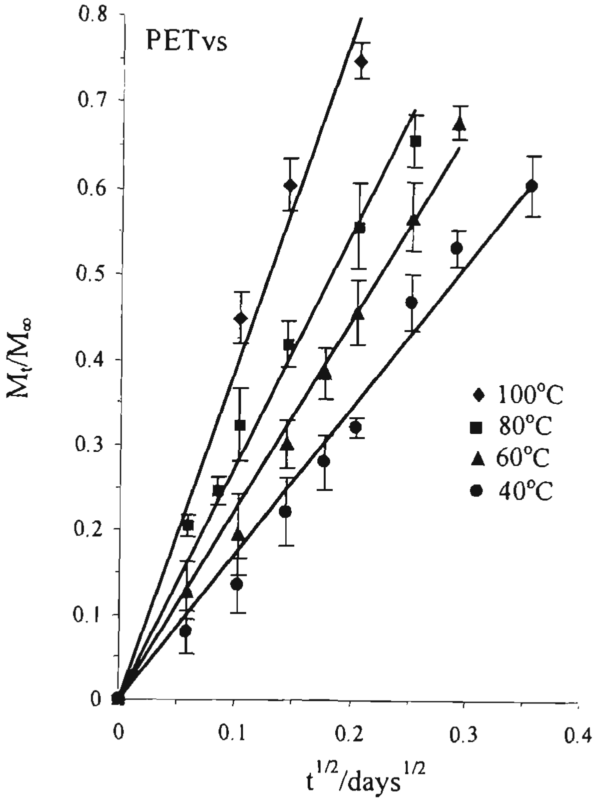
Table 4. 11. Diffusion coefficients for acetaldehyde-PET in different crystallinities

Sample	Crystallinity	$D \times 10^{11}$ /cm^2 s^{-1}	
		Short-term	Long-term
PETvs	18.5 ± 1.0	19.2 ± 1.9	3.6 ± 0.9
	19.8 ± 0.6	40.7 ± 4.2	4.1 ± 0.4
	24.7 ± 1.0	48.6 ± 2.0	4.5 ± 0.2
	29.7 ± 1.5	55.8 ± 2.1	4.7 ± 0.2
PCR-PETs	21.2 ± 0.9	26.8 ± 2.1	1.6 ± 0.6
	24.8 ± 0.3	41.3 ± 6.7	6.5 ± 0.3
	28.9 ± 0.5	95.9 ± 9.6	6.9 ± 0.4
	33.8 ± 0.9	196.6 ±12.5	7.6 ± 0.4

It is also apparent that the diffusion of the migrating compound depends on the morphological structure of the polymer. In general, the higher the degree of crystallinity in the pre-sorbed samples, the higher is the diffusion coefficient determined from the migration studies. This observation is in accordance with the widely accepted assumption that sorption and diffusion of small molecules in semicrystalline polymers occurs primarily in the amorphous regions. Therefore, for a specific concentration of acetaldehyde in the PET, the higher the degree of crystallinity, the higher is the concentration of the migrant in the less abundant amorphous phase. An increased concentration in the amorphous phase may cause swelling of the polymer resulting in an increased diffusion coefficient. This may explain the higher diffusion coefficient obtained in the migration studies for the more crystalline PCR-PET compared to the PETvs. These results are in agreement with those reported by Durning *et al.* (1986).

4.5.4.3 The effect of temperature

The diffusion of a solute through a polymer matrix is commonly considered to be constant and dependent only on the temperature. Figure 4.38 shows a plot of M_t/M_∞ versus $t^{1/2}$ up to $M_t/M_\infty < 0.7$ from the migration studies from PET into water at temperatures of 40, 60, 80 and 100°C and into iso-octane at temperatures of 30, 40 and 50°C. Diffusion coefficients were calculated from the slope of this plot and summarized in Table 4.12.



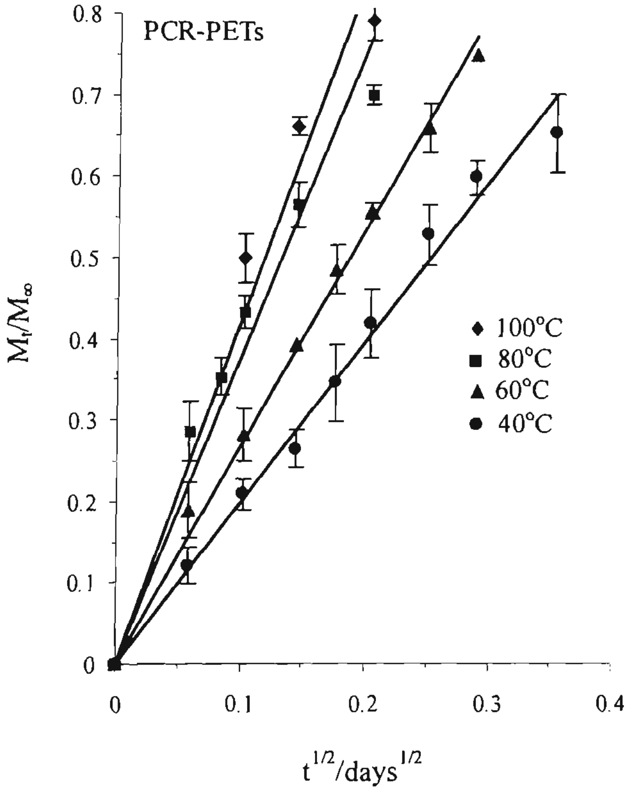


Figure 4. 38. Plot of M_t/M_∞ versus $t^{1/2}$ for acetaldehyde migration from virgin and recycled PET into water at different temperatures. Bars represent standard error of the mean

As expected, the diffusion coefficients of acetaldehyde in PET increased with the increase in temperature. Similar results were also found in many publications. The increase in the diffusion coefficient with temperature is mostly due to the enhanced motion of the polymer segments and the increased energy of the diffusing molecules (Ten Hulscher and Cornelissen, 1996). The diffusion coefficient values for PCR-PETs were higher than those for PETvs across the entire temperature range investigated in the present study. This is due to the fact that PCR-PETs had a higher crystallinity than PETvs (see also Section 4.5.4.2).

Table 4. 12. Diffusion coefficients of acetaldehyde from PET into water and iso-octane

Sample	Food simulant			
	Water		Iso-octane	
	Temperature/ °C	$D \times 10^{11}/cm^{2}s^{-1}$	Temperature/°C	$D \times 10^{11}/cm^{2}s^{-1}$
PETvs	40	4.3 ± 0.1	30	17.1 ± 0.4
	60	7.3 ± 0.1	40	19.4 ± 2.3
	80	10.9 ± 0.3	50	23.8 ± 1.1
	100	21.9 ± 1.4		
PCR-PETs	40	13.6 ± 0.5	30	16.0 ± 2.2
	60	24.8 ± 5.7	40	21.5 ± 3.4
	80	49.5 ± 3.1	50	26.9 ± 1.1
	100	61.7 ± 7.1		

The mass transport of acetaldehyde from the polymer into iso-octane was much faster than from the polymer into water at the same temperature of exposure, for both, PETvs and PCR-PETs. Iso-octane may cause a larger structural change in the polymer, resulting in swelling, higher polymer free volume, and as a consequence, faster diffusion. However, water is known to be a plasticizer for PET, whereas iso-octane is a better solvent for some organic apolar species. These results are consistent with those of a previous study (Garde *et al.*, 2001). The values of the diffusion coefficient obtained from the current migration studies are 4.3×10^{-11} and 19.4×10^{-11} cm^2 s^{-1} for PETvs and 13.6×10^{-11} and 21.5×10^{-11} cm^2 s^{-1} for PCR-PETs into water and iso-octane respectively at a temperature of 40°C (see Table 4.12).

The effect of temperature on the diffusion coefficients of acetaldehyde in PETvs and PCR-PETs is shown in Figure 4.39 for water and iso-octane as the respective food simulants, when plotted according to the Arrhenius-type correlation.

In the case of migration into water, a similar temperature sensitivity of the diffusion coefficient during migration from the virgin and recycled polymers can be noticed. In the case of iso-octane however, the diffusion coefficient is much more temperature dependent in the PCR-PETs samples than in the PETvs ones. The reason for this could be that with the increase in temperature, iso-octane may increasingly disrupt more of the crystallites in the more crystalline PCR-PETs as compared to the less crystalline PETvs samples and which is manifest in the increase the temperature sensitivity of the diffusion coefficient in PCR-PETs compared to PETs.

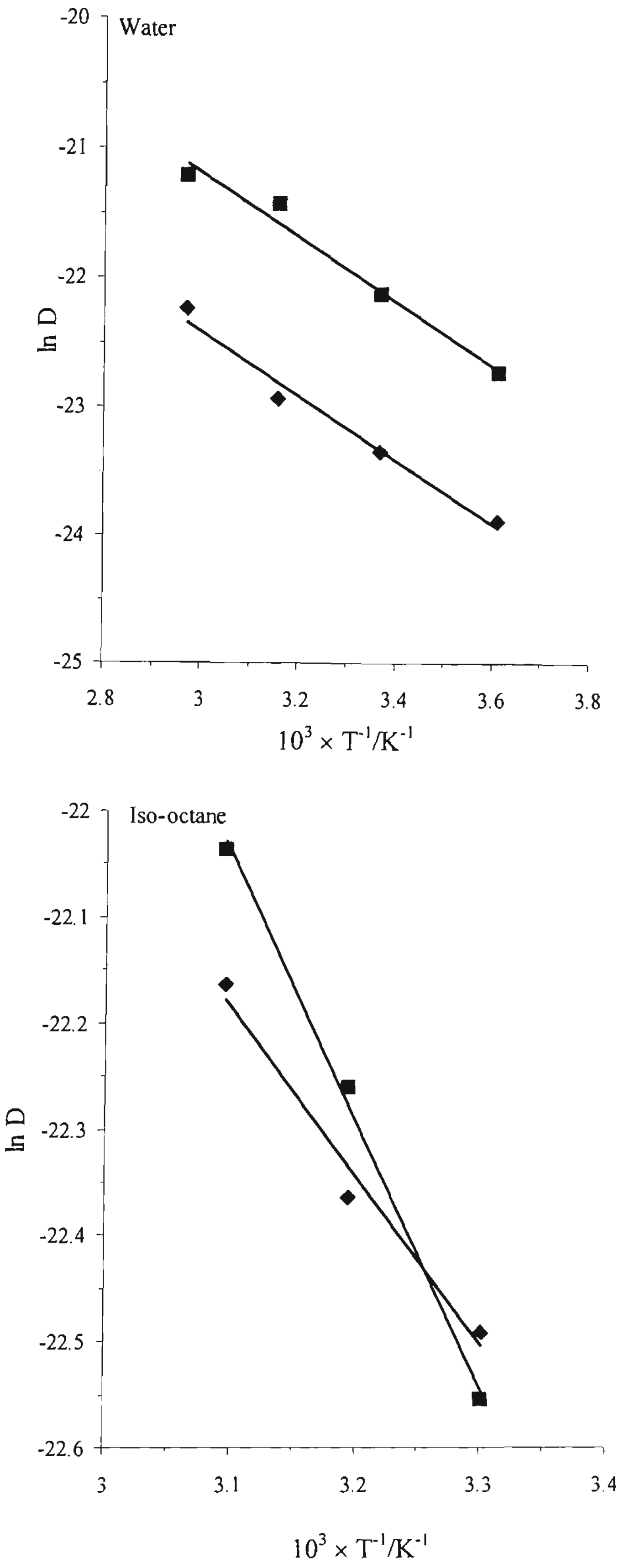


Figure 4. 39. Arrhenius plots of ln D versus 1/T for acetaldehyde-PET

The activation energies of diffusion, E_D, calculated from the slopes of the fitted lines in Figure 4.39 are presented in Table 4.13.

Table 4. 13. Value of activation energy of diffusion (E_D/kJ mol^{-1})

Sample	Water	Iso-octane
PETvs	20.59	12.61
PCR-PETs	20.44	21.17

The value of E_D for PETvs and PCR-PET are almost identical in the water system. In the iso-octane system, on the other hand, the activation energy for PCR-PETs is about 70% higher than that for PETvs.

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A number of conclusions can be drawn from the results of the current study:

5.1.1 Physical properties of the studied PET

1. The intrinsic viscosity of the virgin PET was significantly higher than that of the recycled material, therefore the virgin PET had a higher viscosity average molecular weight than the recycled counterpart.
2. The tensile test experiments revealed that there were no major differences between the mechanical properties of virgin and recycled PET sheet except in elongation at break. However, the recycled PET is more brittle and stiffer than the virgin one, due to the reduced molecular weight.
3. A thermal treatment at 120°C followed by quenching changed the crystallinity of the PET sheet samples. Thermal analysis suggested that increasing the heating time during the thermal treatment led to an increase in the endothermic (melting) peak and a decrease in the exothermic peaks (additional crystallization). A linear correlation between the heating time and the degree of polymer crystallinity was found in this study. A 25% degree of crystallinity was found to be the maximum crystalline content at which PET still exhibited an exothermal peak on the DSC thermograms.
4. The different volumes (dimensions) of virgin PET bottles affected the degree of crystallinity of the samples although the differences were not very large. It

can be concluded that stretching of these bottles during the blow moulding process has induced additional crystallisation.

5.1.2 Sorption of acetaldehyde into PET

1. The transport parameters (k, K_s, E_a, ΔH_s, ΔS and D) showed a systematic dependence on the degree of crystallinity of PET samples and on the temperature at which the experiments were performed. The functional relationship between the crystallinity and the transport parameters, however, do not follow simple linear correlations.
2. The PET samples exhibit transport behaviour ranging from a Pseudo-Fickian to a Super Case II mechanism. The higher the crystallinity of the samples and the lower the temperatures of sorption, the more complex the transport behaviour leading to a Super Case II mechanism. However, during the early stage of sorption, Fickian behaviour was prevalent.
3. Comparison between the virgin PET and the recycled PET revealed that virgin PET absorbs more acetaldehyde and requires a shorter time to reach equilibrium than the recycled counterpart. However, at the same degrees of crystallinity, the amount of acetaldehyde sorbed was similar in the two kinds of PET samples.
4. Entropy analysis suggests that the crystalline structures were more ordered in the virgin PET than in the recycled PET.
5. The interactions between the PET and acetaldehyde were exothermic as indicated from the negative values of the enthalpy of sorption. Therefore, the

sorption process followed the Langmuir sorption mode rather than Henry's law.

5.1.3 Overall migration

1. The values of the overall migration obtained for all PET samples tested by the conventional total-immersion method were significantly below the limits allowed by European Directive 90/128/EEC. Therefore, it can be concluded that the PET samples could be used for food packaging applications as long as the temperature of exposures does not exceed 40°C. However, specific migration studies, particularly for toxic or carcinogenic compounds, should be carried out to guarantee the safety of those containers.
2. The reflux method gave significantly higher total migration levels in all PET samples, sometimes more than 10 times higher, than those obtained in the conventional method. It was assumed that a high temperature has probably accelerated the decomposition and degradation process resulting in more residues being released from this polymer.
3. The PCR-PETs produced the highest overall migration in all tested food simulants. In the reflux method, these samples released a value exceeding 10 mg dm^{-2}, the maximum allowed by regulatory agencies, in the two alternative fatty food simulants (95% (v/v) aqueous ethanol and iso-octane). Oligomers were suspected to be the compounds released from this sample. Therefore, this recycled PET material is not suited for high temperature applications in contact with food.

4. The post-consumer PET bottles had a lower level of total residues migrating into the food simulant compared to the virgin PET bottles. It was assumed that some adjuvants had been leached out into the product originally contained in these bottles.
5. Based on the food simulants, a trend of decreasing overall migration was observed in the order: iso-octane > 95% (v/v) aqueous ethanol > 3% (v/v) aqueous acetic acid > 15% (v/v) aqueous ethanol > distilled water. Based on polymer samples, total migration values decreased in the order: PCR-PETs > PETvs > PETvb > PC-PETb.

5.1.4 Migration of acetaldehyde into food simulants

1. The results indicate that migration of acetaldehyde from PET depends primarily on the initial concentration of the migrant in the polymer. Neogi's model for the effect of concentration on the diffusion coefficient fitted well the results of the present work. It was noted that the dependence of the diffusion coefficient on the initial migrant concentration was larger in the recycled compared to the virgin PET.
2. The structure and morphology of the polymer also affected the migration process. The higher the degree of crystallinity, the higher was the calculated diffusion coefficient of acetaldehyde in the polymer. PCR-PETs, with a higher degree of crystallinity, exhibited a higher diffusion coefficient than PETvs.
3. Increasing the temperature of exposure resulted in an increase in the diffusion coefficient as well as an increase in the acetaldehyde migration levels. The

Arrhenius-type plot could be used to study the effect of temperature on migration within the temperature range used in the current study both for PETvs and PCR-PETs. The temperature dependency on the diffusion coefficient was higher in the recycled PET than in the virgin material.

4. The mass transport of acetaldehyde from PET into iso-octane was much faster than from the PET into water under the same conditions of exposure. It was suggested that iso-octane causes swelling and results in a higher free volume and therefore faster diffusion rates.

5.2 Recommendations

In this study, the major research objectives were accomplished satisfactorily and additional information was generated. However, several questions remain unanswered due to limitation in the techniques and time constraints. Therefore the following studies are proposed to extend the current work:

1. Only acetaldehyde was studied in the present work. Other principal degradation products resulting from PET degradation are toluene and oligomers. It is recommended to study the migration behavior of toluene and oligomers from (recycled) PET into food or food simulants.
2. In the doping method, high concentrations of acetaldehyde in the PET material were obtained. These concentrations might be higher than contained in PET in actual applications. Consequently, there is a need to establish methods to incorporate acetaldehyde in PET at levels comparable to actual use.

3. Iso-octane causes swelling of PET and might have altered the diffusion coefficient. However, the effect of swelling on the diffusion coefficient was not investigated in the present study. Therefore, it is recommended to include the swelling effect in the model of transport in order to better predict the diffusion coefficient.

BIBLIOGRAPHY

Aminabhavi, T. M. and Shivaputrappa, B. H. 1991, 'Thermodynamic study on the sorption of liquids by polymer films', *Journal of Chemical Education*, Vol. 68, No. 4, pp. 343 - 346.

Aminabhavi, T. M. and Munnolli, R. S. 1994, 'An assessment of chemical compatibility of bromobutyl rubber, chlorosulfonated polyethylene and epichlorohydrin membranes in the presence of some hazardous organic liquids', *Journal of Hazardous Materials*, Vol. 38, No. 2, pp. 223 - 242.

Aminabhavi, T. M., Harlapur, S. F., Balundgi, R. H. and Ortego, J. D. 1996a, 'Sorption kinetics and diffusion of alkanes into tetrafluoroethylene/ propylene copolymer membrane', *Journal of Applied Polymer Science*, Vol. 59, pp. 1857 - 1870.

Aminabhavi, T. M., Phayde, H. T. S., Ortego, J. D. and Vergnaud, J. M. 1996b, 'Sorption/diffusion of aliphatic ester into tetrafluoroethylene/propylene copolymeric membranes in the temperature interval from 25 to 70°C', *European Polymer Journal*, Vol. 32, No. 9, pp. 1117 - 1126.

Aminabhavi, T. M., Phayde, H. T. S., Ortego, J. D. and Vergnaud, J. M. 1996c, 'A study of sorption/desorption profiles and diffusion anomalies of organic haloalkanes into a polymeric blend of ethylene-propylene random copolymer and isotactic polypropylene', *Polymer*, Vol. 37, No. 9, pp. 1677 - 1684.

Aminabhavi, T. M., Phayde, H. T. S., Ortego, J. D. and Stahl, W. M. 1997, 'Sorption and migration of aliphatic organic ester into VITON fluoroelastomer membranes', *Journal of Applied Polymer Science*, Vol. 63, pp. 1223 - 1235.

Aminabhavi, T. M. and Naik, H. G. 1999, 'Sorption/desorption, diffusion, permeation and swelling of high density polyethylene geomembrane in the presence of hazardous organic liquid', *Journal of Hazardous Materials*, Vol. 64, No. 3, pp. 251 - 262.

Anon. 1999, 'Strong growth in plastic packaging recycling', *Packaging*, May, p.14.

Arthur, C. L. and Pawliszyn, J. 1990, 'Solid phase micro-extraction with thermal desorption using fused silica optical fibers', *Analytical Chemistry*, Vol. 62, pp. 2145 - 2148.

Arthur, C. L., Potter, D. W., Bucholz, K. D., Motlagh, S. and Pawliszyn, J. 1992, 'Solid phase micro-extraction for direct analysis of water : Theory and Practice', *Liquid Chromatography - Gas Chromatography*, Vol. 10, pp. 656 - 661.

Ashby, R. 1988, 'Migration from polyethylene terephthalate under all condition of use', *Food Additives and Contaminants*, Vol. 5, pp. 485 - 492.

Ashby, R. 1992, 'Standard methods of test for plastics intended to come into contact with food', in *Food Packaging Migration and Legislation*, ed Robert Ashby, Ian Cooper, Derek Shorten and Philip Tice, Pira International, London, UK, pp. 16 - 41.

ASTM D 638 - 93. 1996, '*Standard test method for tensile properties of plastics (metric)*', Annual Books of ASTM Standard, Vol. 08. 01, Plastic (I), p. 57 – 66.

ASTM D 1601 - 86. 1996, '*Standard test method for dilute solution viscosity of ethylene polymers*', Annual Books of ASTM Standard, Vol. 08. 01, Plastic (I), p. 366 – 372.

ASTM D 1746 - 92. 1996, '*Standard test method for transparency of plastic sheeting*', Annual Books of ASTM Standard, Vol. 08. 01, Plastic (I), p. 424 – 426.

Baner, A. L., Beiber, W., Figge, K., Franz, R. and Piringer, O. 1992, 'Alternative fatty food simulant for migration testing of polymeric food contact materials', *Food Additives and Contaminants*, Vol. 9, pp. 137 - 226.

Baner, A. L., Brandsch, J., Franz, R. and Piringer, O. 1996, 'The application of a model for evaluating the compliance of plastics materials with food regulation', *Food Additives and Contaminants*, Vol. 13, No. 5, pp. 587- 601.

Baner, A. L. 2000, 'The Estimation of partition coefficients, solubility and permeability coefficient for organic molecules in polymer', in *Food Packaging. Testing Methods and Applications*, ed S. J. Risch, American Chemical Society, Washington DC, p. 37 - 55.

Bashir, Z., Al-Aloush I., Al-Raqibah, I. and Ibrahim, M. 2000, 'Evaluation of three methods for measurement of crystallinity of PET resin, preforms and bottles', *Polymer Engineering and Science*, Vol. 40, No. 11, pp. 2442 - 2455.

Bayer, F. L., Myers, D. V. and Gage, M. J. 1995, 'Consideration of poly(ethylene terephthelate) recycling for food use', in *Plastics, Rubber, and Paper Recycling: A Pragmatic Approach*, ed Charles P. Rader, Sherly D. Baldwin, David D. Cornell, George D. Sadler and Richard F. Stockel, American Chemical Society, Washington DC, p. 458 - 471.

Bayer, F. L. 1997, 'The threshold of regulation and its application to indirect food additive contaminants in recycled plastics', *Food Additives and Contaminants*, Vol. 14, No. 6 - 7, pp. 661 - 670.

Bayer, F. L. 2002, 'Polyethylene terephthalate recycling for food-contact applications: Testing, safety and technologies: a global perspective', *Food Additives and Contaminants*, Vo. 19, pp. 114 - 134.

Bednas, M. E., Day, M., Ho, K., Sander, R. and Wiles, D. M. 1981, 'Combusion and pyrolysis of poly(ethylene terephthalate). I. The role of flame retardants on product of pyrolysis', *Journal of Applied Polymer Science*, Vol. 26, pp. 277 - 283.

Begley, T. H. and Hollifield, H. C. 1990a, 'High-performance liquid chromatographic determination of polyethylene terephthalate oligomers in corn oil', *Journal Agricultural and Food Chemistry*, Vol. 38, pp. 145 - 148.

Begley, T. H. and Hollifield, H. C. 1990b, 'Evaluation of polyethylene terepthalate cyclic trimer migration from microwave food packaging using temperature-time profiles', *Food Additives and Contaminants*, Vol. 7, No. 3, pp. 339 -346.

Begley, T. H. and Hollifield, H. C. 1990c, 'Migration of dibenzoate plasticizer and polyethylene terephthalate cyclic oligomers from microwave susceptor', *Journal of Food Protection*, Vol. 53, No. 13, pp. 1062 - 1066.

Begley, T. H., Biles, J. E. and Hollified, H. C. 1991, 'Migration of epoxy adhesive compound into a food simulating liquid and food from microwave susceptor packaging, '*Journal of Agricultural and Food Chemistry*, Vol. 39, pp. 1944 - 1945.

Begley, T. H. and Hollifiled, H. C. 1993, 'Recycled polymers in food packaging: Migration consideration. When recycled polymer are used in packaging the possibility that toxic contaminants may migrate into food must be determined', *Food Technology*, Vol. 47, pp. 109 - 112.

Begley, T. H. 1997, 'Methods and approaches used by FDA to evaluate the safety of food packaging materials', *Food Additives and Contaminants,* Vol. 14, No. 6 - 7, pp. 545- 553.

Begley, T.H., Mc.Neal, T. P., Biles, J. E. and Paquette, K. E. 2002, 'Evaluating the potential for recycling all PET bottles into new food packaging', *Food Additives and Contaminants*, Vol. 19, pp. 135 - 143.

Benfenati, E., Natangelo, M., Davoli, E. and Fanelli, R. 1991, 'Migration of vinyl chloride into PVC-bottled drinking assessed by gas chromatography-mass spectrometry', *Food and Chemical Toxicology*, Vol. 29, pp. 131 - 1334.

Billovits, G. F. and Durning, C. J. 1988, 'Penetrant transport in semicrystalline poly(ethylene terephtalate)', *Polymer*, Vol. 29, pp. 1468 - 1484.

Bills, D. D., Yang, C. S., Morgan, M. E. and Bodyfelt, F. W. 1972, 'Effect of sucrose on the production of acetaldehyde and acid by yoghurt culture bacteria, '*Journal of Dairy Science*, Vol. 55, pp. 1570 - 1573.

Bird, R. B., Stewart, W. E. and Lightfoot, E. N. 1975, *Transport Phenomena,* John Willey and Sons, New York, p. 502.

Boersma, A., Cangialosi, D. and Picken, S. J. 2003, 'Mobility and solubility of antioxidant and oxygen in glassy polymer. III. Influence of deformation and orientation on oxygen permeability', *Polymer*, Vol. 44, pp. 2463 - 2471.

Borodinsky, L. 1991, 'Toward a threshold of regulation for packaging components', in *Food and Packaging Interactions II*, ed Sara J. Risch, Joseph H. Hotchkiss, American Chemical Society, Washington DC, p. 79 - 103.

Brandrup, J., Immergut, E. and Grulke, H. E. 1998, *Polymer handbook.* John Wiley and Son Inc., New York.

Briston, J. H. 1994, *Rigid and Semi-rigid Plastic Container,* Longman Group Limited, London, .p. 33 - 37.

Brodkey, R. S. and Hersey, H. C., 1988, *Transport Phenomena. A unified Approach,* McGraw-Hill Book Company, New York, p. 14 - 59.

Brody, A. L. and Marsh, K. S. (ed). 1997, 'Polyester, thermoplastic', in *The Wiley Encyclopedia of Packaging Technology 2nd edn*, New York, John Wiley and Sons Inc., p. 742 - 745.

Bryk, M. T. 1991, *Polymeric components of composite and their thermal stability. Degradation of filled polymer. High temperature and thermal-oxidative processes*, Elliss Horwood, New York, p. 9 - 44.

Blundell, D. J. and Osborn, B. N. 1983, 'The morphology of poly(aryl-ether-ether-ketone)', *Polymer*, Vol. 24, pp. 953 -958.

Castle, L., Jickells, S. M., Sharman, M., Gramshaw, W. and Gilbert, J. 1988, 'Migration of the plasticizer acethyltributyl citrate from plastics film into foods during microwave cooking and other domestic use', *Journal of Food Protection*, Vol. 5, No. 12, pp. 916 - 919.

Castle, L., Mayo, L., Creus, C. and Gilbert, J. 1989, 'Migration of PET oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages', *Journal of Food Protection*, Vol. 52, No. 5, pp. 337 - 342.

Castle, L., Jickles, S. M., Gilbert, J. and Harrison, N. 1990. ' Migration testing of plastics and microwave-active materials for high-temperature food-use applications', *Food Additives and Contaminants*, Vol. 7, No. 6, pp. 779-796.

Castle, L. 1994, 'Recycled and re-use plastics for food packaging', *Packaging Technology and Science*, Vol.7, pp. 291 - 297.

Castle, L., Honeybone, C. A., Jickells, S. M., Philo, M. R. and Sharman, M. 1994, 'Practical aspects of testing food contact materials for migration', *Food Additives and Contaminants*, Vol. 11, No. 2, pp. 177 - 185.

Chaari, F., Chaouche, M. and Doucet, J. 2003, 'Crystallization of poly(ethyelene terephthalate) under tensile strain: crystalline development versus mechanical behaviour', *Polymer*, Vol. 44, pp. 473 - 479.

Chalykh, A. Y., Puchkov, N. I., Orlova, S. P. and Shcipacheva, N. A. 1979. 'Diffusion and sorption of solvent in polypropylene', *Polymer Science*, Vol. 21, pp. 1486 - 1496.

Chang, S. S., Guttman, C. M., Sanchez, I. C. and Smith, L. E. 1988, 'Theoretical aspect of migration of package components to food', *ACS Symposium Series*, American Chemical Society, Washington DC, Vol. 365, pp. 106 - 117.

Cheeseman, M. A., Machuga, E. J. and Bailey, A. B. 1999, 'A tiered approach to threshold of regulation', *Food and Chemical Toxicology*, Vol. 37, pp. 387 - 412.

Chin, H. W., Benhard, R. A. and Rosenberg, M. 1996. 'Solid phase micro-extraction for cheese volatile compound analysis', *Journal of Food Science*, Vol. 61, pp. 1118 - 1128.

Choudhry, M. S., Lox, F. and Decroly, P., 1994, 'The migration of plastic components: the quantification of influences from mechanical stresses and vibration', *Packaging Technology and Science*, Vol. 7, p. 163 - 167.

Choudhry, M. S., Lox, F., Buekens, A., and Decroly, P. 1998,'Evaluation of migrational behaviour of plastics food contact materials: A comparison of method', *Packaging Technology and Science*, Vol. 11, p. 275 - 283.

Coe, J. S. 1971, '*Chemical Equilibrium. An Introduction*', Methuen Educational Ltd., London, p. 1 - 7.

Commission Directive 90/128/EEC, Official Journal of the European Communities L346, p. 26 , 13/12/1990 of 23rd February 1990.

Commission Directive 92/39/EEC, Official Journal of the European Communities L168, p. 21, 23/6/1992 of 14th May 1992.

Commission Directive 93/9/EEC, Official Journal of the European Communities L090, p. 26, 14/4/1993 of 15th March 1993.

Commission Directive 95/3/EEC, Official Journal of the European Communities L041, p. 44, 23/2/1995 of 14th February 1995.

Commission Directive 96/11/EEC, Official Journal of the European Communities L061, p. 26, 12/3/1996 of 5 March 1996.

Commission Directive 99/91/EC, Official Journal of the European Communities L310, p. 41, 4/12/1999 of 23rd November 1999.

Commission Directive 2001/62/EC, Official Journal of the European Communities L221, p. 18, 17/08/2001 of 9 August 2001.

Commission Directive 2002/17/EC, Official Journal of the European Communities L058, p. 19, 28/02/2002 of 21 February 2002.

Commission of European Communities. 1994, 'European parliament and council directive 94/62/EC of 20 December 1994', [Online]. Available : http//: europa.eu.int/eur-lex/en/lif/dat/1994/ en_394L0062.html, Accessed 28 May 2001.

Cornell, D. D. 1995, 'Plastics recycling: An overview', in *Plastics, Rubber, and Paper Recycling: A Pragmatic Approach,* ed Charles P. Rader, Sherly D. Baldwin, David D. Cornell, George D. Sadler and Richard F. Stockel, American Chemical Society, Washington DC, p. 72-79.

Council Directive 82/711/EEC, Official Journal of the European Communities L297, p. 26, 23/10/1982 of 18th October 1982.

Council Directive 89/109/EEC, Official Journal of the European Communities L40, p. 38, 11/2/1989 of 21st December 1988.

Crank, J. 1975, *The Mathematics of Diffusion,* Clarendon Press, Oxford, p. 137 - 159.

Crank, J. and. Park, J. S. 1978, *Diffusion in Polymer,* Academic Press, London.

Crosby, N. T. 1981, '*Food Packaging Material: Aspect of Analysis and Migration of Contaminats*', Applied Science Publisher, London.

Czerniawski, B. and Pogorzelska, Z. 1997, 'Investigations on overall migration of various plastic materials and articles used in contact with foodstuffs', *Packaging Technology and Science*, Vol. 10, p. 267 - 270.

Dábrowska, A., Borcz, A. and Nawrocki, J. 2003, 'Aldehyde contamination of mineral water stored in PET bottles', *Food Additives and Contaminants*, Vol. 20, No. 12, pp. 1170 - 1177.

D'Aniello, C., Guadagno, L., Gorrasi, G. and Vittoria, V. 2000, 'Influence of the crystallinity on the transport properties of isotactic polypropylene', *Polymer*, Vol. 41, pp. 2515 - 2519.

Dargent, E., Grenet, J. and Dahoun, A. 1997, 'Evolution of hot strain induced crystalline texture of poly(ethylene terephthalate) films', *Polymer Engineering and Science*, Vol. 37, No. 11, pp. 1856 - 1857.

Dawson, P. C., Gilbert, M. and Maddams, W. F. 1991,' Comparison of X-ray diffraction and thermal analysis methods for assessing order in poly(vinyl chloride)', *Journal of Polymer Science*, Vol. 29, pp. 1407 - 1418.

De Kruijf, N., Rijk, M. A. H. and Soethardi, L. A. 1983a, 'Investigation of suitability of isooctane as fatty food simulant', *Food Additives and Contaminants*, pp. 125 - 132.

De Kruijf, N., Rijk, M. A. H. and Soetardi, L. A. 1983b, 'Selection and application of new volatile solvent as food simulant for determining the global migration of constituents of plastic materials', *Food and Chemical Toxicology*, Vol. 21, No. 2, pp. 187 - 191.

De Kruijf, N. and Rijk, M. A. H. 1988, 'Iso-octane as fatty food simulant: possibilities and limitation', *Food Additives and Contaminants*, Vol. 5, pp. 467-483.

De Kruijf, N. and Rijk, R. 1994, 'Test method to simulate high-temperature exposure', *Food Additives and Contaminants*, Vol. 11, No. 2, pp. 197-222.

De Kruijf, N. and Rijk, M. A. H. 1997, 'The suitability of alternative fatty food simulant for overall migration testing under both low and high temperature test condition', *Food Additives and Contaminants*, Vol. 14, pp. 775-789.

Dekoninck, J. M., Legras, R. and Mercier, J. P. 1989, 'Nucleation of poly(ethylene terephthalate) by sodium compounds: a unique mechanism', *Polymer*, Vol. 30, pp. 910 -913.

De Leiris, J. P. 1986, 'Water activity and permeability', in *Food Packaging and Preservation*, ed M. Mathlouthi, Elsevier Applied Science, New York, p. 213 - 233.

Demertzis, P. G., Johansson, F., Lievens, C. and Franz, R. 1997, 'Development of quick inertness test procedure for multi-use PET container-sorption behavior of bottle wall strips, '*Packaging Science and Technology*, Vol. 10, pp. 45 - 58.

Devlieghere, F., De Meulenaer, B., Demyttenaere, J. and Huygherbaert, A. 1998, 'Evaluation of recycled HDPE milk bottles for food applications', *Food Additives and Contaminants*, Vol. 15, No. 3, pp. 336 – 345.

Dong, M., DiEdwardo, A. H. and Zitomer, F. 1980, 'Determination of residual acetaldehyde in poly(ethylene terephthalate) bottles, preforms and resin by automated headspace gas chromatography', *Journal of Chromatography Science*, Vol. 18, pp. 242 - 246.

Donnelly, A., Ohara, T. and Birkinshaw, C. 1997, 'Characterization of physical and molecular structure of thermal elongation poly(ethylene terephthalate)', *Journal of Applied Polymer Science*, Vol. 66, pp. 989 - 995.

Dröscher, M. and Wegner, G. 1978, 'Poly(ethylene terephthalate): a solid state condensation process', *Polymer*, Vol.19, pp. 43 - 47.

Duda, J. L. and Zielinski, J. M. 1996, 'Free-volume theory', in *Diffusion in Polymers*, ed. P. Neogi, Marcel Dekker Inc., New York, p. 143 - 171.

Dulio, V., Riccardo Po, Borrelli, R., Guarini, A. and Santini, C. 1995, 'Characterization of low-molecular-weight oligomers in recycled poly(ethylene terephthalate)', *Die Angewandte Makromolekulare Chemie*, Vol. 225, pp. 109 - 122.

Dumas, T. 1980, 'Determination of formaldehyde, acetaldehyde and associated components in solution and vapors by gas chromatography', *Journal of Chromatography A*, Vol. 200, pp. 206 - 210.

Durning, C. J., Rebenfeld, L. and Russel W. B. 1986, 'Integral sorption with induced crystallization', *Polymer Engineering and Science*, Vol. 26, pp. 1066 - 1078.

Dzięcioł, M. and Trzeszczyński, J. 1998, 'Studies of temperature influence on volatile thermal degradation product of polyethylene terephthalate', *Journal of Applied Polymer Science*, Vol. 69, pp. 2377 - 2381.

Dzięcioł, M. and Trzeszczyński, J. 2000, 'Volatile product of poly(ethylene terephthalate) thermal degradation in nitrogen atmosphere', *Journal of Applied Polymer Science*, Vol. 77, pp. 1894 - 1901.

Eberhartinger, S., Steiner, I., Washüttl, J. and Kroyer, G. 1990, 'Study of the migration of acetaldehyde from PET bottles into soft driks containing carbonic acid', *Z. Lebensn Unters Forsch*, Vol. 191, pp. 286 - 289.

Edlund, P. O. 1987, 'Chromatography analysis of acetaldehyde and formaldehyde', *Chromatographia*, Vol. 23, pp. 709 - 712.

European Standard EN 1186-1 (Part 1). 1999, Guide to the selection of condition and test method for overall migration.

European Standard EN 1186-2 (Part 2). 1999, Test method for overall migration into olive oil by total immersion.

European Standard EN 1186-3 (Part 3). 1998, Test method for overall migration into aqueous food simulants by total immersion.

European Standard EN 1186-10 (Part 10). 1999, Test method for overall migration into olive oil (modified method for use in cases where incomplete extraction of olive oil occurs).

European PreStandard ENV 1186-15 (Part 15). 1999, Alternative test method to migration into fatty food simulant by rapid extraction into iso-octane and/or 95% ethanol.

Fazzalari, F. A. 1973, *'Compilation of odor and taste threshold value data',* American Society for Testing and Materials, Philadelphia, Pensylvania.

Feigenbaum, A., Laoubi, S. and Vergnaud, J. M. 1997, 'Kinetics of diffusion of pollutant from a recycled polymer through a functional barrier; recycling plastics for food packaging', *Journal of Applied Polymer Science*, Vol. 66, pp. 597 - 607.

Feldman, D. and Barbalata, A. 1996, *Synthetic Polymer. Technology, Properties, Applications,* 1st edn, Chapman and Hall, New York, p.177.

Feron, V. J., Kruysse, A., and Woutersen, R. A. 1982, 'Respiratory tract tumor in hamsters exposed to acetaldehyde vapor alone or simultaneously to benso[a]pyrene or diethylnitrosamine', *European Journal of Cancer and Clinical Oncology*, Vol. 18, pp. 13 - 31.

Feron, V. J., Jetten, J., De Kruijf, N. and Van den Berg, F. 1994, 'Polyethylene terephthalate bottles (PBRs): A health and safety assessment', *Food Additives and Contaminants*, Vol. 11, No.5, pp. 571 - 594.

Fordham, P. J., Gramshaw, J. W., Crews, H. M. and Castle, L. 1995, 'Element residues in food contact plastics and their migration into food simulant, measured by inductively-coupled plasma-mass spectrometry', *Food Additives and Contaminants*, Vol. 12, No. 5, pp. 651 - 669.

Franck, V., Cuodane, J. and Vert, M. 1994, 'Titration of aldehyde present in poly(ethylene terephthalate)', *Journal of Applied Polymer Science*, Vol. 52, pp. 55 - 60.

Franck, V., Coudane, J. and Vert, M. 1995, 'Thermal degradation of polyethylene terephthalate : Study of polymer stabilization', *Polymer Degradation and Stability*, Vol. 49, pp. 393 - 397.

Franz, R. 1999, 'Migration of plastics constituent', in *Plastics Packaging Material for Food: Barrier Function, Mass Transport, Quality Assurance and Legislation,* ed O. G. Piringer and A. L. Baner, Wiley-VCH, New York, p. 287 - 357.

Franz, R. 2002, 'Program on the recyclability of food-packaging materials with respect to food safety considerations: polyetylene terphthalate (PET), paper and board and plastics covered by functional barriers', *Food Additives and Contaminants*, Vol. 19, pp. 93 - 110.

Franz, R., Huber, M. and Piringer, O. G. 1994, 'Testing and evaluation of recycled plastics for food packaging use-possible migration through a functional barrier', *Food Additives and Contaminants*, Vol. 11, No. 4, pp. 479 - 496.

Franz, R., Huber, M., Piringer, O. G., Dumant, A. P., Jicklles, S. M. and Castle, L. 1996, 'Study of functional barrier properties of multiplayer recycled poly(ethylene terephthalate) bottles for soft drinks', *Journal of Agricultural and Food Chemistry*, Vol. 44, pp. 892 - 867.

Franz, R., Huber, M. and Piringer, O. G. 1997, 'Presentation and experimental verification of physico-mathematical model describing the migration across functional barrier layers into foodstuffs', *Food Additives and Contaminants*, Vol. 14, pp. 627 - 640.

Freire, M. T. De A., Castle, L., Reyes, F. G. R. and Damant, A. P. 1998, 'Thermal stability of polyethylene terephthalate food contact materials : formation of volatiles from retail samples and implications for recycling', *Food Additives and Contaminants*, Vol. 15, No. 14, p. 473 - 480.

Freire, M. T. De. A., Damant, A. P., Castle, L. and Reyes, F. G. R. 1999, 'Thermal stability of polyethylene terephthalate (PET): Oligomer distribution and formation of volatiles', *Packaging Technology and Science*, Vol. 12, pp. 29-36.

Galić K. and Ciković, N. 2001, 'Permeability characterization of solvent treated polymer materials', *Polymer Testing*, Vol. 20, pp. 599 - 606.

Galotto, M. J. and Guarda, A. 1999, 'Comparison between thermal and Microwave treatment on the overall migration of plastic material intended to be in contact with food', *Packaging Science and Technology*, Vol. 12, pp. 277 - 281.

Garde, J. A., Catala, R., Gavara, R. and Hernandez, R. J. 2001, 'Characterizing the migration of antioxidants from polypropylene into fatty food simulant', *Food Additives and Contaminants*, Vol. 18, No. 8, pp. 750 - 762.

Gavara, R. and Hernandex, R. J. 1994, 'The effect of water transport on oxygen through Nylon-6 films', *Journal of Polymer Science. Polymer Physics Edition*, Vol. 32, pp. 2375 - 2382.

Geil, P. H. 1997, 'Polymer Morphology', in *Introduction to Polymer Science and Technology: An SPE Textbook*, ed Herman. S. K. and Joshep J. F., John Wiley and Sons Inc., New York, p. 206 - 238.

Gilbert, J. and Rossi, L. 2000, 'European priorities for research to support legislation in the area of food contact material and articles', *Food Additives and Contaminants*, Vol. 17, No. 1, pp. 83 - 127.

Gnanasekharan, V. and Floros, J. D. 1997, 'Migration and sorption phenomena in packaged foods', *Critical Reviews in Food Science and Nutrition*, Vol. 37, pp. 519 - 559.

Gogolewski, S. and Mainil Varlet, P. 1996, 'The effect of thermal treatment on sterility, molecular and mechanical properties of various polyactides', *Biomaterials*, Vol. 17, pp. 523 - 528.

Goydan, R., Schwope, A. D., Reid, R. C. and Cramer, G. 1990, 'High-temperature migration of antioxidants from polyolefins', *Food Additives and Contaminants*, Vol. 7, No. 3, pp. 323 - 337.

Gramshaw, J. W. Vandenburgh, H. J. and Lakin, R. A. 1995, 'Identification of potential migrants from samples of dual-ovenable plastics', *Food Additives and Contaminants*, Vol. 12, No, 5, pp. 211-222.

Gray, A. P. 1970, 'Polymer crystallinity determination by DSC', *Thermochimica Acta*, Vol. 1, No. 6, pp. 563 - 579.

Griffin, N., Moore, A. and Renvoize, I., 1996, 'EC Legislation on food contact materials and article', in *Food Science Reviews. Volume 2. Chemical Migration from Food Packaging*, ed Watson D. H. and. Meah M. N., Woodhead Publishing Ltd., p. 35 - 42.

Groeninckx, G., Reynaers, H., Berghmans, H. and Smets, G. 1980, 'Morphology and melting behavior of semi-crystalline poly(ethylene terephthalate). I. Isothermally crystallized PET', *Journal of Polymer Science. Polymer Physic Edition*, Vol. 18, pp. 1311 - 1323.

Gümther, B. and Zachmann, H. G. 1982, 'Influence of molar mass and catalyst on the kinetics of crystallization and on the orientation of poly(ethylene terephthalate)', *Polymer*, Vol. 24, pp. 1008 -1014.

Hadjilambrinos, C. 1996, 'A review of plastics recycling in the USA with policy recommendations', *Environmental Conservation*, Vol. 23, No. 4, pp. 298 - 306.

Hagemeyer, H. J. 1987, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons Inc., New York, p. 97 - 112.

Hamdani, M. and Feigenbaum, A. 1996, 'Migration from plasticized poly(vinyl chloride) into fatty media : Importance of stimulant selectivity for the choice of volatile fatty acid stimulant', *Food Additives and Contaminants*, Vol. 13, pp. 717 - 730.

Hamdani, M., Feigenbaum, A. and Vergnaud, J. M. 1997, 'Prediction of worst case migration from packaging to food using mathematical models', *Food Additives and Contaminants*, Vol. 14, No. 5, pp. 499 - 506.

Han, J., Selke, S. E., Downes, T.W. and Harte, B.R. 2003. 'Application of a computer model to evaluate the ability of plastics to act as functional barrier', *Packaging Technology and Science*, Vol. 16, pp. 107-118.

Hatakeyama, T. and Quinn, F. X. 1999, *Thermal Analysis. Fundamental and Applications to Polymer Science,* John Wiley and Sons Inc., New York.

Hayashi, H., Sakai, H. and Matsuzawa, S. 1994, 'Diffusion of methyl esters of higher fatty acid in polypropylene', *Journal of Applied Polymer Science*, Vol. 51, pp. 2165 - 2173.

Hedenqvist, M., Trakner, T., Varkalis, A., Johnsson, G. and Gedde, U. W. 1993, 'Sorption of liquid propane in polyethylene', *Thermochimica Acta*, Vol. 214, pp. 111 - 122.

Hollifield, H. C. and Begley, T. H. 1991, 'Food and drug administration studies of high temperature food packaging', in *Food Packaging Interaction II*, ed Sarah J. R. and Joseph H. Hotchkiss, American Chemical Society, Washington DC, p. 22 - 36.

Huber, M. and Franz, R. 1997, 'Studies on contamination of post consumer plastics from controlled resources for recycling into food packaging application', *Deutshe Lebensmittel-Rundschau*, Vol. 93, No. 10, pp. 328-331.

Improta, C., Nota, G., Ferretti, C. and Papale, U. 1984, 'Determination of formaldehyde and acetaldehyde (as cyanohydrins) in water by gas chromatography', *Journal of Chromatography*, Vol. 285, pp. 385 - 388.

Incarnato, L., Di Maio, L., Acierno, D., Denaro, M. and Arrivabene, L. 1998, 'Relationships between processing-structure-migration properties for recycled polypropylene in food pakaging', *Food Additives and Contaminants*, Vol. 15, No. 2, pp. 195-201.

Jabarin, S. A. 1987a, 'Crystallization kinetics of polyethylene terephthalate. I. Isothermal crystallization from the melt', *Journal of Applied Polymer Science*, Vol. 34, pp. 85 - 96.

Jabarin, S. A. 1987b, 'Crystallization kinetics of poly(ethylene terephthalate). II. Dynamic crystallization of PET', *Journal of Applied Polymer Science*, Vol. 34, pp. 97 - 102

Jabarin, S. A. 1987c, 'Crystallization kinetics of poly(ethylene terephthalate). III. Effect of moisture on the crystallization behavior of PET from the glassy state', *Journal of Applied Polymer Science*, Vol. 34, pp. 1083 - 108.

Jacquiss, D. B. G., Borman, W. F. H. and Campbell, R. W. 1982, in *Encyclopedia of Chemical Technology*, ed M. Grayson, John Wiley and Sons Inc., New York, p. 549.

Jayakannan, M. and Ramakrishnan, S. 1999, 'Effect of branching on the crystallization kinetics of poly(ethylene terephthalate)', *Journal of Applied Polymer Science*, Vol. 74, pp. 59 - 66.

Jetten, J., Kruijf, N. and Castle, L. 1999, 'Quality and safety aspects of reusable plastic food packaging materials: A European study to underpin future legislation', *Food Additives and Contaminants*, Vol. 16, No. 1, pp. 25 - 36.

Kashtock, M. and Breder, C. V. 1980, 'Migration of ethylene glycol from polyethylene terephthalate bottles into 3% acetic acid', *Journal of Association Official Analytical Chemistry*, Vol. 63, pp. 168-172.

Katan, L. 1996, 'Introduction', in *Migration from Food Contact Material*, ed L.L. Katan, Blackie Academic & Professional, London, p. 1 - 10.

Kay, J. F. 1991, 'Food-contact materials and articles: Standards for Europe', in *Food and Packaging Interactions II*, ed Sara J. Risch and Joseph H. Hotchkiss, American Chemical Society, Washington DC, p. 104 - 110.

Khemani, K. C. 2000, 'A novel approach for studying the thermal degradation, and for estimating the rate of acetaldehyde generation by chain scission mechanism in ethylene glycol base polyester and copolyester', *Polymer Degradation and Stability*, Vol. 67, pp. 91 - 99.

Khinnavar, R. S., Aminabhavi, T. M., Balundgi, R. H., Kutac, A. and Shukla, S. S. 1991, 'Resistance of barrier elastomers to hazardous organic liquid', *Journal of Hazardous Materials*, Vol. 28, pp. 281 - 294.

Kitano, Y., Kinoshita, Y. and Ashida, T. 1995, 'Morphology and crystal structure of an axis oriented, highly crystalline poly(ethylene terephthalate)', *Polymer*, Vol. 36, No. 10, pp. 1947 - 1955.

Komolprasert, V. and Lawson, A. R. 1995, 'Residual contaminants in recycled poly(ethylene terephthalate): Effect of washing and drying', in *Plastics, Rubber and Paper Recycling*, ed Charles P. Rader, David D. Cornell, George D. Sadler, Richard F. Stockel, American Chemical Society, Washington DC, p. 435 - 440.

Komolpraset, V. and Lawson, A. R. 1997, 'Consideration for reuse of poly(ethylene terephthalate) bottles in food packaging: Migration study', *Journal Agricultural and Food Chemistry*, Vol. 45, pp. 444 – 448.

Komolprasert, V., Lawson, A. R. and Begley, T. H. 1997, 'Migration of residual contaminants from secondary recycled poly(ethylene terephthalate) into food stimulating solvents, aqueous ethanol and heptane', *Food Additives and Contaminants*, Vol. 14, No. 5, pp. 491 – 498.

Komolpraset, V., McNeal, T. P., Agrawal, A., Adhikari, C. and Thayer, D. W. 2001, 'Volatile and non-volatile compounds in irradiated semi-rigid crystalline poly(ethylene terephthalate) polymers', *Food Additives and Contaminants*, Vol. 18, No. 1, pp. 89 - 101.

Kong, Y. and Hay, J. N. 2002, 'The measurement of the crystallinity of polymers by DSC', *Polymer*, Vol. 43, pp. 3873 - 3878.

Kroes, R., Galli, C., Munro, I., Schilter, B., Tran, L. A., Walker, R. and Wurtzen, G. 2000, 'Threshold of toxicological concern for chemical substances present in the diet: a practical tool for assessing the need for toxicity testing', *Food and Chemical Toxicology*, Vol. 38, pp. 255 - 312.

Laoubi, S. and Vergnaud, J. M. 1995, 'Process of contaminants transfer through a food package made of a recycled film and a functional barrier', *Packaging Science and Technology*, Vol. 8, pp. 97 - 110.

Laoubi, S., Feigenbaum, A. and Vergnaud, J. M. 1995, 'Safety of recycled plastics for food contact materials: Testing to define a functional barrier', *Packaging Technology and Science*, Vol. 8, pp. 17 - 27.

Lau, O. and Wong, S. 1996, 'The migration of plasticizer from cling film into food during microwave heating-effect of fat content and contact time', *Packaging Technology and Science*, Vol. 9, pp. 19 - 27.

Lau, O. and Wong, S. 2000, 'Contamination in food from packaging material', *Journal of Chromatography*, Vol. 882, pp. 255 - 270.

Leber, A. P. 2001, 'Human exposure to monomers resulting from consumer contact with polymers', *Chemico-Biological Interaction*, Vol. 135 - 136, pp. 215 - 220.

Li, B., Yu, J., Lee, S. and Ree, M. 1999, 'Crystallization of poly(ethylene terephthalate co ethylene isophthalate)', *Polymer*, Vol. 40, pp. 5371 - 5375.

Linssen, J. P. H., Verheul, A., Roozen, J. P. and Posthumus, M. A. 1991, 'Absorption of flavor compounds by packaging material: Drink yoghurt in polyethylene bottles', *International Dairy Journal*, Vol. 1, pp. 33 - 40.

Linssen, J., Reitsma, H. and Cozijnsen, J. 1995, 'Static headspace gas chromatography of acetaldehyde in aqueous food and polyethylene terephtalate', *Zeitschrift fur Lebensmittel-Untersuchung und-Forschung*, Vol. 201, No. 3, pp.253 - 255.

Liu, H., Li, J. and Hu, Y. 1999, 'A transport model for sorption and desorption of penetrants in glassy polymer membrane', *Fluid Phase Equilibria*, Vol. 158 - 160, pp. 1035 - 1044.

Lo Russo, S., Gramiccioni, L., Di Marzio, S., Milana, M. R., Pospero, P. and Papetta, A. 1985, 'Acetaldehyde from polyethylene (PET) container. Chemical determinations and toxicological assessment', *Annali di Chimica*, Vol. 75, pp. 403 - 414.

Lox, F., Van Dael, S. and Machiels, V. 1992, 'Organoleptic and migrational properties of PP film produced with various amounts of scrap', *Packaging Technology and Science*, Vol. 5, pp. 307 - 312.

Lu, X. F. and. Hay, J. N. 2001, 'Crystallization orientation and relaxation in uniaxially drawn poly(ethylene terephthalate)', *Polymer*, Vol. 42, pp. 8055 - 8067.

Lucht, L. M. and Peppas, N. A. 1987, 'Transport of penetrants in the macromolecular structure of coals. V. Anomalous transport in pretreated coal particle', *Journal of Applied Polymer Science*, Vol. 33, pp. 1557 - 1566.

Luong, J., Sieben, L., Fairhurst, M. and Dezeeuw, J. 1996, 'Determination of low levels of formaldehyde and acetaldehyde by gas chromatography flame ionization detection with a nickel catalyst', *HRC-Journal of High Resolution Chromatography*, Vol. 19, pp. 591 - 594.

Lupien, J. R. 1997, 'Food packaging, international standards related to food safety and quality, and trade', *Food Additives and Contaminants*, Vol. 14, No. 6-7, p. 519 - 527.

Lützow, N., Tihminlioglu, A., Danner, R. P., Duda, J. L., De Haan, A., Warnier, G. and Zielinski, J. M. 1999, 'Diffusion of toluene and n-heptane in polyethylenes of different crystallinity', *Polymer*, Vol. 40, pp. 2797 - 2803.

Maarse, H. 1991, *Volatile Compounds in Foods and Beverages,* Marcell Dekker Inc., New York.

MacElroy, J. M. D. 1996, 'Diffusion in Homogeneous Media', in *Diffusion in Polymer*, ed P. Neogi, Marcel Dekker Inc., New York, p. 1 - 65.

Manabe, S. 1996, 'Supermolecular structure of polymer solid and its effect on penetrant transport', in *Diffusion in Polymer*, ed P. Neogi, Marcel Dekker Inc., New York, p. 211 - 250.

Mancini, S. D. and Zanin, M. 1999, 'Recyclability of PET from virgin resin', *Materials Research*, Vol. 2, No. 1, pp. 33 - 38.

Mancini, S. D. and Zanin, M. 2000, 'Consecutive steps of PET recycling by injection: Evaluation of the procedure and of the mechanical properties',*Journal of Applied Polymer Science*, Vol. 76, pp. 266 - 275.

Mariani, M. B., Chiacchierini, E. and Gesumundo, C. 1999, 'Potential migration of di-isopropyl naphthalene from recycled paperboard packaging into dry foods', *Food Additives and Contaminants*, Vol. 16, No. 5, p. 207 - 213.

Mark, J. E. 1999, *Polymer Data Handbook,* Oxford University Press, New York, p. 558 - 560.

Mark, H. F. and. Atlas, S. 1977, 'Introduction to Polymer Science', in *Introduction to Polymer Science and Technology: An SPE Textbook*, ed Herman. S. K. and Joshep J. F., John Wiley and Sons Inc., New York, p. 1 - 23.

Markarewicz, P. J. and Wilkes, G. L. 1978, 'Diffusion studies of poly(ethylene terephthalate) crystallized by non-reactive liquids and vapors', *Journal of Polymer Science. Polymer Physics Edition*, Vol. 16, pp. 1529 - 1544.

McDowell, C. C., Freeman, B. D. and McNeely, G. W. 1998, 'Acetone sorption and uptake kinetic in poly(ethylene terephthalate)', *Polymer*, Vol. 40, pp. 3487 - 3499.

McDowell, C. C., Partin, J. M., Freeman, B. D. and McNeely, G. W. 1999, 'Acetone solubility and diffusivity in poly(ethylene terephthalate) modified with low levels of 2,6-naphthalene dicarboxylic acid, isophthalic acid, and 2,5-bis-(4-carboxyphenyl)-1,3,4-oxadiazole', *Journal of Membrane Science*, Vol. 163, pp. 39 - 49.

Mercea, P. 1999, 'Model for Diffusion in Polymer' in *Plastic Food Packaging Materials: Barrier Function, Mass Transport, Quality Assurance, Legislation*, ed O. G. Piringer and A. L. Baner, Wiley-VCH, New York, 125 - 157.

Mehta, A., Gaur, U. and Wunderlich, B. 1978, 'Equilibrium melting parameter of poly(ethylene terephthalate)', *Polymer Science. Polymer Physic Edition*, Vol. 16, pp. 289 - 296.

Miltz, J. 1992, 'Food Packaging', in *Hand Book of Food Engineering*, ed D. Heldman and D. Lund, Marcel Dekker Inc., New York, pp. 667 - 718.

Miltz, J., Ram, A. and Nir, M. M. 1997, 'Prospect for food application of post-consumer used plastics in food packaging', *Food Additives and Contaminants*, Vol. 14, No. 6-7, pp. 649 - 659.

Miyake, T. and Shibamoto, T. 1993, 'Quantitative analysis of acetaldehyde in food and beverages', *Journal of Agricultural and Food Chemistry*, Vol. 41, pp. 1968 - 1970.

Mogri, Z. and Paul, D. R. 2001, 'Gas sorption and transport in side-chain crystalline and molten poly(octadecyl acrylate)', *Polymer*, Vol. 42, pp. 2531 - 2542.

Mohney, S. S., Hernandez, R. J., Giacin, J. R. and Miltz, J. 1988, 'Permeability and solubility of d-limonene vapor in cereal package liner', *Journal of Food Science*, Vol. 53, pp. 253 - 257.

Monarca, S., De Fusco, R., Biscardi, D., De Feo, V., Pasquini, R., Fatigoni, C., Moretti, M. and Zanardini, A. 1994, 'Studies of migration of potentially genotoxic compound into water stored in PET bottles', *Food and Chemical Toxicology*, Vol. 32, pp. 783 - 788.

Morrison, G.H. and Freiser, H. 1957, *Solvent Extraction in Analytical Chemistry*, John Wiley and Son, New York.

Murthy, N. S., Khanna, Y. P. and Signorelli, A. J. 1994, 'Crystallinities of poly(chlorotrifluoroethylene) and its copolymers by differential scanning calorimetry, X-ray diffraction and density measurements', *Polymer Engineering and Science*, Vol. 36, No. 16, pp. 1254 - 1259.

Myung, H. S, Yoon, W. J., Yoo, E. S., Kimm, B. C. and Im, S. S. 2001, 'Effect of shearing on crystallization behavior of poly(ethylene terephthalate)', *Journal of Applied Polymer Science*, Vol. 80, pp. 2640 - 2464.

Nawrocki, J., Dàbroswka, A. and Borcz, A. 2002. 'Investigation of carbonyl compounds in bottled waters from Poland', *Water Research,* Article in Press.

Neogi, P. 1996, 'Transport Phenomena in Polymer Membranes', in *Diffusion in Polymer*, ed P. Neogi, Marcel Dekker Inc., New York, p. 173 - 209.

Ner, C., Asensi, E. and Batle, R. 2000, 'Supercritical fluid extraction of additives and degradation product from both virgin and recycled PET', Vol. 19, pp. 205 - 212.

Nerin, C., Salafranca, C., Rubio, C. and Cacho, J. 1998, 'Multicomponent recycled plastics: Considerations about their use in food contact applications', *Food Additives and Contaminants*, Vol. 15, No. 7, pp. 842 - 854.

Nerin, C., Acosta, D. and Fernandez, C. 2001, 'Temperature profile of several plastic containers and food packages in microwave ovens and behaviour of several solid adsorbents used as food simulates', *Food Additives and Contaminants. Article in Press.*

Nerin, C., Acosta, D. and Rubio, C. 2002, 'Potential migration release of volatile compunds from plastic container destined for food used in microwave ovens', *Food Additives and Contaminanants*', Vol. 19, No. 6, pp. 594 - 601.

Neway, B., Westberg, A., Mattozzi, A., Hedenqvist, M. S., Baschetti, M. G., Mathot, V. B. F. and Gedde, U. W. 2004, 'Free volume and transport properties of homogeneous poly(ethylene-*co*-octene)s', *Polymer,* Article in Press.

Newton, J. 1997, 'Film, Oriented Polyester', in *The Wiley Encyclopedia of Packaging Technology 2nd edn*, ed Brody A. L. and Marsh. K. S., John Wiley and Sons Inc., Inc., New York, pp. 408 - 415.

Nichols, M. E. and Robertson, R. E., 1992. 'The original of multiple melting endotherm in thermal analysis of polymers'. *Journal Polymer Science. Part B, Polymer Physic*, Vol. 30, pp. 305 - 306.

Nijssen, B., Kamperman., T and Jetten, J. 1996, 'Acetaldehyde in meneral water stored in polyethylene terephthalate (PET) bottles : Odour treshold and quantification', *Packaging Technology and Science*, Vol. 9, pp. 175 - 185.

Nir, M. M., Ram, A. and Miltz, J. 1996, 'Sorption and migration of organic liquids in poly(ethylene terephthalate)', *Polymer Engineering and Science*, Vol. 36, No. 6, pp. 862 - 868.

Nouri, B., Fouilet, B., Toussaint, G., Chambon, R. and Chambon, P. 1996, 'Complementary of purge-trap and trap and headspace capillary gas chromatography methods for determination of methyl-*ter*-butyl ether in water', *Journal of Chromatography A*, Vol. 726, pp. 153 - 159.

O'Brien, A. Leach, A. and Cooper, I. 2000, 'Polypropylene: Establishment of a rapid extraction test for overall migration limit compliance testing', *Packaging Science and Technology*, Vol. 13, 13 -18.

O'Brien, A. and Coper, I. 2002, 'Practical experience in the use of mathematical models to predict migration of additives from food-contact polymers', *Food Additives and Contaminants*, Vol. 19, Supplement, pp. 63 - 72.

O'Malley, J. J. 1975, 'Crystalline isomeric polyester block copolymers. Scanning calorimetry and density measurements', *Journal of Polymer Science. Polymer Physic Edition*, Vol. 13, pp. 1353 - 1363.

Overton, B. W. 1994, 'Impact of recycling and environmental legislation', *Food Additives and Contaminants*, Vol. 11, pp. 285 - 293.

PACIA (Plastics And Chemicals Industries Association Inc.). 2003, 'National plastics recycling survey 2003. Main survey report, September 2003", [Online], Available: http://www.pacia.org.au/Recycling/PACIARecycling Rpt1-3-2003.pdf, Accessed 27 May 2004.

Pan, L., Adams, M. and Pawliszyn, J. 1995, 'Determination of fatty acid using solid-phase microextraction', *Analytic Chemistry*, Vol. 67, pp. 4396 - 4403.

Patton, C. J., Felder, R. M. and Koros, J. 1984, 'Sorption and transport of benzene in PET', *Journal of Polymer Engineering and Science*, Vol. 29, pp. 1095 - 1110.

Philo, M. 1994, 'Stability of plastics monomer in food simulating liquid under European union test condition, '*Journal of Agricultural and Food Chemistry*, pp. 1487 - 1501.

Pierce, D. E., King, D. B. and Sadler, G. D. 1995, 'Analysis of contaminants in recycled poly(ethylene terephthalate) by thermal extraction gas chromatography-mass spectroscopy', in *Plastics, Rubber, and Paper Recycling: A Pragmatic Approach*, ed Charles P. Rader, Sherly D. Baldwin, David D. Cornell, George D. Sadler and Richard F. Stockel, American Chemical Society, Washington DC, p. 458 - 471.

Piringer, O. G. 1999, 'Permeation of gases, water vapor and volatile organic compounds', in *Plastic Packaging Material for Food: Barrier function, Mass transport, Quality Assurance and Legislation*, ed O. G. Piringer and A. L. Baner, Wiley-VCH, New York, p. 239 - 285.

Poretta, S. and Minuti, E. 1995, 'Acetaldehyde in PET-package commercial mineral waters and soft drink: Determination of its content and evaluation of its taste threshold', *Industria Conserve*, Vol. 70, PP. 266 - 274.

Possanzini, M. and Di Palo, V. 1997, 'Determination of formaldehyde and acetaldehyde in air by HPLC with fluorescence detection', *Chromatographia*, Vol. 46, No. 5/6, pp. 235 - 420.

Qureshi, N., Stepanov, E. V., Schiraldi, D., Hiltner, D. and Baer, E. 2000, 'Oxygen-barrier properties of oriented and heat-set poly(ethylelene terephtalate)', *Journal of Polymer Science. Part B: Polymer Physic*, Vol. 38, No. 13, pp. 1679 - 1686.

Ram, A. 1997, *Fundamentals of Polymer Engineering*, Plenum Press, New York.

Ram, A., Meir, T. and Miltz, J. 1980, 'Durability of polyethylene films', *International Journal of Polymeric Materials*, Vol. 8, pp. 323 - 366.

Ramakrishna, A., Srivatsa, A. N., Siddaramaiah and Varadarajulu, A. 1997, 'The effect of thermal treatment on the properties of PP film and laminated', *Packaging Science and Technology*, Vol 10, pp. 83 - 86.

Richard, R. E., Boon, W. H., Martin-Shultz, M. L. and Sisson, E. A. 1992, 'Incorporating post consumer recycled poly(ethylene terephthalate): A new polyester', in *Plastic Recycling, ACS Symposium Series 513*, ed G.D. Andrewa and. P. M. Subraminiam, American Chemical Society, Washington DC.

Ritchie, M. 1966, *'Chemical Kinetics in Homogeneous System'*, Oliver & Boyd, London, p. 1 - 15.

Robert, R. C., 1969, 'Poly(ethylene terephthalate). I-Heat fusion', *Polymer'*, Vol. 10, pp. 113 - 116.

Robertson, G. L., 1993, *Food Packaging. Principle and Practice,* Marcel deckker Inc., New York, p. 73 – 100.

Rogers, C. E. 1985, 'Permeation of gases and vapors in polymers', in *Polymer Permeability*, ed J. Comyn, Elsevier Applied Science, London, p. 11.

Rubin, I. 1990, *Handbook of Plastics Material and Technology,* John Wiley and Sons Inc., New York, pp. 664 -645.

Sadler, G., Pierce D., Lawson, A. and Suvannunt, V. 1996, 'Evaluating organic compound migration in poly(ethylene terephthalate) a simple test with implications for polymer recycling', *Food Additives and Contaminants*, Vol. 13, No. 8, pp. 979 - 988.

Salame, M. 1989, 'The use of barrier polymers in food and beverage packaging', in *Plastic Film Technology, Volume One - High Barrier Plastics Film for Packaging*, ed Finlayson K.M., Technomic Publishing Company, Lancaster, Pensylvania, p. 132 - 145.

Samperi, F., Puglisi, C., Alicata, R. and Montaudo, G. 2003, 'Thermal degradation of polyethylene at the processing temperature', *Polymer Degradation and Stability*, Article in Press.

Scheirs, J. 1998, 'Recycling of PET', in *Polymer Recycling Science, Technology and Applications*, John Willey and Sons Inc., New York, pp. 121 - 181.

Schwartz, P. S. 1994, 'Update on migration research and regulatory initiatives', *Food Additives and Contaminants*, Vol. 1, pp. 261 - 270.

Selikhova, V. I. 1989, 'Effect of orientation and annealing on melting and recrystallization processes in polypropylene', *Polymer Science*, Vol. 31, pp. 804 - 808.

Selke, S. E. 1988, 'Recycling of plastics packaging in the United States', *Packaging Technology and Science*, Vol. 1, pp. 93 - 98.

Selke, S. E. M. 1990, *Packaging and the Environment: Alternatives, Trends, and Solutions*, Lancaster, Pennsylvania., USA, Technomic Publishing Company Inc., p. 119 - 139.

Shieh, L. Y. and Peppas, N. A. 1991, 'Solute and penetrant diffusion in swellable polymer. XI. The dynamic swelling behavior of hydrophilic copolymers containing multiethylene glycol dimethacrylates', *Journal of Applied Polymer Science*, Vol. 42, pp. 1579 - 1587.

Shimoda, M., Matsui, T. and Osajima, Y. 1987, 'Effects of the number of carbon atoms of flavor compound on diffusion, permeation and sorption with polyethylene films', *Journal of Japan Nutrition and Food Science*, Vol. 34, pp. 353 - 539.

Shiono, S. 1979, 'Determination of poly(ethylene terephthalate) oligomers in refrigeration oils by adsorption column chromatography-gel permeation chromatography', *Analytical Chemistry*, Vol. 51, No. 14, pp. 2398 - 2400.

Shirataki, H., Nakashima, A., Sato, K. and Okajima, K. 1997, 'Correlation between tensile properties and network draw range of molecular orientation and crystallinity', *Journal of Applied Polymer Science*, Vol. 64, pp. 2631 - 2646.

Siripatrawan, U., Burgess, G. and Harte, B.R. 2000, 'The effect of repeated microwave heating, fill level and temperature on the impact resistance of polypropilene syrup bottle', *Packaging Technology and Science*, Vol. 13, pp. 205 -210.

Slatter, G. 1999, 'PET bottle collection, we top the world', *Packaging News,* August, p. 6.

Smith, E. B. 1993, *Basic Chemical Thermodynamic,* Clarendon Press, Oxford, p. 36 - 62.

Springer, H., Brinkmann, U. and Hinrichsen, G. 1981, '*Colloid and Polymer Science*, Vol. 259, pp. 38 - 45.

Starkweather, H. W., Zoller, P and Jones, G. A. 1983, 'The heat of fusion of poly(ethylene terephthalate), '*Polymer Science. Polymer Physic Edition*, Vol. 21, pp. 295 - 299.

Sugaya, N., Nakagawa, T., Sakurai, K., Morita, M. and Onodera, S. 2001, 'Analysis of aldehydes in water by head space-GC/MS', *Journal of Health Science*, Vol. 47, No. 1, pp. 21-27.

Sun, Y., Lin, C., Chen, Y. and Wu, C. 1997, 'Sorption and diffusion of organic vapors in poly[bis(trifluoroethoxy phosphazene] and poly[bis(phenoxy) phosphazene] membrane', *Journal of Membrane Science*, Vol. 134, pp. 117 - 126.

Suttles, M. L. and Marshal, R. T. 1993, 'Interactions of package and fluorescent light with the flavor of ice cream', *Journal of Food Protection*, Vol. 56, pp. 622 - 624.

Svensson, K., Nielsen, P. A., Svendsen, S., Sipilainen-Malm, T., Hammarling, L., Petersen, J. H., Hellstrom, T., Vaz, R. and Hallikainen, A. 1993, 'Packaging materials and cooking ware for food contact at high temperature', *Vardofa,*, p. 635.

Takami, K. K., Sugimae, A. and Nakamoto, M. 1985, 'Trace determination of aldehydes in water by high-performance liquid chromatography', *Analytical Chemistry*, Vol. 57, pp.243 - 245.

Ten Hulscher, Th. E. M. and Cornelissen, G. 1996, 'Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants-a review', *Chemosphere*, Vol. 32, No.4, pp. 609 - 626.

Thorsheim, H. R. and Armsrong, D. J. 1993, 'Recycled Plastics for food packaging : How do FDA policy and research ensure that recycled plastics are safe for food contact use?' *Chemtech*, Vol. 33, No. 8, pp. 55 - 58.

Tice, P. A. and Cooper, I. 1996, 'Migration test for food packaging', in Food Science Reviews : Chemical Migration from Food Packaging Volume 2, ed Watson, D. H. and Meah, M. N., Woodhead, England, p. 3 - 33.

Till, H. P., Wountersen, R. A. and Feron, V. J. 1988, 'Evaluation of the oral toxicity of acetaldehyde and formaldehyde in a 4-week drinking-water study in rats', *Food Chemical Toxicity*, Vol. 26, pp. 447 - 452.

Torres, N., Robin, J. J. and Boutevin, B. 2000, 'Study of thermal and mechanical properties of virgin and recycled poly(ethylene terepthalate) before and after injection molding', *European Polymer Journal*, Vol. 36, pp. 2075 - 2080.

Urdahl, K. G. and Peppas, N.A. 1987, 'Anomalous penetran transport in glassy polymer. V. Cyclohexane transport in polystyrene, '*Journal of Applied Polymer Science*, Vol. 33, pp. 2670 - 2687.

US Food and Drug Administration. June 1995, 'Recommendation for chemistry data for indirect food additive petitions', [Online], Available : http://vm. cfsan.gov/~dms/opa-cg5.html, Accessed 25 June 2003.

Van Aardt, M., Duncan, S. E., Bourne, D., Marcy, J. E., Long, T.E., Hackney, C. R., Heisey, C. 2001, 'Flavor threshold for acetaldehyde in milk, chocolate milk, and spring water using solid phase micro extraction gas chromatography for quantification', *Journal of Agricultural and Food Chemistry*, Vol. 49, pp. 1377 - 1381.

Van Krevelen, D. W. 1990, *Properties of Polymer. Their Correlaion with Chemical Structure; Their Numerical Estimation and Prodiction from Additives Group Contribution,* 3rd edn, Elsevier, New York.

Van Lune, F. S., Nijssen, L. M. and Linssen, J. P. H. 1997, 'Absorption of methanol and toluene by polyester-based bottles', *Packaging Science and Technology*, pp. 221 - 227.

Vergnaud, J. M. 1991, *Liquid Transport Process in Polymer Materials. Modeling and Industrial Application,* Prentice Hall, New York.

Verhoyen, O., Dupret, F. and Legras, R. 1998, 'Isothermal and non-isothermal crystallization kinetics of polyethylene terephthalate-mathematical modeling and experimental measurement', *Polymer Engineering and Science*, Vol. 38, No. 9, pp. 1594 - 1610.

Vermylen, V., Lodifier, P., Devaux, J., Legras, R., Mac Donald, W. A., Rozenberg, R. and De Hoffmann, E. 1999, 'Study of the thermal evolution of the cyclic-oligomer formation in a cyclic-oligomer-free PET', *Journal of Polymer Science*, Vol. 38, pp. 416 - 422.

Vilanova, P. C., Guzman G. M. and Ribas, S. M. 1985, 'Isothermal crystallization of poly(ethylene terephthalate) of flow molecular weight by differential scanning calorimetry: I. Crystallization kinetics', *Polymer*, Vol.26, pp. 423 - 428.

Villain, F., Coudane, J. and Vert, M. 1995, 'Thermal degradation of polyethylene terephthalate : study of polymer stabilization', *Polymer Degradation and Stability*, Vol. 49, pp. 393 - 397.

Vrentas, J. S. and Vrentas, J. M. 1994, 'Solvents self diffusion in glassy polymer-solvent system', *Macromolecules*, Vol. 27, pp. 5570 - 5576.

Wang, Z. G., Hsiao, B. S., Sauer, B. B. and Kampert, W. G. 1998, 'The nature of secondary crystallization in poly(ethylene terephthalate)', *Polymer*, Vol. 40, pp. 4615 - 4627.

Weast, R. C. 1969, *Handbook of Chemistry and Physics,* The Chemical Rubber Co., Ohio, USA, p. C-75.

Woodward, A. E., Crissman, J. M. and Saver, J. A. 1960, 'Investigations of dynamic mechanical properties of some polyamides', *Journal of Polymer Science*, Vol. 23, pp. 20 - 25.

Wyatt, D. M. 1983, 'Semi-automation of headspace GC as applied to determination of acetaldehyde in poly(ethylene terephthalate) beverage bottles', *Journal of Chromatography Science*, Vol. 21, pp. 508 - 511.

Yasuhata, A. and Shibamoto, T. 1991, 'Determination of volatile aliphatic aldehydes in headspace of heated food oils by derivatization with 2-aminoethabethiol', *Journal of Chromatography*, Vol. 547, pp. 291 - 298.

Yaws, C. L. 1999, Chemical properties handbook: physical, thermodynamic, environmental, transport, safety, and health related properties for organic and inorganic chemicals, McGraw-Hill Company, New York, p. 340 – 363.

Yoon, J., Jung, H., Kim, M. and Park, E. 2000, 'Diffusion coefficient and equilibrium solubility of water molecules in biodegradable polymers', *Journal of Applied Polymer Science*, Vol. 77, pp. 1716 – 1722.

Zaroulis, J. S. and Boyce, M. C. 1997, 'Temperature, strain rate, and strain state dependence of the evolution in mechanical behaviour and structure of poly(ethylene terephthalate) with finite strain deformation', *Polymer*, Vol. 38, No. 6, pp. 1303 - 1315.

Zhang, W. D. and. Shen, D. Y. 1998, 'The effects of thermal histories on crystallization of poly(ethylene terephthalate)', *Polymer Journal*, Vol. 30, No. 4, pp. 311 – 314.

Zimmermann, H. 1984, 'Degradation and stabilisation of polyester', in *Development in Polymer Degradation*, ed N. Grassie, Applied Science Publisher, New York.

APPENDIX A

Plot of ln (C_∞ - C_t) versus t

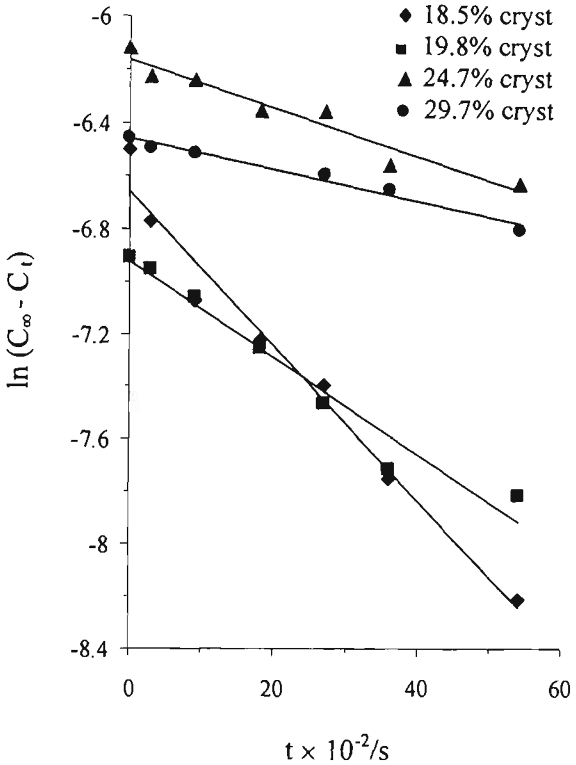


Figure A.1. Plot of ln (C_∞ - C_t) versus t for virgin PET sheet at 15°C

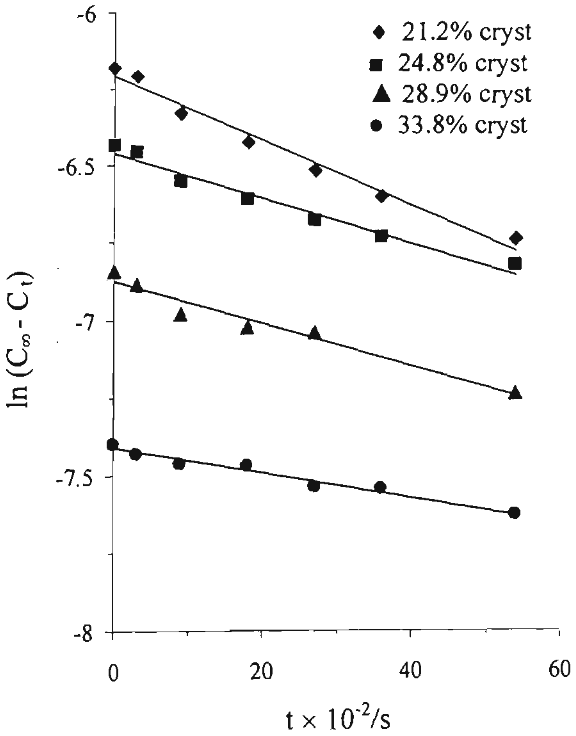


Figure A.2. Plot of ln (C_∞ - C_t) versus t for recycled PET sheet at 15°C

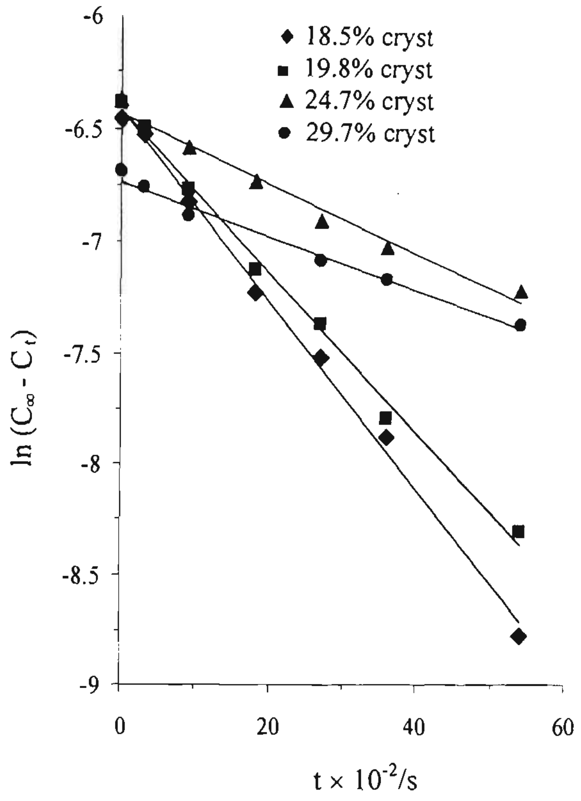


Figure A.3. Plot of ln (C_∞ - C_t) versus t for virgin PET sheet at 20°C.

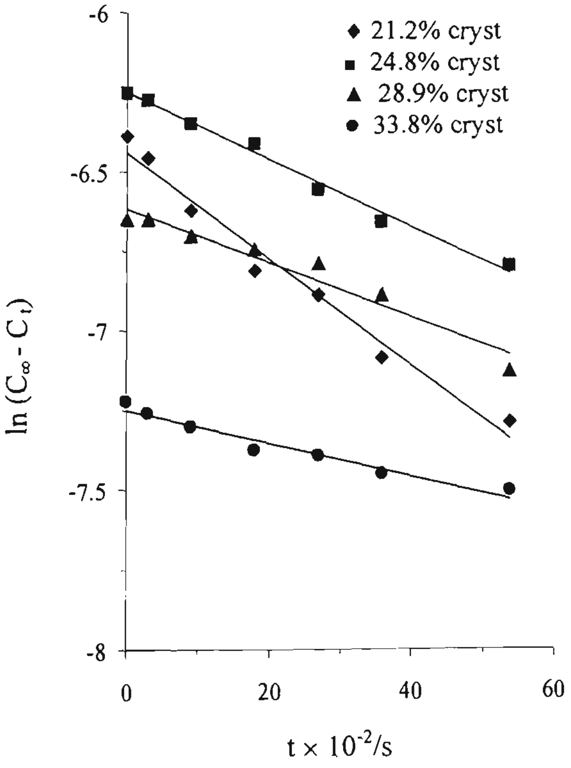


Figure A.4. Plot of ln (C_∞ - C_t) versus t for recycled PET sheet at 20°C

APPENDIX B

Example of calculation coefficient diffusion

Sorption of acetaldehyde into PET

Sample : Virgin-non heated PET

$T_{sortion}$: 5°C

Thikness (L) = 0.0250 ±0.0003 cm

Phi (π) = 3.1459

t/days	$t^{1/2}$	Mass/g	M_t	M_t/M_∞	ln $(1-M_t/M_\infty)$
0	0	0.3118	0	0	0
300	17.32	0.3143	0.0025	0.075758	-0.07878
900	30.00	0.3153	0.0035	0.106061	-0.11212
1800	42.43	0.3168	0.0050	0.151515	-0.1643
2700	51.96	0.3192	0.0074	0.224242	-0.25392
3600	60.00	0.3207	0.0089	0.269697	-0.3143
5400	73.48	0.3234	0.0116	0.351515	-0.43312
7200	84.85	0.3243	0.0125	0.378788	-0.47608
9000	94.87	0.3260	0.0142	0.430303	-0.56265
10800	103.92	0.3276	0.0158	0.478788	-0.6516
14400	120.00	0.3314	0.0196	0.593939	-0.90125
18000	134.16	0.3326	0.0208	0.630303	-0.99507
21600	146.97	0.3353	0.0235	0.712121	-1.24522
25200	158.75	0.3366	0.0248	0.751515	-1.39237
86400	293.94	0.3391	0.0273	0.827273	-1.75604
172800	415.69	0.3440	0.0322	0.975758	-3.71965
259200	509.12	0.3445	0.0327	0.990909	-4.70048
345600	587.88	0.3448	0.0330	1	

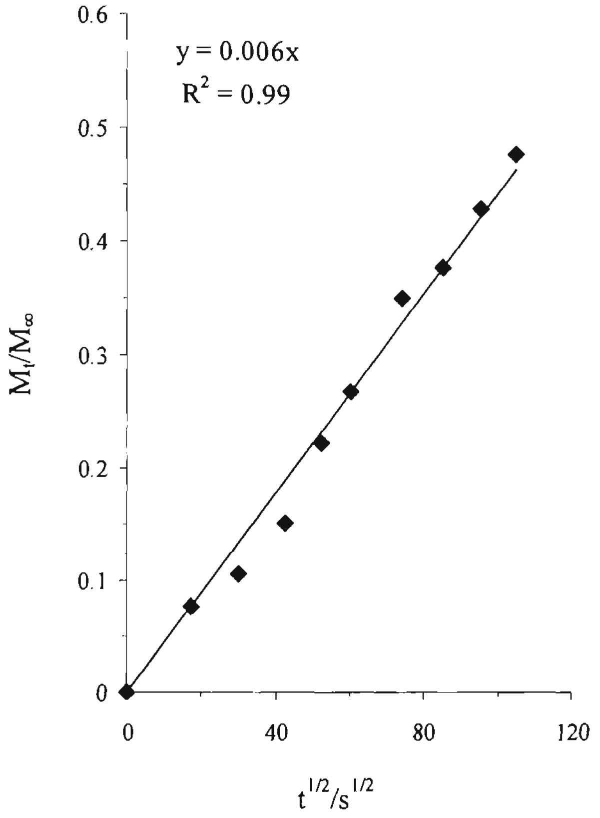


Figure B.1. Plot of M_t/M_∞ versus $t^{1/2}$ up to $M_t/M_\infty < 0.6$

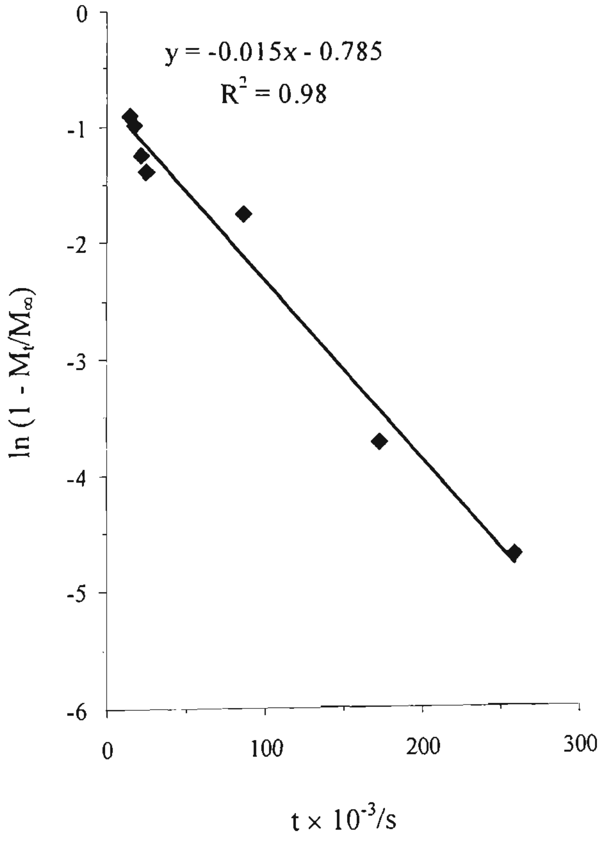


Figure B.2. Plot of ln (1-M_t/M_∞) versus t when $M_t/M_\infty > 0.6$

Coefficient diffusion, D, calculation

For short-term absorption:

Slope = $4(D/\pi L^2)^{1/2}$

D = $(0.006^2 \times 3.1459 \times 0.0250^2)/16$

= 4.4×10^{-9} cm^2 s^{-1}

For long-term absorption:

Slope = $-\pi^2 D/L^2$

D = $(0.0154 \times 10^{-3} \times 0.0250^2)/3.1459^2$

= 9.7×10^{-10} cm^2 s^{-1}

APPENDIX C

Concentration profile by a numerical method

C.1 Computer program to calculate the concentration profile of acetaldehyde in PET

```
% This program are used to calculate and plot the concentration profiles of actealdehyde
% sorbed into polyethylene terephthalate by solving the second Fick's law using numerical method
n=20; % number of x panels
D=4.42e-6 ; % diffusion coefficient
dx=1/n;% size of x panels, indeks i
dt=10;  % size of t panel, indeks j
alpha=D*dt/dx^2;
Y=eye(n+1);
for j=1:1;
   %Matriks Y
   for i=1:n+1;
      Y(i,i)=1+2*alpha;
   end

   for i=2:n+1;
      Y( i,i-1)=-alpha;
      Y(i-1,i)=-alpha;
   end
   %matriks M
   M=zeros(n+1,1);
   M(1,1)=1;
   M(n+1,1)=1;
   for i=1:n-1;
      M(i+1,1)=4*((i)*dx-0.5)^2;
   end
end
W=Y\M;

%M;
%W;
x=0:dx:1;
%plot (x,M,x,W);
for j=2:10000;
   for i=1:n+1;
      Y(i,i)=1+2*alpha;
   end

   for i=2:n+1;
      Y( i,i-1)=-alpha;
      Y(i-1,i)=-alpha;
```

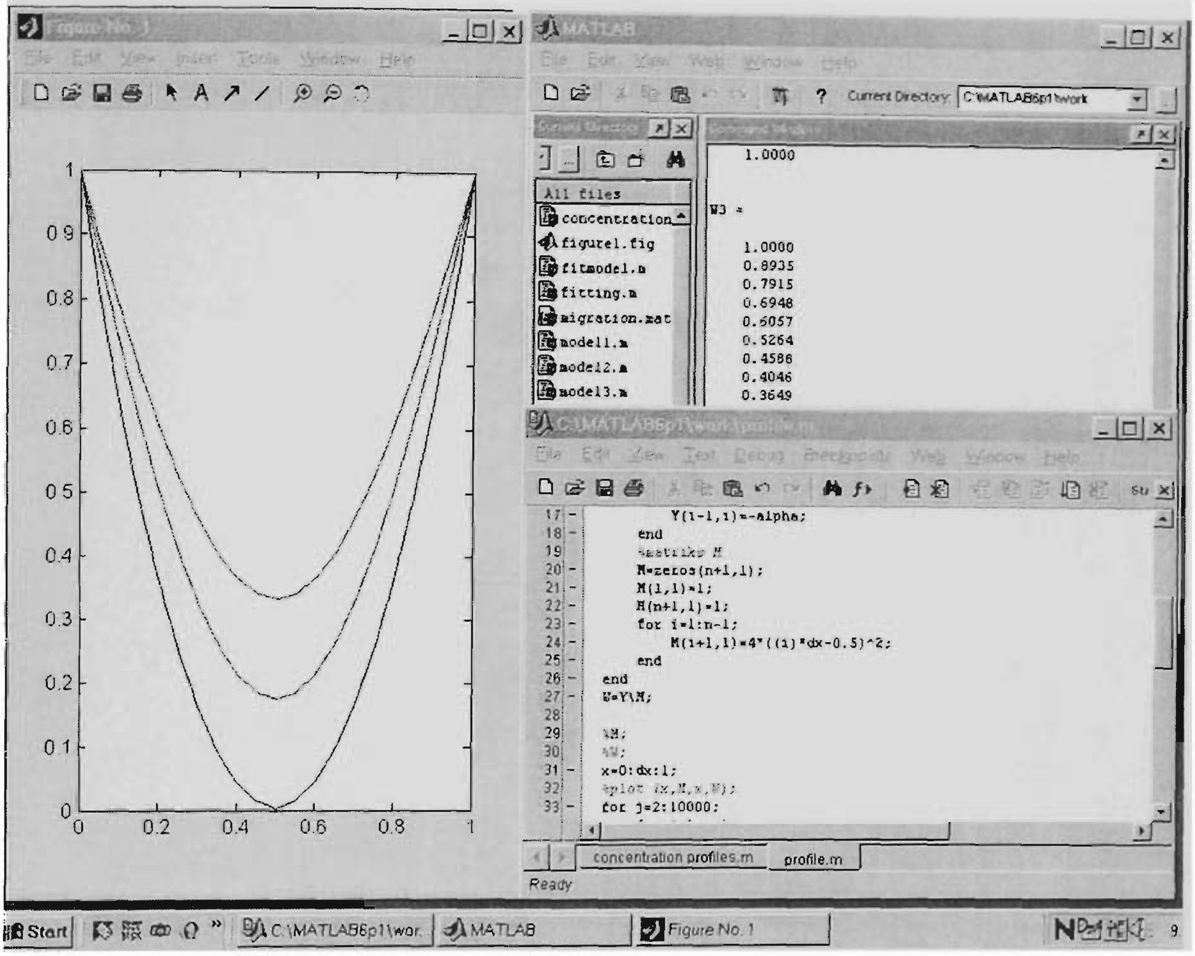
```
  end
  M=W;
  W=Y\M;
  W(1,1)=1;
  W(n+1,1)=1;
  W

 if j==100
    W1=W
 end

 if j==5000
     W2=W
  end
  if j==10000
     W3=W
  end

end
plot (x,W1,x,W2,x,W3)
```

C. 2 Display the profile.m program on the computer screen



```
All files
concentration
figure1.fig
fitmodel.m
fitting.m
migration.mat
model1.m
model2.m
model3.m
```

```
    1.0000


W3 =

    1.0000
    0.8935
    0.7915
    0.6948
    0.6057
    0.5264
    0.4586
    0.4046
    0.3649
```

```
            Y(i-1,i)=-alpha;
        end
        %matrike M
        M=zeros(n+1,1);
        M(1,1)=1;
        M(n+1,1)=1;
        for i=1:n-1;
            M(i+1,1)=4*((i)*dx-0.5)^2;
        end
    end
    W=Y\M;

    %M;
    %W;
    x=0:dx:1;
    %plot (x,M,x,W);
    for j=2:10000;
```