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# **The Influence of Chemically Treated Natural Fibers in Poly(Lactic Acid) Composites Containing Thymol**

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## **Keywords**

Poly(lactic acid); Natural fibers; Polymer composites; Mechanical properties; Thermal properties; Degradation

## **Abstract**

The mechanical, thermal and morphological properties of poly(lactic acid) (PLA) composites incorporated with 30% w/w untreated kenaf (UK) or treated kenaf (TK) fibers was explored together with the inclusion of 5-10% w/w thymol for potential antimicrobial packaging material applications. The TK fiber composites had significantly higher tensile strength than those containing UK fibers. Scanning electron micrograph images showed a better adhesion between the TK fibers and the matrix was achieved resulting in improved reinforcement of the PLA/TK fiber composite. The neat PLA and composites containing 10% w/w thymol exhibited lower processing torque, tensile strength, and glass transition temperatures than those without thymol suggesting a possible lubricating and/or plasticizing effect. However, the incorporation of thymol into PLA at this level as well as into the composites did not influence the flexibility of the materials as a whole. Decomposition in compost progressed rapidly for neat PLA and PLA/thymol resulting in complete disintegration within 35 days. The presence of kenaf slightly inhibited the decomposition although complete disintegration of the composite was achieved within 48 days. The results suggest that PLA composites containing kenaf have the potential to be developed as rigid, compostable food packaging items such as trays from biodegradable and renewable resources.

## 1. Introduction

To date, many researchers have studied bio-composite materials that are either derived from natural resources or renewable resources for various applications where the focus has been on creating materials that have a perceived low environmental impact. Poly(lactic acid) (PLA) is a relatively new and promising bio-based thermoplastic polyester that can be derived from renewable, bio-derived monomers obtained from a range of plants containing polysaccharides [1]. For packaging applications, in particular, this polymer provides good strength and optical properties, low toxicity, is readily compostable, and is easily formed using equipment that processes conventional, commercial polyolefin plastics [1, 2]. Although the potential of PLA for use in packaging applications has been established [3], there are some inherent limitations of this material such as its high production costs, poor water vapour and gas barrier properties, low heat resistance, and brittleness that limit its widespread application in this industry [4, 5].

Naturally-sourced fibers or lignocellulosic materials such as wood, kenaf, jute, ramie and flax are commonly used as cost-reducing biofillers and/or reinforcements for PLA. These can render the PLA more environmentally friendly in the sense that they can enhance the bio/hydro-degradability of the polymer [6, 7]. Furthermore, during processing PLA generally exhibits a better compatibility and interaction with natural fibers than petroleum-based polymers [8]. Thus, the incorporation of natural fibers into PLA matrices has recently gained attention in order to reduce costs and improve mechanical properties as well as enhance compostability and biodegradability [9, 10]. Bast fibers obtained from the outer stem layer of the kenaf plant (*Hibiscus cannabinus* L.) have good mechanical properties that enable this material to be used as a reinforcement in bio-polymer composites as an alternative to glass fibers [11]. However, the inherent hydrophilicity of this fiber requires that some chemical modifications need to be made in order to impart good surface adhesion between the polymer and the filler. Moreover, for potential applications related to disposable packaging materials such as food service products, alkali fiber treatment is an important processing step. Such treatments are required to: (i) remove impurities thereby producing safer packaging materials for food contact and (ii) improve the interaction between the polymer matrix and the fibers [12]. There are several well-established and recommended pre-treatments for kenaf fibers including graft copolymerization and the use of coupling agents as well as alkali chemical treatments [12]. Such modifications can improve the wettability of the fibers with polymer matrices, reduce moisture absorption, and facilitate ease of processing.

Nevertheless, the ability of fibers to reinforce PLA is also influenced by its size, quantity and dispersion as well as processing conditions [7, 13]

In addition to the use of biofillers, the use of some naturally-derived additives can also provide additional functional properties of PLA packaging materials [14]. For example, the incorporation of essential oil extracts such as thymol (2-isopropyl-5-methylphenol) into packaging materials may extend the shelf life of packaged food products by minimizing the growth of microorganisms due to the inherent antimicrobial (AM) properties of this extract. Thymol is a well-established natural AM agent that can reportedly exhibit antioxidant and AM activity against wide spectrum of microorganisms such as bacteria, fungi, mould and yeast [15-17]. For a continuous AM activity, a migratory release system can be used where volatile additives such as thymol, that often seem a safer alternative to synthetically-derived chemical additives, are released from the package into the headspace surrounding the food product [18]. Moreover, the AM activity of PLA-based materials can be increased with the inclusion of hydrophilic fibers that promote and facilitate the release of the AM agent [14, 19]. The combination of the main elements in a composite system comprised of a PLA matrix, kenaf and natural AM substances could potentially improve the key properties and contribute to the sustainability of the system as a whole. However, few studies have reported the development of bio-composites containing both natural fibers and AM additives for use as food packaging materials [20].

The aim of this study was to explore the mechanical, thermal and morphological properties of PLA composites incorporated with untreated or alkali-treated kenaf fibers and thymol. Moreover, a visual qualitative analysis of the degradation under thermophilic aerobic conditions was also performed as a preliminary assessment of the compostability of these PLA-based composites.

## **2. Materials and Methods**

### **2.1. Materials**

Film and bottle-grade poly(lactic acid) 7001D Ingeo™; specific gravity 1.24; weight average molecular weight,  $M_w = 1.1 \times 10^5 \text{ g mol}^{-1}$  [21]; melt flow index (MFI) 6 g/10 min at 210°C and 2.16 kg; melting temperature range 145-160°C was purchased from NatureWorks LLC, USA. Short kenaf fiber bundle (bast) was purchased from Ecofiber Industries, Australia. The aspect ratio (L/D) of the kenaf fibers was approximately 9 with an average length of  $920 \pm 0.40 \text{ }\mu\text{m}$  and an average diameter of  $100 \pm 0.03 \text{ }\mu\text{m}$ . The diameter and length of the fibers were determined by using scanning electron microscopy (SEM) with more than 90 fibers

measured. Generally, raw kenaf bast fibers consist of *ca.* 63.5% cellulose, 17.6% hemicellulose, 12.7% lignin and 4% extractive [22]. Thymol (T0501, MW = 150.22 g mol<sup>-1</sup>) a white crystalline substance with purity of 99.5% was purchased from Sigma-Aldrich Pty. Ltd., Australia. Sodium hydroxide (NaOH) and acetic acid were purchased from Merck Chemicals, Australia.

## **2.2. Preparation of Composites**

The surface treatment of the kenaf was performed by immersing it in 5% w/v NaOH for 2 h at room temperature. Acetic acid was used to adjust the pH during the washing and rinsing of the fibers with distilled water. The treated fibers were removed from the solution and dried overnight in an air circulating oven at 105°C. Prior to mixing with the PLA resin, both the treated and untreated fibers, as well as the PLA resin, were dried in an oven at 60°C overnight before blending with thymol. Drying of the fibers before mixing is necessary in order to avoid fibers debonding at the fiber-matrix interface due to the presence of moisture on their surface [7] and drying also avoids hydrolysis of the polymer. Formulations containing a 30% w/w kenaf loading were prepared with thymol concentrations at zero, 5 or 10% w/w.

The neat PLA and PLA composites containing thymol were compounded using an internal mixer with torque recording capabilities (Haake PolyLab OS, Germany) at 50 rpm and 155°C for 8 min. The PLA resin was introduced in the chamber and mixed for *ca.* 2 min to obtain a constant torque. The kenaf fibers and/or thymol were then added step-by-step in small amounts during the next 7 to 8 min whilst the mixture was continuously mixed. Films and slabs of 0.3 and 3 mm thickness respectively were prepared using a laboratory press (L0003, IDM Instrument Pty. Ltd., Australia). The samples were preheated at 150°C for 2 min and pressed at the same temperature for 3 min under a force of 50 kN before cooling to 30°C. A hand-held micrometer (Hahn & Kolb, Stuttgart, Germany) was used for measuring film thickness.

## **2.3. Imaging of Fibers and Composites**

Scanning electron microscopy (SEM) was performed to observe the morphology of the tensile fracture surface of the composites using a JOEL NeoScope (JCM-5000) scanning electron microscope (SEM) instrument under high vacuum and using an accelerating voltage of 10 kV. Prior to imaging, all samples were coated with a thin layer of gold (up to 6 nm) using a NeoCoater device (MP19020NCTR).

## **2.4. Infrared Analyses**

A Shimadzu IR Prestige Fourier transform infrared (FTIR) spectrophotometer with an attenuated total reflectance (ATR) attachment was used to undertake the infrared spectral analyses. All spectra were recorded

in the range of 550-4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and with 32 scans recorded at every point using Happ-Genzel apodization. A small portion of thymol, untreated and treated fibers was mixed in an agate mortar and pestle with a few drops of paraffin oil. The sample was then applied to a KBr disc and its FTIR spectrum recorded. Ten scans were performed for each acquisition.

For FTIR mapping analysis, the spectra were acquired using a Bruker Hyperion 2000 IR microscope (Bruker Optik GmbH, Ettlingen, Germany) equipped with a liquid nitrogen cooled detector. The apparatus was connected to the infrared microspectroscopy beamline at the Australian Synchrotron (Clayton, Australia). The microscope was coupled to a Bruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany). The line scan and spectral mapping were performed on the surface of PLA film containing 10% w/w thymol and were collected in transmission mode by scanning the film using a computer-controlled microscope stage at an aperture of  $10\ \mu\text{m} \times 10\ \mu\text{m}$  with a 25 $\times$  IR objective. The spectral data were collected in the IR range 4000-800  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  and with 64 scans. All spectra were processed using Opus 6.0 software (Bruker Optics, GmbH, Ettlingen, Germany). A two dimensional (2D) IR map was produced using the software where integrated areas were calculated for bands attributable to the PLA carbonyl group and thymol ring aromatic functional group.

## **2.5. Tensile Testing**

Tensile tests were performed using a Model 4301 Instron Universal Testing Machine with a load cell of 1 kN. Six tensile specimens were prepared from each sample set *via* heat press moulding using a dog-bone die. The tests were conducted at a cross-head speed of 5  $\text{mm min}^{-1}$  on tensile specimens with dimensions of 63  $\text{mm} \times 10\ \text{mm} \times 2\ \text{mm}$  in accordance with the ASTM D638 [23] Type V method until tensile failure was detected. The average tensile strength, tensile modulus and percentage extension at break were measured and calculated using Instron BlueHill Series IX software.

## **2.6. Thermal Property Testing**

A differential scanning calorimetry (DSC) instrument (Mettler Toledo) was used to study the thermal properties of the PLA and composites under an inert gas (nitrogen) atmosphere. Samples of *ca.* 8-9 mg each were weighed and sealed in aluminium crucibles. The heating was performed over the range 30 to 300 $^{\circ}\text{C}$  at a rate of 10 $^{\circ}\text{C min}^{-1}$  and with a nitrogen flow rate of 20  $\text{mL min}^{-1}$ . The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ), cold crystallization enthalpy ( $\Delta H_{cc}$ ), and melting enthalpy ( $\Delta H_m$ ) were obtained from the DSC thermograms using the first heating scan. The maximum

percentage crystallinity (%X<sub>c</sub>) of each sample during the DSC heating was determined by calculating the ratio between the melting enthalpy of the sample and that of 100% crystalline PLA [24] as shown in Equation (1):

$$\%X_c = \Delta H_m / \Delta H_{m0} \times 100 / w \quad (1)$$

where *w* is the weight fraction of PLA in the formulations and  $\Delta H_{m0}$  is the enthalpy of melting for 100% crystalline PLA (93.7 J g<sup>-1</sup>) [25, 26]. The samples were also characterized using a thermogravimetric analyser (TGA) (Mettler Toledo TGA/DSC1) in order to determine their thermal stability. The mass-loss curves of the active composites were recorded when heated from 30 to 500°C at a heating rate of 5°C min<sup>-1</sup> and at a nitrogen flow rate of 0.2 L min<sup>-1</sup>.

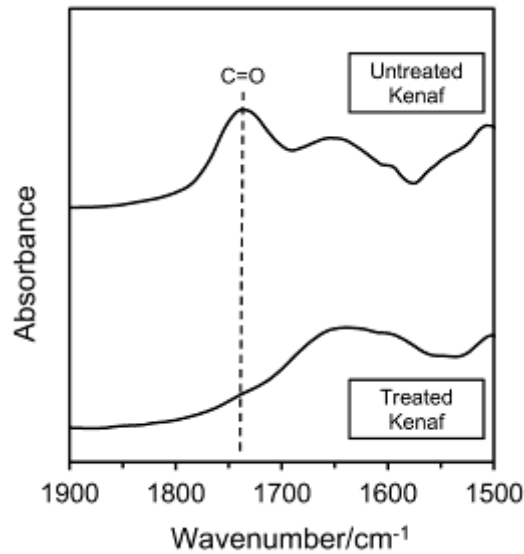
## 2.7. Disintegration Studies

A qualitative/visual study of the decomposition under composting conditions was performed on composite samples cut into pieces (20 × 20 × 3 mm). Samples were buried in a commercial compost at 5 cm depth in perforated boxes and incubated at 58°C. Aerobic conditions were maintained by mixing the compost periodically and by the addition of water to maintain a moisture content equivalent to 60% relative humidity. Samples were removed from the compost after 7, 14, 21, 28, 35 and 48 days, were immediately washed with distilled water to remove traces of compost, and then photographed.

## 3. Results and Discussion

### 3.1. Structural Analysis

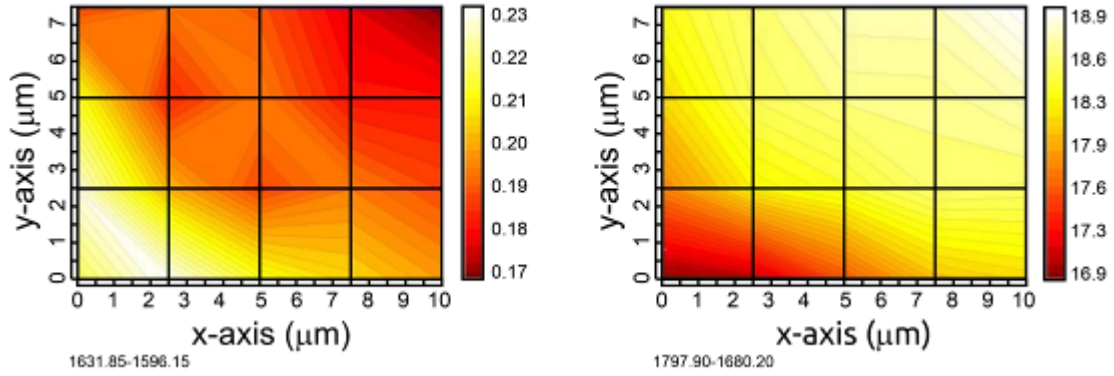
To confirm the effect of alkali treatment on the kenaf fibers, surface FTIR spectra of UK and TK fibers were obtained and are shown in Fig. 1. In the spectrum of the UK fibers, a sharp absorption peak at approximately 1740 cm<sup>-1</sup> is observed which corresponds to the carbonyl group (>C=O) stretching. The existence of this peak in the UK fibers has been ascribed to the acetyl and ester group in hemicellulose or carboxylic acid group in the ferulic and *p*-coumeric components of lignin [12]. This particular peak is not apparent in the case of the TK fibers which indicates the elimination of non-lignocellulose components due to the alkali treatment [12, 27]. A similar finding was also reported by Cao et al. [27] who treated kenaf fibers with 5 to 15% v/w NaOH solution at 25°C for 2 h.



**Fig. 1** Infrared spectra of untreated and treated kenaf fibers in the region 1900-1500  $\text{cm}^{-1}$ .

The FTIR structural analysis of thymol and PLA containing 10% w/w thymol in this study have been discussed in detail previously [14]. However, in that study the presence and distribution of thymol at the surface of the PLA containing 10% w/w thymol film was not investigated and was therefore further analysed using an IR mapping technique in the present study. Fig. 2 shows the intensity of the IR band mapped over PLA film containing 10% w/w thymol at 1618 and 1700  $\text{cm}^{-1}$  that represent the ring aromatic group of thymol and the carbonyl group of PLA respectively [14]. Fig. 2(a) shows that a small amount of thymol is present on the film surface with a higher concentration of thymol detected at the left bottom edge of the area tested. This finding is also consistent with the intensity distribution of the PLA carbonyl group (see Fig. 2(b)) and suggests that this technique can be used to observe the distribution of thymol on the PLA matrix surface and within a relatively small film area. Moreover, the localization of thymol molecules within the matrix or the fibers and at the fiber-matrix interface is an important parameter in further understanding the behaviour of thymol-based bio-composites but is beyond the scope of the present study.

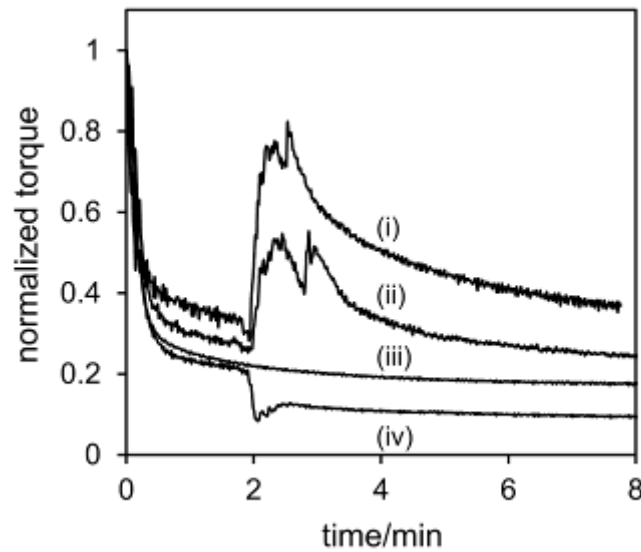




**Fig. 2** Intensity of the IR band mapped over a PLA sample containing 10% w/w thymol at: (a)  $1622\text{ cm}^{-1}$  (aromatic ring of thymol) and (b)  $1700\text{ cm}^{-1}$  (carbonyl group of PLA).

### 3.2. Processing of PLA and Composites

The processing torque profiles of PLA and PLA filled with 30% w/w UK fibers in the presence of thymol are shown in Fig. 3. Generally, the addition of 5-10% w/w thymol to PLA and PLA/kenaf composites imparts a lubricating effect during processing resulting in a significant reduction in the normalized torque value. This lubricating effect could also be due to the diffusion of thymol molecules to the walls of the internal mixer. Similar trends were observed for active PLA filled with TK fibers containing thymol with no significant differences observed in comparison with the PLA/UK fiber composites [20].



**Fig. 3** Normalized torque as a function of time for melts of: (i) PLA/UK fiber composite, (ii) PLA/UK fiber composite with 10% w/w thymol, (iii) neat PLA and (iv) PLA with 10% w/w thymol.

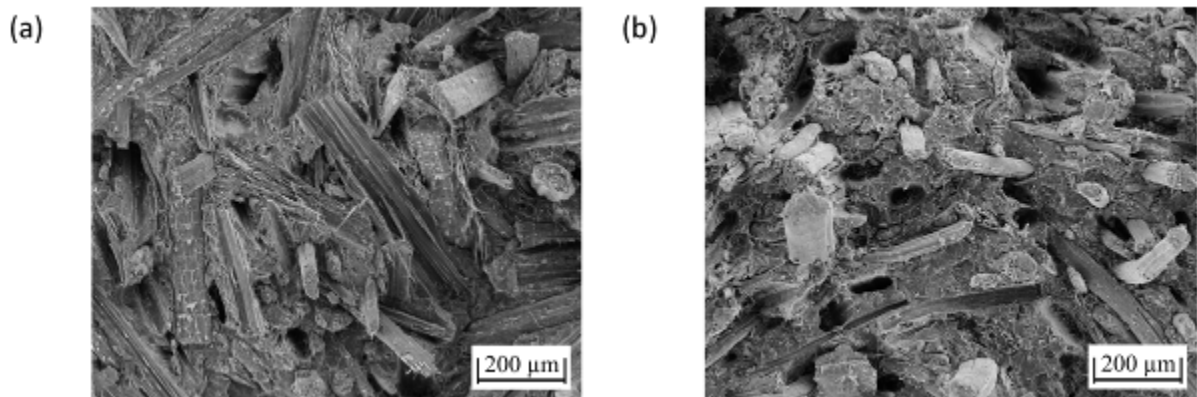
The peak in the melt torque observed at *ca.* 2 min for PLA composite containing UK fibers (see Fig. 3) corresponds to the time when the fibers are introduced into the mixer but this peak is absent when thymol is incorporated into the PLA formulation. For the PLA containing thymol, the torque decreased momentarily and achieved an equilibrium torque value almost immediately where it was maintained throughout the mixing process. These results clearly suggest that the thymol acts as a lubricant for the system. Furthermore, this finding is also supported by the significantly lower equilibrium torque observed after *ca.* 8 min in the formulation containing thymol compared with the formulation without thymol. Similar findings have been reported by Sungsanit [28] who studied the rheology of plasticized PLA blends that contain oligomer polyethylene glycol (PEG) at 5-20% w/w content. It was found that higher loadings of PEG in the PLA blends produced a lower melt viscosity compared to neat PLA.

It is interesting that the presence of thymol, which is a relatively small molecule compared to typical PEG oligomers, has a noticeable effect on the viscosity of the melt. The lower PLA melt viscosity observed in the presence of 10% w/w thymol may be due to the thymol weakening the intermolecular forces between adjacent polymer chains, spacing them further apart and creating a possible free volume [28]. The hydroxyl group in the thymol is also expected to develop a hydrogen bond with the polymer and thus interfere with the polymer-polymer interactions thereby acting in a similar fashion to that of an oligomeric plasticizer [29].

### **3.3. Composite Morphology**

The aim of chemical treatment of the fibers is to remove impurities, pectin, waxy substances, lignin and hemicellulose in order to create a rough fiber surface and increase hydroxyl group accessibility for a better interaction with the matrix [30]. Hydrogen bonding is also likely to occur in the composites between the hydroxyl groups in the UK and TK fibers, the terminal hydroxyl groups of PLA, and the carbonyl groups of the ester linkages of PLA [31]. Figs. 4(a) and (b) show SEM micrographs of the tensile fracture surfaces of PLA composites containing TK fibers with and without thymol. For both of these composites, it appears that the fibers are well dispersed throughout the polymer matrix. For the PLA composite containing no thymol (Fig. 4(a)), the TK fibers appear to be more tightly bound to the matrix compared to the composite in which thymol is present (Fig. 4(b)). This observation is in agreement with the work of Yousif et al. [32] who treated kenaf fibers with 6% w/v NaOH. They observed a slight improvement in the interfacial adhesion and the porosity of the epoxy/kenaf composites that prevented the de-bonding, detachment or “pull-out” of fibers. The presence of thymol in the matrix appears to facilitate the slippage of the fibers out of the matrix during fracture and this

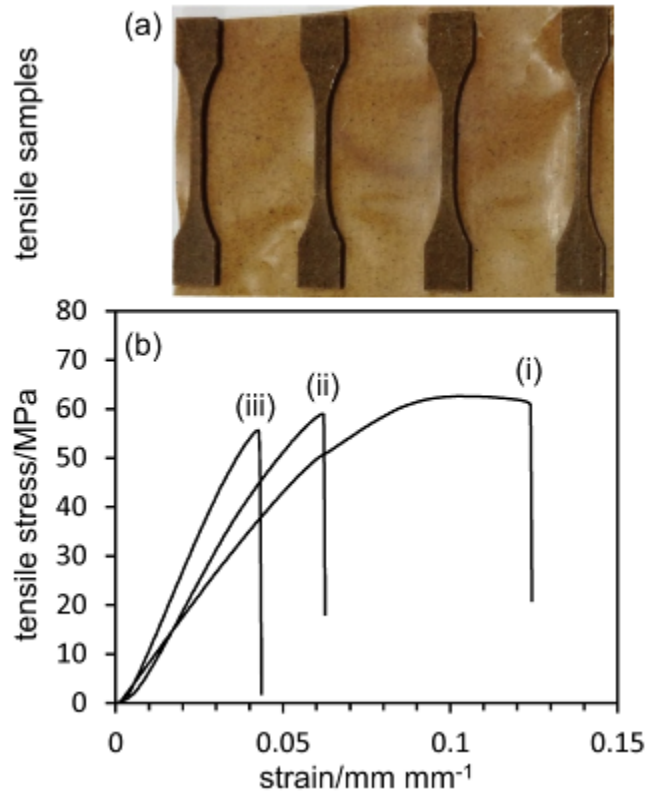
is seen in Fig. 4(b) with the presence of more protruding fibers at the matrix surface. Moreover, the thymol that is present on the surface of the kenaf fibers will lower the coefficient of friction and further facilitate the slippage of the fibers within the matrix. The smooth surfaces of some of the fibers, as well as the voids, suggests that there is weaker adhesion between the fibers and the PLA matrix when thymol is present in the formulation compared to systems where thymol is absent.



**Fig. 4** Scanning electron micrographs of: (a) PLA/TK fiber composite and (b) PLA/TK fiber composite with 10% w/w thymol at 200× magnification.

### 3.4. Mechanical Properties

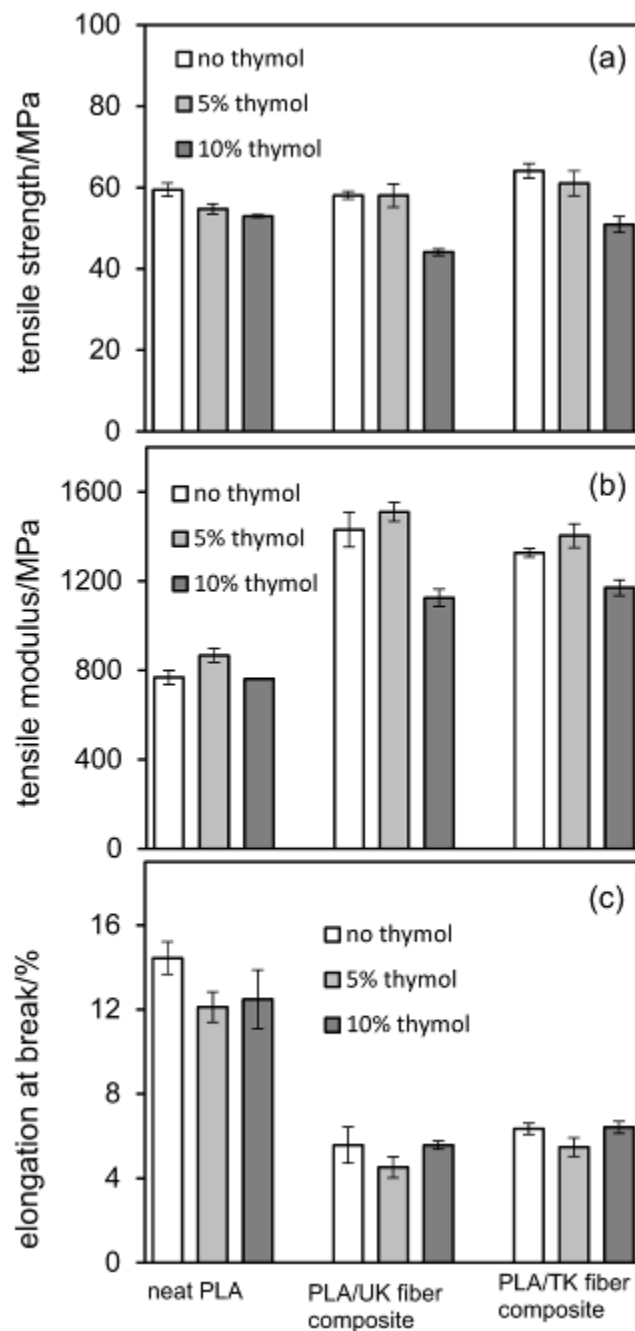
Fig. 5 shows a photograph of the prepared tensile specimens containing 30% w/w TK fibers and typical stress-strain curves of the PLA and PLA composites containing 5% w/w thymol. In all cases, the curves are consistent with a brittle failure mode that is common for fiber-reinforced PLA materials [33]. Fig. 6 shows the effect of the presence of UK or TK fibers on the tensile properties of PLA composites containing zero, 5 or 10% w/w thymol. The tensile strength of PLA filled with TK fibers and containing no thymol was slightly higher than that of the UK composites as well as that of the neat PLA (see Fig. 6(a)). The TK fibers act as reinforcement and impart an approximate 8% increase in tensile strength whereas no significant changes in the tensile strength of the neat PLA were imparted in the case of the composite containing the UK fibers. The slight improvement in the tensile strength is possibly due to better interfacial adhesion between the matrix and the TK fibers as well as better mixing or compatibility within the composite system [13, 34].



**Fig. 5** Photograph of tensile specimens (a), and typical stress-strain curves (b) of composites containing 5% w/w thymol: (i) PLA, (ii) PLA with 30% w/w TK fibers, and (iii) PLA with 30% w/w UK fibers.

The addition of 10% w/w thymol into the neat PLA and the PLA/kenaf composites containing UK and TK caused a significant reduction in the tensile strength compared to those composites without thymol. The percentage reduction in the tensile strength was found to be 11%, 24% and 21% for neat PLA, PLA composites containing UK, and those containing TK fibers respectively. The localized plasticizing effect between the PLA and the thymol whereby the thymol molecules diffuse into the bulk of the matrix between the PLA chains is, in some respects, akin to the case of PLA containing low molecular weight PEG plasticizer [35]. This suggests that the thymol additive interferes with the interaction between the polymer matrix and the fiber in the presence of the applied stress due to the aforementioned slippage effect [36]. This finding is consistent with the observations made in assessing the SEM micrograph images in Fig. 4. In addition, the latter composites demonstrated lower tensile strength than the neat PLA containing only 10% w/w thymol. Thus, thymol may increase end slipping of fibers from the polymer matrix and subsequently reduce the tensile strength. Similarly, Taib et al. [37] reported a reduction of up to 15% in the tensile strength of PLA/30% w/w kenaf

composites containing 10% w/w PEG. Interestingly, the PLA/kenaf composite containing TK fibers and 10% w/w thymol exhibited a higher tensile strength (51 MPa) than the composite containing UK fibers and 10% w/w thymol (44 MPa). This suggests that the reinforcement offered by the TK fibers may prevail over the fiber slippage effect of thymol in PLA at this level of additive in the system. In addition, changes in the tensile strength that may arise due to the effect of the thymol may not be significant at a low level of thymol (5% w/w).



**Fig. 6** Tensile properties of PLA composite with UK or TK fibers containing zero, 5 or 10% w/w thymol: (a) tensile strength, (b) tensile modulus, and (c) percentage elongation at break.

The effect of UK and TK fibers on the tensile modulus and elongation at break of the composites containing zero, 5 or 10% w/w thymol is shown in Figs. 6(b) and (c) respectively. As expected, the tensile modulus (or "stiffness") of the composites containing UK or TK fibers is significantly greater than that of the neat PLA by *ca.* 80% (see Fig. 3(b)). This may be due to the inherently high stiffness of the fiber [4]. This finding is also in agreement with the work of Sujaritjun et al. [38] who incorporated PLA with 30% w/w bamboo fibers and found an increase in the tensile modulus of *ca.* 17%. In this case, the tensile modulus of PLA filled with TK fibers was slightly lower than the composite containing UK fibers. A similar finding was observed by Xia et al. [13] who investigated the tensile modulus of PLA composites containing untreated and alkaline-treated jute fiber reinforcements. Cao et al. [27] reported that treating kenaf fibers with 5% NaOH solution reduces the size of fiber diameter and increases the tensile strength of the fiber with no significant changes in the tensile modulus when compared with untreated kenaf fiber. Nevertheless, it is important to note that the removal of surface components from the fibers during the alkaline treatment cannot be solely responsible for the observed decrease in the stiffness of the composite systems. This is because the stiffness of composites containing natural fibers is mainly related to the cellulose microfibrils that are the major structural components within the microstructure. The reduction in tensile modulus also occurs upon the addition of 10% w/w thymol to the systems containing kenaf with no changes in the tensile modulus observed upon the addition of 10% w/w thymol to neat PLA. This finding is in sharp contrast with the findings of Ramos et al. [16] who reported a 15% reduction in the tensile modulus of PLA films impregnated with 8% w/w thymol but the reasons for the difference in findings are unclear. Nonetheless, the decrease in the stiffness of the composites containing UK and TK fibers are more pronounced due to the effect of the thymol as evidenced in Fig. 4(b).

Fig. 6(c) shows the effect of UK and TK fibers on the elongation at break of composites containing zero, 5 or 10% w/w thymol. In general, the elongation at break of these composites decreases with the addition of the fibrous filler. This suggests that the kenaf does not contribute to the elasticity or the final composite flexibility and this observation is likely to be related to the high stiffness of the composites as indicated by the results in Fig. 6(b). In contrast, the elongations at break of PLA/flax composites were found to be 100% higher than neat PLA with no significant changes having been found between the untreated and treated PLA/flax fibers composites [13]. No significant changes in the elongation at break of any of the composites containing

UK and TK fiber were observed upon the addition of 5-10% w/w thymol. Liu et al. [39] incorporated 5% w/w loadings of both Nisaplin and EDTA into plasticized PLA/glycerol triacetate films and observed a significant reduction of the elongation at break from 108.5 to 62.5% compared to the plasticized PLA. However, a slight increase in the elongation at break was found in extruded PP containing 8% w/w thymol resulting in an increase in ductile properties [36]. The reason for this difference in behaviour of the two systems is unclear nonetheless it is possible that a higher loading of 10% w/w thymol in PLA may produce an enhancement of the elastic properties of the system but this has not been verified in the present study.

In the case of PLA/kenaf composites containing thymol it appears that the presence of thymol does not contribute to or enhance the flexibility of the composites as a whole. This finding is supported by the work of Taib et al. [37] who prepared PLA plasticized with PEG and found a higher strain at break (42%) compared to neat PLA (4%) whereas the addition of 30% w/w kenaf in the plasticised PLA reduced the strain at break significantly to 1%. The addition of UK and TK significantly reduces the flexibility and has been attributed to the stiffening effect of kenaf. The addition of kenaf to the system restricts the mobility of PLA chains and increases the number of the stress-concentrated areas at the fiber ends that can ultimately contribute to the mechanical failure of the composite [37]. The further inclusion of a small molecular species such as thymol to the PLA/kenaf composite system undoubtedly increases the complexity of the system and further complicates any explanation of the experimental observations. Nonetheless, it can be suggested that the type of active PLA/kenaf composites under investigation in the present study is more suitable for use as a rigid packaging material than a flexible packaging material due to the high stiffness of this material [40]. Whence, these materials are potentially suitable for thermal processing into food trays or containers with moderate strength requirements for the packaging of ready-to-eat food products such as fruits and processed deli meats.

It is important to note that the mechanical properties of these composite systems also depend on the fiber size distribution and/or aspect ratio of the fibers. High shear stresses developed during the compounding with an extruder or mixer may lead to fiber damage or breakage resulting in a smaller fiber aspect ratio [9]. Moreover, alkaline treatment reduces the fiber diameter and thereby increases the fiber aspect ratio [41]. The effect of fiber size distribution of the alkali-treated fibers on the mechanical properties of composite containing AM additives should be considered in the future in order to fully understand the complexities of stress transfer in these ternary composite systems.

### 3.5. Thermal Properties

Table 1 shows a summary of the key data obtained from the analysis of the DSC thermograms of PLA and PLA composites containing UK or TK fibers with zero, 5 or 10% w/w thymol. Neat PLA exhibited an onset  $T_g$  at 59.5°C, a  $T_{cc}$  at 92.2°C, and  $T_m$  values at 142.3 (shoulder) and 149.6°C (peak), the latter of which is higher than the value of 141.7°C reported by Byun et al. [42]. The onset of  $T_g$ ,  $T_{cc}$  and  $T_m$  of the PLA composites containing UK or TK fibers demonstrated no significant differences however, some of these values such as  $T_g$ ,  $T_{cc}$ ,  $T_m$ ,  $\Delta H_{cc}$ , and  $\Delta H_m$  for both of the composites were slightly lower than that of neat PLA. The maximum values of  $\%X_c$  calculated using equation (1) for the composites containing UK or TK fibers was slightly higher than that of neat PLA and this finding is in agreement with the work of Du et al. [24] who investigated PLA containing 30% w/w pulp fibers from hardwood, softwood and bleached Kraft wood.

**Table 1** Thermal analysis parameters obtained from DSC thermograms of neat PLA, PLA/kenaf and PLA/kenaf/thymol composites.

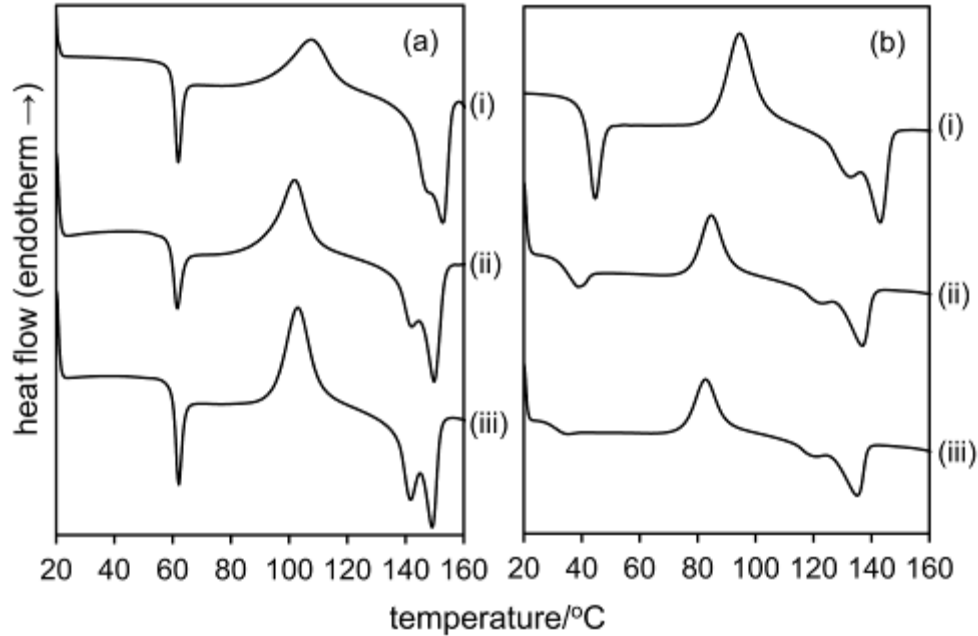
Formulation %w/w thymol	$T_g$ /°C	$T_{cc}$ /°C	$T_{m1}$ /°C	$T_{m2}$ /°C	$\Delta H_{cc}$ /J g <sup>-1</sup>	$\Delta H_m$ /J g <sup>-1</sup>	$X_c$ /%
Neat PLA							
0	59.5	93.3	142.3 <sup>a</sup>	149.6	18.8	26.1	28.0
5	47.9	86.9	131.9	143.0	20.0	23.4	26.7
10	41.6	85.6	124.5	137.4	22.1	22.7	27.1
PLA/UK fibers							
0	59.6	93.5	138.1	146.2	19.7	19.4	29.8
5	46.6	82.9	123.3	134.6	16.0	15.9	26.3
10	30.1	75.7	115.5	129.3	15.9	15.7	28.1
PLA/TK fibers							
0	58.8	94.9	137.8	145.5	19.0	19.1	29.2
5	46.9	85.9	125.5	136.18	16.3	16.6	27.4
10	31.3	78.5	116.7	129.8	15.8	15.8	28.3

<sup>a</sup> Shoulder on the main PLA peak

Fig. 7 presents the DCS thermograms of the PLA and PLA composite systems and, as shown in Fig. 7(a), the neat PLA exhibits a double melting peak with a dominant peak at higher temperature ( $T_{m2}$ ). With the addition of kenaf fibers, the double melting peaks become more distinct. The appearance of these dual melting peaks is in accordance with other reports where the addition of fibers resulted in the development of a small melting peak that shifted to a lower temperature,  $T_{m1}$ , upon further addition of fibers [19, 20, 24]. The



minor peak may be due to either a different PLA crystal type formed only in presence of the fibers and/or the melting of the transcrystalline zone as reported by Yussuf et al. [43].



**Fig. 7** DSC thermograms of (a) neat PLA and PLA composites without thymol: (i) neat PLA, (ii) PLA/UK fiber, (iii) PLA/TK fiber and (b) neat PLA and PLA composites with 10% w/w thymol: (i) neat PLA, (ii) PLA/UK fiber, (iii) PLA/TK fiber.

For the PLA and PLA composites containing 5-10% w/w thymol, the addition of the additive resulted in a decrease in  $T_g$  (see Table 1 and Fig. 7(b)) and this might be attributed to the resultant increase in the free volume of polymer matrix as well as segmental mobility of the PLA chains that change the thermal properties in a way that is akin to a plasticizing effect [20, 44]. In particular, the incorporation of thymol in the PLA decreases the  $T_g$  value which may be a similar effect as that previously observed in the case of PLA containing low and high molecular weight PEG at a 10% w/w loading [35, 37]. Furthermore, Halász and Csóka [10] reported a similar finding where the addition of 10% w/w PEG decreased the  $T_g$  of neat PLA and PLA composite containing 5% w/w microcrystalline cellulose (MCC). The observed plasticizing effect reflected in the  $T_g$  values indicates that the thymol is miscible with the PLA and this is consistent with the observations made from the morphology images, tensile strength, and tensile modulus of neat PLA and PLA kenaf composites (UK and TK) containing thymol (see Figs. 4(b) and 5). It can be observed that, as the content of thymol is increased to 10%

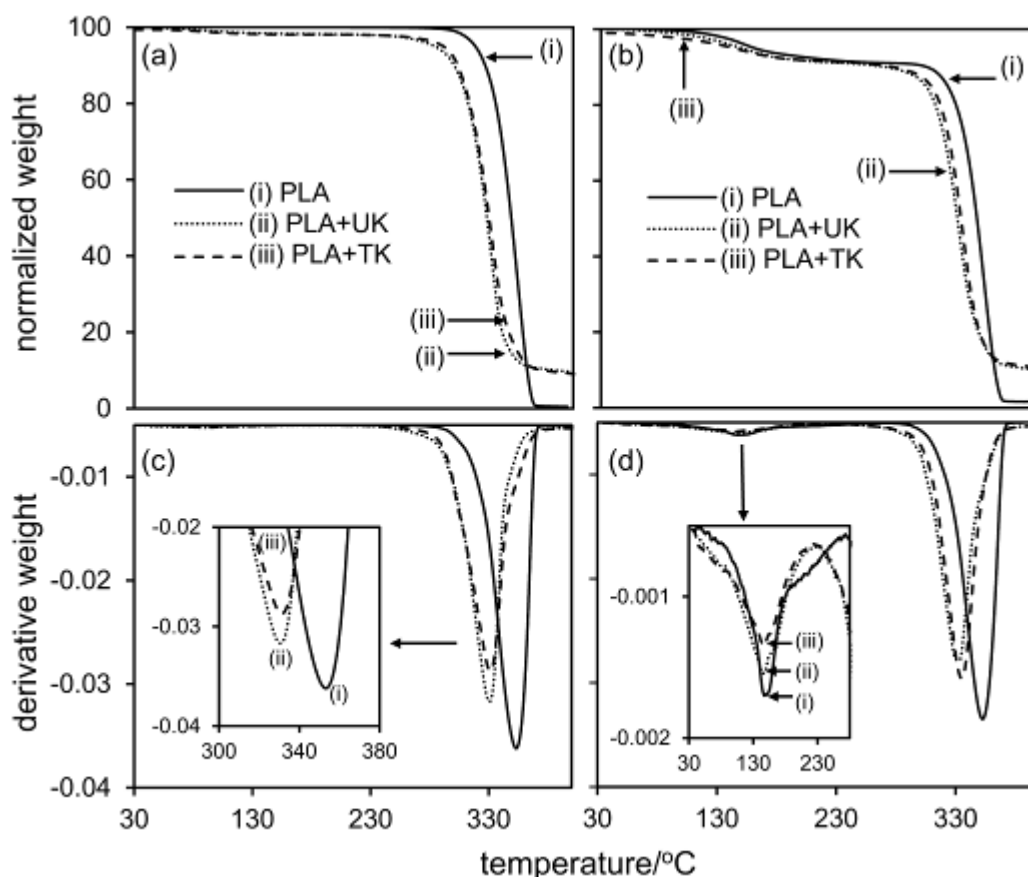
w/w, the  $T_{cc}$  peak becomes broader and shifts to lower temperature, which suggests that the additive enhances the ability of PLA to undergo cold crystallization [45].

Two melting peaks were also observed for PLA containing thymol. The additional melting peak exhibited by the active PLA formulation is more pronounced than that of the neat PLA (see Fig. 4) and this may also be related to the reorganization of the crystal structure. These observations contrast with other findings in the literature where no additional melting peak arose upon the addition of plasticizer such as low molecular weight PEG200 in PLA blends [35]. In general, slight decreases were observed for the  $T_g$ ,  $T_{cc}$ , and  $T_m$  of PLA/kenaf composites containing 10% w/w thymol irrespective of the fiber pre-treatment.

### **3.6. Thermogravimetric Analysis**

It is important to investigate the decomposition and degradation of composites at higher temperature especially if these materials are intended for use in food packaging applications. Low levels of degradation products produced during the thermal processing of such polymers may taint and/or contaminate foodstuffs upon contact thereby causing concerns regarding organoleptic properties or indeed safety. Furthermore, the thermal stability of these materials is also of relevance to the ultimate disposal in composting or land-fill where degradation usually takes place at elevated temperatures.

The thermogravimetric (TG) profiles of neat PLA and PLA composites containing UK and TK fibers with zero or 10% w/w thymol are shown in Fig. 8 in the form of the normalized weight loss as a function of temperature. The corresponding derivative weight loss curves are also shown in Fig. 8 to enable a more detailed analysis of the TG data to be made. The thermal degradation of neat PLA takes place in a single step with a maximum rate of weight loss in the range of 280 to 355°C [16]. In general, the maximum degradation temperature of the neat PLA was higher than any of the PLA composites (see Fig. 8(a)) and this is more clearly reflected in the derivative TG analysis curves. As expected, the presence of fibers in the PLA destabilised the PLA matrix in the composite as has been previously reported by Yussuf et al. [43]. The temperature at which the maximum rate of degradation occurs for the composite containing TK fibers was slightly higher than that of the composite containing UK fibers with degradation temperatures of 331 and 328°C respectively. This may be due to the better interfacial adhesion between the TK fibers and the PLA matrix [46].



**Fig. 8** TGA profiles of (a) neat PLA and PLA composites without thymol: (i) neat PLA, (ii) PLA/UK fiber, (iii) PLA/TK fiber and (b) neat PLA and PLA composites with 10% w/w thymol: (i) neat PLA, (ii) PLA/UK fiber, (iii) PLA/TK fiber.

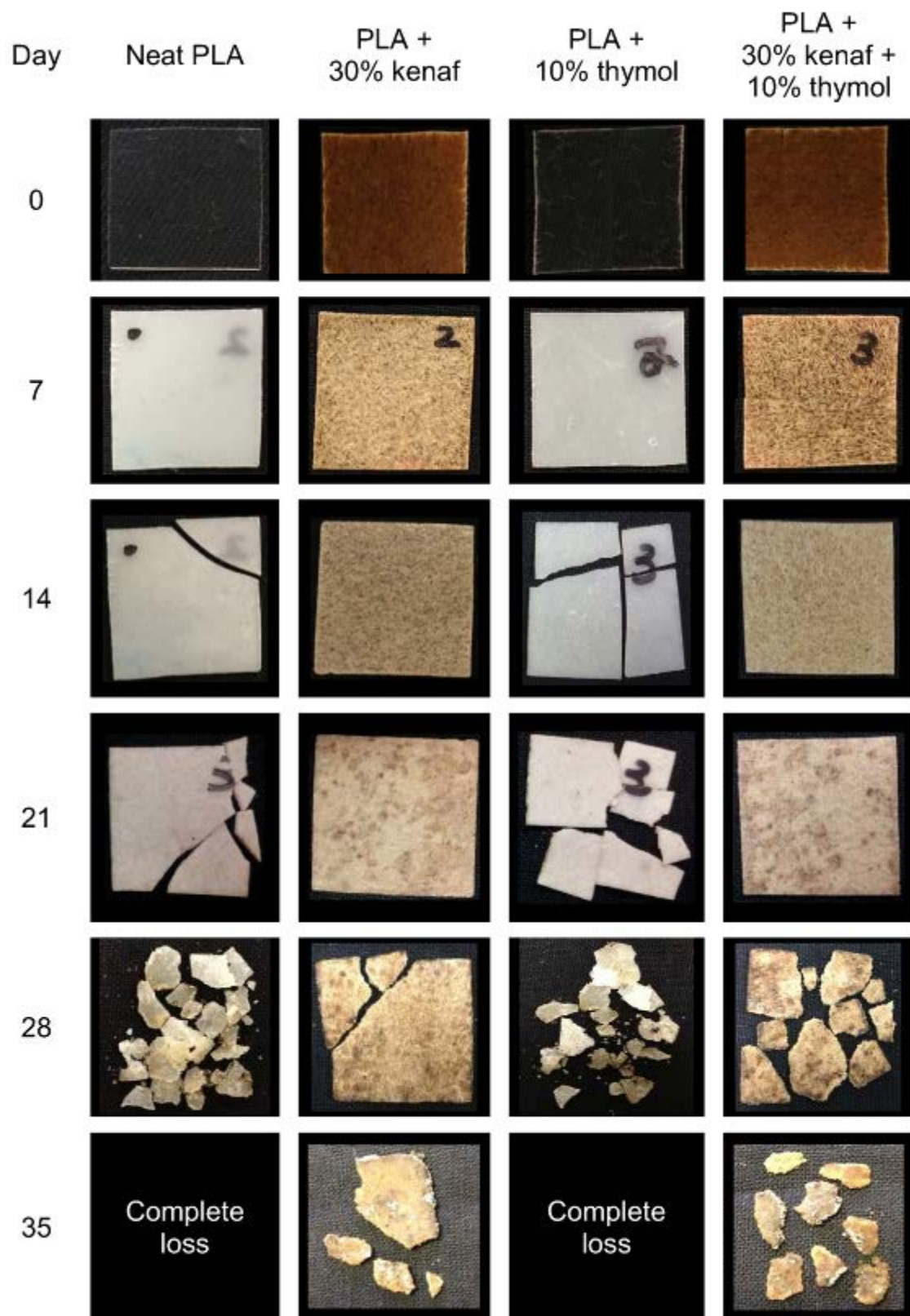
The TG profile of PLA containing a nominal 10% w/w thymol in the formulation exhibits two main steps during the analysis (see Fig. 8(b)). The first step occurs gradually over the temperature range of *ca.* 30 to 300°C and is attributable to the release of thymol from the polymer matrix. This step corresponds to a *ca.* 7% loss in total mass and suggests that the neat PLA and PLA composites that were formulated with 10% w/w thymol retain *ca.* 7% w/w of the thymol that was originally added to the formulation. Thymol release during melt processing due to the high friction between the barrel and the screw, is primarily responsible for the loss of thymol from the formulation [47]. This observation is in agreement with the work by Ramos et al. [16] who investigated by TG analysis the retention of thymol in a PLA matrix after processing. The temperature corresponding to the maximum rate of release of thymol was slightly higher for the composites containing TK fibers (148°C) compared to those containing UK fibers (141°C) suggesting that the thymol interacts more strongly with the TK fibers. The second step observed in the TG profiles of the PLA and PLA composites

containing thymol occurs over the temperature range of *ca.* 310 to 350°C and is attributable to the complete degradation of the polymer matrix.

The temperature corresponding to the maximum rate of degradation for the composite containing TK fibers after the release of 10% w/w thymol was slightly higher than that of the composite containing UK fibers. This may be due to the increased thermal stability of the almost complete cellulosic material that comprises the TK fibers and the absence of other components such as waxy substances, hemicellulose, and lignin that may otherwise destabilize the system [34, 48]. Overall, the addition of thymol to the formulation seems to have little effect on the thermal stability of the PLA whereas the addition of fiber decreases the thermal stability.

### **3.7. Decomposition in Compost**

Although many studies have focused on the biodegradation and/or composting of PLA and PLA incorporated bio-filler composites, few have investigated the composting of PLA-based materials containing AM agents. Moreover, there is still a question of whether the AM property of the material would compromise or affect the ultimate degradation by the microorganisms in soil [49]. In the present study, a preliminary and qualitative analysis of the disintegration under controlled compost-like conditions of PLA and PLA/kenaf films containing the AM agent thymol was conducted as a prelude to future controlled composting studies of these materials. Fig. 9 shows images of PLA and PLA composites containing 30% w/w TK fibers with and without 10% w/w thymol that were removed from controlled composting conditions at different times. Overall, a considerable change in color of all samples was observed with a change from clear to opaque for the neat PLA and PLA containing 10% w/w thymol and changes also observed for the composites. A similar observation was reported by Ramos et al. [50] who investigated the disintegration of PLA and PLA nano-composites containing thymol and silver nanoparticles under controlled composting conditions. These color changes are primarily due to the hydrolytic degradation and crystallization of the PLA matrix [51]. Moisture absorption may lead to hydrolysis that breaks down the macromolecular chains of the polymer with a consequent erosion of the sample surface as demonstrated by the whitening of the surfaces followed by microbial assimilation [52].



**Fig. 9** Images of PLA and PLA containing TK fiber and/or thymol at different stages of decomposition in compost. Sample sizes at day 0 are *ca.* 20 x 20 mm.

One may expect that the incorporation of an AM agent into the PLA-based films will delay the degradation process. However, the neat PLA and PLA containing 10% w/w thymol commenced degradation within 14 days as evidenced by sample fragmentation although no significant differences were observed between the PLA formulations with and without thymol. This may be due to the inherent volatility of thymol, an essential oil extract, that one expects will be released into the atmosphere under the thermal conditions in the compost, . For composite samples containing kenaf, degradation was not apparent until 28 days under the test conditions and in these cases, the PLA surrounding the fiber was observed to have subsequently degraded, dislodging the fibers and thereby roughening the surface. The differences in the degradation rate of these two systems may be attributed to the resistance in water uptake and the diffusion through the composites with the PLA readily adsorbing water [53, 54]. The relatively high degradation rate of the PLA under the aerobic composting conditions is to be expected under the high humidity and temperature (58°C) conditions applied [54]. A more comprehensive biodegradation test such as that outlined in ASTM D5538 [55] is recommended to fully analyse the compostability of the materials developed in this study. Compost monitoring such as pH, evolved CO<sub>2</sub>, and the molar mass of PLA as well as microstructural analysis of the composites by SEM imaging and DSC during biodegradation will be required for further investigation in order to illustrate the effect of thymol on the biodegradation processes.

#### **4. Conclusions**

Bio-based PLA composites containing TK or UK kenaf fibers and thymol were prepared and characterized. The incorporation of thymol into the PLA/kenaf composites imparted a lubricating effect whereby the equilibrium torque value was decreased during processing. A relatively weak adhesion between the PLA matrix and the kenaf fibers was confirmed microscopically in composites containing thymol. The tensile strength of PLA composites containing TK fibers was slightly higher than that of composites containing UK fibers suggesting the alkaline treatment imparts a reinforcing effect within the polymer matrix. The incorporation of the higher level of 10% w/w thymol into the PLA/kenaf composites decreased the tensile strength and stiffness irrespective of the fiber pre-treatment with no significant changes in the elasticity. Thermal analysis by DSC showed a general decrease in  $T_g$ ,  $T_{cc}$  and  $T_m$  in PLA and PLA composites containing 10% w/w thymol compared to the formulations without thymol suggesting changes in the phase structure of the polymer. The TG decomposition temperature of the PLA composite containing TK fibers and 10% w/w thymol

was slightly increased indicating an increase in the thermal stability of the PLA matrix. Under qualitative controlled composting conditions, the disintegration of the PLA and PLA containing TK fibers progressed rapidly resulting in a complete loss within 48 days. In general, the presence of TK fibers in combination with thymol in the PLA composite resulted in significant improvement in the overall properties of the material suggesting that this composite has the potential to be used as a rigid, active bio-based packaging material.

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