

1           Diffusion of Linalool and Methylchavicol from  
2           Polyethylene-Based Antimicrobial Packaging Films

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4           Panuwat Suppakul<sup>a</sup>, Kees Sonneveld<sup>b</sup>, Stephen W. Bigger<sup>c</sup>, Joseph Miltz<sup>d\*</sup>

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6           <sup>a</sup>*Department of Packaging and Materials Technologys, Faculty of Agro-Industry,*  
7           *Kasetsart University, 50 Phaholoyothin Rd., Chatuchak, Bangkok, 10900, Thailand*

8           <sup>b</sup>*KS PackExpert & Associates, PO Box 399, Mansfield, 3724, Australia*

9           <sup>c</sup>*School of Engineering and Science, Faculty of Health, Engineering and Science,*  
10           *Victoria University, P.O. Box 14428, Melbourne, 8001, Australia*

11           <sup>d</sup>*Department of Biotechnology and Food Engineering, Technion-Israel Institute of*  
12           *Technology, Haifa, 32000, Israel*

13  
14           **Abstract**

15  
16           The diffusion of linalool and methylchavicol from thin (45-50  $\mu\text{m}$ ) antimicrobial low-  
17           density polyethylene-based films was evaluated after immersion in isooctane and the  
18           effect of temperature (4, 10, or 25  $^{\circ}\text{C}$ ) on the diffusion rate was evaluated. The kinetics of  
19           linalool and methylchavicol release showed a non-Fickian behavior at the lowest  
20           temperature. An increase in temperature from 4  $^{\circ}\text{C}$  to 25  $^{\circ}\text{C}$  resulted in an increase in the  
21           diffusion coefficient from  $4.2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  to  $2.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for linalool and from  $3.5 \times$   
22            $10^{-13} \text{ m}^2 \text{ s}^{-1}$  to  $1.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for methylchavicol. The effect of temperature on the  
23           diffusion coefficient followed an Arrhenius-type model ( $r^2 = 0.972$ ) in relation to a time-  
24           response function with a Hill coefficient. Activation energies of 57.8  $\text{kJ mol}^{-1}$  (linalool)  
25           and 42.8  $\text{kJ mol}^{-1}$  (methylchavicol) were observed.

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27           \*Corresponding author. Tel.: +972 48292451; fax: +972 48293603 (direct) or +972-  
28           48293399 (Dept).

29           *E-mail address:* [jmiltz@tx.technion.ac.il](mailto:jmiltz@tx.technion.ac.il) (J. Miltz).

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31                           food packaging

32

## 33 **1. Introduction**

34 In solid and semi-solid foods, surface growth of microorganisms is one of the  
35 major causes of food spoilage (Maxcy, 1981). To overcome this problem, attempts are  
36 being made to develop antimicrobial (AM) packages in which AM agents are incorporated  
37 into the packaging material and slowly released onto the food surface (Han, 2000;  
38 Appendini & Hotchkiss, 2002; Suppakul Miltz, Sonneveld, & Bigger, 2003a). Such  
39 materials may have a crucial effect on the food quality and safety and/or on the shelf life  
40 extension of packaged food products. The controlled release of different AM agents from  
41 food packaging materials has been studied and reported in the literature (Mastromatteo,  
42 Mastromatteo, Conte, & Del Nobile, 2010).

43 Naturally-derived AM agents are perceived by consumers as having a low health  
44 risk. Therefore, there is an increasing interest in the evaluation and possible application of  
45 these compounds (Nicholson, 1998). The principal constituents of basil, linalool and  
46 methylchavicol, exhibit an AM effect against a wide range of microorganisms (Suppakul,  
47 Miltz, Sonneveld, & Bigger, 2003b). These compounds are generally recognized as safe  
48 (i.e. possess “GRAS” status), are relatively stable at high temperatures and therefore have  
49 the potential to be used in AM film applications. In recent studies (Suppakul, Miltz,  
50 Sonneveld, & Bigger, 2006; Suppakul, Miltz, Sonneveld, & Bigger, 2008), linalool and/or  
51 methylchavicol were incorporated into polyethylene-based films. The physical properties  
52 of the films (mechanical, barrier, optical and thermal) and the antimicrobial efficacy of the  
53 films were investigated. Apart from the properties and AM efficacy of the films, an  
54 understanding of the diffusion controlled release rate is an essential aspect for developing  
55 appropriate AM food packaging materials.

56 Antimicrobial films represent an application in which active substances (AM  
57 agents) present in the polymeric matrix migrate onto the surface of packaged products.

58 The release profile from an AM film occurs in the opposite direction to sorption (such as  
59 flavor scalping) (Sadler & Braddock, 1991). The diffusivity of the AM agent in the  
60 polymer is a characteristic parameter providing important information required for the  
61 prediction of the rate of release of the AM agent from the film (Han & Floros, 2000).

62 The present paper concentrates on evaluating the rate of diffusion of linalool and  
63 methylchavicol in AM low-density polyethylene-based films (LDPE films) and their  
64 migration into isooctane, simulating to some extent the migration of these agents onto the  
65 non-polar regions on the surface of hard cheeses that are created by fats, lipids and such  
66 species.

67

## 68 **2. Materials and methods**

### 69 *2.1 Antimicrobial films*

70 Low-density polyethylene-based films of 45-50  $\mu\text{m}$  in thickness with and without  
71 linalool (MW = 154.25 g mol<sup>-1</sup>, purity 97%, b.p. = 198.5C; L260-2, Aldrich  
72 Chemical Company, Inc., USA,) or methylchavicol (MW = 148.20 g mol<sup>-1</sup>, purity 98%,  
73 b.p. = 216C; AUSTL 21320, Aurora Pty. Ltd., Australia) were prepared from  
74 commercially obtained LDPE pellets (Alkathene XJF 143, Qenos Pty. Ltd., Australia). A  
75 pre-blended master batch of ethylene vinyl acetate (EVA, ELVAXR®\_3120, Dupont Ltd.,  
76 Australia) copolymer powder containing approximately 15% w/w linalool or  
77 methylchavicol was mixed with virgin LDPE pellets and manufactured into films with a  
78 concentration of 1.5% w/w linalool or methylchavicol at a ratio of 10% w/w EVA to 90%  
79 w/w LDPE master batch by extrusion film blowing in a single screw extruder (Telford  
80 Smith, Australia). The temperature in the extruder was approximately 160°C (all zones).  
81 Films without linalool or methylchavicol were prepared under similar conditions by the  
82 same method and were used as controls.

83

## 84 *2.2 Film thickness measurement*

85 A hand-held micrometer (Hahn & Kolb, Stuttgart, Germany) was used for  
86 measuring film thickness. Five readings were taken for each sample, one at the sample  
87 center and four around the perimeter.

88

## 89 *2.3 Quantification of agents by gas chromatography*

90 The amount of linalool or methylchavicol in the samples was determined by gas  
91 chromatography (GC). The procedure was as follows: the film (5 g) was extracted for 18 h  
92 by Soxhlet extraction using 150 mL of isooctane. An aliquot of the extract with a  
93 precisely known volume was then sampled for GC analysis. A Varian Star 3400-CX GC  
94 equipped with a fused silica capillary column DB-5 (30 m × 0.25 mm i.d., film thickness  
95 0.25 μm, J & W Scientific, USA) was used. The following conditions were applied:  
96 sample volume, 1.0 μL; initial column temperature, 80°C; heating rate, 5°C min<sup>-1</sup> to  
97 180°C that was then held for 5 min more; injector temperature, 250°C, split ratio, 1:100;  
98 FID detector temperature, 300°C; carrier gas, nitrogen. The linalool and methylchavicol  
99 contents of the samples were calculated from prepared standard curves.

100

## 101 *2.4 Diffusion experiments*

102 The release of linalool and methylchavicol from the AM LDPE-based films was  
103 investigated by immersing 4 pieces (5 × 5 cm) of the test film in 100 mL of isooctane  
104 (Unichrom 2516-2.5L, GL grade, APS Chemicals Ltd., Australia), as a fatty food  
105 simulant, in a closed system and storing at 4, 10 or 25°C in an incubation shaker  
106 (Innova™ 4230, New Brunswick Scientific, U.S.A.) with a continuously rotating speed of  
107 30 rpm. The flasks were incubated with mild agitation, simulating agitation during storage

108 and transportation (Appendini & Hotchkiss, 2002). It is believed that under these  
109 conditions a steady-state transfer of AM agents from the film occurs. Aliquots were  
110 sampled at various times. Experiments were performed in triplicate.

111 The amount of linalool or methylchavicol in the aliquot was determined using GC.  
112 An aliquot of the extract of a precisely known volume was injected into the GC for  
113 analysis. The GC was operated using the conditions described above. The linalool and  
114 methylchavicol contents of the samples were calculated from previously prepared  
115 standard curves.

116

### 117 *2.5 Kinetics analysis of linalool and methylchavicol release from LDPE-based films*

118 The relationship between the sorption and the desorption of a given species within  
119 a polymeric matrix is given in Eq. 1:

120

$$121 \quad [M_t/M_\infty]_{\text{desorption}} = 1 - [M_t/M_\infty]_{\text{sorption}} \quad (1)$$

122

123 where  $M_t$  is the total amount of a species that has migrated after time  $t$ , and  $M_\infty$  is the  
124 maximum amount of the species that can migrate after an infinite time, ( $t = \infty$ , namely, at  
125 equilibrium). The ratio  $M_t/M_\infty$  is known as the fractional mass release.

126 Several methods have been reported to be appropriate for measuring diffusion of  
127 small molecules in a polymer (Crank, 1975; Giannakopoulos & Guilbert, 1986; Miltz,  
128 1987; Lim & Tung, 1997). Redl, Gontard & Guilbert (1996) suggested a relatively rapid  
129 and convenient method to determine diffusivity of a species in AM films by immersion in  
130 food simulants (Feigenbaum, Riquet & Scholler, 2000; McCort-Tipton & Pesselman,  
131 2000) such as distilled water, buffer solution, isooctane, ethanol, acetic acid and rectified  
132 olive oil.

133 In the current study, the question of whether the fractional mass release ratio is  
134 directly proportional to  $t^{1/2}$  was considered first, since such a linearity would indicate  
135 compliance with the general law of diffusion (Crank, 1975). The diffusion coefficient  $D$   
136 ( $\text{m}^2 \text{s}^{-1}$ ) of linalool and methylchavicol were later calculated using the half-time method  
137 given in Eq. 2 (Miltz, 1987; Lim & Tung, 1997; Han & Floros, 2000; Ouattara, Simard,  
138 Piette, Begin & Holley, 2000):

139

$$140 \quad D = 0.0491 \times L^2/t_{0.5} \quad (2)$$

141

142 where  $L$  is the thickness of the film, and  $t_{0.5}$  is the time required for 50% of the migrating  
143 species to be released into the simulant (i.e. when  $M_t = 0.5M_\infty$ ).

144 Theoretical values of the fractional mass release as a function of time were  
145 calculated assuming an exponential rise to a maximum level as indicated in Eq. 3  
146 (Schwartzberg, 1975; Lim & Tung, 1997):

147

$$148 \quad M_t/M_\infty = 1 - \exp(-kt) \quad (3)$$

149

150 where  $k$  is the empirically obtained rate constant ( $\text{s}^{-1}$ ) that depends on the mass transfer  
151 properties, geometry and other conditions of the film material (Han & Floros, 2000).

152 In order to determine the temperature dependence of the diffusion coefficient, the  
153 well-known Arrhenius equation (Eq. 4) was used (Chatwin, 1996):

154

$$155 \quad D = D_0 \exp(-E_a/RT) \quad (4)$$

156

157 where  $D_0$  is a pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the ideal gas  
158 constant and  $T$  is the absolute temperature. The parameters  $D_0$  and  $E_a$  can be obtained by  
159 curve fitting of the experimental data (Helmroth, Rijk, Dekker & Jongen, 2002).

160 The data were also analyzed by the time response function using a Hill coefficient  
161 in accordance with Eq. 5:

162

$$163 \quad M_t/M_\infty = 1/[1 + (k/t)^n] \quad (5)$$

164

165 where  $k$  is a rate constant and  $n$  is the Hill coefficient, indicating the degree of  
166 “cooperativity” of the agent (Hill, 1984).

167

## 168 *2.6 Data analysis*

169 The initial part of the migration curves (i.e. values of  $M_t/M_\infty < 0.6$ ), that has been  
170 defined as the “short-term migration” (Miltz, 1987), was plotted against the square root of  
171 time,  $t^{1/2}$ , and tested for linearity using a linear correlation procedure (KyPlot 2.0 for  
172 Windows, Kyence Inc, Japan). The kinetic results were also analyzed using a time-  
173 response function with a Hill coefficient to determine the rate constant of the kinetic  
174 equation. A two-way ANOVA with replication procedure was applied to evaluate the  
175 significance of the main effects of temperature and time as well as their interaction.

176

## 177 **3. Results and discussion**

### 178 *3.1 Film preparation*

179 A constant temperature of approximately 160°C was applied along the extruder in  
180 order to minimize the loss of active agents by evaporation, as recommended in the  
181 literature (Han, 2000). Although a loss of the active agents was observed during the

182 extrusion process, it was significantly lower than the losses observed in a previous study  
183 with linear low-density polyethylene (LLDPE) alone (Suppakul et al., 2006). The actual  
184 amount of linalool or methylchavicol in the extruded films was found to be 0.34% w/w in  
185 each film. This increased retention of the active agent (compared to 0.05% w/w in the  
186 previous study) may be attributable to the lower extruder temperature and/or the  
187 interaction between the active agent and the EVA copolymer. This copolymer may assist  
188 in solubilizing or partially “anchoring” the active molecules within the polymeric matrix.  
189 Linalool-LDPE-based and methylchavicol-LDPE-based films were 47.6  $\mu\text{m}$  and 48.1  $\mu\text{m}$   
190 thick, respectively.

191

### 192 3.2 Migration of linalool and methylchavicol from LDPE into isooctane

193 The experimental migration data of linalool and methylchavicol from the LDPE-  
194 based films immersed in isooctane (used as a fatty food simulant) at different temperatures  
195 are shown in Fig. 1. The migration curves at 4°C for linalool and methylchavicol using  
196 curve fitting involving Hill coefficients of 1.92 and 1.72 respectively are shown in Fig. 2.  
197 It can be seen that the migration rate is at a maximum immediately after a lag time of *ca.*  
198 60 s and declines progressively thereafter until the extent of migration becomes nearly  
199 complete after *ca.* 1800 s for both AM agents. The linearity achieved in all cases when the  
200 data associated with the initial portions of the curves (i.e.  $M_t/M_\infty < 0.6$ ; Miltz, 1987) in  
201 Figure 1 were fitted with respect to the  $t^{1/2}$  model of the initial portion of the curve was  
202 quite good ( $r^2$  ranging from 0.899 to 0.985). However, the kinetics of linalool and  
203 methylchavicol release from the films was fitted considerably better ( $r^2 = 0.994$  and  $r^2 =$   
204 0.993 respectively) with a nonlinear, least-squares fit of the time-response function using  
205 a Hill coefficient (Eq. 5).



206 In view of the latter, the release of linalool and methylchavicol from LDPE-based  
207 films immersed in isooctane, might be described by the “swelling-controlled” model for  
208 drug release that was previously reported by [Armand, Magbard, Bouzon, Rollet, Taverdet,  
209 & Vergnaud \(1987\)](#). According to this model, a simulant such as isooctane penetrates first  
210 into the polymer matrix and dissolves the AM agents thereby enabling their subsequent  
211 release. Indeed, it is expected that an isooctane uptake will cause polymer swelling  
212 ([Feigenbaum et al., 2000](#)) because the solubility parameter of isooctane is close to that of  
213 LDPE ([Brydson, 2000](#)). The migration of linalool and methylchavicol is thus expected to  
214 increase with an increase in isooctane penetration into the LDPE-based film, reaching a  
215 plateau when the matrix is saturated with isooctane ([Armand et al., 1987](#)). The  
216 experimental results obtained in the current study are described well by this model and  
217 evidence for this is the slight lag time that is apparent in the release curves shown in  
218 Figure 2. Nonetheless, the importance of swelling could be further investigated by  
219 following its extent as a function of the temperature in order to more fully characterize the  
220 lag time. In reality, the situation may be more complex and the “swelling-controlled”  
221 model may only be valid in some cases. Many interactions take place during the migration  
222 of species from polymers into liquids. Moreover, [Lim & Tung \(1997\)](#) reported that a  
223 time-dependent relaxation process occurs as a result of the swelling that takes place during  
224 the diffusion of the liquid into the polymer. As a consequence, release rates change  
225 continuously and the accurate mathematical analysis of the migration is difficult  
226 ([Gnanasekharan & Floros, 1997](#)).

227 In the present study, the initial portion of the migration curves was found to be,  
228 more or less, in accordance with the predictions of Fick’s law for diffusion. However,  
229 evidence for the non-Fickian nature of the diffusion appears in the sigmoidal shape of the  
230 migration curves, especially at low temperatures. This indicates interactions that cause the

231 migration curves to display sigmoidal kinetics. The upward curvature of the experimental  
232 sorption curve shows a constant increase in the diffusion coefficient. The penetration of  
233 isooctane molecules facilitates further penetration by the plasticization of the polymer  
234 matrix, until a plateau is reached (Feigenbaum et al., 2000). This suggests that the release  
235 of linalool and methylchavicol from LDPE-based films is not determined by diffusion  
236 alone (Peppas, 1985). Furthermore, the fractional mass release, plotted as a function of  
237 time, was better fitted by a time-response function with a Hill coefficient (Eq. 5) than by  
238 an exponential rise of  $M_t/M_\infty$  to a maximum level (Eq. 3). These findings are in agreement  
239 with those of Ouattara et al. (2000) who reported a non-Fickian behavior for the diffusion  
240 of acetic and propionic acids from chitosan-based films into buffer solutions.  
241 Consequently, the non-Fickian behavior observed in the present study is most likely due  
242 to simultaneous swelling (due to isooctane uptake) and outward diffusion of linalool or  
243 methylchavicol (Ouattara et al., 2000).

244

### 245 *3.3 Effect of temperature on diffusion*

246 The migration data showed a significant effect of temperature on the release of  
247 linalool and methylchavicol from the polymeric matrix, as qualitatively indicated in Fig. 1  
248 where raising the temperature from 4 to 25°C clearly causes a faster rate of migration for  
249 both agents. In particular, the time required to release half the amount of linalool  
250 contained initially in the LDPE-based film decreases from 238 s at 4°C to 165 s at 10°C  
251 and to 42 s at 25°C, whereas the corresponding times for methylchavicol at the respective  
252 temperatures are 327 s, 231 s, and 97 s. Furthermore, the diffusion coefficient,  $D$ , of  
253 linalool calculated from the half-time method (Eq. 2) increased from  $4.2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  to  
254  $2.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , and the corresponding rate constant  $k$  (Eq. 5) decreased from 251 to 44

255 s<sup>-1</sup>, when the temperature was increased from 4 to 25°C. Similar behavior is observed in  
256 the case of methylchavicol (see Table 1).

257 At all temperatures both linalool and methylchavicol showed a positive affinity for  
258 isooctane as indicated by the Hill coefficients being greater than unity. Furthermore, in the  
259 case of linalool there is no statistically significant difference ( $p > 0.05$ ) in the Hill  
260 coefficient within the temperature range of 4 to 25°C. This is in agreement with the  
261 notion that the Hill coefficient of a given system is temperature-independent. However, at  
262 10°C, the Hill coefficient of methylchavicol was found to be 1.35 which lies outside the  
263 expected range of between 1.67-1.72. The reasons for this apparent anomaly remain  
264 unclear at present.

265 In order to further explore the effect of temperature on the kinetics of migration,  
266 Arrhenius plots of the data presented in Table 1 were constructed and these appear in  
267 Figure 3. It can be seen from the plots that each of the analysis methods indicates the rate  
268 of linalool migration is more temperature-sensitive than that of methylchavicol within the  
269 temperature range investigated. The temperature dependence of the diffusion coefficient  
270 is well described by an Arrhenius relation with activation energies of 58.0 kJ mol<sup>-1</sup> and  
271 38.2 kJ mol<sup>-1</sup> obtained for linalool and methylchavicol respectively. The activation  
272 energies obtained from the analysis of a time-response function with a Hill coefficient  
273 were found to be 57.8 kJ mol<sup>-1</sup> and 42.8 kJ mol<sup>-1</sup> for linalool and methylchavicol  
274 respectively. Taken collectively, these data confirm the consistency between the two  
275 methods of analysis used in this case. In particular, the activation energy is a measure of  
276 the sensitivity of the diffusion coefficient to temperature (Chung, Papadakis & Yam,  
277 2001) and the values of the activation energies derived from the diffusion coefficient data  
278 are close to those derived from the half-time method equation. The latter is normally used  
279 for the evaluation of the approximate diffusion coefficients (Lim, & Tung, 1997; Ouattara

280 et al., 2000; Teerakarn, Hirt, Acton, Rieck & Dawson, 2002). These data also reflect the  
281 expected doubling of the diffusion coefficient for approximately every 10°C rise in  
282 temperature.

283 The dependency of the rate of diffusion of linalool and methylchavicol from  
284 LDPE-based films from the point of view of a pure diffusion model is in many cases  
285 explained by temperature effects on the solubility of the diffusing molecules in films, on  
286 the nature of adhesive forces at interfaces (Brydson, 2000), and on the molecular mobility  
287 (Myint, Daud, Mohamad, & Kadhum, 1996). As the molecular weight of linalool is only  
288 slightly higher than that of methylchavicol, it is likely that the different mobility of these  
289 species within the polymer matrix may be due to either their different shapes or polarities.  
290 Indeed the higher polarity of the linalool molecule compared with methylchavicol may  
291 explain its greater mobility and sensitivity of its diffusion coefficient to temperature. This  
292 is because the exudation of a polar species from a non-polar matrix such as LDPE occurs  
293 more readily compared to a non-polar species that will tend to be retained in the matrix.  
294 The fact that the relationship between diffusion and temperature is well described in the  
295 present study by the Arrhenius equation, suggests that the effect of temperature is  
296 thermodynamic in nature, regulated essentially by the proportion of energy provided to the  
297 activation energy (Daniels, & Alberty, 1972).

298

#### 299 **4. Conclusions**

300 Low-density polyethylene-based films containing linalool and methylchavicol  
301 have been proposed as AM packaging materials. In migration studies of the AM agents  
302 into isooctane, used as a fatty-food stimulant, the diffusion coefficient and the temperature  
303 sensitivity of migration of linalool were found to be higher than those of methylchavicol.  
304 Sigmoidal-shape diffusion curves, especially at low temperatures, indicated that diffusion

305 of the AM agents in the polymer was not purely Fickian in nature. The fractional mass  
306 release, plotted as a function of time, was better fitted by a time-response function with a  
307 Hill coefficient than by an exponential rise in this value to a maximum.

308

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318

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400 **Table 1:** Effect of temperature on the migration of linalool and methylchavicol from

401 LDPE-based films into isoctane

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	Temperature	Thickness <sup>[1]</sup>	Diffusion Coeff. <sup>[2]</sup>	Rate Constant <sup>[3]</sup>	Hill Coeff. <sup>[4]</sup>
	T/°C	L × 10 <sup>6</sup> /m	D × 10 <sup>12</sup> /m <sup>2</sup> s <sup>-1</sup>	k/s <sup>-1</sup>	n
Agent					
linalool	4	47.0±1.8	0.42 <sup>a</sup>	250.7 <sup>c</sup>	1.92
	10	47.3±2.0	0.68 <sup>b</sup>	167.2 <sup>b</sup>	1.87
	25	48.4±1.4	2.46 <sup>c</sup>	44.5 <sup>a</sup>	1.93
methylchavicol	4	48.0±1.6	0.35 <sup>a</sup>	346.0 <sup>c</sup>	1.72 <sup>b</sup>
	10	48.7±1.1	0.44 <sup>b</sup>	296.7 <sup>b</sup>	1.35 <sup>a</sup>
	25	47.5±0.3	1.10 <sup>c</sup>	99.1 <sup>a</sup>	1.67 <sup>b</sup>

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<sup>[1]</sup> For each AM agent, thickness values are non-significantly different ( $p > 0.05$ ).

<sup>[2]</sup> For each AM agent,  $D$  values with different letters are significantly different ( $p \leq 0.01$ ).

<sup>[3]</sup> Rate constant obtained by nonlinear regression. For each AM agent,  $k$  values with different letters are significantly different ( $p \leq 0.01$ ).

<sup>[4]</sup> For each AM agent,  $n$  values with different letters are significantly different ( $p \leq 0.05$ ).