

Characterisation of Water Absorption of Biodegradable Poly(lactic Acid)/Halloysite Nanotube Nanocomposites at Different Temperatures

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Abstract: *Poly(lactic acid) (PLA)/6 wt% halloysite nanotube (HNT) nanocomposites were prepared using melt compounding followed by compression molding. Two types of impact modifiers, i.e., maleic anhydride grafted styrene-ethylene/butylene-styrene copolymer (SEBS-g-MA) and N,N'-ethylenebis(stearamide) (EBS) were used to toughen the PLA nanocomposites. The effects of water absorption on the thermal and impact properties of PLA/HNT at three different temperatures (i.e. 30°C, 40°C and 50°C) were investigated. The diffusion coefficient (D) of PLA was decreased by the incorporation of HNT and impact modifiers. It was found that the activation energy of water absorption (E_a) of PLA/HNT6/EBS is higher than that of PLA/HNT6/SEBS-g-MA nanocomposites. The reduction of impact strength, glass transition temperature (T_g), cold-crystallisation temperature (T_{cc}), and melting temperature (T_m) of the PLA samples is attributed to the hydrolytic degradation of PLA.*

Keywords: Poly(lactic acid), halloysite nanotube, impact modifiers, water absorption

1. INTRODUCTION

Biodegradable polymer is originated from renewable sources; as a result it will have a less negative effect on our environment compared to petroleum based materials.¹ Besides, a shortage of petroleum resources have driven efforts aimed at biodegradable polymer, such as poly(lactic acid) (PLA) will partly or completely replace non-renewable petroleum-based polymers in the future.² PLA is suitable for a variety of applications, such as food packaging, automotive, disposable tableware, sutures, drug delivery device etc.^{3,4}

Halloysite nanotube (HNT) is a two-layered aluminosilicate clay with the chemical composition $Al_2(OH)_4Si_2O_5(2H_2O)$. HNT has hollow nanotubular structure and similar chemical composition of kaolinite.⁵ Recently, the HNT has been used as a new type of filler for various polymer, such as poly(propylene)

(PP), vinyl ester, polyamide (PA), poly(vinyl chloride) (PVC), epoxy, natural rubber for enhancing the mechanical, thermal, crystallisation, fire and other specific properties.⁶⁻¹³

PLA is prone to hydrolytic degradation in the presence of water. The absorbed water in the polymer composites could result in substantial deterioration of mechanical and physical properties. The hydrolysis of PLA is governed by the immersion temperature that is possible to accelerate the diffusion of water.¹⁴

This paper reports on the effects of water absorption on the properties of PLA/HNT nanocomposites (with and without impact modifiers) at immersion temperature of 30°C, 40°C and 50°C. The maximum water absorption (M_m), diffusion coefficient (D), activation energy (E_a), impact strength and thermal properties of PLA nanocomposites upon subjected to water absorption are determined.

2. EXPERIMENTAL

2.1 Materials

PLA (Ingeo™ 3051D, NatureWorks LLC®, USA) was selected in this study. The specific gravity and melt flow index of the PLA were 1.25 g/cm³ and 25 g/10 min (2.16 kg load, 210°C), respectively. Halloysite nanotube (HNT) was supplied by Sigma-Aldrich (Malaysia). The diameter of the HNT was in the range of 30–70 nm, while its length was 1–3 μm. SEBS-g-MA, with a maleic anhydride (MA) grafting level of 1.4–2.0 wt% and styrene/rubber ratio of 30/70 (wt%), was purchased from Shanghai Jianqiao Plastic Co. Ltd. (China). The melt flow index and specific gravity of the SEBS-g-MA were 1.0 g/10 min (2.16 kg load, 230°C) and 0.91 g/cm³, respectively. EBS was supplied by Sigma-Aldrich (USA). The melting point and density of EBS is 140°C and 0.97 g/cm³, respectively. The molecular weight of EBS is 593 g/mol.

2.2 Preparation of PLA/HNT Nanocomposites

Melt compounding was carried out by using an internal mixer (Haake PolyDrive R600, Germany) at 180°C for 10 min. The rotor speed was set at 50 rpm. Prior to compounding, PLA, HNT and impact modifiers were dehumidified in a vacuum oven at 80°C for 24 h. Table 1 shows the materials designations and compositions for PLA/HNT6 nanocomposites. The compression molding was performed at 185°C using a hot press machine (Go Tech, Taiwan). The

preheating, compression molding and cooling times were 7 min, 3 min, and 3 min, respectively.

Table 1: Materials designations and compositions of PLA/HNT6 nanocomposites.

Materials designation	PLA (wt%)	HNT (wt%)	SEBS-g-MA (wt%)	EBS (wt%)
PLA	100	–	–	–
PLA/HNT6	94	6	–	–
PLA/HNT6/SEBS-g-MA5	89	6	5	–
PLA/HNT6/SEBS-g-MA10	84	6	10	–
PLA/HNT6/SEBS-g-MA15	79	6	15	–
PLA/HNT6/SEBS-g-MA20	74	6	20	–
PLA/HNT6/EBS5	89	6	–	5
PLA/HNT6/EBS10	84	6	–	10
PLA/HNT6/EBS15	79	6	–	15
PLA/HNT6/EBS20	74	6	–	20

2.3 Characterisation of PLA Nanocomposites

2.3.1 Water absorption and hygrothermal aging tests

The specimens (dimension: $65 \times 13 \times 3$ mm) were dried at 50°C in vacuum oven until a constant weight was attained. Then, they were immersed in water in a thermostated stainless steel water bath at 30°C , 40°C and 50°C . Weight changes were recorded by periodic removal of the specimens from the water bath and weighing on a balance with a precision of 1 mg. The percentage change at any time t , (M_t) as a result of water absorption was determined by Equation 1:

$$M_t = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where, W_d and W_w denote the weight of dry material (the initial weight) and weight of materials after exposure to water absorption, respectively. The percentage at maximum water absorption (M_m) was calculated as the average value of several consecutive measurements that showed no appreciable additional absorption. The weight gain, resulting from moisture absorption, can be expressed in terms of two parameters, the diffusion coefficient (D) and the M_m , using Equation 2.

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right] \quad (2)$$

where h is the thickness of the specimens. The D value can be calculated after rearranging Equation 2 into Equation 3, as follow:

$$D = \frac{\pi h^2 (M_2 - M_1)^2}{16 M_m^2 (t_2^{1/2} - t_1^{1/2})^2} \quad (3)$$

where $\frac{(M_2 - M_1)^2}{(t_2^{1/2} - t_1^{1/2})^2}$ is the initial linear portion of the slope of M_t versus $t^{1/2}$.

The activation energies of water diffusion for the PLA nanocomposites were determined by using Arrhenius Equation (see Equation 4).

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where D is the diffusion coefficient of the sample; D_0 is the initial diffusion coefficient of the sample; E_a is the activation energy of water diffusion; R is gas constant (8.314 J/K mol) and T is the temperature. By plotting the graph of $\ln(D)$ (diffusion coefficient), $\ln(D)$ of the samples versus reciprocal of temperature, $1/T$, activation energy of the water diffusion can be obtained (c.f. Equation 5).

$$\ln D = -\left(\frac{E_a}{RT}\right) + \ln D_0 \quad (5)$$

2.3.2 DSC measurement

The melting and crystallisation behaviour of the composites were scanned under nitrogen atmosphere by DSC 1 (Mettler Toledo STAR^c, USA) using approximately 10 mg samples sealed in aluminum pans. The specimens were scanned from 30°C to 200°C at a heating rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m), cold crystallisation temperature (T_{cc}) and degree of crystallinity (χ_c) of the PLA nanocomposites were determined. The degree of crystallinity (χ_c) of PLA nanocomposites was evaluated according to Equation 6.

$$\chi_c = \frac{\Delta H_m}{\Delta H_f \times w_{PLA}} \times 100\% \quad (6)$$

where, ΔH_m is the enthalpy of melting; ΔH_f is the enthalpy for 100% crystalline PLA, and w_{PLA} is the net weight fraction of the PLA. The heat of fusion for 100% crystalline PLA is approximately 93.6 J/g.^{15,16}

2.3.3 Impact tests

The Charpy impact strength of the samples was determined according to ASTM D6110 by using a pendulum impact machine (model 5101, Zwick, Germany). The dimension of sample was $65 \times 13 \times 3$ mm (length \times width \times thickness). The testing was performed with pendulum of 7.5 J with a velocity of 3.54 m/s. The Charpy impact strength was calculated in kilojoules per square meter (kJ/m^2) using the Equation 7.

$$a_{cU} = \frac{W}{h \times b} \quad (7)$$

where, W is the corrected energy absorbed by breaking the test specimen, h is the thickness of the test specimen and b is the width of the test specimen.

The percentage retention of impact strength of PLA specimens was determined after water absorption according to Equation (8).

$$\% \text{ retention} = \frac{a_{cU(\text{before})} - a_{cU(\text{after})}}{a_{cU(\text{before})}} \times 100\% \quad (8)$$

where, the $a_{cU(\text{before})}$ and $a_{cU(\text{after})}$ denote to the impact strength of PLA specimens before and after exposure to water absorption, respectively.

3. RESULTS AND DISCUSSION

3.1 Kinetic of Water Absorption

Table 2 shows the maximum water absorption (M_m), diffusion coefficient (D) and activation energy (E_a) of PLA nanocomposites at immersion temperature of 30°C, 40°C and 50°C. The M_m values of all PLA/HNT6 are higher than that of

unfilled PLA at immersion temperature of 30°C, 40°C and 50°C. This indicates that the presence of hydroxyl group in HNT is prone to water absorption, which can be associated with its hydrophilicity. The M_m values of HNT filled PLA (with and without impact modifiers) at 40°C and 50°C increased dramatically compared to the samples immersed at 30°C. It is suggested that at higher immersion temperatures (i.e., 40°C and 50°C), the swellable HNTs and the polymer chains became more flexible which create more free volume in PLA nanocomposites to enable more penetration sites for water molecules, and thus increase the M_m value. The addition of SEBS-g-MA decreased the M_m value of PLA/HNT6 nanocomposites at all immersion temperatures. This may be due to the hydrophobic nature of bulky hydrocarbons segment from SEBS-g-MA that hinders the interaction between the hydroxyl group of HNT and water molecules. Most of the PLA/HNT6/EBS show higher M_m compared to that of PLA/HNT6/SEBS-g-MA. This can be associated with the presence of amide group (-CONH-) in EBS, which is more capable to interact with water molecules than SEBS-g-MA.

The D values of PLA decreased with the incorporation of HNT and SEBS-g-MA. The addition of HNT and SEBS-g-MA into PLA increases the tortuous path for the diffusion of water molecules through the nanocomposites. This is due to the physical hindrance of HNT and SEBS-g-MA in the PLA matrix increased the tortuous path of the water diffusion through the specimen. It was found that, regardless of immersion temperature, the D value of PLA/HNT6/SEBS-g-MA < PLA/HNT6 < PLA. On the other hand, the D value of PLA/HNT6 < PLA/HNT6/EBS < PLA. Note that the D value of PLA/HNT6/EBS is governed by the EBS loading. The D values decreased as the increasing of EBS loading. At lower loading, the EBS is unable to restrict the water molecule diffusion because of its short hydrocarbon chain and small droplet dispersion in PLA. However, at higher loading, the EBS form agglomerate (i.e. bigger droplets in PLA matrix) and become obstacles for the water molecule diffusion. The presence of hydroxyl group in HNT and amide group in EBS may increase their polarity and facilitate water uptake, which always contributes to a high value in M_m value. However, a high M_m value does not always lead to a high D value. Accordingly, the lower D value of PLA/HNT nanocomposite compared to that of PLA is attributed to the barrier effect induced by HNT nanofiller geometry (e.g. HNT nanotubular shape with high aspect ratio) and EBS which could result in the hindrance of the diffusion process during water transportation. It is noticed that all specimens exhibited an increase in D value with temperature increment in all conditions. The increase in diffusion coefficient is due to the fact that at higher temperature, the thermal energy increased. Subsequently, the mobility of water molecules, free void volume in the

polymer matrix and flexibility of the polymer chains increased.¹⁷ Thus, it leads to a fast access of water into the polymer matrix.

The E_a is an energy barrier that a substance has to resist the diffusion of water.¹⁸ The E_a values of PLA/HNT6 and PLA/HNT6/SEBS-g-MA nanocomposites are higher than that of neat PLA. The E_a value of PLA increased drastically from 3.50 to 29.72 kJ/mol in PLA/HNT6 nanocomposites. Note that, the addition of SEBS-g-MA further increased the E_a value of PLA/HNT nanocomposites. This phenomenon indicates that water molecules need more energy to diffuse through the PLA/HNT nanocomposites due to barrier effect induced by HNT and SEBS-g-MA. For the PLA/HNT nanocomposites containing EBS, it was found that the E_a of PLA < PLA/HNT6 < PLA/HNT6/EBS. The increment of E_a values indicate that water molecules need more energy to diffuse into PLA matrix due to the barrier effect by HNT and EBS. It is interesting to note that the E_a values of PLA/HNT6/EBS specimens are higher than PLA/HNT6/SEBS-g-MA. This may be related to the barrier contribution of HNT and EBS to water transportation. The increase of E_a values of PLA/HNT6/EBS may suggest a reduction of microvoids for water accumulations due to better interaction of HNT and EBS in PLA nanocomposites. Consequently, the water molecules need more energy to diffuse into the PLA nanocomposites.

Table 2: Maximum water absorption (M_m), diffusion coefficient (D) and activation energy (E_a) of PLA nanocomposites at immersion temperature of 30°C, 40°C and 50°C.

Material designation	Maximum water absorption, M_m (%)			Diffusion coefficient, D ($\times 10^{-12}$) (m ² /s)			E_a (kJ/mol)
	30°C	40°C	50°C	30°C	40°C	50°C	
PLA	0.40	0.91	1.86	2.79	2.92	3.04	3.50
PLA/HNT6	1.25	3.00	4.11	0.81	1.21	1.68	29.72
PLA/HNT6/SEBS-g-MA5	1.19	2.97	3.88	0.78	1.09	1.61	29.48
PLA/HNT6/SEBS-g-MA10	1.09	2.93	3.89	0.75	1.02	1.41	25.69
PLA/HNT6/SEBS-g-MA15	1.06	2.80	4.04	0.74	0.97	1.47	27.88
PLA/HNT6/SEBS-g-MA20	1.03	2.75	3.91	0.70	0.80	1.41	28.47
PLA/HNT6/EBS5	1.21	3.09	3.92	0.90	1.51	2.29	38.24
PLA/HNT6/EBS10	1.26	3.15	3.67	0.84	1.34	2.30	39.36
PLA/HNT6/EBS15	1.27	2.96	3.52	0.85	1.28	2.21	36.39
PLA/HNT6/EBS20	1.30	2.96	3.18	0.81	1.25	2.08	37.38

3.2 DSC Measurement in PLA/HNT Nanocomposites After Hygrothermal Aging

Table 3 represents the DSC data of PLA/HNT nanocomposites after being subjected to water absorption at three different temperatures (i.e. 30°C, 40°C and 50°C). The thermal characteristics of the PLA samples are summarised in Table 3. There is no significant change in T_g , T_{cc} and T_m for all PLA nanocomposites when immersed in 30°C. The thermal properties (i.e. T_g , T_{cc} and T_m) of PLA nanocomposites were affected at the immersion temperatures of 40°C and 50°C. As can be seen in Table 3, the T_g , T_{cc} and T_m of the PLA sample were shifted to lower temperature and the effect was more pronounced at 50°C. The T_g shifts to lower temperature was affected by the reduction of molecular weight and plasticising effect of lactic acid oligomers formed upon the hydrolysis degradation of PLA. The reduction of T_g is also due to the plasticisation effect of water, which increased the polymer chain mobility.¹⁹ The chain cleavage of PLA shortened the polymer segment, which causes the ease of chain mobility.

Table 3: Thermal characteristics of PLA/HNT6 nanocomposites before and after being subjected to water absorption.

Materials designation	T_g (°C)	T_{cc} (°C)	T_m (°C)		ΔH_m (J/g)	ΔH_c (J/g)	χ_c (%)
			$T_{m'}$	T_m			
PLA (control)	58.7	113.5	150.7	157.5	28.0	–	29.9
PLA (30°C)	59.0	114.3	–	150.0	27.2	–	29.0
PLA (40°C)	57.4	102.2	147.5	153.2	31.0	–	33.1
PLA (50°C)	30.5	83.2	110.0	131.3	33.1	–	35.4
PLA/HNT6 (control)	60.3	109.0	150.7	154.3	27.5	–	31.3
PLA/HNT6 (30°C)	62.5	109.0	149.6	155.1	24.5	–	27.9
PLA/HNT6 (40°C)	62.8	101.5	–	154.9	29.5	–	33.5
PLA/HNT6 (50°C)	39.6	86.5	124.6	131.5	30.3	–	35.5
PLA/HNT6/ SEBS-g-MA5 (control)	60.9	107.6	150.0	153.6	23.2	–	27.8
PLA/HNT6/SEBS-g-MA5 (30°C)	62.4	102.8	147.8	154.7	25.2	–	30.3
PLA/HNT6/SEBS-g-MA5 (40°C)	61.6	98.3	–	153.8	23.3	–	28.0
PLA/HNT6/SEBS-g-MA5 (50°C)	37.8	88.0	–	129.6	30.9	–	37.1
PLA/HNT6/SEBS-g-MA20 (control)	61.7	116.6	149.9	154.0	12.3	–	17.7
PLA/HNT6/SEBS-g-MA20 (30°C)	63.5	109.7	148.0	153.8	19.0	–	27.4
PLA/HNT6/SEBS-g-MA20 (40°C)	63.3	99.3	–	153.5	22.6	–	32.6

(continued on next page)

Table 3: (continued)

Materials designation	T_g (°C)	T_{cc} (°C)	T_m (°C)		ΔH_m (J/g)	ΔH_c (J/g)	χ_c (%)
			$T_{m'}$	T_m			
PLA/HNT6/SEBS-g-MA20 (50°C)	37.7	92.7	107.2	124.8	23.3	–	33.7
PLA/HNT6/EBS5 (control)	58.3	106.4	147.3	152.8	31.0	4.8	31.4
PLA/HNT6/EBS5 (30°C)	61.9	104.5	148.1	154.6	29.1	4.0	30.1
PLA/HNT6/EBS5 (40°C)	61.7	100.4	145.1	153.1	32.2	4.3	33.5
PLA/HNT6/EBS5 (50°C)	38.6	88.6	–	137.0	36.0	3.9	38.5
PLA/HNT6/EBS20 (control)	58.7	109.9	147.9	–	34.2	14.4	28.6
PLA/HNT6/EBS20 (30°C)	62.2	102.8	147.7	153.6	42.2	12.6	42.7
PLA/HNT6/EBS20 (40°C)	62.4	97.1	146.6	154.4	40.1	15.6	35.4
PLA/HNT6/EBS20 (50°C)	43.8	93.0	130.5	137.9	41.5	14.9	38.4

Broadened melting peaks of about 110°C–140°C were observed for all the samples after exposure to a 50°C immersion temperature. Double melting endotherms were observed for PLA and all PLA/HNT6 nanocomposites after being subjected to water absorption at 40°C and 50°C. This is attributed to the melting of crystalline structure domains of different sizes which suggests that chain orientations and morphological rearrangement occur when molecular weight was decreased during the hydrolytic degradation process.²⁰ The decrease of T_m was attributed to the lower molecular chains resulting from degradation. Additionally, T_g of PLA nanocomposites was reduced as the outcome of lower molecular weight of oligomeric chains formation by hydrolytic cleavage and water plasticising effects.²¹ It is noted that the T_{cc} was shifted to lower temperature while degree of crystallinity (χ_c) of PLA samples increased after being subjected to hydrothermal aging. According to Fukushima et al.,²² shorter polymer chains with higher mobility show a higher rate of crystallisation, leading to a lower T_{cc} .

3.3 Effects of Water Absorption on the Impact Properties

Table 4 summarises the impact strength of PLA and PLA/HNT nanocomposites (with and without impact modifiers) after being subjected to water absorption at 30°C and 40°C. It is noticed that the impact strength of PLA and PLA/HNT6 nanocomposites was slightly increased after moisture absorption at 30°C and 40°C. Water diffuses into polymer chains and leads to a swelling effect of composite and physical relaxation of molecular chains. This phenomenon evidence that there is no further degradation in polymer composite (such as filler/matrix interfacial hydrolysis or polymer crazing) as long as the composite continue remains in moist condition.²³

Prior to water absorption (control sample), the adding of SEBS-g-MA gave higher impact strength for PLA/HNT6 nanocomposites. This is attributed to the elastomeric nature of SEBS-g-MA which can induce higher energy absorption during impact testing. However, the entire PLA/HNT nanocomposite with SEBS-g-MA experiences reduction in impact strength after being subjected to water absorption at 30°C and 40°C. This can be due to the fact that the diffusion of water molecules weakened the interfacial adhesion between PLA, HNT and SEBS-g-MA. Before exposure to moisture, it was found that there was an increment in PLA/HNT6 nanocomposites which contain EBS. The impact strength of PLA/HNT6/EBS was decreased after exposure to water absorption. The water diffused predominantly into the matrix causing plasticisation of the matrix and induced volumetric expansion between the matrix and the filler. When the stress exceeds the strength of the interphase region, debonding may take place between filler and matrix leading in irreversible damage of composite.²⁴ In this study, it was found that the adding of EBS is predominantly affecting the reduction of impact strength when the specimen was exposed to water. It was suggested that the amide group in EBS tends to absorb moisture into polymer nanocomposites. The excessive diffusion of water molecules along the polymer nanocomposites may deteriorate the bonding between PLA, HNT and EBS leading to the formation of microcavities. The microcavities act as stress concentrators and initiate matrix cracking, leading to the reduction of impact strength. The percentage of retention for PLA/HNT6/SEBS-g-MA is considerable good if compared to that of PLA/HNT6/EBS nanocomposites. This indicates that the SEBS-g-MA is able to hinder the water diffusion into PLA/HNT nanocomposite, and thus sustain higher impact properties.

Table 4: Impact strength of PLA/HNT nanocomposites (with and without impact modifiers) after being subjected to water absorption at 30°C and 40°C.

Materials designation	Impact strength (kJ/m ²)		
	Control	30°C	40°C
PLA	9.0	9.6	12.3
PLA/HNT6	11.4	12.7	13.4
PLA/HNT6/SEBS-g-MA5	20.2	16.0 (79.2)	17.6 (87.1)
PLA/HNT6/SEBS-g-MA10	19.7	18.1 (91.9)	15.9 (80.7)
PLA/HNT6/SEBS-g-MA15	16.4	18.7 (114.0)	15.9 (97.0)
PLA/HNT6/SEBS-g-MA20	16.6	17.8 (107.2)	10.4 (62.7)
PLA/HNT6/EBS5	22.6	15.3 (67.7)	10.2 (45.1)
PLA/HNT6/EBS10	17.9	6.0 (33.6)	6.4 (35.8)
PLA/HNT6/EBS15	15.3	10.3 (67.3)	5.8 (37.9)
PLA/HNT6/EBS20	13.9	13.4 (96.4)	4.7 (33.8)

Remarks: The values in parentheses () are the percentage retention of the impact strength after water absorption in immersion temperatures of 30°C and 40°C.

4. CONCLUSION

The diffusion coefficient of PLA/HNT6 nanocomposites is lower than that of PLA due to the physical hindrance of HNT and impact modifiers (SEBS-g-MA and EBS) which could restrict the diffusivity of water. The E_a value of PLA/HNT6/EBS is higher than that of PLA/HNT6/SEBS-g-MA nanocomposites. The T_g , T_{cc} , T_m and impact strength of the PLA nanocomposites decreased after exposure to water absorption at 40°C and 50°C.

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