

Influence of Heat Treatment on the Heat Distortion Temperature of Poly(lactic acid)/Bamboo Fiber/Talc Hybrid Biocomposites

Q. F. Shi, H. Y. Mou, Q. Y. Li, J. K. Wang, W. H. Guo

Polymer Alloy Laboratory, Key Laboratory for Preparation and Application of Ultrafine Materials of Ministry of Education, School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT: Influence of heat treatment and fillers on the heat distortion temperature (HDT) of poly(lactic acid) hybrid biocomposites was intensively studied through HDT testing, polarizing microscope (POM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). With loading 20 wt % BF or 20 wt % talc, improvement of HDT in PLA composite was about 10°C comparing with neat PLA after heat treatment. Moreover, there was a great improvement (above 45°C) of HDT in PLA composites with loading 20 wt % BF and 20 wt % talc simultaneously after heat treatment. Transcrystallization was observed during heat treatment and isothermal crystallization of PLA composites with loading BF and talc

simultaneously. There was no similar phenomenon in other PLA composite with loading only one filler. The possible mechanism of forming transcrystallization was proposed. DSC and DMA were also used to clarify the variation in HDT before and after heat treatment, and the results suggest that the crystallinity, modulus and glass transition changed, especially formation of transcrystallization played a key role in improvement of HDT in PLA composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2828–2836, 2012

Key words: annealing; composites; biodegradable; thermal properties; heat distortion temperature

INTRODUCTION

The growing demands to substitute petroleum-based products have increased the focus on biopolymers or biopolymers composites. Biodegradable polymers like poly(lactic acid) (PLA), a corn-based polymer, have been the subject of many studies during the past decade.^{1–3} And it is a polymer of lactic acid and commonly produced by ring-opening polymerization of the cyclic lactide dimer.⁴ PLA provides good strength and easy process ability with perfect degradable in most products. However, poor heat distortion temperature (HDT) and other low physical properties of PLA limit its applications.^{2,3}

HDT of a polymeric material is an index of its heat resistance towards applied load. There are sev-

eral ways to improve the HDT of polymers. Forming crosslink in polymer⁵ and improving the glass transition of polymer⁶ are the effective methods for increasing the HDT value. In addition, the easy way to increase the HDT value of polymer is to increase the crystallinity of polymeric with loading fillers (such as natural fibers and inorganic filler).^{1,2}

Advantages of natural fibers over man-made fibers include low density, low cost, recyclability, and biodegradability, which make natural fibers potential replacement for glass fibers in composite materials. The use of natural fibers to reinforce thermoplastics such as polypropylene and polyethylene as an alternative to synthetic or glass fibers has been and continues to be the subject of research and development.^{7,8} Therefore, many investigations have been made on the potential of the natural fibers as reinforcements for composites,^{9–11} especially in PLA composites¹² and in several cases the results have shown that the natural fiber composites exhibit good HDT and high strength.^{13–15} Inorganic fillers (including clay, talc, and CaCO₃) in composites can improve the thermal and crystallization properties of polymers. The changes produced by treated talc addition to biopolymer are well studied^{16,17} whose thermal mechanical properties have been greatly improved. Talc or MMT clay¹⁸ in combination with

Correspondence to: J. K. Wang (wang326@ecust.edu.cn) or W. H. Guo (guoweihong@ecust.edu.cn).

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other fillers is an ideal to improve the stiffness, creep resistance, and HDT of PLA composites. An investigation on hybrid composites from wood fiber, talc, and polyhydroxybutyrate-co-valerate (PHBV) was reported by Sanjeev et al.¹⁹ Synergistic of talc and wood fiber improved the mechanical and thermal properties of PHBV-wood fiber, which was due to the additional reinforcement of micro sized talc. Shaobo et al.²⁰ recognized that the increases in the crystallinity, the glass transition temperature, and the order degree of hydrogen bonding may account for the noticeable increases in the HDT of the nylon-6/clay nanocomposites after annealing. Although few literatures²¹ reported the increase of HDT with improving of crystallinity and special crystallization, the mechanism was not very clearly and it's very difficult in improving of crystallinity for the slowly crystallized polymer (such as PLA). Therefore, the effect of crystallinity on HDT of PLA was also investigated in this article.

Therefore, in this study, attention was focused on the synergism and effect of BF with talc in PLA/BF/talc biocomposites after the heat treatment. Moreover, there might be the remarkable increase in HDT after heat treatment, which was studied by HDT testing, polarizing microscope (POM), dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). It is seldom concerned that the influence of heat treatment on HDT and synergism between BF and talc in PLA/BF/talc hybrid biocomposites. At last, the synergism and mechanism was investigated here in details.

EXPERIMENTAL

Materials

PLA was supplied by NatureWorks (Minnetonka, MN) as a semicrystalline grade (PLA 4032D). It comprises around 2% D-LA and was dried in the 80°C vacuum oven for 4 h before use. Microsized talc was obtained from Shanghai Fei DGM (Shanghai, China). The dimensions of the talc range from 1000 to 2000 mesh, and it was directly used without further purification. The bamboo fiber (BF80, aspect ratio is about 5–6, diameter is 10–20 μm , its structure as shown in Fig. 1) was kindly supplied by Zhejiang MingZ BWP (Zhejiang, China), and it was dried in the 80°C vacuum oven for 24 h before used.

Composites preparation

BF and talc loaded in PLA were prepared in Haake Rheomix600p (Haake Technik GmbH, Coesfeld, Germany), melting at 180°C and a rotor speed of 60 rpm for 10 min. BF and talc were premixed at different ratios, and then added into PLA and melt blend-

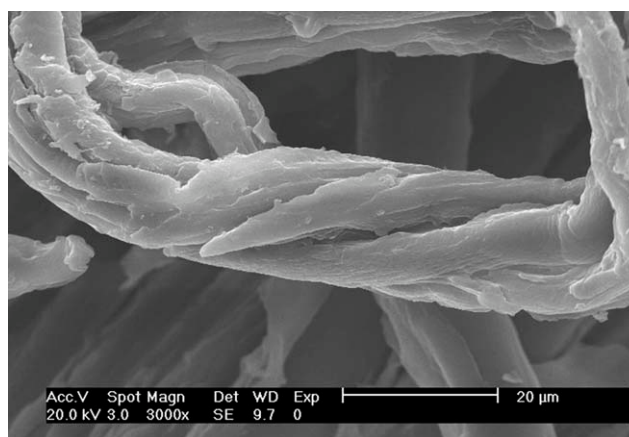


Figure 1 SEM photograph of bamboo fiber structure.

ing under strong shearing. These composites were compression molded at 180°C into sheets for subsequent measurements. Moreover, for the heat treatment, samples were hold at designated temperature for 30 min, which were directly moving from 180°C molding.

Characterization

HDT testing

HDT testing was conducted for both nonheat treatment and heat treatment bars according to ASTM D 648, using a WKW-300 apparatus (Changchun instrument equipment, Changchun, China) at a heating rate of 2°C/min and a load of 1.82 MPa.

Polarizing microscope with heating stage (POM-HS)

Crystal growing of PLA composites has been investigated by POM (Nikon Fi1, Japan) with heating stage (FP90 Central Processor, Mettler Toledo, Switzerland). Sample was cooled down to the designated temperature after melting at 200°C for 10 min.

Differential scanning calorimetry

Thermal analysis of PLA composites was carried out on a NETZSCH DSC 200PC calorimeter (Bayern, Germany). The calorimeter was calibrated with indium standard. For each measurement, a sample of 5–8 mg was placed in an aluminum pan and heated to 200°C at a heating rate of 10°C/min.

Dynamic mechanical analysis

The dynamic mechanical properties of PLA composites have been tested by Rheogel-E4000 DMA (UBM, Japan). The specimens were heated from 20 to 120°C with heating rate of 3°C/min and frequency of 11 Hz. The size of specimen was 30 × 5 × 2 mm³.

TABLE I
HDT of PLA Composites Before and After Heat Treatment

Composites sample	Non Heat Treatment (°C)	Heat Treatment (°C)	Increment (°C) ^a
Neat PLA	50.4 ± 1.2	54.6 ± 5.3	4.2
PLA/20 wt % BF	52.0 ± 3.3	63.8 ± 0.8	11.8
PLA/20 wt % talc	48.8 ± 0.8	63.9 ± 2.2	15.1
PLA/20 wt % BF/20 wt % talc	49.2 ± 6.6	94.5 ± 3.8	45.3
PLA/40 wt % BF	53.2 ± 1.0	68.5 ± 1.1	15.3

^a Increment was calculated by comparing the main value of each sample before and after heat treatment.

X-ray diffraction

X-ray diffraction (XRD; Rigaku-D/max 2550VB /PC, Japan) has been used to investigate the crystal form of PLA composites. The scanning range and rate was 5–50° and 2(°)/min, respectively.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a STA 449 C Jupiter instrument (NETZSH, Bayern, Germany) at a heating rate of 10°C/min from RT to 800°C in a flow of nitrogen.

RESULTS AND DISCUSSION

Heat Distortion Temperature

HDT testing results of PLA composites were summarized in Table I. Specifically, HDT of neat PLA is about 50°C, which is drastically inferior to the heat resistant temperature of products used in our daily life (above 90–100°C). The HDT values of PLA composites were not greatly improved without heat treatment and there was no significant increment of HDT of neat PLA after the heat treatment (120°C for 30 min). After the heat treatment and with loading BF and talc simultaneously, HDT value of PLA/20 wt % BF/20 wt % talc was about 94.5°C, which was

much higher than that of PLA/20 wt % BF and PLA/20 wt % talc, which was only loaded one filler (BF or talc). Moreover, it was noticed that the HDT value of PLA/20 wt % BF/20 wt % talc is about 30°C higher than that of PLA/40 wt % BF, although the weight fractions of fillers in the two PLA composites were the same.

Figure 2 is the TGA curves of PLA/20 wt % BF/20 wt % talc before and after heat treatment. The TGA curves of PLA/20 wt % BF/20 wt % talc and the remaining mass of samples were almost the same before and after treatment. The remaining mass was nearly 20 wt % of each sample, which was the talc and ash content. Due to the increasing of char formation from heat treatment, the remaining mass of PLA/20 wt % BF/20 wt % talc after heat treatment was few more than that of the composites before heat treatment. Otherwise, the degradation temperature of the two samples was almost the same temperature, about 310°C. As mentioned in Shaobo's²⁰ work, the HDT of PA composites had been studied before and after annealing. The differences of HDT between PA composites were due to the different crystal pattern and the dispersion of filler in matrix. Furthermore, the HDT of annealing PA had higher value due to the improvement of relative crystallinity. Here, Figure 3 shows the XRD spectra

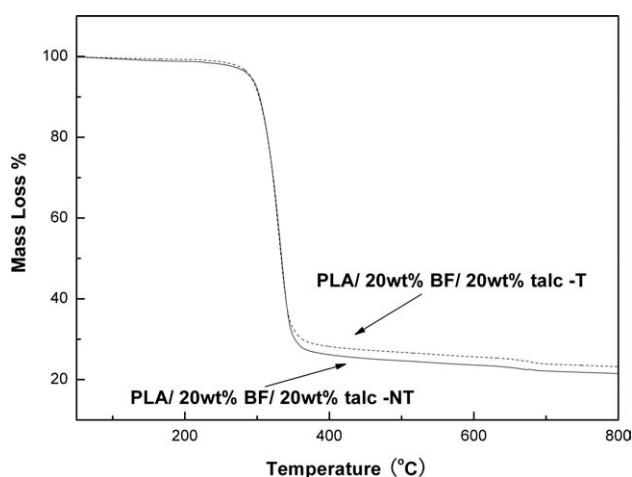


Figure 2 TGA of PLA/20 wt % BF/20 wt % talc before (–NT) and after (–T) heat treatment.

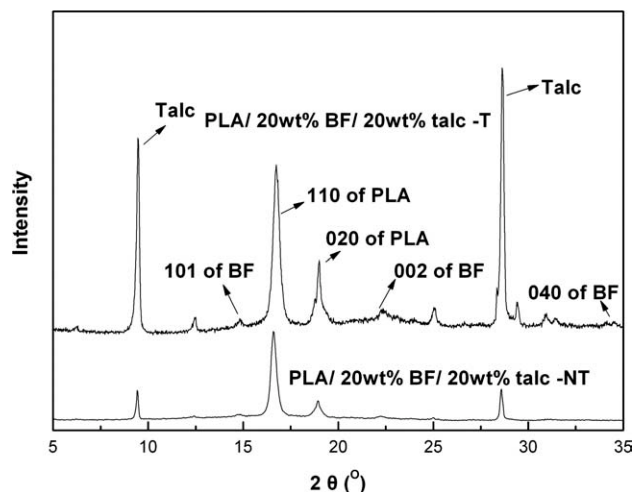


Figure 3 XRD of PLA/20 wt % BF/20 wt % talc before (–NT) and after (–T) heat treatment.

TABLE II
DSC Data of PLA Composites Before and After Heat Treatment

Sample	Heat treatment	Glass Transition (T_g) (°C)	Melting Point (°C)	Melting Enthalpy (ΔH_m /J/g)	Conversion value ^a (ΔH_m /J/g)	Cold crystallization Enthalpy (ΔH_{cc} /J/g)	Crystallinity Value of PLA (%)
Neat PLA	Non	62.9	169.3	39.12	39.12	23.46	12.5
	Yes	69.9	168.8	50.31	50.31	0	54.1
PLA/20 wt % BF	Non	53.9	170.7	40.15	50.18	29.3	14.6
	Yes	60.9	170.0	47.94	59.93	0	64.4
PLA/20 wt % talc	Non	59.7	169.7	36.17	45.21	21.99	19.1
	Yes	66.1	168.7	42.31	52.89	0	56.9
PLA/20 wt % BF/20 wt % talc	Non	53.0	168.0	26.51	44.18	16.49	18.0
	Yes	58.9	169.2	29.91	49.85	0	40.2

^a Melting Enthalpy Converted to 100 wt % PLA.

of PLA/20 wt % BF/20 wt % talc before and after heat treatment. The intensity of reflections at the angular positions 16.7° and 19.0° correspond to the 110 and 020 plane of PLA,²² respectively, and the peaks found at $2\theta = 15.0^\circ$, $2\theta = 22.9^\circ$, and $2\theta = 34.7^\circ$ are related to the 101, 002, and 040 plane of bamboo fiber, respectively (clearly in treated sample).²³ Also, the 9.2° and 28.5° of 2θ agrees to the characteristic XRD of talc.²⁴ There were no obviously crystal patterns changed of PLA or characteristic peak reduced and increased before and after heat treatment. But, the perfect crystal was possibly formed or degree of crystallinity was possible increased after heat treatment, which could be viewed in XRD spectra (higher and more sharply peaks formed). Therefore, there was no chemical reaction or formation of new crystals patterns between fillers and matrix after heat treatment. These results were in accordance with Shaobo's work²⁰ and the results of DSC for PLA composites have been shown in Table II. Melting points of all PLA composites were almost the same and no obviously influence on melting point with loading BF and talc. After the heat treatment, the glass transition of neat PLA and all PLA composites increased distinctly due to the crystallization of PLA. The PLA chain segment was restricted by the crystallinity improvement of PLA composites after the heat treatment as shown in the Table II. Melting Enthalpy (related with relative crystallinity) of PLA composites were all increased after heat treatment. The improvement of melting enthalpy and crystallinity in PLA composites had greatly values except the PLA/20 wt % BF/20 wt % talc, which had the lowest improvement. Of course, the improvement of crystallinity could promote the increase of HDT in PLA composites. However, the HDT of PLA/20 wt % BF/20 wt % talc was the highest value in all PLA composites, which had the lowest improvement of crystallinity after heat treatment. So, the crystallinity is not the key factor for increase of HDT especially in PLA/20 wt % BF/20 wt % talc. HDT measures

the thermomechanical property of polymer. The key factor resulting in the improvement of HDT of PLA composites after heat treatment will be investigated in next discussion. Therefore, influences of BF and talc on HDT of heat-treated PLA composites were clarified in detail through POM-HS and DMA methods in below.

POM-HS

The spherulite growing of PLA composites were observed clearly through POM-HS from melting to designated temperature. Figure 4 shows the POM photographs of PLA/20 wt % BF/20 wt % talc, crystallized under isothermal conditions at 120°C [Fig. 4(a)] and 130°C [Fig. 4(b)], and for 20 minutes. The nonisothermal crystallization, from melting to room temperature, is shown in Figure 4(c). The isothermal crystallization represents the heat treatment process and nonisothermal crystallization represents the nonheat treatment process. It was very interesting that the transcrystallization, which was first mentioned in Jenckel et al. work²⁵ was clearly observed in Figure 4(a,b) during the isothermal crystallization. The first and fast growing crystals were around single BF and the transcrystallization was formed around BFs in the PLA/20 wt % BF/20 wt % talc. The transcrystallization might be formed at a designated temperature and after several minutes, because there was no similar transcrystallization in Figure 4(c), representing directly cooling to the room temperature from melting. Therefore, there might be a relationship between forming transcrystallization and the heat treatment, which also influenced the HDT of PLA composites. Furthermore, there were also relationships between loading two kinds of fillers simultaneously and forming transcrystallization because there was no obviously transcrystallization forming after isothermal crystallizing at 120°C for 20 min in PLA/20 wt % BF and PLA/20 wt % talc, which was only one filler loaded [Fig. 5(a,b)].

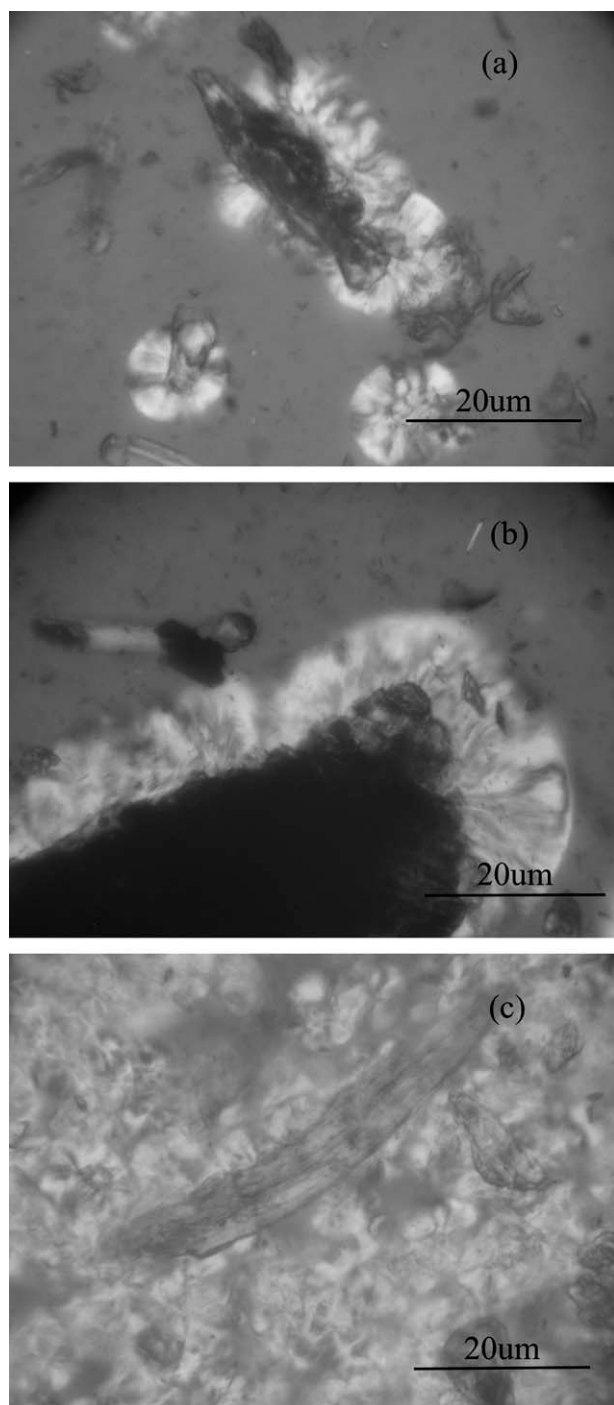


Figure 4 POM isothermal crystallization photographs of PLA/20 wt % BF/20 wt % talc at 120°C (a), 130°C (b), and nonisothermal crystallization from melting to room temperature (c).

Therefore, BF and talc have a synergetic effect in PLA/20 wt % BF/20 wt % talc composites.

To investigate the influence of BF and talc on forming transcrystallization in PLA/20 wt % BF/20 wt % talc, the isothermal crystallization process was studied in details. Fillers of BF and talc had played the different role simultaneously in forming transcrystallization in PLA/20 wt % BF/20 wt % talc dur-

ing the isothermal crystallization process. Moreover, a schematic mechanism of the forming transcrystallization is shown in Figure 6. From observing the growing of spherulite in PLA/20 wt % BF/20 wt % talc through POM-HS [original state, Fig. 6(a)], talc acted as a nucleating agent. Crystallization begins from the powder state [nucleation state in matrix, Fig. 6(b)], and growing of crystals was promoted by BF's filler. Crystals were growing faster and larger around BF's, compared to the growing kinetics of crystals within matrix after nucleation [crystals growing state in matrix, Fig. 6(c)]. At last, transcrystallization was formed around BF's during isothermal crystallization for few minutes.

Forming transcrystallization in PLA/20 wt % BF/20 wt % talc was observed at different isothermal crystallization temperature after 20 minutes remaining as shown in Figure 7. No transcrystallization was formed in the matrix at the lower isothermal crystallization temperature [Fig. 7(a)]. Otherwise, petty crystals were formed around the BF at higher isothermal crystallization temperature [Fig. 7(c)] and these petty crystals may not benefit to the properties of PLA composites especially the mechanical and

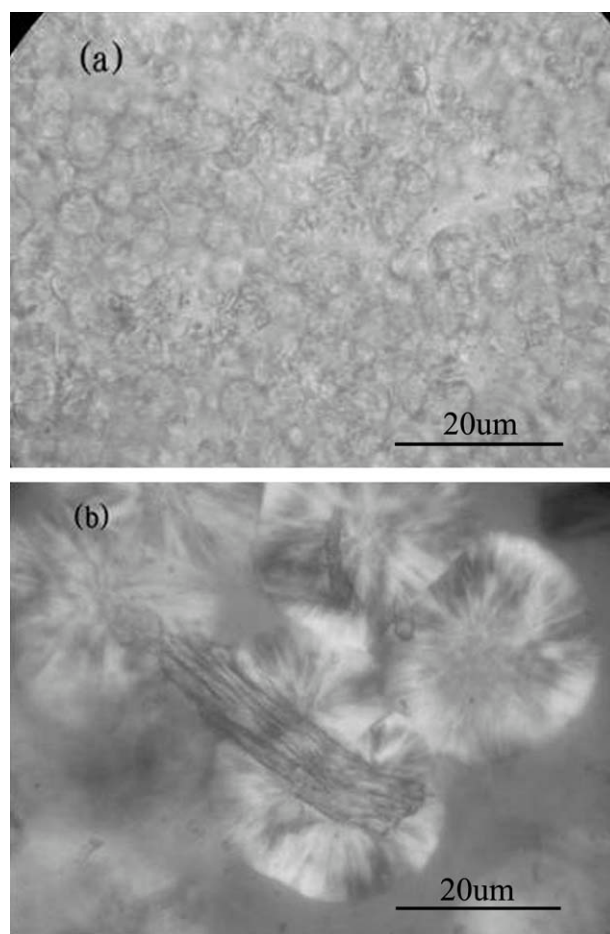


Figure 5 POM isothermal crystallization photographs of PLA/20 wt % BF (a) and PLA/20 wt % talc (b) at 120°C.

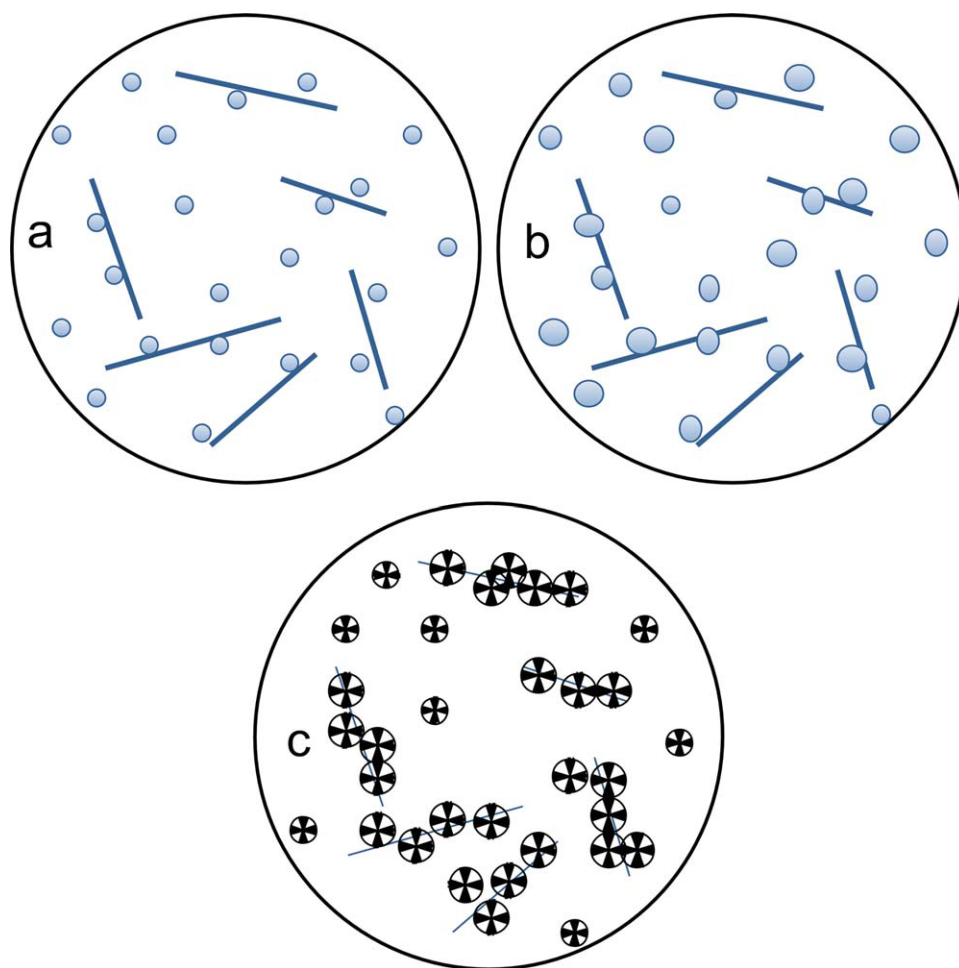


Figure 6 Schematic mechanism of transcrystallization formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

HDT properties (as shown in Table III). Therefore, in this research, the temperature of 120°C was chosen for isothermal crystallization and heat treatment.

In Table III, the HDT of PLA composites were given after heat treatment at different temperature. There was lower improvement of HDT at 110°C and 130°C treatment than that at 120°C especially in PLA/20 wt % BF/20 wt % talc composites. This is due to no transcrystallization forming at 110°C treatment and lots of kind petty crystals formed at 130°C treatment, which induced decreasing the value of HDT in the PLA matrix as shown in Figure 7.

Nowadays, the influence of transcrystallization on properties of polymer composites has been reported in several studies; transcrystallization had the advantages or disadvantages for the properties of polymer composites.^{26,27} In this study, the transcrystallization was benefit to improvement of HDT in PLA composites. Crystals around BF's played an important role in PLA composites especially in PLA/20 wt % BF/20 wt % talc. Furthermore, the improvement of HDT was also due to BF and talc reinforcement together in PLA/20 wt % BF/20 wt % talc.

There was not a lot of nucleation at the beginning of crystallization of PLA composites without talc. As the similar reason, the growing of crystals was not rapid after the nucleation processing in PLA composites without BF. Therefore, the synergism between talc and BF was just playing different role in crystallization and forming transcrystallization.

Through POM-HS experiment, improvement of HDT in PLA/20 wt % BF/20 wt % talc was studied and analyzed in crystallization and reinforcement. The deeply investigation should be proposed in the internal of PLA matrix. Therefore, the viscoelastic properties of samples were studied to clarify the influence of BF and talc on HDT in PLA composites, since HDT reflects the ability of polymeric material to withstand loads at elevated temperature, which is also a modulus-temperature behavior as elucidated by DMA.

Dynamic mechanical analysis

Figure 8 is the DMA thermograms results of PLA composites without heat treatment and the DMA

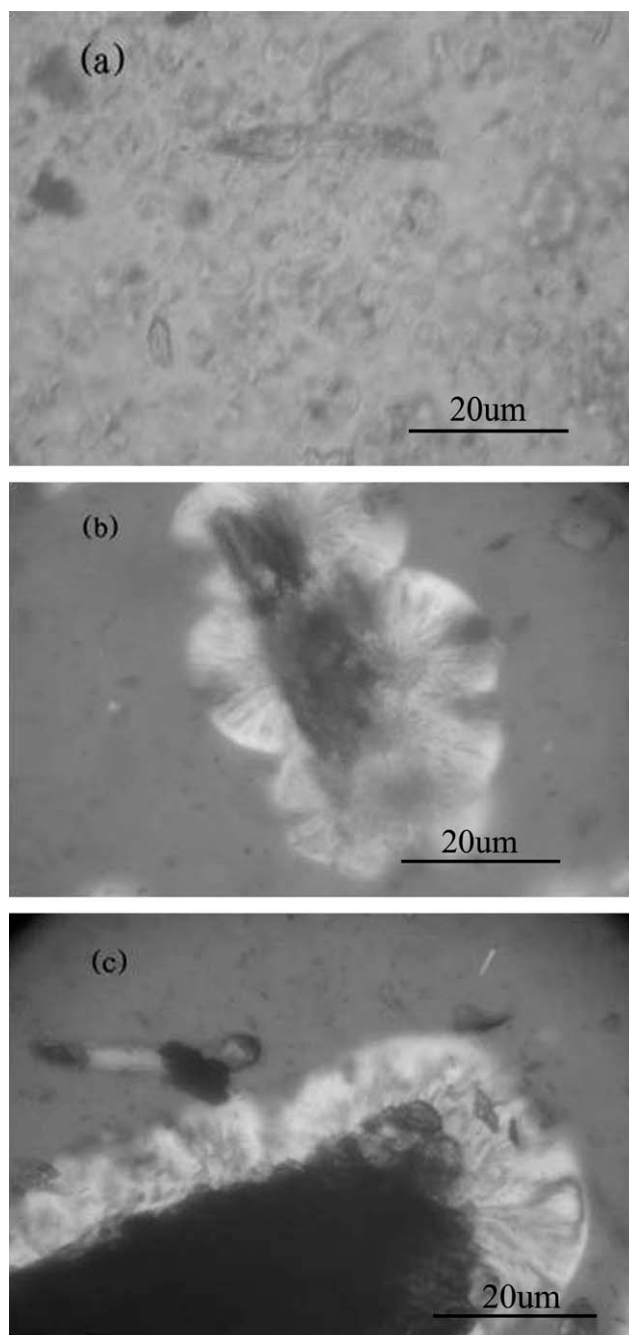


Figure 7 POM isothermal crystallization photographs of PLA/20 wt % BF/20 wt % talc at 110°C (a), 120°C (b), and 130°C (c).

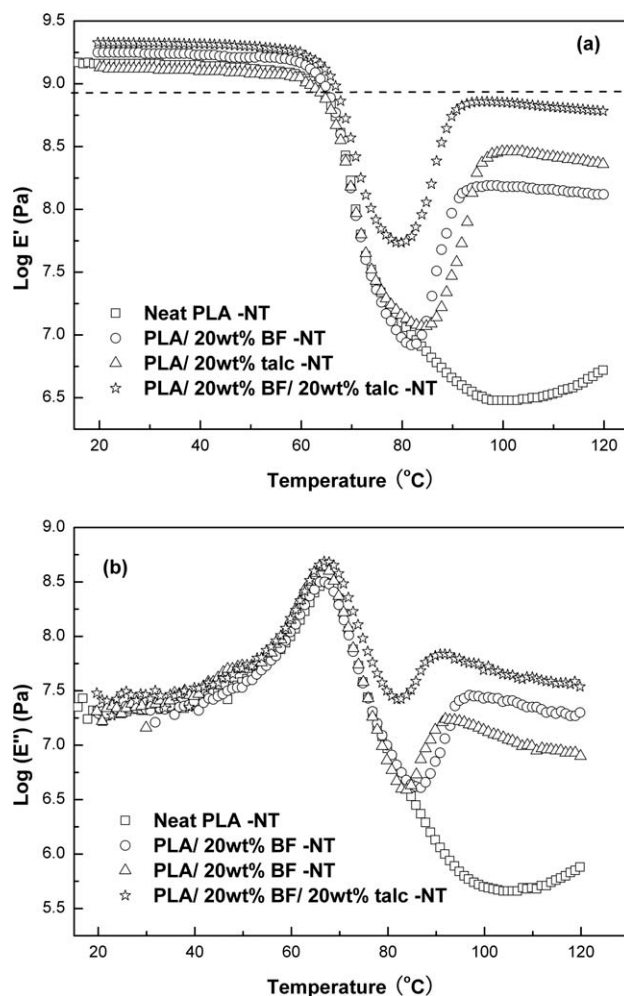


Figure 8 DMA thermograms [storage modulus (a) and loss modulus (b)] of PLA composites with non heat treatment (–NT).

data were summarized in Table IV. For nonheat-treated PLA composites, the storage modulus (E') was nearly the same, and there was the same phenomenon at T_g values ($\tan \delta$ peak in Table IV). PLA/20 wt % BF/20 wt % talc had the highest E' in Figure 8(a), due to the reinforcement of BF and talc simultaneously. E' of PLA composites was greatly improved with heat treatment especially in the PLA/20 wt % BF/20 wt % talc with loading BF and talc simultaneously.

TABLE III
HDT of PLA Composites at Different Temperature Treatment

Composites sample	110°C Heat treatment (°C)	120°C Heat treatment (°C)	130°C Heat treatment (°C)
Neat PLA	52.2 ± 3.0	54.6 ± 5.3	54.0 ± 1.8
PLA/20 wt % BF	60.2 ± 4.0	63.8 ± 0.8	58.9 ± 4.9
PLA/20 wt % talc	57.6 ± 4.5	63.9 ± 2.2	55.0 ± 8.1
PLA/20 wt % BF/20 wt % talc	78.8 ± 2.8	94.5 ± 3.8	74.8 ± 2.9
PLA/40 wt % BF	67.8 ± 4.2	68.5 ± 1.1	58.9 ± 5.5

TABLE IV
Summary of DMA and HDT Data for PLA Composites

Sample	Heat Treatment	Estimated HDT (°C)	Measured HDT (°C)	Tan δ peak (°C)	Peak height of tan δ
Neat PLA	Non	63.0	50.4 \pm 1.2	72.8	1.785
	Yes	71.8	54.6 \pm 5.3	78.8	0.210
PLA/20 wt % BF	Non	64.4	52.0 \pm 3.3	72.8	1.654
	Yes	84.5	63.8 \pm 0.8	77.8	0.141
PLA/20 wt % talc	Non	62.8	48.8 \pm 0.8	72.8	2.014
	Yes	75.7	63.9 \pm 2.2	76.8	0.155
PLA/20 wt % BF/20 wt % talc	Non	66.3	49.2 \pm 6.6	72.8	1.317
	Yes	115.8	94.5 \pm 3.8	74.8	0.105

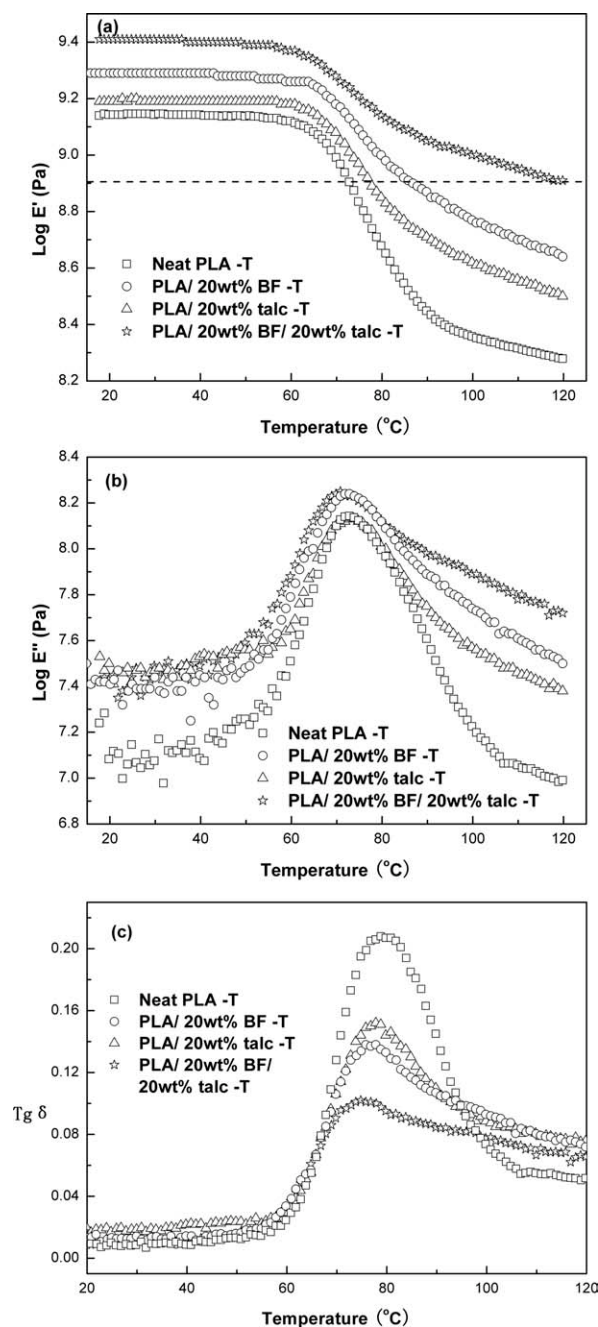


Figure 9 DMA thermograms of PLA composites with heat treatment (-T): (a) storage modulus, (b) loss modulus, and (c) loss factor.

The HDT values of polymer also could be estimated by DMA results.^{20,28} The HDT at a stress of 1.82 MPa corresponds to the temperature at which the logarithm of storage modulus (Pa; $\log E'$) is 8.9, considering the specimen dimensions used for DMA analysis. The estimated HDT values in Table IV had the similar tendency with the measured values. However, the estimated absolute values were higher than the ones measured. The overestimation increases with filler concentration and was very sensitive to small changes in $\log E'$ and the discrepancy might be attributed to many reasons. Physical reasons may stem from crystalline morphology differences, filler concentration effects, that is, agglomeration, decreases in particle aspect ratio, particle-particle interactions, etc.²⁹ In PLA composites, the filler agglomeration and crystalline morphology could be the main reasons because of the difficult dispersion of BF and the transcrystallization forming in matrix.

The alpha peak in loss factor [$\tan \delta$, Fig. 9(c)] is related to T_g of PLA. There was nearly no influence of BF and talc on T_g of PLA composites before heat treatment, which has been shown in Table IV. After the heat treatment, the T_g showed same shift to high temperature in all PLA composites and T_g values obtained by DSC scanning (Table II) showed the similar tendency.

The magnitude of the $\tan \delta$ peak attributed to T_g of PLA composites decreased with loading BF and talc. This was due to the transcrystallization of PLA composites with BF and talc after heat treatment, leading the restriction on mobility of polymer chains in PLA composites. There were obviously decreases in the magnitude of the $\tan \delta$ peak in all PLA composites (Table IV), especially PLA/20 wt % BF/20 wt % talc, which were due to the increased crystallinity and restricted polymer chains during heat treatment.³⁰ The peak loss modulus (E'') of PLA/20 wt % BF/20 wt % talc also decreased after heat treatment [Figs. 8(b) and 9(b)], although there were little differences among the PLA samples. In PLA/20 wt % BF/20 wt % talc, its main chain motion was further constrained after heat treatment because of the increase in T_g , decreases of (i) magnitudes of \tan

δ and (ii) loss modulus. T_m of PLA was about 170°C, which limits its using in high loading and temperature. Therefore, the modulus, T_m and T_g partly affected the HDT of polymer composites whose value was between T_g and T_m .

In conclusion, PLA composites with loading BF or talc hardly enhanced its modulus incrementally, leading no obvious changes in HDT. This work suggests that the HDT of PLA composites, which value was greatly improved by heat treatment under adequate conditions, especially in PLA/20 wt % BF/20 wt % talc in which the transcrystallization occurred. Therefore, the main reason of the great improvement of HDT was the occurrence of transcrystallization in matrix, which increased its crystallinity.

CONCLUSION

Remarkable increase in HDT of PLA hybrid biocomposites was obtained thanks to loading of BF and talc simultaneously. However, there was small improvement in HDT of PLA composites which has only 20 wt % BF or talc loaded. With loading 20 wt % BF and 20 wt % talc, the HDT of PLA composites increased about 45.3°C and the HDT value is suitable to use in daily life. And this was due to the synergism of BF and talc in PLA composites. Transcrystallization was observed in PLA composite with loading BF and talc simultaneously and no similar phenomenon in other PLA composite. In some certain, improvement in HDT of PLA composite was due to the effect of crystallinity. However, the formation of transcrystallization was the main effect on HDT of PLA composites. DMA showed the relationship between viscoelastic properties and HDT of PLA composites. Moreover, mechanism of forming transcrystallization was proposed.

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