

CRYSTALLIZATION BEHAVIOR, THERMAL AND MECHANICAL PROPERTIES OF PHBV/GRAPHENE NANOSHEET COMPOSITES*

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Abstract Biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/graphene nanosheet (GNS) composites were prepared *via* a solution-casting method at low GNS loadings in this work. Transmission electron microscopy revealed that a fine dispersion of GNSs was achieved in the PHBV matrix. The thermal properties of the nanocomposites were investigated by thermogravimetric analysis, and the results showed that the thermal stability of PHBV was significantly improved with a very low loading of GNSs. Nonisothermal melts crystallization behavior, spherulitic morphology and crystal structure of neat PHBV and the PHBV/GNSs nanocomposites were investigated, and the experimental results indicated that crystallization behavior of PHBV was enhanced by the presence of GNSs due to the heterogeneous nucleation effect; however, the two-dimensional (2D) GNSs might restrict the mobility of the PHBV chains in the process of crystal growing. Dynamic mechanical analysis studies showed that the storage modulus of the PHBV/GNSs nanocomposites was greatly improved.

Keywords: PHBV; Graphene nanosheets; Nanocomposites; Solution-casting films.

INTRODUCTION

Graphene is an atomically thick, tow-dimensional (2D) sheet composed of sp^2 carbon atoms arranged in a honeycomb structure. It has attracted great research interest due to high aspect ratio, remarkable thermal, mechanical and electrical properties. The polymer/graphene nanocomposites have recently attracted considerable attention from both academic and industrial viewpoints because they exhibit tremendously improved properties compared with the polymer matrix^[1–3]. Recent studies showed that graphene as nanofiller may be preferred over other conventional nanofillers, such as sodium montmorillonite (Na-MMT), layered double hydroxide (LDH), carbon nanotubes (CNTs), exfoliated or expanded graphite (EG), *etc.* due to its unique properties^[4]. In previous studies, polymer/graphene nanocomposites were prepared by solution blending^[5–7], melt blending^[8, 9], *in situ* polymerization^[10, 11] and so on. Due to the low viscosity of the mixture system in solution, solution blending has been a widely used technique for the preparation of polymer/graphene nanocomposites.

Several studies on the crystallization behavior, mechanical and thermal properties of polymer/graphene nanocomposites have been reported. Xu *et al.* reported that graphene in the Nylon-6 matrix acted as reinforcing filler; it enhanced the Young's modulus and tensile strength of the nanocomposites^[12]. The crystallization

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behaviors of PCL/graphene and PE/graphene nanocomposites were studied by Zhang *et al.*^[13] and Cheng *et al.*^[14], respectively. It was shown that graphene was an effective nucleation agent for PCL and PE, moreover, the presence of a small amount of graphene can dramatically improve the thermal stability of PE. By this means, only a small amount of graphene is required to achieve a high performance of the polymer matrix, which is important for its practical application.

As a biodegradable and biocompatible polyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has recently attracted considerable attention from both academic and industrial viewpoints. It can be produced by bacterial fermentation from renewable natural materials^[15, 16]. However, its wide practical application has been restricted by some disadvantages such as brittleness, poor thermal and mechanical properties, because PHBV has a comparatively low crystallization nucleation ability and slow crystallization rate. Moreover, the secondary crystallization of the amorphous phase in PHBV can take place at the ambient temperature during storage. The solidification process tightly constrains the amorphous chains between the crystals, making the material brittle^[17]. Numerous efforts have been made to overcome these disadvantages. The use of nanoparticles as nucleating agents has become attractive because the nanoparticles are not only useful in nucleating of the polymer but also beneficial to thermal and mechanical properties of the composites. It has been reported that clay, carbon nanotubes and metal oxides, especially MgO, can improve the thermal stability of PHBV^[18–20]. Ma *et al.* studied the effects of fumed silica on the crystallization kinetics of PHBV^[21]. It was shown that the overall crystallization rate and crystallinity increased at low silica concentrations (≤ 2 wt%) and decreased at high concentration (5 wt%). The authors suggested that the high concentration of silica may act as large impurities and hinder crystallite growth. Similarly, PHBV/organophilic montmorillonite (OMMT) nanocomposites were prepared by solution intercalation method^[22]. Their research showed that a small portion of OMMT can increase the crystalline nuclei thus causing a more rapid crystallization rate. However, the crystallinity decreased with increasing amount of OMMT owing to the OMMT layers restricted the motion of PHBV chains. The nanoparticles play important roles in thermal, crystallization and mechanical performance of PHBV. Compared with other nanoparticles, graphene has remarkable thermal and mechanical properties due to its 2D geometry. Moreover, because of its large aspect ratio and unique layered structure with nanoscale thickness, graphene is expected to be alternative nanoparticles in preparing high performance PHBV nanocomposites with a very low addition.

In this article, we presented a convenient solution mixing method to prepare PHBV/GNSs nanocomposites and studied the influence of GNSs on the thermal properties, nonisothermal melt crystallization behavior, spherulitic morphology, crystal structure and dynamic mechanical properties of PHBV nanocomposites with various techniques in detail. This research is expected to be of great interest for better understanding the influence of GNSs on the properties of a biodegradable polymer.

EXPERIMENTAL

Materials

Graphite was purchased from Qindao Jiuyi Graphite Co., Ltd. (Shandong, China) with a mean particle size of 50 μm . PHBV containing 20 mol% hydroxyvalerate (HV) monomer was kindly supplied by Tianan Biologic Co., Ltd. (Ningbo, China). The weight-average molecular weight (M_w) was approximately 380000. PHBV with low molecular weight was prepared by acid degradation according to the method reported by Yu^[23]. After degradation, the M_w of PHBV was reduced to 29000, with the PDI of 2.3 as determined by gel-permeation chromatography (GPC). Sulfuric acid, potassium nitrate, potassium permanganate, hydrogen peroxide, succinic acid, ethyl alcohol, paratoluenesulfonic acid, dimethyl sulfoxide (DMSO), chloroform and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

Preparation of GNSs

GNSs were prepared through thermal exfoliation of graphene oxide (GO). Aksay and coworkers have prepared

GNSs by the exfoliation of graphite oxide^[24, 25]. In our work, we use GO as the starting materials to prepare GNSs following the same method, which ensures the production of single-layer graphene sheet. GO was prepared from graphite powder according to a modified Hummers' method^[26, 27]. The GO colloid suspension was spray-dried with an inlet air temperature of 200 °C and outlet air temperature of 100 °C. The dried sample was stored in a vacuum oven at 60 °C until it was ready for use. The GO suspension used for atomic force microscope (AFM) studies was prepared directly from the GO colloid suspension prior to spray-drying. Thermal exfoliation of GO as prepared above was achieved by placing dried GO powders into a quartz tube, and then the GO powders were annealed at 1050 °C for 30 s under argon atmosphere to produce the final graphene powders, which was similar to the method Aksay and coworkers used.

Preparation of PHBV/GNS Nanocomposites

Solid PHBV/GNS nanocomposites films with various GNS concentrations of 0.1 wt%, 0.5 wt% and 1.0 wt% were prepared *via* a solution-casting method. In a typical procedure, GNSs were dispersed in chloroform with a mass concentration of 0.2 mg/mL by ultra-sonication for 4 h at room temperature. The obtained graphene/chloroform suspension was directly used for transmission electron microscope (TEM) measurements. 6 wt% PHBV was dissolved in the chloroform at 40 °C. The GNSs suspension was then put into the PHBV solution followed by stirring vigorously for 3 h at 40 °C. After that, the mixture was cast onto a clean glass substrate and evaporated overnight at room temperature. The films were subsequently dried in a vacuum oven at 70 °C for 24 h. The neat PHBV film was also prepared according to the same procedure in the absence of GNSs. All films were kept in a desiccator containing allochroic silicagel at room temperature for 1 week prior to any test. In this way, PHBV was mixed with the addition of 0.1 wt%, 0.5 wt% and 1.0 wt% GNSs, respectively. For brevity, they were abbreviated as PHBV/GNSs-0.1, PHBV/GNSs-0.5 and PHBV/GNSs-1.0, respectively, in this work from now on.

Instrumental Analyses

Atomic force microscopy (AFM) images of GO was conducted by a Veeco Dimension 3100 V scanning probe microscope at ambient conditions using a tapping mode.

Transmission electron microscopy (TEM) images of GNSs and PHBV/GNSs nanocomposites were obtained on an FEI Tecnai G² F20 transmission electron microscope with an accelerating voltage of 200 kV. The PHBV/GNSs nanocomposites were embedded in epoxy and cut into 70–90 nm thick slices using an ultramicrotome.

Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo thermal analyzer to determine the thermal stability of the prepared samples. The samples of neat PHBV and PHBV/GNSs nanocomposites were heated to 500 °C at 10 K/min under 50 mL/min nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC under nitrogen atmosphere. The samples of neat PHBV and PHBV/GNSs nanocomposites were first heated to 190 °C at a heating rate of 40 K/min (first heating), and equilibrated at 190 °C for 3 min to remove the thermal history. Subsequently, the samples were cooled to –30 °C at a scanning rate of –10 K/min (first cooling). Finally, the samples were reheated to 190 °C at a heating rate of 10 K/min (second heating). The crystallization temperature (T_c), crystallization enthalpy (ΔH_c) and crystallinity (C_{rc}) were determined from the first cooling traces. The cold crystallization temperature (T_{cc}), cold crystallization enthalpy (ΔH_{cc}), melting point temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating traces.

Spherulitic morphology of neat PHBV and PHBV/GNSs nanocomposites was observed using a polarizing optical microscope (Olympus BX51) (POM) equipped with an Instec HCS601 hot stage. The samples were first heated to 190 °C with a heating rate of 50 K/min on the hot stage and held there for 3.5 min to erase any thermal history, and then they were cooled to desired crystallization temperatures with a cooling rate of 100 K/min. Here, the crystallization temperatures were set at 90 °C and 100 °C. Sequential images of PHBV spherulites were taken by an attached digital camera every 60 s for measuring of spherulite growth rate and nucleation density.

Wide angle X-ray diffraction (WAXD) patterns were recorded on a Bruker D8 diffractometer, using Ni-

filtered Cu K α radiation at 40 kV and 30 mA at room temperature in a 2θ range from 5° to 40° at a scanning rate of $3.5^\circ/\text{min}$.

Dynamic mechanical analysis (DMA) was performed on the samples of $33\text{ mm} \times 5\text{ mm} \times 0.15\text{ mm}$ in size with a dynamic mechanical analyzer from Mettler Toledo Company under tension film mode in a temperature range of -50°C to 80°C at a frequency of 1 Hz with a heating rate of 5 K/min.

RESULTS AND DISCUSSION

Characterization of GO

The GO nanosheets were first characterized by AFM. Figure 1(a) shows the AFM image of typical GO nanosheets from a homogeneous GO aqueous suspension with a mass concentration of 0.1 mg/mL. The average thickness of GO nanosheets was measured to be 1.8 nm from the height profile (Fig. 1b), which demonstrates the GO nanosheets in suspension are mostly single layers.

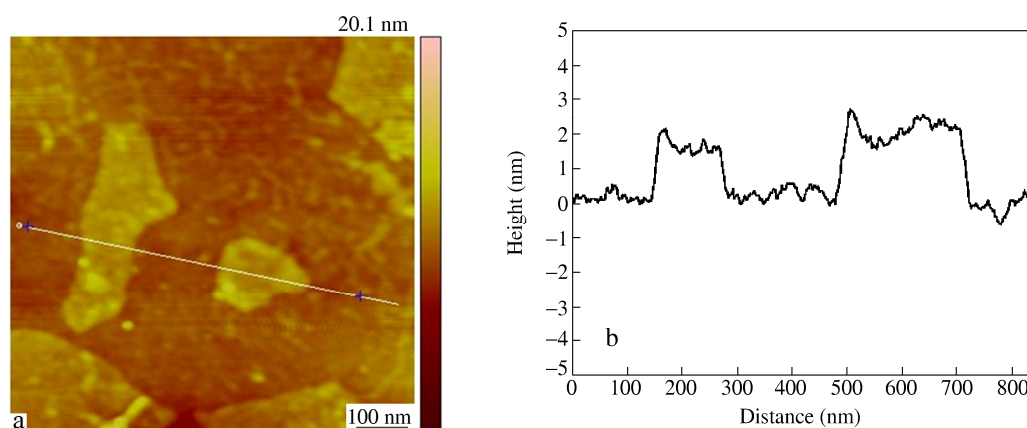


Fig. 1 AFM height image (a) and cross-sectional analysis (b) of GO on Si substrate

Dispersion of Graphene in Chloroform and PHBV Matrix

It is well known that the homogeneous dispersion of GNSs in the polymer matrix plays an important role in influencing the physical properties of the polymer. In our work, we tried to disperse the GNSs in chloroform for the successful preparation of PHBV/GNSs nanocomposites. GNSs dispersion could be stable for more than one week after sonicated in chloroform for 4 h. Figure 2(a) presents the TEM image of GNSs in chloroform. The wrinkled thin sheet-like structure was observed. The dispersion of GNSs in PHBV was also investigated by TEM. Figures 2(b) shows the TEM image of the PHBV/GNSs nanocomposites with 1.0 wt% GNSs content, from which it can be seen that GNSs with wrinkled structure are randomly dispersed in the PHBV matrix without any obvious aggregations. It should be noted that functionalization and defects may distort flat GNSs into wrinkled sheets during the thermal exfoliation, thereby resulting in the wrinkled nature of GNSs^[3, 13]. This well-dispersed structure would be the basis for improving the performance of the PHBV/GNSs nanocomposites.

Thermal Stability Properties

The thermal stability of PHBV/GNSs nanocomposites was evaluated by TGA under nitrogen atmosphere, as shown in Fig. 3. The temperatures for 5% (T_5) and 50% (T_{50}) weight loss of neat PHBV and PHBV/GNSs nanocomposites are summarized in Table 1. For example, inclusion of as low as 0.1 wt% GNSs sheets led to a 12 K increase of T_5 with respect to that for neat PHBV. Meanwhile, with the GNSs content increasing from 0.1 wt% to 1.0 wt%, the T_{50} values for the PHBV/GNSs nanocomposites increased from 251°C to 263°C , whereas the T_{50} values for neat PHBV was 245°C . Obviously, increasing GNSs content (from 0.1 wt% to 1.0 wt%) gradually shifted the degradation temperature (T_5 and T_{50}) of the polymer to higher temperatures, which indicated that the thermal stability of the PHBV/GNSs nanocomposites was greatly improved compared

with that of neat PHBV. These results show that the addition of GNSs into the PHBV matrix at extremely low filling content could dramatically improve the thermal properties of the matrices. This substantial enhancement of thermal stability can be attributed to two reasons: first, the GNSs have high efficiency for capture of free radicals generated by polymer chain scission during the degradation process at high temperatures^[14, 28]. Secondly, the homogeneously distributed GNSs, possessing high aspect ratio, may act as barrier and hinder the diffusion of volatile decomposition products in the PHBV matrix^[29, 30].

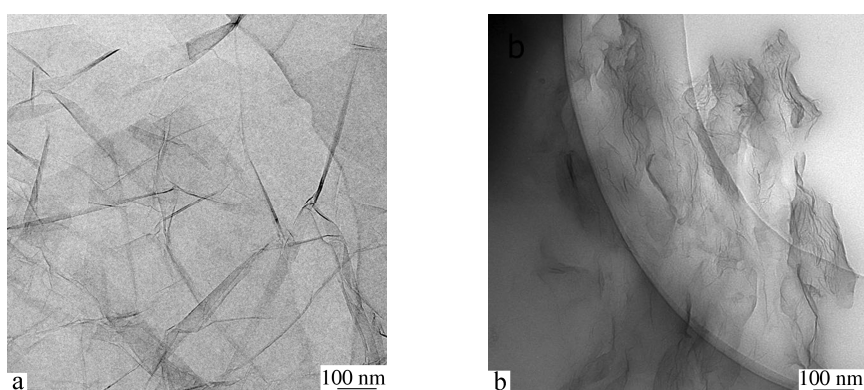


Fig. 2 TEM images of the GNSs (a) and PHBV/GNSs-1.0 nanocomposite film (b)

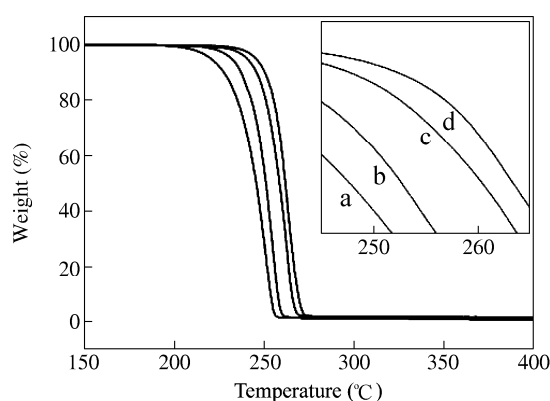


Fig. 3 TGA curves of neat PHBV and PHBV/GNSs nanocomposites with various GNSs contents: (a) neat PHBV, (b) PHBV/GNSs-0.1, (c) PHBV/GNSs-0.5 and (d) PHBV/GNSs-1.0

Table 1. TGA data of neat PHBV and PHBV/GNSs nanocomposites

Sample	T_5 (°C)	T_{50} (°C)
PHBV	220	245
PHBV/GNSs-0.1	232	251
PHBV/GNSs-0.5	240	257
PHBV/GNSs-1.0	245	263

Crystallization Behavior

The crystallization behavior affects the crystalline structure and morphology of the semicrystalline polymers. The influence of GNSs on the crystallization behavior of PHBV is of interest. Therefore, nonisothermal crystallization/melting behavior, spherulitic morphology and crystal structure studies of neat PHBV and its nanocomposites were investigated with various techniques for a better understanding of the influence of the 2D GNSs on the PHBV matrix.

DSC curves of cooling and second heating scans of neat PHBV and PHBV/GNSs nanocomposites are

shown in Figs. 4(A) and 4(B), respectively. The thermal analysis parameters derived from Fig. 4 are summarized in Table 2. The C_r values of PHBV and PHBV/GNSs nanocomposites can be calculated *via* Eq. (1):

$$C_r = (\Delta H / \Delta H_0) \times 100\% \quad (1)$$

where ΔH_0 is the thermodynamic enthalpy of fusion per gram of PHB (146.6 J/g) and ΔH is the apparent enthalpy of crystallization (ΔH_c), cold crystallization (ΔH_{cc}) or fusion (ΔH_m) per gram of PHBV with different GNSs contents.

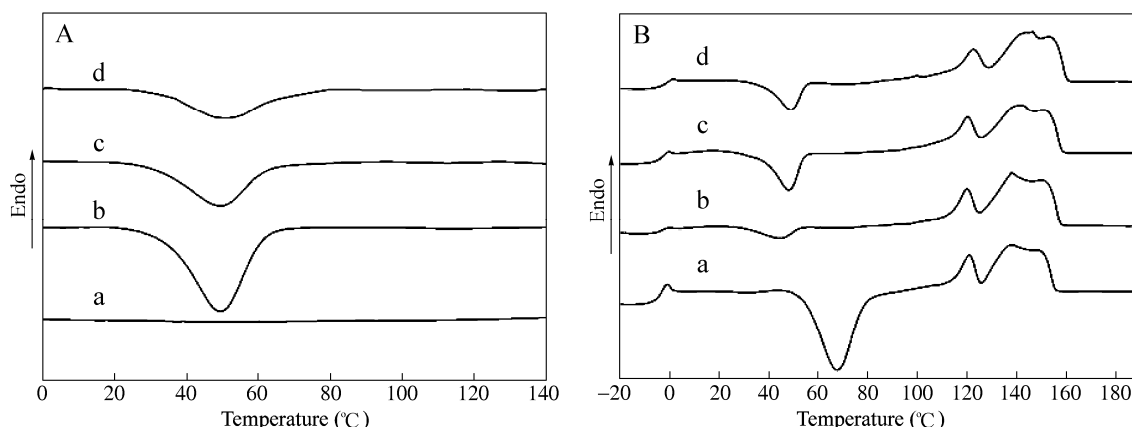


Fig. 4 DSC curves of neat PHBV and PHBV/GNSs nanocomposites from the cooling (A) and second heating (B) scans with various GNSs contents: (a) neat PHBV, (b) PHBV/GNSs-0.1, (c) PHBV/GNSs-0.5 and (d) PHBV/GNSs-1.0

As shown in Fig. 4(A), neat PHBV could not crystallize during the cooling scans. Obviously, all the PHBV/GNSs nanocomposites have an obvious crystallization peak, indicating that the presence of GNSs has enhanced the nonisothermal melt crystallization of PHBV in the nanocomposites relative to neat PHBV. This conclusion has been proved from Fig. 4(B) that all the T_{cc} values of PHBV/GNSs nanocomposites shift to lower temperature range compared with neat PHBV. This can be attributed to that: parts of the PHBV crystallize at the cooling process with the presence of GNSs, which act as the nuclei for the remanent PHBV to crystallize at the second heating process. For this reason, all the T_{cc} and ΔH_{cc} values of PHBV/GNSs nanocomposites are lower than those of the neat PHBV. Such variations of T_c and T_{cc} indicate that the GNSs act as nucleating agent for the crystallization of PHBV, which reduce the energy barrier to form PHBV nuclei. Interestingly, the T_{cc} progressively shifts to higher temperatures when the contents of GNSs increase from 0.1% to 1.0%. From Fig. 4(B), T_{cc} is around 45 °C for PHBV/GNSs-0.1; however, T_{cc} shifts upward to 48 °C and 50 °C for PHBV/GNSs-0.5 and PHBV/GNSs-1.0, respectively. The obvious changes of T_{cc} values indicate that 2D GNSs might restrict the mobility of the PHBV chains and hinder the effective diffusion of chains to growing crystalline lamella. As shown in Fig. 4(a), the ΔH_c and C_{rc} diminished as the GNSs content increased, corresponding to the conclusion that 2D GNSs could hinder the mobility of the PHBV chains. Similar results had been reported in several other studies^[31, 32].

Neat PHBV and PHBV/GNSs nanocomposites exhibit triple melting peaks (T_{m1} , T_{m2} and T_{m3}). A weak single melting peak in the range of 115–125 °C (T_{m1}) is observed, which is caused by the melt of thin PHBV lamellae. Furthermore, all the samples show a double melting peak at two higher nearby temperatures (T_{m2} and T_{m3}), demonstrating a melting-recrystallization-melting process^[33]. PHBV crystals with low perfection melted at low temperature (T_{m2}) and subsequently recrystallized to higher perfection, causing the third melting peak (T_{m3}). This means that the second endothermic peak (T_{m2}) should be used as the melting temperature of the samples. Figure 4(B) shows that all the T_{m2} values of the nanocomposites are higher than that of the neat PHBV. It is of interest to note that the difference in T_{m2} between neat PHBV and PHBV/GNSs-1.0 is around 6 K. One of the factors for the increase of T_m in PHBV nanocomposites is that slower PHBV spherulite growth leads to the

formation of more perfect crystalline lamellae. In other words, the presence of GNSs gives more time for polymer chains to fully grow crystalline lamellae, even if the activity of the polymer chain decreases^[34].

Table 2. DSC data of neat PHBV and PHBV/GNSs nanocomposites

Sample	Cooling			Second heating			Melting		
	T_c (°C)	ΔH_c (J/g)	C_{rc} (%)	T_{cc} (°C)	ΔH_{cc} (J/g)	C_{rec} (%)	T_m (°C)	ΔH_m (J/g)	C_{rm} (%)
PHBV	N/A	N/A	N/A	68	43.8	29.9	137	42.2	28.8
PHBV/GNSs-0.1	50	40.9	27.9	45	5.2	3.5	139	44.9	30.6
PHBV/GNSs-0.5	50	27.4	18.7	48	15.1	10.3	141	40.9	27.9
PHBV/GNSs-1.0	51	24.3	16.6	50	14.3	9.8	143	37.3	25.4

Spherulitic morphology of the neat PHBV and PHBV/GNSs nanocomposites was further studied with POM. PHBV spherulites with characteristic Maltese cross and ring bands could be clearly seen under POM in Fig. 5. As an example, Fig. 5(b) shows that the number of PHBV spherulites is significantly greater in the PHBV/GNSs-0.1 nanocomposites than in neat PHBV, indicating that the nucleation density of PHBV spherulites has been enhanced apparently in the PHBV/GNSs nanocomposites. The spherulite growth rate of the neat PHBV and its nanocomposites is 20.7, 20.3, 18.1 and 17.3 $\mu\text{m}/\text{min}$ for PHBV, PHBV/GNSs-0.1, PHBV/GNSs-0.5 and PHBV/GNSs-1.0, respectively, when isothermally crystallized at 100°C. The results indicate that the addition of GNSs could hinder the mobility of the PHBV chains to growing crystalline lamellae. These POM observations clearly suggested the present of GNSs could act as an effective nucleation agent for PHBV to enhance the nucleation density; however, the spherulite growth rate decreased with the increase of 2D GNSs. This result was concordant with the conclusion obtained from DSC.

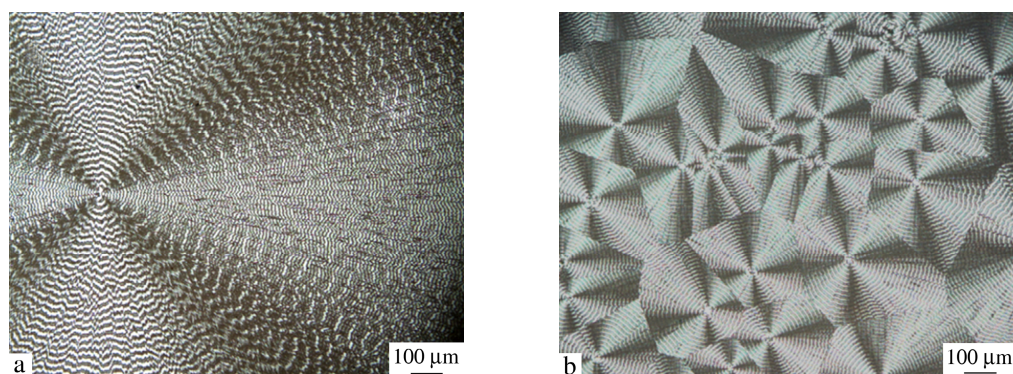


Fig. 5 POM images of (a) neat PHBV and (b) PHBV/GNSs-0.1 crystallized at 90 °C

WAXD was used to study the effect of GNSs on the crystal structure of PHBV matrix in the PHBV/GNSs nanocomposites. Figure 6 shows the WAXD patterns of neat PHBV and its nanocomposites at low GNSs loading. Neat PHBV presents three typical diffraction peaks at $2\theta = 13.56^\circ$, 17.07° and 30.8° corresponding to (020), (110) and (200) crystal planes, respectively^[35]. It can be seen from Fig. 6 that the PHBV and PHBV/GNSs nanocomposites show the similar diffraction peaks, suggesting that the crystal structure of PHBV remains unchanged despite the presence of 2D GNSs in the PHBV/GNSs nanocomposites.

Dynamic Mechanical Properties of PHBV/GNSs Nanocomposites

With Young's modulus of 1 TPa and ultimate strength of 130 GPa^[36], GNSs may result in an improvement in mechanical properties of polymer matrix in the nanocomposites. The effects of GNSs on the dynamic mechanical properties of the PHBV/GNSs nanocomposites were examined by DMA. Figure 7 shows the temperature dependence of storage modulus (E') for both neat PHBV and its nanocomposites. It can be seen that E' generally increased with the presence of GNSs, indicating that the addition of GNSs induces the

reinforcement effect. The presence of GNSs in the PHBV matrix enhanced E' within a wide temperature range of -50 °C to 80 °C. For example, the values of E' at -50 °C increase from around 1395 MPa for neat PHBV to 2670 MPa for PHBV/GNSs-1.0. Compared with neat PHBV, the E' values of the nanocomposites are significantly improved by about 25%, 87% and 91%, respectively, with incorporating only 0.1 wt%, 0.5 wt% and 1.0 wt% GNSs.

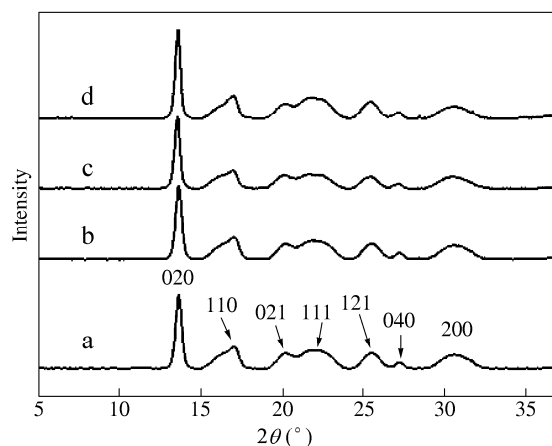


Fig. 6 WAXD patterns of neat PHBV and PHBV/GNSs nanocomposites with various GNSs contents: (a) neat PHBV, (b) PHBV/GNSs-0.1, (c) PHBV/GNSs-0.5 and (d) PHBV/GNSs-1.0

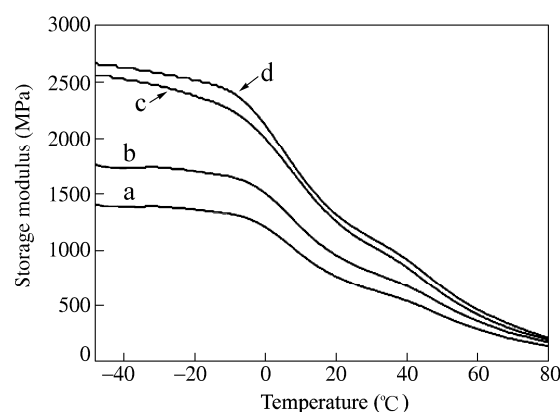


Fig. 7 DMA curves of neat PHBV and PHBV/GNSs nanocomposites with various GNSs contents: (a) neat PHBV, (b) PHBV/GNSs-0.1, (c) PHBV/GNSs-0.5 and (d) PHBV/GNSs-1.0

CONCLUSIONS

In this study, the nanocomposites of biodegradable PHBV and GNSs were prepared *via* the solution mixing method at low GNSs loading. GNSs were found to be uniformly dispersed in PHBV matrix, and the thermal stability of PHBV/GNSs nanocomposites was enhanced compared with neat PHBV. The 2D GNSs could not only act as a heterogeneous nucleation agent for the crystallization of PHBV but also restricted the mobility of the PHBV chains, which were confirmed by both DSC and POM results. It should be noted that the presence of GNSs does not change the crystal structure of PHBV. The storage modulus of the PHBV/GNSs nanocomposites was significantly enhanced by the addition of GNSs. This research is expected to be of great interest for better understanding the influence of GNSs on the properties of a biodegradable polymer. Further researches on using the modified GNSs are underway.

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