

EFFECTS OF MATRIX MOLECULAR WEIGHT ON STRUCTURE AND REINFORCEMENT OF HIGH DENSITY POLYETHYLENE/MICA COMPOSITES*

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Abstract Three types of high-density polyethylene (HDPE) with different molecular weights (high, medium and low) were adopted to evaluate the influence of matrix molecular weight on the structure-property relation of injection-molded HDPE/mica composites through a combination of SEM, 2d-WAXS, DSC, DMA and tensile testing. Various structural factors including orientation, filler dispersion, interfacial interaction between HDPE and mica, *etc.*, which can impact the macroscopic mechanics, were compared in detail among the three HDPE/mica composites. The transcrystallization of HDPE on the mica surface was observed and it exhibited strong matrix molecular weight dependence. Obvious transcrystalline structure was found in the composite with low molecular weight HDPE, whereas it was hard to be detected in the composites with increased HDPE molecular weight. The best reinforcement effect in the composite with low molecular weight HDPE can be understood as mainly due to substantially improved interfacial adhesion between matrix and mica filler, which arises from the transcrystallization mechanism.

Keywords: Polyethylene/mica composite; Molecular weight; Transcrystallization.

INTRODUCTION

The reinforcement of platelet-like particle, mica, in polymeric materials has been investigated for long time mainly to improve the thermal and mechanical properties and reduce production cost of polymer/mica composites. Strong interaction between polymer matrix and filler, highly oriented structure, matrix molecular architecture and even special crystallization mechanism (epitaxy or transcrystallization) of polymer on filler are important factors to achieve excellent properties in polymer/mica composites.

Tailoring the interfacial behavior between mica filler and polymer matrix is regarded as an effective approach to achieve reinforcement of properties. Using compatibilizer or coupling agent is a common way to achieve good interfacial adhesion, which has been investigated extensively^[1–9]. However, there are few studies considering the effect of appropriate processing conditions on the interface interaction, filler dispersion and orientation in polymer/mica composite^[10]. And in the authors' group, it has been demonstrated clearly that intensive shearing during the packing stage of injection-molded processing can effectively improve filler-matrix interaction, filler dispersion and orientation degree^[11]. Obviously, strong interfacial interaction, uniform filler dispersion and highly oriented morphology all play the positive roles on the enhancement of properties.

The oriented structure of polymer/inorganic filler composites, including the alignment of filler particles and matrix polymer chains, has attracted many researches due to its potential for obtaining excellent properties. For

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the polypropylene (PP)/talc composite, as reported by Choi *et al.*^[12], talc particles were oriented parallel to the flow direction in the skin zone of injection-molded bar ($f > 0.95$), resulting in a relative high value for PP orientation. Naiki *et al.*^[13] found that, in the injection-molded talc-filled *i*PP, the lamellae were generated from talc particle and ascribed as a *b*-axis orientation behavior for the orientation relation between molecular chains and talc plate-planes taken respect to the shear flow field. While some studies focused on the epitaxial nucleation of polymers, such as polyolefin, polyester and polyamide^[14], on talc or mica plates. Rybníkar *et al.*^[15] found that poly-4-oxybenzoate tended to epitaxially crystallize into a hexagonal orientation regime with *c*- and *b*-axes lying in mica cleavage surface. Otherwise, in the injection-molded bar of PP/talc composite, a transcrystallization superstructure that PP lamellae arranged perpendicular to the cleavage surface of talc with an interlamellar spacing of 50 nm determined by AFM^[12]. Moreover, shear rate is a crucial factor impacting orientation and thus mechanical reinforcement in the molded products. As a common thought, the critical orientation molecular weight (M^*) shifts to a lower value with increase of shear rate, namely, low molecular weight polymer requires high shear rate to realize orientation^[16]. Thus matrix molecular weight is an important factor for determining structure and properties in polymer/inorganic filler composites. The effect of matrix molecular weight on the mechanical properties of nylon 6/montmorillonite nanocomposites was demonstrated by Fornes *et al.*^[17]. For a higher molecular weight nylon 6 matrix a superior tensile property is available. Recently, Ning *et al.*^[18] found a fine hybrid shish-kebab (HSK) structure in the HDPE/whisker composites obtained *via* a special injection molding technique, dynamic packing injection molding, and demonstrated that the formation of hybrid shish-kebab structure was PE molecular weight dependent^[19]. An obvious HSK structure with PE lamellae closely packed on the surface of whisker was detected in the samples with low molecular weight PE matrix and medium molecular weight PE matrix; however, an incomplete, loose HSK structure was observed in the samples with high molecular weight PE matrix. Moreover, it was found that the tensile properties of HDPE/whisker composites could be well related to the completion extent of HSK structure.

In this work, our effort is devoted to manifest the molecular weight dependence of PE matrix on the mechanical properties, mica filler dispersion, orientation structure, crystalline behavior and especially transcrystalline morphology of the injection-molded bar of HDPE/mica composites prepared under intensive shearing field. To achieve high degree of orientation and strong shearing influence, a unique processing method, the so-called dynamic packing injection molding (DPIM), was applied to exert oscillatory shear on the molten composites through two pistons that moved repeatedly with the same frequency during the solidification process. A systematic investigation associated with various characterizations, such as SEM, 2d-WAXS, DSC, DMA and tensile testing, was performed on the HDPE/mica composites with PEs of three different molecular weights (low-, medium- and high-molecular weight of PE matrix), to finally establish a distinct structure-property relationship of HDPE/whisker composites

EXPERIMENTAL

Materials

Three kinds of commercially available high-density polyethylene (HDPE), trade-marked as 5000S, 8008 and 2911, with different molecular weights (M_w) and polydispersities (PD), were adopted in this study as matrix resin. A PL-GPC220 instrument (Polymer Laboratories Ltd., USA) was used to measure the molecular weight parameters of HDPE resins. The gel permeation chromatography (GPC) experiments were implemented upon 160°C and with calibration of the standard polystyrene. Mica, wet ground muscovite, was obtained from Sanbao Co. Ltd., China. The mica is in powder profile with a mesh size of 800, and the morphology of raw mica powders is exhibited in Fig. 1. Silicohydride, KH-550, used as the coupling agent for mica treatment, was purchased from Chenguang Research Institute of Chemical Industry (Chengdu, China). Mica was first immersed into a 10 wt% KH-550 solution in a high-speed mixer (the rotation speed was 800–1000 r/min) for 8 min. After that, the precipitate was exposed to atmosphere for 3–4 h and then was dried at 85°C for 4 h.

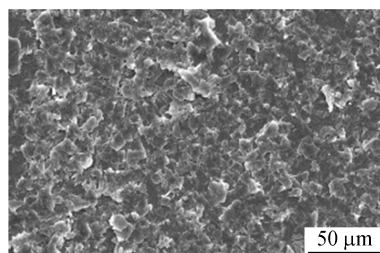


Fig. 1 SEM microphotograph of raw mica powers

Preparation of the Injection-molded Samples

With fixed contents of mica as 10 wt%, the melt blending of HDPE/mica composites with different PE molecular weights (low, medium and high) was conducted in a TssJ-2S co-rotating twin-screw extruder and the temperatures were maintained at 165°C, 180°C, 190°C, 200°C, 200°C and 195°C from hopper to die. In a concision manner, thereafter the low-, medium- and high-molecular weight PE matrixes are abbreviated as LMW-, MMW- and HMW-PE, respectively.

After the pelletizing and drying processes, the as-prepared composites were injected into a mold with the aid of an SZ 100 g injection-molding machine with a barrel temperature of 190°C and injection pressure of 900 kg/cm². Then dynamic packing injection-molding (DPIM) technology was applied to introduce oscillatory shear to the cooling melt during packing stage by two pistons that moved repeatedly with the same frequency (1.0 Hz). Shear rate was about 10 s⁻¹ calculated from the geometry of the mold. The processing parameters, the characteristics and detailed experiment procedure of the DPIM, and the geometrical sizes of molded bar were described in Refs. [20, 21]. The injection-molded bars prepared through DPIM consisted of three zones: the skin, oriented zone and core. We also carried out injection molding under static packing by using the same processing parameters but without shearing for comparison purpose. The specimen obtained by dynamic packing injection molding was called dynamic sample, and the specimen obtained by static packing injection molding was called static sample. The width and thickness of the test samples were about 6.0 and 3.5 mm. Macroscopically, the main feature of the dynamic sample is the shear-induced morphologies with a core layer in the center, an oriented zone surrounding the core, and a skin layer in the cross-section area of the sample. The static sample usually shows skin-core structure as viewed in the cross-section area.

Tensile Testing

An Instron Universal Testing Machine was used to measure the tensile properties under a crosshead speed of 50 mm/min according to the standard of GB/T1040-92, and the temperature was around 25°C. In the mechanical testing, at least five samples were measured and the average values were reported.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed using a DMAQ800 supplied by TA Instruments. The experiments were conducted in a single cantilever mode under nitrogen conditions at a frequency of 1 Hz. The specimens with a dimension of 9.35 mm × 9.8 mm × 4 mm were heated from -80°C to 120°C at a heating rate of 3 K/min. The storage and loss moduli were recorded as a function of temperature.

Two-dimensional Wide-angle X-ray Scattering

The two-dimensional wide-angle X-ray scattering (2d-WAXS) experiments were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromated X-ray from CuK α radiation was 0.154 nm and the transmission mode was used. Before the 2d-WAXS measurement, the injection-molded bars were sliced into three rectangle pieces, namely the skin, oriented zone and core from the outer to the center, which are parallel to the shear flow direction. The samples were placed with the orientation (flow) direction perpendicular to the beam. All of the 2d-WAXS patterns in this article are given with background extraction, which thus allows a qualitative comparison between various samples. Azimuthal scans (0–360°) of 2d-WAXS were made

for the (200) plane of PE at a step of 1° . The orientation degree of crystalline planes could be estimated by calculating the orientation parameter f from the following equation:

$$f = \frac{3\langle \cos^2 \psi \rangle - 1}{2} \quad (1)$$

$$\langle \cos^2 \psi \rangle = \frac{\int_0^{\pi/2} I(\psi) \sin(\psi) \cos^2 \psi d\psi}{\int_0^{\pi/2} I(\psi) \sin \psi d\psi} \quad (2)$$

where ψ is the angle between the normal of a given (hko) crystal plane and the shear flow direction and I is the intensity. The critical values of orientation parameter f , taking $\psi = 0$ as the shear flow direction, are -0.5 for a perfect perpendicular orientation and 1.0 for a perfect parallel orientation. For an isotropic sample, $f = 0$ ^[22].

Differential Scanning Calorimetry

A Perkin Elmer Pyris-I differential scanning calorimeter (DSC) with nitrogen as the purge gas was used to investigate the crystallization behavior of all the prepared samples. The nonisothermal crystallization behavior of the specimens was investigated by melting the samples (about 5 mg) at 200°C for 5 min to erase any thermal history and then cooling them to 30°C at a cooling rate of 10 K/min. After that the specimens were heated again to the melting point at a heating rate of 10 K/min. The melting temperatures (T_m) were determined from the maxima of the fusion peaks. The crystallinity (X_c) of the samples was calculated from the equation $X_c = \Delta H_f / (\phi_i \times \Delta H_i^m)$, where ΔH_f is the enthalpy of fusion of the prepared samples, directly obtained by DSC, and ϕ_i is the mass fraction of HDPE in the blends, ΔH_i^m , the enthalpy of fusion of 100% crystalline polymer, is 293 J/g for HDPE^[23]. For isothermal crystallization, the samples (about 5.0 mg) were first heat-treated to 200°C for 5 min in order to eliminate any thermal history; then, the specimens were cooled at a rate of 100 K/min to the desired crystallization temperature and maintained at that temperature during the whole process of matrix crystallization. The exothermic enthalpy was calculated by integrating area under the exothermic peak with proceeding of crystallization time. Meanwhile, the half-crystallization time, $t_{1/2}$, can be determined when the integrated area of exothermic peak is 1/2 of the total area of exothermic peak.

Scanning Electron Microscopy

The scanning electron microscopy (SEM) was used to investigate the dispersion of mica and the crystal morphology of HDPE in the composites. The crystal morphology of HDPE was studied by preferential etching the amorphous phase in 1% solution of potassium permanganate in a mixture of sulfuric acid: orthophosphoric acid 85:15 (V/V) for 30 min at 60°C ^[24]. The samples were fractured in liquid nitrogen prior to etching. Then the surface was coated with gold and subsequently examined by using a JEOL JSM-5900LV scanning electron microscope with an accelerated voltage of 20 kV.

RESULTS

GPC Analysis of HDPE Resin

Obviously, it is important to identify the molecular weight characters of PE resins used in this study before investigating the effects of matrix molecular weight on structure and reinforcement in the injection-molded bars of polyethylene/mica composites. Some molecular weight parameters of HDPE resin are listed in Table 1 including M_w , M_n and PD, and the relevant GPC spectra are also plotted as Fig. 2 for clarity. The PD becomes broader with increasing M_w , that the PD of HMW-PE is significantly larger than that of MMW-PE, whereas the PD of MMW-PE is slightly larger than that of LMW-PE. Correspondingly, from the GPC spectrum, the obvious low and high Mw tails can be seen for the HMW-PE, while only the low MW tail is distinct for the MMW- and LMW-PE and the mass fraction of the low MW tail is higher in the former. Furthermore, it should be noted that although the differences of absolute value of molecular weight are mild among the three HDPE resins, *i.e.*, the

M_w of HMW-PE is about three times over that of LMW-PE, the differences in PD and low MW tail can dramatically impact the viscous flow property. The melt flow index of HMW-PE is 1.2 g/10min (upon 190°C and 2.16 kg loading), while it is 7.6 and 20.5 g/10min for MMW- and LMW-PE, respectively. This causes obvious alterations in microstructure, crystallization behavior and mechanical performance of injection-molded articles, as ascribed in the following sections.

Table 1. Molecular weight characters of HDPEs used in this study

Brand	M_w	M_n	PD (M_w/M_n)	Type
5000S	3.1×10^5	5.2×10^4	5.9	HMW-PE
8008	2.3×10^5	6.3×10^4	3.6	MMW-PE
2911	1.3×10^5	4.2×10^4	3.2	LMW-PE

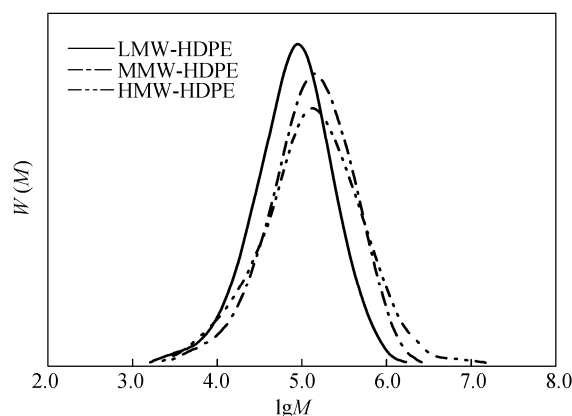


Fig. 2 GPC spectra of HDPE resins

Orientation Structure

The oscillatory shearing exerted by DPIM can cause high orientation structure in the injection-molded bar, which was estimated by 2d-WAXS measurements. The 2d-WAXS patterns shown in Fig. 3 illustrate the orientation situation of orthorhombic PE crystals in the skin, oriented and core zones of dynamic sample and the core zone of static sample of LWM-PE/mica composite. The characteristic reflections of orthorhombic PE crystal are (110) plane, 2θ ca. 21.6° , and (200) plane, 2θ ca. 24° . Meanwhile, the diffused arcs located at 2θ ca. 19.5° are denoted to the contribution of the amorphous chains based on the azimuthal intensity distribution of the halo^[25], and in Fig. 3(d) the weak scattering signals near the beam stop is attributed to the ordered stacking structure of mica layers. For the static sample, two circles corresponded to (110) and (200) planes are observed, indicating a random lamellae orientation. While a tripled-zone structure is formed in the dynamic sample, divided into skin, oriented and core zone. Two intensive diffraction arcs of (110) and (200) planes are focused on the equatorial direction only for the oriented zone of dynamic samples, indicating a highly oriented crystalline structure due to shearing imposed during DPIM process, whereas, the orientation character is weak in the skin and core zones.

Since the orientation feature is most obvious in the oriented zone of dynamic samples, the effect of matrix molecular weight on the orientation of PE crystals is elucidated through the 2d-WAXS patterns for the oriented zones of the dynamic samples with HMW-, MMW- and LMW-PE, as shown in Figs. 4(a) to 4(c), respectively. The corresponding azimuthal scans of (200) plane are also included in Fig. 4(d) for clarity. In our study, the crystalline reflections of the (110) and (200) planes can be only found, whereas the reflection of (002) plane, which is corresponded to the c -orientation directly, is unavailable. However, in an orthorhombic crystal, the (200) plane is parallel to both of the b - and c -axes while the (110) plane parallel to the c -axis only. There has high reliability to estimate the orientation degree using (110) or (200) plane, which has been approved by many previous publications^[26, 27]. So we would like to estimate the orientation degree of PE crystals mainly depended on the azimuthal intensity distribution of the (200) plane. The reflections representing different matrix molecular weights exhibit focused arcs, indicating significant lamellae orientation for all of the dynamic samples.

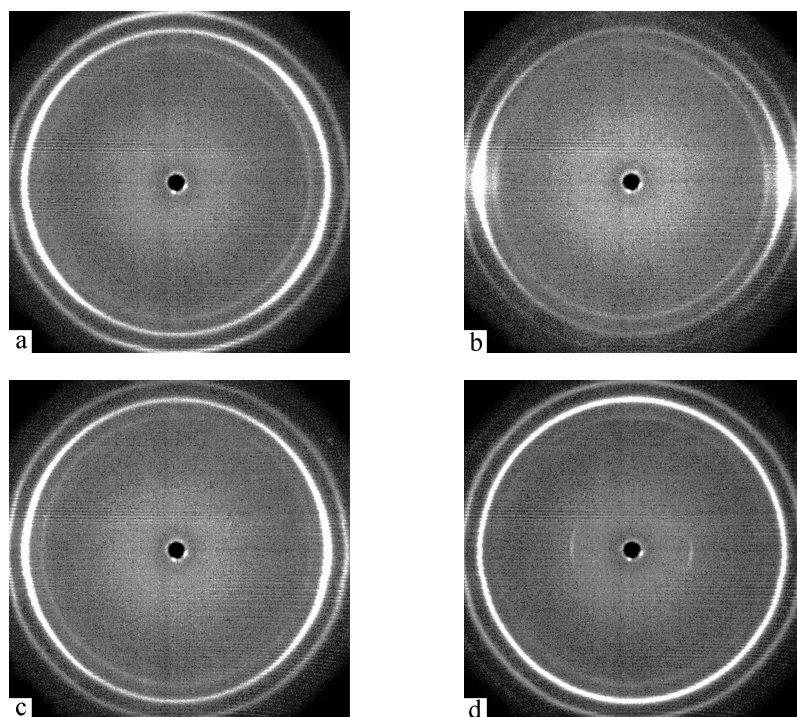


Fig. 3 2D-WAXS patterns of HDPE/mica injection-molding bars at different zones: (a) skin, (b) oriented, (c) core of dynamic sample and (d) core of static sample

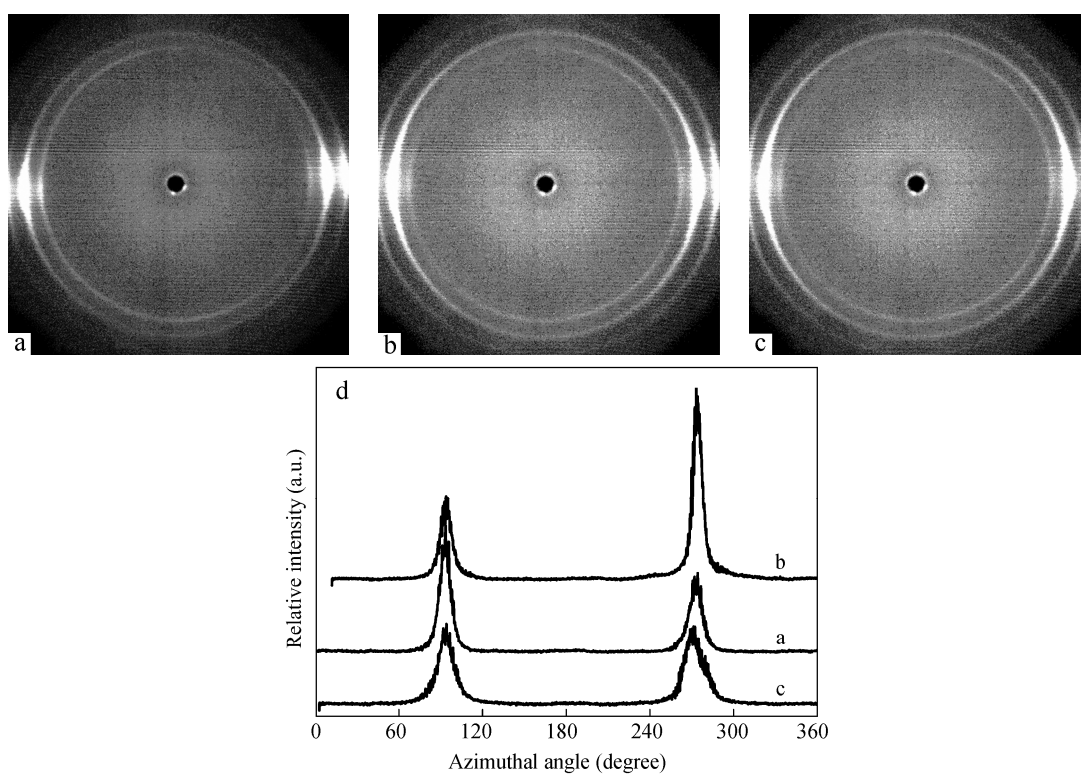


Fig. 4 2D-WAXS patterns of the as-prepared dynamic samples at oriented zone: (a) HMW-PE/mica, (b) MMW-PE/mica, (c) LMW-PE/mica and (d) Azimuthal scans of (200) plane of the three samples

A quantitative estimation of lamellae orientation depending on matrix molecular weight can be achieved through comparing the orientation degrees listed in Table 2. One can find that the addition of mica can induce the highest crystal orientation for HMW-PE matrix with around 0.73, followed by MMW-PE matrix (0.70) and LMW-PE matrix (0.65). It can be envisaged that the relaxation rate of extended chain is slow for HMW-PE, which may be responsible for the highest extent orientation formed in the HMW-PE/mica composite after shearing process.

Table 2. Orientation degree of HDPE in the oriented zone of dynamic samples

Sample	Orientation degree
HMWPE/mica	0.73
MMWPE/mica	0.70
LMWPE/mica	0.65

Microscopic Observation

It is well known that good dispersion and high orientation of inorganic filler in polymer matrix may induce an effective enhancement of property for composites. The oscillatory shearing exerted by DPIM is anticipated to improve dispersion and orientation of mica plates in the injection-molded bars. In this work, SEM was employed to assess the mica dispersion and orientation in HDPE matrix. The SEM micrographs in Fig. 5 represent typical fractured surface of the oriented zone of dynamic molded bars viewed parallel to the flow direction. For all HDPE matrixes, one can observe that most of mica platelets are oriented parallel to the flow direction, indicating no difference of mica orientation state among three matrix molecular weights. However, the dispersion states of mica are not identical for the three PE matrixes. By careful examination, one can find some agglomerations of mica exist in the HMW-PE matrix, whereas thin mica plates with uniform size distribution are observed in the MMW- and LMW-PE, particularly, the size of mica plate in the LMW-PE is the smallest among three composites. This result indicates that LMW-PE can facilitate the high orientation and good dispersion of mica in matrix. Besides, the aggregation and/or ordering stacking of mica platelets can be characterized by WAXS analysis. For the static sample of LMW-PE/mica composite, the mica aggregate causes the reflection at lower 2-theta angle near the beam stopper, as seen in Fig. 3(d). Whereas, no such reflection is found in the dynamic sample of composites (Figs. 3a–3c), indicating DPIM technique induced the exfoliation of mica. Moreover, no reflection of mica aggregate and/or stacking can be found in the oriented zone of dynamic composite for all three HDPE matrixes, as seen in Figs. 4(a)–4(c). From the WAXS analysis, it can be concluded that the effect of matrix molecular weight on exfoliation of mica is weak in the DPIM process.

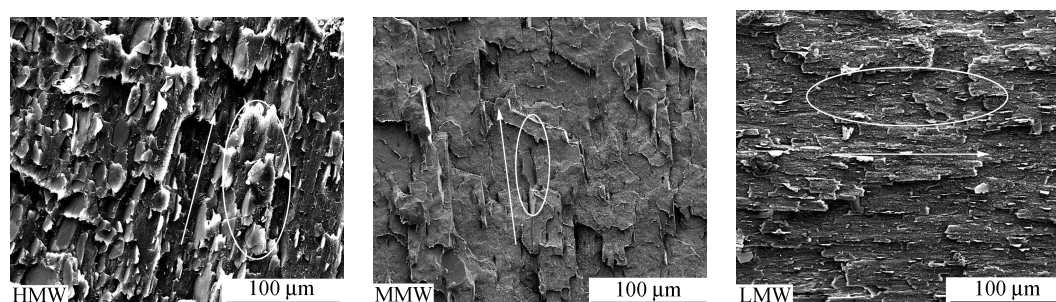


Fig. 5 SEM microphotographs of the oriented zone of dynamic HDPE/mica composites with arrows representing the flow direction

Transcrystallization of HDPE on Mica

Crystal morphology of the injection-molded bar was obtained by etching away the amorphous fraction of PE. The main feature of DPIM PE-sample is preferential orientation of crystalline morphology with PE lamellae aligned perpendicular to the shear flow direction, particularly in the oriented zone. The typical crystalline morphologies of the oriented zone and core zone for various HDPE/mica composites obtained *via* DPIM, are presented in Fig. 6. It seems that the lamellar thickness examined by SEM microscopy is distinctly larger than

the actual thickness of mono-layer lamella. This discrepancy may be derived from the pre-treatment of gold coating before SEM experiments. Importantly, there is an obvious matrix molecular weight dependence of transcrystallization behavior between PE matrix and mica filler. An obvious transcrystallization morphology that many LMW-PE lamellae randomly attached on the surface and cleavage of mica plate is visible in the oriented zone, as shown in the chosen region of Figs. 6(a) and 6(b); otherwise, in the core zone, the transcrystallization morphology disappears but the lamellae keep orientation perpendicular to the flow direction, as shown in Fig. 6(c). Figures 6(d) and 6(e) show the crystal morphologies of dynamic samples of MMW-PE/mica composite. One can find only a few PE lamellae crystallized on mica platelet in the oriented zone, while a spherulitic structure exists in the core zone. However, in the sample with HMW-PE matrix (as shown in Figs. 6f and 6g), there is no transcrystallization between PE lamellae and mica platelet even in the oriented zone; similar to the MMW-PE/mica sample, the oriented structure disappears and PE lamellae align randomly in the core zone. Consequently, it is strongly suggested that lower matrix molecular weight is more favorable for the transcrystallization mechanism.

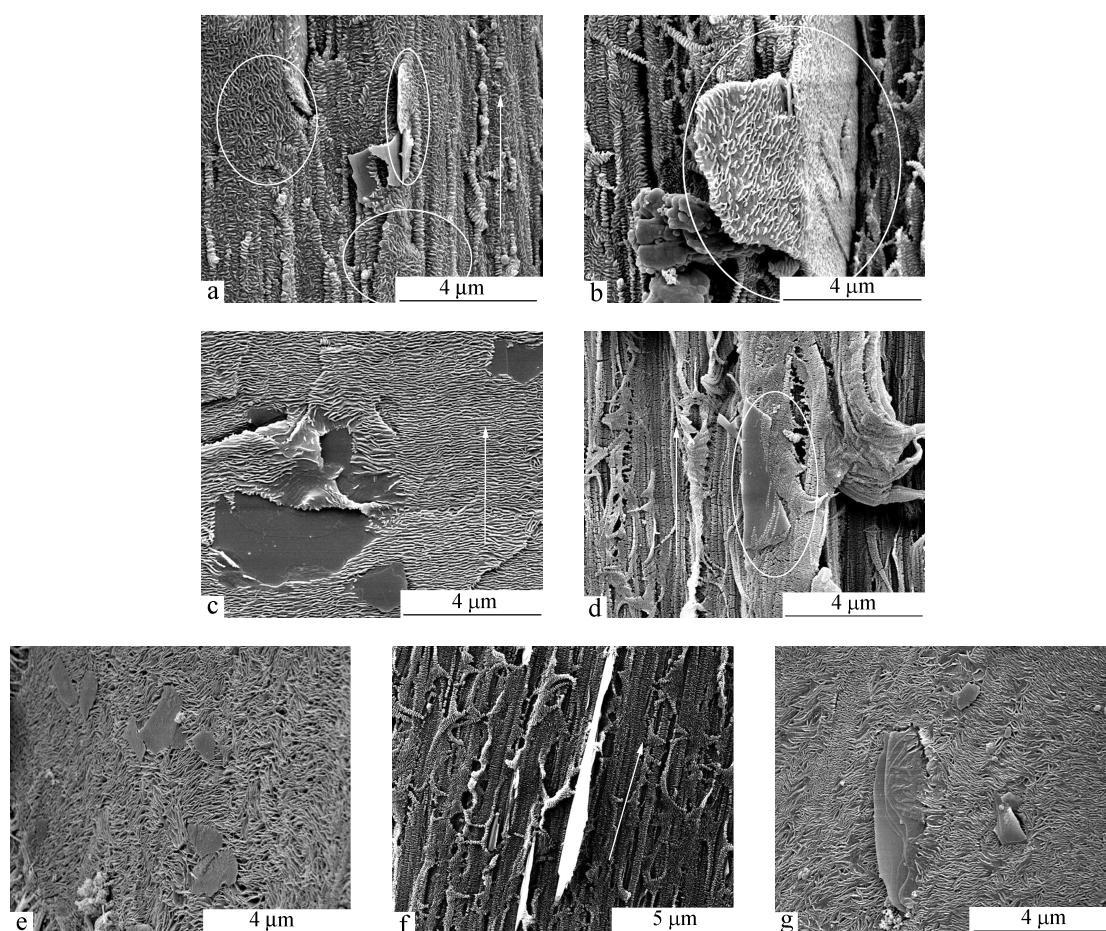


Fig. 6 SEM microphotographs of etched dynamic HDPE/ mica composites with arrows representing the flow direction: (a) and (b) LMW-PE/mica composites, the oriented zone, (c) LMW-PE/mica composites, the core, (d) MMW-PE/mica composite, the oriented zone, (e) MMW-PE/mica composite, the core, (f) HMW-PE/mica composite, the oriented zone and (g) HMW-PE/mica composite, the core

One may argue that the observed phenomenon of PE crystals attached on the surface of mica plate should be related to the epitaxy mechanism. Maybe, a surface of small mica plate will have a nature of single crystal.

Thus, if epitaxial growth occurs, all the crystals will be aligned along the preferred orientation which matches to the substrate (mica). In our case, PE crystals orient randomly on the local surface of mica, which will be approximately a single crystal plane. It is observed that PE single crystal attached on the mica surface occurs obviously only for LMW-PE. LMW-PE chains will have very short relaxation time and crystallization after shear will not be aligned well. Thus the transcrystallization mechanism seems to be reasonable.

Calorimetric Analysis

To understand the effect of PE molecular weight on the crystallization behavior of various HDPE/mica composites, the nonisothermal and isothermal crystallization processes were investigated through DSC. For probing the crystalline behaviors between various samples under the same processing and thermal history, the slices for DSC measurements were all cut from the oriented zone of dynamic bars, and the original crystalline structure was completely erased before crystallization processes. The nonisothermal crystallization curves for the pure HDPEs and the HDPE/mica composites at a cooling rate of 10 K/min are shown in Fig. 7(a). For the pure HDPEs, the crystallization temperature, T_c , of MMW-PE and LMW-PE is higher than that of HMW-PE. Meanwhile, the changes of T_c induced by addition of mica are different among the three HDPE matrixes. A detectable decrease of T_c is found for HMW-PE, while it is unchanged for MMW-PE and increased for LMW-PE. This phenomenon means that the heterogeneous nucleation ability of mica is weak for all the HDPEs used in our study. The corresponding heating curves are plotted in Fig. 7(b). The melt point, T_m , in the specimens containing MMW-PE is somewhat lower than that in the other two types of specimen. On the other hand, adding mica cannot alter T_m for all HDPE matrixes. The detail values of T_c and T_m for the composites and pure HDPEs are listed in Table 3. Moreover, one can find the values of crystallinity, X_c , in the same table. The alteration of X_c induced by adding mica is more obvious than that of T_c and T_m , and is prominently dependent on PE molecular weight. One can observe a constant crystallinity (about 56%) for the pure HMW-PE and HMW-PE/mica composites. However, for MMW-PE and LMW-PE, the crystallinity has a detectable increase, especially in the LMW-PE/mica composite, having an increase of 15% comparing with the pure LMW-PE.

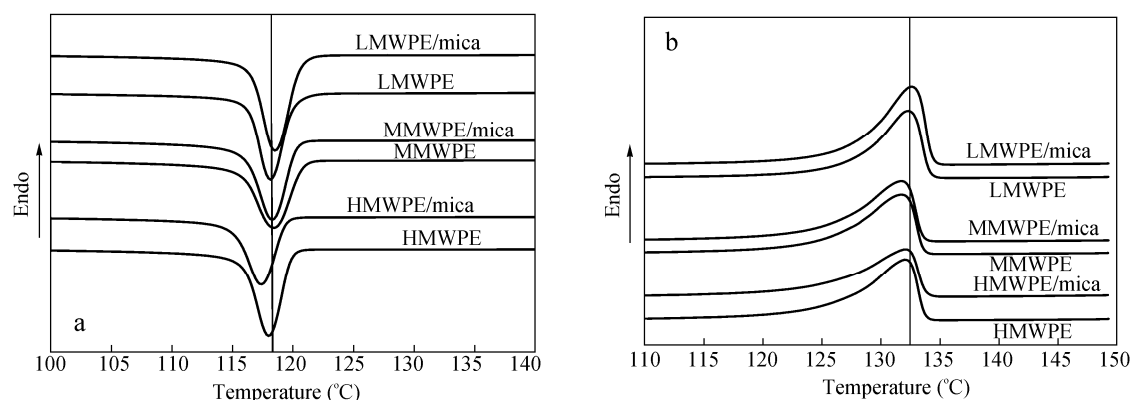


Fig. 7 DSC nonisothermal crystallization curves (a) and corresponding melting curves (b) of pure HDPE and HDPE/mica composites

Table 3. Nonisothermal crystallization and melting data of the prepared samples

	T_c (°C)	T_m (°C)	X_c (%)
HMWPE	117.9	132.0	57.7
HMWPE/mica	117.3	132.4	55.8
MMWPE	118.3	131.9	57.5
MMWPE/mica	118.2	131.8	60.4
LMWPE	118.1	132.6	59.7
LMWPE/mica	118.6	132.8	68.4

T_c , crystallization peak temperature; T_m , melting peak temperature; X_c , wt% crystallinity of HDPEs

Mechanical Reinforcement

In this section, the mechanical properties are measured for the injection-molded bars through DMA and tensile testing. The effect of matrix molecular weight on storage modulus and loss modulus versus temperature is manifested in Fig. 8, and all the measured samples are the DPIM bars of HDPE/mica composites. As a common anticipation, higher molecular weight matrix should result in better mechanical modulus. But an unexpected PE molecular weight dependence of dynamic mechanical properties is achieved for these highly oriented injection-molded bars of composites. For both of storage modulus and loss modulus, the LMW-PE/mica composite possesses the highest property values among the three composites, while the HMW-PE/mica composite and MMW-PE/mica composite have the lowest value and the middle value of modulus, respectively. It should be noted that, in the loss modulus versus temperature spectrum of Fig. 8(b), the β -transition peak (glass transition, -15°C) of PE amorphous chains is very weak for the LMW-PE/mica composite. This phenomenon may be due to strong geometric confinement of mica plates on the relaxation and motion of PE molecular chains. As already demonstrated in the previous work^[28], the mica stacks can be delaminated into thin flakes and oriented along the flow direction, meanwhile the matrix chains intercalate into the galleries between mica plates under shear, and thus the mica platelets can restrict the movement of molecules and result in the increase of damping force for the motion of molecules, and make the polymer chains become much stiffer. This result approves indirectly a better interaction exists between mica plates and LMW-PE matrix.

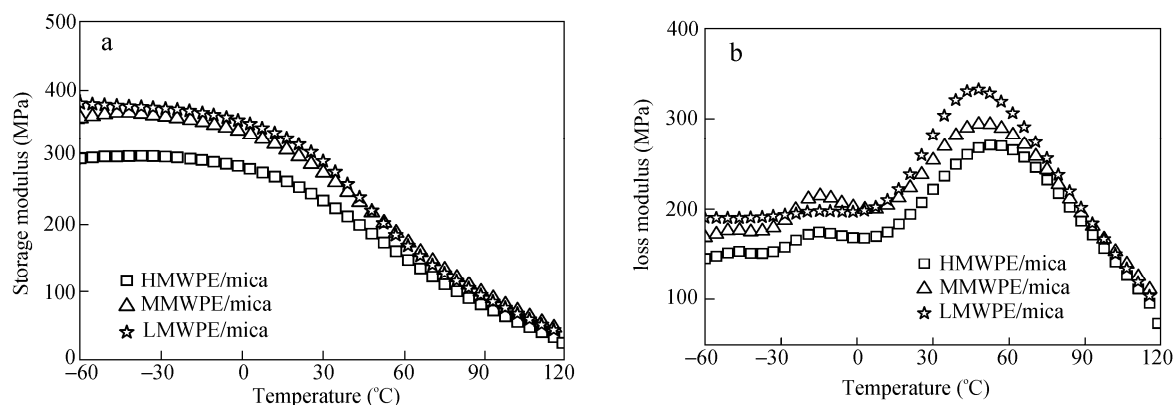


Fig. 8 DMA results of LMW-PE/mica, MMW-PE/mica and HMW-PE/mica composites: (a) the storage modulus-temperature curves, (b) the loss modulus-temperature curves

Some typical stress-strain curves for various pure HDPEs and composites are plotted in Figs. 9(a) and 9(b) for static samples and dynamic samples, respectively. The corresponding values of tensile strength and modulus, which were extracted from the stress-strain curves, are listed in Tables 4 and 5. It is unexpected that in some cases the absolute values of mechanical strength are not accordant with sequence of matrix molecular weight. For example, the tensile strength of the static LMW-PE is higher than that of the static MMW-PE and HMW-PE. This may be due to the wider PD in MMW-PE and HMW-PE. It can be envisaged that the low molecular tails with a relative high mass fraction in MMW-PE and HMW-PE can weaken mechanical strength efficiently. As to the case of composites, for both of static and dynamic samples, the MMW-PE composite has a highest tensile strength. Obviously, to estimate the mechanical strength of composites, one should not merely consider the matrix molecular features (M_w and PD), other factors including filler dispersion, interaction between matrix and filler, orientation structure, crystallinity, etc., might also play important role. A clear demonstration about the absolute value of mechanical strength needs a complicated analysis taking into account so many factors. However, our major purpose in this study is to estimate the mechanical reinforcement efficiency of adding mica into different HDPE matrixes. To realize this purpose in a simple manner, we would like to adopt the increase ratio, defined as $(V_{\text{composite}} - V_{\text{HDPE}})/V_{\text{HDPE}}$, to evaluate the mechanical reinforcement of adding mica in three types of composite.

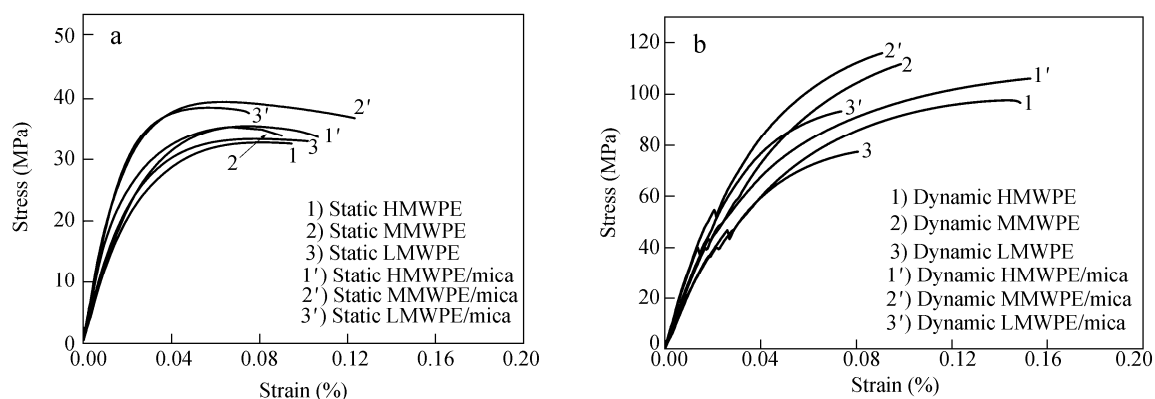


Fig. 9 Typical stress-strain curves for various pure HDPEs and composites: (a) and (b) for static samples and dynamic samples, respectively

Table 4. Tensile strength of injection-molded bars

	Tensile strength (MPa)		Increase ratio (%)	
	Dynamic	Static	Dynamic	Static
HMWPE	97.4	31.6		
HMWPE/mica	106.1	35.5	9.0	12.4
MMWPE	105.8	31.4		
MMWPE/mica	116.2	39.5	9.6	25.9
LMWPE	70.4	32.3		
LMWPE/mica	93.3	38.6	32.5	19.4

Table 5. Tensile modulus of injection-molded bars

	Tensile modulus (MPa)		Increase ratio (%)	
	Dynamic	Static	Dynamic	Static
HMWPE	2192.9	1110.1		
HMWPE/mica	2682.1	1842.8	22.3	66.0
MMWPE	2261.7	1198.0		
MMWPE/mica	3424.4	2035.9	51.4	69.9
LMWPE	1821.9	1347.2		
LMWPE/mica	3466.0	2033.2	90.2	50.9

Similar to the result of DMA, more obvious reinforcement in tensile properties is found on the composite with LWM-PE, which is estimated quantitatively as follows. For the static samples, the tensile strength shows a slight increase with addition of mica. The increase ratio is 19.4% in the samples with LMW-PE matrix, and the tensile strength increases by 25.9% in the samples with MMW-PE matrix, while the value of increase ratio decreases to 12.4% for the samples with HMW-PE matrix. As for the dynamic samples, however, an obvious increase in tensile strength is seen, compared with the corresponding static ones. The increase ratio of the tensile strength is 9% in the samples of HMW-PE/mica composite; the value promotes to 9.6% in the samples containing MMW-PE compared with the pure MMW-PE; furthermore comparing the pure LMW-PE, the value of increase ratio is elevated to 32.5% in the samples with LMW-PE. Obviously, the dynamic sample of LMW-PE/mica composite has the highest increase ratio. The varying trend of tensile modulus between various samples is similar to the case of tensile strength. The LMW-PE/mica composite has the highest increase ratio both for the dynamic and static samples. Especially, for the dynamic sample, the increase ratio of tensile modulus reaches 90.2%. On the contrary, in the samples of MMW-PE/mica and HMW-PE/mica composites, the increase ratio of static bars is higher than that of dynamic bars. So according to tensile testing and dynamic mechanical analysis, a better enhancement in mechanical properties is available for the composite with LMW-PE.

DISCUSSION

Structure-Property Relation of HDPE/Mica Composites

The relation of structure and property enhancement is first discussed for the HDPE/mica composites with different PE molecular weights. In this work, mechanical reinforcement is dependent on matrix molecular weight for that: significant property improvement is achieved for the composites with LWM-PE and MMW-PE matrix, whereas promotion of property for the composite with HMW-PE is limited. Based on the 2d-WAXS results as listed in Table 2, mica can induce the highest crystalline orientation of HMW-PE matrix with the orientation parameter around 0.97, which suggested an effective reinforcement effect should appear in the HMW-PE/mica composite. However, the effects of dispersion of mica filler and crystallinity obey a sequence of LWM-PE > MMW-PE > HMW-PE, particularly, the fine transcrystallization structure is found in the composite with LMW-PE matrix, whereas such crystalline structure is almost absent in the composites with MMW-PE and HMW-PE. Transcrystallization can extremely improve interfacial adhesion between PE matrix and mica filler, thus leads to the best reinforcement efficiency in the LWM-PE composite.

Matrix Molecular Weight Dependence of Transcrystallization

The structural feature in the LMW-PE/mica composite differed dramatically to that in the MMW-PE/mica and HMW-PE/mica composites is the transcrystallization behavior. Subsequently, the matrix molecular weight dependence of transcrystallization will be highlighted. Crystallization capability varied with PE molecular weight is manifested in Fig. 10, in which the half-crystallization time, $t_{1/2}$ (defined as the time required to reach 50% of the complete crystallization), is plotted versus crystallization temperature for various pure HDPEs and composites. An interesting phenomenon is that the crystallization rate decreases ($t_{1/2}$ increases) with the addition of 10 wt% mica for HMW-PE and MMW-PE, but increases ($t_{1/2}$ decreases) with addition of mica for LMW-PE, meaning the crystalline property of the composite with LMW-PE matrix is quite different to that of the composites with HMW- and MMW-PE, and incorporation of mica can only accelerate the crystallization rate of LMW-PE, namely, LMW-PE possesses high crystallization capability in the composite. Moreover, from a detail observation of transcrystallization in Fig. 6(b), PE lamellae randomly align on surface of mica platelet with weak preferential orientation character. This phenomenon implies the molecular chains that can crystallize on mica should have high mobility to easily diffuse and align into mica lattice in various directions. So molecular chain mobility and crystallization capability dominate that fine transcrystallization structure existed in the composite with LMW-PE matrix.

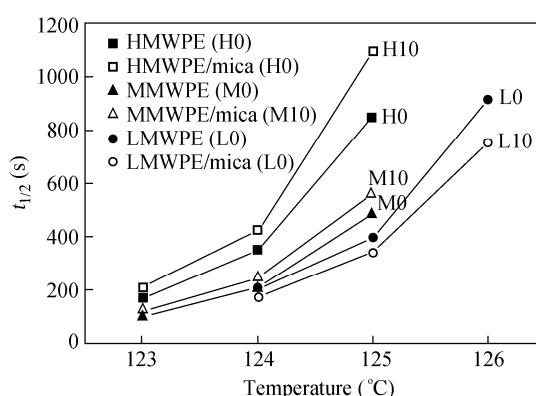


Fig. 10 Half-crystallization time ($t_{1/2}$) versus crystallization temperature curves

CONCLUSIONS

By combination of SEM, 2d-WAXS, DSC, DMA measurements and tensile testing, the matrix molecular weight dependence of the structure-property relation for the injection-molded bars of HDPE/mica composites obtained

via DPIM has been demonstrated in detail. For all three HDPE matrixes, the orientation situation of mica particles and lamellar thickness of PE are almost identical. The highest orientation extent of PE matrix is for the composite with HMW-PE. However, a better dispersion of mica and higher crystallinity are observed for the composite with relatively low molecular weight PE. Particularly, transcrystal growth between PE matrix and mica filler is observed under effect of shear, and strongly dependent on matrix molecular weight. A fine transcrystallization structure with many PE lamellae densely and randomly attached on the surface of mica has been detected for the composite with LMW-PE matrix; a few loose PE lamellae crystallized on mica platelet is found for the composite with MMW-PE matrix; whereas, there is no transcrystallization between PE lamellae and mica filler for the composite with HMW-PE matrix. More obvious reinforcement in mechanical properties is available for the composite with lower matrix molecular weight. Obviously, the unusual reinforcement effect is mainly dominated by transcrystallization between matrix and mica filler, which is extremely distinct in the composite with LMW-PE matrix.

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