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Studies on the morphology and the thermal properties of high-density polyethylene filled with graphite

QIQIONG DONG, QIANG ZHENG*
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: zhengqiang@zju.edu.cn

MINGQIU ZHANG
Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China

Incorporation of graphite (GP) particles into polymer matrix may offer composites a great quantity of advantages over pure polymer systems, such as increased strength [1–3], enhanced electrical and thermal conductivity [1–4]. Hence, increasing academic and applied interests have been devoted to developing polymer/GP composites for their important applications in which electrical or/and thermal conductivity is needed to be involved.

Our previous work [5, 6] mainly dealt with the rheological properties of high-density polyethylene (HDPE)/GP, for dynamic rheological measurement is a preferred method of characterizing the morphology of materials [7]. In this paper, we pay our attention to the morphology and thermal signature of those composites in order to explore the relationship between the phase morphology and the macro-properties.

Three kinds of GP (HuaDong Graphite Processing Factory, China) with density of 2250 kg/m^3 were used as fillers (GP-1 and GP-2 are disk-shaped particles with volume mean diameter of 6 and 130 μm, respectively; GP-3 is spherical particle with mean diameter of 12 μm). HDPE (H005239 0430A, Samsung General Chemicals Co., LTD., Korea) with density of 970 kg/m^3 was used as the matrix. After GP was pretreated by the silicane-coupling agent (SCA, SCA/GP = 3 wt.%) and antioxidant 1010 (with 0.2 wt.% of HDPE) was added to HDPE, composites of HDPE/GP were prepared by using a Hakke Rheomix at 175 °C for 10 min.

Scanning electron microscopy (JSM-5510LV SEM, JEOL., Japan) was used to observe the polished fracture surface after specimens were broken in the liquid nitrogen. The influence of the filler on the thermal characteristics of the polymer composites, such as the melting and crystallization temperatures (T_m and T_c, respectively), enthalpy of crystallization (ΔH_c) of HDPE, were measured by differential scanning calorimetry (DSC-7, Perkin Elmer, USA) within the temperature range from 60–160 °C at heating and cooling rates of 10 °C/min.

The rheological properties of HDPE/GP composites obtained by our previous studies [5, 6], as shown in Fig. 1, indicate that the deviation of viscoelasticity for composites from that of matrix increases with increasing filler concentration (Φ) and plateaus of the dynamic storage modulus (G') at low frequencies (ωs) occur in high-loaded systems [8, 9]. This phenomenon is referred to as "*pseudo solid-like*" behavior and is believed to be a result of the particle percolated network structure. The threshold (Φ_c) obtained for rheological percolation at 160 °C is 14 vol% [5], which is beyond the scope of present study of the morphology and thermal properties. Considering the significant thermal expansion of matrix and the inert and relatively incompressible filler, the true value of Φ_c corresponding to percolated structure is certainly less than 14 vol%.

Fig. 2 gives SEM photographs of polished surface for the composites with different filler loading. The GP-1 particles appearing as the bright sheets dispersed in the dark HDPE background are identified to be uniformly and anisotropically distributed. Cross-sectional images in Fig. 2b–d also show some evidence of a preferred orientation of GP-1 sheets. The planes of lamellar sheets are in some degree parallel to each other and perpendicular to the fracture surface.

Virgin HDPE system appears much smoother fracture surface than that of the composites. The higher the filler loading, the rougher the fracture surface. As for the composites with low filler loading ($\Phi = 5$ vol%), as shown in Fig. 2b, GP-1 sheets disperse separately in the matrix; while for those with high filler loading ($\Phi = 16, 22$ vol%), the distance between the adjacent particles decreases and there appear some particles packing together. It can be seen in Fig. 2b and c that the interface region between the particles and the matrix becomes vague, and it is difficult to separate particles from the matrix. Obviously, the

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* Author to whom all correspondence should be addressed.

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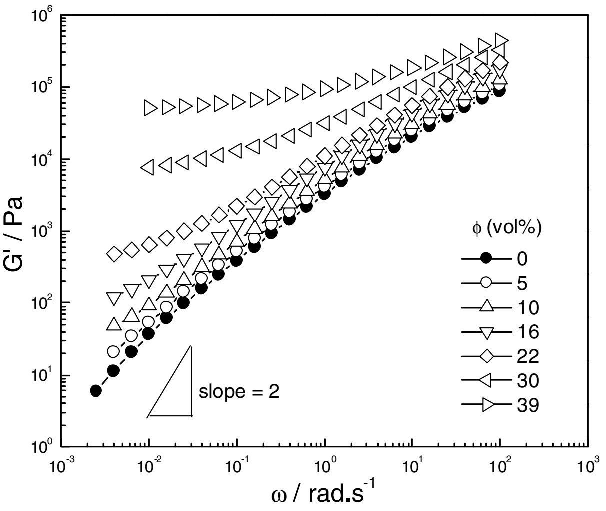

Figure 1 Dynamic storage modulus G' as functions of frequency ω at 160 °C for HDPE filled GP-1 of various concentration Φ (vol%) [5].

TABLE I Thermal properties of HDPE/GP composites (obtained from DSC performed at heating and cooling rates of 10 °C/min)

Samples (vol%)	T_c (°C)	T_m (°C)	T_h (°C)	ΔH_c (J/g)	χ_c (%)
HDPE	117.8	130.6		201	82
HDPE/GP-1–5	119.6	133.2		138	63
HDPE/GP-1–16	120.5	130.7	128.5	143	83
HDPE/GP-1–50	121.9	129.6	128.4	43	58
HDPE/GP-2–50	121.3	129.2	128.7	57	77
HDPE/GP-3–50	121.1	129.7	128.5	61	83

percolated network structures form in those two composites, which is agree with Φ_c of the rheological percolation obtained in our previous work [5, 6].

Fig. 3 and Table I reveal the cooling DSC scan of samples and the thermal signatures obtained from DSC measurements, respectively. It should be noted that no heat effect appears for GP in the temperature range measured, as shown in Fig. 4. A remarkable exothermic peak appears in the scan of virgin HDPE, centered at 118 °C, with an exothermic heat flow of $\Delta H_c = 201$ J/g, which is attributed to the crystallization of HDPE. Moreover, the transition temperature of virgin HDPE is quite low, as compared with the composites filled with GP. The values of T_c for the composites, as determined by the onset of exothermic peak in DSC curves, increase with the increasing GP loading. Meanwhile, the crystallization peak of the sample also broadened significantly. The particle-dependence of T_c also lies in the variation of T_c with particle kinds.

When the filler loading is constant, the disk-shaped particles dispersed system as shown in Fig. 3 and Table I has a higher T_c, as compared with the spherical particles dispersed system. On the basis of the comparison of T_c for HDPE/GP-1 and HDPE/GP-2 composites with $\Phi = 50$ vol%, it is found that composite with smaller dispersed particles also has a higher T_c. In the process of

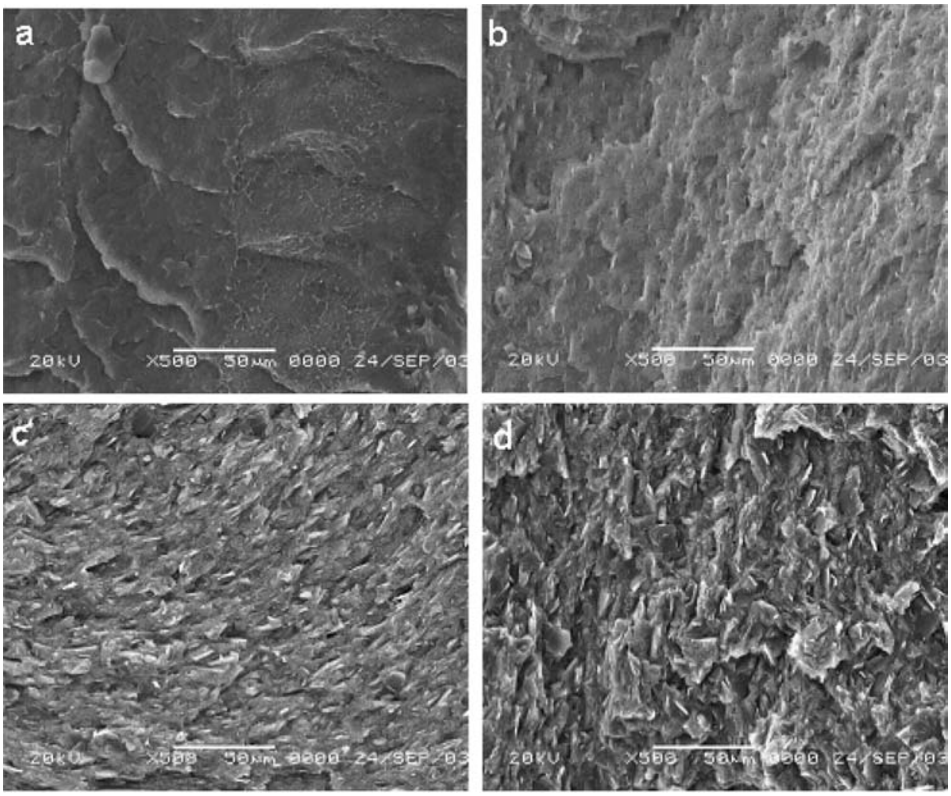

Figure 2 SEM photographs of HDPE and HDPE/GP-1 composites. (a) HDPE; (b–d) HDPE/GP-1 composites (filler contents are 5, 16, and 22 vol%, respectively).

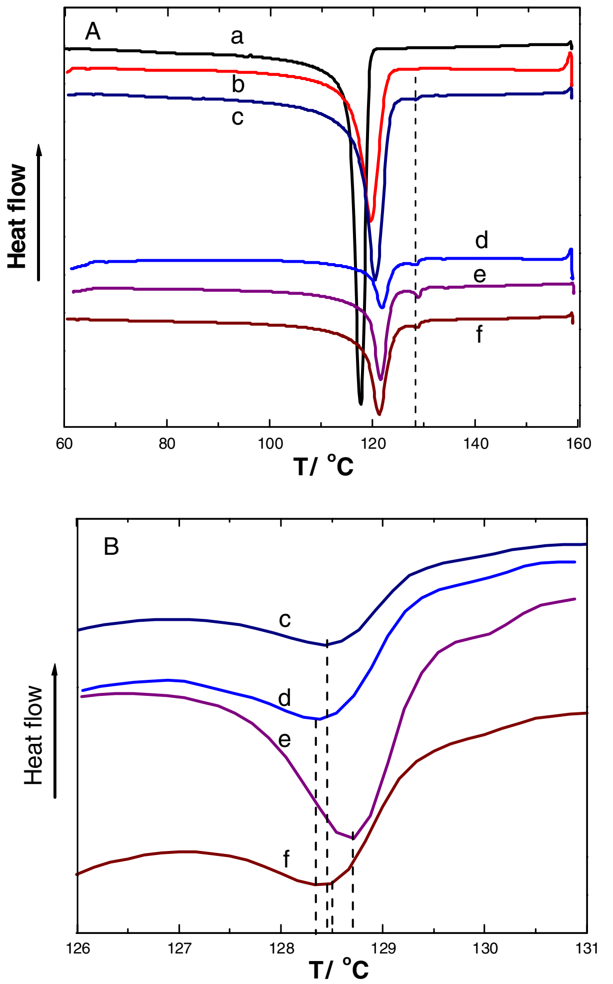

Figure 3 The effect of filler loading on the DSC curves measured from 60 to 160 °C at a cooling rate of 10 °C/min (B) Zoom of a region of (A). (a) HDPE; (b) HDPE/GP-1, 5 vol%; (c) HDPE/GP-1, 16 vol%; (d) HDPE/GP-1, 50 vol%; (e) HDPE/GP-2, 50 vol%; (f) HDPE/GP-3, 50 vol%.

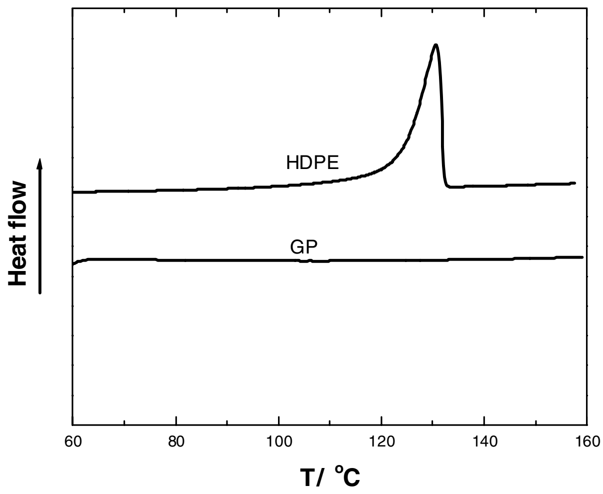

Figure 4 The DSC curves of HDPE and GP measured at a temperature range from 60 to 160 °C at a heating rate of 10 °C/min.

crystallization which takes place during cooling of a molten polymer, a dispersed nucleating additive (such as carbon black, GP, etc.) becomes a nucleation centre leading to crystal growth [10, 11]. As a result of the heterogeneous nucleation, the crystallization temperature T_{c} increases. T_{c} for HDPE/GP composites is consistently several degrees higher than that of the neat polymer system, which strongly suggests that GP particles act as heterogeneous nucleation sites for HDPE crystals. Based on the data of T_{c}, we can draw a conclusion that the polymer matrix in composites containing smaller and disk-shaped particles crystallize earlier (at a higher temperature) during cooling of the molten sample.

On the other hand, T_{m} is also virtually dependent on the filler parameters. T_{m} first increases with Φ to some degree and then decreases. The T_{m} of high-loaded composites is even lower than that of virgin HDPE.

It is interesting that for composites with $\Phi > \Phi_{c}$, there exists an extra and unexpected little exothermic peak (T_{h}) as shown in Fig. 3. And T_{h} is very closed to T_{m}, and 8°C higher than T_{c},. Such phenomenon indicates that the sufficient addition of GP particles can alter the thermal properties of the polymer matrix, which disagrees with the results of composites consisting of HDPE with mixtures of GP and carbon fiber [3, 12]. It is also difficult to interpret it according to the heterogeneous nucleation induced by filler, for the fact that composite with $\Phi = 5$ vol% ($<\Phi_{c}$) does not have such extra exothermic peak.

Though we can not give thorough interpretation for the extra exothermic peak centered at T_{h}, we attempt to present a probable reason for such phenomenon that such extra exothermic peak could be attributed to increased particle agglomeration during the cooling process and the surface inactivity of GP. More and more particles aggregate accompanied by the shrink of HDPE during the cooling process. Due to the inert of GP and the aggregation of particles, the polymer-filler interface decreases. We proposed that such decrease of interface should be accompanied by the weak exothermic reaction, resulting in the appearance of the extra exothermic peak centered at T_{h}. Hence, it is suggested that the main reason for the appearance of T_{h} is the particle aggregation and the heat change accompanied by the decrease of interface area between particle and matrix.

Finally, we discuss the crystallization of the HDPE in all these systems. The crystallinity (χ_{c}) of HDPE as given in Table I is ascertained by Equation (1):

$$\chi_{c} = \frac{\Delta H_{c}}{W_{\mathrm{HDPE}} \times \Delta H_{c}^{\circ}} \tag{1}$$

in which ΔH_{c}° is the enthalpy of crystallization of a 100% crystalline polyethylene (245.3 J/g) [13] and W_{HDPE} is the weight fraction of HDPE component.

It is found that similarly to T_{m}, the change of χ_{c} with filler parameters is also not monotonous. According to the data as listed in Table I, it seems that both insufficient and extra amount of filler lead to the decrease of χ_{c}. The effect of the filler geometrical parameters on the χ_{c} is converse to that on the T_c. The reason is believed to be that morphological reorganization depends upon the mobility of polymer chains which can be largely hindered by the particle aggregation [5, 8]. The formation of particle aggregates depends on the probability of particle contact which is controlled by particle parameters, such as size, shape, and filler content, etc. [5]. The smaller and disk-shaped particles are easier to contact each other and form aggregates, leading to smaller χ_c for particles dispersed composites.

In this paper, we have provided three simple methods (rheological, micrographic, and thermal methods) to characterize the evolution of the material morphology/structure and the properties of composites. We have found that the dispersion of filler particles alters the morphology/structure of the composites and results in the changes of properties of the polymer matrix, especially when the particle percolated structure is formed. We have concluded that the results obtained by three methods are effective for characterizing particles filled composites.

Acknowledgments

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