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Melt flow properties of polypropylene/EPDM/glass bead ternary composites

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The flow properties of polypropylene(PP)/ethylene-propylene-diene monomer copolymer(EPDM)/glass bead (GB) ternary composites were measured in a wide scope of shear rates by using a Rosand capillary rheometer. The apparent shear rates varied from 10 to 10^5 s^{-1}, and the test temperature was from 210 to 240°C. The results showed that the flow behavior of the composite melts may be considered to approximate that of a power law fluid although the slope of the melt flow curves somewhat varied around shear rate of 700 s^{-1}. The dependence of the melt shear viscosity on the test temperature was roughtly consistent with the Arrhenius expression. The melt shear viscosity increased dramatically with increasing the volume fraction (ϕ_g) of GB under lower shear rate level, white it increased gently with an addition of ϕ_g under higher shear rate level. Furthermore, there were certain effects of the filler surface treatment on the melt shear viscosity and its sentivity to the filler content at higher concentration of the beads at lower shear rates.

1. Introduction

The stiffness, impact toughness and thermal properties of polymers can be improved in some extent, but the tensile strength or fracture elongation may be drop down when they are filled with rigid inorganic particles (RIPs), such as calcium carbonate ($CaCO_3$), talc, mica, etc. In order to increase or improve further the toughness of polymer/RIP composites, they are usually filled with elastomer as a toughness promotor [1]. Because glass bead (GB) has smooth and spherical surface, the effects of the beads on the processing properties and the product surface quality of the composites should be relatively insignificant, and the internal stress in the product can be reduced if they are used as a kind of filler [2].

Polypropylene (PP) is extensively used in automobile and electronic applications. However, its application is somewhat limited due to its high shrinkage rate, and relatively poor impact resistance at room or low temperatures. To improve its toughness and dimensional stability, PP filled with RIP is widely used in industry. There have been a number of studies on the mechanical properties of particulate filled PP composites [2–8]. However, it is necessary to know how do the fillers affect the processability of the composites. Melt shear viscosity is an important characteristic of the processing properties of polymeric materials. It has, therefore, received extensive attention in the past two decades. Most of these previous works have focused on measuring the melt shear viscosity under the conditions of low shear rates [9–11]. Lepez *et al.* [12] carried out thermorheological analysis of glass bead-filled high-density polyethylene (HDPE) and polystyrene (PS) melts within a frequency range from 10^{-2} to 10^3 s^{-1} by means of a parallel plate rheometry, and proposed a new empirical model to predict the complex viscosity of these filled-systems. Ou *et al.* [13] also used a parallel plate rheometry to investigate the effects of interfacial adhesion on the microdamage and rheological behaviour of glass bead-filled nylon 6 melt at shear rate limits of 10^{-1} to 10^2 s^{-1}. The results showed that the interfacial strength affected the rheological behaviour of the melt significantly. In addition, the melt shear viscosity of nylon/treated glass bead-filled system was obviously higher than that of the unfilled nylon and nylon/raw glass bead system at lower shear rates. In the previous work, Liang and Li [14] investigated the influence of glass bead content and extrusion conditions on the melt flow properties of glass bead-filled low-density polyethylene (LDPE) composites by using a capillary rheometer, and found that the filler effect was insignificant. It may be attributable to the relatively weak polymer-particle adhesion or interaction of these composites that the flow resistance does not increase obviously like other inorganic rigid fillers, especially at high shear rates, leading to improvement in flow properties owing to the shear-thinning effect of polymer melts.

Injection moulding and extrusion are conducted at higher flow rates for most polymer materials processing. The objectives of this work are to investigate the effects of temperatures, the filler content and its surface treatment on the melt flow behaviour of glass bead-filled PP/ethylene-propylene-diene monomer copolymer (EPDM) composites in a wide range of extrusion flow rates.

2. Experimental

2.1. Raw materials

A polypropylene with trademark of Pro-fax 6331 supplied by Himont Inc. was used as the matrix resin in this test. This is a homopolymer resin and the density in solid state and the melt flow rate (2.16 kg, 230°C) of the resin were 900 kg/m^3 and 12 g (10 min)$^{-1}$, respectively.

The fillers used in this work included two kinds of A-glass beads and an ethylene-polypropylene-diene monometer copolymer (EPDM). Glass beads were fine solid spheres with trademark of Spheriglass®, supplied by Potters Indust. Inc. in USA. One was pretreated by the supplier with silane coupling agent (CP-03) named GB, the other was raw particles named GBu. The mean diameter and density of the GB were 35 μm and 2.5 g cm^{-3}, respectively. The EPDM (Nordel® 2470) was a semi-crystalline grade hydrocarbon rubber supplied by Du Pont Company. The density (22°C) and Mooney viscosity ($ML_{2+10}^{125^\circ\mathrm{C}}$) were 870 kg/m^3 and 68 ± 5 respectively. The elastomer grafted by maleic anhydride (MA) and dicumyl peroxide (DCP) was called EPDM-MA.

2.2. Preparation of materials

All fillers and the PP pellets were compounded by a twin-screw extruder (Brabender, Plasticorder PL 2000) in a range of temperature from 180 to 230°C and screw speed about 15 rpm to produce the composites after they were mixed simply. The length-diameter ratios of the screw and the head die were 42/7 and 8/1, respectively. The volume fraction of the glass beads were varied from 0 to 30%, and the volume fraction of either EPDM or EPDM-MA particles was fixed as 10%. The resin and fillers were weighed with weight fraction in experiments to sure the target compositions were achieved in practice. The relationship between volume fraction (ϕ_f) and weight fraction (w_f) may be determined by following expression [15]:

$$w_\mathrm{f} = \frac{\phi_\mathrm{f}\rho_\mathrm{f}}{\rho_\mathrm{c}} \tag{1}$$

where ρ_f is the filler density, and ρ_c is the average density of the composite.

2.3. Instrument and methodology

The melt flow properties of the composites were measured by means of a Rosand rheometer. This is a constant rate type of capillary rheometer with two bores whose diameter was 15 mm, supplied by Rosand Precision Ltd. A short die ($L/D \approx 0$) and a long die ($L/D = 16$) were used, and the diameter was 1 mm. They were respectively installed at the two reservoirs in order to make the entry correction automatically. In this case, the shear stress at the die wall (τ_w) is given by:

$$\tau_\mathrm{w} = \frac{(\Delta P_\mathrm{L} - \Delta P_\mathrm{S})D}{4L} \tag{2}$$

where ΔP_L and ΔP_S are the pressure drops of the long die and short die respectively. D and L are the diameter and length of the long die.

The tests were conducted over a temperature range of 180–230°C and a piston speed (V) range of 5–240 mm/min. In this work, the corresponding apparent shear rate can be determined by:

$$\dot{\gamma}_\mathrm{a} = \frac{2\beta^2 V}{15D} \tag{3}$$

where β is the channel contraction ratio of the reservoir and die. $\beta = D_\mathrm{R}/D$, D_R and D are the diameter of the reservoir and the capillary die, respectively.

3. Results and discussion

3.1. Flow curves

Fig. 1 shows the apparent shear flow curves (i.e., shear stresses versus apparent shear rates) of PP/EPDM/GBu system at 190°C. It can be seen that the slope of the flow curves changes when apparent shear rate is around 700 s^{-1}. In addition, the shear stress is a linear function of shear rate either in low shear rate region (100–700 s^{-1}) or in high shear rate region (700–10^5 s^{-1}). This suggests that the shear flow of the sample melts obey approximately the power law.

It can also be seen in Fig. 1 that the slope of the flow curves in low shear rate region is higher than that in high shear rate region. This indicates that there is some difference in the melt non-Newtonian property in high/low shear rate zones. Namely, the non-Newtonian property of the sample melts at high flow rate is more obvious than that at low flow rate. Furthermore, τ_w increases with an addition of the volume fraction (ϕ_g) of the beads, and the increase of it reduces with an increase of shear rate, meaning the flow resistance increases somewhat with an addition of the filler concentration

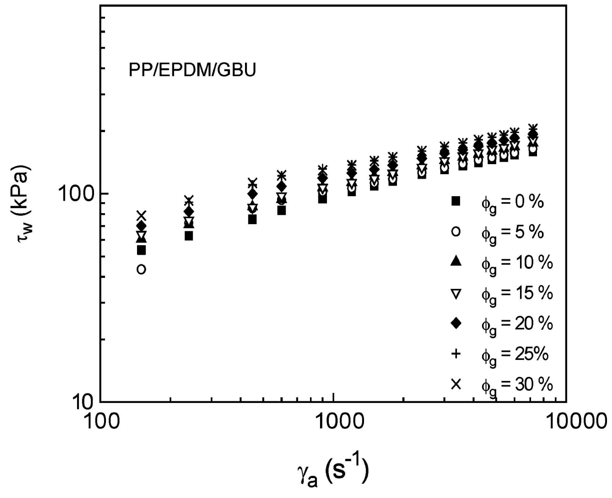

Figure 1 Flow curves of samples (190°C).

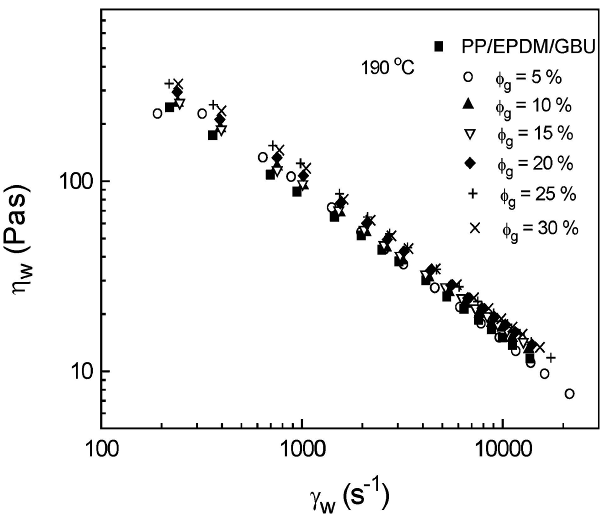

Figure 2 Dependence of shear viscosity on shear rate.

during extrusion of the composite melts. This may be attributed to the reduction of viscosity at higher flow rate due to the shear-thinning effect of polymeric melts.

3.2. Dependence of shear viscosity on shear rate

Fig. 2 illustrates the relationship between shear viscosity (η_w) and true shear rate ($\dot{\gamma}_w$) of PP/EPDM/GBu system at 190°C. When $\dot{\gamma}_w$ is less than 300 s^{-1}, η_w decreases gently with an increase of $\dot{\gamma}_w$; white η_w drops down linearly with increasing $\dot{\gamma}_w$ when shear rate is more than 300 s^{-1}. Here, η_w is defined as follows,

$$\eta_w = \frac{\tau_w}{\dot{\gamma}_w} \tag{4}$$

It can also be seen in Fig. 2 that η_w increases somewhat with an addition of ϕ_g, but the increase is not significant. This phenomenon may be related to the shear thinning property of the resin in addition to the reason as stated above.

3.3. Dependence of shear viscosity on temperature

Fig. 3 displays the dependence of the shear viscosity of the sample melts on test temperature. It can be seen that ln η_w is approximately a linear function of $1/T$(T is the absolute temperature, °K) under fixed wall shear stress. This suggests that the dependence of the shear viscosity of the sample melts on temperature is roughly consistent with Arrhenius expression.

It can also be seen in Fig. 3 that the slope of the ln $\eta_w - 1/T$ curves of PP/EPDM system is lower than that of PP/EPDM-MA and PP/EPDM/GBu systems. The slope of the curves reflects the sensitivity of the melt viscosity to temperature. This shows that the compatibility between PP and EPDM is improved after MA and DCP have grafted the elastomer, and the sensitivity of the shear viscosity of the blending system to temperature is increased. The active ability of the macromolecular chains of resin and the activity of glass beads in the matrix are increased with a rise of temperature, leading to increase of the sensitivity of the shear viscosity to temperature.

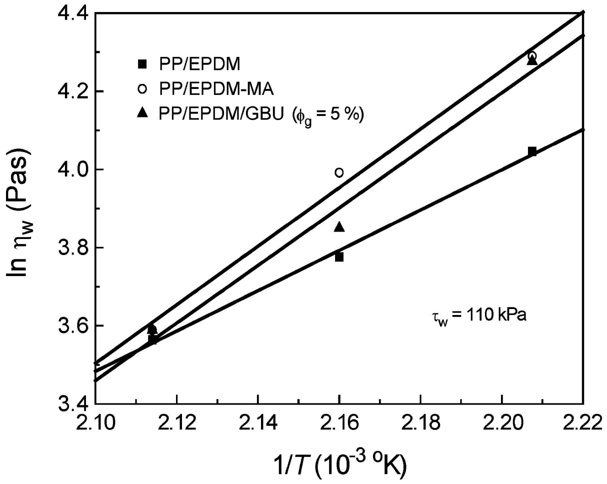

Figure 3 Dependence of shear viscosity on test temperature.

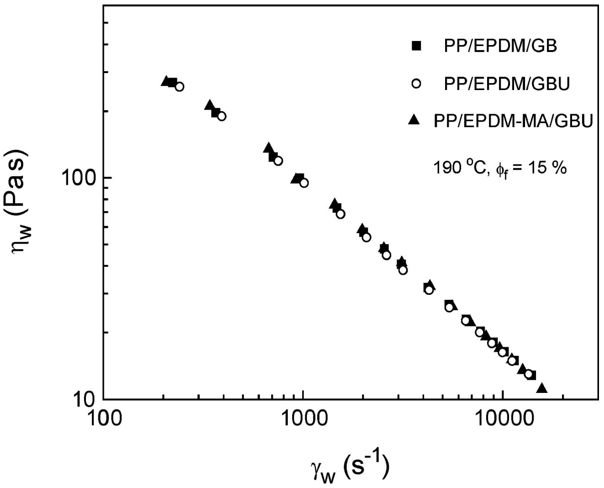

Figure 4 Influence of filler surface treatment on shear viscosity.

3.4. Influence of filler surface treatment on shear viscosity-shear rate dependence

Fig. 4 shows the influence of the surface treatment of the filler particles on the dependence of the melt shear viscosity of the three kinds of composite systems on shear rates at test temperature of 190°C when the volume fraction of the glass beads is 15%. It can be seen that the melt shear viscosity of these composites are close each other under the same shear rates. This means that the influence of the surface treatment of the filler particles on the dependence of the melt shear viscosity of the samples on shear rates is insignificant at lower concentration of the glass beads under these test conditions.

3.5. Relationship between shear viscosity and GB volume fraction

Fig. 5 displays the relationship between the melt shear viscosity and the volume fraction (ϕ_g) of the glass beads of PP/EPDM/GB system when test temperature

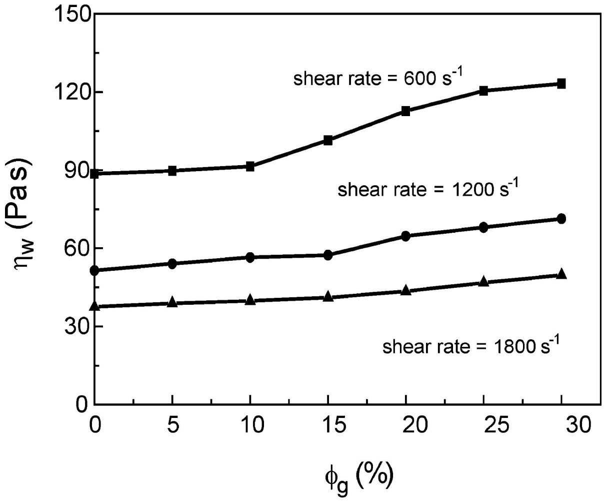

Figure 5 Relationship between shear viscosity and ϕ_f (EPDM/PP/GB system).

is 190°C. The melt shear viscosity of the samples increases with an addition of ϕ_g under the same shear rate, and the increase of it reduces with increasing shear rate. Fig. 6 illustrates the correction between the melt shear viscosity and ϕ_g of PP/EPDM/GBu system at 190°C. Similarly, The melt shear viscosity of the samples increases with an addition of ϕ_g under the same shear rate, and the increase of it reduces with increasing shear rate. It can be seen by comparing Figs 5 and 6 that the melt shear viscosity of PP/EPDM/GB system is slightly higher than that of PP/EPDM/GBu system under the same test conditions. Furthermore, the dependence of the melt shear viscosity on ϕ_g of the former is more significant than that of the latter when ϕ_g is more than 15%. For example, the melt shear viscosity of PP/EPDM/GB composites increases with an addition of ϕ_g at higher apparent shear rate (e.g., 1800 s^{-1}), whereas the melt shear viscosity of PP/EPDM/GBu composites only increases slightly.

At lower apparent shear rate, the increase of the melt shear viscosity of both two composite systems increases significantly with an addition of ϕ_g, and the relationship between them is nonlinear function. On the basis of Einstein equation [4], this expression can be described by:

$$\eta_c = \eta_m\left(1 + K_E\phi_g^{\alpha}\right) \quad (5)$$

where η_m is the melt viscosity of the matrix (i.e., unfilled resin), K_E is the Einstein coefficient, for sphere particle, $K_E = 2.5$. α is the parameter related to the concentration of filler particles, and the interface morphology between the filler and the matrix.

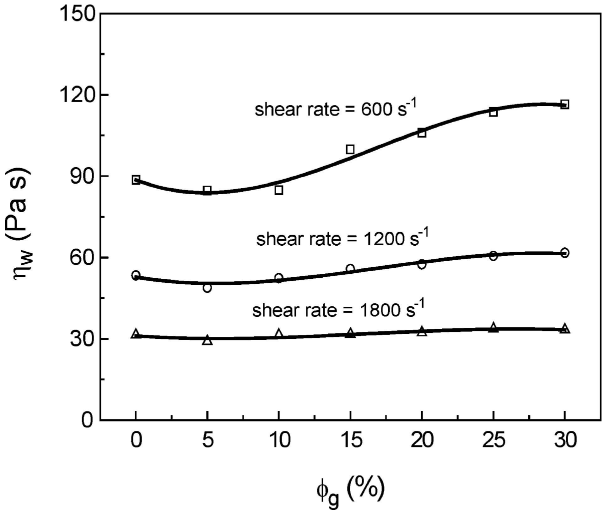

Figure 6 Relationship between shear viscosity and ϕ_f (EPDM/PP/GBu system).

3.6. Discussion

For an inorganic particle-filled polymer composite, the molecular chain motion of matrix resin is blocked to some extent by filler particles, and this resistance increases with an addition of the particle concentration, resulting in increase of the fluid viscosity. Comparing with general inorganic particles (e.g., mica, talc and calcium carbonate), glass bead has relatively weak polymer-particle adhesion owing to its smooth spherical surface and the resistance to the molecular chain movement of the matrix resin is relatively small, especially under higher flow rate conditions, leading to reduction of the sensitivity the fluid viscosity to the particle concentration. It can be seen in Figs 5 and 6 that the dependence of the melt shear viscosity of PP/EPDM/GB and PP/EPDM/GBu on the volume fraction of the fillers is decreased with an increase of shear rates.

In addition to the size and concentration of the filler particles, the influence of the interfacial adhesion between the particles and the matrix on the viscoelasticity of the composite systems is also important. Because the surface of the glass beads is treated with silane coupling agent, the compatibility between the PP resin and the beads is enhanced, and the interfacial adhesion between the beads and the matrix resin is improved, leading to increasing correspondingly the melt shear viscosity and its sensitivity to the particle concentration of the composite systems, especially at higher concentration of the beads (see Figs 5 and 6).

4. Conclusions

The slope of the melt shear flow curves of PP/EPDM/GBu composite systems varied around shear rate of 700 s^{-1}. In general, the flow behavior of PP/EPDM/GB composite systems may be considered approximate to that of a power law fluid under the test conditions.

The dependence of the melt shear viscosity of the samples on test temperature was roughly consistent with the Arrhenius expression under the experimental conditions, and the temperature sensitivity somewhat increased with the improvement of the compatibility between PP and EPDM or with an addition of glass bead concentration.

The melt shear viscosity of the composite systems increased with an addition of the volume fraction of glass beads, white the sensitivity of the viscosity to the filler concentration was enhanced with a reduction of shear rate.

The melt shear viscosity of the surface pretreated glass bead-filled PP/EPDM composite systems and its sensitivity to the filler concentration somewhat increased at higher concentration of the glass beads, especially at lower shear rate.

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