

The Melt Shear Viscosity of Polypropylene/Glass Bead Composites at High Extrusion Flow Rates

J.Z. Liang¹, R.K.Y. Li¹, C.Y. Tang² and S.W. Cheung³

¹*Department of Physics and Materials Science, City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong, P.R. China*

²*Department of Manufacturing Engineering, The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong, P.R. China*

³*Hong Kong Plastics Technology Centre, Kowloon, Hung Hom, Hong Kong, P.R. China*

SUMMARY: The effects of filler content and its surface treatment with silane coupling agent on the melt shear viscosity of glass bead-filled polypropylene (PP) composites have been investigated using a capillary rheometer at a wide shear rate scope of 150 to 7200 s⁻¹ and temperature range of 160 to 200 °C. The melt flow obeys power law, but the slopes of the flow curves have transitions at the shear rate of about 500 s⁻¹. The melt shear viscosity of the coated glass bead-filled system is somewhat higher than that of the uncoated glass bead-filled system when both were subjected to the same conditions. The dependence of the melt shear viscosity on temperatures can be described with Arrhenius relationship, and the temperature sensitivity of the composite melts is greater than that of pure PP. The melt shear viscosity (η_w) increases with the volume fraction of the fillers (ϕ_f) at lower shear rates, while the dependence of η_w on ϕ_f decreases with the increase of shear rates.

KEYWORDS: polypropylene, glass bead, composite, melt viscosity, capillary extrusion

INTRODUCTION

Polypropylene (PP) is extensively used in automobile and electronical appliance applications. However, its application is somewhat limited due to its high shrinkage rate, and relatively poor impact resistance, especially at room or low temperatures. To improve its toughness and dimensional stability, PP filled with rigid inorganic particles, such as calcium carbonates and glass beads, is widely used in industry. There have been a number of studies on the mechanical properties of particulate filled PP composites [1-6]. However, it is necessary to know whether / how the fillers affect the processability of the composites. Melt shear viscosity is an important characteristics 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 flow rates [7-9].

However, polymer materials processing is usually conducted at higher flow rates, such as extrusion and injection shaping. The objectives of this work are to investigate the effects of temperatures, the filler content and its surface treatment on the melt shear viscosity of glass bead filled PP composites at high extrusion flow rates.

EXPERIMENTAL

Materials and Preparation

The PP used in this work was a general purpose resin with trade mark Pro-fax 6331[®]. Its density at solid state and melt flow index (2.16 kg, 230 °C) were 0.9 g cm⁻³ and 12 g (10min)⁻¹, respectively. Two types of A-glass beads were used as the fillers, one of which had the surface pretreated with a silane coupling agent CP-03 (GB2) while the other was uncoated (GB1). All the small solid spheres had density of 2.5 g cm⁻³, they were supplied by Potters Indust. Inc., USA, under trade mark of Spheriglass[®]. After being simply mixed the PP and glass beads were blended by using a twin screw extruder (Brabender PL 2000) at screw speed of 15 rpm and in a range of temperatures from 180 °C to 230 °C to produce the composites.

Apparatus and Methodology

The measurement of the melt flow property was carried out by means of a constant rate type of capillary rheometer with two bores supplied by Rosand Precision Ltd. A long die (L / D = 16) and a short die (L / D ≈ 0) both of which were 1 mm in diameter were selected in order to conduct the entry correction. The shear stress at the wall (τ_w) is given by:

$$\tau_w = \frac{(\Delta P_L - \Delta P_S)D}{L_L} \quad (1)$$

where ΔP_L and ΔP_S are the pressure drop of the long die and short die, respectively, and L_L is the long die length.

The melt flow properties of these composites were measured piston speeds (V) varied from 5 to 240 mm/min (corresponding to apparent shear rates of 10^2 to 10^4 s⁻¹) and test temperatures ranging from 180 to 200 °C. The apparent shear rate at the wall is given by:

$$\gamma_a = \frac{32Q}{\pi D^3} \quad (2)$$

where Q is the volumetric flow rate.

According to the instrumental conditions, γ_a can be expressed as follows:

$$\gamma_a = 30V \quad (3)$$

RESULTS AND DISCUSSION

Melt Flow Curves

Figure 1 shows the melt flow curves of pure PP and PP / GB1 system with different glass bead contents at 190 °C. It can be seen that each melt flow curve can be represented by three linear regions. It means that the melt shear flow of the pure PP and the composites basically obeys the power law under the experimental conditions applied. In addition, the slope of these curves decreases with increasing volume fraction of the inclusions, ϕ_f . It suggests that the power law index decreases with increasing ϕ_f . In other words, the non-Newtonian property of the composite melts is somewhat enhanced with increasing the concentration of the fillers. It can be also seen in Fig. 1 that the slope of the melt flow curves changed at $\gamma_a \approx 500 \text{ s}^{-1}$, and the slope suddenly decreases in a range from 500 to 1100 s^{-1} to form a "plateau". It is suggested that the melt shear flow has experienced wall-slip at this case. This is because when the wall shear stress exceeds the inter-adhesion between the wall and the melt, the melt moves as a form of slip, and the wall shear stress decreases correspondingly in this case.

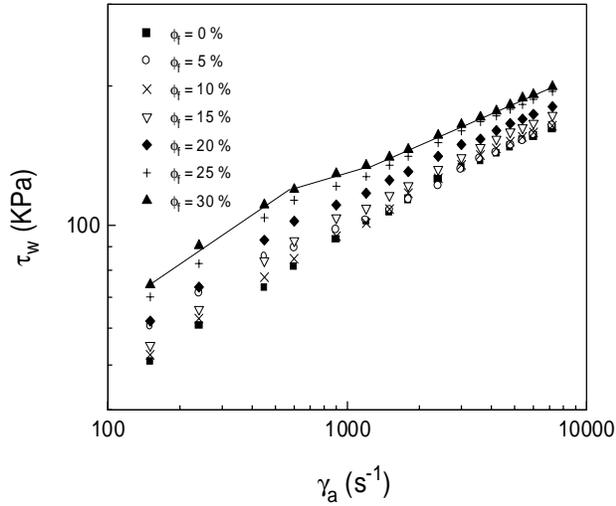


Fig. 1 Melt flow curves (190 °C).

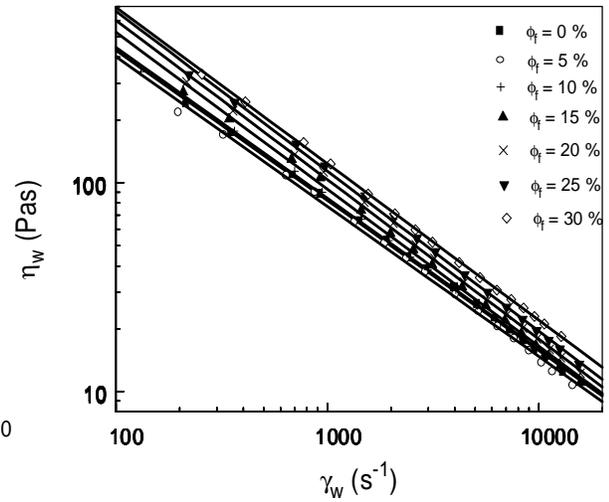


Fig.2 η_w as a function of γ_w (190 °C).

Dependence of η_w on γ_w and Temperature

Figure 2 displays the relationship between the melt shear viscosity (η_w) and true wall shear rate (γ_w) of PP and PP / GB2 system at 190 °C. It can be seen that η_w decreases linearly with increasing γ_w and increases slightly with the increase of ϕ_f , at the lower γ_w region, while it does not vary with ϕ_f at higher γ_w . η_w , and γ_w are defined respectively as follows:

$$\eta_w = \tau_w / \gamma_w \quad (4)$$

and

$$\gamma_w = \frac{3n+1}{4n} \gamma_a \quad (5)$$

where n is the power law index.

Figure 3 illustrates the dependence of the melt shear viscosity of the pure PP and PP / GB2 on temperatures at a shear stress of 152 KPa. It can be seen that $\ln \eta_w$ increases linearly with increasing $1/T$ (T is the absolute temperature). It suggests that the dependence of the melt shear viscosity on temperature is governed by the Arrhenius expression. That is,

$$\eta_w = A \exp(E/RT) \quad (6)$$

where A is the viscosity coefficient, E and R are the activation energy of viscous flow and the universal gas constant, respectively. In addition, the slope of the curve of $\ln \eta_w$ against $1/T$ for the composite is greater than that of the pure PP. It indicates that the sensitivity of the melt shear viscosity of the composite to temperature is higher than that of the pure PP.

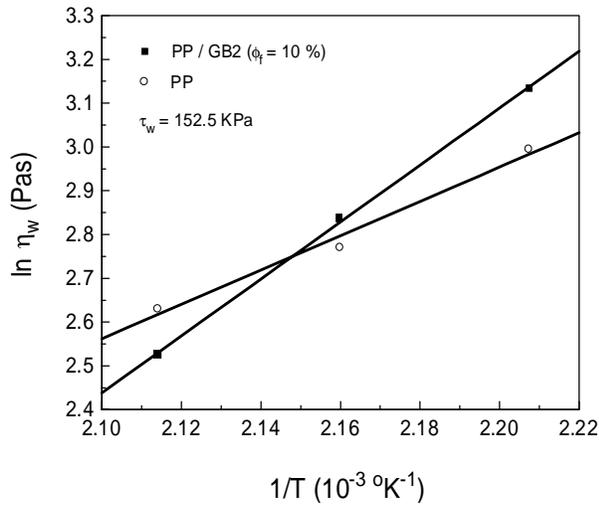


Fig.3 Dependence of η_w on temperature

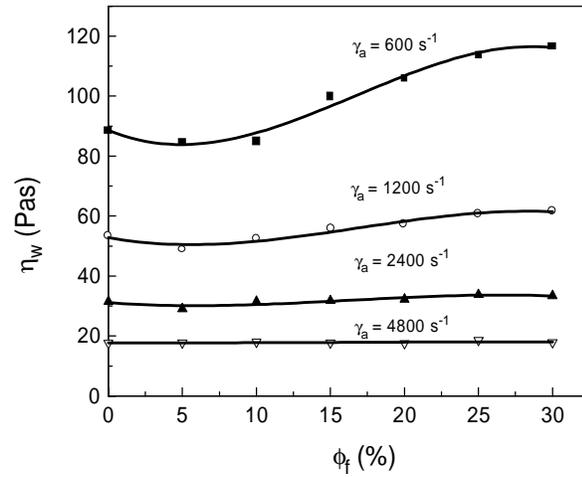


Fig. 4 Effect of ϕ_f on η_w (190 °C)

Effect of Filler Content on η_w

Under different apparent shear rates, the effect of the filler content on the melt shear viscosity of PP / GB1 system is shown in Figure 4. At lower apparent shear rate, η_w increases with increasing volume fraction of the glass beads, especially at higher filler concentration. While at higher apparent shear rate, η_w increases lightly with the increase of ϕ_f . In other words, the dependence of the melt shear viscosity on the filler content weakens with increasing flow rate. When shear rate reaches a high level, the orientation of molecular chains are much obvious, and the melt shear viscosity is very small and it tends to a constant. In this case, the glass beads can move more easily in the matrix melt due to their

smooth spherical surface. Consequently, the dependence of the melt shear viscosity on the filler content decreases significantly.

Influence of Filler Surface Treatment on Melt Flow Property

Figure 5 shows the melt flow curves of PP / GB1 and PP / GB2 systems with $\phi_f = 25\%$ at $190\text{ }^\circ\text{C}$. Under the same experimental conditions, the τ_w values of PP / GB2 system are somewhat higher than those of PP / GB1 system. In addition, the critical apparent shear rate for the onset of the "plateau" phenomenon for the former is higher than the latter. It suggests that the increase of melt flow resistance and flow stability of PP / GB2 system is attributable to the addition of the interfacial adhesion between the filler and matrix melt due to the pretreatment of the particle surface with silane coupling agent.

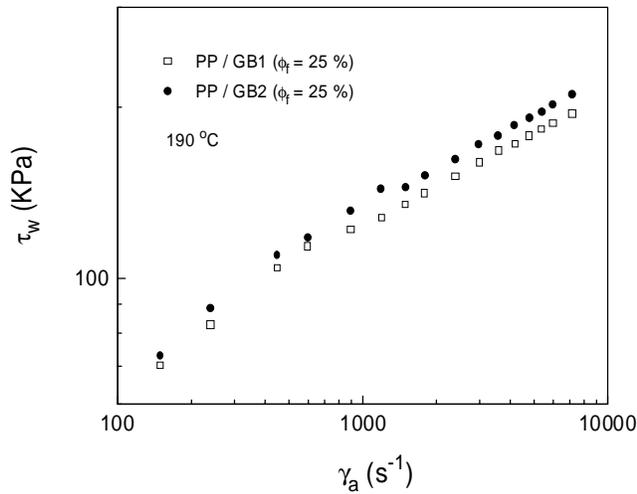


Fig. 5 Comparison of melt flow curves.

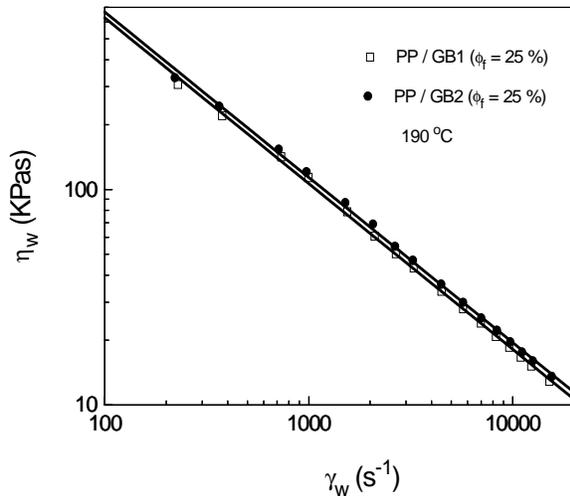


Fig. 6 Comparison of melt viscosity curves.

Figure 6 displays the comparison of the melt shear viscosity curves for PP / GB1 and PP / GB2 systems with $\phi_f = 25\%$ at $190\text{ }^\circ\text{C}$. Similarly, the η_w values of PP / GB2 system are slightly higher than those of PP / GB1 system at the same shear rate. It means that the melt shear viscosity of the composites can be somewhat increased by the surface treatment of glass beads, in addition to the improvement of the interfacial adhesion between the matrix and fillers.

CONCLUSION

Under the conditions of high extrusion rates, glass bead filled-polypropylene composite melts present some flow behaviour being different from that at low flow rates. The melt shear viscosity increases with increasing the volume fraction of the fillers at lower shear rates, while it increases only slightly with the filler content at higher shear rates. The melt flow approximately obeys power law, but the slopes of the flow curves change at the apparent shear rate about 500 s^{-1} . The melt shear viscosity of the coated glass bead-filled system is somewhat higher than that of the uncoated glass bead-filled system at the same conditions applied. The dependence of the melt

shear viscosity on temperatures is governed by the Arrhenius relationship, and the temperature sensitivity of the composite melts is greater than that of the pure PP.

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REFERENCES

1. Pukanszky, B., Influence of Interface Interaction on the Ultimate Tensile Properties of Polymer Composites, *Composites*, Vol. 21, No. 3, 1990, pp. 255-262.
2. Maiti, S.N. and Mahapatro, P.K., Mechanical Properties of Nickel-Powder-Filled Polypropylene Composites, *Polymer Composites*, Vol. 13, No. 1, 1992, pp. 47-52.
3. Jancar, J., Dibenedtto A.T. and Dianselmo, A., Effect of Adhesion on the Fracture Toughness of Calcium Carbonate-Filled Polypropylene, *Polymer Engineering and Science*, Vol. 33, No. 9, 1993, pp. 559-563.
4. Stricker, F., Bruch, M. and Mulhaupt, R., Mechanical and Thermal Properties of Syndiotactic Polypropylene Filled With Glass Beads and Talcum, *Polymer*, Vol. 38, No. 21, 1997, pp. 5347-5353.
5. Sjogren, B.A. and Berglund, L.A., Failure Mechanisms in Polypropylene With Glass Beads, *Polymer Composites*, Vol. 18, No. 1, 1997, pp. 1-15.
6. Liang, J.Z. and Li, R.K.Y., Mechanical Properties and Morphology of Glass Bead-Filled Polypropylene Composites, *Polymer Composites*, Vol. 19, No. 6, 1998, pp. 698-703.
7. Kamal, M.R. and Mutel, A., Rheological Properties of Suspensions in Newtonian and Non-Newtonian Fluids, Vol. 5, No. 4, 1985, pp. 293-382.
8. Metzner, A.B., Rheology of Suspension in Polymer Liquids, *Journal of Rheology*, Vol. 29, No. 6, 1985, pp. 739-775.
9. Khan, S.A. and Prudhomme, R.K., Melt Rheology of Filled Thermoplastics, *Reviews in Chemical Engineering*, Vol. 4, No. 3-4, 1987, pp. 205-270.

