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Rheological Behavior for Mica-filled Polypropylene Composite Melts

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Abstract: The study on rheological properties of a series of mica-filled polypropylene (PP) composites was carried out. The influence of surface-treatment of mica particles on dynamic rheological behavior of the composites were dealt with. The viscosity (η) and dynamic modulus (G') of the composite melts were higher than those of PP matrix, especially those for systems treated with silane, which was attributed to the interfacial adhesion enhancement. However, surface-treatment of mica by titanate resulted in lower η and G', as compared with the treatment by silane. The reason for this is believed to be the formation of the mono-molecular layer on the mica surface.

Keywords: Mica, polypropylene, dynamic rheological behavior.

As a typical two-dimensional silicate sheet, mica has excellent mechanical, electrical properties and thermal stability, which makes it as a universally applied mineral material in reinforced plastics and insulating products [1]. A lot of researches concerning mica-filled polymers have mostly focused on the aspects of mechanical and dielectric properties, while a few reports have been related to rheological behavior of their melts [2-4]. It is well known that a knowledge of the rheology of melt not only gives much useful information for material moulding and processing, but also is an important way to characterize the structure and properties of polymer materials [5, 6]. On the other hand, the character of polymer matrix and filler, as well as interaction of polymer-filler interface influences on the rheological behavior of filled polymer system. The purpose of this article is to investigate the influence of the interaction between matrix and filler on rheological behavior for filled PP composites.

PP used here was homopolymerized one (T300, SINOPEC Shanghai Petrochem, China) and the mica filler had an average particle size of 8 μm. The silane and titanate coupling agents were TM-69($(C_2H_5O)_3Si(CH_2)_3S_4(CH_2)_3Si(OC_2H5)_3$) and NDZ-105 ($(CH_3)_2CHOTi(OCC_{17}H_{35})_3$), respectively. The mica was treated in 1.5 wt% of the solution of the coupling agent and then dried in vacuum at 80°C for 24 h. The samples of PP filled with 50 wt% mica fillers, exposed to different surface-treatment, were prepared using a Haake Rheomix at 180°C, and were marked as PPM5S and PPM5T, standing for PP samples filled with mica treated by silane and titanate, respectively. The appropriate polymer-filler mixtures including antioxidant (1010) with 0.5 wt% of

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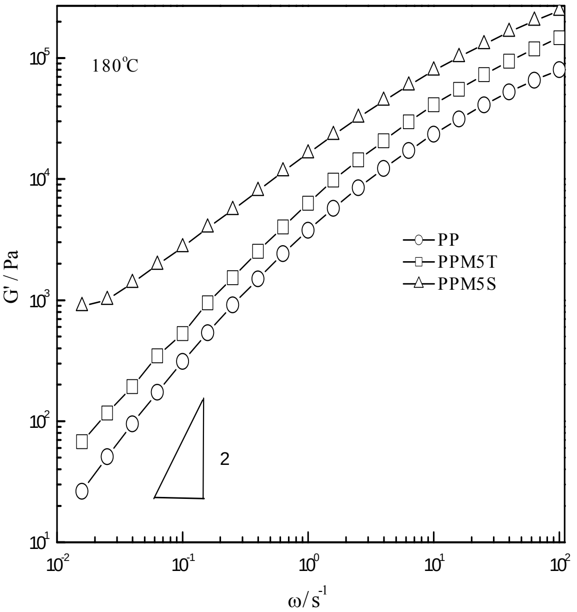
matrix weight were kneaded for 10 min at 60 rpm. All samples were compression-moulded into disks of 25 mm in diameter and 2 mm in thickness at 180 ℃, 10 MPa. The rheological measurements were performed on an Advanced Rheometric Expansion System (ARES) in the parallel plate mode at 180°C. The dynamic frequency scan were realized in 0.015 to 100 s^{-1} and the strain amplitude was maintained 0.5 ~ 5 %. The steady shear tests were carried out in 0.01 ~ 10 s^{-1}. The dynamic time-scan were performed at 0.1 $rad.s^{-1}$.

In general, the increase of dynamic viscoelastic functions in the low frequency (ω) range is related to the extent of heterogeneity for the filled polymers. The higher the G', the more heterogeneous is the system. In other words, the better the value of G' approaches that of the virgin PP, the higher is the level of compatibility of the interface 5. **Figure 1** shows ω dependence of G' for PPM5S and PPM5T at 180°C. Obviously, values of G′ for the filled PP composites are higher than those of virgin PP. However, G' for PPM5T is lower than that of PPM5S, especially in low ω. It is well accepted whether the slope of logG' vs logω at low ω is close to 2 or not, as defined in rheology, is responsible for the existence of heterogeneous or homogeneous structure in multi-component polymers[5,6]. Accordingly, the results above indicated that the surface-treatment of fillers improved the interaction between PP and mica; and furthermore, with respect to the improvement of interface compatibility between filler and PP matrix, the effect of titanate was more effective than that of silane.

Figure 1 Relationship between dynamic storage modulus G' and frequency ω for composites exposed to different surface-treatment



The results of the steady shear tests also confirm the effect of coupling agents. **Figure 2** gives relationship of steady viscosity (η) and shear rate ($\dot{\gamma}$) for composites exposed to different surface-treatment. It can be seen that surface-treatment of fillers results in the change of rheological behavior of composites, especially in low ω. When $\dot{\gamma}$ is lower than $\dot{\gamma}_{co}$ ($\approx 4\times10^{-1}$ s^{-1}), namely, the critical shear rate of virgin PP, the values of η of composites are higher than those of virgin PP, ranking as PPM5S > PPM5T > PP. Also, as compared with that of virgin PP, η of filled polymer presents the characteristic of non-Newtonain fluids at lower ω, *i.e.* the critical shear rate $\dot{\gamma}_{cs}$ at which shear-thinning appears about 4×10^{-2} s^{-1}, lower than $\dot{\gamma}_{co}$ for virgin PP. The reason for this is owed to formation of an active organic mono-layer, induced by the mono-alkoxyl in titanate coupling agent. On the other hand, the mono-layer has the effect of lubricant on the flow. Generally, silane groups in TM-69 can react with carbonyl which was formed in processing of PP [7]. Hence, the formation of chemical link between main chain in matrix and fillers strongly restricts the movement of PP chain, leading to higher η for PPM5S.

Figure 3 displays dynamic time-scan curves of composites exposed to different surface treatment. No significant thermal degradation occurs for filled systems during 1 h in the process of investigation. In other words, both PPM5S and PPM5T are under stable dispersion state and no structure / morphology are destroyed.

Figure 2 Relationship of steady viscosity η and shear rate $\dot{\gamma}$ for composites exposed to different surface-treatment

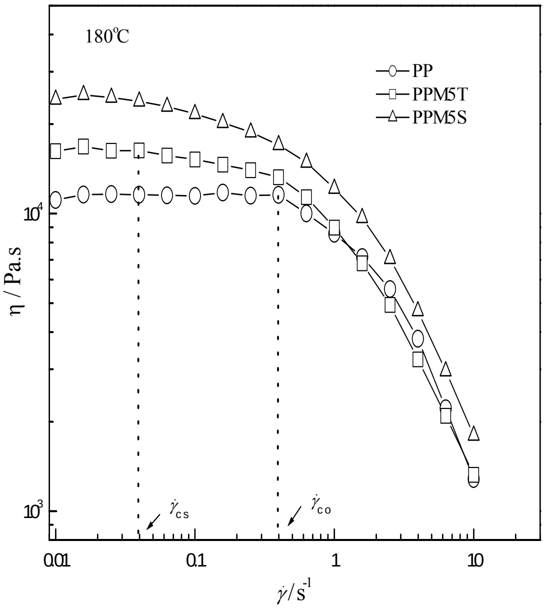
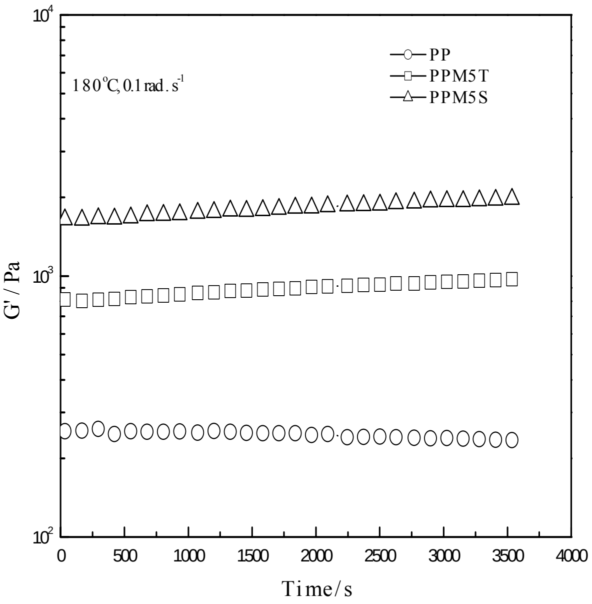


Figure 3 Dynamic time-scan curves of composites exposed to different surface-treatment



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