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Preparing temperature-dependent dynamic rheological properties of polypropylene filled with ultra-fine powdered rubber

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The special toughening effect on polypropylene (PP) using ultra-fine powdered rubber (UFPR) has attracted attention recently [1] because the toughness, stiffness and heat resistance of PP can be improved simultaneously through incorporation of a small amount of UFPR. It is now generally accepted that the properties of immiscible blends strongly depend on the structure and morphology of the system, and they are determined dominantly by the rheological characteristics of the blend. Moreover, dynamic rheological testing is believed to be a preferential method for dealing with structure/morphology of materials because the structure of materials exposed to testing processes is not destroyed under small strain amplitude [2]. To our knowledge, few results concerning the rheological behavior of UFPR/polymer systems have been reported until now.

PP used here is homopolymerized one (S38F, SINOPEC Shanghai Petrochem, China) and the UFPR filler is a styrene-butadiene copolymer (VP-101, Beijing Research Institute of Chemical Industry, China) [1]. The samples of PP filled with various weight fractions of UFPR fillers were prepared using a Haake Rheomix at 160 °C (marked as "*PP160*") and 180 °C (marked as "*PP180*") respectively. The appropriate polymer-filler mixtures including 0.4 g antioxidant (1010) were kneaded for 10 min at 50 rpm. All samples were prepared under identical molding conditions. The rheological measurements were performed on an advanced rheometric expansion system (ARES) in the parallel plate mode. A sample with a radius of 25 mm and thickness of 2 mm was placed between the plates and dynamic torsional shear was applied to the sample under 1% strain. The temperature was held constant during the frequency sweep.

Fig. 1 shows the dependence of dynamic storage modulus G' on frequency ω for PP160 samples with various UFPR content measured at 200 °C. It can be seen that when the UFPR content is below 5 wt%, curves of G' vs. ω for the composites more or less coincide with that of virgin PP, and at the same time the dynamic viscoelastic behavior appears similar to that for virgin PP, implying that the viscoelastic properties of the filled samples are determined dominantly by the polymer matrix. According to linear viscoelastic theory, the dynamic modulus for the homogeneous polymer system are given by [3]

$$G'(\omega)|_{\omega\to 0} = J_e^0 \eta_0^2 \omega^2$$
$$G''(\omega)|_{\omega\to 0} = \eta_0 \omega$$

It is clear that G' and G'' are proportional to ω^2 and ω, respectively, to $\log G' \propto 2 \log \omega$, and $\log G'' \propto \omega$, respectively. In other words, the gradient of $\log G'$ vs. $\log \omega$ at low frequencies (terminal range) is 2 or close to 2 for the homogeneous polymer system. In general, the existence of an heterogeneously ordered structure can result in the departure of the gradient from 2. Both molecular theory and experiment of facts have given verifications [3, 4]. It is worth noting that the rheological model concerning complex fluids has not been satisfactorily developed until now. For the rheological characterization of these systems, it is the main method for studying the departure of the linear viscoelastic functions behavior between complex and the homogeneous systems. Fortunately, it is found that the change of gradient at low frequency is sensitive to the change/formation of structure morphology of the complex system. We suggest there exists a better dispersion

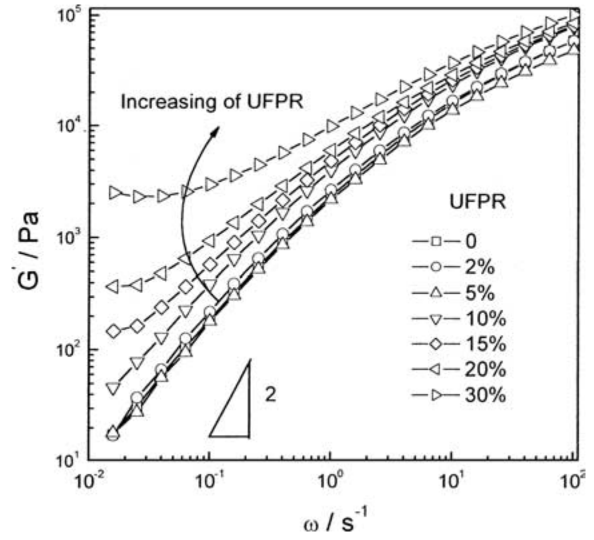

Figure 1 Frequency dependence of dynamic storage modulus G' for PP160 samples with various UFPR content measured at 200 °C.

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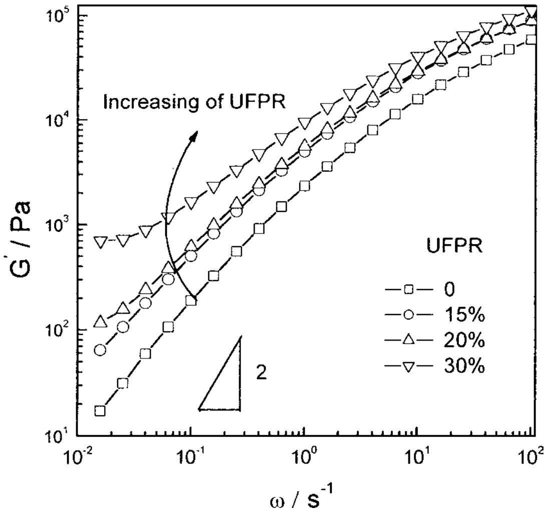

Figure 2 Frequency dependence of dynamic storage modulus G' for PP180 samples with various UFPR content measured at 200 °C.

of fillers for the composites containing UFPR less than or equal to 10%. However, with the increase of filler content, especially when the content is beyond 10 wt%, the corresponding G' values are obviously higher than that of virgin PP. It is interesting that when the content is beyond 15 wt%, curves of G' vs. ω appear to turn up on reducing ω to the lower values in the range measured. This phenomenon generally is called the "*second plateau*" [5] in rheology, which is referred to the formation of ordered structure/morphology induced by aggregation of fillers [6] and a phase-separated system [7].

Fig. 2 displays the case of PP180 samples. It is clear that G' values increase with the increase of UFPR content at the terminal range, similar to PP160. But different from the case in Fig. 1. there is no discernible upturn in curves of G' vs. ω in Fig. 2 for PP180 samples containing either 15 or 20 wt% UFPR.

Fig. 3 gives the comparison of ω dependence of G' and dynamic loss modulus G'' measured at 200 °C between PP160 and PP180 with 20 wt% UFPR. It can be seen that both G' and G'' of PP180 are lower than those of PP160. According to accepted rheological ideas concerning particle-filled polymers [6] and the results discussed above, we conclude that even if there exists heterogeneously ordered structure/morphology in PP160 and PP180 samples, the former appears much more heterogeneous than the latter. In other words, the temperature 180 °C, compared with 160 °C, seems preferable for the dispersion of UFPR in PP matrix.

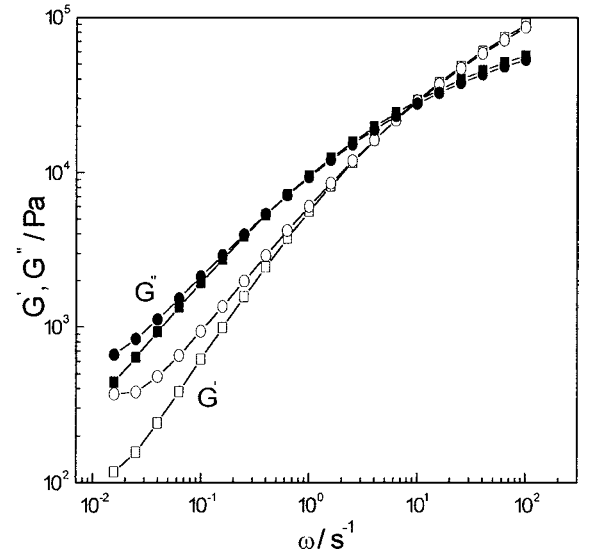

Figure 3 Comparison of frequency dependence of dynamic storage modulus G' (open) and dynamic loss modulus G'' (solid) measured at 200 °C between PP160 (circle) and PP180 (square) with 20 wt% UFPR.

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References

1. Y. Q. LIU, X. H. ZHANG, G. S. WEI, J. M. GAO, F. HUANG, M. L. ZHANG, M. F. GUO and J. L. QIAO, *Chin. J. Polym. Sci.* **20**(2) (2002) 93.
2. L. A. UTRACKI, "Polymer Alloys and Blends" (Carl Hanser Press, New York, 1989) p. 131.
3. J. D. FERRY, "Viscoelastic Properties of Polymers" (Wiley Press, New York, 1980) p. 56.
4. C. D. HAN and J. K. KIM, *Macromolecules* **22** (1989) 4292.
5. Q. ZHENG and T. J. ZHAO, *Chin. J. Mater. Res.* **12**(3) (1998) 225.
6. Q. ZHENG, X. W. ZHANG, Y. PAN and X. S. YI, *J. Appl. Polym. Sci.* **86** (2002) 3166.
7. Q. ZHENG, M. DU, B. B. YANG and G. WU, *Polymer.* 42 (2001) 5743.

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