

DYNAMIC RHEOLOGICAL BEHAVIOR OF POLYPROPYLENE FILLED WITH ULTRA-FINE POWDERED RUBBER PARTICLES*

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Abstract Dynamic rheological characteristics of polypropylene (PP) filled with ultra-fine full-vulcanized powdered rubber (UFPR) composed of styrene-butadiene copolymer were studied through dynamic rheological measurements on an Advanced Rheometric Expansion System (ARES). A specific viscoelastic phenomenon, *i.e.* “the second plateau”, appeared at low frequencies, and exhibits a certain dependence on the amount of rubber particles and the dispersion state in the matrix. This phenomenon is attributed to the formation of aggregation structure of rubber particles. The analyses of Cole-Cole diagrams of the dynamic viscoelastic functions suggest that the heterogeneity of the composites is enhanced on increasing both particle content and temperature.

Keywords Polypropylene, Ultra-fine powdered rubber, Filled polymers, Dynamic rheological behavior, Aggregation of fillers

INTRODUCTION

Fillers are used extensively to improve the mechanical properties of polymer matrix resins such as stiffness, strength and hardness. These properties usually increase with increasing amounts of fillers added. The incorporation of fillers into polymers will also alters their flow behavior and thus their processability. Studies on the rheological properties of particle-filled polymers in the molten state have attracted much attention^[1–5]. Viscoelastic functions such as dynamic storage modulus (G') and dynamic loss modulus (G'') for the multi-component polymers containing particles show peculiar changes in the low frequency region^[6]. For example, the plots of G' or G'' against frequency for ABS exhibit a second plateau at low frequencies^[1], which has been thought to be related to rubber concentration, rubber particle size, and grafting of matrix chains at the surface of the particles and has been attributed to the formation of a network-type structure due to agglomerating particles^[1, 7]. Also this phenomenon has been observed in systems such as acrylic-type particles with core-shell structure^[3, 4].

The special toughening effect on polypropylene (PP) of a small amount of ultra-fine full-vulcanized powdered rubber (UFPR) has become of interest recently^[8] because the toughness, stiffness and heat resistance of PP can be improved simultaneously. It is now generally accepted that the properties of incompatible blends strongly depend on the structure and morphology of the system, and they are determined dominantly by their rheological characteristics. 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^[9]. To our knowledge, few results concerning the rheological behavior of UFPR/polymer systems have been reported until now. The aim of the present work is to study the viscoelastic

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properties of PP melts filled with a new kind of UFPR at long relaxation times and to discuss the effect of particle concentration and experimental temperature on the second plateau phenomenon.

EXPERIMENTAL

Materials and Sample Preparation

The polypropylene (PP) used here is a 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)^[8]. VP-101 is in the form of white powder with an average particle diameter of 96 nm and an apparent density of 0.7 g/cm³. The PP samples filled with various weight fractions of UFPR fillers and 0.4 g antioxidant (1010) were prepared using a Haake Rheomix at 160°C (marked as “PP (I)”) and 180°C (marked as “PP (II)”), 50 r/min for 10 min, respectively. Samples for subsequent dynamic analysis were then compression-molded into disks of 25 mm in diameter and 2 mm in thickness at 180°C, 10 MPa.

Rheological Measurements

The rheological measurements were performed on an Advanced Rheometric Expansion System (ARES) in the parallel plate mode. A sample was placed between the plates and dynamic torsional shear was applied to the sample under 1% strain. The temperature was maintained constant during the frequency sweep.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of dynamic storage modulus G' on frequency ω of PP (I) and PP (II) samples containing different UFPR content at 200°C. When UFPR content is less than 5 wt%, the curves of G' versus ω for the blends almost overlap with that of the virgin PP, indicating that the viscoelastic properties of the filled samples are determined predominantly by the polymer matrix. The curves approximately follow the linear viscoelasticity as given by $G' \propto \omega^2$ in the low frequency region (terminal region). However, as the content of filler is higher than 10 wt%, the relevant G' values of the blends are obviously higher than that of the virgin one. As the content of filler increases further, especially higher than 15 wt%, an upturn appears in the terminal region. This phenomenon, which is called a “second plateau” in rheology, is considered to be the result of formation of ordered structure/morphology induced by aggregation of the fillers and phase-separation in the systems^[6]. It can be seen that for PP (I) and PP (II) samples there exists a discernible difference in the UFPR content, at which the curve of samples exhibits an upturn, the former is at 15 wt% and the latter is at 20 wt%. It is well accepted that the more obvious the phenomenon, the higher is the level of aggregation^[10, 11]. Accordingly, it is reasonable to conclude that if there exists heterogeneously ordered structure/morphology in PP (I) and PP (II) samples, the former has much higher heterogeneity than the latter. In other words, the temperature 180°C, as compared with 160°C, seemed preferable to the dispersion of UFPR in PP matrix during the preparation process.

Figure 2 shows the dependence of loss tangent ($\tan\delta$) on frequency ω for PP (I) and PP (II) samples with different UFPR content at 200°C. For PP (I) samples with 15 wt%, 20 wt%, 30 wt% UFPR, a peak appears in the low frequency region; this peak decreases and shifts toward the higher frequency region with the increase of UFPR content. PP (II) sample possesses higher values of $\tan\delta$ than PP (I) sample. Besides, even when the UFPR content of PP (II) sample reaches 30% the corresponding peak appears at $6 \times 10^{-2} \text{ rad} \cdot \text{s}^{-1}$, and is lower than $3 \times 10^{-1} \text{ rad} \cdot \text{s}^{-1}$ for PP (I). Generally, the absence of $\tan\delta$ peak at lower frequency region is responsible for the existence of disorder or homogeneous structure in the filled polymer system. In other words, the appearance of $\tan\delta$ peak in the lower frequency region, together with the decrease of $\tan\delta$ peak and shifting of $\tan\delta$ peak toward higher frequency region with increase of filler content, have been attributed to the formation of heterogeneous structure/ morphology^[12]. Hence, the above phenomena are considered to be involved in the higher level of UFPR aggregation in PP (I) than in PP (II) at 200°C, which is in accord with the results showed in Fig. 1. On the other hand, the decrease in $\tan\delta$ with increasing UFPR content in PP (I) and PP (II) indicates that the decrease of energy dissipation for the filled system implies the retardation of the relaxation of polymer chain by UFPR.

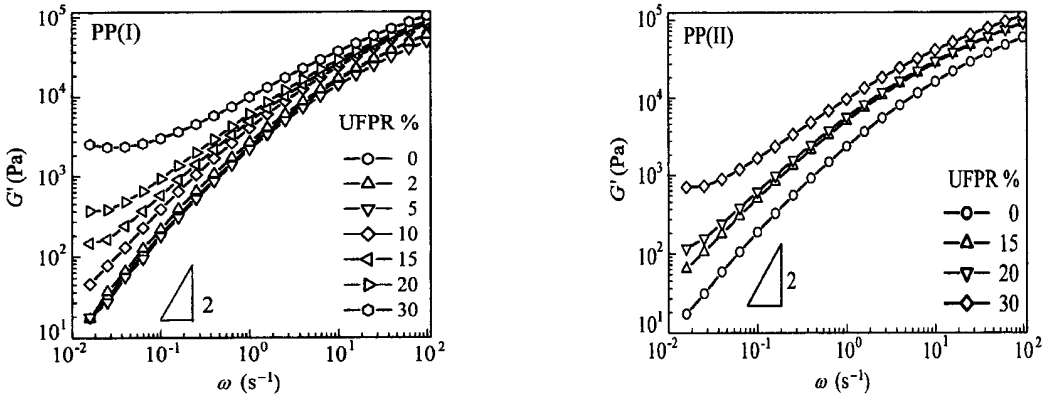


Fig. 1 Dependence of dynamic storage modulus G' on frequency ω for PP (I) and PP (II) samples with various UFPR contents at 200°C

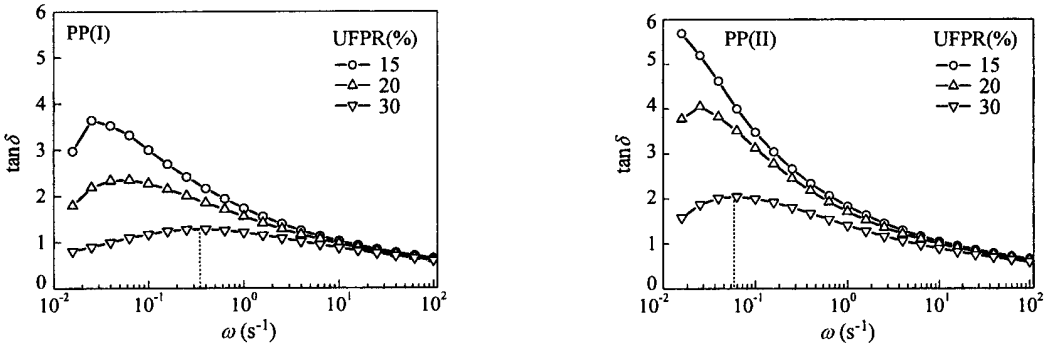


Fig. 2 Dependence of loss tangent $\tan\delta$ on frequency ω for PP (I) and PP (II) samples with different UFPR contents at 200°C

It is well known that the relationship between dynamic viscosity $\eta' (= G''/\omega$, representing the viscous part) and loss viscosity $\eta'' (= G'/\omega$, representing the elasticity part), namely the Cole-Cole diagram, reveals the existence of various groups of relaxation times and gives detailed information on the relaxation processes for the filled polymer melts^[5]. Figure 3 shows the Cole-Cole diagrams measured at 200°C for the virgin PP and PP(II) filled with various contents of UFPR. The Cole-Cole diagrams of the composites containing less than 20 wt% rubber particles demonstrate the form of an arc, similar to that of the virgin PP. With the increase of UFPR content (30 wt%), η'' in the region of long relaxation times (*i.e.*, the low frequency region) dominantly increases as compared with η' , and the form of Cole-Cole diagram changes from arc to linear. It is worth noting that the obvious increase in η'' resulted from the enhanced elasticity due to the increase of content of full-vulcanized rubber particles in the filled polymers. This phenomenon has also been found in other multi-component polymer systems in which there existed phase-separation^[11] or the network-type structure formed by aggregation of filled particles^[5]. Therefore, the aggregation of UFPR is believed to be the main reason for the change of Cole-Cole diagrams and the emergence of the second plateau as presented in Fig. 1.

The effect of temperature on the Cole-Cole diagrams is shown in Fig. 4. Virgin PP shows smooth arcs within the whole frequency range at different measuring temperatures. Exceptionally a tail develops on the right-hand side of the arc for the PP (II) containing 20 wt% particles when the temperature is beyond 190°C. This phenomenon indicates that the higher the temperature, the easier is the movement of the filler particles. In other words, increase of temperature results in the aggregation of UFPR particles. According to our previous reports the appearance of tail is related to the formation of heterogeneous structure/morphology^[5, 11]. Hence, it is

suggested that the structure of the PP (II) containing 20 wt% UFPR is homogeneous when the temperature is below 190°C.

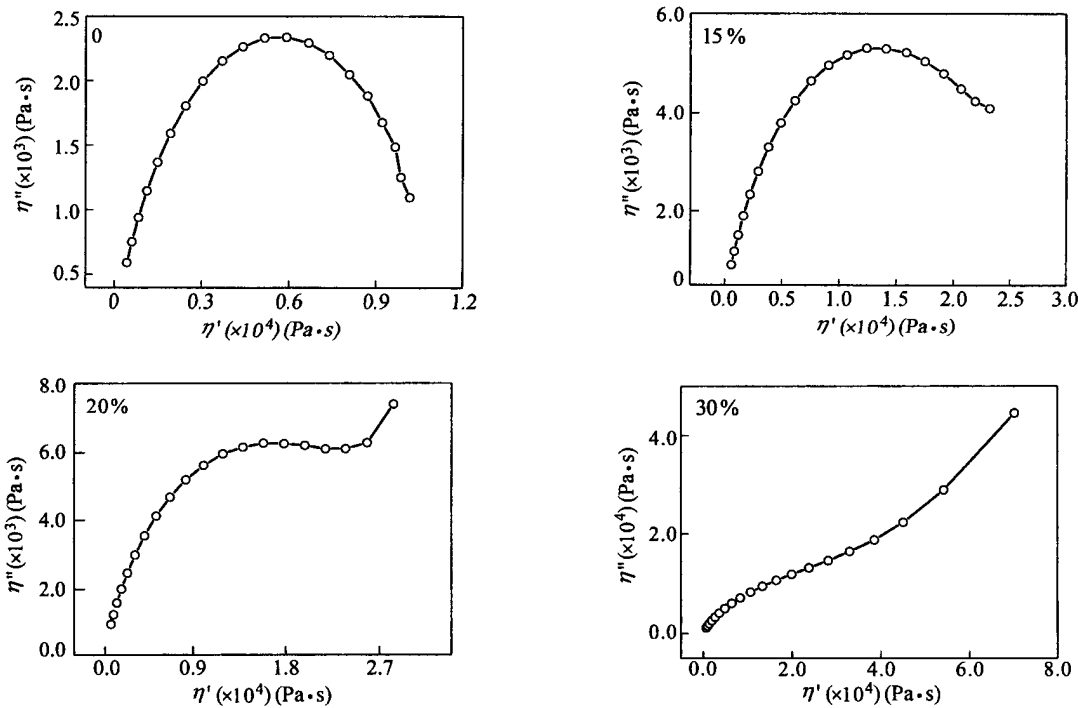


Fig. 3 Cole-Cole diagrams measured at 200°C for PP (II) filled with various contents of UFPR

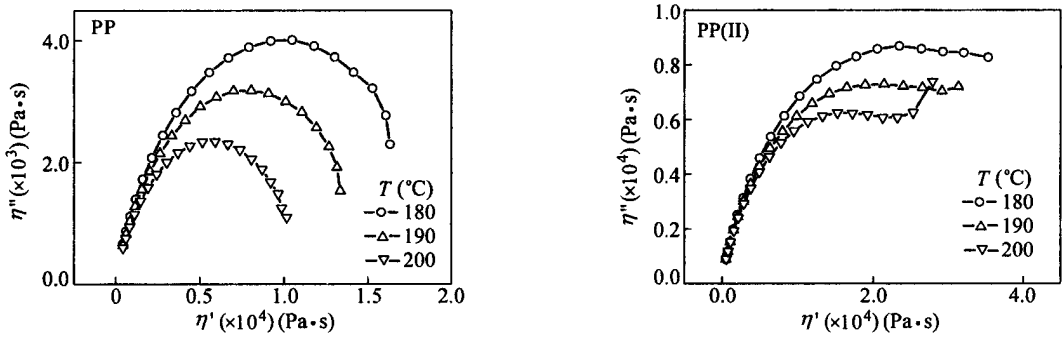


Fig. 4 Cole-Cole diagrams of virgin PP and PP (II) filled with 20 wt% UFPR at different temperatures

CONCLUSIONS

A study on the dynamic rheological behavior of PP filled with ultra-fine powdered rubber (UFPR) was carried out. The results indicate that the second plateau apparent at low frequencies is related to the amount of rubber particles and their dispersion state in the matrix, and is attributed to the aggregation of rubber particles. On the basis of the analyses of Cole-Cole diagrams of the dynamic viscoelastic functions, it is suggested that the heterogeneity of the composites was enhanced with increase of both particle contents and temperature.

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