

RHEOLOGICAL BEHAVIOR OF KAOLIN TOUGHENED POLYPROPYLENE COMPOSITES*

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ABSTRACT

The relation between the rheological behavior and various interfacial properties of Kaolin rigid particle toughened polypropylene(PP/Kaolin) composites were studied by means of parallel-plate rheometer, melt flow rate apparatus, scanning electron microscopy (SEM) and other testing methods. The results show that addition of interfacial modifier to PP/Kaolin composites is advantageous to homogeneous dispersion of filler in PP matrix, formation of flexible interlayer between Kaolin particles and PP matrix and improvement of the melt processibility of the composites.

INTRODUCTION

In recent years, a new method of toughening polymer in which inorganic rigid particle instead of rubbery elastomer as toughening agent was blended into polymer matrix, has been developed gradually^[1,2]. This method has not only great economic value, but also a series of excellent properties which rubbery elastomer toughening polymer can not offer, including high heat distortion temperature (HDT), high hardness, good toughness with high strength of the composites^[3,4]. However, whether the added inorganic rigid particle can toughen the polymer or not it may be affected by many factors. One of the most important factors is how to control interphase structure of these composites, and the formation of interphase structure for the composites is closely related to their rheological properties^[5-7]. Therefore, the studies on the relationship between interphase structure and rheological properties are very necessary. In the present study, the relations between rheological behavior and interphase structure of Kaolin rigid particle toughened polypropylene(PP/Kaolin) composites in the light of the surface treatment of Kaolin particles using interfacial modifier with known structure has been investigated.

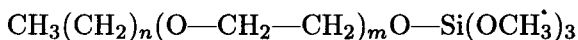
* The project was supported by the National Natural Science Foundation of China.

Received March 6, 1995

EXPERIMENTAL

1. Materials

Inorganic filler used in this work was Kaolin particle, whose size below $2\mu\text{m}$ is no less than 92.6%. PP1330 matrix was obtained from Beijing Yanshan Petrochemical Company. Interfacial modifier with flexible molecular chain was synthesized in our laboratory,



2. Samples

The surface of Kaolin filler was treated with modifier in the presence of alcohol. Untreated or treated Kaolin filler was dried in a vacuum dryer for at least 6 h. Then, the dried filler and PP1330 in definite proportions were mixed by means of high-velocity mixer. PP/Kaolin compounds of different weight fractions of filler φ namely from 0% to 50% and different filler surface treatment were prepared by extruding in a Brabender Plasticorder Model PLE651 equipped with a two-screw extruder at a rotational speed of 30 rpm. Temperature profile of the barrel was 170—210—225—230—205°C (die). These extrudates were pelleted, dried and injected into the standard samples for mechanical tests (injection molding machine Model SZ-160/80NB, made in Ningbo Plastics Machine Factory). The injection molding temperature and injection molding pressure were 220°C and 13.5MPa, respectively.

3. Measurements

(1) Rheology

Rheological measurements were carried out on a plate-and-plate rheometer (RMS-605, made by Rheometrics Company of America) at a temperature of 220°C. Plate-and-plate fixtures (radius 25mm) were adjusted with a gap of about 1.2mm, which varied from sample to sample. The samples were inject-molded from the polymer composites.

(2) Melt index (MI)

The melt index apparatus (μP XRZ-400, made by Jilin University) was used to obtain the melt index values of PP/Kaolin extrudates according to GB3682-83 standard.

(3) Morphology

A scanning electron microscopy, Hitachi S-530 (Japan), was used to observe the morphology of fracture surfaces obtained from samples after their impact tests at room temperature.

(4) Surface energy

The surface energy values of the PP pellet, untreated and treated filler were measured by means of contact angle apparatus Model JY-82, (made in Chende, China), using double-solvent method after these materials were pressed into film.

Parameters are defined by eqs. (1), (2), and (3).

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

$$W_a = 2[(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}] \quad (2)$$

$$W_c = 2\gamma_{LV} \quad (3)$$

where, γ_s is surface energy, γ_s^d is dispersive surface energy, γ_s^p is polar surface energy, W_a is adhesive work, W_c is cohesive work, footmark S, L, V denote filler, polymer, and atmosphere, respectively.

RESULTS AND DISCUSSION

1. Steady rheological behavior

(1) Melt elasticity

Fig.1 is a plot of first normal stress difference (N_1) versus shear rate ($\dot{\gamma}$) of PP and PP/Kaolin systems. It shows that all filled systems, whether the Kaolins are treated or not, have lower N_1 than the virgin resin at the same shear rate. The reason is that the added Kaolin particles act as the physical crosslinking points in the polymer network. It is also seen that, filled samples with various interfacial properties have different melt elasticity. The filled sample by treated Kaolin filler has higher first normal stress difference than that with untreated Kaolin. The reasons for the improvement of N_1 are that the formation of flexible interlayer between PP matrix and Kaolin particles by end group reactions of modifier, namely, the hydrolysis of siloxane group and the physical entanglement of carbon chain group, can improve the interfacial deformability between PP matrix and Kaolin particles.

(2) Melt viscosity

Fig.2 gives plots of apparent viscosity (η) versus shear rate ($\dot{\gamma}$) for PP matrix and PP/Kaolin systems. It is obviously that the apparent viscosity of the filled PP and unfilled PP decrease with increasing shear rate, which indicates the character of pseudoplastic flow of the methods. It can also be seen that, the order of the magnitude of the viscosity of the two Kaolin filled samples and PP melt is as follows:

PP/Kaolin (untreated) > PP > PP/Kaolin (modified)

The apparent viscosity of polymer melt increase rapidly in the presence of Kaolin particles, which is in accord with the common law of rheological behavior for filled sample. For treated Kaolin/PP system, there are two factors affect their apparent

viscosity. First, the modifier treated Kaolin particles have fine dispersion in PP matrix. Second, the formed flexible interlayer by the addition of modifier increases the interfacial deformability between Kaolin particles and PP matrix. The former factor improves the apparent viscosity of filled sample but the latter reduces. According to the results, the possible explanation is that the effect of latter factor is stronger than former.

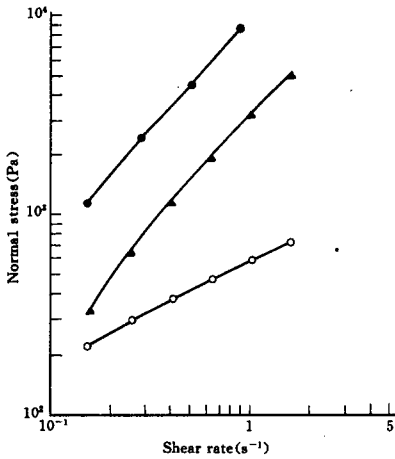


Fig.1 Normal stress (N_1) vs. shear rate (γ) for the PP/Kaolin (100/20) composites and PP
(●) PP; (○) PP/Kaolin (untreated);
(▲) PP/Kaolin (3% modifier)

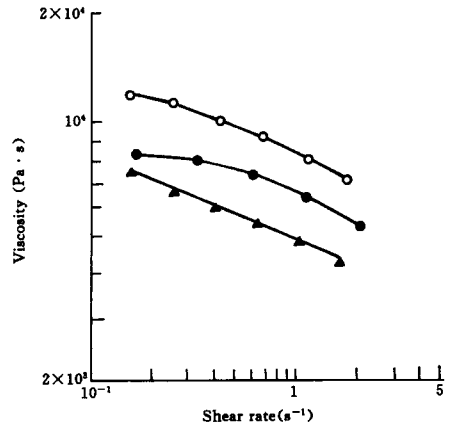


Fig.2 Viscosity (η) vs. shear rate (γ) for the PP/Kaolin (100/20) composites and PP
(●) PP; (○) PP/Kaolin (untreated);
(▲) PP/Kaolin (3% modifier)

2. Dynamic rheological behavior

(1) Storage modulus (G') and loss modulus (G'')

As shown in Fig.3 and Fig.4, the addition of Kaolin particles improves storage modulus (G') and loss modulus (G'') of polymer melt. The result indicates that added filler particles as physical crosslinking points increases the capacity not only in the storage of elastic energy but also in the dispersion of mechanical energy of polymer melt. It is worthwhile to note that the G' and G'' of filled sample decrease obviously while Kaolin filler was treated by modifier. The reasons for the reduction of G' and G'' of filled sample treated by modifier are that Kaolin particles disperse more homogeneously and the interlayer between Kaolin particles and PP matrix becomes more flexible, which increases the activity of PP molecular chains.

(2) Dynamic loss ($\tan\delta$)

Fig.5 gives plot of dynamic loss ($\tan\delta$) versus shear frequency (ω) for PP and PP/Kaolin systems. It shows that all of filled systems, whether the filler was

untreated or treated by modifier, have lower $\tan\delta$ than the virgin resin, and the $\tan\delta$ of untreated one is the lowest. The result indicates that polymer network was damaged by the addition of Kaolin particles, and the above-mentioned damage was restored partly in the presence of modifier.

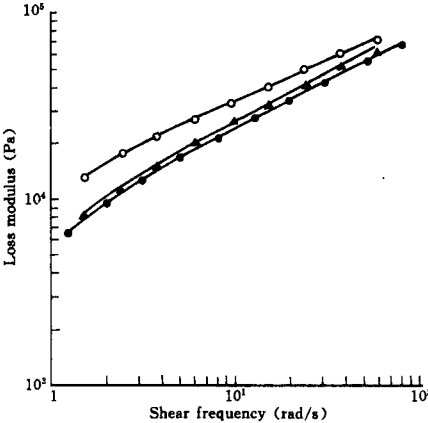
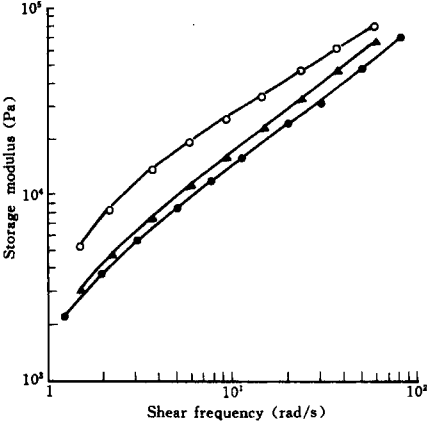


Fig.3 Storage modulus (G') vs. shear frequency for the PP/Kaolin (100/20) composites and PP
(●) PP; (○) PP/Kaolin (untreated);
(▲) PP/Kaolin (3% modifier)

Fig.4 Loss modulus (G'') vs. shear frequency (ω) for the PP/Kaolin (100/20) composites and PP
(●) PP; (○) PP/Kaolin (untreated);
(▲) PP/Kaolin (3% modifier)

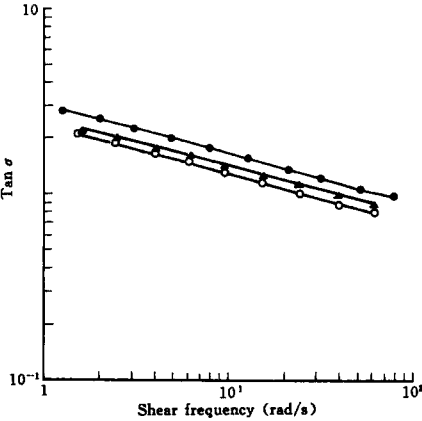


Fig.5 Tendency loss ($\tan\delta$) vs. shear frequency (ω) for the PP/Kaolin (100/20) composites and PP
(●) PP; (○) PP/Kaolin (untreated);
(▲) PP/Kaolin (3% modifier)

Table 1 Data of melt index (MI) for PP/Kaolin (100/20) composites and PP

Component	MI
PP	1.1
PP/Kaolin (untreated)	1.2
PP/Kaolin (3% modifier)	1.7

Table 2 Data of surface energy (γ_s) for PP and Kaolin

Sample	γ_s (mJ/m ²)
PP	29.8
Kaolin (untreated)	71.0
Kaolin (modifier treated)	58.6

3. Melt index

The melt index (MI) data for PP and PP/Kaolin systems were given in Table 1. MI value of PP/Kaolin composite with modifier is larger than that of

PP. Furthermore, this result confirms the conclusion of the apparent viscosity. The higher the *MI* value of filled melt, the better the flow properties of PP/Kaolin composites in the injection-mold processing.

4. Interfacial properties

Table 2 shows data of surface energy (γ_s) of PP and Kaolin filler. It is seen that the differences of γ_s value between modifier treated Kaolin and PP matrix is smaller than that of untreated one. The smaller the differences of γ_s value, the more homogeneous the dispersion of Kaolin particles in PP matrix.

Table 3 shows data of adhesive work (W_a) and cohesive work (W_c) for PP and PP/Kaolin systems. It is seen that the W_a of modifier treated PP/Kaolin system is lower than that of untreated one. This suggests that the formed interlayer by the addition of modifier with flexible molecular chain increases the interfacial deformability between Kaolin particles and PP matrix. It is an advantageous effect to the improvement of the toughness for PP/Kaolin composites, because the decrease of W_a improves the deformability of interlayer in the presence of exterior stress. Data of Izod impact strength (S_I) of PP/Kaolin composite confirmed the conclusion made above.

Table 3 Data of adhesive work (W_a) and cohesive work (W_c) for PP/Kaolin (100/20) composites

Component	W_a (mJ/m ²)	W_c (mJ/m ²)	S_I (J/m)*
PP/Kaolin (untreated)	69.29	59.6	87.7
PP/Kaolin (modifier)	46.83	59.6	343

* S_I : notched Izod impact strength

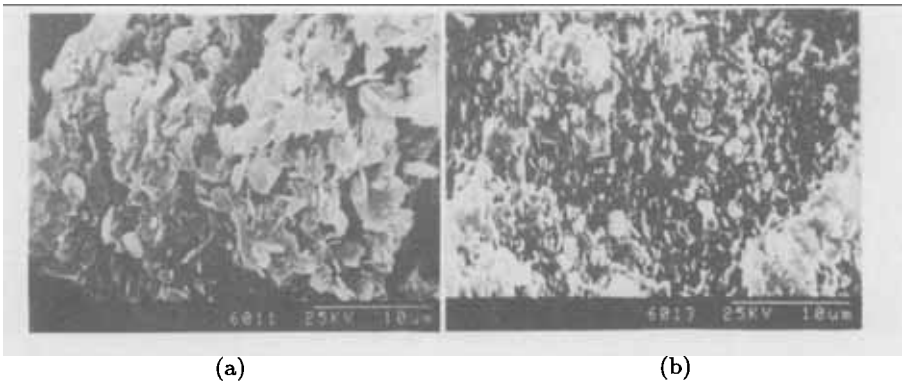


Fig.6 SEM photographs of dispersion of filler for fracture surface of PP/Kaolin composite at room temperature, with Kaolin (a) untreated; (b). 3% modifier treated

5. Morphology

The morphology of dispersion for Kaolin filler was studied by SEM. Untreated Kaolin particles in PP matrix disperse poorly and aggregate together because of their high surface energy. In comparison with untreated one, modifier treated Kaolin particles in PP matrix have finer dispersion and lower aggregative degree between particles. Meanwhile, modifier treated Kaolin particles in PP matrix have two dispersion ways, namely, clubbed particle of single Kaolin particle and spherical particle of PP wrapped Kaolin particle. This spherical particles were formed by the coupling reaction of modifier during processing process. Formed spherical particles are advantageous to the improvement of rheological properties for processing and of toughness for filled composites^[8].

Keywords:

Modifier; Filled polypropylene; Processing rheology

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