

EFFECTS OF COUPLING AGENTS ON THE RHEOLOGICAL BEHAVIOR OF KAOLIN FILLED POLYAMIDE 6*

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ABSTRACT

An experimental study was carried out to investigate the effects of coupling agents on the rheological properties of kaolin filled polyamide 6 (PA6). We have investigated the state of dispersion and interfacial interaction of the filled systems, using scanning electron microscopy (SEM) and Molau test, respectively. It is found that the addition of the coupling agents to the PA6/kaolin (20 wt percent) significantly decreases the melt viscosity and the melt elasticity (first normal stress difference). Moreover, the states of dispersion and the polymer/filler interactions have significant influences on the rheological properties of kaolin/PA6 systems. The rheological behavior of KH550 kaolin/PA6 system is different from that of KH560 kaolin/PA6 system, although chemical reactions have taken place between the surface of KH550 kaolin (or KH560 kaolin) and PA6 matrix during melt processing. This is attributable, in part, to the differences in the state of dispersion of kaolins in PA6 matrix and, to a great extent, to the differences in the extent of chemical reactions that have taken place between the filler and polymer matrix.

The application of coupling agents for the surface modification of fillers and reinforcements in polymers has generally been directed towards improving the mechanical strength and chemical resistance of composites by improving adhesion across the interface^[1,2]. Moreover, the surface modification of the filler particles also affects the rheology (viscosity and elasticity) of the polymer by changing the dispersion of the particles and the interfacial interactions^[3,4]. This paper reports the results of our investigation on the rheology-structure relationships and property-morphology relationships of composites of nylon 6 filled with several kinds of surface-treated kaolin.

EXPERIMENTAL

1. Material

The polymer used in this work was polyamide 6 (PA6), its relative viscosity is 2.6–2.9. The filler is made of kaolin, the average particle size is 0.8 μm , as determined by SEM. The coupling agents used for treating the kaolin are KH550 (Gaixian Chemical Plant), KH560 (Shanghai Yaohua Glass Plant) and titanate coupling agent, NDZ-201 (Nanjing Zhandou Chemical Plant). The chemical structures of the coupling agents are shown in Table 1. The weight concentration of each coupling agent used in the kaolin filler is 1%.

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Table 1 The coupling agent treated kaolin fillers

Coupling agent	Chemical structure
KH550	$(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{NH}_2$
KH560	$(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{CH}_2\text{CH}(\text{O})\text{CH}_2$
NDZ-201	$(\text{CH}_3)_2\text{CHO}-\text{Ti}-(-\text{O}-\text{P}(=\text{O})(\text{OC}_8\text{H}_{17})_2)_3$

2. Melt extrusion

PA6/kaolin composites were prepared by melt extrusion using a Brabender twin screw extruder (35mmΦ) at 30rpm. All composites contained 20 percent by weight of a filler and 80 percent by weight of PA6. The barrel temperatures were 230–240 °C.

3. Rheological measurements

A parallel-plate rheometer (Rheometrics RMS-605) was used at 260 °C to measure (1) steady shearing flow properties, namely, viscosity (η), shear stress (σ_{12}), and first normal stress difference (N_1), (2) oscillatory shearing flow properties, namely, dynamic viscosity (η'), storage modulus (G') and loss modulus (G'').

4. Molau test^[5,6]

Molau test was conducted by mixing about 0.8g of the 20/80 untreated kaolin/PA6 composite with 8ml of 80% formic acid. The mixture was first shaken thoroughly in a beaker and then left alone in a test tube for a long period. We repeated the same procedure with composites of 20/80 KH550 kaolin/PA6, 20/80 KH560 kaolin/PA6, and 20/80/NDZ-201 kaolin/PA6.

RESULTS AND DISCUSSION

1. Steady shearing flow properties of kaolin-filled PA6 composites in the melt state

Figure 1 gives plots of apparent viscosity (η) versus shear rate ($\dot{\gamma}$) for the kaolin/PA6 system with and without coupling agents. It is seen that the viscosity of the composite decreases with increasing shear rate. This behavior is explained by flake interactions, which tend to draw the flakes into orientations unfavorable for flow, leading to high viscosity at low shear rates; but at high shear rates the viscous stresses predominate over particle interaction, alignment is greater and the viscosity becomes less. Moreover, the surface properties of fillers has great influences on the viscosity of the composites with the same loading. The untreated kaolin/PA6 system has a higher melt viscosity than the virgin resin. However, the addition of the coupling agents to the filled systems decreases the melt viscosity in the range of shear rates investigated, the order of the magnitude of the viscosity of the four composites is as follows:

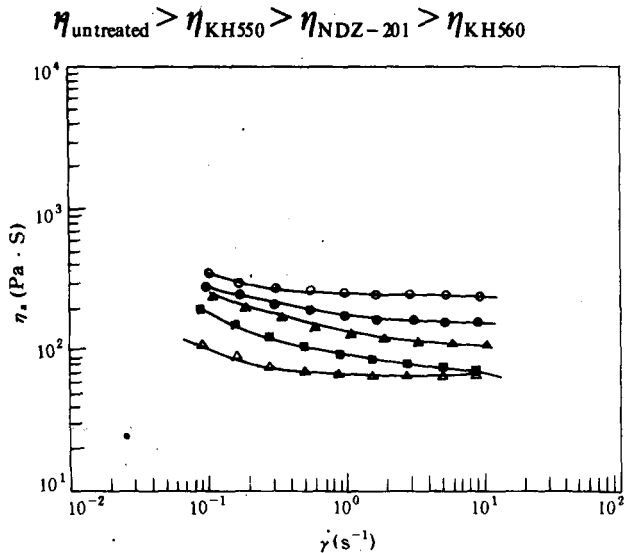


Fig. 1 η_a vs. $\dot{\gamma}$ for the composite system

(●) unfilled PA6; (○) untreated kaolin/PA6=20/80; (▲) KH550 kaolin/PA6=20/80; (△) KH560 kaolin/PA6=20/80; (■) NDZ-201 kaolin/PA6=20/80, 260 °C .

It is also seen that, the melt viscosity of KH550 kaolin (or NDZ-201 kaolin filled PA6) is more sensitive to the shear rate than that of KH560 kaolin system, which relates to the state of dispersion of fillers in PA6 matrix.

Figure 2 gives plots of first normal stress difference (N_1) (a measure of elasticity) versus shear rate ($\dot{\gamma}$) for kaolin/PA6 systems. It shows that all filled systems, whether the kaolins are treated or not, have higher melt elasticity than the virgin resin. But the coupling agents decrease the melt elasticity of the untreated kaolin /PA6 over the limit range of shear rates studied.

The results above indicate that the coupling agents have different influences on the rheological properties of kaolin/PA6 composites. These differences are attributed to the degree of dispersion of fillers in the PA6 matrix and the nature of the interface between filler and matrix^[7].

2. Polymer-filler interaction

In our investigation, Molau test was used to examine the state of interface of

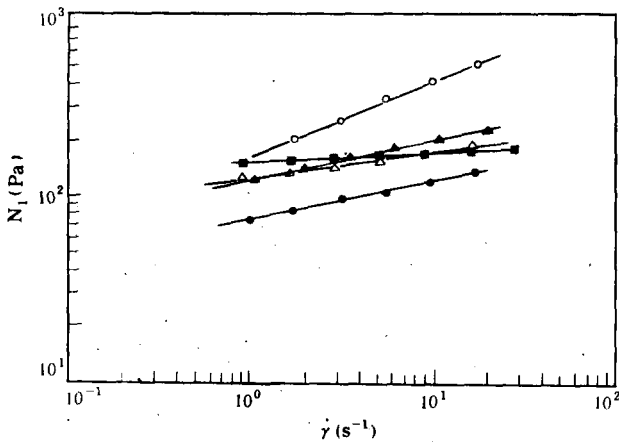
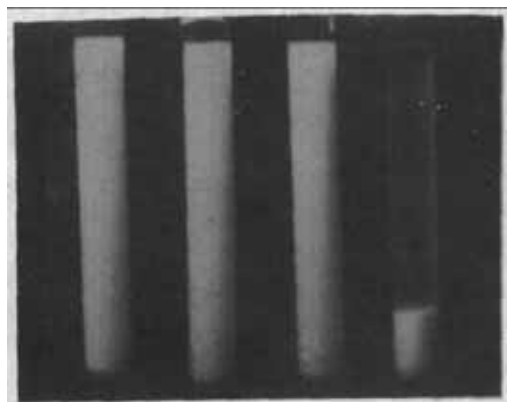


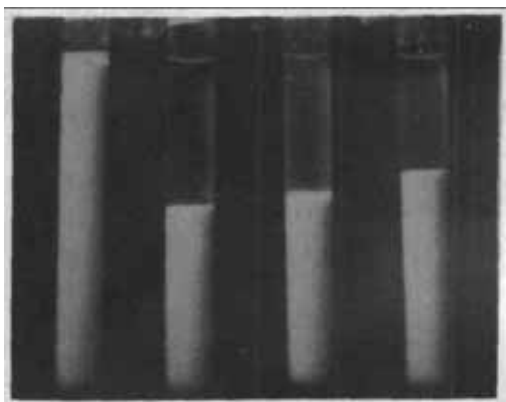
Fig. 2 N_1 vs. $\dot{\gamma}$ for kaolin/PA6 composites
The symbols for the sample are the same as in Figure 1

the kaolin/PA6 composites. Figure 3 shows the results of our Molau test. We observed a phase separation in the 20/80 untreated kaolin/PA6 composite, whereas turbidity persisted in the solution containing the 20/80 KH550 kaolin/PA6 composite, the 20/80 KH560 kaolin/PA6 composite and the 20/80 NDZ-201 kaolin/PA6 composite. Note that, for the untreated kaolin/PA6 system, the lower part of the test tube (the white area) represents a suspension of kaolin particles, and the upper part of the same test tube (the clear area) represents a solution consisting of formic acid/PA6. In comparison, the treated or untreated kaolins were directly mixed in formic acid/PA6 solution in normal atmospheric temperature without processing of melt extrusion, respectively. The mixtures were shaken thoroughly in beakers and then left alone in test tubes for several days, the results are shown in Figure 4. For the untreated kaolin/PA6 mixture, the KH550 kaolin/PA6 mixture, and the KH560 kaolin/PA6 mixture, a phase separation was observed in this case, due to that the basic PA6 molecules interact so strongly with the formic acid that it can not adsorb on the fillers^[8] [see Fig. 4(a), (b) and (c)], whereas turbidity persisted in the formic acid solution containing PA6 and the NDZ-201 kaolin [see Fig. 4(d)]. It is noted that, the NDZ-201 kaolin was suspended in the formic acid/PA6 solution in these two cases [see Fig. 3(d) and Fig. 4(d)]. It is owing to the entanglement between the long hydrocarbon chain in the NDZ-201 and the PA6 molecules, and the complex^[9] between the PA6 (electron donor) and the titanium (electron acceptor) on the surface of NDZ-201 kaolin. By comparison of Fig. 4 with Fig. 3, it indicates that during the melt extrusion of PA6 and KH550 kaolin (or KH560 kaolin), chemical reactions have occurred between the fillers and PA6 matrix, however, no chemical reactions have taken place at the interface between untreated kaolin and PA6. These were confirmed by the infrared spectrum (IR) results^[10].



(d) (c) (b) (a)

Fig. 3 Molau test solutions consisting of 80% formic acid and each of the following composite
(a) Untreated kaolin/PA6; (b) KH550 kaolin/PA6;
(c) KH560 kaolin/PA6; (d) NDZ-201 kaolin/PA6.



(d) (c) (b) (a)

Fig. 4 The dispersive stabilities of the formic acid solutions consisting of PA6 and each of the following filler
(a) Untreated kaolin; (b) KH550 kaolin;
(c) KH560 kaolin; (d) NDZ-201 kaolin.

3. The state of dispersion

It is well-established that the state of dispersion in a filled polymer composite

greatly influences its rheological behavior. Therefore, it is meaningless to considering the rheological behavior of composite without discussing the state of dispersion. It should be pointed out that the state of dispersion in a filled polymer system is determined by the rheological properties of constituent components, the surface properties of the fillers and the processing conditions under which the composites were prepared. Scanning electron microscopy (SEM) was used to investigate the state of dispersion of the kaolin filled PA6 systems. Figure 5 shows representative SEM micrographs of the surfaces of injection—molded specimens of PA6/kaolin composites. In the untreated kaolin filled system, the untreated kaolin is not uniformly dispersed in the PA6 matrix, due to its high surface energy and its agglomeration, and some of which is pulled off clean from the matrix showing no chemical reactions took place between PA6 and the untreated kaolin [See Fig. 5 (a)]. KH560 kaolin has a fine dispersion in the PA6 matrix, whereas

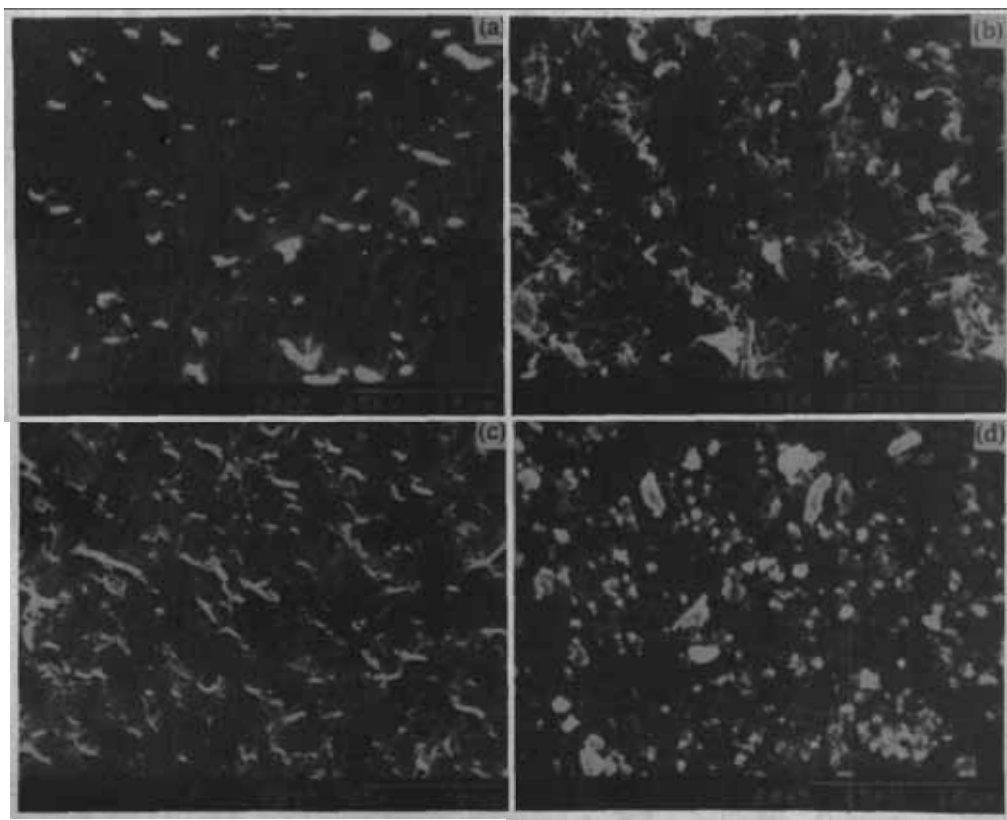


Fig. 5 SEM micrographs of the smooth surface of the kaolin/PA6 composite system:

- (a) Untreated kaolin/PA6; (b) KH550 kaolin/PA6;
(c) KH560 kaolin/PA6; (d) NDZ-201 kaolin/PA6.

KH550 kaolin poor, although their surface energy and their polarity match those of PA6 [see Fig. 5(b) and (c)]. It is attributed to the difference of acid-base properties of the surfaces of the KH550 kaolin and of the KH560 kaolin. The KH560 kaolin with Lewis acidity is easier dispersed in basic PA6 matrix by acid—base interaction than basic KH550 kaolin. NDZ-201 kaolin, not matching PA6 in their respective polarity and surface energy, has a poor dispersion in PA6 matrix.

4. Rheology—structure relationships

Let us examine the observed rheological behavior of the composite systems investigated, from the points of view of the state of dispersion and the chemical reactions taking place between the constituent components in the composites.

Figure 6 gives plots of dynamic viscosity (η') vs. frequency (ω) at 260 °C for kaolin/PA6 composites. Very similar to steady shearing flow properties, precoating the kaolin with coupling agents results in a significant decrease in the viscosity, due primarily to reducing of the surface energy of kaolin on addition of the coupling agents, weakening the interaction of kaolin particles, and improving the compatibility of kaolin particles with PA6 matrix. Another possibility is that

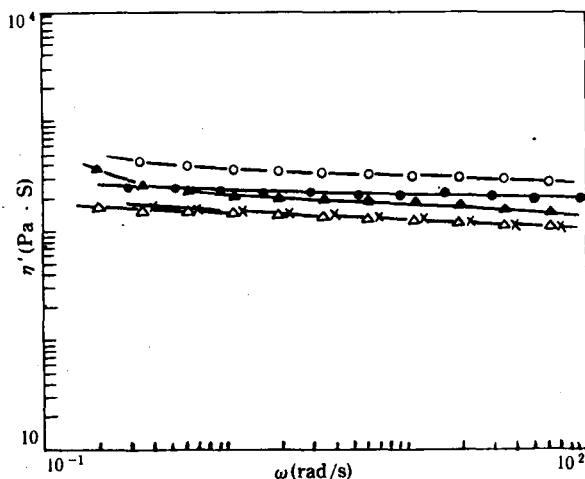


Fig. 6 η' vs. ω for kaolin/PA6 composite system. symbols are the same as in Fig. 1

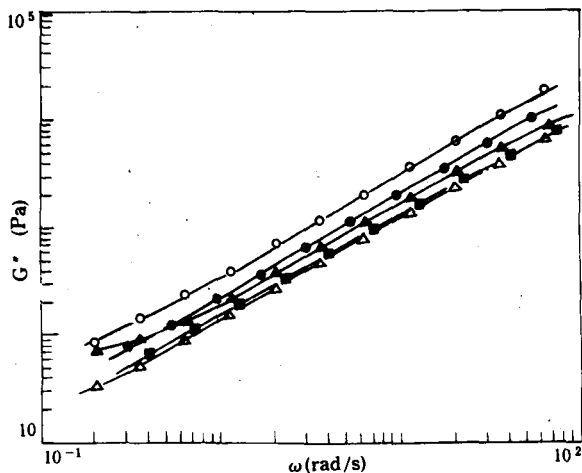


Fig. 7 G' vs. ω for kaolin/PA6 composite system. symbols are the same as in Fig. 1

the coupling agent might have diffused into the polymer matrix, playing the role of an internal plasticizer which would then have decreased the viscosity of the virgin PA6 phase^[11]. It is interesting that the viscosity of KH550 kaolin filled PA6 system is higher than that of KH560 system, despite they all underwent chemical reactions during melt extrusion.

Figure 7 gives plots of dynamic loss modulus (G'') vs. frequency (ω) at 260 °C. It is seen that the use of coupling agents results in a rapid decrease in G'' for kaolin/PA6 composites having the same loading levels, and that the loss modulus is similar in magnitude order to melt viscosity for the four composites.

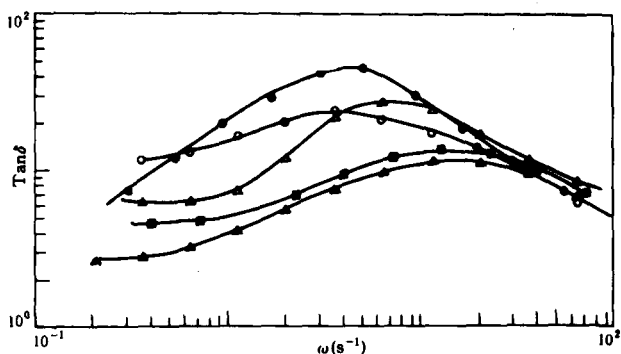


Fig. 8 $\text{Tan}\delta$ vs. ω for kaolin/PA6 composite system. symbols are the same as in Fig. 1.

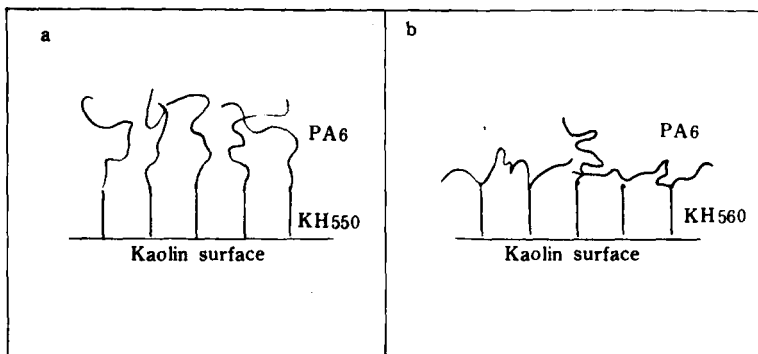


Fig. 9 Interfacial states of (a) KH550 kaolin/PA6 and (b) KH560 kaolin/PA6

Figure 8 gives plots of dynamic loss ($\text{tan}\delta$) vs. frequency (ω) for kaolin/PA6 composites. It is seen that $\text{tan}\delta$ goes through a maximum at a respective certain ω for all composites in the range of frequencies investigated, and that the peaks of $\text{tan}\delta$ for the coupling agent treated kaolin system, all shift to higher ω compared to the untreated kaolin system. It is believed due primarily to the change of interfacial adhesion and the state of dispersion by using the coupling agents. A close examination of Figure 6, 7 and 8 reveals that, compared to 20/80 KH550 kaolin/PA6 composite, KH560 kaolin/PA6 composite having the same component ratio shows a very rapid decrease in η' , G'' and $\text{tan}\delta$, although that they all underwent chemical reactions at interface between kaolin and PA6, during melt processing. These differences are attributable, in part, to the finer dispersion for KH560 kaolin in PA6 matrix compared to KH550 system and, to a great extent, to the differences in the extent of chemical reactions that have taken place between the constituent components in the respective composite systems.

According to the facts that the amino groups at the surface of KH550 kaolin only react with carboxylic group present in the PA6 molecule, whereas the epoxy groups at the surface of KH560 kaolin react with both amino group and amide group in the PA6 molecule during melt extrusion, we deduce that they exhibit such interfacial states as shown in Figure 9. PA6 molecular

chain grafted on the surface of KH550 kaolin by vertical way, namely, there is one grafting point on the KH550 kaolin for one PA6 molecular chain, whereas on the surface of KH560 kaolin in parallel way, namely, there are more than one grafting points on the kaolin surface for one PA6 molecular chain, indicating that the PA6 molecular chains grafted on the KH550 kaolin are more than that on the KH560 kaolin and had a stronger adhesion with the KH550 kaolin in comparison with that of the KH560 kaolin. That is, the extent of interfacial adhesions for the KH550 kaolin system is higher than that of the KH560 system, which partly interpret differences between the rheological behavior of the KH550 kaolin/PA6 system and that of the KH560 kaolin/PA6 system.

Keywords:

Rheology; Interface; Polyamide 6; Coupling agent

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