

Time-Dependent Rheological Behavior of Low-Density Polyethylene White Color Masterbatches Under Dynamic Stress Field

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ABSTRACT: The time-dependent behavior of low-density polyethylene (LDPE) white color masterbatches (WCMBs), which were concentrated suspensions filled with titanium dioxide (TiO_2), was found using dynamic stress rheometer. The viscosity first decreased slightly with time then continuously increased with time, and $T_g(\delta)$ (δ was the angle of loss) decreased with time, which meant the time-dependent behavior of the elastic contribution was more pronounced than that of the viscous contribution. The higher the experimental frequency and temperature, the more pronounced the viscosity increase. However, the higher experimental stress did not lead to pronounced viscosity increase, which was attributed to the existence of small defects at higher stress. The 30 wt % of TiO_2 content was critical to obvious time-dependent behavior. The viscosity increase with time was related to the formation of a hard shell around the melt sample during the test. It was verified by thermogravimetric analysis that the TiO_2 concentration at the outer surface was higher than that at the core of the sample and, because the outer surface contained more TiO_2 , a hard shell was formed, which impeded further deformation of the sample. This was completely different from the other reported systems with time-dependent behavior. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2793–2799, 2002

Key words: color masterbatches; rheology; polyethylene; viscoelastic properties

INTRODUCTION

Color masterbatches are increasingly used in plastics coloring because of their excellent dispersion, slight pollution, and convenience. They are a kind of compound composed of carrier resin, pigments, and dispersant. Many industrial white color masterbatches (WCMBs) are concentrated suspensions filled with titanium dioxide (TiO_2). As a key component in plastics coloring, the rheological behavior of WCMB is very important for

the coloring performance. According to our studies¹ it was shown that the rheological behavior of WCMBs had much in common with the highly filled polymer systems, which showed yield stress, shear thinning, and other characteristics. Up to now their time-dependent rheological behavior has not been reported.

Time-dependent rheological behavior was frequently found in suspension systems.^{2–8} Two time-dependent behaviors, thixotropy and rheopecty, were previously reported. The phenomenon of continuous decrease of apparent viscosity with time under shear was called *thixotropy* and the opposite phenomenon was called *rheopecty*. An extensive review on thixotropy was written by Mewis.⁹ In suspension systems, time-dependent

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behavior was often related to the breakdown or buildup of structures in the dispersions.^{10–17} Schreuder et al.¹¹ studied suspensions of untreated glass particles in dioctylphthalate (DOP), in which time-dependent behavior was found. They considered that during deformation, the solid particles arranged themselves into a closed-packed structure in a part of the system and thus the apparent viscosity increased, which led to an additional accumulation of solid particles and blocked further deformation. Thus, storage modulus and loss modulus continuously increased with time and strain decreased with time under a constant stress. Leighton and Acrivos¹⁸ reported that time-dependent behavior originated from shear-induced diffusion based on their studies on polystyrene spheres in silicone oil. The viscosity decrease was attributed to the shear-induced migration of the particles from the gap between the cylinders in their couette geometry to the reservoir below the cylinders. Time-dependent behavior might also originate from the occurrence of stick-slip of the dispersion in the measuring assembly.¹⁹ These suspensions often contained solvents or other low-molecular liquids.

In this study we present measurements of time-dependent viscosity of a commercial WCMB whose suspending media was high-viscosity melting polymeric matrix [carrier resin was low-density polyethylene (LDPE)] at different temperature, frequency, and stress using a dynamic stress rheometer. To obtain some information about the influence of TiO₂ content on the time-dependent behavior, self-made WCMB with different TiO₂ content was used. The mechanism of the time-dependent behavior was also investigated.

EXPERIMENTAL

Materials

WCMB L071L with 60 wt % TiO₂ content, whose carrier resin was LDPE-F410, was a product of Ngai Hing Hong Plastics Materials Co. (Guangzhou, China). WCMB L0009 with different TiO₂ content (7, 20, 30, 40, and 70 wt %) and with LDPE-F410 as carrier resins were prepared in our laboratory by special equipment that was used to produce high-concentration masterbatches. LDPE-F410 was obtained from TPC Co. Its melt flow index was 17.8 g/10 min, obtained according to ASTM D1238 at 190°C and 5.0 kg. Its melt temperature was 115°C (peak temperature),

which was tested by STA625+ (DSC/TGA simultaneous analyzer made by Rheometric Scientific). TiO₂ was from DuPont (Boston, MA). Its average radius was 0.22 μm and distributed from 0.1 to 0.7 μm according to the information given by the supplier. Its specific gravity was 4.2. Weight loss was less than 0.5% measured by STA625+ at 260°C for 30 min.

Rheological Properties Test

Dynamic rheological behavior was tested on a dynamic stress rheometer (DSR) (SR500, stress-controlled) from Rheometric Scientific. A parallel plate with 25 mm diameter was employed. Particle samples were used and directly compressed on the DSR according to the following procedure. At the experimental temperature, a paper ring (26 mm diameter, 6 mm height) was put on the lower plate of the parallel plate and particles were added. Then the upper plate was lowered until it just contacted the particles. After 15 min the upper plate was lowered until the gap was 3 mm and the paper circle was removed off. The outer edge of the sample was trimmed quickly. After 10 min the upper plate was slowly lowered until the gap was 1 mm and then after another 10 min the test was begun. It was found that 10 min was enough to reach thermal equilibrium. During the whole test period, the sample environment was purged with N₂. No degradation was observed from the color of sample. Storage modulus G' and loss modulus G'' kept constant when pure carrier resin was tested during the whole process, which lasted about 40 min.

At a certain temperature, frequency, and stress the dynamic time sweep test was conducted. Experimental temperatures 180, 190, and 200°C; experimental frequencies 0.5, 10, and 100 rad/s; and experimental stresses 20,000, 40,000, 80,000, and 90,000 dyn/cm² were employed.

Thermogravimetric Test

Thermal gravity was measured by STA625+ from 25 to 600°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Time-Dependent Behavior of WCMB Above Melting Temperature

The time-dependent behavior of L071L and L0009 under dynamic stress field is given in Fig-

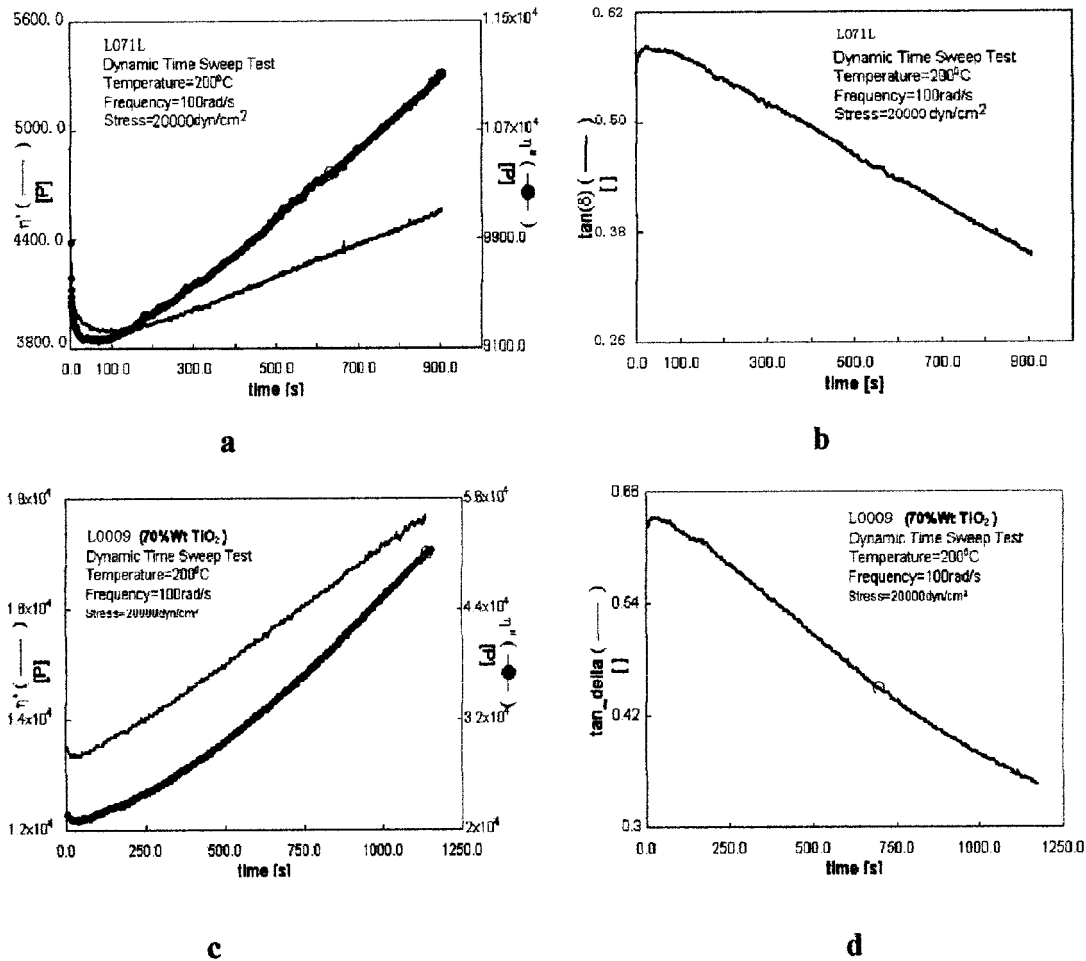


Figure 1 Time-dependent behavior of L071L and L0009 with 70 wt % TiO_2 content. Test conditions are listed in insets.

ure 1. At experimental temperature 200°C , frequency 100 rad/s , and stress $20,000\text{ dyn/cm}^2$, the real viscosity η' and imaginary viscosity η'' were recorded. $T_g(\delta)$ was computed according to the following equation.

$$T_g(\delta) = \eta'/\eta''$$

In Figure 1 time-dependent behavior of WCMB obviously included two periods. During the first period, the viscosity (η' and η'') decreased with time and, after about 60 s, the viscosity increased with time. During this period the increase of η'' was more pronounced than the increase of η' , leading to $T_g(\delta)$ and strain decrease with time, which showed that the elastic contribution to the viscosity was more dependent on time than was the viscous contribution. The viscosity decrease with time during the first period was predictable

because sheet formation, like the wall layer in the capillary, was developing with deformation. However, because of small-amplitude deformation, the development of thin sheet formation was completed in a short time and had much less effect than the wall layer in the capillary on the viscosity. In fact, from the small difference between initial viscosity and the last viscosity of the first period, we concluded that only slight slip occurred in the oscillation shear tests. Obviously, the second period was dominated by a different mechanism.

The time-dependent behavior of WCMB could be caused by the chemical change of the carrier resin such as crosslinking reaction, some change on the interface between the carrier resin and TiO_2 , and the distribution of TiO_2 . There was some crosslinking reaction in the polyethylene resin under thermal influence because of the ex-

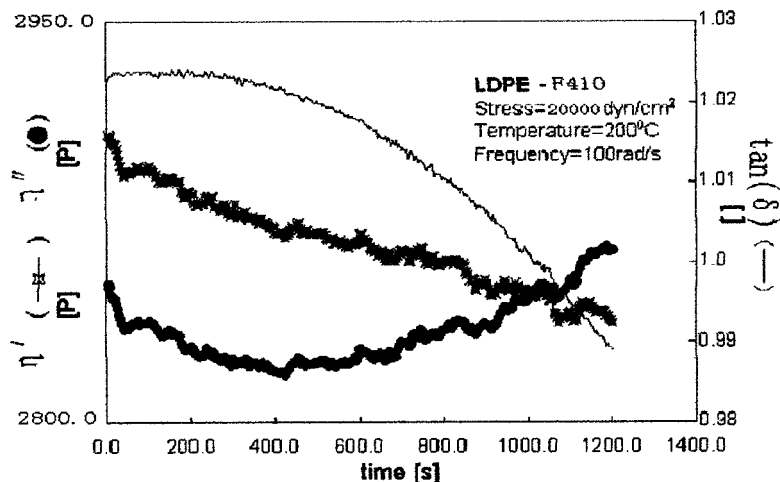


Figure 2 Time-dependent behavior of pure carrier resin LDPE-F410. Test conditions are listed in inset.

istence of initiator,²⁰ which could result in the time-dependent behavior.²¹ However, our results in pure LDPE resin did not prove this. With time a small change of viscosity of pure LDPE resin occurred, as shown in Figure 2. Compared with the pronounced increase in WCMB, the effect of carrier resin of WCMB was excluded.

During the test, after approximately 10 min, a thin hard shell was observed around the melt sample. Therefore it was postulated that it was the formation of the hard shell that impeded the further deformation, which resulted in the viscosity increase with time. The hard shell was related to the higher TiO_2 concentration on the outside of the sample. It was known that during the melt flow, the dispersion phase with higher viscosity and particles tended to move to the area with

lowest shear stress. In the dynamic parallel-plate test, the melt exposed to the outside of the plate (referred to as A) was in the area of lowest shear stress, whereas the melt adjacent to the upper plate (referred to as B) was in the area of highest shear stress. Therefore, the TiO_2 concentration at A should be higher than that at B. TGA results further prove this. After dynamic testing for 0.5 h at 100 rad/s, 200°C, and 20,000 dyn/cm², the melt of L071L from A and B was tested by TGA, the results of which are shown in Figure 3. The TiO_2 concentration in A was higher than that in B, which was in agreement with our hypothesis. The difference of TiO_2 concentration at A and B was small because the hard shell was very thin and the sample used for the TGA test was composed of a higher content of inner sample adjacent to the

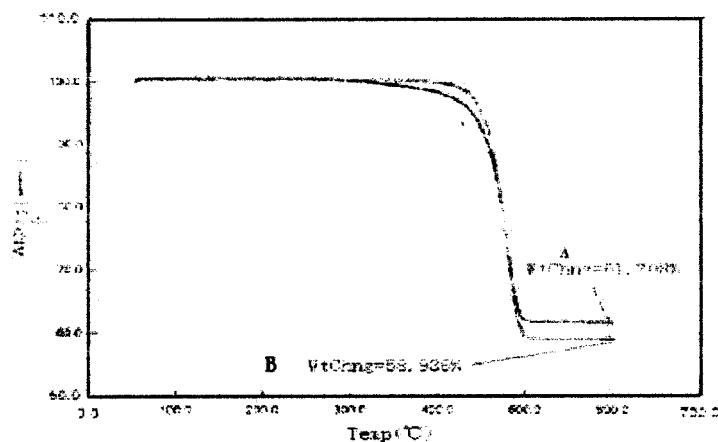


Figure 3 TGA results of melt L071L at highest stress and at lowest stress.

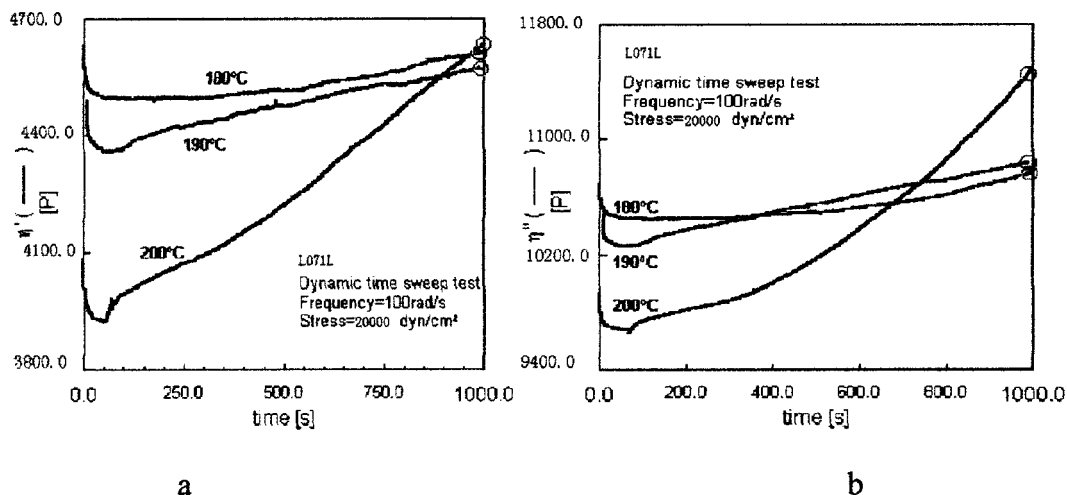


Figure 4 Effect of experimental temperature on the time-dependent behavior of L071L. Test conditions are listed in insets.

hard shell. During dynamic testing, the formation of a hard shell around the sample, which impeded the deformation of melt, was the major reason for the time-dependent rheological behavior of WCMB, which was different from the mechanism reported in suspensions.

Factors Influencing the Time-Dependent Behavior of WCMB

Effect of Experimental Temperature

The viscosity change of L071L with time at dynamic frequency 100 rad/s, stress 20,000 dyn/cm², and three different temperatures, 180, 190, and 200°C, is given in Figure 4. It was found that the higher the experimental temperature, the more pronounced the time-dependent behavior. At 180 and 190°C, the time-dependent behavior was not apparent, whereas at 200°C the time-dependent behavior was very pronounced. The higher the experimental temperature, the faster the migration behavior, resulting in higher TiO₂ concentration at the outside surface and more pronounced impediment of the deformation of melt. In Figure 4, the critical time needed for the viscosity increase was shorter at 200°C than at either 180 or 190°C.

Effect of Experimental Frequency

At 200°C and three different frequencies, 0.5, 10, and 100 rad/s, the time-dependent behavior of L071L was tested, the results of which are shown in Figure 5. K was the viscosity ratio at 1000 and

500 s. At different frequencies, the K of real viscosity increased from 0.985 at 0.5 rad/s to 1.09 at 100 rad/s, and the K of imaginary viscosity increased from 0.976 to 1.15. Therefore it was concluded that the higher the experimental frequency, the more apparent the viscosity increase, which was similar to the effect of experimental temperature.

Effect of Experimental Stress

At 200°C, 100 rad/s, and at four different stresses, 20,000, 40,000, 80,000, and 90,000 dyn/cm², the test of L071L was recorded. The results are shown in Figure 6. It was found that the viscosity increase with time lessened with the increase of stress, which was contrary to the concept that the higher the stress, the more apparent the migration effect of TiO₂. Higher stress led to higher strain, resulting in the emergence of small defects in the sample. These defects, which could not recover themselves, led to the decrease of viscosity, which lessened the effect of time-dependent behavior.

Effect of Content of TiO₂

At 200°C, 100 rad/s, and 20,000 dyn/cm², the time-dependent behavior of WCMB L0009 with different TiO₂ content was studied, as shown in Figure 7. It was found that the WCMB with TiO₂ content less than 30 wt % did not display apparent time-dependent behavior, whereas when the TiO₂ content was more than 30 wt %, the real

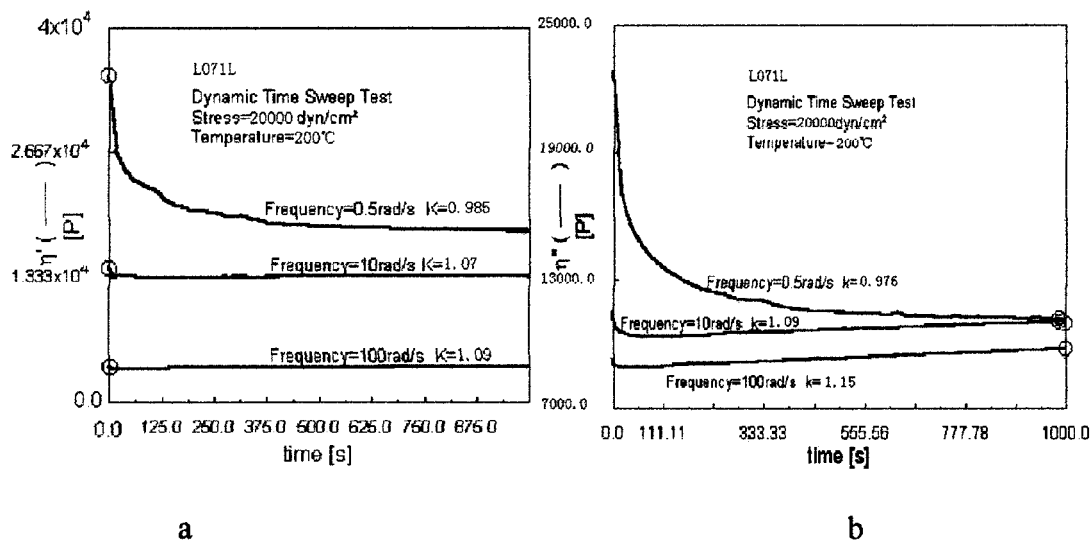


Figure 5 Effect of experimental frequency on the time-dependent behavior of L071L. Test conditions are listed in insets. K is the viscosity ratio at 1000 and 500 s.

viscosity increased 200 P from 500 to 1000 s; the imaginary viscosity increased 650 P.

Moreover, Figure 7 also shows that when the TiO_2 content was less than 30 wt %, the real and imaginary viscosities of WCMB were not very dependent on TiO_2 content. However, when the TiO_2 content was greater than 30 wt %, the viscosity suddenly increased. Therefore 30 wt % TiO_2 content was the critical content for the viscosity increase and pronounced time-dependent behavior.

CONCLUSIONS

Pronounced time-dependent behavior, found in commercial and self-made LDPE white color masterbatches including white pigment TiO_2 was attributed to the higher TiO_2 content on the outside surface of the sample, resulting in the formation of a hard shell that impeded the deformation of the sample, and led to the increase of viscosity with time.

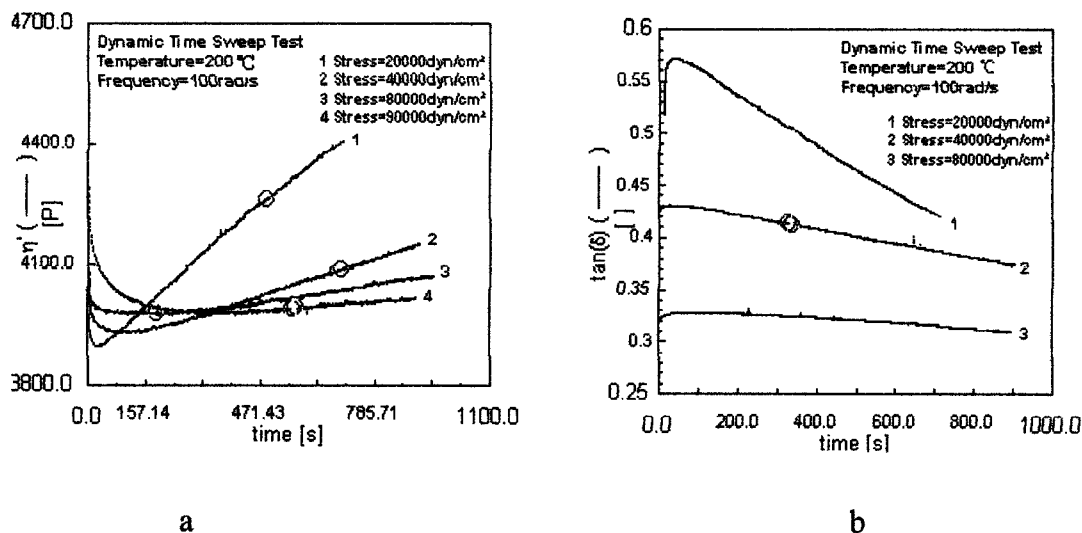


Figure 6 Effect of stress on the time-dependent behavior of L071L. Test conditions are listed in insets.

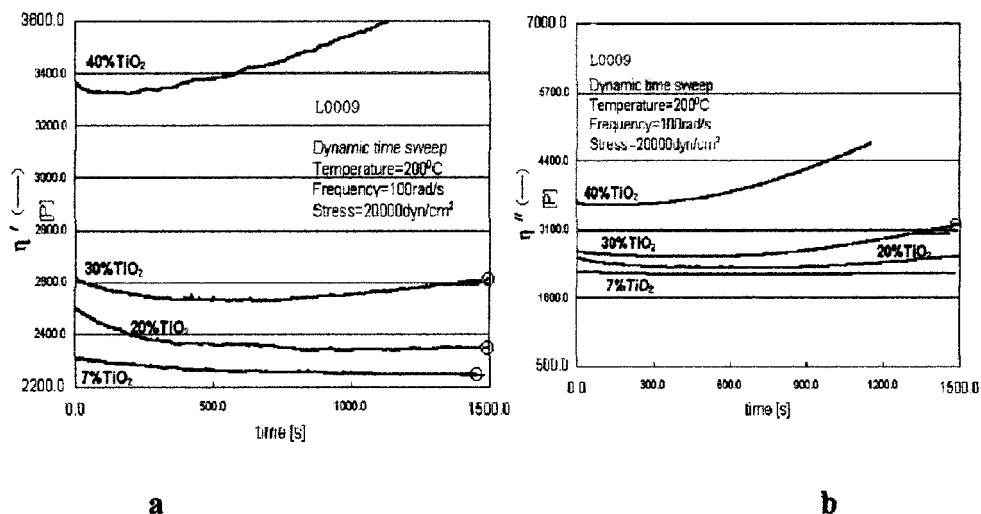


Figure 7 Effect of TiO₂ content on the time-dependent behavior of L0009. Test conditions are listed in insets.

The time-dependent behavior was influenced by the temperature, frequency, stress, and TiO₂ content. The higher the experimental frequency and temperature, the more pronounced the viscosity increase. However, higher stress did not lead to a more apparent increase in viscosity, which was attributed to the formation of small defects at higher stress. Through the test of time-dependent rheological behavior of self-made white color masterbatches L0009 with different TiO₂ contents, it was found that the 30 wt % TiO₂ content was critical for the time-dependent behavior.

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