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The Effects of Storage Temperature on the Rheological Properties of Poly(1-oxotrimethylene) Spinning Dope in an Aqueous Solution of Complex Metal Salts

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ABSTRACT

To investigate the effects of storage temperature on the physical properties of the solution of poly(1-oxotrimethylene) in an aqueous solution of complex metals, the rheological properties of the solution were examined in terms of temperature and time. Stepwise shearing experiment explained the physical state of the solution. Rheological responses suggested that the solution formed a reversible get at 50^{o}C but an irreversible gel at 90^{o}C.

INTRODUCTION

Poly(1-oxotrimethylene) (POTM) fiber is one of the high-performance fibers which can be used as a reinforcement of composite materials.

POTM was first synthesized as early as 1950s. POTM fiber has many merits such as excellent mechanical properties, excellent chemical resistance, good rubber adhesiveness and competitive price. So it is expected to be used as mechanical rubber goods including high-performance tire-cord and other industrial materials. In spite of long developmental history and high cost-performance, however, the POTM fibers have not been commercialized partly because of policy and partly because of technical problems.

POTM fibers are prepared from the aqueous solutions of complex metal salts. It is recognized that the spinning dope of POTM in the solvent is not stable. In addition, it is expected for highly polar polymer solutions that the rheological properties of the solution are greatly affected by storage temperature. Hence it is prerequisite to understand the rheological properties of the spinning dope to design spinning process. In this study we investigated the rheological properties of POTM in the aqueous solution of complex metal salts in terms of shear rate, temperature, and time.

EXPERIMENTAL

Materials

POTM powder was provided from Hyosung Co. (Korea), whose intrinsic viscosity was 5.0 respectively. EP-grade lithium chloride, calcium chloride and zinc chloride were purchased and used without further purification.

Preparation of POTM Solution

POTM powder was mixed in the mixed solutions of calcium chloride / zinc chloride / lithium chloride / distilled water. The concentration of polymer was 8 wt%, and the solution was heated to 55^{o}C and homogenized at the temperature with vigorous stirring for 2 hours in a dissolving tank. It had a real significance to generate pressure during stirring. A transparent solution guaranteed its complete dissolution.

Rheological Measurement

The dynamic viscosity of 8 wt% POTM solutions was measured by Advanced Rheometric Expansion System 2000 (ARES, Rheometric scientific). Parallel-plate geometry with a diameter of 50 mm was adopted. The plate gap and strain level were 1 mm and 5%, respectively. The outside of both two plates was sealed with a heavy mineral oil (Aldrich Co.) to prevent the evaporation of the solvent during rheological measurement. Dynamic frequency sweep test was conducted over the frequency range of 0.05 to 200 rad/s between 30 and 90°C. In addition, time sweep test during stepwise shearing at 1 and 10 rad/s was performed to investigate the time dependent gelation behavior of the solution dope. First, the time sweep experiment of the POTM solution was carried out for 600 seconds. Then solution was relaxed for another 600 seconds. This procedure was repeated three times.

RESULTS AND DISCUSSION

Figure 1 shows the dynamic viscosity curves of 8 wt% solution of POTM in the aqueous solution of complex metal salts at various temperatures. At 30°C this solution seems to form a soft gel. Hence it gives rise to high viscosity. This soft gel proves a reversible gel because it changes to a liquid phase when it is heated to 50°C. Hence, viscosity is decreased and lower Newtonian region is observed at 50°C.

The fact that the gel at 50°C is reversible is further ascertained by stepwise time-sweep experiment. Figure 2 shows time dependence of storage modulus of POTM solutions at 50°C for repeated stressing. Storage modulus was measured for 600 seconds at a constant frequency of 10 rad/sec, then shearing was stopped and relaxed for 600 seconds. This experiment was repeated three times.

As shown in Figure 2 amost of the data obtained during 1^{st}, 2^{nd} and 3^{rd} sweep experiment fall on a master curve. Further, the storage modulus does not change with shearing time by stepwise shearing. This implies that there is little change in gel phase morphology under shear. This results from the fact that the deformation and recovery of the gel are well balanced, and there is no accumulation of deformation during the experiment. That is, the stepwise stresses do not produce permanent deformation. Consequently, little change of storage modulus in the step-stress-relaxation experiment suggests that the gel at 50°C is a reversible gel.

It is also noted in Fig. 1 that the dynamic viscosity of POTM solution is rising again with increasing temperature from 50 to 90°C, particularly in the range of low frequencies. This means that the solution system produces more and more gels when heated from 50 to 90°C. In fact, a notable Bingham behavior is observed at 90°C.

The storage modulus (G′) of POTM solution is plotted against the loss modulus (G′) in Figure 3. Theoretically, plotting of logG′ against logG″ gives rise to a single master curve with slope of 2 in irrespective of measuring temperature if the polymer system is isotropic and homogeneous. In the case of POTM solution, however, the so-called Cole-Cole plot gives rise to several curves of different slopes of ca. 1.7 as shown in Figure 3. It means that the POTM solution

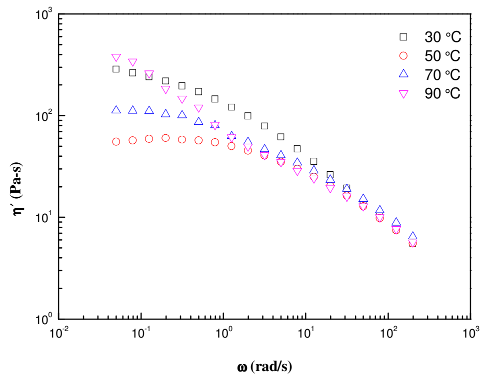

Fig.1. Dynamic viscosity curves of POTM solution at various temperatures.

system is not homogeneous. That is, the slope should be 2 if the shearing does not produces a permanent deformation due to the accumulation of irreversible deformations.

A more close examination of Figures 1 and 2 reveals that there is an inflection point in the curve obtained at 90°C. This seems to result from a phase change by applied stress, which results in the formation of irreversible gel. This can be clearly verified by stepwise shearing experiment at 90°C as shown Figure 4. It is seen that the storage modulus is continuously increased with shearing time. In comparison with Figure 2 one can say that the gel formed at 50°C is reversible but that formed at 90°C is irreversible.

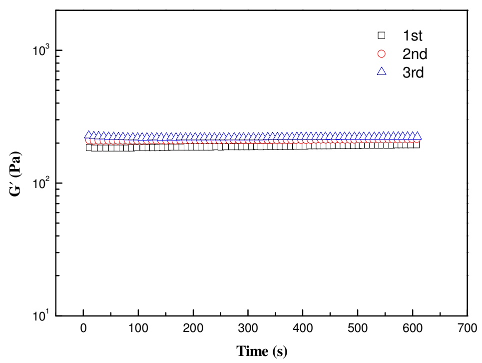

Fig.2. Time dependence of storage modulus of POTM solution at 50°C

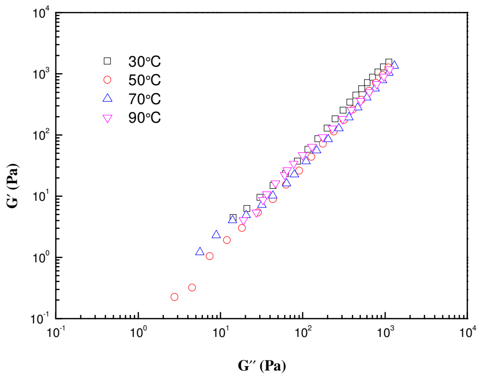

Fig.3. Modified Cole-Cole plot of POTM solution at 50°C.

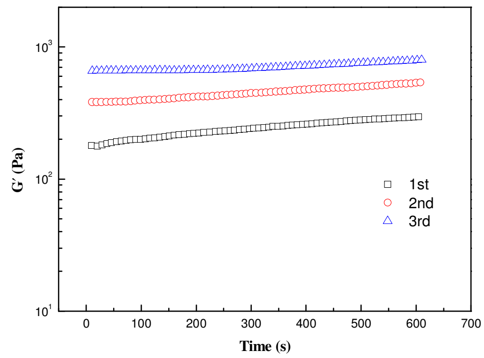

Fig.4. Time dependence of storage modulus of POTM solution at 90°C.

CONCLUDING REMARKS

The rheological responses of the solution dope of POTM in the aqueous solution of complex metal salts ascertained that the solution formed a reversible gel at 50°C but an irreversible gel at 90°C. This may offer a basic information on the design of the spinning system of POTM.

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