The Viscoelastic Properties of PP/Glass Fiber Composites in Molten State

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Synopsis

The molten viscoelastic behavior of polypropylene/glass fiber composites (FRPP) were investigated under steady state and dynamic state. The steady viscosity was measured from both cone-plate rheometer and capillary flow tester. The dynamic viscoelastic properties were measured from cone-plate rheometer. The variation of molten viscoelastic behavior of FRPP with the composition, temperature, shear rate, and coupling agent are examined and discussed in this paper. Die swell phenomena of FRPP at different temperatures, shear rates, and compositions were also observed. The results were that the viscosity and modulus of FRPP increased with increasing the fiber content in FRPP. Pretreatment of glass fibers with coupling agent would enhance the interfacial adhesion between polypropylene and fibers, and the fiber length in FRPP was longer on the average. Die swell of FRPP significantly decreased by the presence of glass fibers.

INTRODUCTION

Polymer products made through different processes have been widely applied in various fields by the characteristics of low-density, high corrosion resistance and easy processing. But the mechanical strength, dimensional stability, and heat deflection temperature of polymer materials are generally not high enough for them to be used as engineering materials. The fiber-reinforced plastics (FRP) have been developed to meet the requirement of engineering uses. The most practical fibers for this purpose are glass fiber, carbon fiber, and kevlar fiber in types of chopped strand mat, chopped strand, roving, and woven roving. The mechanical properties of FRP vary mainly with the processing condition, fiber type, polymer, and composition.[1-3] There have been many papers published on the mechanical properties of FRP in which the fillers are chopped glass fibers. Some of them are theoretical and others experimental. It has been known that polymers filled with chopped glass fibers will increase the stiffness, tensile strength, heat resistance, and dimensional stability.[4]

Recently many works have focused on studing the molten viscoelastic properties of polymer composites. L. A. Utracki[5,6] discussed the zero shear rate viscosity (η_0) of fiber reinforced polymers at different compositions. Chan[7] studied the viscosity, normal stress, and elongational viscosity of FRPE and FRPS with different rates of strain. Kitano and T. Kataska[8] utilized different processes to make FRPE and discussed the length distribution of fibers in FRPE. Han[9] found the viscosity increased when coupling agent was added to PP/glass bead composites. In this work, we study the molten

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viscoelastic behavior of PP/glass fiber composites (FRPP) in steady and dynamic states. The fiber content, temperature, and shear rate will change the viscoelastic properties of FRPP. A certain type of coupling agent is added in these composites in order to improve the interfacial interaction between PP and glass fiber, and then increase the mechanical strength. The effect of coupling agent on the steady or dynamic viscoelastic properties of these composites is observed in our experiments.

Most molten polymers behave like the pseudoplastic fluid, here we define the viscoelastic behavior of FRPP melt in the same way, i.e., the steady viscosity in high shear rate range can be expressed as the form of power law.

$$\eta = m\dot{\gamma}^{n-1} \tag{1}$$

where m and n are parameters dependent on polymer structure, temperature and fibers. As shear rate decreases to a very low value (~ 0), the viscosity will go toward a maximum value, η_0, zero shear rate viscosity. η_0 is again variable with polymer structure, temperature, and fibers. Similarly, a complex viscosity (η^*) and complex modulus (G^*) are obtained as follows from dynamic test:

$$G^* = \frac{\tau^*}{\gamma^*} = \frac{\tau_0}{\gamma_0}(\cos\delta + i\sin\delta) = G' + iG'' \tag{2}$$

$$\eta^* = \frac{\tau^*}{\dot{\gamma}^*} = \frac{\tau_0}{w\gamma_0}(\sin\delta - i\cos\delta) = \eta' - i\eta'' \tag{3}$$

Where γ^* is the imposed strain, τ^* is the resulting stress, and δ is the phase angle between strain and stress. The relationship among η, η', η'', G', G'', and $\tan\delta$ with varying composition of FRPP will be experimentally determined and discussed in this work.

Die swell or extrudate swell of polymers can be an indication of dimensional stability of the materials upon processing. A large amount of research has been done on this problem. Die swell of polymer is decreased largely by filling in fibers or fillers.[10-12] Chan, White, and Oyanagi[7] studied the relation among normal stress coefficient, viscosity, and die swell of FRPS and FRPE. Graessley[13], Racin and Bogue[14] found the die swell of PS increased with increasing the molecular weight and its distribution. In this paper, die swell phenomena for FRPP flowing through a capillary tube are investigated experimentally. The variation of die swell with the shear rate, temperature, and compostion of FRPP are discussed.

EXPERIMENTAL

Materials

Isotactic polypropylene (MI = 5.0 g/10 min) and E-glass fiber of 6 mm chopped strand were the matrix and reinforcing agent of the composities studied. N-β-(Aminoethyl)-γ-aminopropyl trimethoxysilane (KBM 603) was selected as the coupling agent for these composites.

Manufacture of FRPP Specimens

Glass fibers were heated in an oven at 650°C for 30 minutes to burn out all sizing agents over the fiber surface and to obtain the so called clean fibers. Some of the clean fibers were soaked in the 2 wt% aqueous solution of silane couping agent for 10 min and dried at 80°C for over 10 h. PP and glass fibers (either clean or treated with coupling agent) in various weight ratios were then mixed and blended through screw extruder, cut to grains, and hot pressed under 250 kg/cm^2 and 230°C for about 10 min to form a FRPP sheet 2 mm thick. The symbol FRPP 1502 means the fiber-PP composite containing 15 wt% fiber pretreated with 2 wt% silane aqueous solution.

Measurement of Steady Viscosity

A cone-plate rheometer was used to measure the steady viscosity of molten FRPP at low shear rate ($\dot{\gamma} = 10^{-3} \sim 10 \text{ s}^{-1}$). A capillary flow tester was used to measure the steady viscosity of molten FRPP at high shear rate ($\dot{\gamma} = 10 \sim 10^4 \text{ s}^{-1}$). The effects of temperature, shear rate, coupling agent, and fibers on the steady viscosity of FRPP were investigated.

Measurement of Dynamic Viscoelastic Properties

A cone-plate rheometer was used to measure the dynamic modulus, dynamic viscosity, and loss tangent of molten FRPP at different frequencies ($\omega = 10^{-2} \sim 10 \text{ s}^{-1}$) and different temperatures. The effects of temperature, frequency, coupling agent, and fibers on the dynamic viscoelastic behavior of molten FRPP were examined.

Die Swell

A capillary flow tester was also used to study the die swell of FRPP under different experimental conditions. The diameter of extrudate after cooling in air (De) was measured with a micrometer. The effects of temperature, shear rate, coupling agent, and fiber on the die swell of FRPP were observed.

Fiber Length Distributions in FRPP

Most fibers were broken seriously by friction and twisting force in extruder during blending process for making FRPP. The viscoelastic behavior of FRPP was influenced by the fiber length distribution in it. To determine the fiber length distribution in FRPP, the weighted FRPP specimen was heated in an oven at 650°C to burn out PP and the remaining fibers were wetted in glycerine, spread on a glass plate, dried, and observed through a microscope. The lengths of at least 500 fibers were measured carefully in each experiment. The fiber length distributions were then determined under different experimental conditions.

RESULTS AND DISCUSSION

The dependence of viscosity of molten FRPP 1502 on temperature in steady state is shown in Figure 1. The viscosity was lower at higher temperature due to increasing the molecular mobility and free volume of FRPP. In low shear

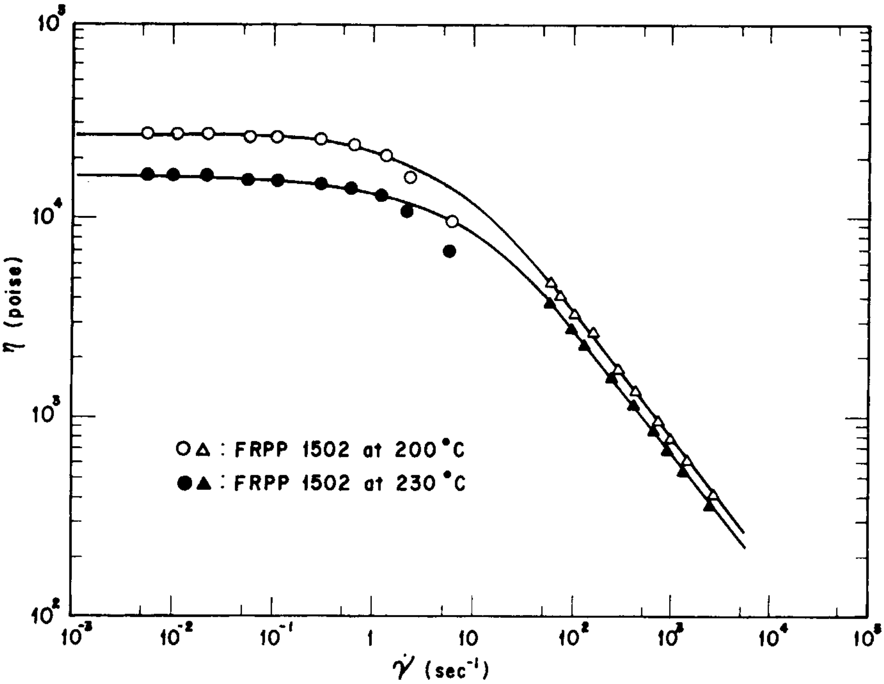

Fig. 1. Dependence of viscosity on shear rate for FRPP 1502 at different temperatures. ○ ● represent data taken from cone-plate rheometer, △ ▲ represent data taken from capillary flow tester.

rate region ($\dot{\gamma} < 0.1\ s^{-1}$), η reached toward a maximum value, η_0, which was very temperature sensitive. In high shear rate region ($\dot{\gamma} > 10^2\ s^{-1}$), η decreased with increasing the shear rate almost linearly in log-log scale. It was again temperature dependent but less sensitive. The viscosity data obtained from both the cone-plate rheometer and the capillary flow tester were linked up well except at $\dot{\gamma} = 1\ s^{-1}$ and $2\ s^{-1}$ points, which were around the limiting operative shear rate in the cone-plate rheometer. In dynamic test, we obtained several viscoelastic properties: dynamic viscosities η' and η'', dynamic moduli G' and G'', and loss tangent $\tan\delta$. The dependences of η' on temperature and frequency (ω) for FRPP 1502 are shown in Figure 2. Within our experimental ω range obtained from the cone-plate rheometer, η' slightly decreased with increasing the frequency and tended toward a maximum value η'_0 at very low ω. The relation of η' vs. ω resembled that of η vs. $\dot{\gamma}$. η' was also very temperature sensitive. Figure 3 showed the plot of η''/ω as a function of frequency at different temperature for FRPP 1502, η''/ω decreased monotonously with increasing the frequency. There were no limits existing at very low ω. η'' was lower at higher temperature too. Figure 4 showed the storage modulus G' as a function of frequency at different temperatures for FRPP 1502. G' increased with increasing the frequency. In high frequency condition, polymer behaved more like an elastic-solid material, hence higher modulus was obtained. However, with temperature rises, polymer would flow more easily with lower viscosity, hence it represented a smaller modulus. Figure 5 showed the loss modulus G'' as a function of frequency at different tempera-

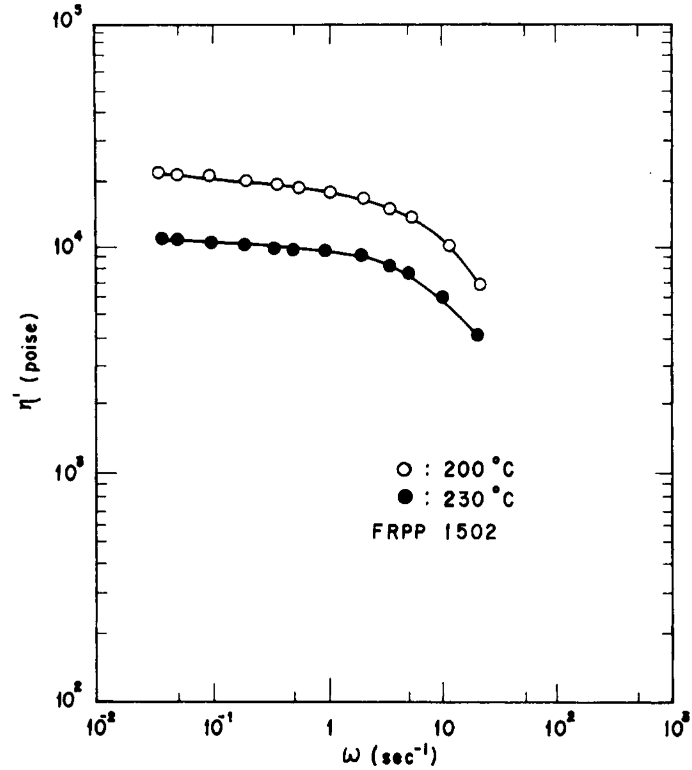

Fig. 2. Dynamic viscosity η' as a function of frequency for FRPP 1502 at different temperatures.

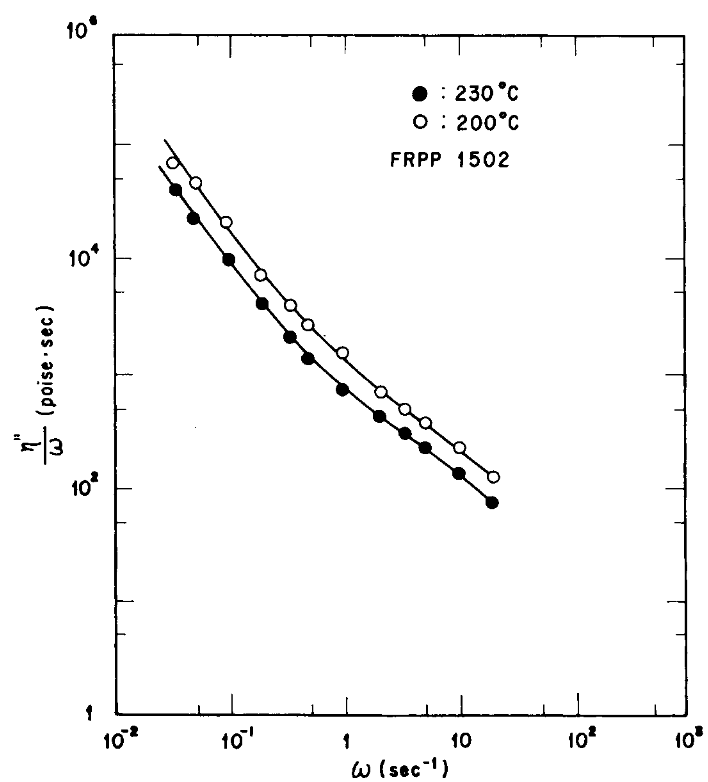

Fig. 3. Plot of η''/ω as a function of frequency for FRPP 1502 at different temperatures.

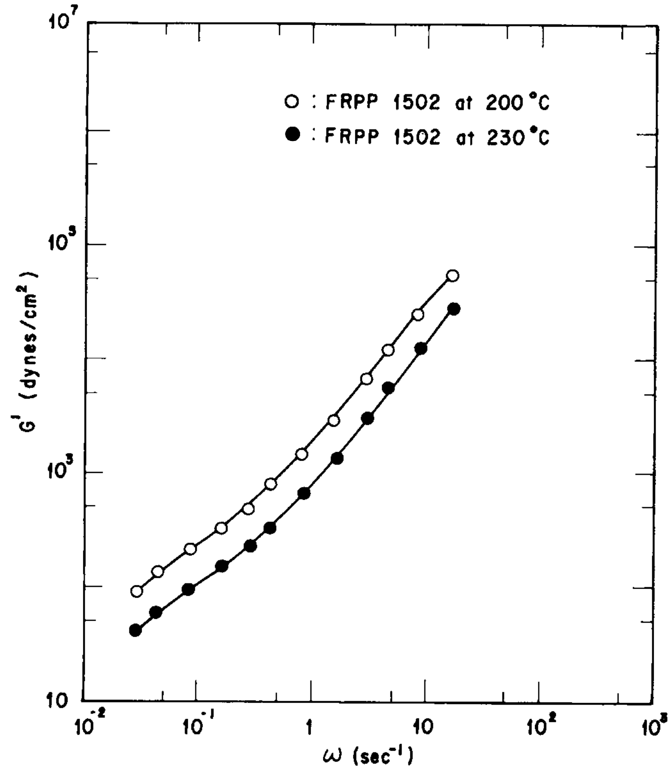

Fig. 4. Storage modulus G' as a function of frequency for FRPP 1502 at different temperatures.

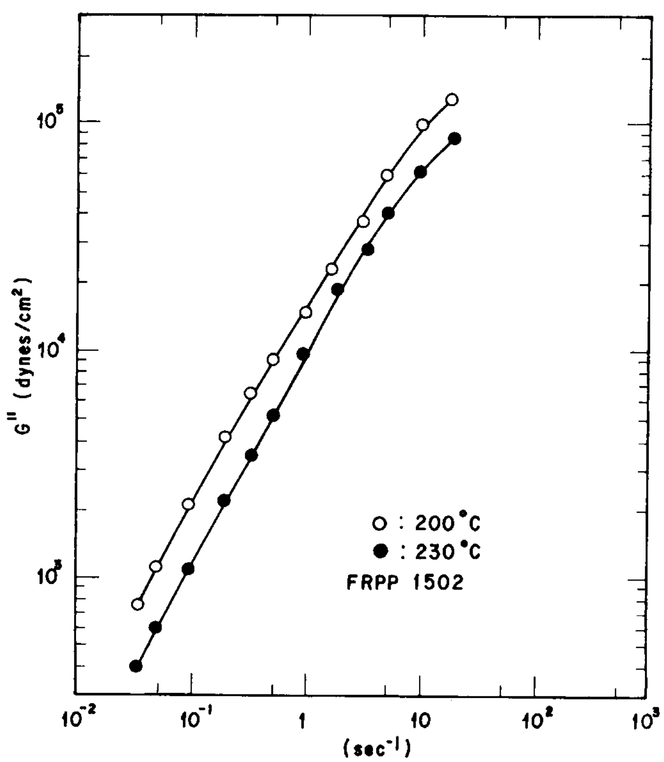

Fig. 5. Loss modulus G'' as a function of frequency for FRPP 1502 at different temperatures.

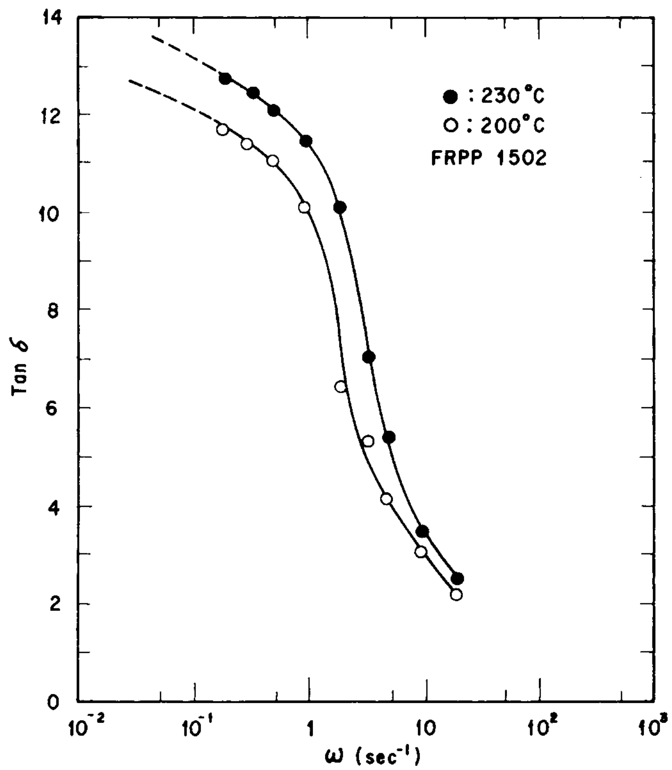

Fig. 6. Loss tangent as a function of frequency for FRPP 1502 at different temperatures.

tures for FRPP 1502. The relationships among G'', ω, and temperature were like those of G', ω and temperature. In our experimental frequency range, curves of modulus versus frequency at two temperatures were almost parallel to each other. Figure 6 showed the dependences of loss tangent $\tan\delta$ on the frequency and temperature for FRPP 1502. $\tan\delta$ decreased sharply with increasing the frequency. As mentioned above, polymer was more rigid at high frequency condition, so $\tan\delta$ decreased significantly. The $\tan\delta$ of an ideal elastic solid should be zero because stress and strain were completely in phase. When temperature rises, polymer would behave more like a liquid and $\tan\delta$ would increase. From Figure 6, the $\tan\delta$ was found to be more temperature sensitive at low ω region. As in Figure 1 ~ Figure 6, it was apparent that the variation of viscoelastic behavior with the temperature, shear rate, and frequency for the FRPP composite followed the same trend as that of homopolymers.

The main objectives of filling glass fibers into PP matrix were to improve the mechanical strength and dimensional stability of PP. However, the viscosity of it increased upon processing and the viscoelastic properties were changed due to the existence of fibers. In this work, we investigated the variation of steady viscosity, dynamic viscosity, dynamic modulus, and $\tan\delta$ with the fiber content, coupling agent, shear rate, and frequency for FRPP. Figure 7 showed the dependence of steady viscosity on shear rate for FRPP with different fiber contents. The viscosity increased with increased fiber

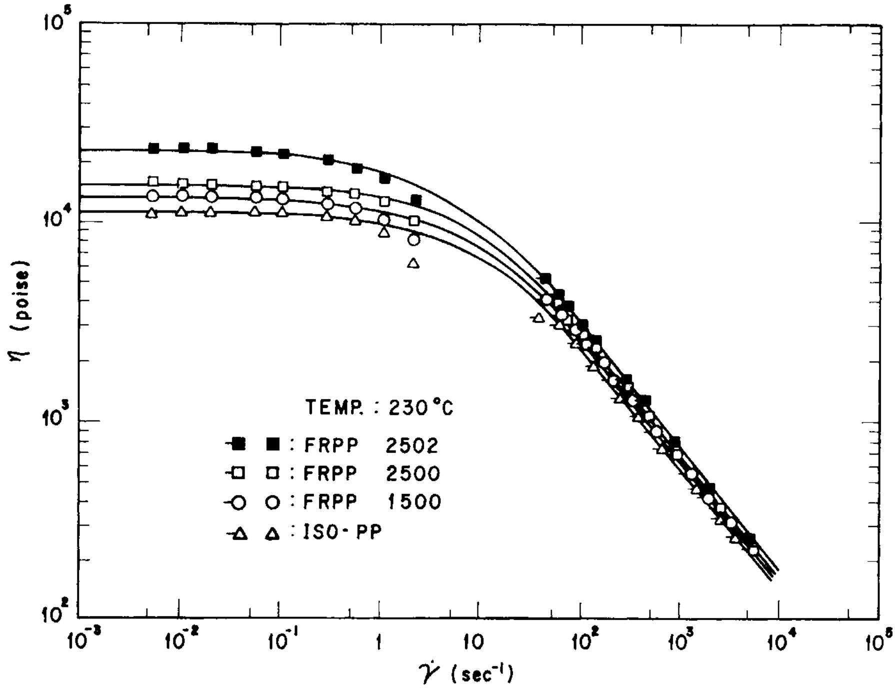

Fig. 7. Dependence of viscosity on shear rate for FRPP with different fiber contents. △, ○, □, ■ represent data taken from cone-plate rheometer, -△, -○, -□, -■ represent data taken from capillary flow tester.

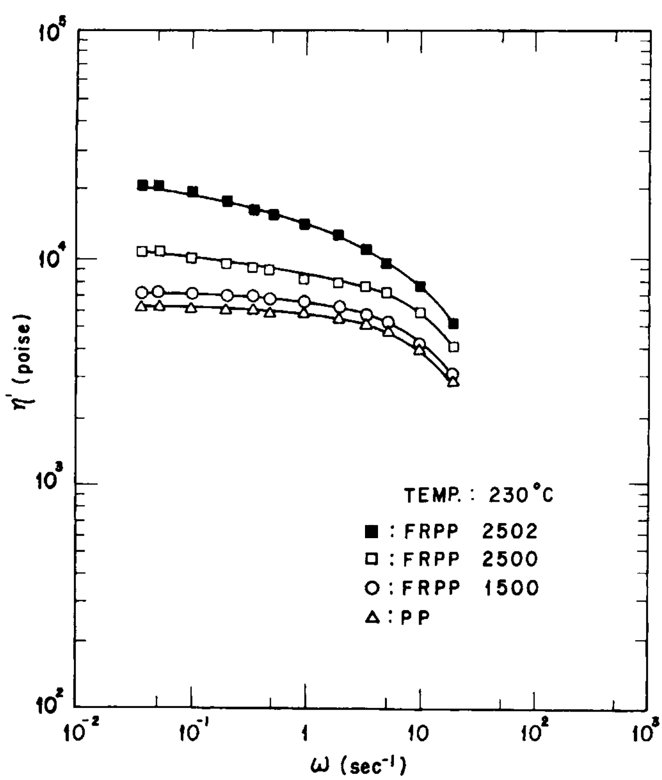

Fig. 8. Dynamic viscosity η' as a function of frequency for FRPP with different fiber contents.

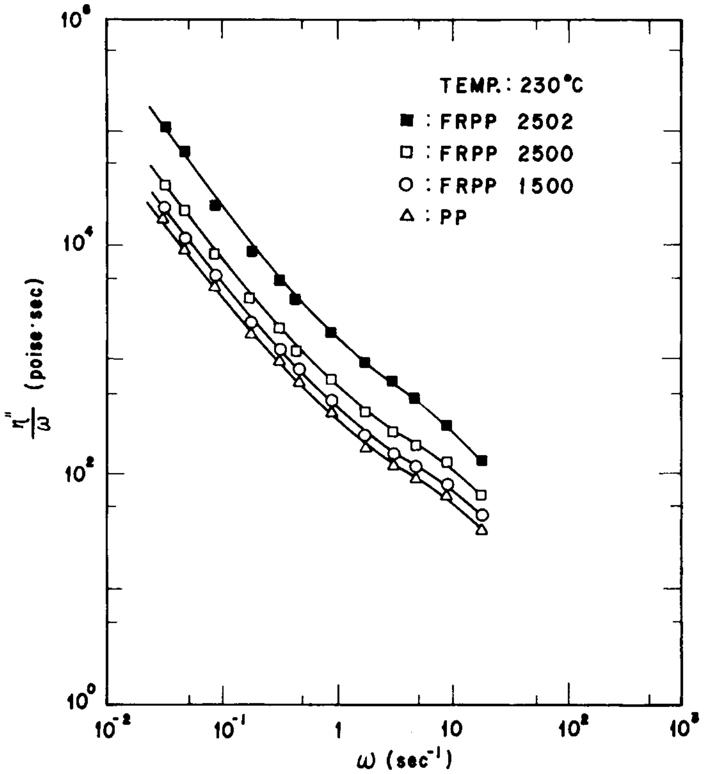

Fig. 9. Plot of η''/ω as a function of frequency for FRPP with different fiber contents.

content, especially in the low shear rate range. The effect of coupling agent on the viscosity was very significant in low shear rate region. The interfacial adhesion between PP and fibers was enhanced by the incorporation of coupling agent. The void content over interfacial surface was extensively decreased, and longer fibers were observed to distribute over the PP matrix in comparison with the case without pretreating fibers by coupling agent. The long fibers in FRPP would contribute more viscous force upon flowing. Therefore, as seen in Figure 7, the viscosity of FRPP increased over the entire range of shear rate with the incorporation of coupling agent. Figures 8 and 9 showed the plots of dynamic viscosities, η' and η''/ω as functions of frequency for FRPP with different fiber contents. η' represented the same trend with respect to frequency, fiber content, and coupling agent as the η' vs. $\dot{\gamma}$ curves in Figure 7. η''/ω decreased monotonously as frequency increased. The filling fibers in PP would make these polymer materials stiffer. The coupling agent performed the same function as discussed above. Hence, higher values of η''/ω where observed in the cases of higher fiber content and pretreating fibers with coupling agent. By the same reasons, FRPP of both cases would possess higher modulus as observed in Figures 10 and 11, in which either storage modulus G' or loss modulus G'' increased monotonously with increasing the frequency. Figure 12 showed the dependences of loss tangent on frequency, fiber content, and coupling agent at constant temperature. All samples represented lower $\tan\delta$ at high frequency. Because the elastic part of polymer

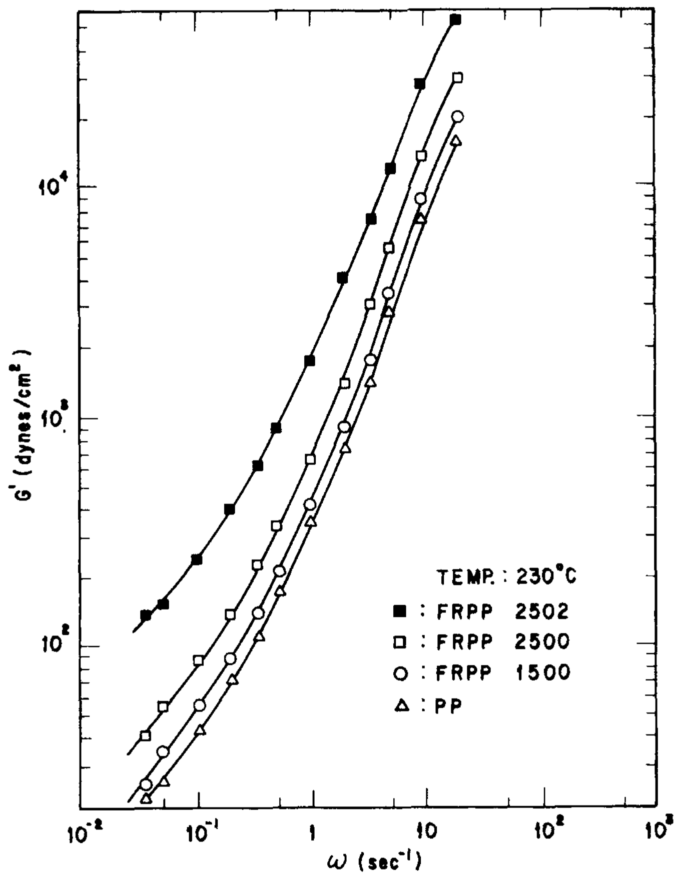

Fig. 10. Storage modulus G' as a function of frequency for FRPP with different fiber contents.

material gave an instantaneous response for the imposed input, while the viscous part responded gradually. Polymer behaved more like elastic material when the imposed frequency of strain was high. Also, we obtained lower tan δ for the composites containing more fibers or coupling agent. The effect of coupling agent on the loss tangent was very pronounced at low frequency.

The die swell of polymers has been found to decrease significantly by adding several types of fillers. The variation of die swell for FRPP with fiber content, temperature, shear rate, and coupling agent were investigated in this work. Figure 13 showed the die swell ratio (De/D) versus shear rate for FRPP 1502 at different temperatures, where De was the diameter of extrudate flowing out from a capillary tube with diameter D. For the same material, die swell ratio increased when shear rate increased or temperature decreased. This was due to the decreases of normal stress and elastic recovery at low shear rate and high temperature. The dependence of die swell on temperature was higher at low γ. Figure 14 showed the die swell ratio versus shear rate for FRPP with different fiber contents. It was seen that the die swell of FRPP dropped to values near 1.0 when a small amount of fibers was filled in. This was explained by the distribution of fibers over the PP matrix retarding the elastic recovery of material and absorbing part of the stress on the material.

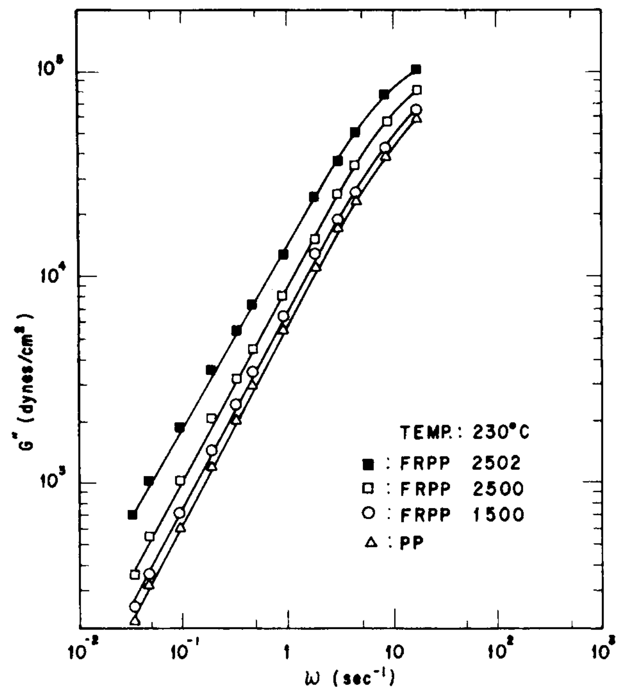

Fig. 11. Loss modulus G'' as a function of frequency for FRPP with different fiber contents.

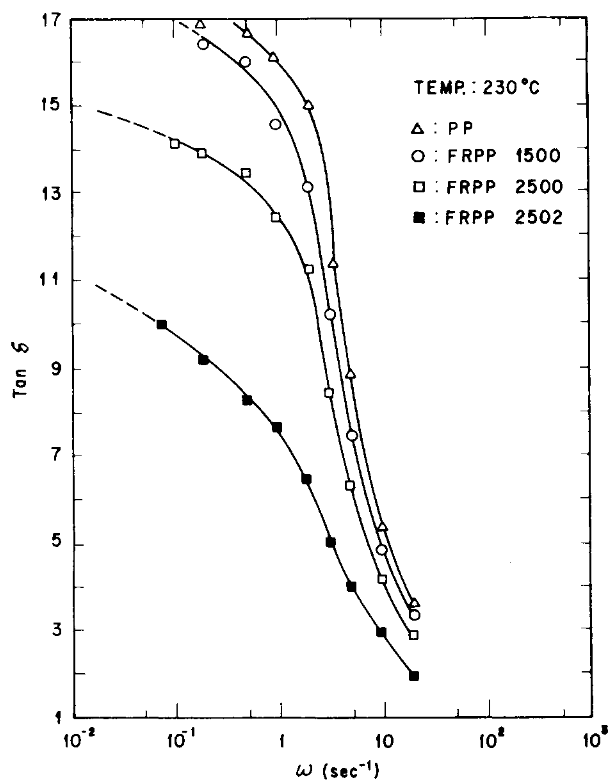

Fig. 12. Loss tangent as a function of frequency for FRPP with different fiber contents.

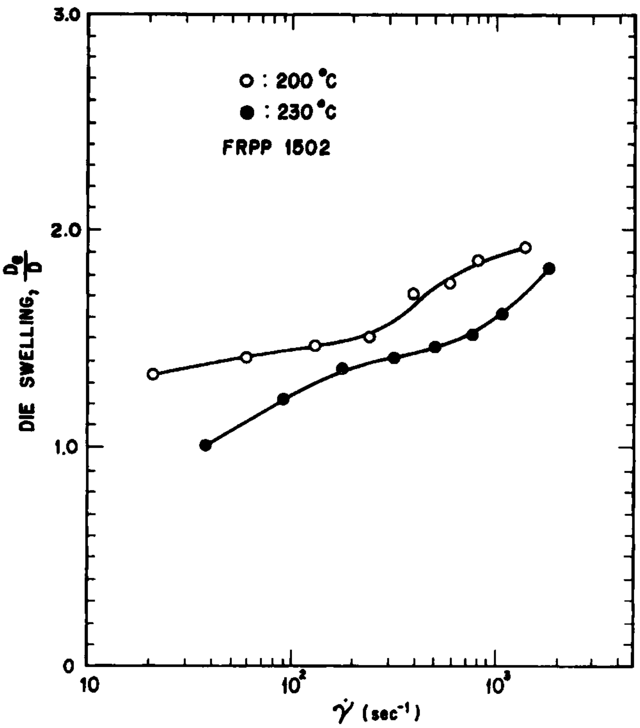

Fig. 13. Die swell ratio De/D versus shear rate for FRPP 1502 at different temperatures.

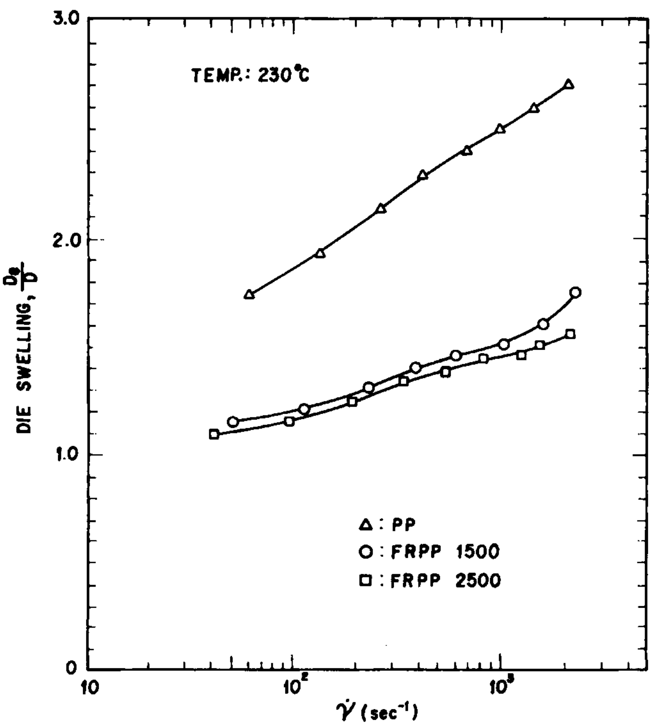

Fig. 14. Die swell ratio De/D versus shear rate for FRPP with different fiber contents.

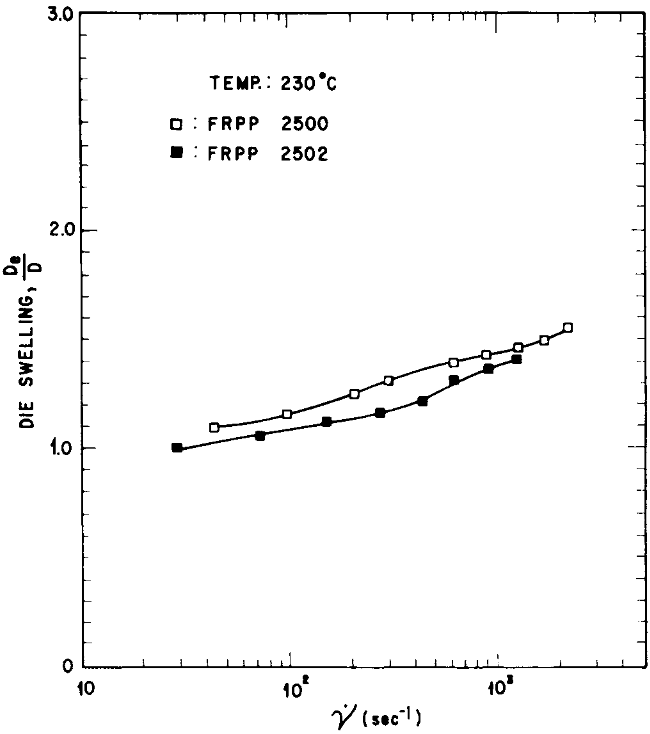

Fig. 15. Effect of coupling agent on the die swell ratio of FRPP.

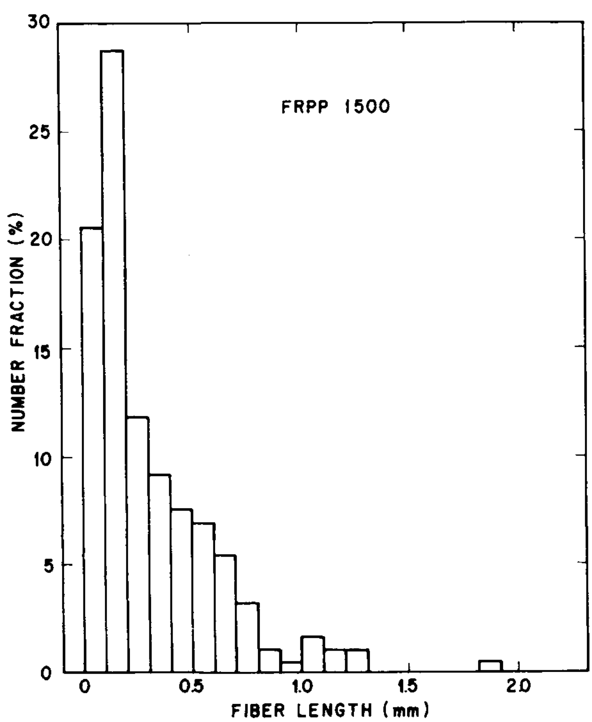

Fig. 16. Fiber length distribution in FRPP 1500.

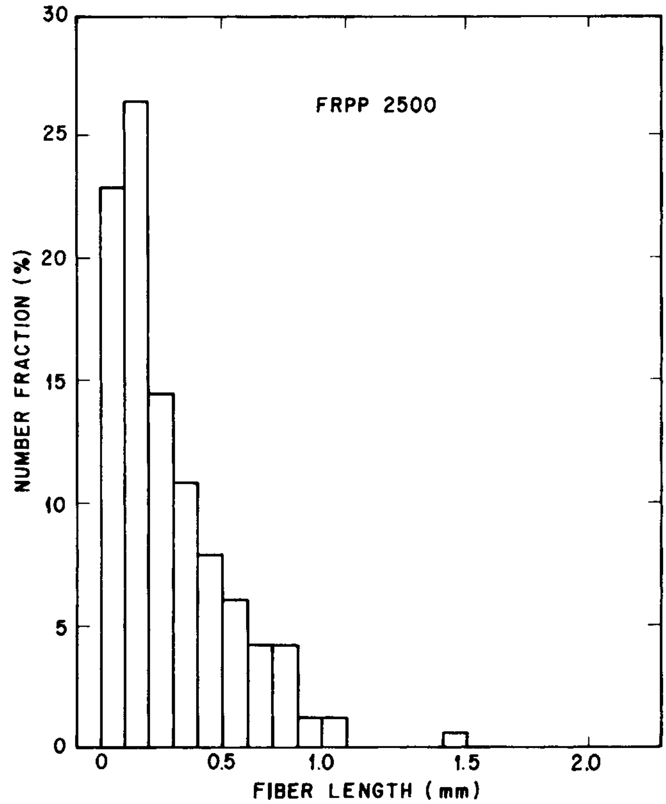

Fig. 17. Fiber length distribution in FRPP 2500.

Therefore, a large decrease of die swell was observed for FRPP systems and the die swell was less shear-rate sensitive than PP. If fibers were pretreated with coupling agent, they were expected to have even lower die swell by the enhancement of interfacial adhesion, which aided in the transfer of stress to fibers from PP matrix and would retard the elastic recovery of PP more efficiently. The effect of coupling agent on die swell ratio of FRPP is shown in Figure 15. Fiber lengths in FRPP would affect the viscosity of composite upon flowing. Most fibers were broken by friction and twisting force when they were mixed and blended with PP through extrusion processing. So the measurement of fiber length distribution in FRPP was needed to interpret some of the viscoelastic data as shown above. Figures 16, 17, and 18 show the fiber length distributions in FRPP 1500, FRPP 2500, and FRPP 2502 specimens, respectively. Table I gives the corresponding number average, weight average, and polydispersity of fiber lengths in different FRPP specimens. By comparing the data in the figures and Table I, fibers unpretreated by coupling agent would break much more easily. The higher the fiber content, the smaller the average fiber length obtained. Since fibers contacted, twisted, and bent more often when more fibers existed in FRPP. That would make the fibers break more frequently. As for the function of coupling agent on fibers, the interfacial adhesion between fiber and PP was improved. It seemed that the fiber surface was smoothed and plasticized by coating layers

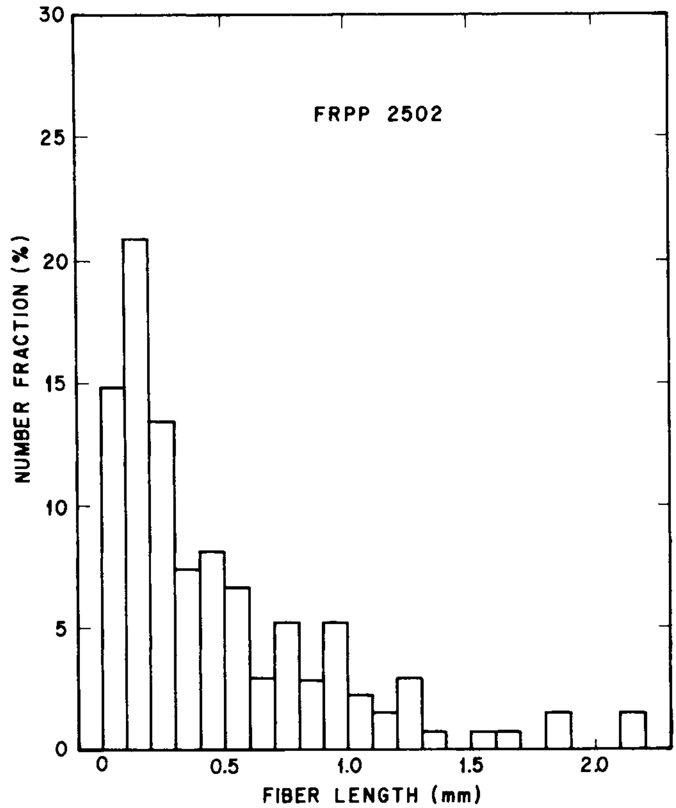

Fig. 18. Fiber length distribution in FRPP 2502.

TABLE I
Number Average, Weight Average, and Polydispersity of Fiber Length in Different FRPP Specimens

Specimen	*Ln* (mm)	*Lw* (mm)	*Lw*/*Ln*
FRPP1500	0.36630	0.59703	1.62988
FRPP2500	0.33313	0.50289	1.50959
FRPP2502	0.52761	0.91641	1.73689

of PP polymer compactly. Then the friction force and twisting force on fibers decreased significantly. So the average fiber lengths in FRPP 2502 were much longer than the other two FRPP specimens. This was one of the reasons for FRPP 2502 having higher viscosity and modulus as discussed above.

CONCLUSION

The objective of this paper was to discuss the viscoelastic properties of FRPP in the molten state. In steady state, the viscosity of FRPP decreased with increasing the shear rate or temperature. When the glass fiber content in FRPP increased, the viscosity increased. For the case of fibers pretreated with coupling agent, the viscosity of FRPP increased significantly due to the enhancement of interfacial adhesion between PP matrix and fiber through the coupling agent, and the fibers were much less broken in FRPP. In the dynamic test, the dynamic viscosity η', η''/ω and loss tangent $\tan\delta$ decreased with increasing the frequency, but the dynamic modulus G' and G'' changed in the opposite trend. The effects of fiber and coupling agent on dynamic viscoelastic properties of FRPP were to increase either the viscosity or the modulus. The dimensional stability of PP was expected to be greatly improved with filling in glass fibers by the fact of large reduction in die swell.

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