A Study on Rheologic Behavior of Polyphenylene Sulfide

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SYNOPSIS

Rheologic behavior of the common Ryton-type poly(phenylene sulfide) (PPS) and Fortron PPS has been studied using a capillary rheometer. The effects of shearing rate, shearing stress, and temperature on the apparent viscosities of PPS are discussed. The non-Newtonian index and the activation energy of the viscous flow were obtained. The results show that the apparent viscosity of the Ryton PPS decreased obviously with increase of shearing rate or shearing stress, and with increase of the temperature, the apparent viscosity is not considerably decreased. On the contrary, the apparent viscosity of the Fortron PPS is more sensitive to temperature than to shearing rate and shearing stress. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Rheologic behavior is an important property of a polymer, for most polymers are processed and shaped by making use of their flowing behavior in the melt condition. Poly(phenylene sulfide) (PPS) is a high-performance engineering thermoplastic, with good thermal stability, excellent chemical resistance, inherent flame resistance, and precision moldability. PPS resin also has excellent electrical and mechanical properties. PPS resin was produced in America by Phillips Petroleum Co. under the trade name Ryton in 1968. Ryton resin has a moderate molecular weight for injection moldings and usually should undergo a "curing" reaction upon heating in the presence of oxygen. The molecular weight of the polymer is increased by chain branching and crossing. Studies on its rheologic behavior have been reported over the last two decades.[1-3] In 1985, PPS with linear and high molecular weight and toughness was commercially produced in Japan by Kureha Chemical Industry Co., which is called the second-generation PPS with the trade name Fortron.[4] Thermal characteristics of Fortron have been reported.[5] To obtain reasonable processing parameters, we present a study on the rheologic behavior of the two types of PPS. A comparison between the two types of PPS is also reported.

EXPERIMENTAL

Materials

PPS used in this study may be divided into two types:

1. PPS pellet: Produced by Phillips Petroleum Co. under the trade name Ryton 6 (R-6). T_m: 276°C; melt index (MI): 41 g/10 min at 316°C; 5 kg load.
2. PPS resin: produced by Kureha Chemical Industry Co. under the trade name Fortron W-205 and Fortron W-214. T_m: 294.1 and 290.2°C; MI: 505 and 140 g/10 min (316°C, 5 kg load); inherent viscosities: 0.211 and 0.348 dL/g (measured at 208°C, using 1-chloronaphthalene as the solvent, at 0.4 g PPS/100 mL solution), respectively.

Instrument

An XLY-II capillary rheometer made by Scientifical Instrumental Factory of Jilin University, was used, whose length-to-diameter ratio of a selected capillary is 40, so the entrance effect need not be considered.

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Journal of Applied Polymer Science, Vol. 56, 581–590 (1995)
 CCC 0021-8995/95/050581-10

Method of Operation

Polymers were heated to a certain melt temperature and maintained for 10 min in the pipe, then extruded through a capillary by a plug (the area of the end of plug is equal to 1 cm^2). The extrusion velocity and temperature were automatically recorded.

Processing of Data

Shearing Stress σ

For a steady flowing, the shearing stress of capillary is shown as

$$\sigma = \frac{\Delta PR}{2L} \tag{1}$$

where ΔP is the pressure difference between two ends of the capillary, and R and L, the radius and length of capillary, respectively.

Apparent Shearing Rate γ

$$\gamma = \frac{4Q}{\pi R^3} \tag{2}$$

where Q is the volume output of the polymer melt.

Non-Newtonian Index N

Generally, non-Newtonian flow is described by the equation

$$\sigma = k\gamma^N \tag{3}$$

(the "power law"), where k is the zero-shearing (Newtonian) viscosity. According to eq. (3), σ and γ were drawn on a double logarithmic coordinate. The log σ vs. log γ should be a straight line. From the straight line, the slope N can be obtained.

Modified Shearing Rate γ_m

The melt fluid of polymer is non-Newtonian, so γ should be corrected by the following equation:

$$\gamma_m = \frac{3N+1}{4N}\gamma \tag{4}$$

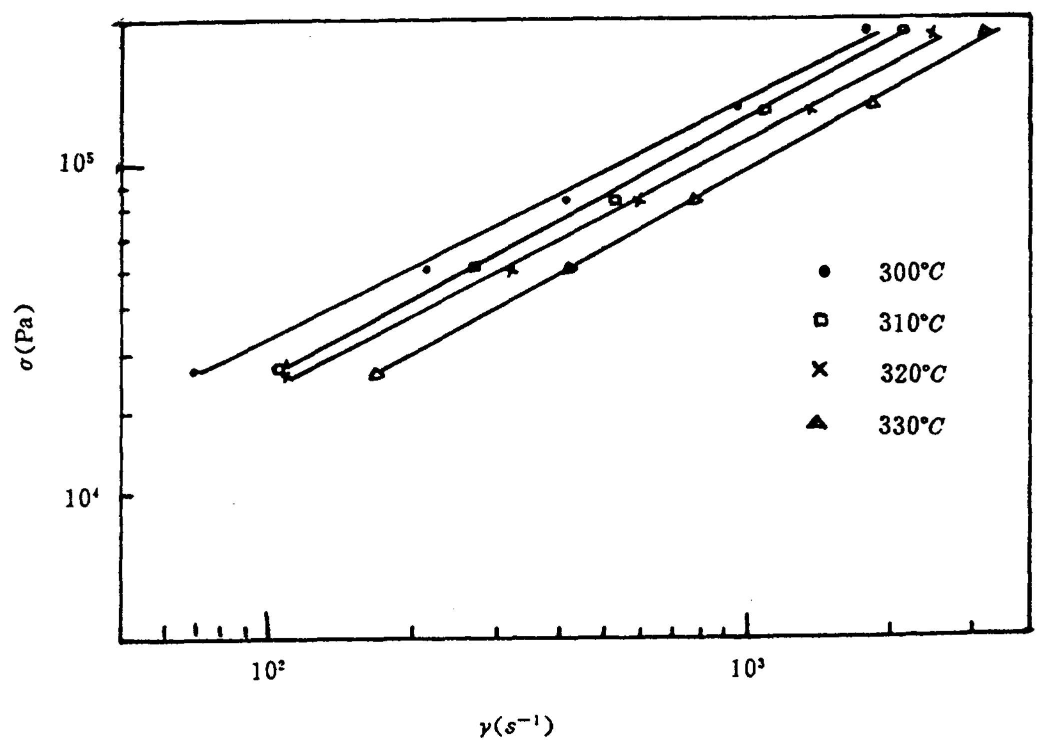


Figure 1 Plot of σ vs. γ of R-6.

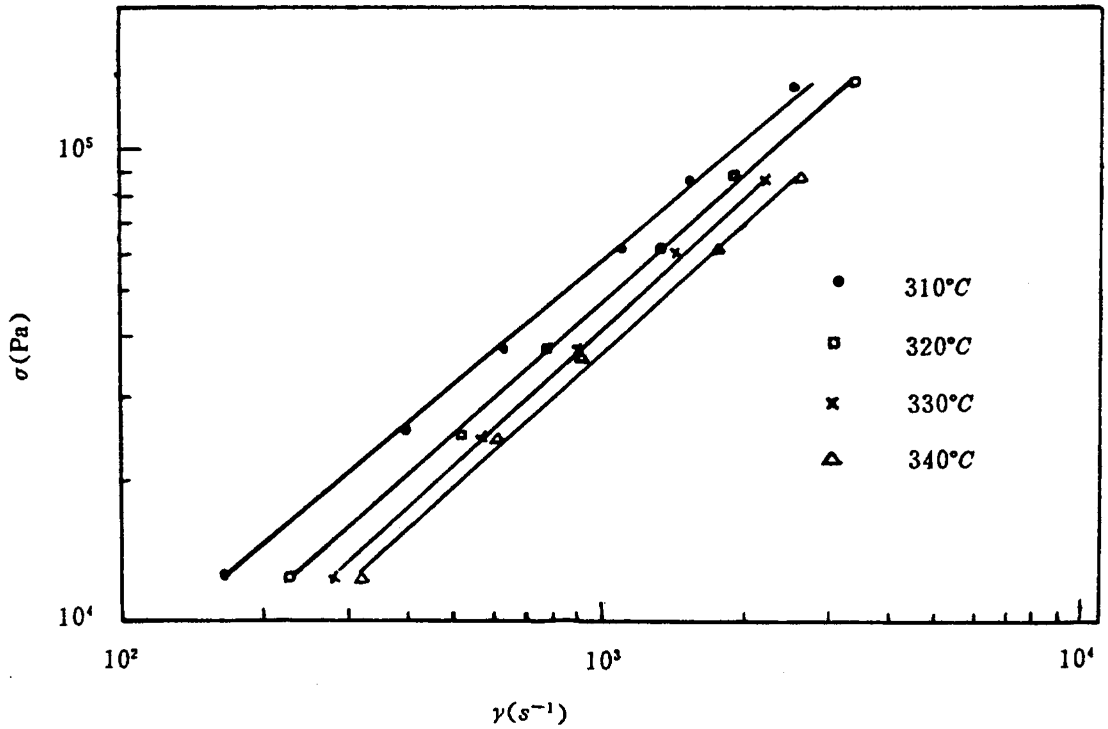


Figure 2 Plot of σ vs. γ of W-205.

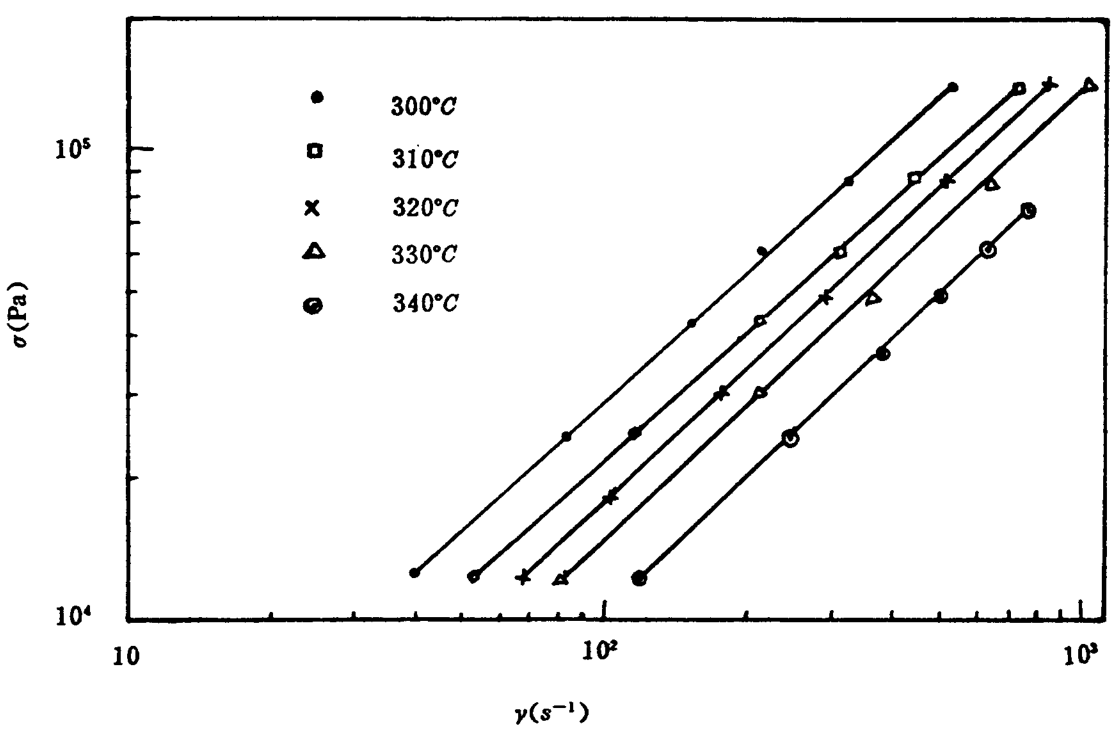


Figure 3 Plot of σ vs. γ of W-214.

Table I Non-Newtonian Indices N of R-6, W-205, and W-214 at Different Temperatures

	Non-Newtonian N				
Sample	300°C	310°C	320°C	330°C	340°C
R-6	0.517	0.552	0.559	0.561	
W-205		0.881	0.891	0.935	0.930
W-214	0.923	0.922	0.947	0.940	0.956

Apparent Viscosity η_{am}

$$\eta_{am} = \frac{\sigma}{\gamma_m} \tag{5}$$

Activation Energy of Viscous Flow ΔE

For polymer melts, the relationship between apparent viscosity and temperature can be expressed as an Arrhenius equation:

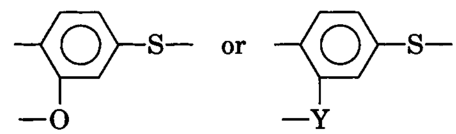
$$\eta_{am} = ke^{\Delta E/RT} \tag{6}$$

where ΔE is activation energy of viscous flow, and k, a constant. According to eq. (6), ln η_{am} against $1/T$ should be a straight line, and ΔE can be calculated from the slope of obtained straight line.

RESULTS AND DISCUSSION

Flowing Curve

The correlations of shearing stress σ on shearing γ of R-6, W-205, and W-214 measured at different temperatures are shown in Figures 1–3. The obtained non-Newtonian indices are listed in Table I. By a modified eq. (4), the flowing curves of R-6, W-205, and W-214 were obtained (Figs. 4–6). From Table I and Figures 4–6, we found that the two types of PPS are all pseudoplastic fluids and N is increased with elevated temperature, which means that the non-Newtonian behavior of the PPS fluid is decreased because the chain motion is more active with increasing temperature. Also, data in Table I show that the Fortron PPS tends more to Newtonian flowing than does Ryton 6, owing to their chain-structure difference. Ryton 6 is pelletized Ryton P-4,[6] which is a cured product of the moderate molecular weight PPS Ryton V-1 heated in the presence of air. The backbones of the cured PPS (Ryton P-4 or Ryton 6) contain crosslinked or branched units such as



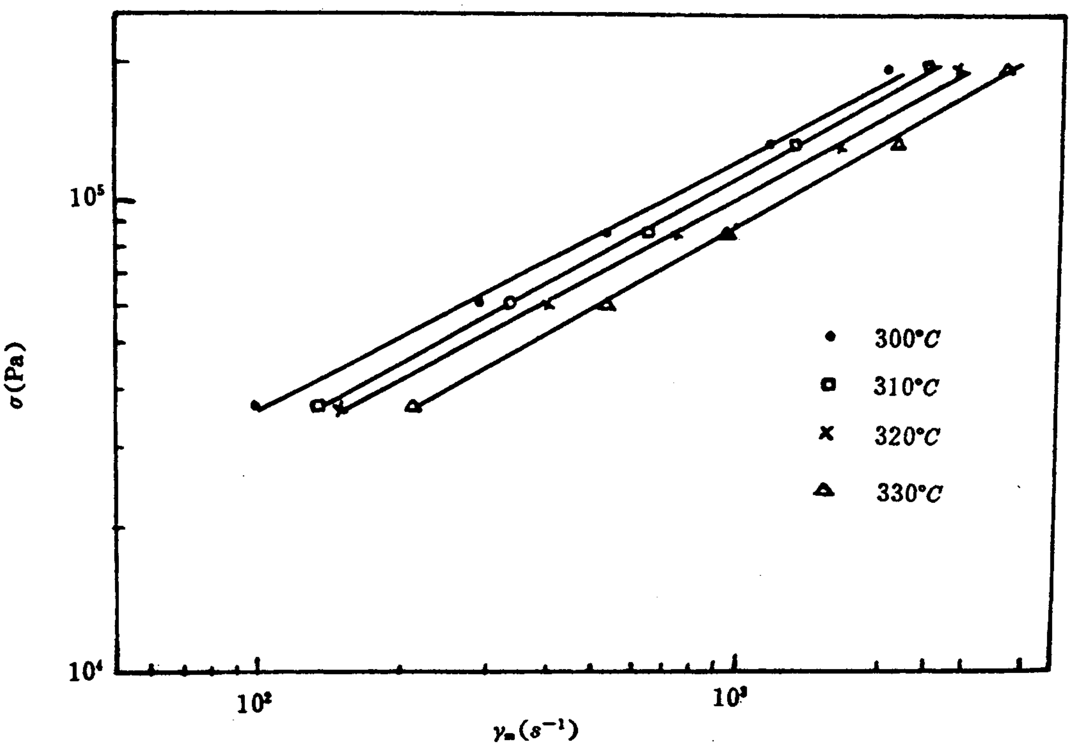


Figure 4 Plot of σ vs. γ_m of R-6.

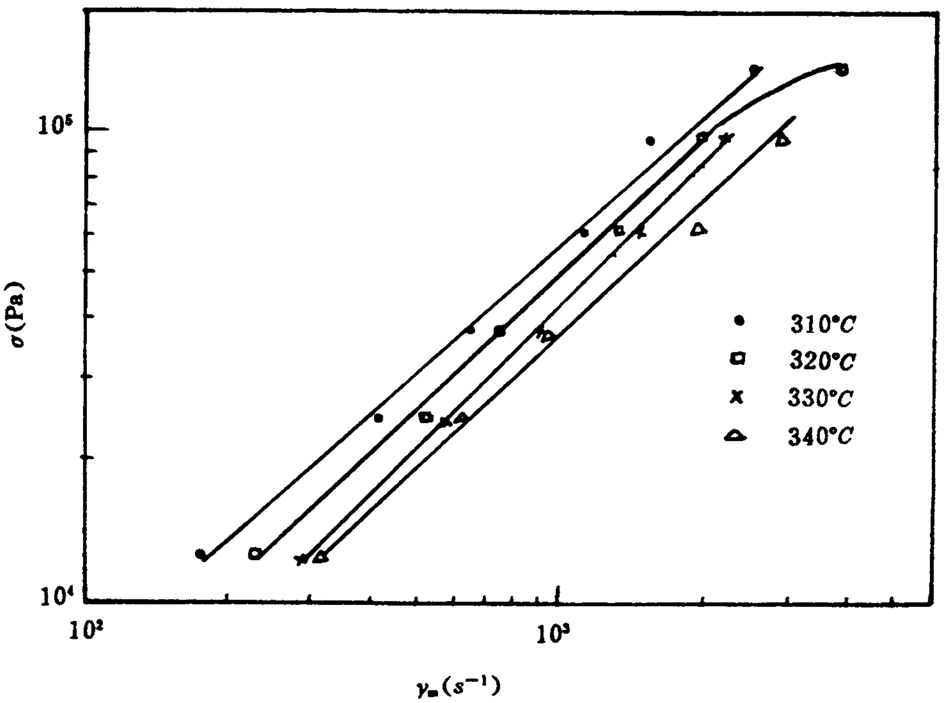


Figure 5 Plot of σ vs. γ_m of W-205.

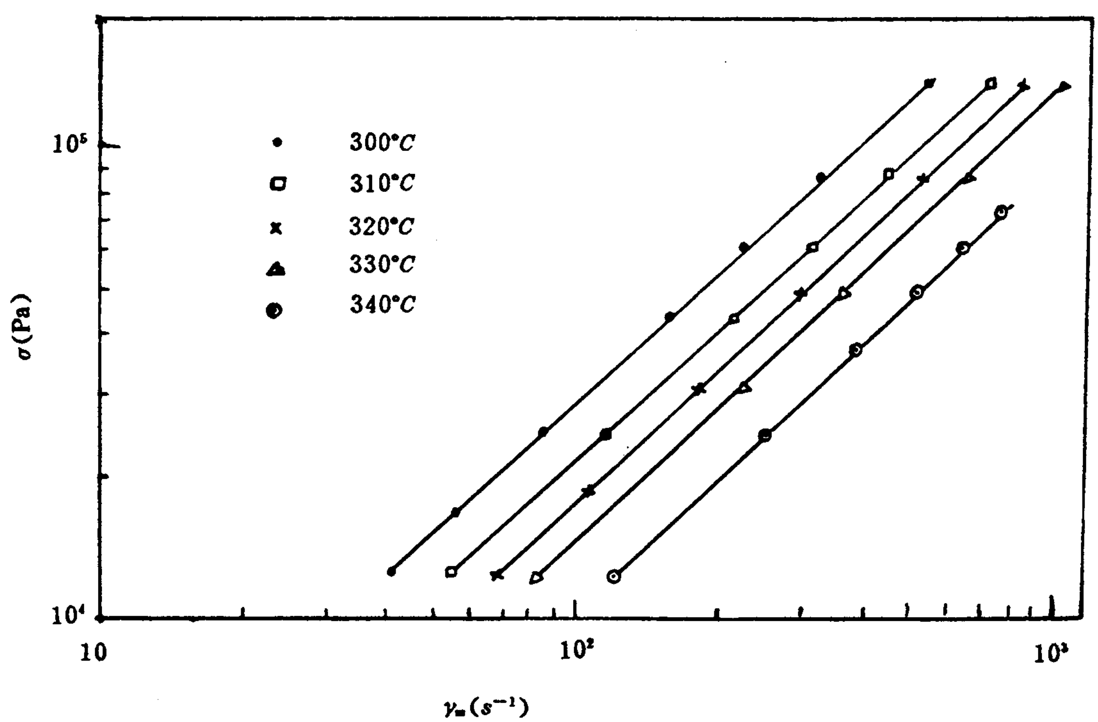


Figure 6 Plot of σ vs. γ_m of W-214.

where Y is S or arylene.[7,8] Both oxidative crosslinking and thermal crosslinking-formed units in the structure affected the flow of Ryton R-6 melt, with the result that N was far less than 1. But Fortron PPS is known to be more linear than is Ryton 6.[5]

Relationship of η_{am} to γ_m and σ

The correlation of apparent viscosity η_{am} and modified shearing rate γ_m are shown in Figures 7–9. Figures 10–12 show the relationship between apparent viscosity η_{am} and shearing stress σ of R-6, W-205, and W-214. From Figures 7–12, it can be observed that the η_{am} of both types of PPS decreases with increase of γ_m or σ due to the orientation of the molecular chain. Because the PPS chain is constituted by the rigid phenylene and soft thioether bond (—S—), and it might therefore be a semirigid polymer chain, its dependence of η_{am} on shearing rate and shearing stress is not obviously the same as that of the soft-chain polymer. Because of the structure difference between Ryton and Fortron, η_{am} of R-6 decreases sharply with increase of γ_{am} and σ, while the η_{am} of W-205 and W-214 are not decreased obviously at the same conditions.

Relationship Between η_{am} and Temperature

As is well known, increasing the temperature of a melted polymer decreases its viscosity. But the effect is considerably different for different types of polymer. For both of Ryton and Fortron, the apparent viscosities η_{am} at different temperatures were obtained at a constant shearing rate from Figures 7–9. From the plots of ln η_{am} against $1/T$ (Figs. 13–15), the activation energies of the viscous flow ΔE of both types of PPS were calculated and are listed in Table II. The results in Figures 13–15 and Table II show that the η_{am} of two types of PPS are decreased with increasing temperature and the activation energy of Fortron PPS, especially of W-214, is much higher than that of Ryton 6. The data indicate that Fortron PPS is more tractable than is Ryton 6. Also, it can be seen that ΔE is decreased

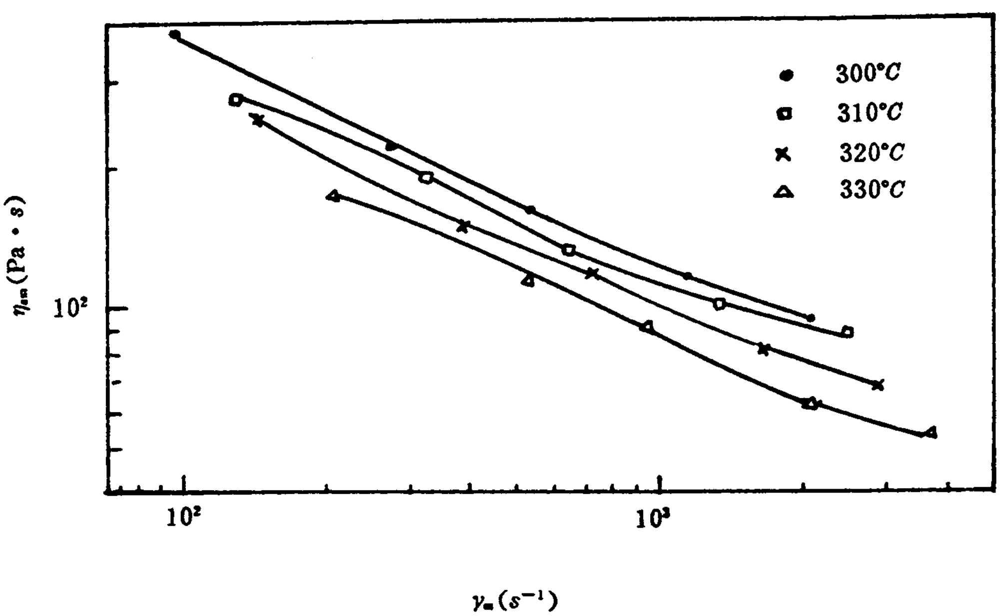


Figure 7 Plot of η_{am} vs. γ_m of R-6.

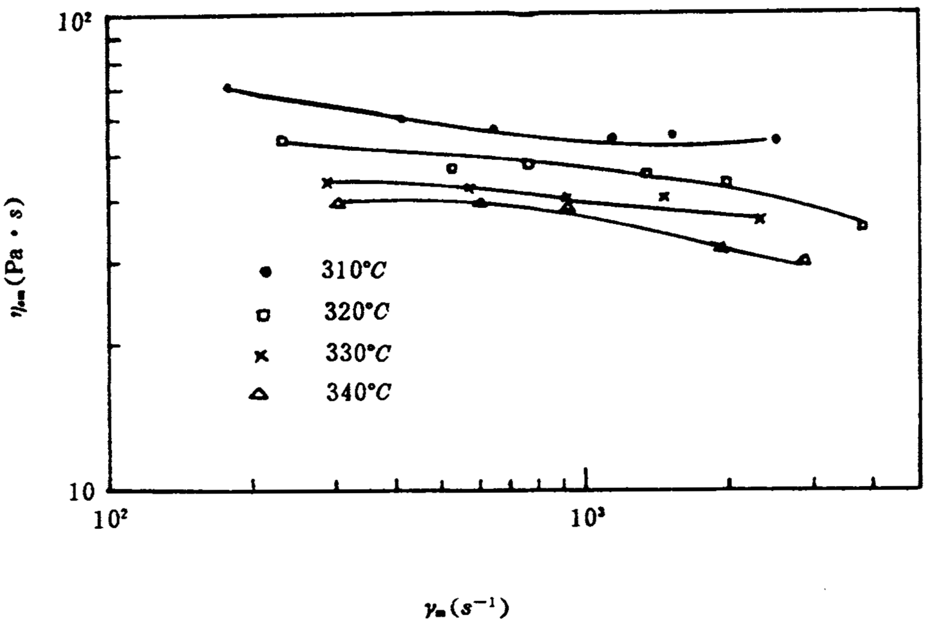


Figure 8 Plot of η_{am} vs. γ_m of W-205.

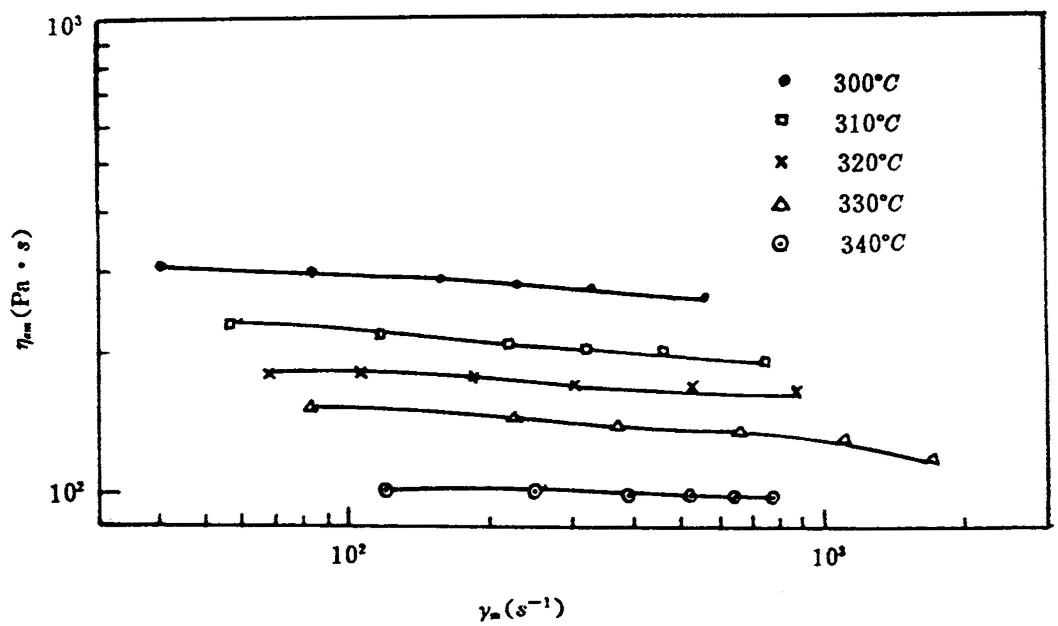


Figure 9 Plot of η_{am} vs. γ_m of W-214.

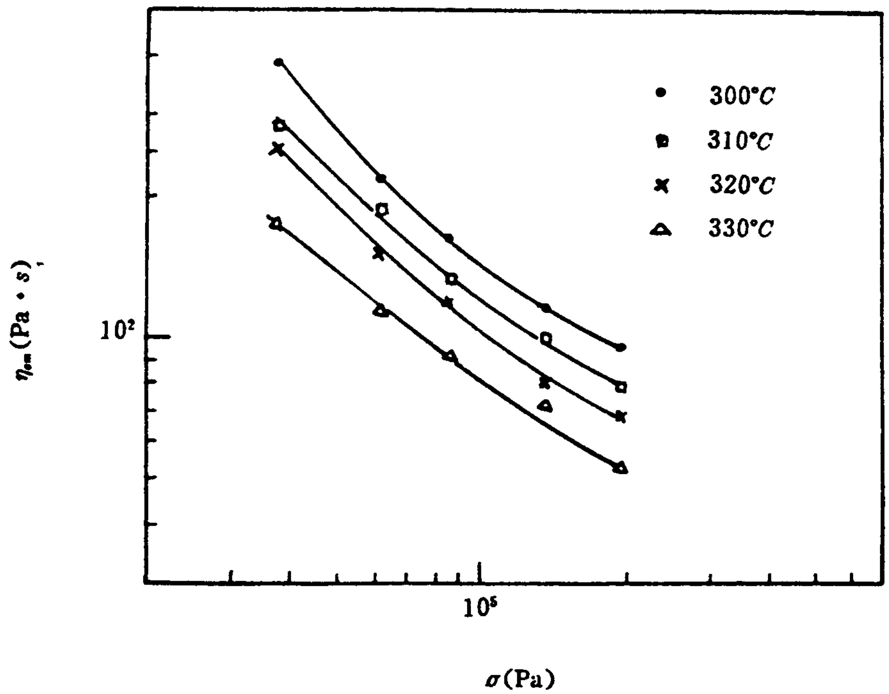


Figure 10 Plot of η_{am} vs. σ of R-6.

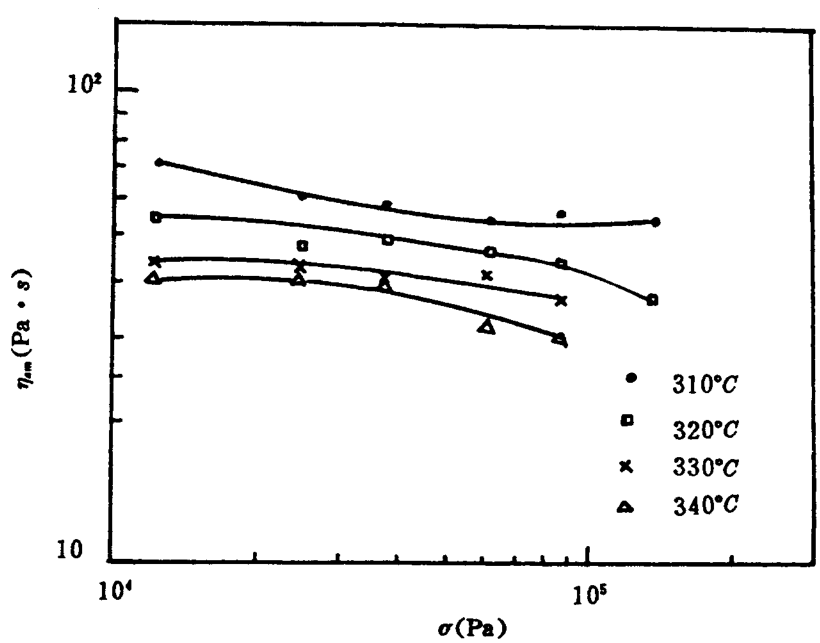


Figure 11 Plot of η_{am} vs. σ of W-205.

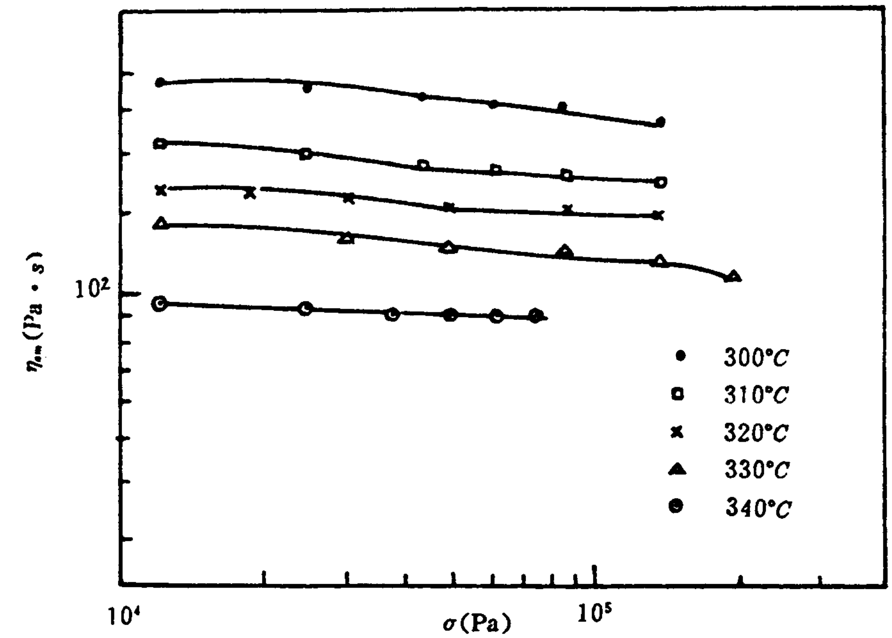


Figure 12 Plot of η_{am} vs. σ of W-214.

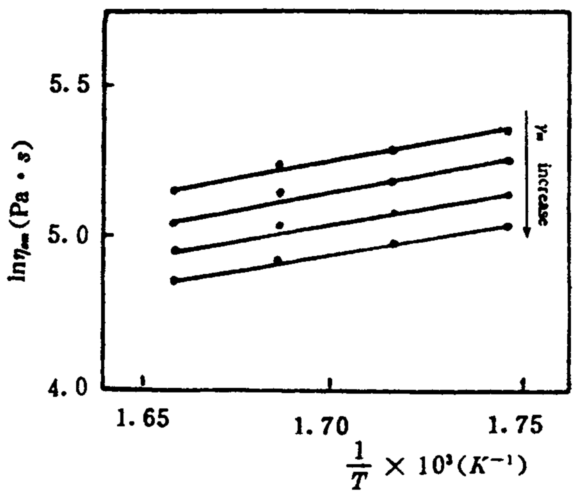


Figure 13 Plot of ln η_{am} vs. $1/T$ of R-6.

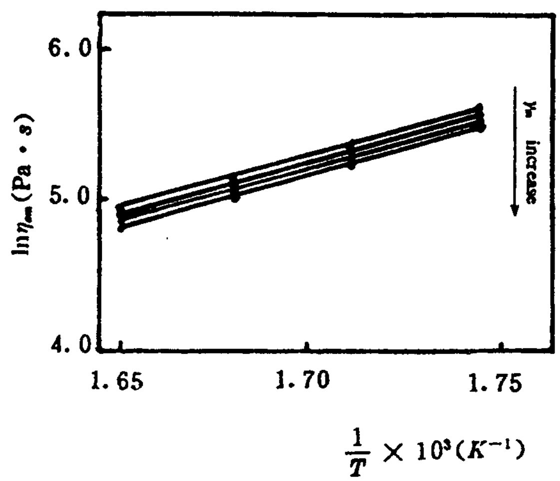


Figure 15 Plot of ln η_{am} vs. $1/T$ of W-214.

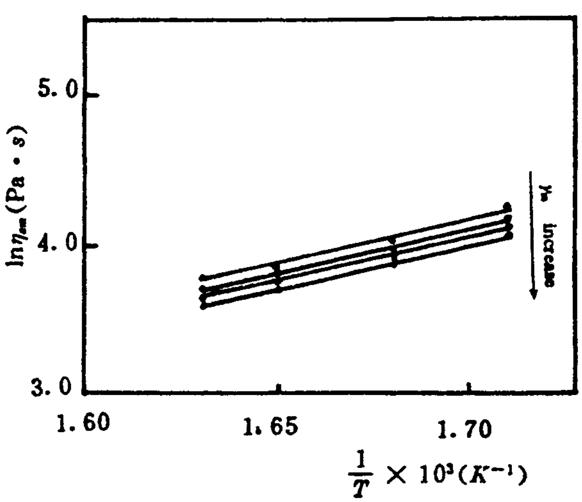


Figure 14 Plot of ln η_{am} vs. $1/T$ of W-205.

Table II Activation Energy of Viscous Flow of R-6, W-205, and W-214 at Different Shearing Rates

	ΔE (kJ/mol)			
Sample	200 s^{-1}	316 s^{-1}	501 s^{-1}	794 s^{-1}
R-6	37.5	36.0	34.6	33.1
W-205	48.3	46.9	45.5	44.0
W-214	69.9	69.2	68.5	67.9

with increasing shearing rate, which is consistent with classical theory.

CONCLUSIONS

From the rheologic behavior of both types of PPS, some conclusions could be obtained:

1. Both types of melted PPS belong to the pseudoplastic fluid.
2. The apparent viscosity of Ryton 6 is more sensitive to shearing rate and shearing stress than to temperature.
3. The apparent viscosity of the Fortron PPS is more sensitive to temperature than to shearing rate and shearing stress.

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Received December 17, 1993
Accepted October 9, 1994