

RHEOLOGICAL BEHAVIOR OF POLYPHENYLENE SULFIDE/POLYAMIDE-66 BLENDS*

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ABSTRACT

Blends of polyphenylene sulfide (PPS) containing trace amounts of branching and/or cross-linking in chain and Polyamide-66 (PA-66) have been prepared by melt blending. The rheological behavior of PPS/PA-66 blends has been studied by means of capillary rheometer, and compared with PPS. The effects of shear rate, shear stress and temperature on the flow of PPS/PA-66 blends and PPS are discussed. The non-Newtonian indexes and the activation energies of viscous flow are obtained. The results show that the apparent viscosity of PPS/PA-66 blends is not sensitive to shear rate and stress, but decreases with the elevation of temperature. On the contrary, the apparent viscosity of the PPS decreases obviously with the increasing of shear rate and shear stress, but it is increased by the elevation of temperature.

INTRODUCTION

Polyphenylene sulfide (PPS) is an engineering thermoplastics. It possesses high temperature resistance, chemical and solvent resistance, excellent electrical and mechanical properties. PPS has been widely used in corrosion resistant coating, mechanical parts, electric and electronic apparatus. PPS is semicrystalline, rather brittle. When PPS blends with PA-66, the properties of PPS such as impact strength, toughness and processing flowability can be improved. So it is an important way of PPS modification. Fisher and Balow^[1] have reported on the mechanical properties at room and elevated temperature of a blended glass-fiber reinforced alloy of PPS and PA-66. Kawashima et al.^[2] have also examined the mechanical properties of PPS and PA-66 alloy with 30 percent glass-fiber reinforced. Recently, the rheological properties of the alloy of PPS and PA-66 have been investigated by

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Akhtar et al.^[3], but only the effect of shear rate on the shear viscosity at 290°C was reported. In this paper the rheological behavior of the blends of PPS and PA-66 at different temperatures and pressures is studied. The parameters obtained are available for processing.

On rheological behavior of PPS, Hou et al.^[4] have studied the differences between common Ryton type PPS and Fortron PPS. Kraus et al.^[5] have reported the relation between melt viscosity and molecular weight of PPS. Zhang et al.^[6] and Wu^[7] have discussed the rheological behaviour of PPS which does not contain any branching or cross-linking in the chains. For comparison, we have also studied the rheological behavior of PPS containing trace amounts of branching or/and cross-linking in chains and PA-66, respectively.

EXPERIMENTAL

Materials

PPS pellets were supplied by Zigong Chemical Reagent Factory, $T_m = 275^\circ\text{C}$. There are trace amounts of branching or/and cross-linking in PPS chains. The melt index (MI) is 41.5g/10min. determined at 316°C, 5kg load, with a die of 2.095mm diameter and 10mm length. The load and the die are also the same for other MI data.

PA-66 pellets were produced by Heilongjiang Nylon Factory, $T_m = 250^\circ\text{C}$. Molecular weight estimated by intrinsic viscosity using Mark-Houwink equation is about 57,000. The MI is 251g/10min at 280°C.

Blends preparation

PPS and PA-66 pellets were dried at 110°C for 4h, they were blended in different proportions and extruded, through a twin screw extruder. Thus, MI of PPS/PA-66 (50/50) and PPS/PA-66 (25/75) was 308 and 553g/10min., respectively, at 300°C.

Instrument

XLY-II capillary rheometer is made by Jilin University. The length to diameter ratio of selected capillary is 40, so the entrance effect is not considered. The pressure range of the rheometer is 1–50MPa while the temperature range is from room temperature to 400°C.

Method of operation

Polymers were heated to a certain temperature and maintained for 10min in the pipe, then extruded under the constant load through a capillary by a plug with end area 1cm². Extrusion velocity and temperature were automatically recorded. The data were processed by computer programs.

Data processing

1. Shear stress σ

When incompressible viscous fluid flows steadily, the shear stress σ on the capillary wall is

$$\sigma = \Delta P R / 2L \quad (1)$$

where ΔP is the pressure difference between two ends of the capillary. R and L are radius and length of the capillary, respectively. If $L/D = 40$, entrance correction can be neglected.

2. Shear rate $\dot{\gamma}$

For a Newtonian fluid, $\dot{\gamma}$ on the capillary wall is as follows:

$$\dot{\gamma} = 4Q / \pi R^3 \quad (2)$$

where Q is the volume output of polymer melt.

3. Non-Newtonian index N

Non-Newtonian index N would be

$$N = d \log \sigma / d \log \dot{\gamma} \quad (3)$$

For a non-Newtonian polymer fluid, $\dot{\gamma}$ should accept non-Newtonian correction, expressed as

$$\dot{\gamma}_m = \frac{3N + 1}{4N} \cdot \dot{\gamma} \quad (4)$$

4. Apparent viscosity η_a

For a non-Newtonian polymer fluid, η_a may be given as

$$\eta_a = \sigma / \dot{\gamma}_m \quad (5)$$

5. Activation energy of viscous flow ΔE

For polymer melt, relationship between η_a and temperature can be expressed as Arrhenius equation:

$$\eta_a = k e^{\Delta E / RT} \quad (6)$$

where ΔE is activation energy of viscous flow, k is a constant, R is gas constant. According to equation (6), ΔE can be calculated from the slope of $\ln \eta_a$ against $1/T$ straight line.

RESULTS AND DISCUSSION

Flow curve

Rheological behavior of PPS/PA-66 blends and PPS was determined at 300°C. The correlation of shear stress σ and shear rate $\dot{\gamma}$ of the blends and PPS is shown in

Fig.1. At different $\dot{\gamma}$ and σ , non-Newtonian indexes N of the blends and PPS can be calculated from tangent in every point on the lines of Fig.1, and are enumerated in Table 1 and 2. According to equation (4), modified shear rate $\dot{\gamma}_m$ can be obtained from shear rate $\dot{\gamma}$. Then the flow curves of the blends and PPS were drawn as shown in Fig.2. From Table 1—2 and Fig.2, it can be seen that the melts of the blends and

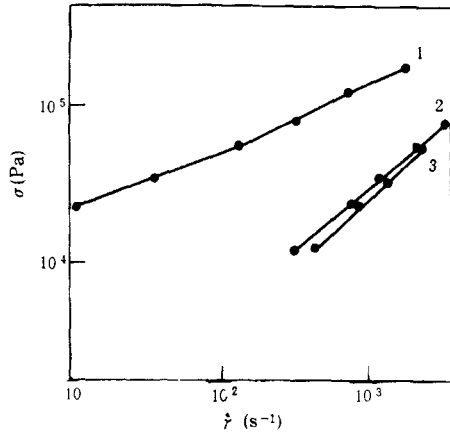


Fig. 1 Relation between σ and $\dot{\gamma}$ of blends and PPS at 300°C
 1) PPS; 2) PPS/PA-66 (50/50);
 3) PPS/PA-66 (25/75)

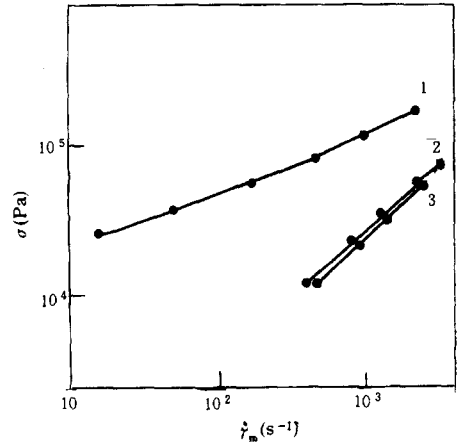


Fig. 2 Flow curve of blends and PPS at 300°C
 1) PPS; 2) PPS/PA-66 (50/50);
 3) PPS/PA-66 (25/75)

Table 1 Effect of different shear rate $\dot{\gamma}$ on N of blends and PPS (at 300°C)

Sample	$\dot{\gamma}(\text{s}^{-1})$	N
PPS	1.01×10	0.311
	3.55×10	0.355
	1.31×10^2	0.401
	3.31×10^2	0.433
	7.28×10^2	0.460
	1.89×10^3	0.493
PPS/PA-66 (50/50)	3.20×10^2	0.824
	7.86×10^2	0.818
	1.20×10^3	0.815
	2.27×10^3	0.810
	3.55×10^3	0.807
PPS/PA-66 (25/75)	4.47×10^2	1.034
	8.93×10^2	0.960
	1.38×10^3	0.913
	2.46×10^3	0.852

Table 2 Effect of shear stress σ on N of blends and PPS (at 300°C)

Sample	$\sigma \times 10^{-4}(\text{Pa})$	N
PPS	2.45	0.311
	3.68	0.355
	6.13	0.401
	8.59	0.433
	13.50	0.460
	19.60	0.493
PPS/PA-66 (50/50)	1.23	0.824
	2.45	0.818
	3.68	0.815
	6.13	0.810
	8.59	0.807
PPS/PA-66 (25/75)	1.23	1.034
	2.45	0.960
	3.68	0.913
	6.13	0.852

PPS belong to pseudoplastic fluids. N increases with the increasing content of PA-66. It shows that non-Newtonian extent of the blends is less than that of PPS. The reason is that PPS contains trace amounts of branching or/and cross-linking in chain structure, and the rheological behavior is determined at a temperature higher

than the melting point of PPS, and much higher than that of PA-66. Therefore, the elastic effect of the melt blends is less than that of PPS. Also, it is found that with increasing $\dot{\gamma}$ and σ , N of the blends decreases, whereas N of PPS increases.

Apparent viscosity

The apparent viscosity η_a is plotted as a function of modified shear rate $\dot{\gamma}_m$ for the blends and PPS at 300°C, as shown in Fig.3. Fig.4 shows the relationship of apparent viscosity η_a and shear stress σ of the blends and PPS, indicating their η_a decreases with increasing $\dot{\gamma}_m$ and σ . This fact proves further that the melts of the blends and PPS are pseudoplastic fluid. The experimental results also show that η_a of various samples is sensitive to $\dot{\gamma}_m$ and σ , but the η_a of PPS is much more sensitive to $\dot{\gamma}_m$ and σ than that of its blends. When $\dot{\gamma}_m$ increases by 10 times, η_a for blends do not change obviously. The reason may be that PPS molecular chains would be orientated along the flow direction with increasing $\dot{\gamma}_m$ and σ , and make η_a to decrease rapidly. Though PA-66 chains in the blends are softer than that of PPS, but PA-66 molecules contain polar groups and are hydrogen-bonded intramolecularly. As $\dot{\gamma}_m$ and σ increase, perhaps only a few hydrogen bonds are interrupted, so η_a does not change greatly. Therefore, during processing, flow property of PPS can be changed by increasing or decreasing $\dot{\gamma}_m$ and σ , however that of its blends can not be changed.

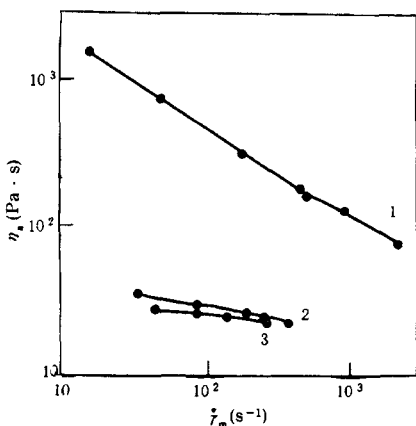


Fig. 3 Plots of η_a vs. $\dot{\gamma}_m$ at 300°C

- 1) PPS; 2) PPS/PA-66 (50/50);
- 3) PPS/PA-66 (25/75)

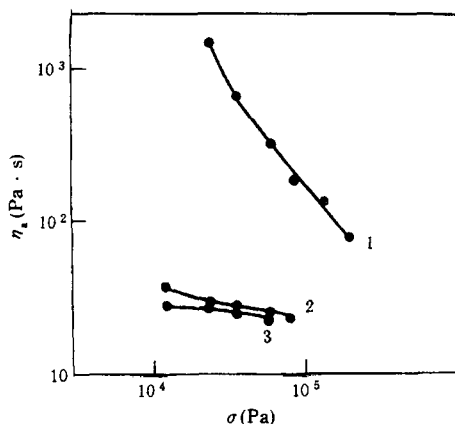


Fig. 4 Plots of η_a vs. σ at 300°C

- 1) PPS; 2) PPS/PA-66 (50/50);
- 3) PPS/PA-66 (25/75)

Activation energy of viscous flow

The η_a of PPS, PA-66 and the blends is determined at different temperatures and different $\dot{\gamma}_m$ as shown in Figs.5—8. According to the plots of $\ln \eta_a$ against $1/T$ (Fig.9 at $\dot{\gamma}_m = 631 \text{ s}^{-1}$), the viscous flow activation energies ΔE of PA-66 and its blends were calculated and listed in Table 3. Also, activation energies were listed

at a constant σ in Table 4. From these experimental results, it can be concluded that by increasing melt temperature the viscosities of PA-66 and its blends decrease at constant $\dot{\gamma}_m$ and σ , but the situation for PPS is on the contrary. PPS chain will be oxidized and crosslinked at high temperature. The rheological behavior of PPS does not obey the Arrhenius equation, and ΔE can not be obtained. η_a for PPS is slightly increased at 300 to 310°C (For instance, 148 and 165 Pa·s⁻¹ at 300 and 310°C at $\dot{\gamma}_m = 900\text{s}^{-1}$, respectively), but η_a of PPS blended with PA-66 is still decreased at 300 to 310°C (for PPS/PA-66= 50/50, 29 and 14 Pa·s⁻¹ at 300 and 310°C at $\dot{\gamma}_m = 900\text{s}^{-1}$, respectively.) due to their good compatibility^[8] and/or change of aggregative structure. The rheological behavior of the blends obeys the Arrhenius equation.

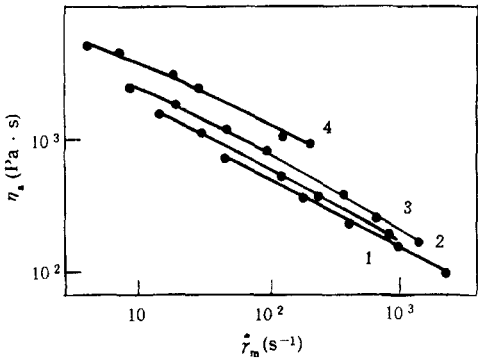


Fig. 5 Plots of η_a vs. $\dot{\gamma}_m$ for PPS
1) 300°C; 2) 310°C; 3) 320°C;
4) 330°C

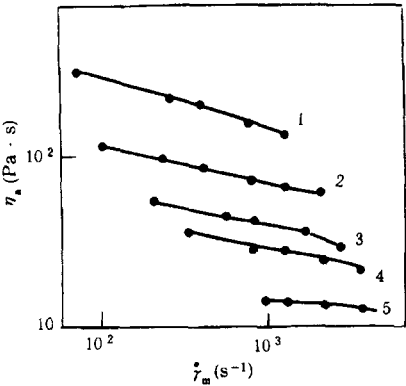


Fig. 6 Plots of η_a vs. $\dot{\gamma}_m$ for PPS/
PA-66(50/50)
1) 270°C; 2) 280°C; 3) 290°C;
4) 300°C; 5) 310°C

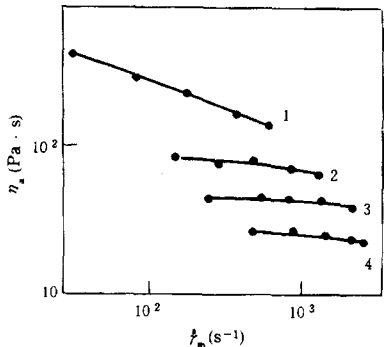


Fig. 7 Plots of η_a vs. $\dot{\gamma}_m$ for PPS/PA-66
(25/75)
1) 270°C; 2) 280°C; 3) 290°C;
4) 300°C

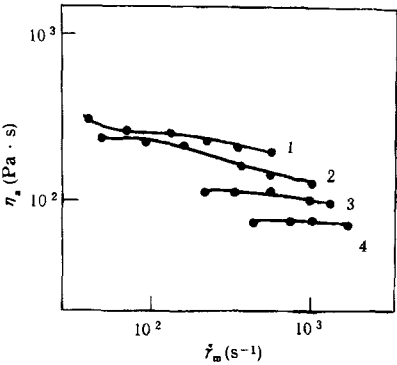


Fig. 8 Plots of η_a vs. $\dot{\gamma}_m$ for PA-66
1) 257°C; 2) 265°C; 3) 275°C;
4) 280°C

Again, it can be seen from Table 3 and Table 4 that activation energies of the blends are greater than that of PA-66. The results show that their viscosities are very sensitive to temperature, and it is possible to improve melt flowability by temperature change during processing. At the same time, the ΔE of the blends decreases with increasing PA-66 content, and the sensitivity of η_a to temperature decreases due to the soft chain of PA-66. On the other hand, Table 3 and Table 4 also indicate that ΔE of samples is decreased with increasing $\dot{\gamma}_m$ and σ , which is similar to the results for other polymers^[9].

Table 3 Activation energy ΔE of viscous flow of blends and PA-66 at a constant $\dot{\gamma}_m$

Sample	$\dot{\gamma}_m(\text{s}^{-1})$	$\Delta E(\text{kJ/mol})$
PPS/PA-66 (50/50)	6.31×10^2	155
	7.94×10^2	153
	1.00×10^3	150
	1.26×10^3	148
	1.56×10^3	145
PPS/PA-66 (25/75)	3.98×10^2	149
	5.01×10^2	144
	6.31×10^2	139
	7.94×10^2	139
PA-66	3.16×10^2	114
	3.98×10^2	109
	5.01×10^2	105
	6.31×10^2	100
	7.94×10^2	96

Table 4 Activation energy ΔE of viscous flow of blends and PA-66 at a constant σ

Sample	$\sigma(\text{MP}_a)$	$\Delta E(\text{kJ/mol})$
PPS/PA-66 (50/50)	2.00×10^4	205
	3.98×10^4	194
	5.49×10^4	188
	7.94×10^4	182
PPS/PA-66 (25/75)	2.00×10^4	207
	3.98×10^4	182
	5.49×10^4	170
	7.94×10^4	156
PA-66	2.00×10^4	141
	3.98×10^4	125
	5.49×10^4	118
	7.94×10^4	109

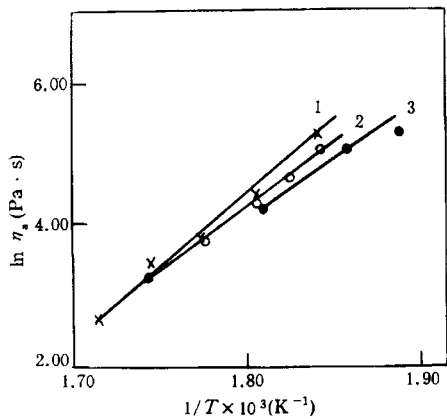


Fig. 9 Plots of $\ln \eta_a$ vs. $1/T$ for PA-66 and its blends at $\dot{\gamma}_m = 631\text{s}^{-1}$
1) PPS/PA-66 (50/50); 2) PPS/PA-66(25/75); 3) PA-66

CONCLUSIONS

From the rheological behavior of the blends and PPS some conclusions could be drawn.

1. PPS containing trace amounts of branching and/or cross-linking in chain and the blends of PPS/PA-66 at 300°C belong to pseudoplastic fluid. The non-Newtonian extent of the blends is less than that of PPS.

2. Apparent viscosity η_a of the blends is less than that of PPS, and the sensitivities of apparent viscosity to shear rate and shear stress are less than that of PPS.

3. Activation energy of viscous flow for the blends is higher, so its flowability is changed with temperature variation.

4. Chemical and oxidized crosslink reactions will take place in PPS chains at high temperature. Therefore, its apparent viscosity increases with elevating temperature, the relationship between $\ln \eta_a$ and $1/T$ does not obey the Arrhenius equation.

Keywords:

Polyphenylene sulfide; Polyamide-66; Polyphenylene sulfide/Polyamide-66 blends; Rheological behavior; Rheometer

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