

Rheological and Morphological Properties of Thermal-Aged Poly(phenylene Sulfide) Resin

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Synopsis

This paper discusses the morphological properties of thermal-aged poly(phenylene sulfide) (PPS) resin by Fourier-transform infrared spectroscopy (FT-IR) and solid-state ^{13}C -NMR. Also included is a method of applying the dynamic melt viscoelastic properties to determine the molecular weight distribution of the PPS resin. For virgin PPS resin, two resonance peaks were detected by NMR magic angle spinning (MAS) and cross polarization (CP) studies. However, four additional peaks can be seen for heat-treated PPS resin, indicating that the aromatic ring in PPS resin was attacked by sulfur-containing species or by the aryl ether group. The two most important reactions are crosslinking and chain extension. However, the chain extension is predominant when PPS is heated in nitrogen. The results coincide with the phenomenon observed in FT-IR studies. The molecular weight distribution of thermal-aged PPS resin was determined from dynamic melt viscoelasticity data. Results show that the longer the preheated time the broader the molecular weight distribution. It indicates that crosslinking and chain-extension reaction may have occurred when PPS resin was heated in air.

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a high-performance semicrystalline thermoplastic resin. From thermal analysis¹ and rheological data,² PPS shows thermoplastic character; however, when it is heated in air at elevated temperature it also shows some thermoset properties. This thermoset-thermoplastic character will affect the processing conditions, cycle numbers for reprocessing, and properties of the finished parts. The molecular structure of PPS may also be changed by heating it in air at processing temperature (315°C). The mechanism of the change of molecular structure is complicated and involves both crosslinking and chain-extension reaction.³

A systematic study was conducted to investigate the PPS-structure change during preheated process in different process conditions and environments (e.g., in ambient air and nitrogen atmospheres) utilizing solid-state ^{13}C -NMR, FT-IR, and ESR. Since PPS has a high melting temperature ($T_m = 285^\circ\text{C}$) and excellent solvent resistance, it is very difficult to determine the molecular weight and molecular weight distribution of PPS by conventional gel permeation chromatography unless a special design column and equipment is used.⁴ In this study, a method⁵⁻⁷ was developed by using dynamic-melt viscoelasticity to determine the molecular weight distribution of thermal-aged PPS.

EXPERIMENTAL

Material

A 77- μm -thick PPS film used in this study was obtained from Toray Company, Japan; it was a commercial material marketed under the trade name Ryton-PPS by Phillips Petroleum Co. (Bartlesville, OK).

Dynamic Mechanical Spectrometer

All of the rheological properties were measured by a Rheometric mechanical spectrometer, Model RMS-605. A strain was applied to the sample and the resultant stress was measured. A disposable 25-mm diameter parallel-plate fixture was employed; a frequency sweep was applied from 0.01 to 100 rad/s at 20% strain. The storage modulus G' and loss modulus G'' were superimposed to obtain the master curves of dynamic modulus at reference temperature, 315°C.

Solid State ^{13}C -NMR

The nuclear magnetic resonance (NMR) spectra were obtained from a Bruker MSL 200 type spectrometer. The line-narrowing techniques such as magic-angle spinning (MAS), high-power decoupling, and cross polarization (CP) were used to increase the resolution of spectra. Different contact times (0.05–8 ms) and delay times (35–70 μs) were applied to distinguish the protonated and nonprotonated carbons.

Infrared Spectroscopy

IR spectra were recorded on a Domen DA3-002 FT-IR spectrometer to detect the transmittance peaks which were the characteristics of the thermal-aged PPS film under different processing environments and conditions.

Electron Spin Resonance

The ESR spectra were recorded on a Bruker ER 2000-SRC spectrometer with an ancillary temperature-control unit. The sample was heated continuously to 220°C and scanned to generate a spectrum every 10 min. The spectrum of PPS heated in air for 60 min was taken to illustrate the appearance of new peaks.

Element Analyzer

Oxygen content of preheated PPS sample was detected by using a Heraeus CHN-O-Rapid Analyzer with a Tacussel Coulomax 78 automatic coulometric titrator.

X-Ray Diffractometer

The X-ray diffraction patterns employed a Shimadzu X-ray Diffractometer Model XD-5, with appropriate counting and recording equipment. Measurements were made with CuK_α radiation. The qualitative and quantitative procedures have been described by Brady.⁸

RESULTS AND DISCUSSION

Morphological Properties

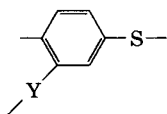
Since PPS is insoluble in most conventional solvents at room temperature, solid-state ^{13}C -NMR and FT-IR were utilized to investigate the molecular structure changes before and after processing. Figure 1 shows the IR absorption bands of virgin PPS, PPS heated in air at 315°C for 60 min, and PPS heated in nitrogen for 4 h; the different shapes of trisubstituted functional groups absorption bands between 1660 and 2000 cm^{-1} were observed. These results indicate that a crosslinking reaction may occur on the aromatic ring when PPS was preheated in air at elevated temperature.

Hawkins³ postulated that the oxygen, sulfur, or aryl ether group may attack the benzene ring when PPS is heated in air above its melting point. From the morphological study of crystallized PPS, the component of functional groups in 1236 cm^{-1} was increased with crystallinity of PPS. This phenomenon can be found in Figure 2. Figure 2 also illustrates the IR spectra of an amorphous PPS, and quenched PPS resins which have been annealed at 87 , 125 , and 162°C , respectively.

The crystallinity of annealed samples could be calculated from the height and half-height width of X-ray diffractometer pattern⁹ as shown in Figure 3. The crystallinity of PPS samples is 52 and 54% which have been annealed at 125 and 162°C , respectively; however, the sample annealed at 87°C is still an amorphous type. This phenomenon is due to the relaxation process of the ether linkage. The molecular chain in the disorder phase will be reoriented and packed better when the temperature is high enough; hence the bands will be changed. The asymmetric stretching mode of the diphenyl ether group in 1244 cm^{-1} of PEEK resin also show the same phenomena.¹⁰

As shown in Figure 1, the isothermal FT-IR spectra between 1660 and 2000 cm^{-1} did not change when the samples were studied in nitrogen atmosphere at 315°C . Hence, the crosslinking reaction may not occur on the benzene ring when PPS was heated in nitrogen atmosphere. Furthermore, from the rheological studies,² the isothermal viscosity of PPS increasing with time is explicit. This indicates that the chain-extension reaction may occur when PPS was heated in nitrogen atmosphere.

To study the curing mechanism of PPS, high-resolution ^{13}C -NMR was utilized. From the earlier study of the CP/MAS spectra of virgin PPS, there are two resonance lines (136 and 133 ppm) that can be seen in the spectra.¹¹ When the crosslinking reaction occurred, the molecular structure of PPS changed. Figure 4 shows the spectra of a cured PPS which was preheated in air for 60 min. The spectra have six resonance peaks. The molecular structure of cured PPS was postulated as:



where Y may be the oxygen, sulfur, or aryl ether functional groups.

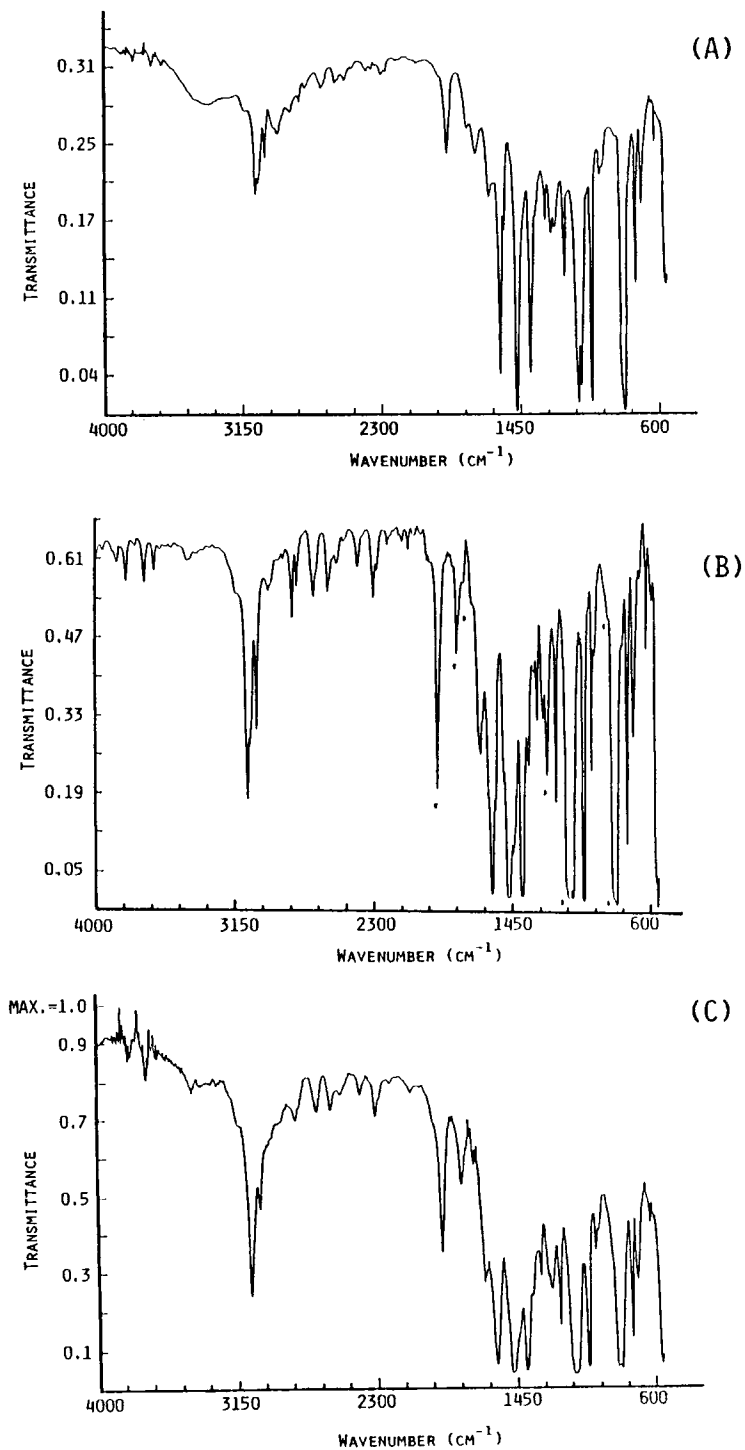


Fig. 1. FT-IR spectrum of: (a) virgin PPS; (b) PPS preheated in air at 315°C for 60 min; (c) PPS continuously heated in N_2 (g) at 315°C for 4 h.

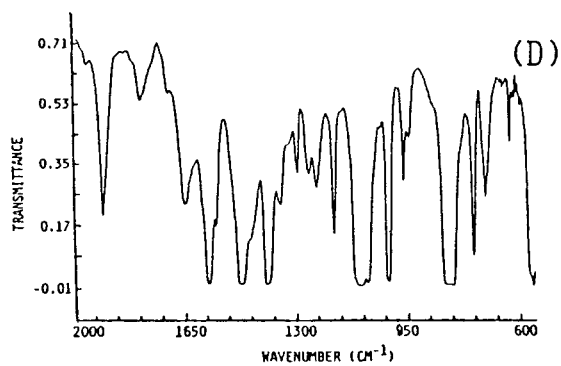
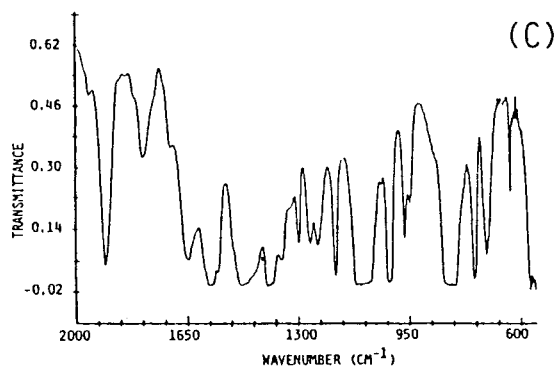
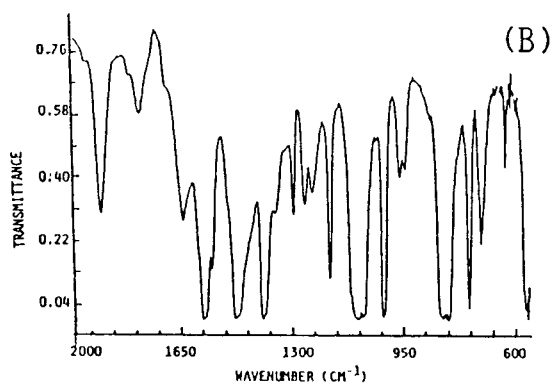
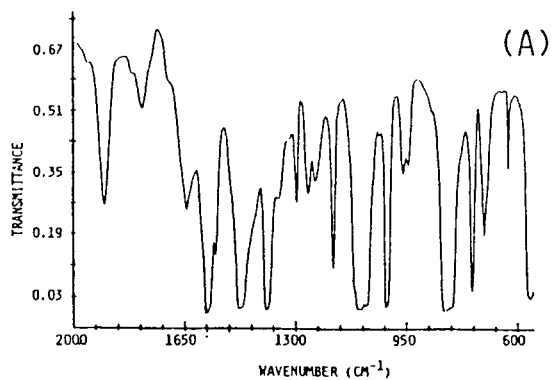


Fig. 2. FT-IR spectrum of PPS quenched at 315°C: (a) amorphous; (b) annealed at 87°C; (c) annealed at 125°C; (d) annealed at 162°C.

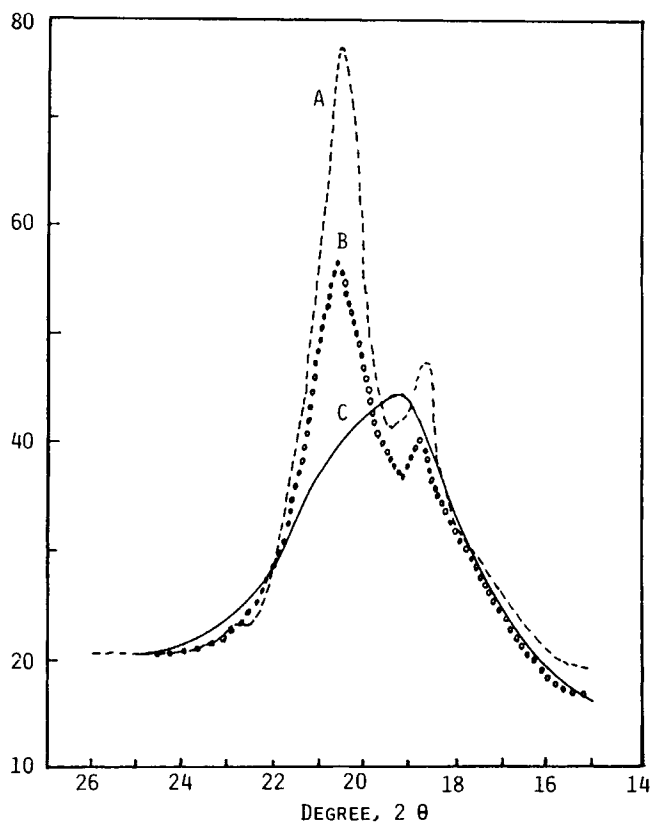


Fig. 3. X-ray diffractograms ($\text{CuK}\alpha$) of PPS annealed at: (a) 162°C; (b) 125°C; (c) 87°C.

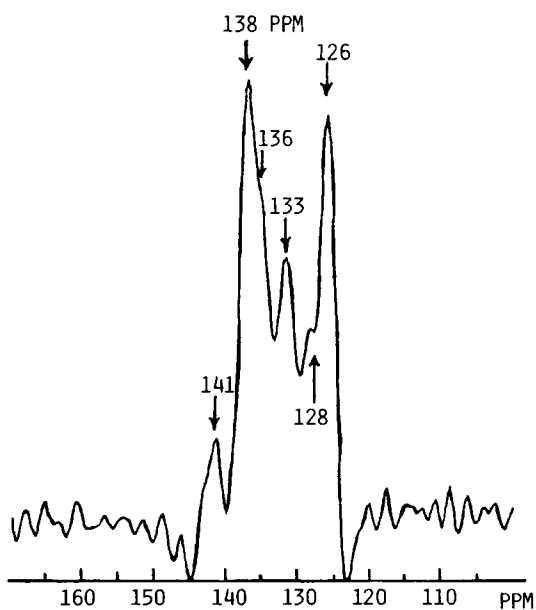


Fig. 4. CP/MAS ^{13}C -NMR spectrum of PPS preheated at 315°C for 60 min in air.

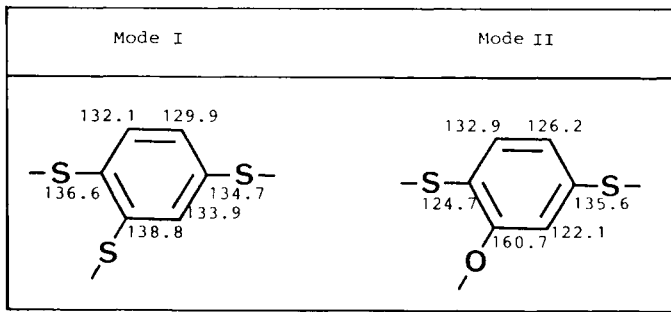


Fig. 5. ¹³C-NMR chemical shift of model monomers.

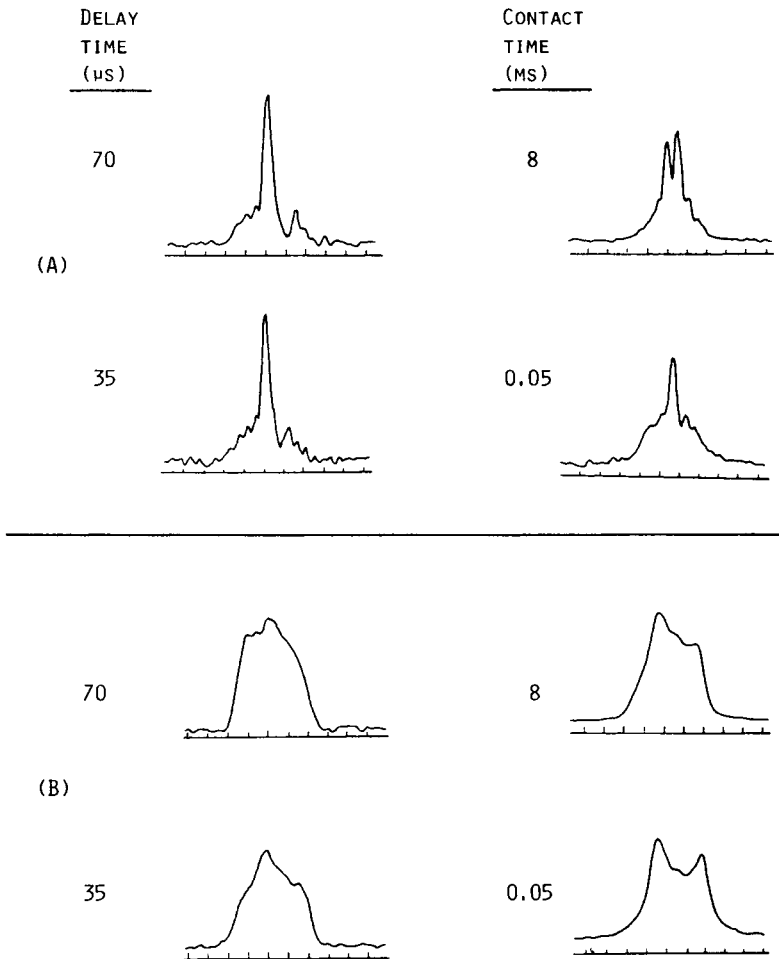
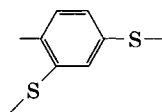


Fig. 6. Effect of contact time and delay time on the CP/MAS ¹³C-NMR spectrum of: (a) crystalline PPS; (b) amorphous PPS preheated at 315°C for 60 min in air.

From linear substituent parameters,¹² two models of molecular structure were obtained, as shown in Figure 5. By employing the experiment of different contact times (0.05–8 ms) and delay time (35–70 μ s), the molecular structure of aged PPS can be analyzed. Figure 6 shows the resonance spectra of crystalline and amorphous PPS, peaks of crystalline PPS are sharper than those of amorphous PPS since the packing of crystalline PPS molecular is tighter than that of amorphous PPS. The height of resonance peak enhanced at 136 ppm with the increasing of contact time and the peak at 133 ppm disappeared when delay time was longer than 35 μ s. This result is related to static dipolar interaction between carbon and the neighboring proton. It also shows that the resonance peaks at 136 and 133 ppm are nonprotonated carbon and protonated carbon, respectively. Although the resonance spectra peaks of amorphous PPS are broader, the information of molecular structure can be obtained by varying contact time and delay time. From the same figure, a small resonance peak at 141 ppm was found and the extent of resonance peak increased with contact time. When the delay time was 70 μ s, two peaks at 141 and 138 ppm still existed which implied that 141 and 138 ppm were resonance absorption peaks of nonprotonated carbons. From these results, the molecular structure of aged PPS can be postulated as Model I (Table I), i.e., the molecular structure of a cured PPS may be proposed as



The aryl ether groups can be detected in IR spectra; however, the oxygen content is too low to be detected by using ¹³C-NMR. When PPS was heated in air for 45 h; the NMR resonances at 158 ppm appeared as shown in Figure 7. According to the Model II mechanism (Fig. 5), the resonance peak at 158 ppm may be caused by aryl ether group. By the study of different contact times and delay times,³ it is clear that the peaks are also presented at longer delay times as shown in Figure 7. The peak at 158 ppm is caused by a nonprotonated carbon which was caused by the Model II mechanism. Figure 8 shows

TABLE I
Zero-Shear Viscosity and Shift Factor of PPS Resin

PPS	Temp (°C)	ETA ₀ ($\times 10^{-4}$)	$a_T = \text{ETA}_0/\text{ETA}_{00}$
Virgin PPS	302	1.83	1.24
	315	1.48	1.00
	330	0.73	0.49
	345	0.42	0.28
	360	0.17	0.12
Preheated 30 min	286	5.34	2.05
	315	2.61	1.00
	345	0.48	0.18
Preheated 60 min	285	11.5	1.41
	290	9.26	1.13
	315	8.20	1.00
	345	2.84	0.35

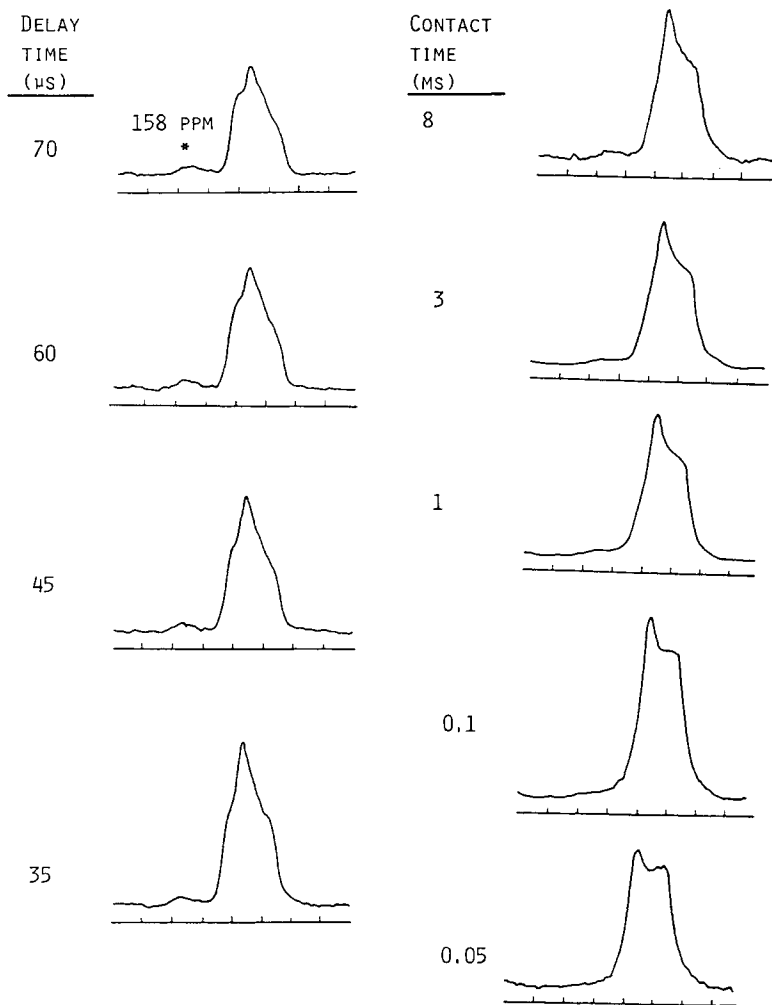


Fig. 7. Effect of delay time and contact time on the CP/MAS ^{13}C -NMR spectrum of PPS preheated at 315°C for 45 h in air.

the oxygen content of PPS at different preheated times. The longer the preheated time, the higher the oxygen content. To investigate the mechanism of chain extension and crosslinking reaction induced by free radicals, ESR studies were conducted. From ESR studies, a peak at 3391G can be found from PPS preheated in air at 315°C for 60 min as shown in Figure 9. The peak height increases with the increasing of heated time at 220°C as shown in Figure 10. These results suggest that free radicals occurred when PPS was heated at high temperature.

Rheological Properties

In general, thermoplastic composite was processed in air above its melting point (e.g., the processing temperature of PPS is 315°C). Although the thermal stability of PPS is very high, its molecular structure may change

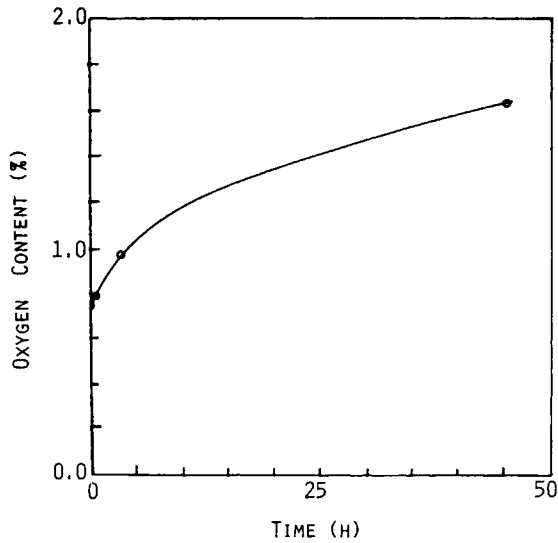


Fig. 8. Effect of aging time on the oxygen content of PPS aging at 315°C in air.

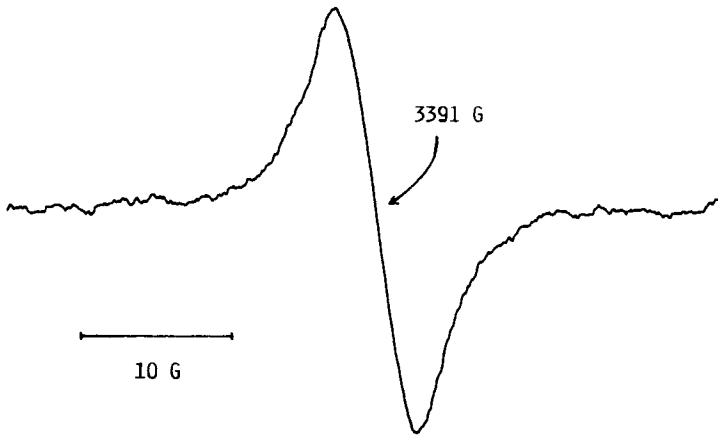


Fig. 9. ESR spectrum of PPS preheated at 315°C for 60 min in air.

during process. When PPS was heated in air above its melting point, the isothermal viscosity changed with time.¹ From the study of the changing of storage modulus and loss modulus of PPS with time, an intersection point between G' and G'' curves (Figs. 11 and 12) can be found. The higher the isothermal temperature, the shorter the time to reach the intersection point. This is analogous to the gel point of thermosetting resin during the curing process. This phenomenon indicates that crosslinking and/or chain extension may occur.

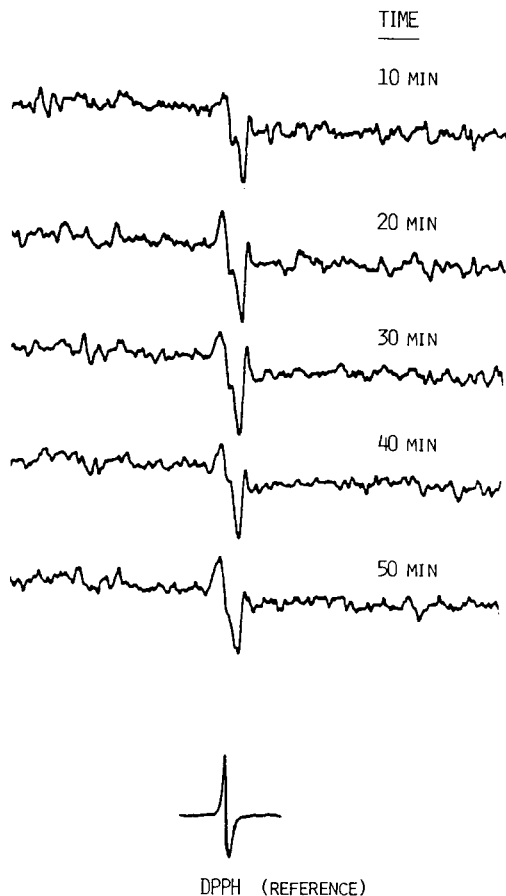


Fig. 10. ESR spectrum of PPS continuously heated at 220°C.

From the FT-IR spectra, it is difficult to find the trisubstituted absorption peaks (Fig. 1). However, the dynamic viscosity of PPS changed with time in nitrogen atmosphere (Fig. 13), and the intersection point between G' and G'' curves was also found. When PPS resin was heated in inert gas at elevated temperature, the predominate reaction was a chain extension reaction. The crosslinking reaction in air was due to oxygen.

Determination of Molecular Weight Distribution

The dynamic storage modulus G' and loss modulus G'' were changed with frequency for PPS preheated in air at various times (at 315°C). The dynamic storage modulus and loss modulus were superimposed to obtain master curves at the reference temperature, 315°C (Figs. 14 and 15). The shifted factor a_T is given by the following equation:

$$a_T = \frac{(\text{ETA}_0)}{\text{ETA}_{00}} \left(\frac{T_0}{T} \right) \left(\frac{L_0}{L} \right) \quad (1)$$

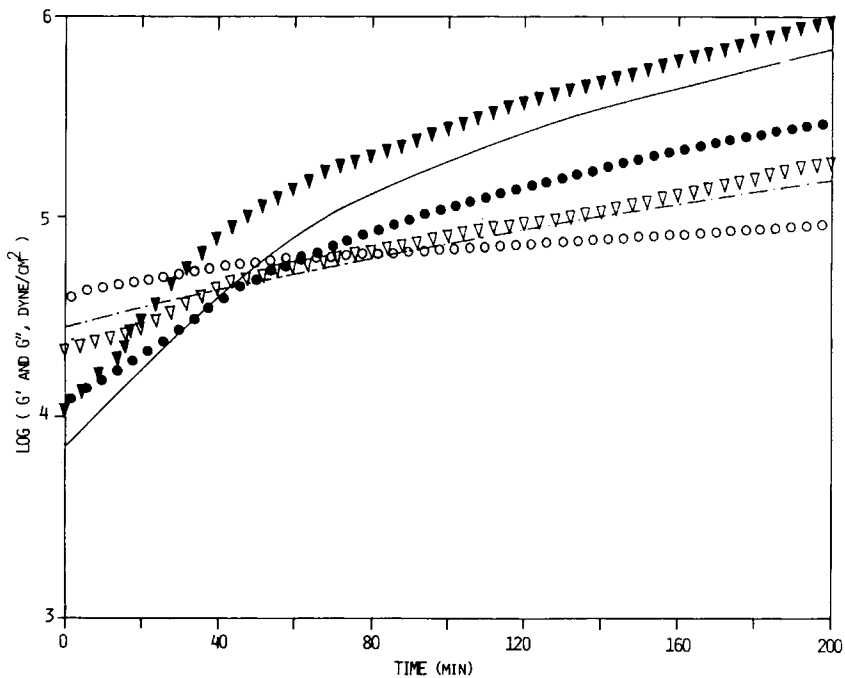


Fig. 11. Time-dependent storage modulus G' and loss modulus G'' of PPS at various isothermal temperatures at 1.0 Hz in air: G' : (●) 300°C; (—) 316°C; (▼) 330°C. G'' : (○) 300°C; (- -) 316°C; (▽) 330°C.

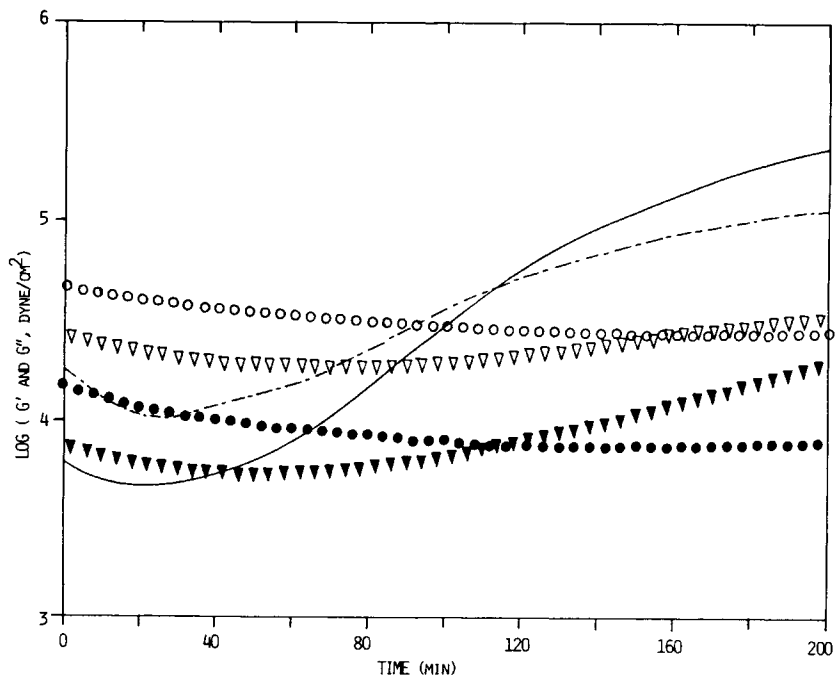


Fig. 12. Time-dependent storage modulus G' and loss modulus G'' of PPS at various isothermal temperatures at 1.0 Hz in N_2 : G' : (●) 345°C; (▼) 360°C; (—) 380°C. G'' : (○) 345°C; (▽) 360°C; (- -) 380°C.

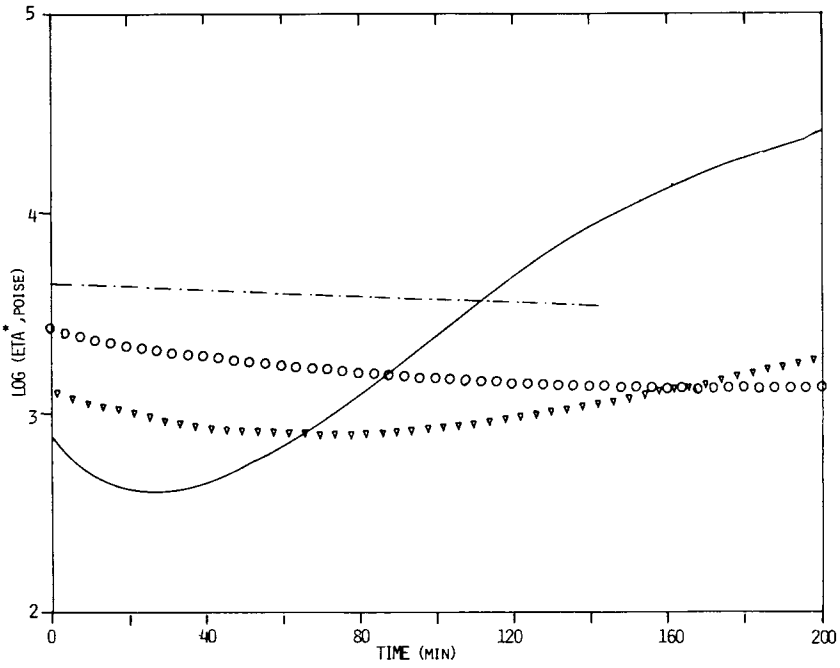


Fig. 13. Time-dependent dynamic viscosity of PPS resin at various isothermal temperatures at 1.0 Hz in N₂: (---) 316°C; (○) 345°C; (▽) 360°C; (—) 380°C.

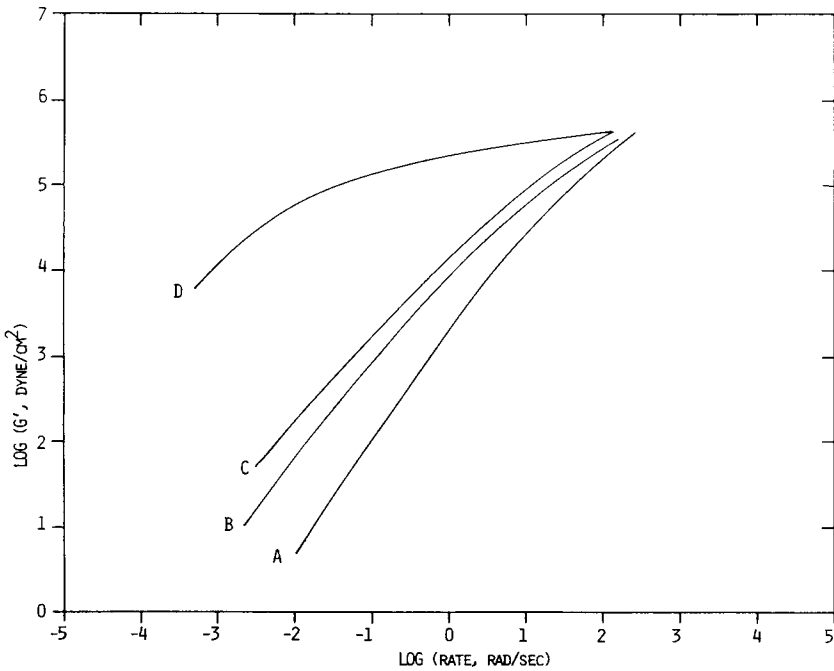


Fig. 14. Master curves of dynamic storage modulus of PPS preheated at 315°C: (A) virgin PPS; (B) 30 min; (C) 60 min; (D) 110 min.

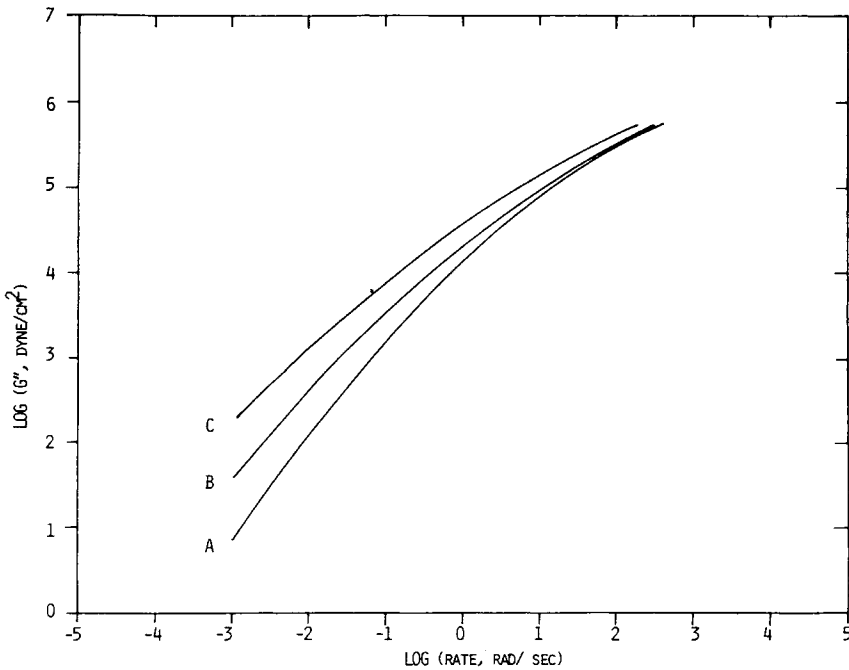


Fig. 15. Master curves of dynamic loss modulus of PPS preheated at 315°C: (A) virgin PPS; (B) 30 min; (C) 60 min.

where ETA_0 is the zero-shear viscosity at T , ETA_{00} is the zero-shear viscosity at the reference temperature, and L is the density. Results are summarized in Table I. The weight-average molecular weight (\bar{M}_w) can be obtained from the zero-shear viscosity ETA_0 by the following equation¹³:

$$\text{ETA}_0 = 2.06M_w^{4.68} \times 10^{-20} \quad (2)$$

The dynamic storage modulus G' in the master curve is fitted to the following empirical relation⁴:

$$\frac{G'}{G_N^0} = (\tau W)^c / (1 + \tau W)^c \quad (3)$$

where G_N^0 is the plateau modulus of the master curve, τ is the characteristic relaxation time, W is frequency, and C is a parameter. G_N^0 is determined by the following equation⁵:

$$G_N^0 = (4/\pi) \int_{-\infty}^{W_{\max}} G'' d \ln W \quad (4)$$

where W_{\max} is the frequency at G''_{\max} . The parameters τ and C are determined by a nonlinear-square method. This result is shown in Table II. The weight-average molecular weight distribution function in time scale can be expressed

TABLE II
Parameters of Dynamic Storage Modulus of PPS in Eq. (3)

PPS Resin	G_N^0	τ	C
Virgin PPS	1,124,000	0.0036	1.166
Preheated 30 min	1,137,000	0.0043	0.970
Preheated 60 min	1,047,000	0.0069	0.896

as eq. (5):

$$D(\tau) = \left| \sum_j \frac{(2G_j^0/\pi)(1/\tau_j)(10)^{C_jx} \sin(\pi c_j/2)}{(1/\tau_j)^2(10)^{2C_jx} + (2/\tau_j)(10)^{C_jx} \cos(\pi c_j/2) + 1} \right|_{\tau=1/w} \quad (5)$$

where $x = \log W$. The relation $\tau = IM^b$ is used to convert $D(\tau)$ to molecular weight scale, where $b = 3.5$ for $M > M_c$, and $b = 2$ for $M < M_c$.¹⁴

M_c can be estimated by

$$M_c = 2\rho RT/G_N^0 = 1.3 \times 10^5 \quad (6)$$

where ρ is density and R is the gas constant. Here, $b = 2$ and $I = 1$ were used to obtain a relative molecular weight scale ($\bar{M}_{w,r}$). Then $\bar{M}_{w,r}$ is converted to the absolute scale by using the scaling factor (S):

$$S = \bar{M}_w/\bar{M}_{w,r} \quad (7)$$

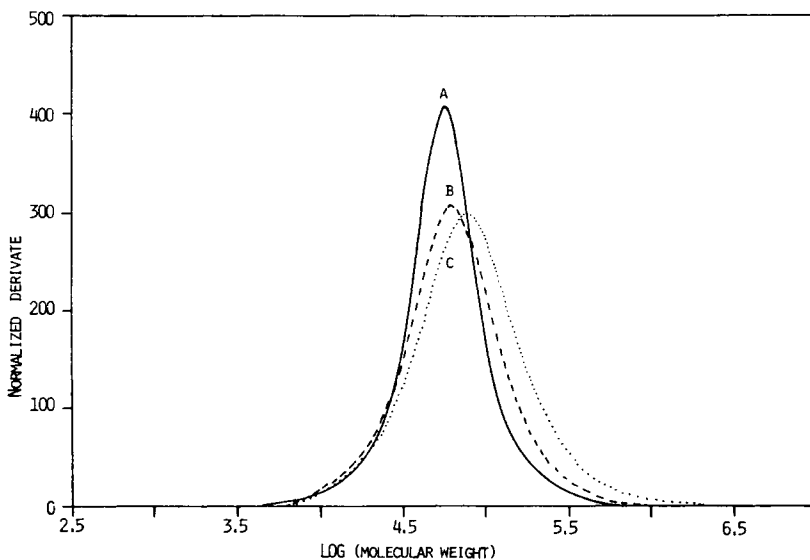


Fig. 16. Differential molecular weight distribution curves obtained from dynamic melt viscosity using exact method for PPS resin: (A, —) virgin; (B, ---) preheated in air for 30 min; (C, ···) preheated in air for 60 min.

TABLE III
Molecular Weights and Polydispersity Indices of PPS Resin

PPS resin	$\bar{M}_w (10^4)$	$\bar{M}_N (10^4)$	\bar{M}_w/\bar{M}_N
Virgin PPS	8.47	4.98	1.7
Preheated 30 min	9.11	4.4	2.1
Preheated 60 min	12.1	4.95	2.4
Preheated 110 min	36.9	—	—

where $\bar{M}_{w,r}$, the relative weight-average molecular weight, and \bar{M}_w , the absolute weight-average molecular weight, were obtained from eq. (2). From the master curve of G' , it was found that the longer the preheated time, the broader the spectrum, which indicates a broad molecular-weight distribution occurred. Figure 16 shows the differential-molecular-weight-distribution curves obtained from dynamic melt viscoelasticity for various preheated PPS resins. Table III summarizes the polydispersity index of PPS resin.

CONCLUSIONS

This research shows that when PPS is heated in air at elevated temperature, its molecular structure may change. A trisubstituted functional group absorption of benzene ring was found in FT-IR spectra. Solid-state ^{13}C -NMR confirmed a trisubstituted function group that was caused by the attack of an aromatic ring with oxygen and sulfur. The two most important reactions are crosslinking and chain extension. However, the chain extension reaction is predominant when PPS is heated in an nitrogen atmosphere. From the dynamic melt viscoelasticity study of preheated PPS resins, the molecular weight and molecular weight distribution can be obtained. The weight-average molecular weight of thermal-aged PPS increased with heating time. The longer the preheated time, the broader the molecular weight distribution.

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