

# Crosslinking of Poly(arylene Ether Ketone)s

## 1. Rheological Behavior of the Melt and Mechanical Properties of Cured Resin

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### Synopsis

Elemental sulfur has been used to crosslink poly(arylene ether ketone)s. Evidence for crosslinking is presented in terms of rheological data of the melt. The effects of crosslinking on mechanical properties have been examined using tensile creep, stress-relaxation, and dynamic-mechanical properties in torsion. The crosslinking elevates the glass transition temperature ( $T_g$ ), as measured by the maximum in the loss tangent, and reduces creep strain at temperatures above  $T_g$ . A new technique for monitoring cure is also presented. One of the advantages of this method for crosslinking poly(arylene ether ketone)s is that the crosslinking can be carried out both in the solid state and in the melt, the rate being dependent on the temperature (above  $T_g$ ) of annealing.

### INTRODUCTION

Poly(arylene ether ketone)s and polyethersulfones are gaining widespread acceptance as high-temperature-resistant, thermoplastic semicrystalline materials. Commercial examples are: a polyetheretherketone (PEEK) sold as VICTREX by ICI, and UDEL, a polyaromatic ethersulfone marketed by Union Carbide. Although these materials perform satisfactorily up to 150°C and are resistant to most organic solvents, some demanding applications require better mechanical performance and better solvent resistance. Crosslinking is an obvious way to achieve these ends. However, conventional techniques such as radiation crosslinking with or without the presence of peroxides or chemical crosslinking with additives do not work with these polymers. We have used elemental sulfur to crosslink poly(arylene ether ketone)s in the solid state and in the melt.<sup>1</sup> This technique is attractive in that the material can be crosslinked at any temperature between the glass transition temperature ( $T_g$ ) and the melt temperature ( $T_m$ ), and that the level of crosslinking can be controlled by varying the temperature of annealing. This method of crosslinking enhances the creep resistance above  $T_g$ , as well as the isochronal modulus above  $T_g$ . There is also an apparent increase of  $T_g$ .

While both PEEK and polyetherketones (PEK) have useful long-term mechanical strength above their glass transition temperatures which are measured to be 145°C (Ref. 2) and 165°C (Ref. 3), respectively, further improvement can be achieved if crosslinking can be introduced in the polymers. Unlike most aliphatic polymers such as polyethylene, aromatic polymers of this kind are not readily crosslinked by electron radiation. Jarrett and Staniland of ICI<sup>4,5</sup> have claimed in their patents that a copolyetherketone/sulfone con-

taining  $-\text{Ar}-\text{CO}-$  (75–90%) and  $-\text{Ar}-\text{SO}-$  (25–10%) repeat units (where Ar is a bivalent aromatic radical) forms crosslinks when mixed with elemental sulfur, upon heating to 300–450°C. It is particularly emphasized in their patents that the presence of  $-\text{Ar}-\text{SO}-$  repeat units is essential for crosslinking to occur. Lewis and Greinke<sup>6</sup> have done an extensive study on the polymerization of aromatic hydrocarbons with sulfur. Their results indicate that sulfur acts as a polymerization agent for polynuclear aromatic hydrocarbons. We have found that crosslinking can occur when a mixture of PEK or PEEK and elemental sulfur was compounded using either a corotating twin-screw extruder (ZSE) or a counter-rotating twin-screw extruder (ZSK).

In the following, we present data for polyetheretherketones (supplied by ICI). We have found that polyetherketones behave in an entirely analogous fashion, and the conclusions presented here apply equally well to polyetherketones.

The second section of this paper describes the experimental details, and the third section discusses the results from the studies of the mechanical and rheological properties for the sulfur-modified materials. The conclusions are presented in the fourth section.

## EXPERIMENTAL

### Sample Preparation

Sulfur and polyetheretherketone were dried before being compounded using either a corotating or counter-rotating twin-screw extruder at 400°C. The compounded pellets were then used to injection-mold tensile bars (T-bars) or to extrude taps or fibers. Sulfur concentration ranges of 0.25–2.0% by weight were used. The T-bars or taps were annealed at different temperatures and for different lengths of time before being tested.

### Mechanical Properties

a. Tensile stress–strain measurements were made on T-bars, using an Instron. A 5-cm/min jaw separation speed was used at room temperature (RT), and 1.27-cm/min at 200°C.

b. Stress–relaxation measurements were also carried out using an Instron. After samples were stretched to 5% elongation, the tensile engineering stress was monitored with time, at RT and at 200°C.

c. Tensile creep was monitored on extruded taps by hanging a weight, and measuring the separation between preset markings as a function of time.

d. Dynamic-mechanical measurements were carried out in torsion using a Rheometrics Mechanical Spectrometer Model 605 (RMS-605). Strain amplitudes varied between 0.03 and 0.5%, and were adjusted to optimize transducer response while remaining in the linear response range of the material. These measurements were carried out on injection-molded specimens.

### Rheological Measurements

Rheological characterization was carried out using a Rheometrics Mechanical Spectrometer 605. Samples were prepared from the injection-molded bars

by pressing them into disks at 20,000 psi in a press. This method of preparation produced virtually void-free disks and gave reproducible results in the RMS.

Testings were done between 25-mm-diameter parallel plates at 385°C. Samples were melted, and subjected to sinusoidal deformation. Two kinds of experiments were carried out: (1) a "frequency sweep," where the frequency of the deformation was varied between 0.1 and 100 rad/s; (2) a "time sweep," where the dynamic response was monitored as a function of time at a fixed frequency. Strain amplitude was varied between 10 and 40% to maximize response while remaining in the linear regime. All data analysis and accumulation, as well instrument control, were carried out using a DEC PDP-11 microcomputer.

## RESULTS AND DISCUSSION

Two effects are observed when sulfur is compounded with polyetheretherketone. Initially, the PEEK undergoes chain scission; subsequently, on aging in the solid state at temperatures above  $T_g$ , the material undergoes crosslinking, presumably with sulfur acting as a covalent crosslinker. The initial chain scission permits easy processability of the PEEK-sulfur melts; subsequent crosslinking enhances mechanical properties as well as chemical resistance. Evidence for both phenomena, as well as their effects, are presented in the following.

### High-Strain Tensile Properties

Experiments were performed on tensile bars in an Instron machine. Figure 1 depicts the stress-strain curves for three PEEK samples, one without sulfur, the others with 0.25 and 2% sulfur. These samples were annealed at 240°C for

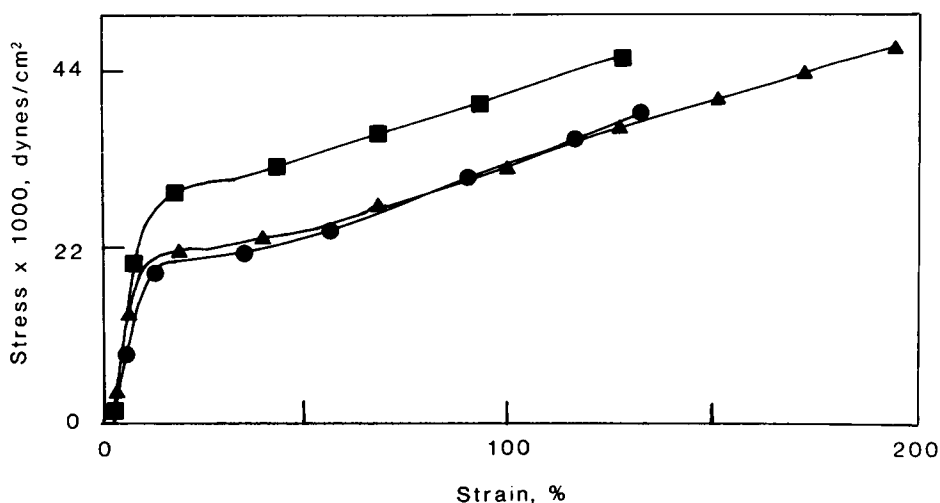


Fig. 1. Stress-strain curves at 200°C for annealed samples, measured on an Instron at 1.27 cm/min. All samples annealed at 240°C for 4 h: (●) PEEK; (▲) PEEK + 0.25% S; (■) PEEK + 2.0% S.

TABLE I  
Mechanical Properties of PEEK and PEEK + S Compounds

Sample	$E$ (dyn/cm <sup>2</sup> )	$\sigma_b$ (dyn/cm <sup>2</sup> )	$\epsilon_b$ (%)
PEEK	$1.28 \times 10^{10}$	$9.23 \times 10^8$	40
PEEK + 0.25% S	$1.46 \times 10^{10}$	$9.80 \times 10^8$	23
PEEK + 0.5% S	$1.41 \times 10^{10}$	$9.32 \times 10^8$	28
PEEK + 1.0% S	$1.46 \times 10^{10}$	$1.02 \times 10^9$	25
200°C			
PEEK	$1.52 \times 10^9$	$3.86 \times 10^8$	160
PEEK + 0.25% S	$1.92 \times 10^9$	$4.35 \times 10^8$	198
PEEK + 0.5% S	$2.10 \times 10^9$	$4.28 \times 10^8$	220
PEEK + 1.0% S	$2.35 \times 10^9$	$4.21 \times 10^8$	240

4 h. In conjunction with Table I, it is clear that:

1. The sulfur compounds show higher initial moduli and higher elongations at break,  $\epsilon_b$ , compared to pure PEEK at 200°C.
2. Increasing the sulfur content increases both modulus and  $\epsilon_b$  at 200°C.
3. The 200°C stress-strain curves deviate from that of PEEK at strains around 5%.
4. The differences in room-temperature properties between PEEK and the PEEK-sulfur compounds are negligible.

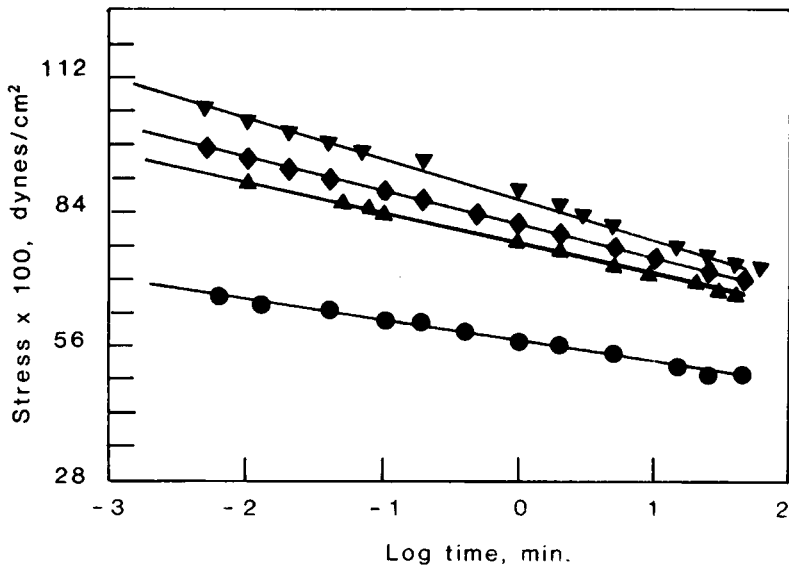


Fig. 2. Stress-relaxation at 200°C for annealed samples, measured on an Instron at 5% elongation. All samples annealed at 240°C for 4 h: (●) PEEK; (▲) PEEK + 0.25% S; (◆) PEEK + 0.50% S; (▼) PEEK + 1.0% S.

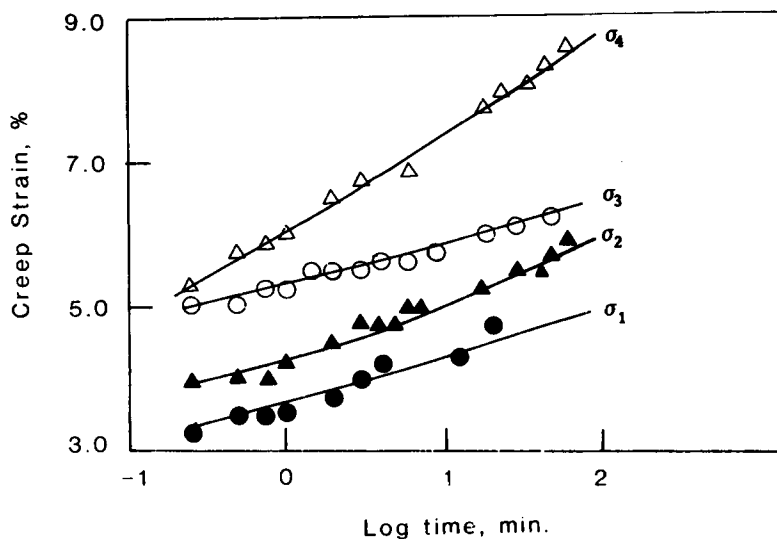


Fig. 3. Creep strain (%) vs. time at 200°C for two different stress levels, measured on an Instron. All samples annealed at 240°C for 4 h: ( $\Delta$ ,  $\circ$ ) PEEK;  $\sigma_3 = 1.17 \times 10^8$  dyn/cm<sup>2</sup> and  $\sigma_4 = 1.40 \times 10^8$  dyn/cm<sup>2</sup>; ( $\blacktriangle$ ,  $\bullet$ ) PEEK + 0.25% S;  $\sigma_1 = 1.16 \times 10^8$  dyn/cm<sup>2</sup> and  $\sigma_2 = 1.51 \times 10^8$  dyn/cm<sup>2</sup>.

These samples were estimated to have comparable degrees of crystallinity (about 40%) by X-ray diffraction (XRD),<sup>7</sup> and so the differences in modulus above  $T_g$  must be attributed to crosslinking of the amorphous phase and morphological differences in the crystalline phase.<sup>7</sup> The increase in  $\epsilon_b$  is harder to interpret; it could be attributed to a "plasticization" effect of sulfur, as has been reported for polyethylene sulfide by Tobolsky,<sup>8</sup> but we have no evidence of  $T_g$  lowering to substantiate this.

Stress-relaxation at 5% elongation and creep at stresses of around  $1.4 \times 10^8$  dyn/cm<sup>2</sup>, at 200°C, reveal interesting, and materially important, features in Figures 2 and 3. The magnitudes of the relaxation moduli increase with increasing amounts of sulfur. The creep strains also decrease with sulfur content. Both features are complementary, and desirable in high-temperature thermoplastics.

### Low-Strain Mechanical Properties

Dynamic-mechanical properties were carried out in the linear response range of the material. The results are shown in Figures 4 and 5. In Figure 4, the samples were annealed at 240°C for 24 h, while the PEEK and the PEEK + 0.25% S compound are similar to one another, the PEEK + 2% S material shows an increase in modulus and a slight shift in  $T_g$ , as reflected in the loss-tangent maximum (not shown). Annealing for 24 h at 290°C enhances the differences, as shown in Figure 5. Now the PEEK + 0.25% S compound shows a higher modulus above  $T_g$  than pure PEEK, as well as a higher  $T_g$ ; the effect is even more pronounced for the 2% S compound. The increase in modulus is about 1.5 times at 200°C, and the apparent  $T_g$  is higher by about 20°C. These results corroborate the tensile (high-strain) results, indicating little differences at room temperature, but appreciable differences above  $T_g$ .

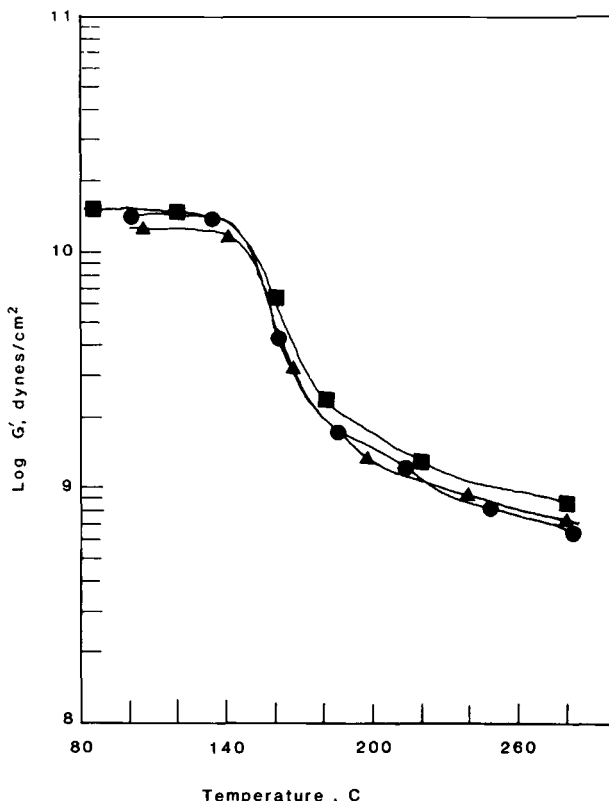


Fig. 4. Dynamic-mechanical properties as a function of temperature. Measurements made on rectangular strips, with an RMS-605, in torsion, at a frequency of 5 rad/s. All samples annealed at 240°C for 24 h: (●) PEEK; (▲) PEEK + 0.25% S; (■) PEEK + 2.0% S.

### Rheological Properties

Figures 6–8 contain the results of RMS measurements on the melt at 385°C. We have verified that the Cox-Merz rule is valid for these melts at 400°C, i.e.,  $\eta^*(\omega) \approx \eta(\dot{\gamma})$  for  $10^{-1} \text{ s}^{-1} < \dot{\gamma} < 10 \text{ s}^{-1}$  and  $10^{-1} \text{ rad/s} < \omega < 10 \text{ rad/s}$ . Thus, in the following,  $\eta^*(\omega)$  results are used exclusively with the implicit assumption that  $\eta(\dot{\gamma})$  reveals the same features. There are two kinds of results in these figures. Figure 6 shows initial frequency sweeps for the “unaged” compounds, i.e., samples which have been mixed and pelletized but not otherwise heat-treated. Then, these same samples were subjected to aging in the melt at 385°C; the dynamic viscoelastic functions were monitored (at a fixed frequency) for these samples as a function of time as shown in Figures 7 and 8.

Evidence that sulfur causes chain scission in PEEK comes directly from the initial, “unaged” frequency sweeps shown in Figure 6. The initial, “unaged” samples were prepared by mixing the PEEK and sulfur in a ZSE at 400°C, followed by pelletization. These pellets were pressed into slabs for the RMS work or injection-molded for tensile/torsion measurements. During the mixing operation, the mixture was exposed to a temperature of about 400°C for a total of approximately 10 min.

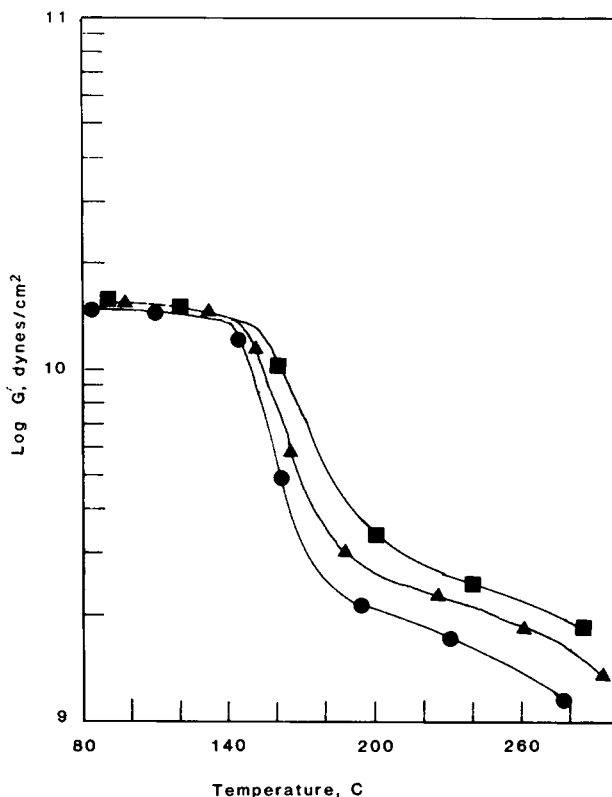


Fig. 5. Dynamic-mechanical properties as a function of temperatures. Samples annealed at 240°C for 24 h and further aged at 290°C for 24 h. Symbols same as in Figure 4.

In Figure 6 the PEEK and the PEEK + 0.25% S samples show virtually identical behavior, indicating that the heat treatment with sulfur has not caused any significant changes in the PEEK. However, the 2% S sample shows a drop in the low-shear viscosity, and also exhibits a marked shear-rate (or frequency) dependence. The viscosity at the high-shear rate (at 100 rad/s) is lower by a factor of 2.5, when compared with that of the PEEK.

This indicates chain scission, and the production of low-molecular-weight (MW) species, or at least, species with markedly lower relaxation times. The shape of the curve also indicates a broadening of the MW distribution, with the weight-average remaining more or less constant, but with a low-molecular-weight-tail developing. The lower melt viscosity and/or the presence of lower-MW species lead to a higher rate of crystallization for the 2% S sample, as well (see Ref. 7). Also the same samples, before being heat-aged, are also completely soluble in  $H_2SO_4$ , indicating the absence of crosslinking at this stage.

When these samples are heat-aged, chain-extension, and crosslinking start to occur. This heat-aging can be done in the melt (400°C) or in the solid state above  $T_g$  (we used 240 and 290°C). When aged in the melt at 400°C in the RMS, the sample viscosity increased with time. We chose a low frequency, 0.5 rad/s, to accentuate any changes in molecular weight as reflected in the

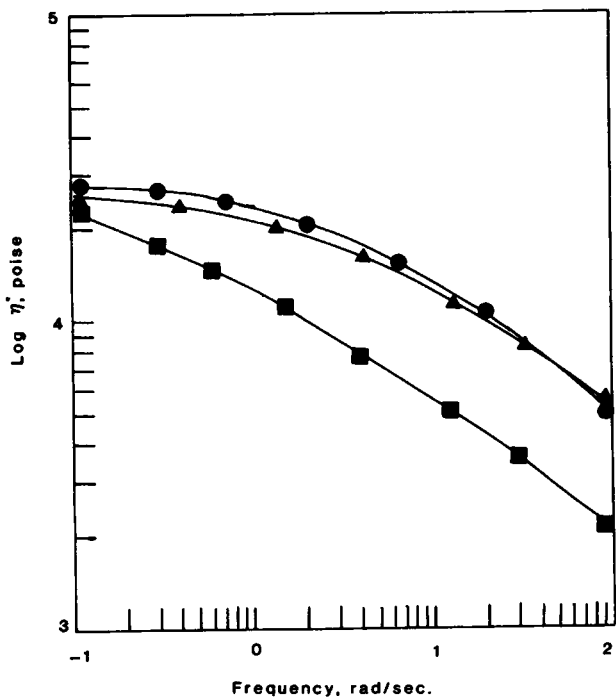


Fig. 6. Dynamic complex melt viscosity as a function of frequency at 385°C, measured between parallel plates on an RMS-605. Symbols same as in Figure 4.

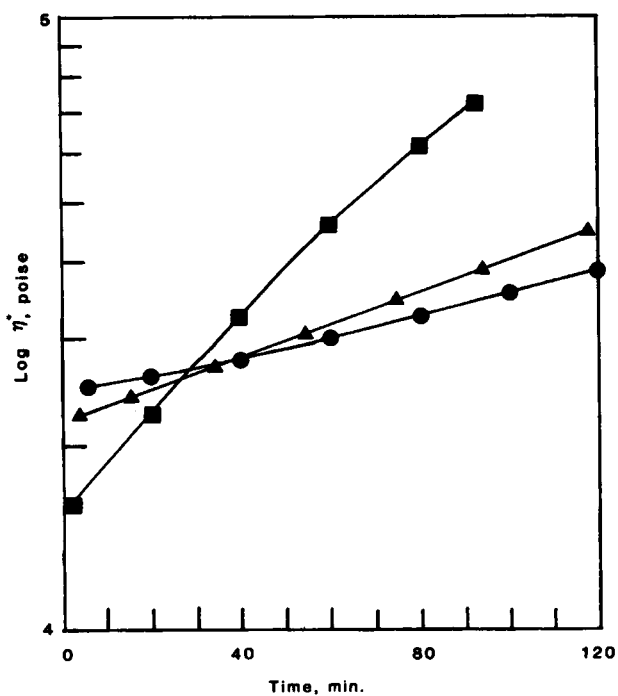


Fig. 7. Increase in complex viscosity with time, in the melt at 385°C. Parallel plates, 10% strain, at 0.5 rad/s. Symbols same as in Figure 4.



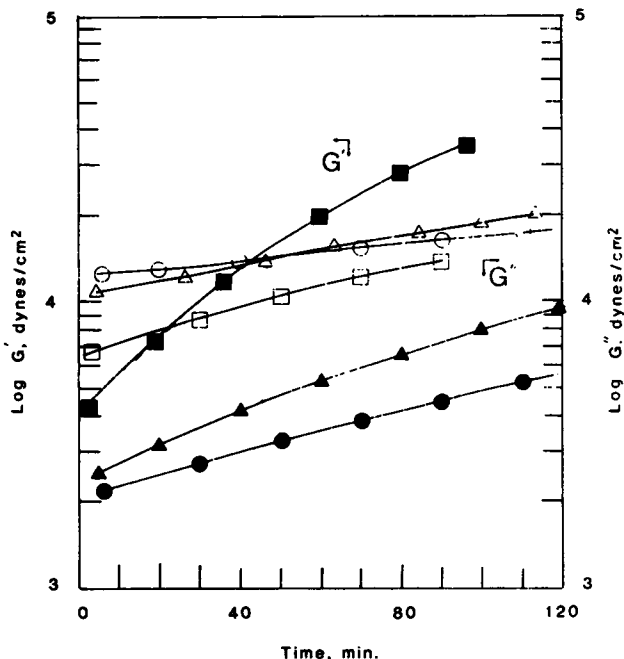


Fig. 8. Elastic and loss moduli of the melt at 385°C as a function of time: 10% strain, at a frequency of 0.5 rad/s; (●,○)  $G'$  and  $G''$  for PEEK; (▲,△)  $G'$  and  $G''$  for PEEK + 0.25% S; (■,□)  $G'$  and  $G''$  for PEEK + 2.0% S.

viscosity. Figure 7 shows that, up to 120 min, the pure PEEK and the PEEK + 0.25% S samples behave similarly, although one discerns a slightly faster rate with the 0.25% S sample. The rate is markedly higher for the 2% S sample.

In Figure 8, we plot  $G'$  and  $G''$  (at 0.5 rad/s) as a function of time for the same samples as shown in Figures 6 and 7. The utility of this type of plot to quantify rates of crosslinking will be elaborated below. Initially, as expected,  $G''$  (at this low frequency) is higher than  $G'$ ; as aging proceeds,  $G'$  increases relative to  $G''$ . This is indicative of an increase in entanglement density and/or degree of crosslinking (see similar arguments in Ref. 9). In general, one can infer, from the increase of  $\eta^*$  in Figure 7, and the behavior depicted in Figure 8, that the molecular weight is increasing in some manner.

To verify whether crosslinking occurs, we have analyzed the gel content in samples aged for different time intervals. We have done this by dissolving the aged samples in 98%  $\text{H}_2\text{SO}_4$ , filtering off any gel, and estimating the concentration of the solution using UV visible spectroscopy at 432 nm (this is a protonated carbonyl absorption). Empirically, we have established a relationship between gel content and a parameter we term the "crossover" time, or  $t_c$ .<sup>10</sup> In Figure 8, this is defined as the time at which  $G'$  and  $G''$  "cross" each other, i.e.,  $G' = G''$  at time  $t = t_c$ .

Figure 9 shows a plot of gel content vs. time of aging,  $t$ , plotted as the distance from  $t_c$ , or as  $(t - t_c)$ .<sup>10</sup> A variety of samples was analyzed, with different values of  $t_c$ . All of them fall on the same curve, however, when plotted against  $(t - t_c)$ . This strongly suggests that  $t_c$  is an indicator of the

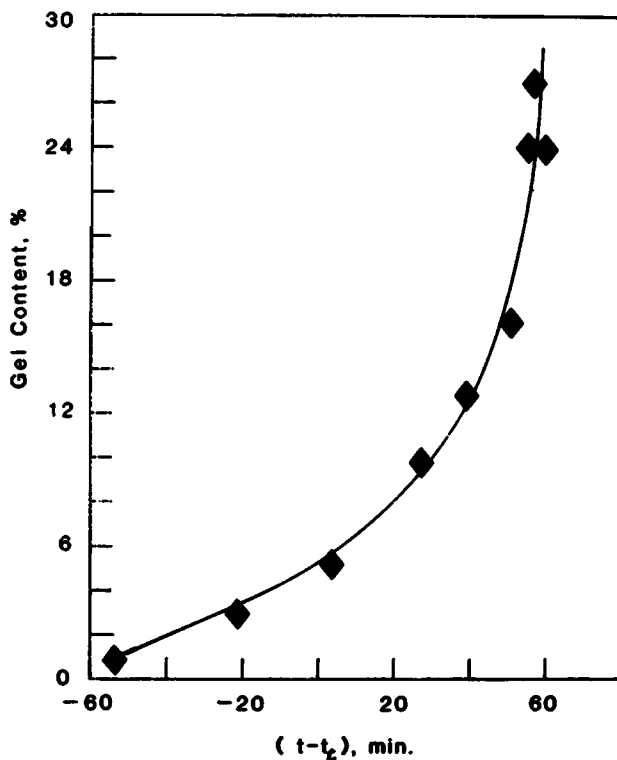


Fig. 9. Gel content as a function of distance from the crossover point ( $t - t_c$ ). Samples analyzed for gel content after aging in the melt at  $385^\circ\text{C}$  for different lengths of time. Data represent several polyetherketones with widely differing values of  $t_c$ .

rate of crosslinking. In other words, the shorter the value of  $t_c$ , the higher the rate of crosslinking. Using this criterion, we see that, in Figure 8, the PEEK + 2% S undergoes crosslinking in the melt faster than the other samples.

The results of the mechanical measurements on the aged solids, and the rheological work on the melts, demonstrate clearly two effects, as mentioned before: (1) an initial chain-scission step, which probably occurs during compounding in the extruder at around  $400^\circ\text{C}$ ; and (2) subsequent crosslinking on heat treatment, either in the melt, or in the solid state, above  $T_g$ .

Poly(arylene ether ketone)s are known to crosslink thermally if aged for a sufficiently long period of time at elevated temperatures (ca.  $400$ – $450^\circ\text{C}$ ). For PEEK, this happens very slowly (see Fig. 8). The introduction of sulfur provides a fast crosslinking process; it can do this either by crosslinking the polymeric chains, or by crosslinking with itself and trapping the polymer within the network. The latter possibility can be ruled out in the view of the fact that (a) low concentrations of sulfur are sufficient to form a network and (b) once completely crosslinked, the polyetheretherketone cannot be leached out with sulfuric acid, at least over a period of several days.

The mechanism for crosslinking poly(arylene ether ketone)s or a copolymer of polyetherketone/sulfone, by sulfur, is still not quite clearly understood; it is almost certain to be fairly complicated based on the fact that even the chemistry of molten sulfur is fairly complex.<sup>11,12</sup>

Sulfur exists predominantly as orthorhombic sulfur at room temperature. On heating, it melts at around 120°C, via an intermediate monoclinic form. At the melting point, it consists mainly of S<sub>8</sub> rings (yellow in color), and a fraction of S<sub>w</sub> (polymeric sulfur, reddish-black in color). The amount of S<sub>w</sub> increases with temperature up to around 200°C; above this temperature, the chains start to break up. Thus the maximum concentration of polymeric sulfur occurs at around 200°C. It is safe to assume that sulfur at temperatures above 200°C consists of polymeric and other reactive radical species, S<sub>n</sub>, where  $n \leq 8$ .

These reactive radicals initiate chain scissions in polyetheretherketones, leading to the production of lower-molecular-weight species and broadening the distribution, accounting for the behavior depicted in Figure 6. Subsequent heating above  $T_g$  in nitrogen or vacuum must lead to crosslinking. The usual mechanisms postulated for sulfur crosslinking in the vulcanization of rubber<sup>13</sup> are not applicable here, since there are no aliphatic double bonds in polyetheretherketones. Without further work, it is difficult to conjecture at this point on the mechanism; all we can deduce is that the mobility of sulfur above 150°C is sufficient to crosslink the polymer in the solid state. The effects of this kind of crosslinking on crystallinity will be elaborated upon in a forthcoming paper.<sup>7</sup>

## CONCLUSIONS

By means of mechanical and rheological studies, we have demonstrated that elemental sulfur can crosslink polyetheretherketones and polyetherketones in the solid state and in the melt. The crosslinked polymer exhibits enhanced properties such as a decrease in creep strain, and an increase in stress-relaxation modulus, as measured above  $T_g$ . The glass transition temperature is also increased upon the incorporation of sulfur and subsequent aging. All of these results point to a convenient technique for enhancing the high-temperature performance of aromatic polyetheretherketones and polyetherketones.

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