

# Effect of Solid-State Curing on the Viscoelastic Properties of Poly(phenylene sulfide)

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## SYNOPSIS

PPS is a thermosetting/thermoplastic resin. The resin, upon exiting the polymerization process, is generally a low viscosity, low molecular weight material. The thermosetting character is therefore exploited in a solid state cure process in the presence of air at elevated temperatures. This produces a resin with a more desirable property profile. Melt state dynamic mechanical measurements have been made on a series of cured PPS resins to elucidate structural changes that occur on the molecular level during the cure process. Increases in viscosity, non-Newtonian behavior, and relative elastic response were observed with increasing cure time and have been attributed to an increasing molecular weight and broadening molecular weight distribution achieved through branching/crosslinking. The effects of various environments on curing have also been investigated. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

High-temperature thermoplastics are currently receiving a great deal of attention due to their thermal stability, chemical resistance, good mechanical performance, and potential for use as matrices in advanced composite materials. Poly(phenylene sulfide) (PPS) is one of these thermoplastic materials. It is of particular interest since it has a unique thermosetting/thermoplastic character. Early studies of this thermosetting (curing) behavior by Hawkins<sup>1</sup> focused on several reaction mechanisms. These include (1) chain extension, (2) oxidative cross-linking to form trisubstituted species, and (3) oxygen uptake followed by loss of SO<sub>2</sub>. From a commercial point of view, these curing reactions can be exploited through two different routes<sup>2</sup>: In the first, PPS [ $T_g = 85^\circ\text{C}$ ,  $T_m = 285^\circ\text{C}$  (Ref. 3)] is cured as a melt at temperatures of 315–425°C. This process is relatively slow since normal processing conditions are known not to affect PPS properties significantly. In the second method, the solid-state resin is cured in the presence of air at temperatures of approximately 175–280°C. In these processes, the rate of cure increases with temperature and melt flow decreases with time.<sup>2</sup> This latter result is an indication of increased molecular weight.

As PPS cures, changes in the molecular structure occur. Although this fact has been well known for some time, there have been few studies of the effect of curing on the bulk properties of PPS, in particular, on the viscoelastic properties.<sup>3</sup>

A more detailed knowledge of the viscoelastic properties of cured PPS can give insight into the structural changes that occur on the molecular level. However, it is unclear whether the curing mechanisms described by Hawkins result in resins with significantly different properties, such that they are detectable by bulk characterizations. Therefore, an indirect measure of structural changes using viscoelastic measurements may be useful. This information, in turn, can be used as an aid in controlling these reactions. Therefore, the molecular architecture and properties may be controlled through appropriate processing. This paper reports the results of a study to examine the melt-state viscoelastic properties of PPS cured in the solid state and the effect of various environments.

## EXPERIMENTAL

### Materials

The resins used in this study were obtained from Tosoh Susteel. The G100 grade (not commercially available) is an uncured reactor powder. It is there-

fore a low viscosity, low molecular weight resin and is not strandable in extrusion. The 160 grade is a version based upon G100 that has been air-cured at temperatures of approximately 255–260°C. The curing process increases the viscosity of the resin so that an extrudable material results.

### Sample Preparation

The uncured G100 resin was supplied in powder form. Prior to curing, it was dried in a vacuum oven at 80°C for 4 h. To cure the resin, a layer of powder approximately 1 cm deep was poured into an uncovered glass dish. The dish was placed in the center of a recirculating air oven at approximately 255–260°C. The resin was then cured for various times. Cured and uncured powders were compression-molded into disks at 300°C and 2 tons pressure for 2 min, followed by cooling in a cold press under pressure.

The 160 grade powder was cured and subsequently processed into disks in a manner identical to that used for G100 powder. In addition to powder curing, the 160 grade was cured as pellets. Pellets

were dried and cured in a glass dish in a manner similar to that described for G100. To examine the effects of different environments, the G100 powder was also cured in a nitrogen environment and under vacuum.

### Instrument

A Rheometrics Dynamic Spectrometer Model 7700 (Rheometrics, Inc, Piscataway, NJ) was used to measure the melt-state dynamic mechanical response of the resins. A parallel plate geometry in a nitrogen-purged environment was used for all tests. Frequencies were varied from 0.1 to 500 rad/s. Temperature was kept constant at 300°C.

### RESULTS

Figure 1 shows capillary and dynamic viscosity data for three PPS grades produced by Tosoh Susteel. As previously described, the 160 grade is a cured version of G100. The 140 grade is cured in a process similar to that used to make 160, but a shorter cure time is used. In the figure, dynamic data for G100

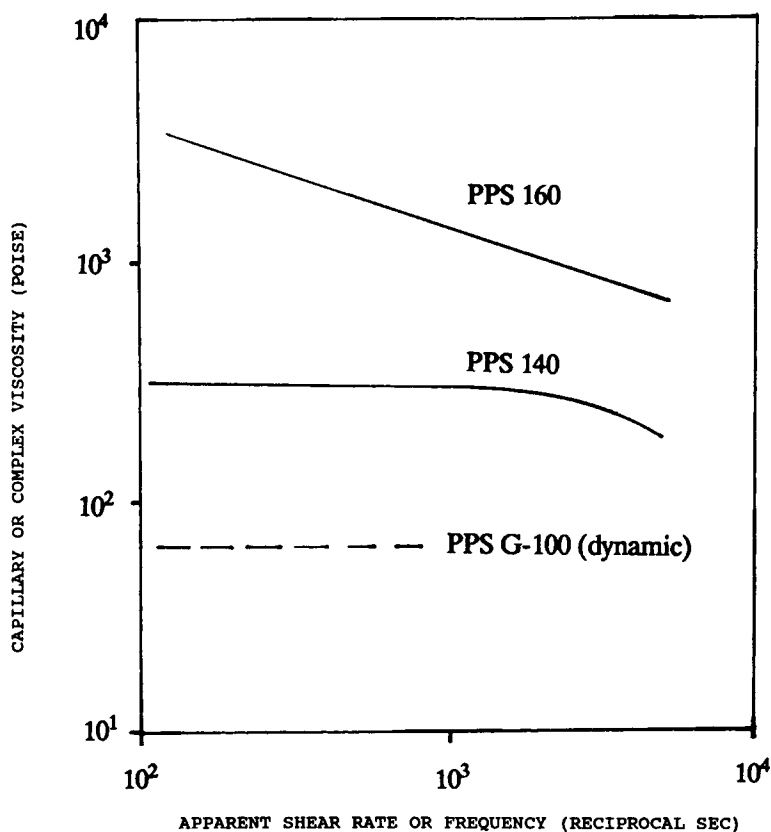


Figure 1 Capillary and dynamic viscosities of various PPS grades.

are compared to capillary viscosity data for the two cured resins.

Figure 2 shows complex viscosity as a function of frequency for the as-received G100 and 160 powders. The lines plotted in these graphs represent the average of three tests. From this figure, it is apparent that the viscosity of G100 is extremely low. Given the limitations of our parallel plate geometry, the low-frequency data were difficult to obtain. Moreover, behavior of this resin appears to be highly Newtonian. Also shown on this plot is the complex viscosity of 160 grade pellets, i.e., 160 powder that has seen one brief melt-state cure in the extruder (approximately 1–2 min residence time). It is seen that under normal processing conditions that complex viscosity is not increased significantly.

Figure 3 shows the results of curing PPS reactor powder in air (presented as complex viscosity as a function of frequency). One observes that the increase in viscosity is faster for the 1 h cure time. For comparison, the curve for the 160 grade resin is also displayed. After curing G100 for more than 4 h, a resin with a viscosity similar to that of the 160 grade is obtained.

The effect of curing on the viscoelastic response of the 160 resin in pellet and powder form is shown

in Figure 4. The difference observed here is related to surface area. Powder obviously has a greater surface area than do pellets. The pellet cure results in a greater non-Newtonian character after 7 h in air.

To further elucidate the general effects of solid-state curing on the viscoelastic response, one can decompose the complex viscosity into loss and storage moduli ( $G''$  and  $G'$ , respectively). This has been done for the curing of 160 pellets in air for several cure times. The 13.5 h cure is shown in Figure 5. In this figure, the  $G'-G''$  crossover is observed to shift to lower frequencies.

In Figure 6, the effect of curing G100 in different environments is shown. The most prominent feature of this comparison is that the presence of oxygen causes a much quicker change in viscosity. There is no significant difference between nitrogen and vacuum curing.

The effects of these two different curing routes can be made clearer if a comparison is made at similar viscosity levels, as shown in Figure 7. It is seen that to cure to similar viscosity levels more time is required for oxygen-free (vacuum) curing (as demonstrated in Fig. 6); however, the lack of oxygen causes a significant increase in non-Newtonian response.

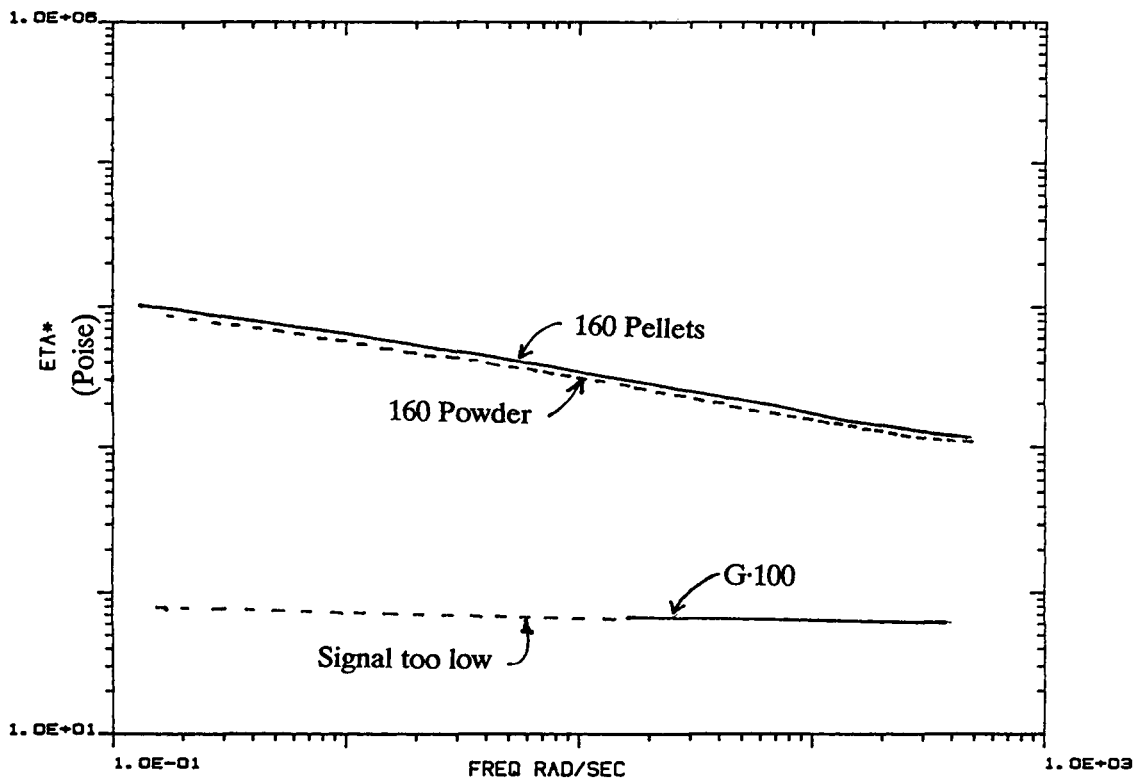


Figure 2 Effect of one extrusion on PPS viscosity.

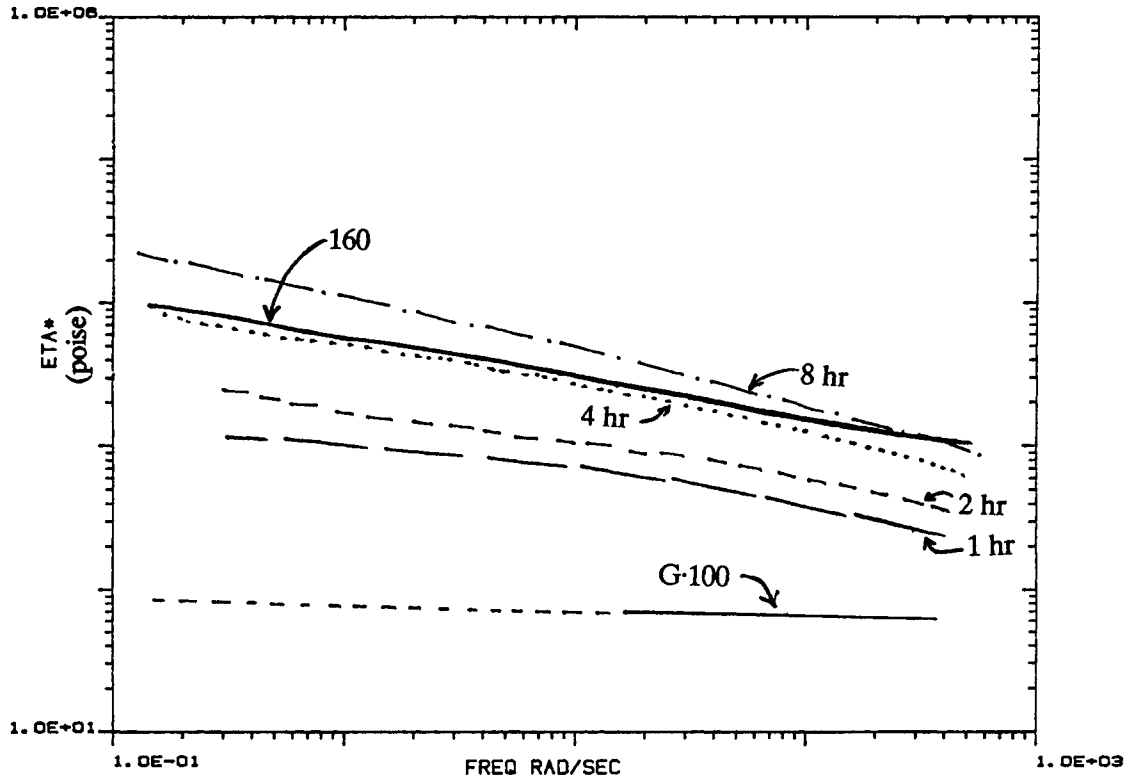


Figure 3 Effect of cure on G100 powder.

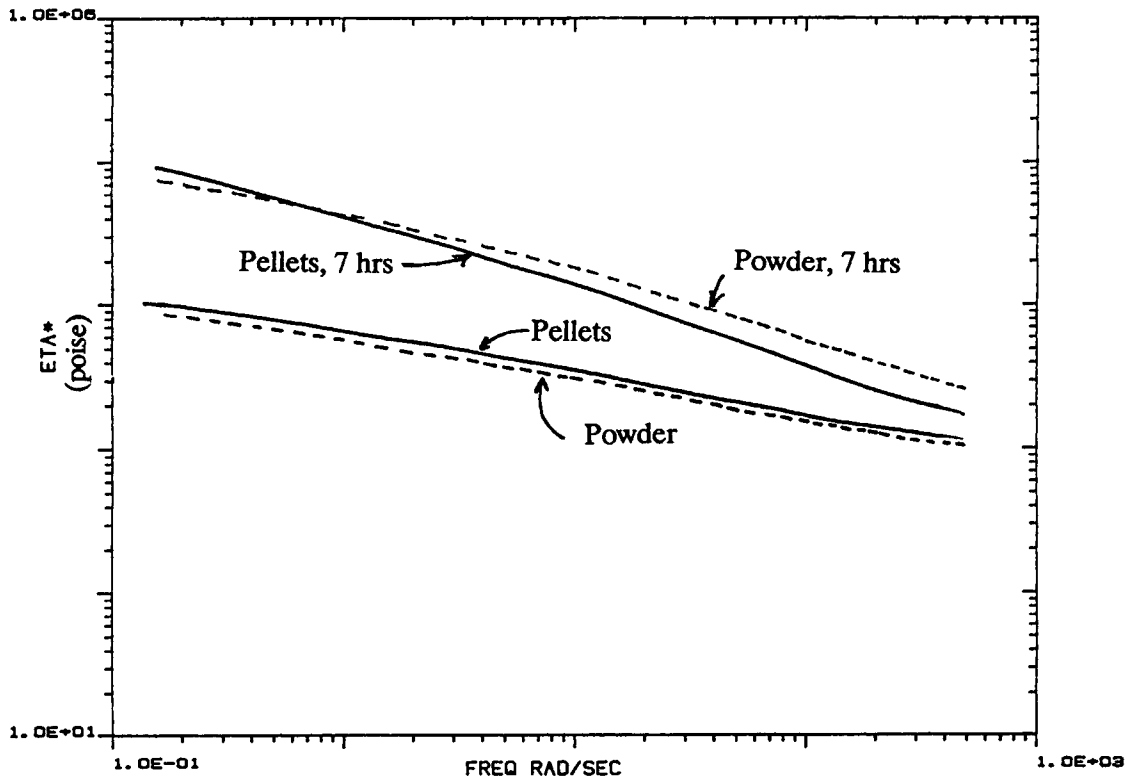


Figure 4 Powder cure vs. pellet cure.

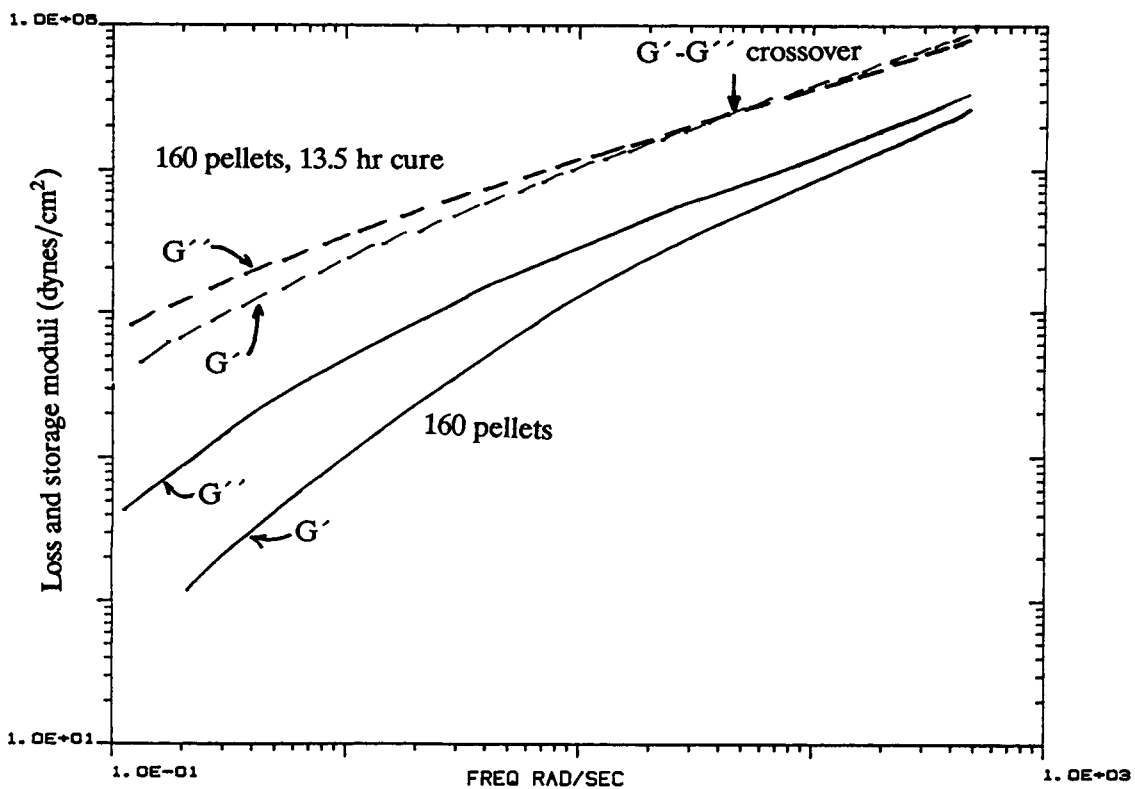


Figure 5 General effect of cure on moduli behavior.

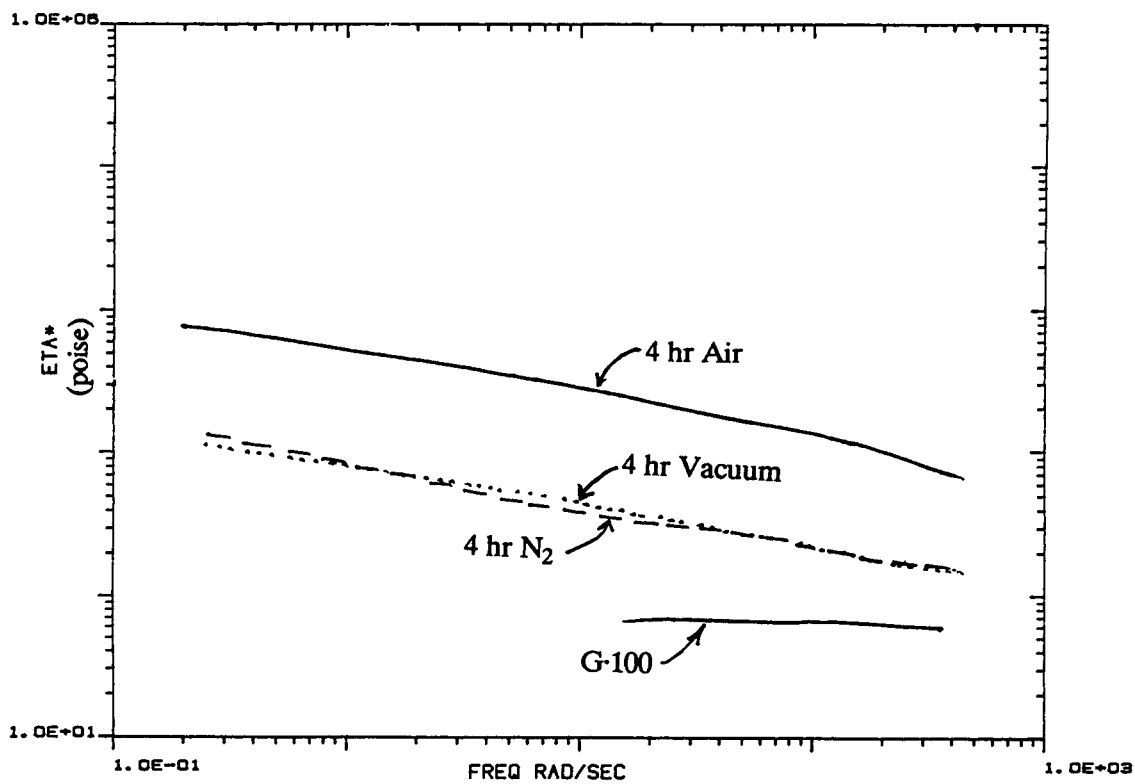


Figure 6 Effect of environment on G100 cure.

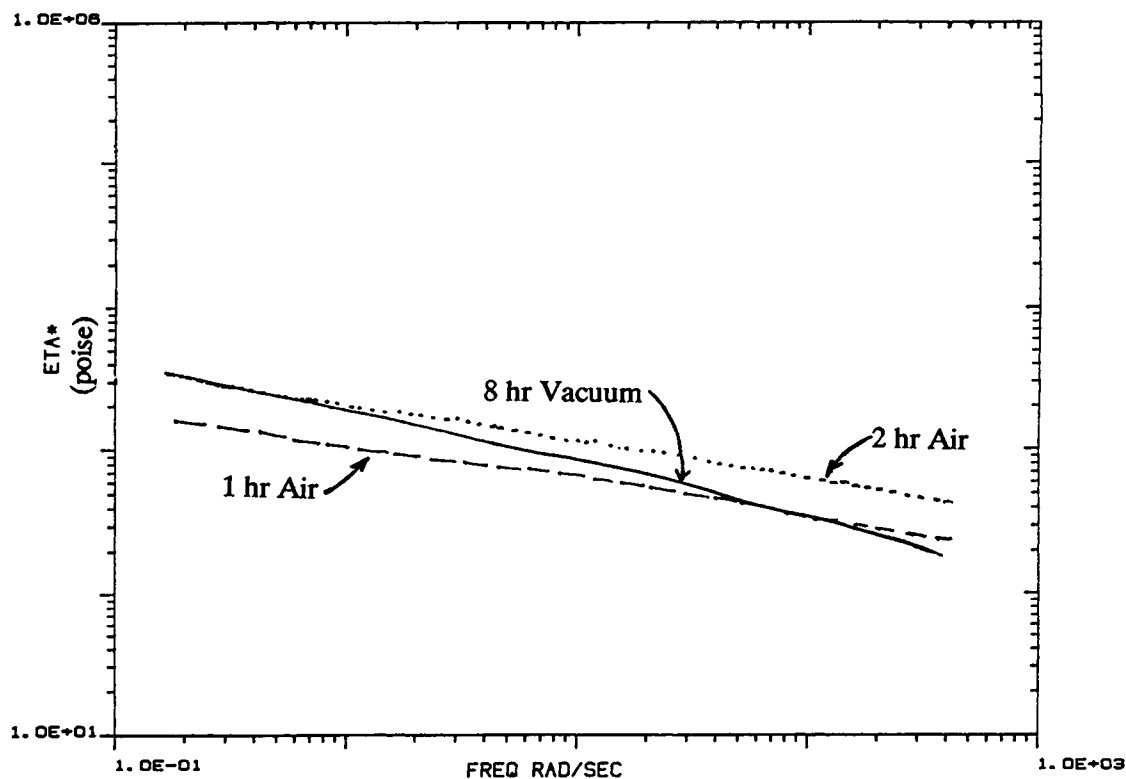


Figure 7 Comparison of air and vacuum curing at similar levels of viscosity.

## DISCUSSION

Several effects of changing molecular structure manifest themselves in rheological behavior and are apparent in Figure 1. First, increasing molecular weight increases viscosity.<sup>4</sup> Second, increasing molecular weight also causes a deviation from Newtonian behavior at lower shear rate.<sup>5,6</sup> Third, broader molecular weight distribution causes a less sharp transition from Newtonian to power law behavior.<sup>7-9</sup> Also, long-chain branching increases the low shear rate viscosity.<sup>10,11</sup> This last point is probably the most important in the current context.

The above points are represented to varying degrees based upon the curing process (environment) used. From Figure 3, the deviation from Newtonian behavior is greater for the G100 cured in our laboratories. This indicates that even though the cure time used approximates the time necessary to commercially cure G100 into 160, the structures or MWDs of 160 and the material cured in our oven are different. This is not surprising since the scale of our laboratory experiments is much smaller than that of the commercial cure process. Furthermore, over the limited range of cure times used in this

study, viscosity increases faster for the 1 h cure, indicating that the greatest change in structure occurs during the initial part of the cure.

From Figure 5, it is seen that the  $G'-G''$  crossover for the 13.5 h cure has shifted down the frequency axis to approximately 45 rad/s. This transition is indicative of the transition from meltlike to rubbery behavior in the frequency (time) domain. This result is consistent with increases in long-chain branching or cross-linking.

It was noted for Figure 4 (and Fig. 5) that there appeared to be an effect of surface area on curing behavior. It is rather surprising though, given the large differences in surface area between powder and pellet forms (and therefore the amount of oxygen that can potentially diffuse into the resin), that larger differences in behavior are not observed. This point is subject to future study.

Apparently, the evolution of volatiles in an oxygen-free environment is negligible as vacuum does not change the effect of cure relative to a nitrogen environment. Effectively, then, these results confirm Hawkins' finding that there are two basic types of curing: (a) air or oxygen-mediated curing and (b) oxygen-free curing for which nitrogen and vacuum

appear identical. The former route involves thermal and oxidative effects, whereas the latter involves thermal effects only.

The behavior described above may be discussed in terms of competing reactions. In the most general case, there is competition between oxygen-induced and thermally induced curing. For each of these types of reactions, there is also competition between branching/cross-linking and chain extension. Air (oxygen) curing is seen to be faster because it involves both oxidative and thermal curing. The air-cured material is more Newtonian than is the thermally cured resin, indicating, perhaps, these different mechanisms.

Since oxidative and thermal curing result in different viscoelastic spectra, effects of temperature, and, hence, chain mobility, may affect the dominant mechanism. Again, these effects are subject to future study.

## CONCLUSIONS

The solid-state curing of PPS at temperatures of 255–260°C has the following effects on the viscoelastic/rheological behavior:

1. Viscosity is increased.
2. Deviation from Newtonian behavior is increased.
3. The presence of oxygen causes a greater rate of cure and decreased deviation from Newtonian behavior relative to an oxygen-free cure.

The above behavior has been attributed to an increase in molecular weight and broadening of molecular weight distribution through branching/

cross-linking, which may dominate chain extension. However, oxygen-induced curing was found to have a viscoelastic response more characteristic of less branched/cross-linked structure relative to pure thermal curing, when compared at similar viscosity levels.

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