

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

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SYNOPSIS

Low molecular weight, low viscosity poly(phenylene sulfide) (PPS) has been cured in the melt state to examine effects of curing time and temperature on the melt-state dynamic viscoelastic behavior. It was found that the Newtonian behavior of the uncured material could largely be retained if melt cure temperatures are properly controlled. This result is in contrast to solid-state curing, where the Newtonian nature of the resin is reduced, presumably due to increased branching and cross-linking as molecular weight builds. The current result indicates that melt-state curing may provide a high molecular weight PPS resin with a predominantly linear molecular architecture. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a unique high-temperature thermoplastic because it displays a thermosetting/thermoplastic character.¹ The thermosetting nature is a result of curing reactions that increase the molecular weight and viscosity.² These reactions can occur with the resin in the solid state (at 175–280°C) or in the melt state (315–425°C).

In a previous study,³ the solid-state cure process was examined using curing temperatures of 255–260°C. Curing effects were evaluated with respect to viscoelastic/rheological behavior as a function of cure time and cure temperature. It was found that in general, curing causes an increase in viscosity that is accompanied by an increased deviation from Newtonian behavior. Furthermore, the relative contribution of elastic behavior increased faster than that for viscous behavior. The effect of environment was also examined. Oxygen was shown to cause a greater rate of cure relative to an oxygen-free environment. The latter environment was shown to correspond to a greater non-Newtonian character when comparing curing in oxygen-rich and oxygen-free environments at similar viscosity levels.

The above behavior was attributed to increasing molecular weight and broadening of molecular

weight distribution that occur as branching/cross-linking occur. It was noted that the viscoelastic behavior of material cured under oxygen-induced curing conditions was more characteristic of chain extension, relative to pure thermally induced conditions.

It was the objective of the current work to extend the previous study of solid-state curing to conditions where the resin is held in the melt state for extended periods of time. Studies such as these are of interest because they may provide methods for preparing resins with desirable molecular architectures, without having to generate new synthetic technology. This paper presents results of a preliminary study where the melt-state viscoelastic properties of PPS are emphasized.

EXPERIMENTAL

Materials

The materials of this study are summarized in Table I. Sample U is an uncured reactor powder and is therefore a low viscosity, low molecular weight resin. It does not have enough melt strength to be strandable in extrusion and must therefore be cured to be useful in typical polymer processing operations. It is produced by reaction of dihalobenzenes and sodium sulfides in a polar organic solvent.⁴ Sample C is also a powder resin. It is identical to sample U

Table I

Sample	Supplier	Grade	Description
U	Tosoh Susteel	G-100	Reactor powder*
C	Tosoh Susteel	160	G-100 that was cured in air 4 hours (branched)
L1	Phillips	Ryton M2588	High MW linear
L2	Phillips	Ryton M2888	High MW linear

* Not commercially available.

except that it has been cured commercially in a proprietary process at approximately 250–260°C (solid-state curing). This process yields a resin with viscoelastic behavior characteristic of a highly branched structure.³ Samples L1 and L2 are produced via a polymerization process that yields resin with linear molecular architecture. Molecular weight is sufficiently high such that the need for the curing reaction necessary for resin C is eliminated.⁵

Sample Preparation

As-received, uncured reactor powder, sample U, was charged to a preheated cylindrical mold with a 25 mm-diameter cavity. Pressure was applied to com-

press the powder as it melted. The melted resin was then allowed to cure in the mold for various times. After curing, the mold was placed in a cold press and cooled to room temperature.

Instrument

Cured disks from the mold (25 mm diameter, approximately 2 mm thick) were characterized on a Rheometrics mechanical spectrometer model 7700 (Rheometrics, Inc., Piscataway, NJ). A parallel plate geometry in a nitrogen-purged environment was used. Frequencies were varied from 0.1–500 rad/s. Temperature was kept constant at 300°C.

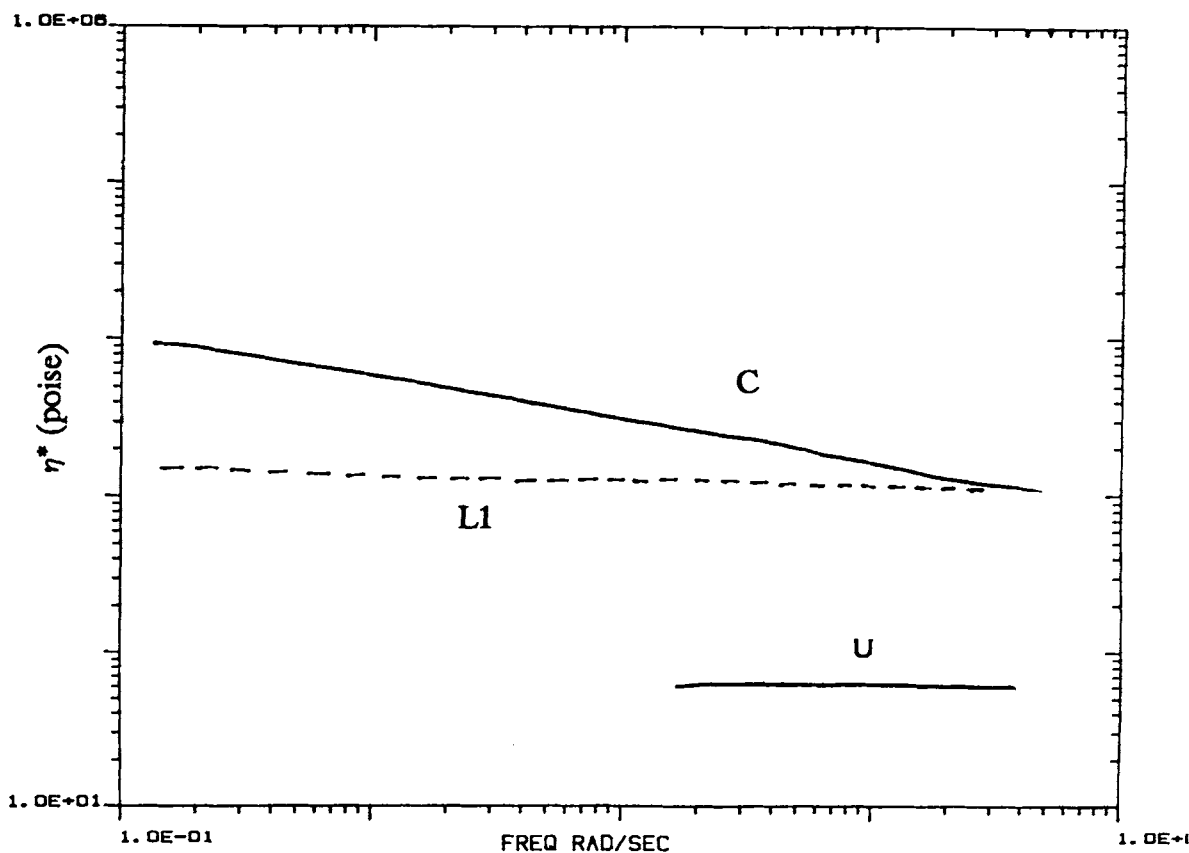


Figure 1 Complex viscosity behavior for samples U, C, and L1 at 300°C.

RESULTS

Figure 1 shows complex viscosity data as a function of frequency for samples U, C, and L1. The lines plotted in these figures represent the average results for two tests.

Sample U needs to be cured to be processable in typical machinery. Therefore, the approach used here is to cure the resin in the melt state to viscosity levels comparable to those for commercial resins C, L1, and L2, by altering the time and temperature of cure. By critically examining the viscoelastic response of the cured resins, one can gain insight into changes in the molecular architecture that may have occurred during curing. Since PPS melts at 280–285°C,¹ curing temperatures have been chosen to be sufficiently above this range to ensure complete melting of the PPS.

Figure 2 summarizes the general effects of cure duration at a temperature of 330–335°C. It is seen that the Newtonian character of the resin is largely maintained under these conditions.

The general effect of temperature can be seen in Figure 3 for a 3.5 h cure. Figure 4 shows a similar comparison made for 7 h cure times.

Comparing Figures 2, 3, and 4, one may surmise that by judicious choice of cure time and temperature it may be possible to cure sample U to give a viscoelastic response similar to resins L1 and L2. This is demonstrated in Figure 5, where a 7 h cure of sample U at 330–335°C is compared to sample L1. Figure 6 shows an analogous plot where sample U, which was cured for 14 h at 312–315°C, is compared to sample L2. To examine the relative contribution of elastic and viscous behavior, the data of Figures 5 and 6 have been decomposed into storage and loss moduli in Figures 7 and 8, respectively.

DISCUSSION

The data of Figure 1 display an important point worth noting. Resin L1 is an uncured resin and displays the same Newtonian behavior as does sample U over the frequency range tested. On the other hand, sample C displays a non-Newtonian behavior. In the former case (L1), the resin structure is known to be highly linear. Likewise, the low molecular weight resin, U, has a similar structure. Therefore, the frequency range of these tests is insufficient to

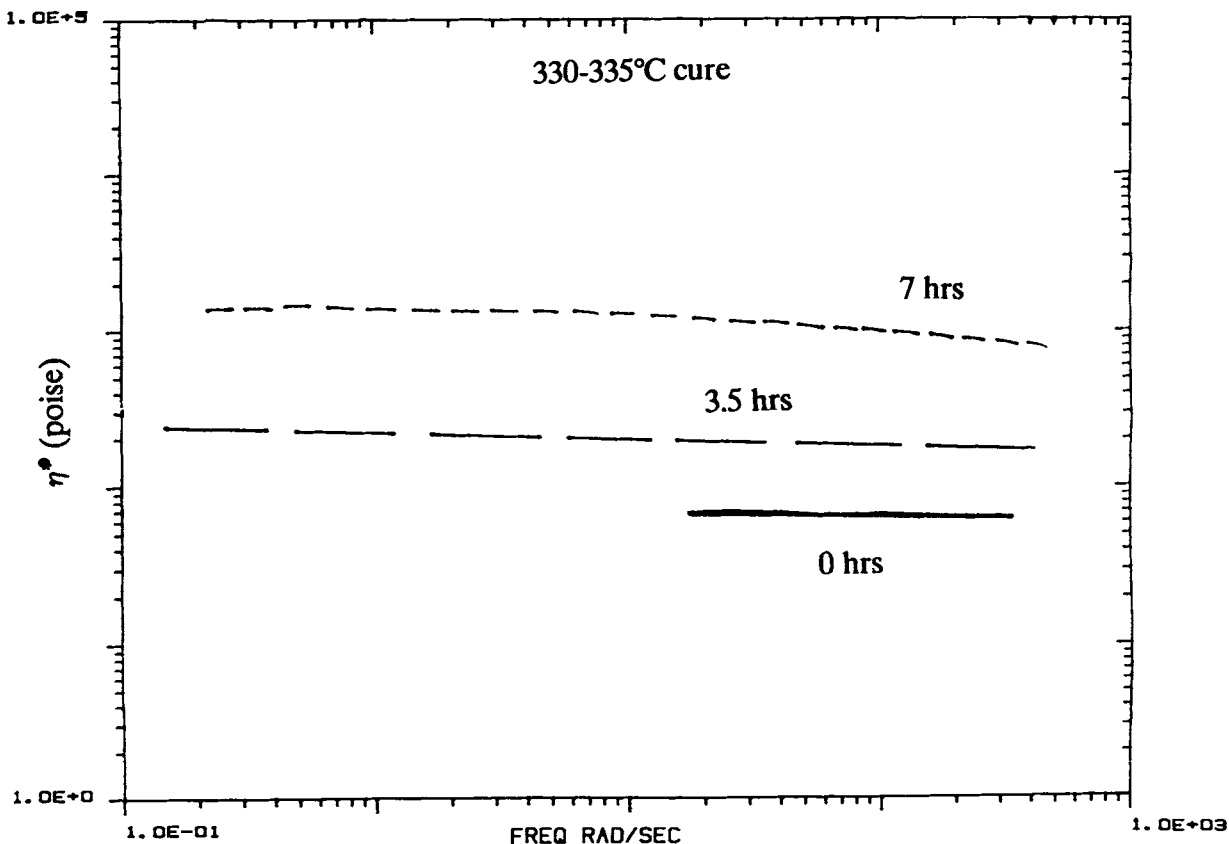


Figure 2 Effect of time on sample U held at 330–335°C.

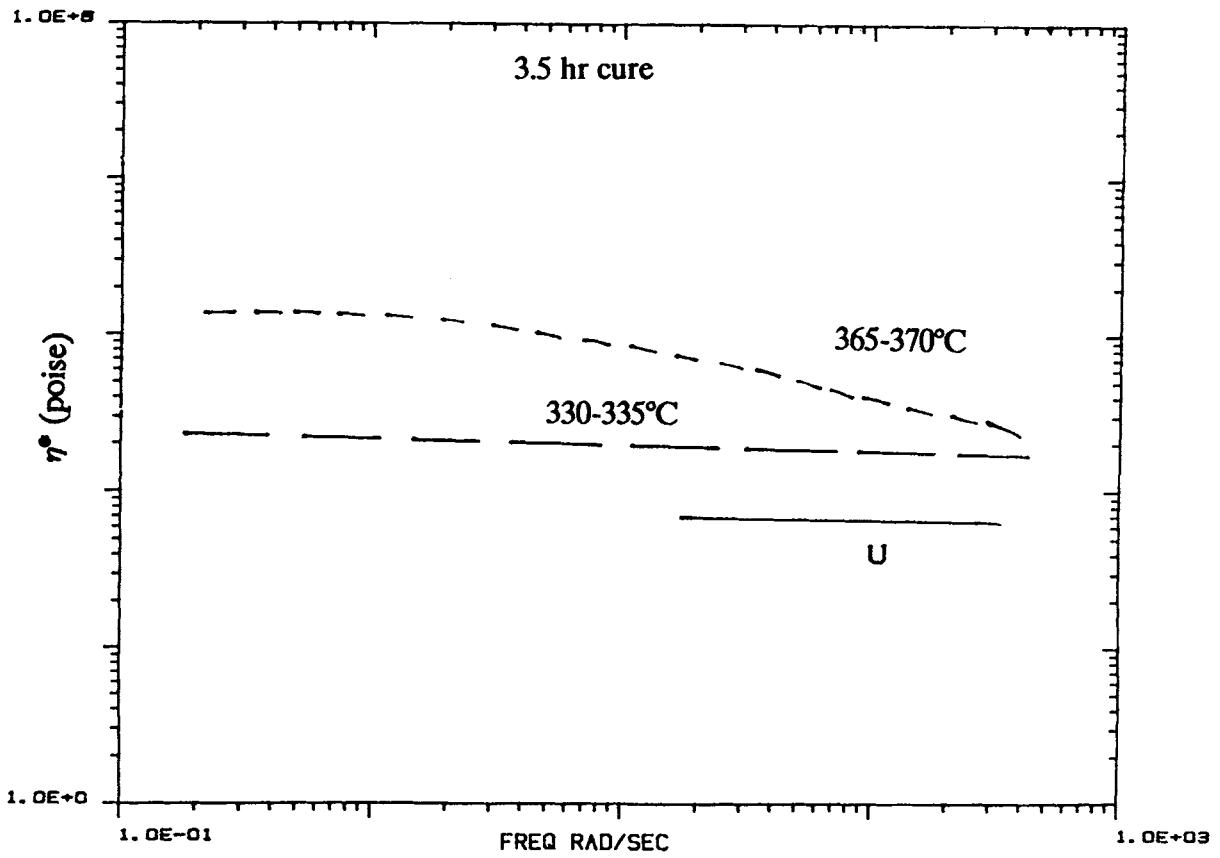


Figure 3 Effect of temperature on sample U for 3.5 h cure time.

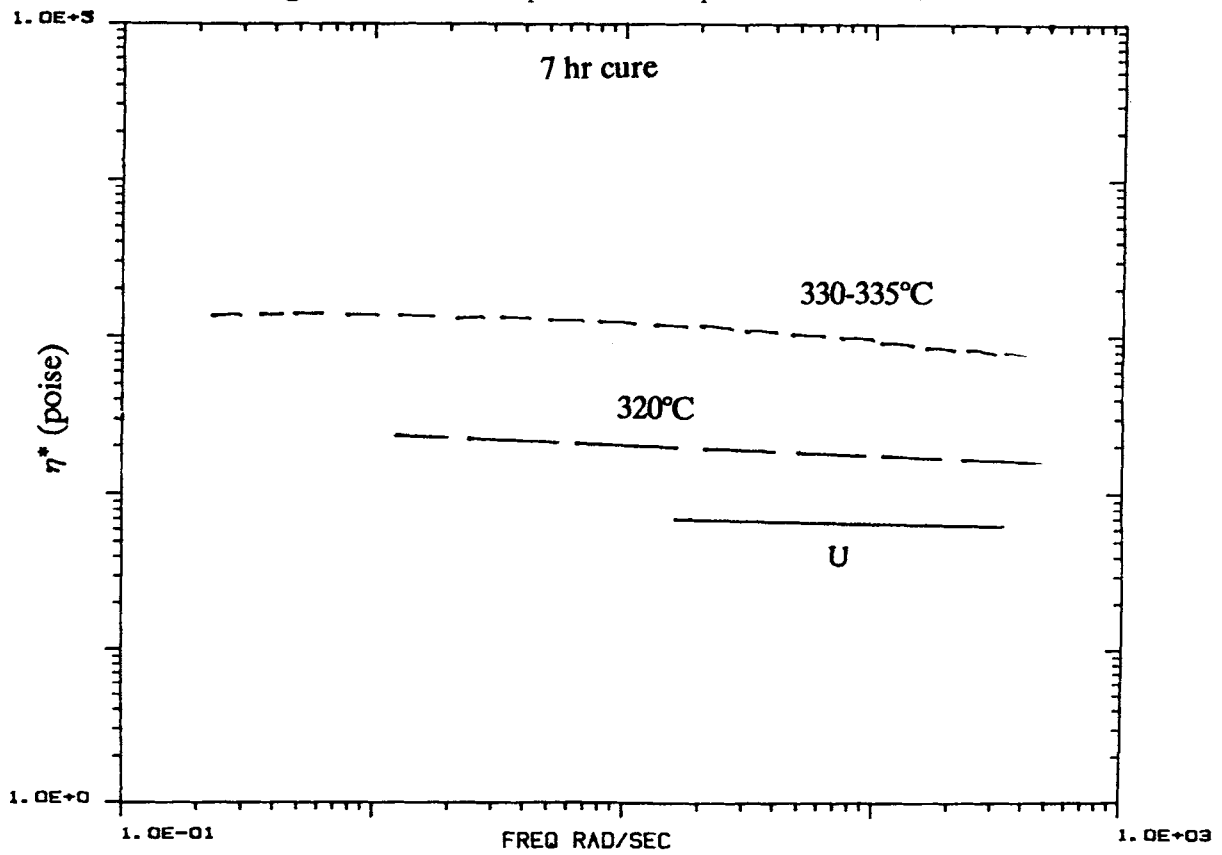


Figure 4 Effect of temperature on sample U for 7 h cure time.

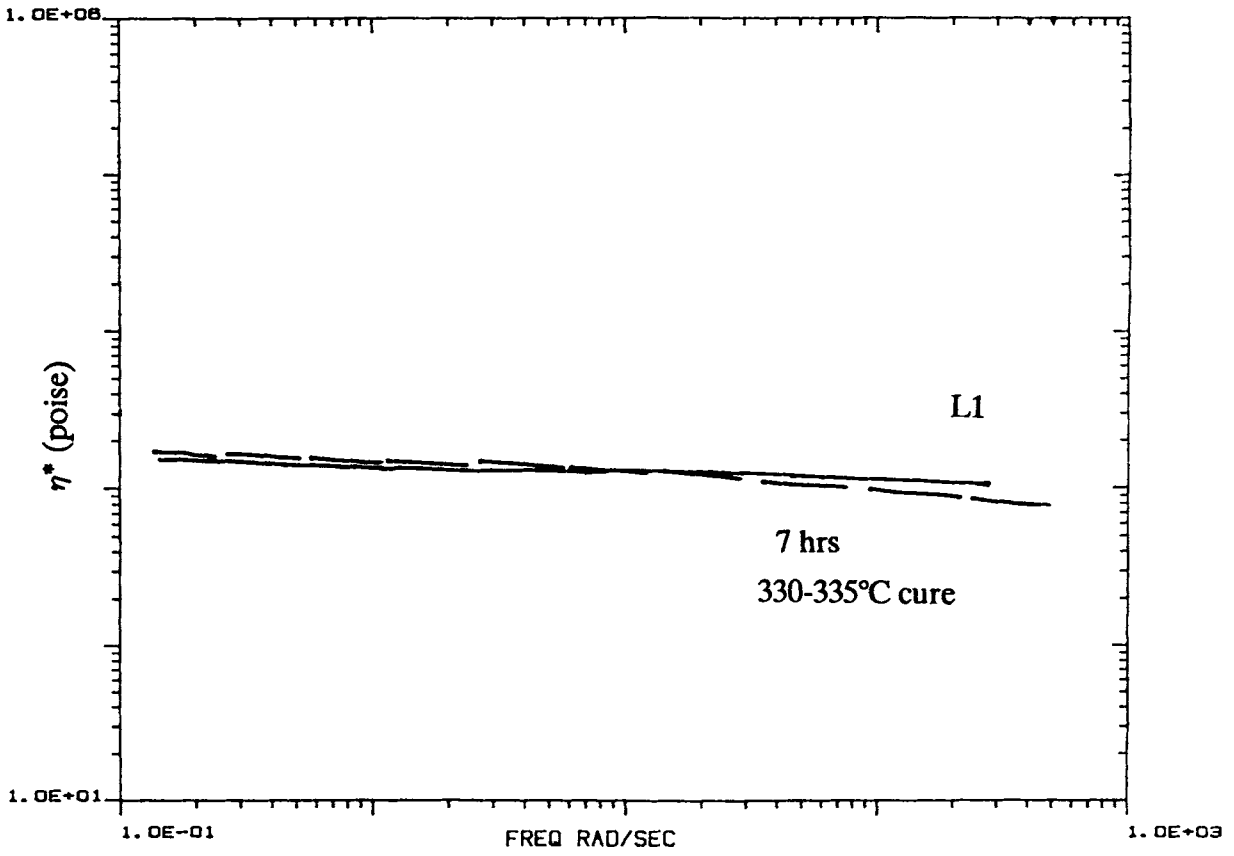


Figure 5 Comparison of sample U cured 7 h at 330-335°C with sample L1.

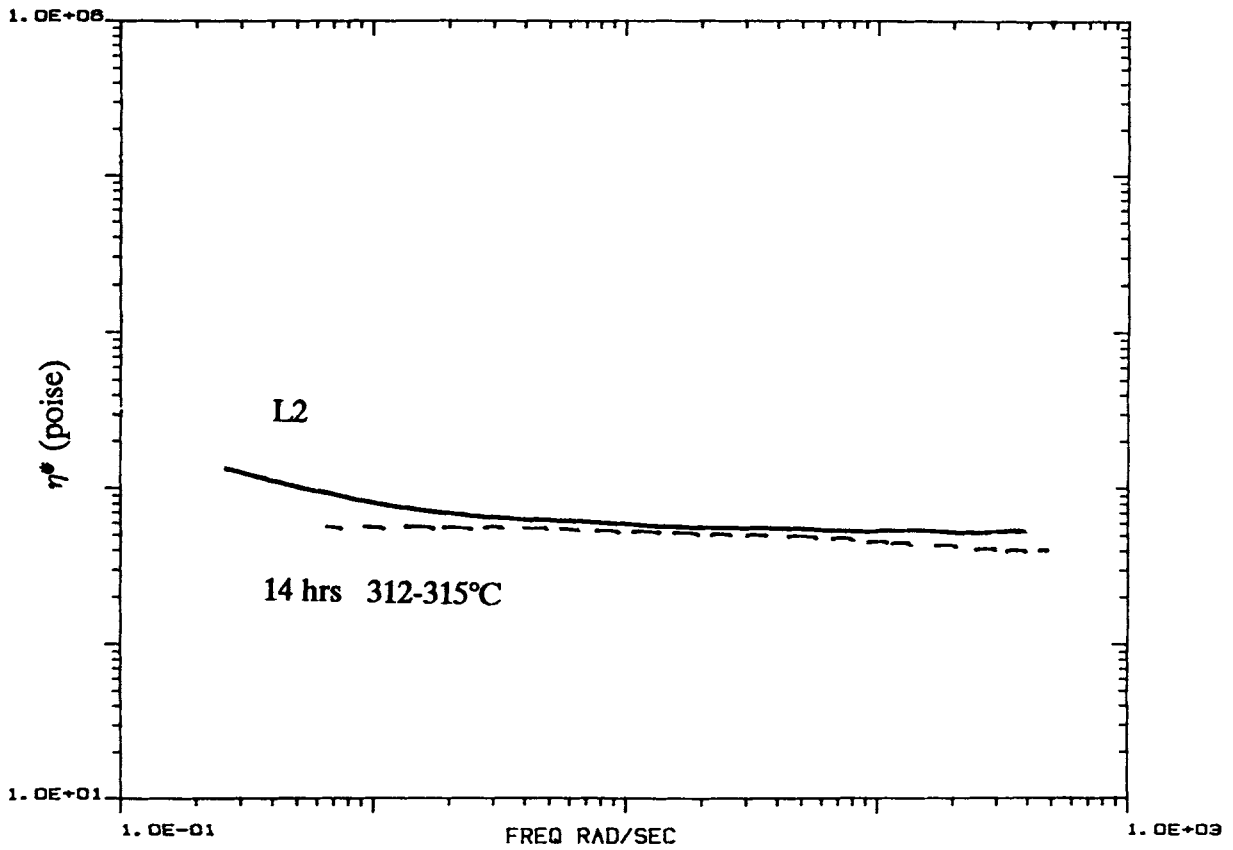


Figure 6 Comparison of sample U cured 14 h at 312-315°C with sample L2.

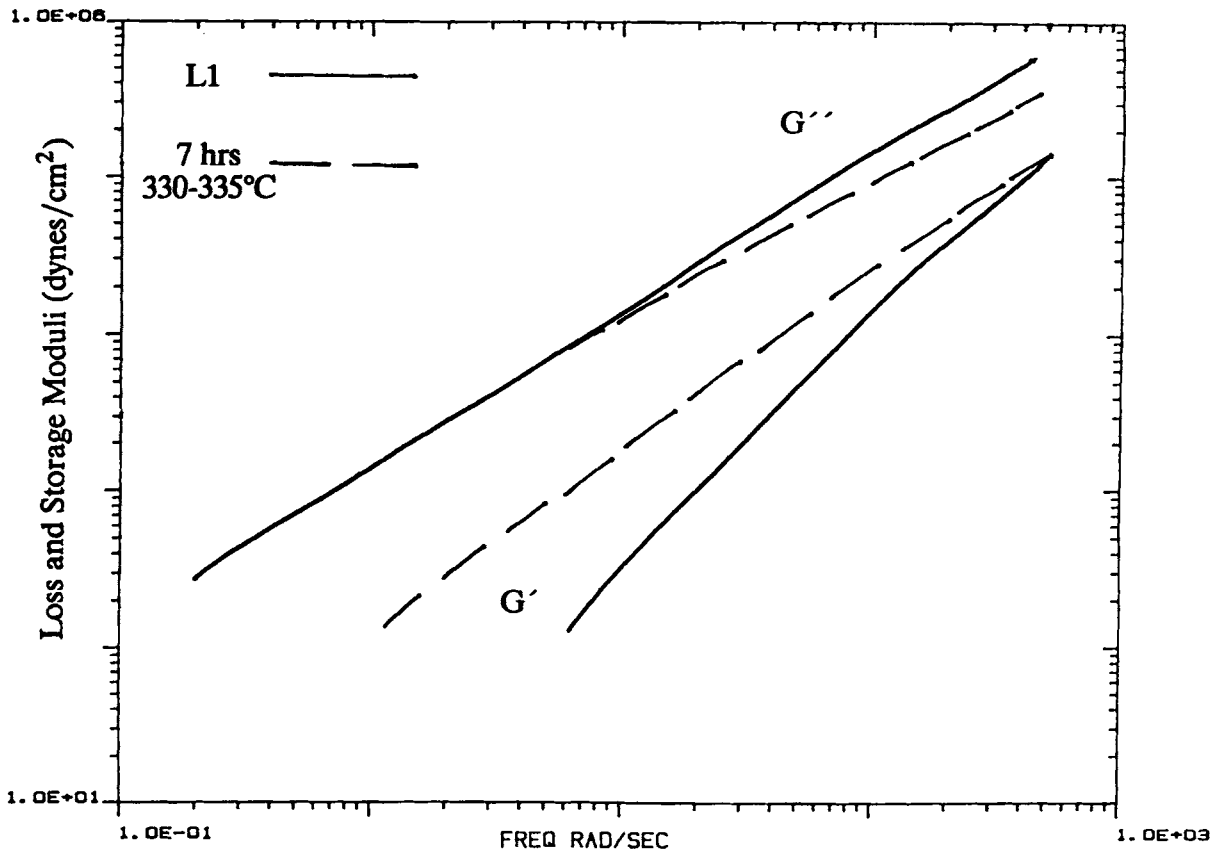


Figure 7 Data of Figure 5 decomposed into loss and storage moduli.

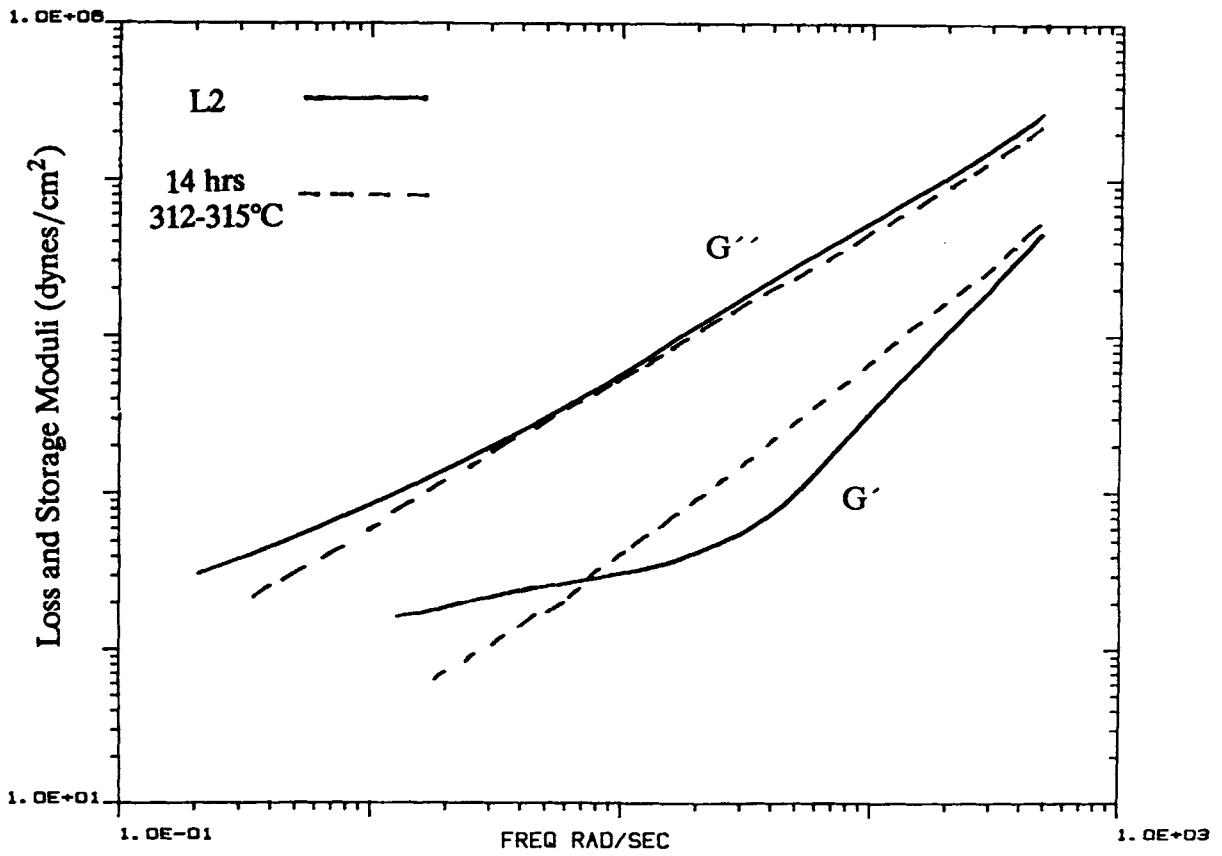


Figure 8 Data of Figure 6 decomposed into loss and storage moduli.

show the high shear-rate (frequency) dependence of viscosity. The non-Newtonian behavior of sample C can be attributed to its different molecular structure, i.e., solid-state curing in an air environment promotes branching as molecular weight builds,³ causing increased deviation from the Newtonian response.

Figure 2 shows results not seen for air curing³ and sample C. Under these conditions of time and temperature (above the melting point of PPS), there is considerable retention of Newtonian character. Curing of sample U in the solid state for comparable times was shown to result in non-Newtonian behavior.

As temperature is raised (Fig. 3), melt-state curing for 3.5 h results in a resin with a significant frequency dependence of complex viscosity. If, on the other hand, the temperature range is lowered, and cure time increased, it can be seen from Figure 4 that longer cure times can be tolerated without significant deviation from Newtonian behavior. This result is significant because it suggests that molecular architectures may be controllable through appropriate curing methods.

The results of Figures 5 and 6 indicate that resins with rheological response similar to linear resins L1 and L2 can be prepared from resin U by curing in the melt state for 7 h at 330–335°C and 14 h at 312–315°C, respectively. Further evidence that these cured resins have molecular structures similar to resins L1 and L2 is seen in the comparison of storage and loss moduli in Figures 7 and 8. In both these figures, the dominant loss modulus, G'' , compares favorably. The storage modulus, G' , is generally larger for the melt-cured resins, indicating some difference in structure.

The above results are in stark contrast to our previous results and make it possible to speculate as to the nature of curing mechanisms. For solid-state curing, storage moduli were relatively much greater (very close in magnitude to G'' , with the $G'-G''$ crossover visible within the frequency range of the tests) and deviation from Newtonian behavior was increased. Solid-state curing is a combination of chain extension and cross-linking.⁶ It was shown that oxygen-induced curing resulted in a resin with a rheological response more characteristic of a more

branched structure, when compared to oxygen-free curing. Furthermore, this oxygen-induced curing was quicker, presumably due to the combined effects of oxygen-induced and thermally induced cure mechanisms. In melt curing, it has been shown that resins can be produced with viscoelastic behavior similar to that for commercial resins of linear molecular structure. This may indicate that in the relatively oxygen-free environment of the melt cure (the bulk of the resin was sealed in the mold) chain extension may be preferred for the lower temperatures, i.e., the molecules have sufficient mobility for chain ends to interact. The contribution of extension relative to cross-linking/branching appears to decrease as temperature is increased.

CONCLUSIONS

Melt-state curing of PPS resin has been studied. It has been shown that curing in the melt allows for resins to be produced that have increased molecular weight while maintaining Newtonian character. The rheological response of resins cured in this manner is similar to that for resins with known linear structure. As melt cure temperature is increased, the viscoelastic behavior begins to deviate from that of linear structures. These findings are of significant value since they point to nonsynthetic routes to high molecular weight PPS that may have linear structure and, therefore, different properties from the more cross-linked materials.

REFERENCES

1. H. W. Hill, Jr. and D. G. Brady, in *Encyclopedia of Chemical Technology*, Wiley, New York, 1982, p. 793.
2. L. C. Lopez and G. L. Wilkes, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **c29**(1), 83 (1989).
3. J. J. Scobbo, Jr., *J. Appl. Polym. Sci.*, to appear.
4. U.S. Pat. 3,354,129 (1967).
5. U.S. Pat. 3,919,177 (1975).
6. R. T. Hawkins, *Macromolecules* **9**, 189 (1976).

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