

The effect of curing on the crystallization of poly(phenylene sulfide)

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Summary

Poly(phenylene sulfide) (PPS) was cured in the melt and solid states under air and/or nitrogen environments. Crystallization behavior of such cured materials as a function of cure time at 320°C and 255°C was studied via differential scanning calorimetry. It was found, in general, that while "short-time" curing leads to an increase in crystallization rate, prolonged curing leads to a decrease in both crystallinity and crystallization rate. In contrast to the enhanced crystallization rate caused by curing in nitrogen at the melt state, no significant change of crystallization rate is observed while curing is done in the solid state (in nitrogen).

Introduction

Poly(phenylene sulfide) (PPS) due to its excellent chemical resistance and thermal properties is a very attractive candidate for applications in hostile environments, such as under-hood applications in automobiles. In addition, its superior flow properties qualify this material for the possible application of thin-wall parts. The general property profile of this materials can be found in a review article by López and Wilkes¹.

PPS is known to undergo so-called "curing" reaction(s) at a prolonged exposure of elevated temperature. The detailed chemistry of curing has been studied by Hawkins et al.² and Port et al.³ It is generally believed that three types of reactions in regard to the molecular structure are involved (1) chain extension; (2) chain branching, either via oxidative cross-linking or cross-linking by the radical reaction of thiol end groups; (3) chain scission. Several reports has been published to address the curing kinetics^{3,4,5}. It is found that curing rate is greater in the presence of oxygen as compared to that in the absence of oxygen. Therefore, the oxidative cross-linking reaction appears to be the most efficient curing reaction relative to the others. However, it is confirmed that the "branching", one of the most important curing reaction, can still occur in the absence of oxygen through thiol groups, although at a lower rate or at a higher temperature.

It has been shown that curing can lead to an enhancement of the crystallization rate of PPS^{4,6,7}. However, to the authors' knowledge, the effect of curing on the crystallization rate at a temperature close to its melting temperature, whether at the solid state or at the melting state, has not been examined at extended curing times and thus is the main focus of this short paper.

Experimental

Ryton® (® Registered trademark of the Philips Petroleum Company).grade of PPS PR26 was chosen for this study and was used as received. This grade of PPS has a dynamic

viscosity of ~600 poise at frequency of 0.5 rad/sec and temperature of 300°C. The curing was carried out in a Perkin Elmer DSC-7 calorimeter with air or/and nitrogen atmosphere. The curing temperature was 255°C and 320°C. PPS melts at around 290°C and thus curing at 255°C and 320°C is referred as solid and melt state curing, respectively. In addition, an oven with air circulation was also used for curing at 255°C. The exotherms of the crystallization at 245°C were recorded with the calorimeter to evaluate the crystallization rate. This crystallization temperature was chosen based on the convenience of experimental time scale. It is a typical and necessary practice for crystallization study that the polymer is held in the melt state for a sufficient time to eliminate existing nuclei generated from the previous thermal treatment. Since the thermodynamic melting temperature is typically less than 320°C for a low to moderate molecular weight PPS^{8,9}, we thus chose the melt holding condition to be 320°C for 4 minutes. Crystallization were repeated selectively to check for the reproductivity of data.

Results and Discussions

The thermal evolution of crystallization monitored by DSC can be used to obtain important information on the crystallization kinetics. A typical example of the isothermal crystallization exotherm is shown in Figure 1. The time (t_{peak}) to reach the minimum of the crystallization exotherm, t_{peak} is conveniently chosen to be used as an index to evaluate the crystallization rate. As seen in Figure 1, an 8hr oven cured PPS shows a smaller t_{peak} in comparison with that of an un-cured PPS. This enhancement of crystallization rate caused by curing is consistent with the observations reported by Lee et al.⁴ and Zeng et al.⁶ Figure 2 shows the t_{peak} as a function of curing time for oven and DSC curing at 255°C in air, respectively. As seen in both cases, the t_{peak} first decreases and then increases with increasing curing time. This occurrence of minimum t_{peak} is mostly clearly observed for curing at 320°C in air as shown in Figure 3. These results indicate that the crystallization rate can be enhanced greatly if a proper curing time is chosen. The time to reach the minimum t_{peak} is significantly less at 320°C than that at 255°C, suggesting a faster curing rate at higher curing temperature. In addition, the minimum t_{peak} at 320°C is found to be ~1 min which is much less than ~3.5 min found at 255°C. These findings imply that not only the curing kinetics are different at different temperatures but also the type or the partition of different reactions are different.

It is noted that the crystallization rate remains unchanged while the materials are cured at 255°C up to 8 hours in N₂. However, if the curing temperature is raised to 320°C, a similar curing effect seen for air cured PPS is also observed. This observation illustrates the curing can effectively improve the crystallization rate even without the presence of air if the curing temperature is high enough. Nevertheless, the minimum t_{peak} for N₂ cured PPS is higher than that for air cured materials. Based on these results on different curing temperatures, the higher curing temperature as well as air atmosphere are likely to bring more benefits in regard to the crystallization rate.

The oven curing appears to give a slower curing rate relative to the DSC curing, as indicated by the delayed occurrence of minimum t_{peak} . Some variation of t_{peak} for the oven cured specimens is also noted. Such observations are believed to be due to the heterogeneity of curing which is caused by a continuous consumption of air by the materials residing at the surface during the curing process. The specimens of the oven cured powder are sampled in such a way that the specimen would represent a uniform mixture of the overall cured pile of powders. To demonstrate the importance of the surface contact with air to the curing efficiency, a very thin layer of powder was purposely spread

in the sample pan to increase the surface area exposed to the air during curing (curing time of 8 hours). Indeed as shown by the cross symbol in Figure 2, such a specimen exhibits a lower t_{peak} and reasonably close to that of DSC cured specimen. This observation illustrates that good "contact" between the air and the materials is essential for efficient curing.

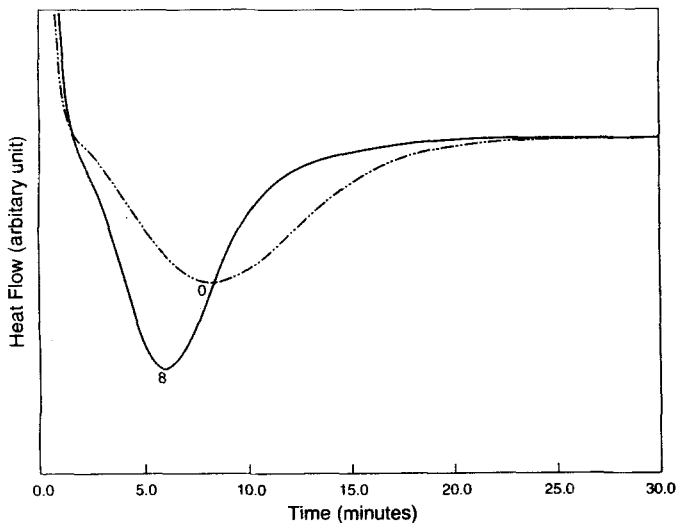


Figure 1 DSC traces for crystallization at 245°C of a un-cured specimen and a specimen oven cured at 255°C for 8hr, respectively. The cure time is marked in the figure.

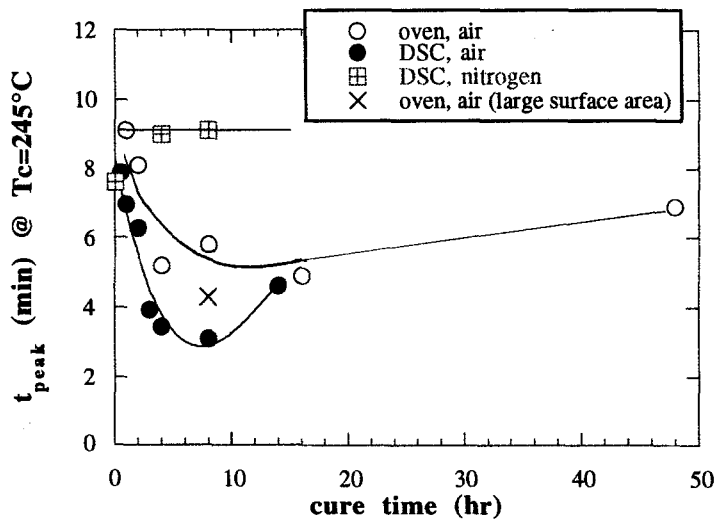


Figure 2 t_{peak} as a function of cure time at solid state curing (255°C). Lines are the guides to the eye.

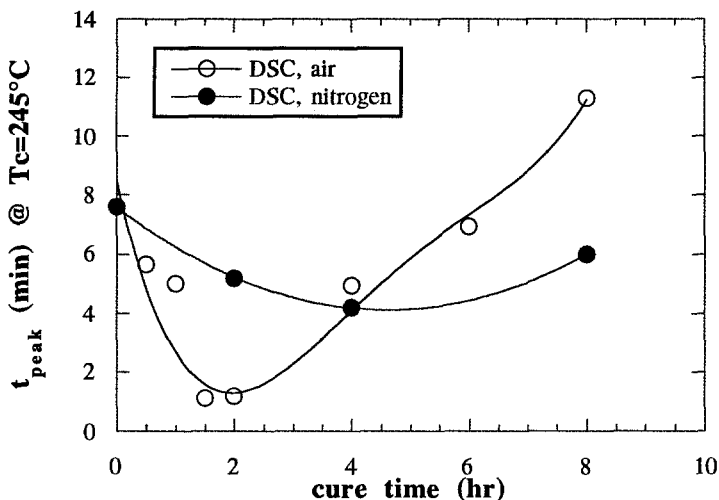


Figure 3 t_{peak} as a function of cure time at melt state curing (320°C). Lines are the guides to the eye.

The oven curing appears to give a slower curing rate relative to the DSC curing, as indicated by the delayed occurrence of minimum t_{peak} . Some variation of t_{peak} for the oven cured specimens is also noted. Such observations are believed to be due to the heterogeneity of curing which is caused by a continuous consumption of air by the materials residing at the surface during the curing process. The specimens of the oven cured powder are sampled in such a way that the specimen would represent an uniform mixture of the overall cured pile of powders. To demonstrate the importance of the surface contact with air to the curing efficiency, a very thin layer of powder was purposely spread in the sample pan to increase the surface area exposed to the air during curing (curing time of 8 hours). Indeed as shown by the cross symbol in Figure 2, such a specimen exhibits a lower t_{peak} and reasonably close to that of DSC cured specimen. This observation illustrates that good "contact" between the air and the materials is essential for efficient curing.

Our observation on the enhancement of crystallization rate by curing (at "short" curing time) is consistent with those reported by Lee et al.⁴ and Zeng et al.⁶ It was proposed by Zeng that the branching points act as nucleation sites leading to such an increase of crystallization rate during curing. However, by expanding the curing time, we have achieved a full picture of the curing effect which does not always give rise to an enhancement of crystallization rate. It is suspected that the structure of PPS for prolonged curing may approach a structure resembling "crosslinked" materials. Therefore, the "distance" between crosslinks is shortened to an extent that diminishes the crystallizability of the materials. This hypothesis seems to be supported by the observation that the heat of crystallization (the area of the crystallization exotherm), thus crystallinity, of PPS with long curing time is much lower than that of the uncured material, as indicated in Figure 4.

The crystallinity decreases as curing time increases both at 320°C and 255°C , as shown in Figure 4. In general, lower crystallinity corresponds to higher crystallization rate.

However, the increase in crystallization rate appears to be greater at 320°C than at 255°C while the decrease of crystallinity is comparable at both temperature. It is thus concluded that curing in the melt state would be more beneficial than that in the solid state regarding the crystallization rate.

In conclusion, we have reported the observations on the effect of curing to crystallization rate: in general "short-time" curing leads to an increase in crystallization rate while prolonged curing leads to a decrease in both crystallinity and crystallization rate. Curing is found to be more effective in the melt state (higher temperature) and/or in air relative to solid state and in nitrogen, respectively. As to why the crystallization rate increases upon curing is an on-going research subject.

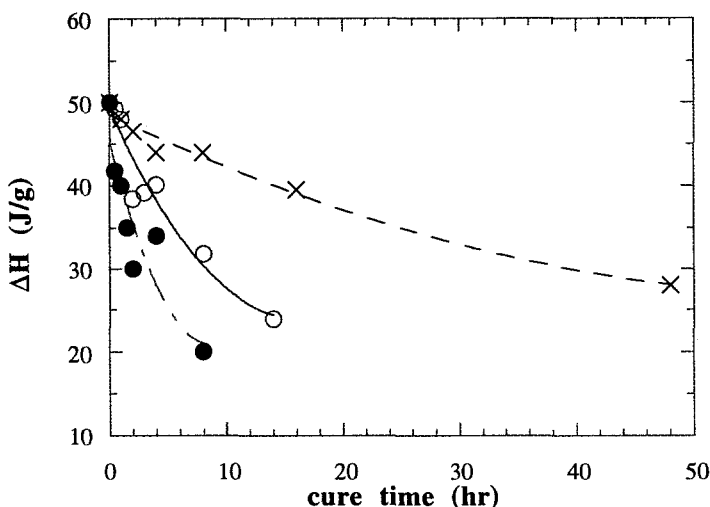


Figure 4 Heat of crystallization as a function of curing time under various curing environments. O DSC cure at solid state (255°C), ● DSC cure at melt state (320°C), × oven cure at solid state (255°C).

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