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DSC Studies upon Thermal Curing of Methylsilsesquinoxane

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DSC Studies upon Thermal Curing of Methylsilsesquinoxane

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A conventional DSC was used to investigate the thermal curing behavior of methylsilsesquioxane (MSSQ) which transforms into the low dielectric constant material, poly(MSSQ). Temperature scan of MSSQ up to 350 °C revealed that the curing of MSSQ is an endothermic reaction that occurs over the wide temperature range. From the isothermal scan of MSSQ, it was found that the curing of MSSQ follows the first-order reaction.

Keywords Methylsilsesquioxane; Low dielectric constant material; Thermal curing

INTRODUCTION

Poly(methylsilsesquioxane) (PMSSQ) is one of the promising low dielectric constant (k) materials for its low k between 2.7 and 2.9 with low moisture absorption, good thermal stability, and high mechanical hardness in a fully cured state [1]. We have previously reported that the lower k (k = 2.1) could be achieved by incorporating the nanoscale air voids (k = 1) in PMSSQ through inorganic/organic polymer hybrid templates [2]. In this work, we investigate the thermal curing behavior of methylsilsesquioxane (MSSQ) using a conventional DSC.

EXPERIMENTAL

MSSQ prepolymer received from TECHNEGLAS was fractionated and a fraction of M_n = 4,800 was obtained. Curing behavior of powdery MSSQ prepolymer was investigated using Perkin Elmer Pyris1 DSC with N_2 purge. In an isothermal scan, the net heat flow was obtained using the heat flow of the second run as a baseline.

RESULTS AND DISCUSSION

As shown in Figure 1, the first temperature scan of uncured MSSQ exhibited a glass transition at 51 °C with a broad endothermic peak above 200 °C. In the following second scan, the glass transition disappeared and the endothermic heat flow above 200 °C was reduced to the negligible level. It indicates that MSSQ prepolymer was cured into the crosslinked PMSSQ during the first scan and the curing of MSSQ is an endothermic reaction with onset temperature of 200 °C, which is dependant upon the experimental scan rate.

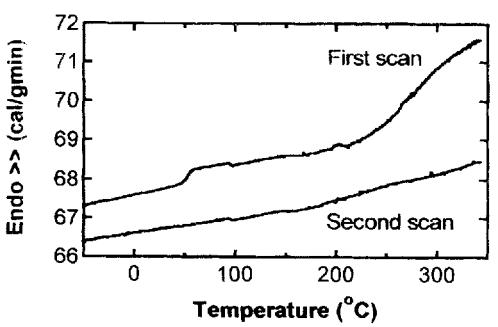

FIGURE 1. DSC temperature scan of MSSQ prepolymer at a scan rate of 10 °C/min.

Figure 2 shows the effect of scan rate upon the onset temperature of MSSQ curing. As the scan rate was decreased from 10 to 2 °C/min, the onset temperature of endothermic curing was reduced to about 100 °C, which implies that the curing of MSSQ may happen at room temperature after sufficiently long period of time. Actually, we have experienced the insolubility of MSSQ stored at room temperature for several months, indicative of the partial curing of MSSQ. The glass transition of MSSQ was more clearly observed at the higher scan rate.

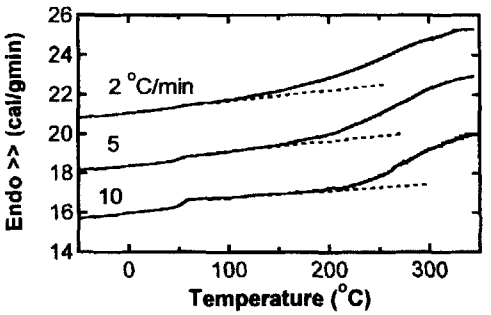

FIGURE 2. DSC temperature scan of MSSQ prepolymer at different scan rates.

Figure 3 shows the curing behavior of MSSQ at a constant temperature of 270 °C with the time. Sample was loaded at 30 °C and the temperature was elevated to 270 °C at 100 °C/min. The endothermic heat flow was recorded until 300 minutes showing maximum value of 2.8 cal/g min at 6.6 minutes indicating that the maximum reaction rate was achieved at that time. Such a maximum reaction rate that occurs at the initial stage is the distinguishing characteristic of an *n*th-order reaction.

To obtain the order (n) of reaction, we assumed that the full conversion ($\alpha = 1$) was achieved after 300 minutes, since the rate of

conversion in an *n*th-order reaction is expressed as $d\alpha/dt = k (1 - \alpha)^n$ where k is a rate constant. The calculated order of reaction for the curing at 270 °C was 0.72, suggestive of a first-order reaction.

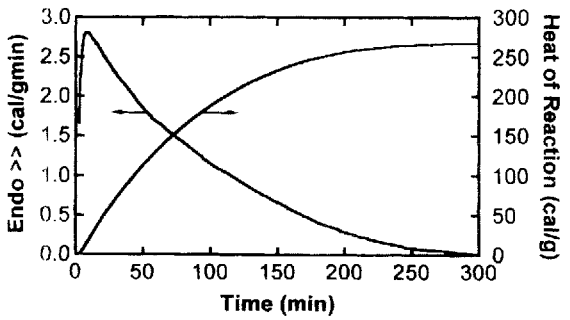

FIGURE 3. DSC isothermal scan of MSSQ at 270 °C.

CONCLUSIONS

The onset temperature of MSSQ curing was decreased as the scan rate decreased. The curing of MSSQ occurred remarkably above 200 °C following the first-order reaction. This work will help to establish optimum cure cycle.

ACKNOWLEDGMENT

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