Effects of Sonication on Curing Process in Furan Resin

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Sonication was carried out through the curing process of furan resin by using an ultrasonic homogenizer at the frequency of 20 kHz and the intensity of 50 W/cm². Carbonaceous fine particles were added to furan resin to investigate the sedimentation behavior in cured resin. Curing rate of furan resin was accelerated by sonication, which was effective to remove out the included larger pores and also to avoid the sedimentation of the particles. The additives were dispersed uniformly in the cured furan resin by sonication. Therefore, it was clarified that the additives were able to be distributed homogeneously in the furan resin by the ultrasonic treatment.

KEYWORDS Sonication, Furan resin, Curing process, Sonochemistry

1. Introduction

Furfuryl alcohol condensate (furan resin) is commonly used as a matrix precursor of carbon fiber/carbon matrix composites because of the convenience at carbonization process due to thermosetting properties. However, its curing and carbonization processes take a long time to prevent the formation of cracks and to remove out the induced pores. Recently, Park et al. added small amount of inorganic fine particles in furan resin to control the microstructure of the furan resin derived carbon or to improve the oxidation resistance of carbon. They reported that even though mixed furan resin with additives were ball-milled for 24 hours, powder sedimented after pouring into polystyrene container. Matrix modification by fine-grained powder is required to attain the homogeneous distribution of the additives in the matrix. Increasing in the reaction temperature and the amount of catalyst to furan resin did not result in homogeneous and crack free carbon materials. To solve these problems, the authors applied sonication for the curing process of furan resin. The purpose of this study is to examine the effect of ultrasonic treatment on the curing process in furan resin, and to show the potential method for the homogeneous preparation of cured resin.

2. Experimental Procedure

Hitafuran 302 (Hitachi Chemical Co., Ltd.) was used as furfuryl alcohol condensate. Curing catalyst (p-toluenesulfonic acid) was added to the furan resin in the proportion of 0.3 mass%. After stirred at room temperature for 30 minutes, temperature of the furan resin was controlled at 50 °C. In this condition, ultrasound was applied through the curing process by using an ultrasonic homogenizer (Branson, model 450) at the frequency of 20 kHz and the intensity of 50 W/cm². The viscosity change of furan resin in the curing process was determined at a constant temperature (50 °C) with a viscometer (Brookfield, DV-II+). The rotation speed of the viscometer was 100 rpm. Polymer molecular weights were measured by Gel Permeation Chromatography (GPC : JASCO, GULLIVER SERIES, column; Shodex GPC K802+K803+K804+K805, eluent : chloroform), with polystyrene as a standard material. The furan resin was diluted with chloroform for GPC measurement. Then, the aggregated samples were filtered through a membrane filter. Phenol resin beads heat-treated at 1000 °C were added to furan resin to investigate the sedimentation condition in cured resin. The amount of additives was fixed at 5 mass% of furan resin. After sonication, these samples were hardened at 50 °C for 2 days. The hardened samples were post-cured at 100 °C for 96 hours, and then heat-treated at 1000 °C for two hours in Ar gas atmosphere. Distribution of pores and additives in cured resin were investigated through an optical microscope under polarized light with a gypsum plate (Nikon, HFX-II).

3. Results and Discussion

In general, a direct curing process of furan resin is initiated with the presence of acid catalyst such as p-toluenesulfonic acid and progressed by polycondensation reaction. In the final stage of polycondensation reaction, furan resin is gelled by cross-linkage. Therefore, one of the most important characterizations of furan resin in the curing process is molecular weight measurement. Fig.1 shows the molecular weight distributions of furan resin at various curing time. The higher molecular weight component was increased with the increase of reaction time and the distributions became broader.

Fig.2 shows the degree of polydispersion change of furan resin as a function of the curing time. Polydispersity of furan resin was estimated based on the number average molecular weight (Mn) and the weight average molecular weight (Mw). The Mn and Mw are calculated with equation (1) and (2), respectively.

\[ M_n = \sum N_i M_i / \sum N_i \]  \hspace{1cm} (1)
\[ M_w = \sum N_i M_i^2 / \sum N_i M_i \]  \hspace{1cm} (2)

where \( N_i \) is the number of molecules of kind \( i \) (\( i \) being the degree of polymerization) present in furan resin, \( M_i \) is its
molecular weight$^{3}$. The ratio of $M_w/M_n$, called the dispersity, is a useful parameter of the spread of a polymer distribution. When $M_w/M_n = 1$, all polymeric molecules have the same molecular weight and there is no spreading. In this study, polydispersities of furan resin before and after the curing process were above 10 and 50, respectively. These values were much higher than a commercial polymer$^{4}$ such as polystyrene ($M_w/M_n=2.4$), which indicated a very wide spread, from monomer to high molecular weight over a million.

Fig. 3 shows the viscosity change of furan resin as a function of average molecular weight. An approximately linear relationship was found between the logarithms of the viscosity and the average molecular weight before gelation point. In the vicinity of the gelation point, the viscosity and the molecular weight could not be measured accurately due to Weisenberg effect$^{5}$ and the increase of chloroform insoluble component. Consequently, it was difficult to discuss the relationship of the viscosity and the molecular weight after gelation point. On the other hand, GPC measurement of sonicated sample before gelation point was difficult because of its curing behavior, that is, the curing time was much faster than the sample without sonication. Therefore, the average molecular weight of sonicated sample was calculated by the viscosity, using Fig. 3.

Fig. 4 shows the degree of polymerization (the number of furan ring) plotted against curing time with and without sonication. The rate constants for with and without sonication were $1.4 \times 10^{-1}$ and $2.2 \times 10^{-2}$ s$^{-1}$, respectively. The increase of curing rate was considered to result from that cavitation$^{6}$ took
Fig. 5  Pores and beads distributions in sonicated furan resin derived carbon (HTT 1000°C), (a) no sonication, (b) sonication, (c) sonication to the resin with 5 mass % GC beads (HTT 100°C).

place during sonication. The cavitation process is attributed to the behavior of the small bubbles. The local pressures and temperatures generated by collapse of these bubbles are enormous and beneficial effects such as greater yields, higher product purity and rate accelerations are resulted directly from this phenomenon. At this point it should be stressed that the curing reaction is little proceeded in the absence of cavitation and stirring (without sonication) fails to produce such marked increases in the rate of reaction.

The optical micrographs of furan resin after cured at 100°C and carbonized at 1000°C are presented in Fig. 5. Sonication was effective to remove out the included pores. Large size of carbon spheres of 15 μm could be dispersed uniformly by sonication. The terminal velocity of sedimentation was calculated in the Stokes range\(^9\). When the curing time was 45 minutes, that is, gelation point for sonication, these values were 0.80 and 0.03 mm/h for stirring and sonication, respectively. The result of calculation suggested that sonication avoided the sedimentation of particles.

4. Conclusions

In this study, ultrasound was applied to the curing process of furan resin. The results are summarized as follows. (1) Curing rate of furan resin was accelerated by sonication. (2) Sonication was effective to remove out the included larger pores and also succeeded in to avoid the sedimentation of the added particles. (3) The additives were dispersed well in the cured furan resin by sonication.

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References