JOURNAL OF MATERIALS SCIENCE **39** (2004) 4913–4915 LETTERS

Cross-linking behavior of a polysiloxane in preceramic foam processing

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Ceramic foams possess some unique characteristics, such as low density, high specific strength, low thermal conductivity, high permeability, high chemical resistance, and high thermal shock resistance. With these unique characteristics, the application fields of ceramic foams have been observed to expand to gas diffusers, flame barriers, catalyst supports, and various filters [1, 2]. Since the open-cell content and cell morphology in porous ceramics, i.e., the cell density, cell size, and cell-size distribution, directly relates to their ability to perform desired functions in a particular application, it has been emphasized to fabricate a porous ceramic structure with controlled porosity, open-cell content, and cell morphology [2–4].

In decades past, various processing routes had been proposed for the production of porous ceramics, such as direct foaming of ceramic slurries or of sol–gel solution [5, 6], chemical vapor deposition of various refractory materials on foamed carbon skeletons [7], sintering of hollow spheres [8], and replication of polyurethane foam with ceramic slurries [9]. Recently, our study demonstrated that a controlled and uniformly distributed porous structure could be developed from polysiloxane by foaming and then using controlled pyrolysis [10–12]. The followings are the basic steps that will be involved in producing porous ceramics: (i) compounding the polysiloxane and additives to produce a foamable composition, (ii) saturating the samples using high pressure gaseous or supercritical fluid, (iii) nucleating and growing a large number of bubbles using a thermodynamic instability, and (iv) transforming by pyrolysis the foamed polysiloxane articles into porous silicon oxycarbide ceramics.

Since the polysiloxane used in the present experiment can be cross-linked at elevated temperatures, the processing procedures will alternate the average molecular weight of the polysiloxane and, in turn, alternate the rheological properties and foaming behaviors of the blends. If the degree of cross-linking is too low, then the melt strength and viscosity of polysiloxane will be too low to promote a good foam structure. In contrast, too high a degree of cross-linking will also negatively affect cell formation. Therefore, inducement of an optimum degree of cross-linking will be critically important in microcellular foam processing of polysiloxane. In this context, the information regarding the cross-linking behavior of polysiloxane and the corresponding viscosity change are required. In this research, the viscosity of polysiloxane YR3370 at various temperatures was measured using a rotational rheometer while varying the degree of cross-linking. Preceramic foams were produced from these cross-linked polysiloxane samples to demonstrate the effectiveness of cross-linking.

A commercially available polysiloxane resin (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo) was used for this experiment. Its molecular weight is about 7000 g/mol and it has a glass transition temperature of around 86 °C. Its pyrolysis in inert atmosphere yields a $Si_xO_yC_z$ ceramic, with a weight loss of about 19%.

This kind of polysiloxane resin shows severe room-temperature brittleness because of its low molecular weight. In order to fulfill the application for the proposed foaming method and increase the melt strength at foaming temperature, a different cross-linking was induced to the YR3370, which was thermally achieved by condensation reactions.

The cross-linking behaviors of YR3370 were measured using a rheometer (RS-200, Rheometrics Inc., Piscataway, USA) with a parallel-plate geometry (plate diameter of 25 mm and a gap of 0.5 mm). The material was rheologically characterized by recording dynamic time sweeps at different temperatures from 120 to 190 °C at an interval of 10 °C. The dynamic time sweep can indicate the effect of heating time on the complex viscosity of the measured materials. Herein, the complex viscosity refers to a frequency-dependent viscosity function determined during forced harmonic oscillation of shear stress. It is related to the complex shear modulus and represents the angle between the viscous stress and the shear stress. The measurements under dynamic time sweep mode lasted for 3600 s, and were carried out in an open atmosphere.

Fig. 1 shows that the complex viscosity of YR3370 kept almost constant during the measuring period when tested at 120 and 140 °C. This indicates the cross-linking phenomenon of YR33370 is not severe at these temperatures. With an increased testing temperature, the rate of increase in complex viscosity was remarkably accelerated. It reveals that the cross-linking of

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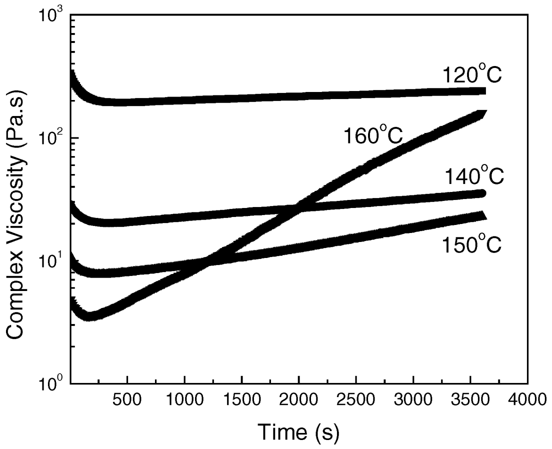

Figure 1 The effect of various cross-linking temperature on the complex viscosity of YR3370.

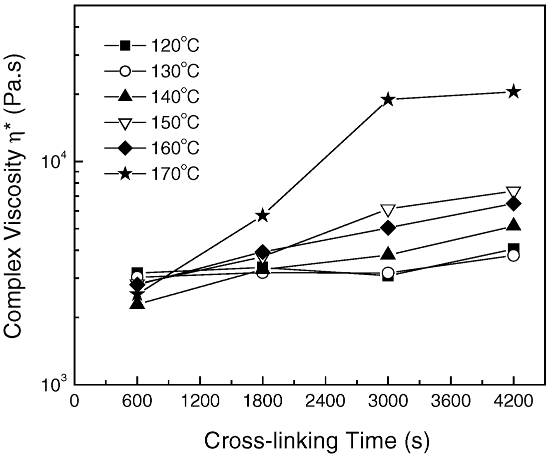

Figure 2 The effect of cross-linking conditions on the complex viscosity of pure YR3370.

YR3370 will take place at a more rapid speed at higher temperature.

However, in order to optimize the processing windows, further quantitative analysis of the melt viscosity had to be carried out. On the basis of our previous research on low-density microcelluar polyolefin foaming, we found that the melt viscosity of cross-linked polysiloxane should be precisely controlled to a limited range, in order to prevent cell coalescence during bubble growth and increase the expansion ratio.

For the purpose of simulation, the desired melt viscosity of cross-linked polysiloxane was assumed to be similar with that of the optimized melt viscosity of foaming polystyrene (PS). On the basis of previous study on PS foaming [13], the optimized complex viscosity for polysiloxane was hypothesized to be about 4×10^3 Pa · s. The effect of various cross-linking conditions of polysiloxane on the complex viscosity was investigated and an optimized cross-linking procedure was selected.

Herein, several batches of YR3370 were cross-linked at various temperatures at fixed times, such as 600, 1800, 3000, and 4200 s, respectively. Then the cross-linked materials were cooled to 110 °C, at a cooling rate of 15 °C and stabilized at 110 °C, for 1200 s. The change of rheological properties during this procedure was characterized by recording the dynamic temperature ramp.

The effect of cross-linked conditions on the complex viscosity is shown in Fig. 2. It reveals that the viscosity of YR3370 generally increased with the expansion of cross-linking time. The rate of increase in viscosity was much higher at high-cross-linking temperatures. These results are at close agreement with that which was obtained from the dynamic time sweep test. Moreover, from this figure, it can be quantitatively seen that in order to get the desired melt viscosity, remarkably different cross-linking times should be induced to YR3370 when heated at various temperatures. As the previous hypothesis, the optimized melt viscosity for polysiloxane foaming is assumed to be 4×10^3 Pa · s. In order to increase the viscosity of YR3370 to this level, several different cross-linking procedures can be selected (seen in Fig. 2), They can be thermally cross-linked for 1200 s at 170 °C, 1800 s at 160 °C, 2000 s at 150 °C, 3200 s at 140 °C or for a longer time at a lower temperature. However, when governed by the practical capability of heating equipments and accuracy of controlling apparatus, a relatively longer cross-linking time, at a lower temperature is favorable, which means the condition of 1800 s/160 °C or 2000 s/150 °C may be preferable. The other processing conditions will increase the product cost dramatically and even worsen the final foam structure.

In order to demonstrate the feasibility of the proposed foaming method and to verify whether the preliminary optimized cross-linking conditions work, a sheet of cross-linked pure YR3370 polysiloxane resin was fabricated using a compression-molding machine. The temperature for molding and cross-linking were set as 160 °C; the cross-linked time was 1800 s. After

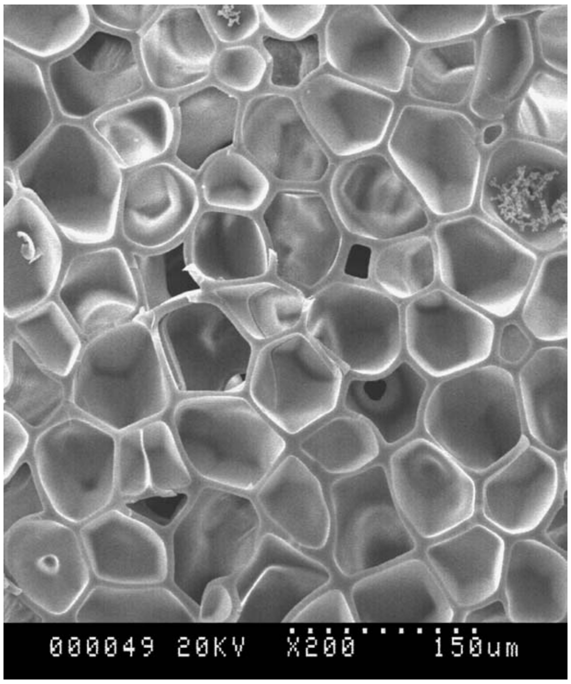

Figure 3 Typical fracture surface of cross-linked YR3370 specimen; molded using a compression molding machine, heated at 160 °C for 1800 s, then saturated under 800 psi gaseous CO_2 at room temperature for 2 hr and depressurized immediately.

molding and cross-linking, parts of the obtained sheet were placed in a pressure chamber where the samples were saturated for 2 hr with high pressure CO_2. The saturation pressure was maintained at 800 psi and saturation temperature was room temperature. Next, a thermodynamic instability was introduced by rapidly dropping the pressure at room temperature, and then a foamed preceramic structure was produced after cell nucleating and growth.

The SEM morphology shows that a uniformly fine-celled structure has been fabricated from the cross-linked YR3370 using the proposed method (seen in Fig. 3) and that the assumed cross-linking condition was acceptable for producing fine preceramic foam structures. The average cell size of the produced preceramic foam was smaller than 100 μm.

These results demonstrate the feasibility of producing porous preceramics with polysiloxane by cross-linking and subsequent foaming. Furthermore, a cross-linking condition was preliminarily optimized after investigating the changing of rheological properties during cross-linking.

Acknowledgments

This work (at the University of Seoul) was supported by the Center for Advanced Materials Processing (21C Frontier R&D Program of Korea Ministry of Science and Technology) under Grant No. PM003-3-00-01.

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Received 17 February
and accepted 1 April 2004