JOURNALOF

Ceramic Processing Research

# Fabrication of porous ceramics from polysiloxane-metallocene polyethylene blends with carbon dioxide

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Porous silicon oxycarbide (SiOC) ceramics with controllable open-cell content were made by compounding, foaming, and pyrolyzing polysiloxane and metallocene-polyethylene (mPE) polymer blends. Aimed at the development of desired foamable polysiloxane-polyolefin blends, the rheological properties of the polysiloxane and the mPE polymer were characterized, and the effects of mPE content and processing temperature on the compounding behaviors of the polysiloxane-mPE blend system were investigated. Furthermore, porous preceramics were fabricated from the polysiloxane-mPE blends with high pressure CO<sub>2</sub> using batch foaming technology. Finally, the preceramic foams were converted to porous silicon oxycarbide ceramics by completing the organic-inorganic transition via controlled pyrolysis, and open-channels were made in the cell walls by burning out the sacrificial dispersed mPE phase during pyrolysis.

Key words: Porous ceramics, Silicon oxycarbide, Foaming, Polysiloxane, Polyethylene.

### Introduction

Recent investigations in ceramic foams has increased markedly due to the rapidly growing interesting of ceramic foams as filters, catalyst supports, burners, hightemperature gas diffusers, flame barriers, biomaterial for bone replacement, and carriers for enzymes and bacteria [1-7]. Numerous technologies for fabricating ceramic foams have been developed in the past decade in a bid to produce tailored foams for various applications. The following methods represent the various attempts researchers have made to fabricate porous ceramics with a tailored foam structure: replication methods [3-5], the direct foaming of a ceramic slurry [6-9] or of a sol-gel solution [10, 11], the CVD deposition of various refractory materials on a foamed carbon skeleton [12], the sintering of hollow spheres [13], the siliciding of carbon preforms [14], the pyrolyzing of preceramic polymers containing PMMA microbeads [15, 16], the pyrolyzing of preceramic polymers foamed with expandable microspheres [17], and the pyrolyzing of preceramic polymer blends foamed with CO<sub>2</sub> [18-22].

Recently, our feasibility study demonstrated that a lowdensity, fine-celled porous ceramic structure could be developed from the blends of polysiloxane and low density polyethylene(LDPE) [21, 22]. Three stages were involved in the processing: (i) development of desired foamable polysiloxane-LDPE blends in which the LDPE phase is uniformly dispersed in the polysiloxane matrix, (ii) foaming the polysiloxane-LDPE blends obtained by implementing the thermodynamic instability principle to produce a porous ceramic precursor structure, and (iii) completing the organic-inorganic transition without sacrificing the porous structure obtained and inducing openchannels in the cell walls by burning out the sacrificial LDPE at elevated temperatures [22]. Utilizing this processing method, porous silicon oxycarbide (SiOC) ceramics with an average pore size less than 50 µm, and pore density higher than 10<sup>8</sup> cells/cm<sup>3</sup>, have been developed from the blends of polysiloxane and LDPE. The pore size distribution of the ceramic foams produced is very uniform; moreover, the pore shape and the open-cell content of the ceramic foams produced can be tailored by varying the viscosity and concentration of sacrificial LDPE phases [22].

However, since the melt temperature of LDPE is around 110 °C, in order to get fine-celled porous preceramic foams by utilizing a conventional polymer foaming system, i.e., continuous extrusion foaming or injection-molding foaming, the processing temperature of LDPE-polysiloxane has to be correspondingly higher than 110 °C in the proposed strategy. On the other hand, the polysiloxane material is highly temperature sensitive and will easily cross-link at such a high temperature [21]. Once the polysiloxane is cross-linked, the viscosity of the blends will increase dramatically and consequently the internal pressure in the extruder will increase quickly, as reflected by a signal from a pressure gauge indicating increased loading of the extrusion screw. Consequently, the polymer flow may cease and the motor used to drive the extruder often has to be turned

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off due to excessive torque requirements. Therefore, the manipulation of processing parameters, especially temperature control, is critically important and difficult during processing.

In order to overcome this difficulty, a type of metallocene polyethylene (mPE) with a low melt temperature was utilized to decrease the compounding temperature and thus to prevent the potential thermal cross-linking of polysiloxane. In this paper, a desirable blend morphology was produced from a polysiloxane-mPE system with a compounding temperature lower than 90 °C, and the cell morphology of the preceramic foams produced was tailored by varying the concentration of sacrificial polyethylene phases and the compounding temperatures. Furthermore, the feasibility of batch foaming porous preceramics from compounded polysiloxane-mPE blends with high pressure  $CO_2$  was demonstrated with several examples.

## **Experimental Procedure**

A commercially available polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan) was used as a preceramic polymer. Its pyrolysis in inert atmospheres yielded a silicon oxycarbide (SiOC) ceramic, with a weight loss of about 13%. A type of metallocene polyethylene (mPE, Engage 8200, Dupont Dow Elastomers, Melt peak 60 °C and Melt Flow Index according to ASTM standard D1238 of 5 g/10 min) was selected as the sacrificial polymeric material.

Six batches of mixtures were prepared and the amount of mPE in the mixtures was varied from 2 wt% to 40 wt%. Polysiloxane materials were ground into coarse powder before dry blending them with mPE pellets. After dry blending, the mixtures were compounded using an inner mixer (3-piece Mixer, C.W. Brabender Instruments, Inc., Hackensack, U.S.A.). The compounding temperature was set at 80 °C. The driver speed was 50 rpm and the compounding time was 15 minutes for each batch.

In order to investigate the effect of compounding temperature on the blend morphology, a particular study was carried out in the inner mixer under fixed material parameters. For this case, the concentration of mPE was fixed to 10 wt%. The compounding temperatures were varied from 80 °C to 110 °C.

After compounding, parts of each blend obtained were placed in a pressure chamber where the samples were saturated for 24 h with high pressure  $CO_2$ . The saturation pressure was maintained at 5 MPa and the saturation temperature was room temperature (approx. 22-25 °C). Next, a thermodynamic instability was introduced in the saturated blends by rapidly dropping the pressure at room temperature, and then a foamed preceramic structure was produced with bubble nucleation and growth.

The foamed specimens were cross-linked by sucking an aminoalkylalkoxysilane condensation catalyst into the structure, subsequently heating up the specimens to 180 °C, and then maintaining that temperature for 2 h in the air. Finally, the mPE-polysiloxane polymer blends were pyrolyzed at 1,200 °C for 1 h in nitrogen atmosphere at a heating rate of 2 Kminute<sup>-1</sup>.

The rheological behaviors of the mPE and polysiloxane were measured using a rheometer (RS-200, Rheometrics Inc., Piscataway, U.S.A.) with a parallel plate geometry (plate diameter of 25 mm and a gap of 1.0 mm). The materials were rheologically characterized by recording the dynamic frequency sweep and dynamic temperature ramps, respectively. In the measurement of dynamic frequency sweep, the frequencies were decreased from 100 rad/s to 0.1 rad/s and the subtractions were logarithmically scaled. In the testing of dynamic temperature ramps, the frequencies were fixed to 100 rad/s and the stress was 500 Pa, then the temperature was reduced from 125 °C to 85 °C at a constant rate of 1 Kminute<sup>-1</sup>.

The microstructures of the foamed mPE-polysiloxane specimens were observed by scanning electron microscopy (SEM, S-4300, Hitachi High Technologies Co., Tokyo, Japan). The microstructures of the pyrolyzed ceramic specimens were observed using another SEM (JSM-6060, JEOL Ltd., Tokyo, Japan). The cell densities of the porous mPE-polysiloxane specimens were measured by counting the number of cells in a two-dimensional image of the microstructure and converting it to 3-dimensions [17]. The particle density, which means the number of the dispersed mPE domains per unit volume (cm<sup>3</sup>) was determined from:

$$N_0 = \left[\frac{n}{A}\right]^{\bar{2}} M^3 \tag{1}$$

where n is the number of domains in the two-dimensional SEM picture, M the magnification of the micrograph, and A the area of the micrograph.

#### **Results and Discussion**

The overall strategy of the research has been described in detail previously [22]. The central idea is: in order to improve the processability of the polysiloxane and to control the cell morphology of the final ceramic articles, an appropriate amount of polyethylene polymer should be uniformly integrated into the polysiloxane substrate [22]. Therefore, an important element of this research was concerned with the dispersion and mixing of polysiloxanemetallocene polyethylene (mPE) blends in compound processing equipment such as an inner mixer. In other words, with the objective of controlling factors to produce desirable foamable blends, the amount of mPE, and the size and shape of the dispersed mPE phase as functions of compounding parameters, were investigated.

Generally, the minor mPE phase in the immiscible polysiloxane-mPE blends is deformable, as opposed to the composite materials containing a rigid minor phase such as solid particles or microspheres. A wide range of sizes and shapes can thus be obtained for this dispersed phase during processing. With careful manipulation, the



**Fig. 1.** Complex viscosity ( $\eta^*$ ) as a function of heating temperature for both mPE (Engage 8200) and polysiloxane (YR3370); shear rate is fixed to 100 rad/s and stress is 500 Pa.



**Fig. 2.** Complex viscosity ( $\eta^*$ ) as a function of shear rate for both mPE (Engage 8200) and polysiloxane (YR3370).

dispersed mPE domains can range in size from submicrometre to hundreds of micrometres. Furthermore, spherical, ellipsoidal, fiber-like, ribbon-like or co-continuous morphologies can be produced under various conditions. The final morphology obtained is a balance between the deformation-disintegration phenomena and coalescence [23]. In the present study, factors affecting the manipulation of shape and size of dispersed mPE were demonstrated.

The ratio of the viscosity of the dispersed phase to the viscosity of the matrix, has been shown to be one of the most important variables for controlling blend morphology [23]. Generally, it is believed that the viscosity ratio should be approximately unity when designing new polymer blends. If the minor component has a lower viscosity than the major one, the minor component will be finely and uniformly dispersed; conversely, the minor component will normally be coarsely dispersed if its viscosity is higher than that of the major component [23]. In this study, we investigated the viscosity change of both polysiloxane and mPE with

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changes in melt temperature by recording the dynamic temperature ramp sweeps of the two materials in a rheometer; consequently, the optimized compounding temperature regime was selected by choosing the temperature range where the viscosity ratio between mPE and polysiloxane was slightly lower than 1.

From Figs. 1 and 2 it may be seen that the viscosity change of polysiloxane (YR3370) is much more temperature sensitive than for mPE (Engage8200), and when the temperature is lower than 100 °C, the viscosity of polysiloxane is higher than that of the mPE material. However, since the polysiloxane would solidify around 86 °C, the compounding temperature could not be decreased too much.

Since the temperature profile of a polymer melt in an extruder or mixer depends on the material and processing parameters such as the molecular structure, the heat conductivity, the melt flow rate, the screw speed and the screw geometry, it is difficult to measure the exact compounding temperature in the extruder or mixer. However generally, the actual processing temperature is still close to the setting temperature. In our experiments, the compounding temperatures were set from 80 °C to 110 °C to prevent the potential thermal cross-linking of polysiloxane during processing, so that the influence of compounding temperature on particle size was investigated.

The mPE concentration was fixed at 10 wt%. By decreasing the compounding temperature, the viscosities of mPE and polysiloxane were increased, respectively



Fig. 3. The effect of compounding temperature on the average size of dispersed mPE phase, compounded under condition 50 rpm/ 15 minutes, mPE content is fixed to 10 wt%: (a) 80 °C, (b) 90 °C, (c) 100 °C and (d) 110 °C,

(see Fig. 2). However, the viscosity change of polysiloxane was much more sensitive to temperature alteration than that of mPE; in the temperatures that range lower than 107 °C, the viscosity ratio between polysiloxane and mPE increased markedly and higher than 1. Moreover, due to the dramatic increase of the viscosity of the polysiloxane matrix, the force used to induce deformation and disintegration of mPE phases increased correspondingly and the resistance to prevent coalescence between dispersed mPE domains increased also. Therefore, the number-average particle size decreased when the compounding temperature decreased (see Fig. 3). At 110 °C, the average particles size is around 6.2  $\mu$ m; whereas, when the temperature is decreased to 80 °C, the particle size is changed to around 1.9  $\mu$ m only.

But as mentioned previously, since the polysiloxane would solidify around 86 °C, the compounding temperature could not be decreased much. In the actual compounding, when the compounding temperature was decreased to 70 °C, the polysiloxane would not be fully softened.

When the compounding conditions were fixed, the concentration of mPE in the system strongly affected the blend morphology. The present research indicated that at about 30 wt% Engage8200, there was an intermediate region in which both Engage8200 and YR3370 were co-

continuous, and as the content of polyethylene decreased to 20%, some cylinder-like Engage8200 phases were observed in the compounded blend (see Fig. 4). At lower polyethylene concentrations, there was a gradual decrease in the dispersed phase dimensions with a decrease in the Engage8200 concentration. A further decrease in the fraction of the dispersed metallocene polyethylene phase, resulted in a decrease in the particle size due to the mitigated coalescence. When the mPE concentration was lower than 10%, the dimension of most minor phases could be decreased to less than  $3\mu m$  and the dispersion of them was quite uniform.

Once the controlled well-dispersed polysiloxane-mPE blends were developed, porous structures were created by introducing a thermodynamic instability into the blend system to promote a large cell density and a large void fraction. In the present research, a batch foaming system was utilized to identify the possibility of utilizing the thermodynamic instability to produce porous ceramic precursors.

The first step of the processing involved dissolving carbon dioxide under high pressure into the polysiloxane-mPE polymer blends to saturate them up to the equilibrium gas concentration, i.e., the solubility. Once saturated blends were formed after 24 hours of saturation, a number of



**Fig. 4.** The effect of mPE concentration on the blends morphology, compounded under condition 80 °C/50 rpm/15 minutes. Melt flow index of mPE is equal to 5 g/10 minutes:(a) 2%, (b) 5%, (c) 10%, (d) 20%, (e) 30% and (f) 40%.



Fig. 5. The effect of dispersed mPE particles on cell density.

microvoids were rapidly nucleated by introducing a thermodynamic instability via a rapid pressure drop in the polysiloxane-mPE blends.

Cell nucleation could occur homogeneously throughout the YR3370 matrix or heterogeneously at interfacial regions such as the boundaries between the mPE and polysiloxane melt phases. Well dispersed mPE particles could not only control the open-cell content by inducing open channels Chunmin Wang, Jin Wang, Chul B. Park and Young-Wook Kim

in the cell walls after being burnt out, but also act as a nucleating agent in foam processing by inducing large amounts of nucleating sites with an interfacial region. As is shown in Fig. 5, when there were more dispersed mPE domains in the compounded blends, a higher cell density was observed in the foamed preceramic samples. Meanwhile, the dispersed mPE phases could also have acted as a type of enhancement additive to alternate the melt strength of the blend system, and thus affect the foam growth and expansion ratio.

The experimental results suggest that gaseous  $CO_2$  which was dissolved into polysiloxane had a plasticizing effect and lowered the softening temperature to below room temperature (R.T.). This resulted in foaming occurring when depressurized even at room temperature. The cell size and cell density were strongly dependent on their blend compositions (see Fig. 6). Generally, the dispersed mPE particles increased the viscosities of the polysiloxane melt, and the phases with greater mPE contents would hinder the quick expansion of bubbles and alleviate the cell coalescence. As the concentration of mPE became lower than 5%, the incorporated mPE phase failed to increase the melt strength of the polysiloxane-mPE system due to its tiny fraction in the blends. Consequently, the cell density decreased dramatically and the average cell



Fig. 6. The effect of mPE concentration on foam morphology, compounded under conditions 80 °C/50 rpm/15 minutes, foamed after saturation for 24 h at R.T under 5.5 MPa CO<sub>2</sub>: (a) 2%, (b) 5%, (c) 10%, (d) 20%, (e) 30% and (f) 40%.



Fig. 7. SEM morphologies of typical porous ceramic structures; compounded under conditions 80  $^{\circ}$ C/50 rpm/15 minutes, foamed after saturation for 24 h at R.T. under 5.5 MPa CO<sub>2</sub>, and then pyrolyzed in N<sub>2</sub> for 1 h at 1,100  $^{\circ}$ C. (a) and (b) specimen with 5% mPE, (c) and (d) specimen with 30% mPE.

size increased to above 100  $\mu$ m, the magnitude of which was similar to the cell size of pure YR3,370 foams [21]. With an increase of the mPE content (> 10%), the cell size of the foamed polysiloxane-mPE blends was decreased and also the cell density was increased. When the mPE content in the blends was higher than 30%, the morphology of the mPE phase in the foamed blends was changed from isolated to continuous. As a result, the continuous structure of mPE prevented the expansion and coalescence of polysiloxane by limiting the flow of the preceramic polymer inside the network structure. Compared with the cells produced in the blends with 2% mPE, the average cell size was much smaller.

The foamed blends were subsequently cross-linked with a catalyst and pyrolyzed into a ceramic in a  $N_2$  atmosphere. Typical microstructures of silicon oxycarbide foams are shown in Fig. 7. The foam structure was well maintained. The open-cell content was determined by the concentration of mPE in the original blends. The cell morphology showed major open cells at a high mPE concentration and major closed cells when the mPE content was lower than 10 wt%. At high mPE concentrations, the mPE phase was dispersed continuously or in long fiber-like shapes throughout the polysiloxane matrix because of the high shear effect in the mixer. After foaming and pyrolysis, numerous tangled void channels were formed when the oriented mPE phase was burnt out. The ceramics obtained, therefore, are fully opencelled. In contrast, the mPE phase was dispersed as short fibers or even as isolated domains in blends that contained lower amounts of mPE; after foaming and pyrolysis, only isolated channels or voids were induced into the ceramics and the porous ceramics produced were fully close-celled.

#### Summary

The relationships between the compositions of blends, processing temperatures in compounding, dispersed phase behaviors and foam morphologies were investigated and discussed. It can be concluded that the processing temperature of the polysiloxane can be successfully decreased to 90 °C by utilizing a type of mPE (Engage8200), and that the undesirable thermal cross-linking of polysiloxane (YR3370) can thus be minimized during the compounding. The dispersed mPE phase morphology in the immiscible polysiloxane-mPE polymer system can be manipulated by deliberate control of the materials and processing temperatures. The feasibility of producing porous preceramics from compounded polysiloxane-mPE blends

by utilizing the thermodynamic instability is identified using a batch foaming system. Finally, ceramic foams with tailored cell morphologies were fabricated from the porous preceramic templates via controlled pyrolysis.

## Acknowledgments

This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21<sup>st</sup> Century Frontier R&D Program funded by the Ministry of Knowledge Economy (MKE), Republic of Korea.

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