

## Processing of porous silicon oxycarbide ceramics from extruded blends of polysiloxane and low-density polyethylene

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The aim of this paper is to demonstrate a new technology to fabricate controlled and uniformly distributed porous ceramic structures from the blends of polyolefin and preceramic polymers by compounding and subsequent pyrolysis. As examples, porous silicon oxycarbide ceramics with either fully open-celled or major close-celled structures, with cell porosities ranging from 20.5% to 79.8%, cell densities higher than  $10^8$  cells/cm<sup>3</sup> and cell diameters smaller than 50  $\mu$ m, were made from low-density polyethylene (LDPE) and polysiloxane blends. The LDPE powders and polysiloxane were directly compounded using a counter-rotated twin-screw extruder with a filamentary die, and then the specimens obtained were transformed into porous silicon oxycarbide ceramics by controlled pyrolysis.

**Key words:** Porous ceramics, Silicon oxycarbide, Polysiloxane, Extrusion.

### Introduction

Ceramic foams possess some unique characteristics such as: low density, high specific strength, low thermal conductivity, high fluid permeability, high chemical resistance, and high thermal shock resistance. Due to these unique characteristics, ceramic foams have many applications. For example, high porosity open-celled ceramic foams can be used as fluid filters, catalyst supports, burners, gas diffusers, flame barriers, liquid aerators and as carriers for cells, enzymes and bacteria. Furthermore, close-celled ceramic foams can be used as energy absorbers and as lightweight structure materials [1-7]. Since the open-cell content and cell morphology in porous ceramics directly relate to their ability to perform a desired function in a particular application, emphasis has been put on fabrications a porous ceramic structure with controlled porosity, open-cell content and cell morphology [3-7].

In decades past, various processing routes have been proposed for the production of porous ceramics [3-14]. Among them, utilization of preceramic polymers is relatively novel and effective because the variable rheological properties of preceramics allow a great deal of control over the processing. In addition, some well-established plastic foaming techniques can be effectively used to get tailored foam structures [10-14].

Recently, our feasibility study demonstrated that a

controlled and uniformly distributed porous structure could be developed from various blends of a polyolefin and preceramic polymers by fully compounding and subsequent controlled pyrolysis. The following are the basic steps to produce porous ceramics: (i) compounding preceramic polymers and a polyolefin; (ii) molding the shape of articles; and (iii) transforming the articles obtained into porous ceramics by pyrolysis and optionally subsequent sintering.

Utilizing the mentioned processing technology, a preceramic polymer would be transformed into the backbone of the porous ceramic after completing the polymer-to-ceramic conversion; and the polyolefin would act as the sacrificial phase and leave the pores after burning out during pyrolysis. With a well-established technique for polymer processing, varying the compounding parameters and polyolefin content of the blending could control the blend morphology. For instance, if the polyolefin content were high enough to make the polyolefin/preceramic polymer co-continuous, the porous ceramic after pyrolysis would be fully open-celled. However, if the polyolefin content is low, the separately isolated polyolefin phase could be dispersed in the matrix of the preceramic polymer by combining a precise control of the compounding conditions; and in turn, a close-celled porous ceramic structure could be produced after burn out of the polyolefin and completing the polymer-to-ceramic conversion.

Compared to the traditional technique of producing porous ceramics through extrusion and pyrolysis of a ceramic powders/binder system [15], the present process has general advantages of polymer-derived ceramics such as low-temperature processing, additive-free densification,

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and chemical homogeneity [16]. Furthermore, with the present technology, it is feasible to realize shapes that are impossible or difficult to achieve using the classical procedures [17].

In the present paper, a successful example of fabricating porous silicon oxycarbide (SiOC) ceramic structures with a controlled open-cell content, uniformly distributed cell size, and fine-celled morphology is demonstrated.

## Experimental Procedure

A commercially available polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan) was used as the preceramic polymer. Its pyrolysis in inert atmospheres yielded a silicon oxycarbide (SiOC) ceramic, with a mass loss of about 13%. The SiOC is an amorphous phase and when heated at temperatures above 1300 °C, precipitation of nanometre-sized SiC particles embedded in amorphous SiO<sub>2</sub> takes place [18]. SiOC ceramics show improved thermal and mechanical properties at high temperatures. For example, they are resistant to oxidation and stable in the amorphous state upto approximately 1500 °C [19]. Furthermore, polysiloxane (YR3370) material offers very good air stability (long shelf life in the monomer form at room temperature) and non-toxicity which enable easy storage and processing and consequently, cost reduction [20].

Low-density polyethylene (LDPE, LC0520, Nova Chemical, Canada) was used as the sacrificial polymeric material. Four batches of powder were mixed (Table I).

The powders were directly compounded using a counter-rotated twin-screw extruder with a filament die 2.3 mm in diameter and 11.9 mm in length. The temperatures for the two heated sections of the barrel were set at 90 °C and 115 °C, respectively. The die temperature was 130 °C and the extruder speed was 40 rpm. The extruded specimens were cross-linked by doping a condensation catalyst (aminoalkylalkoxysilane) and subsequently heating up to 180 °C and held at temperature for 2 h in air. Then, the blends of the polyolefin-preceramic polymer were pyrolyzed at 1200 °C for 1 h in nitrogen with a heating rate of 2 Kminute<sup>-1</sup>.

The rheological behaviors of YR3370 and LDPE were characterized using a strain-controlled 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 microstructures of the pyrolyzed specimens were observed by scanning electron microscopy (SEM, S-4300, Hitachi High Technologies Co., Japan). The void fraction of the obtained porous ceramics was measured on a polished surface using an image analyzer (Image-Pro Plus, Media Cybernetics, USA). The cell density of the porous ceramics was measured by counting the number of the cells in a two-dimensional image on the microstructure and by converting it to 3-dimensions [11].

## Results and Discussion

A uniformly mixed blend of polyolefin-preceramic polymer could be achieved using a counter-rotated twin-screw extruder. When pyrolyzed at elevated temperatures, LDPE was burned out and only SiOC was obtained and maintained after the polymer-to-ceramic conversion of the polysiloxane (YR3370). Therefore, the final porous morphology in the ceramic articles was mostly governed by the content, distribution, and morphology of the LDPE phase in the compounded blends.

However, the distribution and morphology of the LDPE phase in the blends were correspondingly controlled by the rheological behaviors of the polysiloxane and LDPE polymers investigated. In order to better understand the rheological properties under actual compounding condition, both LDPE and YR3370 were rheologically characterized by recording the dynamic time sweeps at a temperature 130 °C with a high stress and a relatively high shear rate (500 Pa, 100 rad/s). Fig. 1 showed the change of storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) as a function of heating time. It may be seen the  $G'$  and  $G''$  remained stable for LDPE; however, both  $G'$  and  $G''$  increased for YR3370 except for the initial stage, and this was explained by considering the cross-linking behavior of YR3370 at high temperatures [21]. In addition, for LDPE,  $G'$  was higher than  $G''$ , meaning that the LDPE

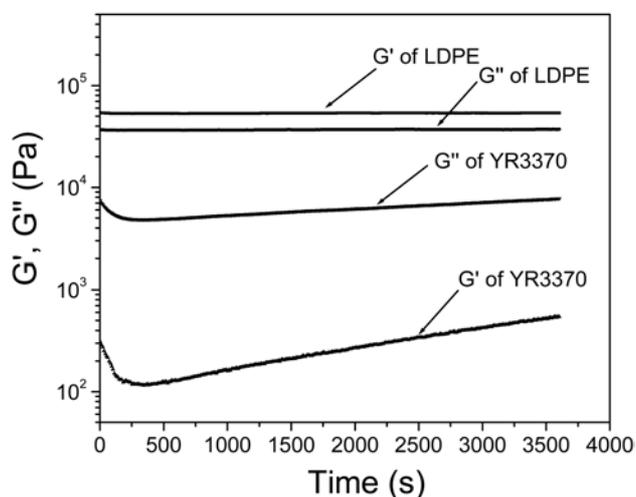


Fig. 1. Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) as a function of heating time for both LDPE and YR3370 at 130 °C.

Table 1. Batch composition and sample designation

Sample designation	Batch composition (wt%)	
	Polysiloxane*	LDPE**
50YR50LDPE	50	50
70YR30LDPE	70	30
85YR15LDPE	85	15
90YR10LDPE	90	10

\* YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan

\*\* LC0520, Nova Chemical, Canada

was principally solid-like; however, for YR3370,  $G'$  was lower than  $G''$ , meaning that the material was more liquid-like. Taking the magnitude of the complex viscosity (see in Fig. 2) for both LDPE and YR3370 into account, it was reasonable to state that compounding actually occurred in the system with a soft-matrix and a stiff-dispersed phase.

Because of the remarkable difference in viscosity, it will be difficult to get a uniformly dispersed, tiny spherical LDPE phase under common compounding conditions [22]. On the contrary, the dispersed LDPE phase will be likely to be elongated to a fibrous structure in the strong shear field during compounding.

Another parameter that affects the morphology of final porous ceramic articles will be the LDPE content. After burning out of the LDPE, voids will be induced into the articles and consequently, the porosity of the porous ceramic will be mostly controlled by the initial composition of blends. Furthermore, coalescence and entanglement in polymer blends will be significantly affected by the composition of the blends as well as by the processing conditions. Deliberately selecting a proper content of LDPE, combining it with an appropriate compounding condition, one can control the degree of entanglement and the distribution of the LDPE phase in the polymer blends and thus, control the final open-cell content and porosity of the porous ceramics obtained.

The morphology of pyrolyzed SiOC samples indirectly demonstrated the above conclusions. Fig. 3 shows the morphology of the pyrolyzed porous SiOC ceramic from the 50YR50LDPE specimen. It is evident that the LDPE phase and YR3370 phase were dispersed co-continuously and elongated along the flow direction in the compounding because of the strong shear effect during the convergence and flow through the die. As a result, by burning out of the co-continuously connected LDPE, the structure of the pyrolyzed 50YR50LDPE specimen was completely open-celled (see in Fig. 3(b)).

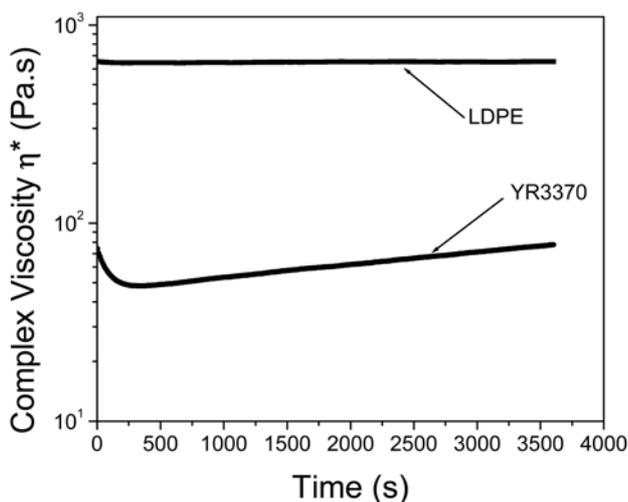


Fig. 2. Complex viscosity ( $\eta^*$ ) as a function of heating time for both LDPE and YR3370 at 130 °C.

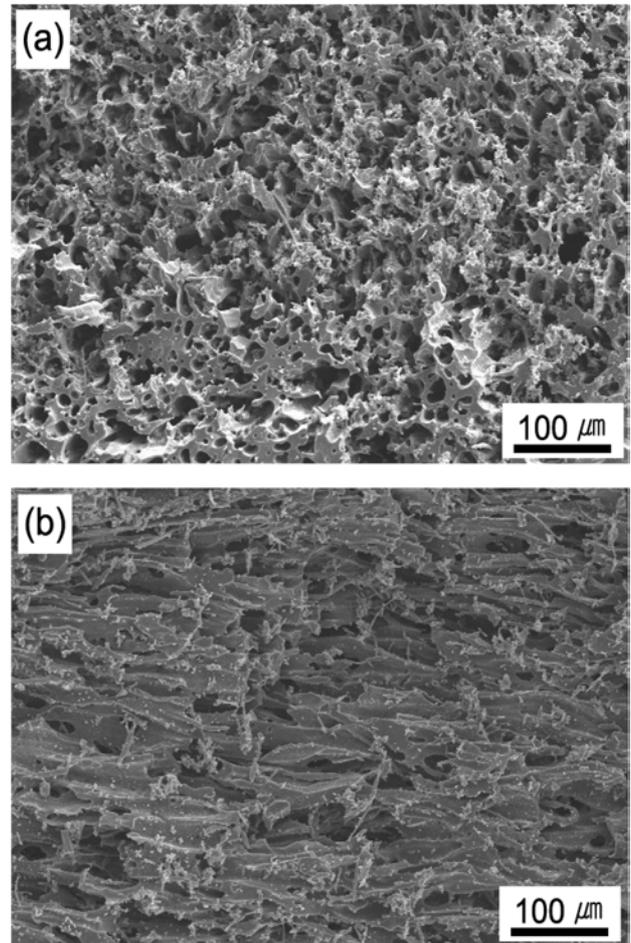
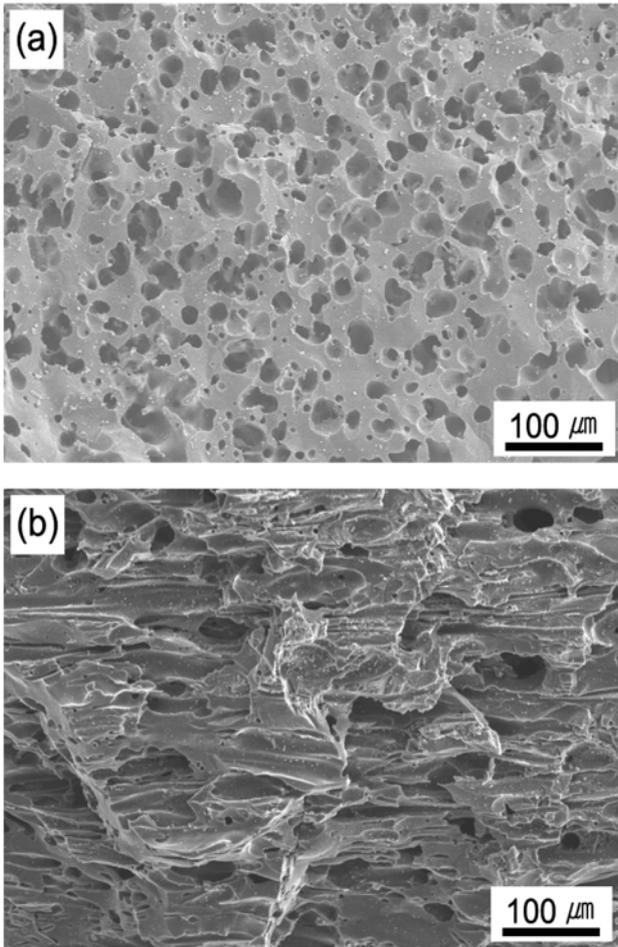


Fig. 3. Typical fracture surfaces of 50YR50LDPE specimens; mixed using a counter-rotated twin-screw extruder then pyrolyzed at 1200 °C for 1 h in  $N_2$ : (a) cross section and (b) flow direction.

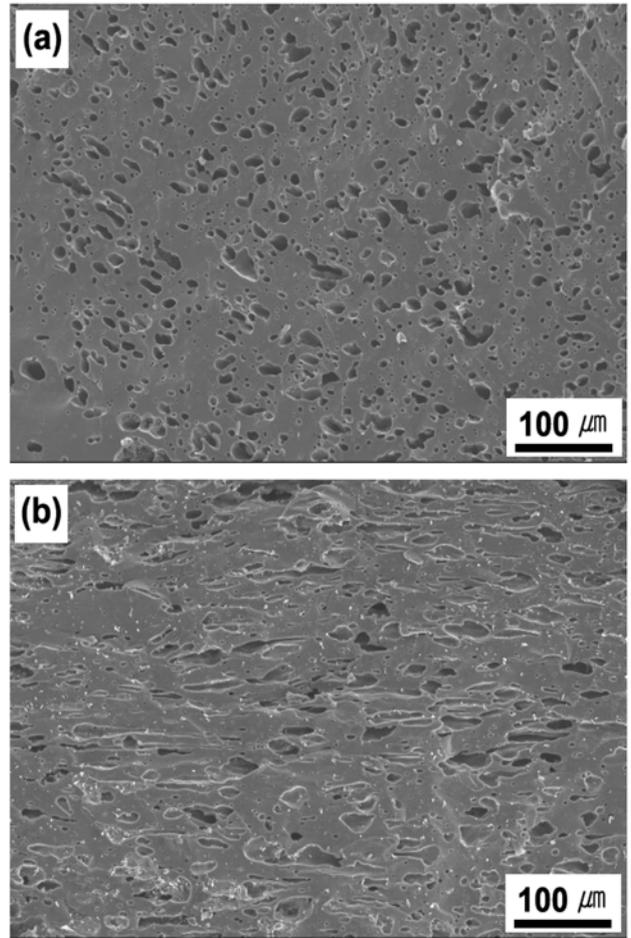
With a smaller content of LDPE, the minor LDPE was expected to disperse in the matrix of the YR3370 as an isolated second phase. From Fig. 4(a), major closed cells and minor island-continuous cells co-existed in the pyrolyzed 70YR30LDPE specimens, which confirms the above assumption. However, it seems that the 30 mass% content of LDPE was still high enough to cause coalescence of the LDPE phase in the mixture during compounding and extrusion. The shear generated especially by the flow in the die, caused some severe coalescence. Therefore, some elongated large voids could be observed in part of the pyrolyzed 70YR30LDPE specimens (see Fig. 4 (b)).

By further decreasing the content of LDPE to 15 mass%, a mostly close-celled porous ceramic structure could be fabricated (see Fig. 5). The pores left by burning out the LDPE phase were mainly fiber-like and highly orientated. As mentioned above, this phenomenon was determined by the viscosity ratio of LDPE and YR3370 under the compounding conditions. The morphology of the pyrolyzed 90YR10LDPE was similar with that of 85YR15LDPE.

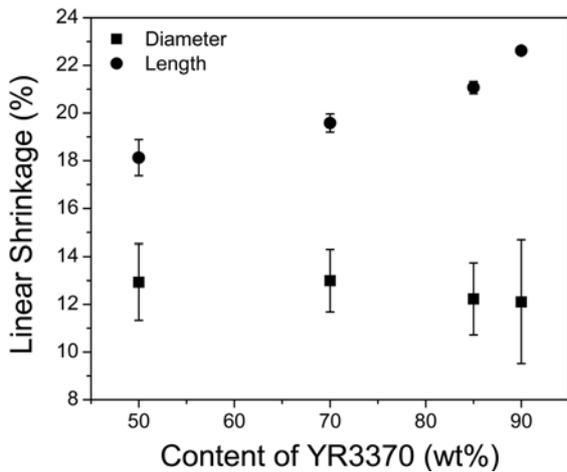
Fig. 6 and Fig. 7 show the linear shrinkage and porosity for all of the four compositions investigated. These indicate that, for the given compounding and pyrolysis conditions,



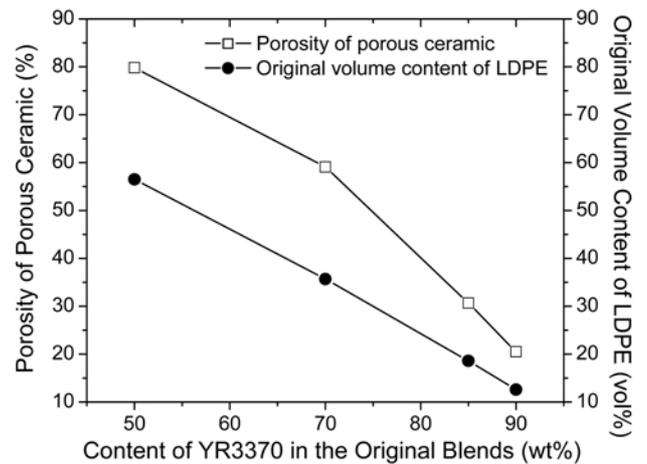
**Fig. 4.** Typical fracture surfaces of 70YR30LDPE specimens; mixed using a counter-rotated twin-screw extruder, then pyrolyzed at 1200 °C for 1 h in N<sub>2</sub>: (a) cross section and (b) flow direction.



**Fig. 5.** Typical fracture surfaces of 85YR15LDPE specimens; mixed using a counter-rotated twin-screw extruder then pyrolyzed at 1200 °C for 1 h in N<sub>2</sub>: (a) cross section and (b) flow direction.



**Fig. 6.** Linear shrinkage of pyrolyzed specimens as a function of YR3370 content in the initial blends.



**Fig. 7.** Porosity of pyrolyzed specimens as a function of YR3370 content in the initial blends.

the linear shrinkage increased with a decrease in the amount of LDPE; and the amount of porosity in the porous ceramics decreased with a decrease in the amount of LDPE. However, the amount of porosity for all samples was

higher than the initial volume content of LDPE in the blends. The increase in porosity after pyrolysis was ascribed to the complex reactions occurring in the cross-linking and the pyrolysis procedures, such as the thermolysis

that gives off oligomers and other decomposition gases. According to the literature, the pyrolytic conversion process of a cured preceramic has been found to involve a number of stages [23-26]. During the organic-inorganic transition, the polymeric network is locally reconstructed and new bonds are formed, which in turn is accompanied by a volume and density change of the products. Usually, degradation of low molecular weight molecules and decomposition of organic side groups occur up to about 800 °C, and large weight losses and gaseous evolution of mainly H<sub>2</sub> and CH<sub>4</sub> are associated with these reactions [23-26].

The average cell diameter was about 10-50 μm for all specimens after pyrolysis. The cell densities of the pyrolyzed SiOC ceramic specimens were  $2.7 \times 10^8$ ,  $1.4 \times 10^8$ ,  $8.1 \times 10^8$  and  $7.4 \times 10^8$  cells/cm<sup>3</sup> for 50YR50LDPE, 70YR30LDPE, 85YR15LDPE and 90YR10LDPE specimens, respectively. The anomalous behavior for the 70YR30LDPE sample is probably due to an opened-to-closed transition cell structure. This type of cell morphology was very close to the transition level from major open to major closed morphology, therefore, in this sample, coalescence of LDPE probably was very severe and in turn, the cell density of pyrolyzed sample will decrease. However, further research needs to be conducted to clarify this issue.

The current results demonstrate the feasibility of producing porous SiOC ceramics with blends of polyolefin-preceramic polymers using blending and sintering. By implementing the principle of this method to other plastic shaping techniques, i.e. injection molding and compression molding, various porous ceramic articles with the required cell morphology and complex shapes can be fabricated easily and conveniently.

### Summary

An example of fabricating porous SiOC ceramics from various blends of LDPE and polysiloxane (YR3370) has been demonstrated in this paper. According to the content of LDPE in the blends, the cell structure of the porous SiOC ceramics can be fully open-celled or major closed. The porous SiOC ceramics obtained have porosities from 20.5% to 79.8%; cell densities higher than 10<sup>8</sup> cells/cm<sup>3</sup> and average cell diameters smaller than 50 μm.

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### References

1. J. Saggio-Woyansky, C.E. Scott and W.P. Minnear, *Am. Ceram. Soc. Bull.* 71[11] (1992) 1674-1682.
2. P. Sepulveda, *Am. Ceram. Soc. Bull.* 76[10] (1997) 61-65.
3. P. Colombo and M. Modesti, *J. Am. Ceram. Soc.* 82[3] (1999) 573-578.
4. P. Sepulveda and J.G. P. Binner, *J. Europ. Ceram. Soc.* 19 (1999) 2059-2066.
5. H.X. Peng, Z. Fan, J.R.G. Evans and J.J.C. Busfield, *J. Europ. Ceram. Soc.* 20 (2000) 807-813.
6. Y.-W. Kim, H.D. Kim and C.B. Park, *J. Am. Ceram. Soc.* 88[12] (2005) 3311-3315.
7. J.H. Eom, Y.-W. Kim, I.H. Song and H.D. Kim, *Mater. Sci. Eng. A* 464 (2007) 129-134.
8. P. Colombo and E. Bernardo, *Comp. Sci. and Tech.* 63 (2003) 2353-2359.
9. M.R. Nangrejo, X. Bao and M.J. Edirisinghe, *J. Mat. Sci. Lett.* 19 (2000) 787-789.
10. Y.-W. Kim, J.H. Eom, C. Wang and C.B. Park, *J. Am. Ceram. Soc.* 91 (2008) 1361-1364.
11. Y.-W. Kim and C.B. Park, *Comp. Sci. and Tech.* 63[16] (2003) 2371-2377.
12. J. Zeschky, F. Goetz-Neunhoeffler, J. Neubauer, S. H. Jason Lo, B. Kummer, M. Scheffler, and P. Greil, *Comp. Sci. and Tech.* 63[16] (2003) 2361-2370.
13. Y.-W. Kim, S.H. Kim, X. Xu, C.H. Choi, C.B. Park and H.D. Kim, *J. Mater. Sci. Lett.* 21[21] (2002) 1667-1669.
14. Y.-W. Kim, S.H. Kim, C. Wang and C.B. Park, *J. Am. Ceram. Soc.* 86[12] (2003) 2231-2233.
15. F.A. Cantaloupe, R.I. Frost and L.M. Holleran, US Patent 3919384, Method for extruding thin-walled honeycombed structures, 1975.
16. R. Rice, in *Advanced Ceramics Processing and Technology*, Vol.1, 1990, edited by J.G.P. Binner (Noyes Publications, 1990) p.123.
17. P. Greil, *Adv. Eng. Mater.* 2 (2000) 339-348.
18. H.J. Kleebe, C. Turquat and G.D. Soraru, *J. Am. Ceram. Soc.* 84[5] (2001) 1073-1080.
19. G.D. Soraru and D. Suttor, *J. Sol-Gel Sci. Tech.* 14[1] (1999) 69-74.
20. YR3370 Material Safety Data Sheet (MSDS), GE Toshiba Silicones, Tokyo, 2002.
21. C. Wang, J. Wang, C.B. Park and Y.-W. Kim, *J. Mater. Sci. Lett.* 39 (2004) 4913-4915.
22. B.D. Favis, in *Polymer Blends*, Vol. 1, 2000, edited by D.R. Paul and C.B. Bucknall (John Wiley & Sons, 2000) p. 501.
23. G.M. Renlund, S. Prochazka and R.H. Doremus, *J. Mater. Res.* 6[12] (1991) 2716-2722.
24. G.M. Renlund, S. Prochazka and R.H. Doremus, *J. Mater. Res.* 6[12] (1991) 2723-2734.
25. S.H. Yu, R.E. Riman, S.C. Danforth, R.Y. Leung and S.T. Gonczy, *Ceram. Trans.* 42 (1994) 71-79.
26. F. Babonneau, L. Bois, C.Y. Yang and L.V. Interrante, *Chem. Mater.* 6 (1994) 51- 57.