Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 497-507

HEAT CAPACITY MEASUREMENT OF BORON NITRIDE-FILLED POLYBENZOXAZINE
The composite structure-insensitive property

H. Ishida[*] *and S. Rimdusit*

The NSP Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland
Ohio 44106-7202, USA

(Received March 8, 1999)

Abstract

Specific heat capacity of boron nitride-filled polybenzoxazine has been investigated by using temperature-modulated differential scanning calorimetry, TMDSC, to study that it is a composite structure-insensitive property, i.e. independent of the degree of filler network formation. Many aspects of boron nitride filler such as particle size, particle surface area, particle shape, and filler loading are investigated. At the same filler loading, we observe insignificant change in composite specific heat capacity due to the effect of particle size, particle surface area, and particle shape. Filler loading is found to be the only aspect of filler that can change the specific heat capacity of this filled system. A linear relationship between the composite heat capacities and filler loading is observed and can be predicted by the rule of mixture with an error within ±1%. Within the temperature range betwen 0 and 80°C, the temperature dependent heat capacity of this composite can simply be expressed in the form of a linear equation: $C_p=A+BT$.

Keywords: heat capacity of polymer composite, rule of mixture, TMDSC

Introduction

In composite materials, the effect of adding filler on the overall specific heat capacity of the composites has not been widely investigated as the determination of specific heat capacity for composite materials is tedious and difficult to accurately determine [1, 2]. Specific heat capacity of composite materials is an essential parameter especially in the determination of thermal conductivity because it relates thermal diffusivity and thermal conductivity. Thermal diffusivity can be easily determined, but thermal conductivity, the more useful and more important parameter in many applications, is difficult to directly determine. They can be related by the relationship: $\lambda=k/\rho C_p$, where λ is thermal diffusivity ($m^2\ s^{-1}$), ρ is density ($kg\ m^{-3}$), C_p is

---

[*] Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

specific heat capacity (J K^{-1} kg^{-1}), and k is thermal conductivity (W m^{-1} K^{-1}) of the composite.

This experiment is also intended to show the important characteristic of a composite's structure-insensitive property. A structure-insensitive property is a property that depends only on the amount of filler in the composite. On the contrary, a path-dependent property depends strongly on the formation of the filler network in the composite system. A structure-insensitive property character is typically observed in non-transport properties such as specific heat capacity and density and in some transport properties where the difference between the transport property values between the filler and the matrix is small such as that observed in the thermal conductivity of glass-filled polymers [3]. This property is normally observed as having a linear relationship with filler loading, i.e. being predicted by the rule of mixture.

Most transport properties of filled systems such as electrical conductivity, thermal conductivity, and viscosity are path-dependent properties. That is, the properties will greatly change with the transformation from discontinuous to continuous filler network and vice versa. This behavior is usually called the filler dispersion effect. These properties normally have a non-linear relationship with the filler loadings and the properties usually change more rapidly with the formation of a more perfect filler network [4]. The properties can typically be predicted by percolation theory [5].

Most specific heat capacity values of composites at different filler contents are normally obtained by using the rule of mixture when the heat capacities of the filler and the matrix are known [6–8]. However, by utilizing the new temperature-modulated differential scanning calorimetry technique, the determination of the absolute value of heat capacity of the material is much quicker, easier, and more accurate [9, 10]. It is the purpose of this study to investigate the effect of boron nitride filler on the specific heat capacity of filled polybenzoxazine as these composite systems exhibited extraordinarily high values of thermal conductivity [11]. The effect of particle size, shape, surface area, and filler loading on composite specific heat capacities as a function of temperature is studied to verify its structure-insensitive property characteristic.

Experimental

Materials

The polybenzoxazine used is a bisphenol-A – methylamine type. The monomer was synthesized by the method reported by Ning and Ishida [12]. Figure l shows the monomer and polymer structures of the benzoxazine resin used in this studies. The resin was used as synthesized without further purification. The monomer is solid at room temperature.

Figure 2 exhibits the SEM picture of boron nitride flake-like crystals. The boron nitride filler used in this study includes various grades of hexagonal-type boron nitride supplied by Advanced Ceramics Corporation. There are two major classes of hexagonal boron nitride. The first class consists of flake-like crystals having diameter ranging from 3–10 μm. The other class consists of aggregates of the flake-like

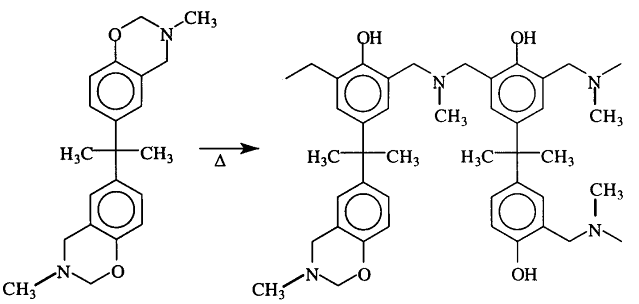

Fig. 1 Chemical formula for monomer and polymer of benzoxazine resin used in this studies

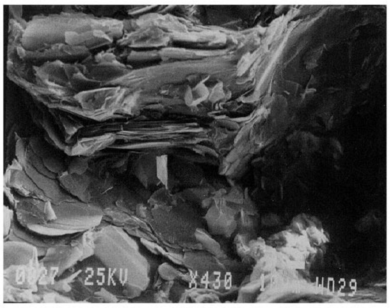

Fig. 2 SEM picture of flake structure of boron nitride crystals

crystals having many ranges of particle size and particle size distribution as classified by different grades of the boron nitride filler.

Sample preparations

The monomer powder was dry mixed well with boron nitride at a desired volume fraction. The mixture was then heated to about 80°C in the mixer and mixed by hand for about ten minutes. The compound in the form of paste was then compression molded into a disk-shaped specimen with 50 mm in diameter and 2 mm in thickness. All specimens were thermally cured at 200°C with pressure of 0.1 MPa for 2 h. The specimens were left to cool to room temperature in the open mold for about 2 h before using. The specimens were cut into smaller size with dimensions of 10×50 mm using a diamond saw. They were polished to reduce their thickness and smooth the contact surface to obtain good thermal contact with the aluminum pan. All specimens were cut again to obtain samples having a size equivalent to 25 mg. All samples were dried in an oven at 50°C for 24 h and kept in a closed container before testing.

Heat capacity measurement

Specific heat capacity of the sample was measured by a temperature-modulated differential scanning calorimeter (TMDSC) model 2920 from TA Instruments. All samples were crimped in non-hermetic aluminum pans with lids. The mass of the reference and sample pans with lids were measured to within 23±0.1 mg. The sample was purged with dry nitrogen gas using a flow rate of 60 ml min^{-1}. Liquid nitrogen was used as a coolant for the experiment at the low temperature range. The instrument was calibrated for heat capacity measurement using sapphire as a reference material. The calibration method and the experiment were performed at the same conditions as follows: 1) isothermal equilibration for 10 min at –10°C, 2) temperature amplitude of ±1°C with period of 80 s, 3) temperature ramp at 5°C min^{-1} to 100 or 200°C. Temperature calibration was performed using the onset of melting temperature of indium (156.6°C). The measurement condition was suitably chosen for this high thermal conductivity composite. As a matter of fact, these materials have thermal conductivity about 2 orders of magnitude greater than that of polymeric materials [11]. All specific heat capacity values were normalized by the filler content analysed by thermal gravimetric analysis (TG) measured on the same sample used for TMDSC.

The thermogravimetric analyzer used is model 2950 from TA Instruments. The experiment was done using the heating rate of 20°C min^{-1} under air. The temperature was ramped from 30 to 900°C in order to burn out all organic portion of the composites.

Results and discussion

Figure 3 shows plots of specific heat capacity of boron nitride-filled polybenzoxazine using seven grades of boron nitride filler at the same filler content at 60% by mass. Each grade of boron nitride has different average particle size, shape, and particle surface area as summarized in Table 1. From the plot, we observed almost no differences among the specific heat capacities of these filled systems at constant filler content. The effect of temperature on specific heat capacity can be indicated by the slope of the plot between specific heat capacity and temperature. The slopes of

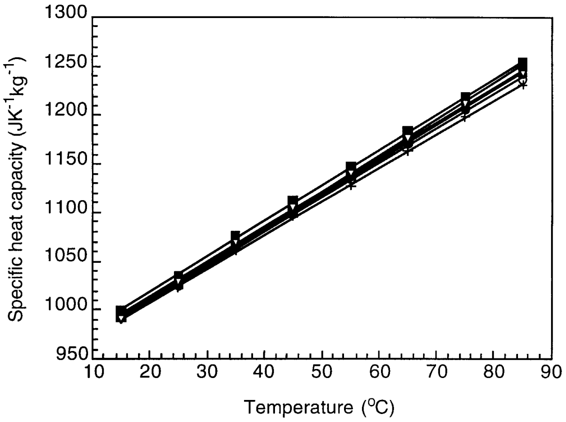

Fig. 3 Specific heat capacity as a function of temperature of different grades of boron nitride o – HCPH, □ – HCPL, △ – AC6063, • – AC6004, + – HCJ325, ■ – TS1890, ▽ – HCJ48

Table 1 Properties of various grades of boron nitride used in the experiment [23]

Grades	Surface area/ $m^2\ g^{-1}$	Mean particle size/ μm	Particle shape	Tap density/ g cm–3
TS1890	0.88	75	aggregate	0.40
HCJ48	0.91	225	aggregate	0.86
HCJ325	2.85	45	aggregate	0.77
AC6004	3.17	10.5	flake	0.52
AC6063	6.34	8.0	flake	NA
HCPL	7.00	9.5	flake	0.50
HCPH	17.0	9.0	flake	0.35

all plots are positive signifying an increase in specific heat capacities as temperature increases. In the vicinity of the glass transition temperature, specific heat capacity at constant pressure can be explained due to the contributions of molecular vibrations and free volume. In the solid state far below a glass transition temperature, the heat capacity of the material is mostly due to molecular vibrations as other contributions are normally negligible [13]. Thus,

$$C_p = C_v^{vib} \tag{1}$$

where C_p is the specific heat capacity at constant pressure, C_v^{vib} is the specific heat capacity at constant volume due to molecular vibrations. As a result, the greater C_p values of the composites at elevated temperature are normally due to the greater degrees of molecular vibrations at higher temperature.

Generally, small particle size filler or high aspect ratio filler will form a more perfect conductive network than large particle size filler or low aspect ratio filler at the same filler content [14–16]. In this case, boron nitride grades AC6004, AC6063, HCPL, and HCPH have flake-shaped structures which possess higher aspect ratios compared with boron nitride grades TS1890, HCJ48, and HCJ325 which are aggregates of the flake crystals. Li *et al*. reported that these flake fillers can form the conductive network more readily than the lower aspect ratio filler [17]. Hence, at a moderate boron nitride loading, such as at 60% by mass (42.8% by volume), it should form a higher degree of network than the lower aspect ratio filler. As a result, the first group of boron nitride should give a higher degree of network than the second group. Furthermore, in the same class of filler of the second group, the particle size of boron nitride grade varies as HCJ325<TS1890< HCJ48. Therefore, at the same moderate filler content beyond the percolation threshold, the smallest particle size, HCJ325, will give the highest degree of conductive network formation among the three grades. As a result, if heat capacity is a path-dependent property, it will show different values of heat capacities at different degrees of network formation as mentioned above. Nonetheless, we observed similar specific heat capacities of all these composites indicating that the formation of different degrees of network due to differences in particle size and shape do not affect the heat capacity of the composites as shown in Fig. 3.

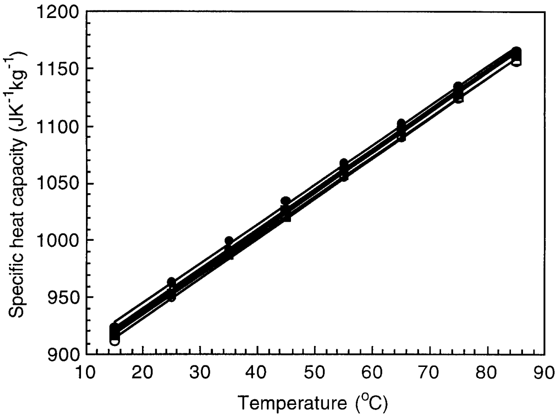

Fig. 4 Effect of particle size on the specific heat capacity of boron nitride-filled polybenzoxazine. HCJ48:TS1890: o – 100:0, □ – 80:20, △ – 60:40, • – 40:60, + – 20:80, ■ – 0:100

The lack of the effect of particle size on the specific heat capacity of the composite is again confirmed in Fig. 4. In this experiment, we mixed two grades of boron nitride which have similar surface area together i.e. HCJ48 with average particle size of 225 μm and TS1890 with average particle size of 75 μm. The composition of the boron nitride in the composites was fixed at 75% by mass. From the figure, as we varied the composition of the large particle grade, we also observed insignificant change in the specific heat capacities of the composites. This confirmed the structure insensitive property behavior of the specific heat capacity of the composite as it is independent on the degree of filler network formation due to the particle size variation. In contrast to the thermal conductivity of this filler-matrix system, we observed a considerable dependence of the composite thermal conductivity on the variation of particle size of the filler [11].

Particle surface area was found to play a significant role in the composite thermal conductivity as it is a major source of phonon scattering which leads to thermal resistance in composite materials [18–20]. The effect of filler surface area on composite heat capacity is shown in Fig. 5. Boron nitride grade HCJ325 with surface area about 2.85 m^2 g^{-1} and grade TS1890 with surface area about 0.88 m^2 g^{-1} were mixed together. The filler content was fixed at 75% by mass. As we varied the composition of the high surface area particle, we observed insignificant change in specific heat capacity of the composites.

Figure 6 shows the effect of filler loading on the specific heat capacities at room temperature of boron nitride-filled polybenzoxazine. Due to the structure-insensitive characteristic of composite specific heat capacity, the effect of filler loading on the composite heat capacity should be predicted by the rule of mixture as expressed in the equation below.

For a two-phase system,

$$C_{pc} = C_{pf}w_f + C_{pp}(1-w_f) \qquad (2)$$

C_{pc}, C_{pf} and C_{pp} are the specific heat capacities of the composite, filler, and polymer respectively, w_f is the mass fraction of the filler.

Figure 6 shows the plot of the composite specific heat capacity as a function of filler loading ranging from 40 to 90% by mass of filler at 25°C. The plot reveals a linear relationship between specific heat capacity and filler loading. By extrapolating the experimental results to 100% by mass filler loading, we obtain the specific heat capacity value of pure boron nitride with the value of 792 J K^{-1} kg^{-1}. The value is close to the published value of 780 J K^{-1} kg^{-1} at the same temperature of 25°C [21].

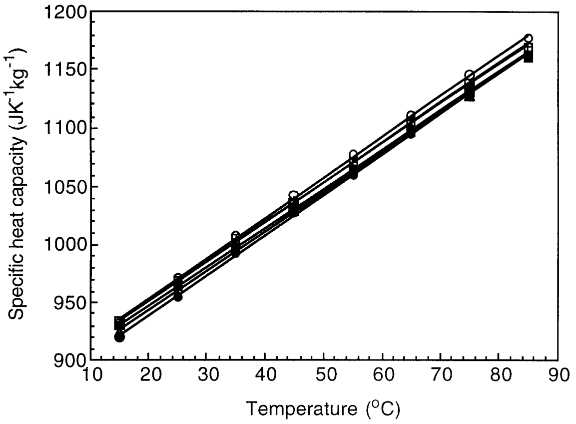

Fig. 5 Effect of particle surface area on the specific heat capacity of boron nitride-filled polybenzoxazine. HCJ32S:TS1890: o – 100:0, ▫ – 80:20, △ – 60:40, • – 40:60, + – 20:80, ▪ – 100:0

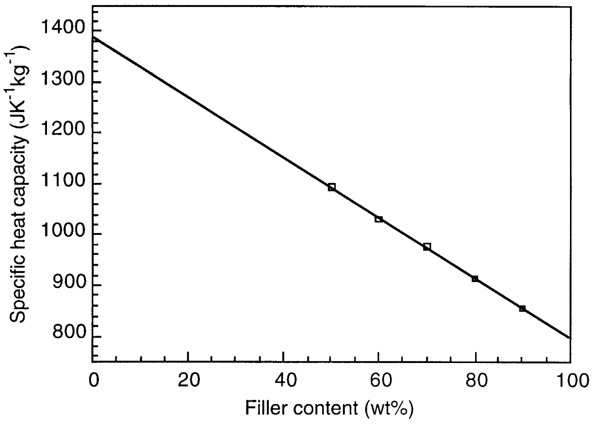

Fig. 6 Effect of boron nitride contents on the specific heat capacity of its filled polybenzoxazine composites

Also, by extrapolating the experimental results to 0% by mass filler to predict the specific heat capacity of the neat polybenzoxazine resin, we obtain a predicted value of 1383 J K^{-1} kg^{-1} which is close to the measured value of 1415 J K^{-1} kg^{-1}. The specific heat capacity values of different filler contents from the experimental results are thus in good agreement with those predicted by the rule of mixture, Eq. (2), with an error within ±1.0 % as shown in Table 2.

Table 2 Heat capacity values of boron nitride-filled polybenzoxazine at different filler contents

Filler content/ wt%	Heat capacity/J K^{-1} kg^{-1}		Error/ %
	Experimental	Calculated	
50	1098	1104	–0.54
60	1037	1041	–0.38
70	987	979	+0.82
80	916	917	–0.11
90	860	854	+0.70

The effect of temperature on composite specific heat capacity at different filler loading is shown in Fig. 7. The effect of temperature on the specific heat capacities of the composites can be identified by the slope of the plots. From the experimental results, we observed fairly low and stable slopes in our composite systems up to about 200°C. This is due to the high thermal stability and T_g of the polybenzoxazine matrix used. However, within this temperature range, we observed the inflection of the slope of the plot at the temprature about 110°C which can be due to the β-transition of this composite material. This transition temperature was first observed by Ishida and Allen using dynamic mechanical analysis [22].

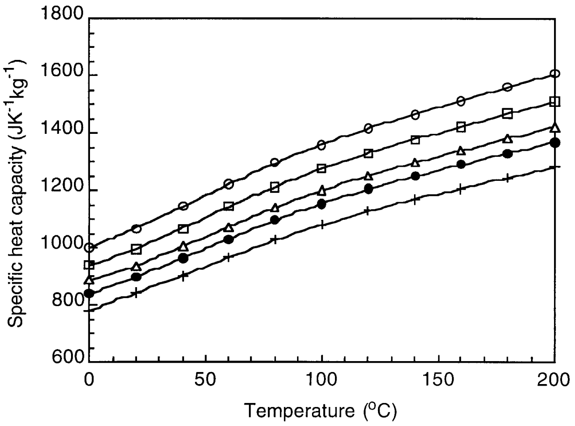

Fig. 7 Specific heat capacity of boron nitride-filled polybenzoxazine as a function of temperature at different filler loading. o – 50 wt%, □ – 60 wt%, △ – 70 wt%, • – 80 wt%, + – 90wt%

In general, the specific heat capacity of the material away from its transition temperature and within moderate temperature range can be predicted by the following linear equation

$$C_p = A + B(\Delta T) \tag{3}$$

where ΔT is the temperature difference from the reference temperature, A and B are numerical constants.

In a composite system, substituting Eq. (3) into Eq. (2) we obtain,

$$C_{pc}(T) = (A_f + B_f\Delta T)w_f + (A_p + B_p\Delta T)(1 - w_f) \tag{4}$$

Rearranging Eq. (4), we obtain

$$C_{pc}(T) = (A_f w_f + A_p(1 - w_f)) + (B_f w_f + B_p(1 - w_f))\,\Delta T \tag{5}$$

$$C_{pc}(T) = \alpha + \beta\Delta T \tag{6}$$

where α is the mass average specific heat capacity of filler and matrix at the reference temperature, β is the mass average slope.

Table 3 Slopes of the plot between heat capacity and temperature at different filler loading

Filler content/ wt%	Slopes×10^3 (J K^{-2} kg^{-1}) at temperature between 0–80°C	
	experimental	calculated
50	3.81	3.75
60	3.64	3.60
70	3.44	3.45
80	3.34	3.30
90	3.09	3.15

Table 3 exhibits the values of the slopes at different filler contents of the plots between heat capacity and temperature in Fig. 7. In the temperature range between 0–80°C, as expected, the slopes, β, decrease with increasing filler contents. The change in slopes was predicted by Eq. (5) which was the mass average of slopes of the plot between the specific heat capacity and temperature of polybenzoxazine resin and boron nitride filler at this temperature range as shown in the same table. Temperature dependence of the specific heat capacity of polybenzoxazine and boron nitride as well as the corresponding slopes at this temperature range were obtained from Fig. 8. The polybenzoxazine shows no transition temperature in the temperature range between 0 and 80°C which is the general range of service temperature of electronic packaging materials. Therefore, the prediction of the temperature dependence of specific heat capacity of this electronic packaging material for the purpose of thermal management simulation can be easily obtained by using Eq. (5).

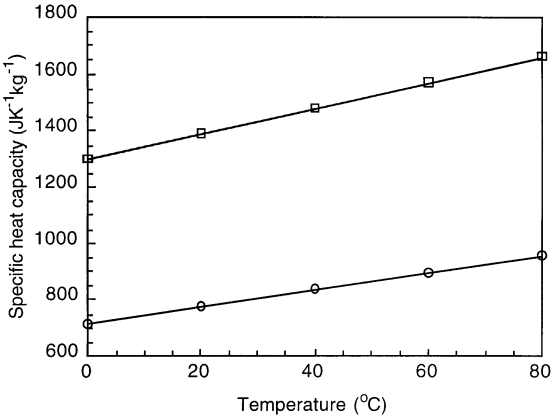

Fig. 8 Specific heat capacity in the temperature range between 0–80°C of neat polybenzoxazine and boron nitride. ○ – boron nitride, □ – polybenzoxazine

In the temperature range between 0 and 80°C and using 0°C as a reference temperature, we obtained an empirical equation to predict the temperature-dependent specific heat capacity of boron nitride-filled polybenzoxazine as:

$$C_p(T) = (1301 - 584w_f) + (4.5 - 1.5w_f)T \qquad (7)$$

where w_f – percent by mass of boron nitride filler, and T – temperature in °C.

Conclusions

Temperature-modulated differential scanning calorimetry was used as a quick and reliable tool for the measurement of an absolute value of heat capacity of boron nitride-filled polybenzoxazine. Heat capacity of this filled system was shown to be a structure-insensitive property of the composite materials, i.e. independent of the degree of formation of filler network in the composite system at the same filler content. The composite specific heat capacity in the temperature range between 0 and 80°C can be predicted well by the empirical equation:

$$C_p(T) = (1301 - 584w_f) + (4.5 - 1.5w_f)\,T$$

References

1 K. H. Hsieh and Y. Z. Wang, Polym. Eng. & Sci., 30 (1990) 476.
2 G. M. Nasr and M. M. Badawy, Polym. Inter., 38 (1995) 249.
3 D. W. Sundstrom and S. Y. Chen, J. Comp. Mat., 4 (1970) 113.
4 D. M. Bigg, Polym. Eng. Sci., 17 (1977) 842.
5 M. Sahimi, 'Applications of Percolation Theory,' Taylor & Francis, London 1994.
6 P. Bujard, G. Kuhnlein, S. Ino and T. Shiobata, IEEE Transac. Compn. Packg. Manu. Tech. Part A, 17 (1994) 527.

7 G. Johansson, M. Joelsson and M. Bastos, Polymer, 33 (1992) 152.
8 G. P. Krielaart, C. M. Brakman and S. Vanderzwaag, J. Mat. Sci., 31 (1996) 1501.
9 P. S. Gill, S. R. Sauerbrunn and M. Reading, J. Thermal Anal., 40 (1993) 931.
10 A. Boller, Y. Jin and B. Wunderlich, J. Thermal Anal., 42 (1994) 307.
11 H. Ishida and S. Rimdusit, Thermochim. Acta, 320 (1998) 177.
12 X. Ning and H. Ishida, J. Polym. Sci. Chem. Ed., 32 (1994) 1121.
13 A. Boller, C. Schick and B. Wunderlich, Thermochim. Acta, 226 (1995) 97.
14 G. R. Ruschau and R. E. Newnham, J. Comp. Mat., 26 (1992) 2727.
15 G. R. Ruschau, S. Yoshikawa and R. E. Newnham, Proceedings IEEE 1992, Piscataway, 1992, p. 481.
16 R. M. German, 'Particle Packing Characterics,' Metal Powders Industries Federation, Princeton 1989.
17 L. Li and D. D. L. Chung, Composites, 22 (1991) 211.
18 S. Pettersson and G. D. Mahan, Phys. Rev. B, 42 (1990) 7386.
19 A. Bellosi, L. Esposito, E. Scafe and L. Fabbi, J. Mat. Sci., 29 (1994) 5014.
20 D. P. H. Hasselman and L. F. Johnson, J. Comp. Mat., 21 (1987) 508.
21 S. J. Schneider, Jr., 'Engineered Materials Handbook, Vol. 4, Ceramics and Glasses,' ASM International, USA (1991).
22 X. Ning and H. Ishida, J. Polym. Sci. Part B: Polym. Phys., 32 (1994) 921.
23 Advanced Ceramic Corporation literatures.