Thermal Properties of Polytetrafluoroethylene/ $Sr_2Ce_2Ti_5O_{16}$ Polymer/Ceramic Composites

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ABSTRACT: Polytetrafluoroethylene (PTFE) composites filled with $Sr_2Ce_2Ti_5O_{16}$ ceramic were prepared by a powder processing technique. The structures and microstructures of the composites were investigated by X-ray diffraction and scanning electron microscopy techniques. Differential scanning calorimetry showed that the ceramic filler had no effect on the melting point of the PTFE. The effect of the $Sr_2Ce_2Ti_5O_{16}$ ceramic content [0–0.6 volume fraction (vf)] on the thermal conductivity, coefficient of thermal expansion (CTE), specific heat capacity, and thermal diffusivity were investigated. As the vf of the $Sr_2Ce_2Ti_5O_{16}$ ceramic increased, the thermal conductivity of the specimen increased, and the CTE decreased. The thermal conductivity and thermal expansion of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites were improved to 1.7 W m^{-1} °C^{-1} and 34 ppm/°C, respectively for 0.6 vf of the ceramics. The experimental thermal conductivity and CTE were compared with different theoretical models. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1716–1721, 2008

Key words: composites; fillers; microstructure; polytetrafluoroethylene (PTFE); thermal properties

INTRODUCTION

The electronics industry is responding to increasing consumer demand in telecommunication devices and computers for cost-effective product miniaturization.[1–5] The requirement for denser and faster microelectronic circuits limits the use of conventional packaging materials.[1–5] The thermal conductivity and coefficient of thermal expansion (CTE) of packaging and substrate materials are critically important as they have to dissipate heat and must prevent mismatch with the CTE of Si.[1–9] Polymers and ceramics have extreme electrical, mechanical, and thermal properties for packaging materials. Hence, polymers filled with low-loss ceramics are suitable for electronic packaging and substrate applications.

Polytetrafluoroethylene (PTFE) has been used as an electronic substrate and in packaging applications because of its excellent dielectric properties ($\varepsilon_\gamma = 2.1$ and $\tan \delta = 10^{-4}$ at 800 MHz) and chemical resistances.[10,11] However, its applications are limited because the polymer has a low thermal conductivity (0.265 W/m °C)[12] and a high CTE (100 ppm/°C).[13] Even though metals have a high thermal conductivity, they cannot be used as fillers because they affect the dielectric properties of the composites adversely. Hence, ceramics with low thermal expansion coefficients, high thermal conductivities, and low dielectric losses are preferred fillers. $Sr_2Ce_2Ti_5O_{16}$ is a high-dielectric- constant, low-loss material[14] with a very low CTE (1.72 ppm/°C) and a moderate thermal conductivity.

The precise prediction of the thermal conductivity and CTE of a composite material is very important for the design of packaging materials and substrates. Several quantitative rules[15–19] and simulation techniques[20–23] have been proposed for the prediction of thermal conductivity and CTE. In this article, we report the thermal properties of PTFE/$Sr_2Ce_2Ti_5O_{16}$ polymer ceramic composites. Also, the experimentally observed thermal conductivity and CTE are compared with that predicted by theoretical models.

EXPERIMENTAL

$Sr_2Ce_2Ti_5O_{16}$ ceramics were prepared by the solid-state ceramic route. High-purity $SrCO_3$ and TiO_2 (99.9 + %, Aldrich Chemical Co., Inc., Milwaukee, WI) and CeO_2 (99.99%, Indian Rare Earth, Ltd., Udyogamandal, India) were used as the starting materials. Stoichiometric amounts of ceramic powders

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were ball-milled in a distilled water medium with yttria-stabilized zirconia balls in a plastic container for 24 h. The slurry was dried and calcined at 1300°C for 5 h. The calcined material was ground into a fine powder. $Sr_2Ce_2Ti_5O_{16}$/PTFE (Hindustan Fluorocarbons, Hyderabad, India) composites were prepared by powder processing technology. To create an active surface for binding with the polymer, the fine powder of $Sr_2Ce_2Ti_5O_{16}$ was mixed with an acrylic acid solution for 1 h and dried.[10] Acrylic acid is a well-known polymerizing agent. The dried powder was again treated with 2 wt % tetrabutyl titanate. The use of titanate-based coupling agents provides excellent mechanical and electrical properties compared to other organic functional coupling agents such as silane. The evaporation of the solvent gave $Sr_2Ce_2Ti_5O_{16}$ powders cladded with coupling agents. The volume fraction (vf) of the ceramics is given by

$$\phi = V_2/(V_1 + V_2) \tag{1}$$

where V_1 and V_2 are the volumes of PTFE matrix and $Sr_2Ce_2Ti_5O_{16}$ ceramic, respectively.

Different vf's (0–0.6) of treated ceramics and PTFE powders were dispersed in ethyl alcohol with an ultrasonic mixer for about 30 min. A dried powder mixture was obtained by the removal of the solvent at 70°C under stirring. The homogeneously mixed PTFE/$Sr_2Ce_2Ti_5O_{16}$ powders were then compacted under a uniaxial pressure of 50 MPa for 1 min. The cylindrical pellets thus obtained were kept at 310°C for 2 h and were then slowly cooled to room temperature.

The composites were characterized by the X-ray diffraction (XRD) technique with Cu Kα radiation (Philips X-ray diffractometer, Eindhoven, The Netherlands). The surface morphology of the composites was studied by scanning electron microscopy (Jeol-JSM 5600 LV, Tokyo). Differential scanning calorimetry (DSC) analysis was done with a PerkinElmer DSC 7 instrument (Waltham, MA). The instrument was computer-controlled, and calculations were done with Pyris software. Samples (5–10 mg) were sealed in aluminum pans and heated from 25 to 400°C at rate of 5°C/min and were cooled to 25°C at the same rate. An improved photopyroelectric (PPE) technique[24,25] was used to determine the thermal conductivity of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. A 70-mW He–Cd laser with a wavelength of 442 nm and an intensity modulated by a mechanical chopper (model SR540, Stanford Research Systems, Sunnyvale, CA) was used as the optical heating source. A PVDF film with a thickness of 28 μm and with Ni–Cr coating on both sides was used as the pyroelectric detector. The out put signal was measured with a lock-in amplifier (model SR 830, Stanford Research Systems, Sunnyvale, CA). The modulation frequency was kept above 60 Hz to ensure that the detector, sample, and backing medium were thermally thick during the measurements. We verified the thermal thickness of the composites by plotting the PPE amplitude and phase with frequency at room temperature. Thermal diffusivity (γ) and thermal effusivity were also measured from the PPE signal phase and amplitude.[26] From the values of γ and thermal effusivity, the thermal conductivity and specific heat capacity of the samples were obtained.

Heat-treated cylindrical samples of dimensions (diameter = 8 mm and height = 10 mm) were used to measure the coefficient of thermal expansion (CTE_z) of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites using thermomechanical analyzer (TMA-60 H, Shimadzu, Kyoto, Japan) in the temperature range of 25–270°C.

RESULTS AND DISCUSSION

Figure 1 gives the XRD patterns of PTFE and its $Sr_2Ce_2Ti_5O_{16}$-filled composites. The pattern of PTFE [Fig. 1(a)] showed a strong crystalline peak superimposed over an amorphous halo, as reported earlier.[27] Figure 1(b,c) shows the XRD patterns of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites with ceramic vf's of 0.3 and

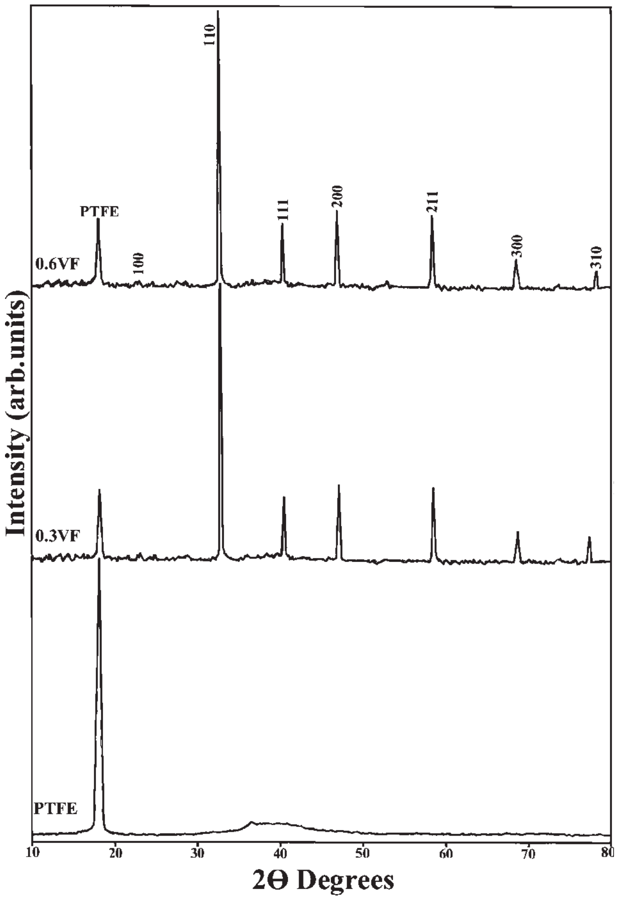

Figure 1 XRD patterns recorded with Cu Kα radiation: PTFE, PTFE/0.3-vf $Sr_2Ce_2Ti_5O_{16}$ and PTFE/0.6-vf $Sr_2Ce_2Ti_5O_{16}$ composites.

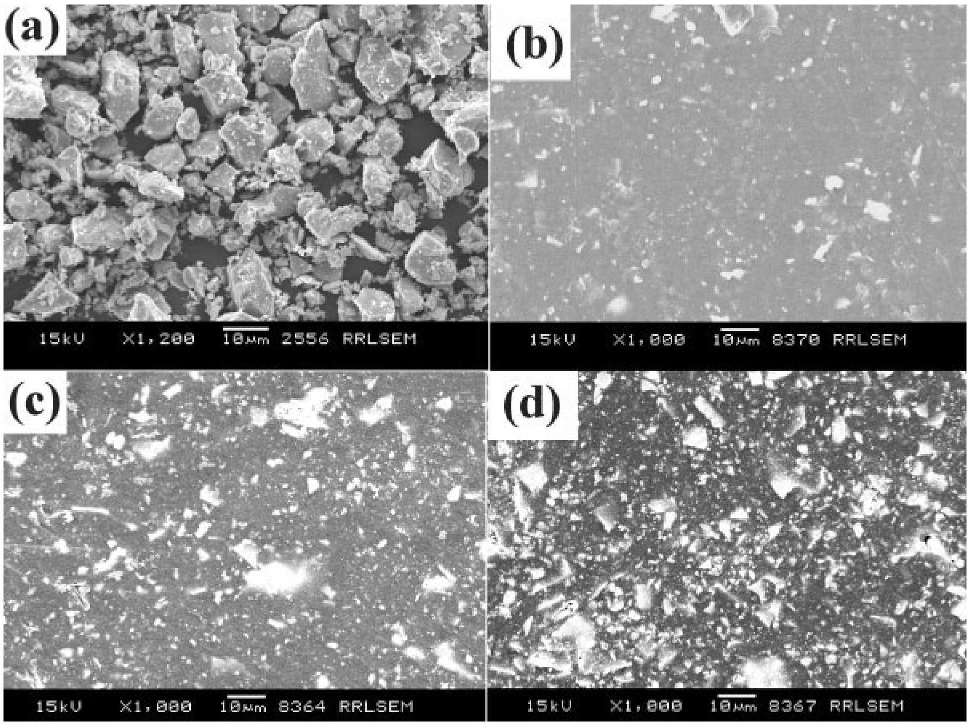

Figure 2 SEM micrographs of the (a) $Sr_2Ce_2Ti_5O_{16}$ powders and (b) PTFE/0.1-vf $Sr_2Ce_2Ti_5O_{16}$, (c) PTFE/0.3-vf $Sr_2Ce_2Ti_5O_{16}$, and (d) PTFE/0.6-vf $Sr_2Ce_2Ti_5O_{16}$ composites.

0.6. The XRD peaks corresponding to $Sr_2Ce_2Ti_5O_{16}$ were indexed based on JCPDS File No. 49-1554.

Figure 2 shows SEM pictures of the $Sr_2Ce_2Ti_5O_{16}$ particles and PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites with different vf's. As shown in Figure 2(a), the average particle size of the $Sr_2Ce_2Ti_5O_{16}$ powders used for the composite preparation was less than 10 μm. Also, the particles were of irregular shape with a nonuniform distribution. The nonuniformity in size, shape, and distribution of the particle was attributed to the grinding of the samples prepared at high temperatures (1300°C). The $Sr_2Ce_2Ti_5O_{16}$ particles were well dispersed in the PTFE matrix; however, at higher mixing ratios, crowding of the ceramic particles was observed [see Fig. 2(d)]. Hence, for higher mixing ratios, the connectivity among the ceramic particles increased, which in turn, increased the conductive properties.

DSC measurements provide qualitative and quantitative information as a function of time and temperature for transitions in materials that involve endothermic or exothermic processes. Figure 3 shows the DSC thermogram of the PTFE/0.3-vf $Sr_2Ce_2Ti_5O_{16}$ composites. The melting point of PTFE was 327°C. As shown in Figure 3, the PTFE/0.3-vf $Sr_2Ce_2Ti_5O_{16}$ composites melted at 327°C. Hence, no change in the melting point of PTFE was observed with the ceramic fillers. A similar result was also observed for PTFE/SiO_2 composites by Chen et al.[13]

Figure 4 shows a comparison of the experimental and theoretical thermal conductivities of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. As the vf of $Sr_2Ce_2Ti_5O_{16}$ increased, the thermal conductivity also gradually increased. A sudden rise in the thermal conductivity was observed at 0.6 vf of the $Sr_2Ce_2Ti_5O_{16}$ composites. This was due to the presence of more connecting path between the filler without the disturbing matrix. A similar observation was reported by Kim

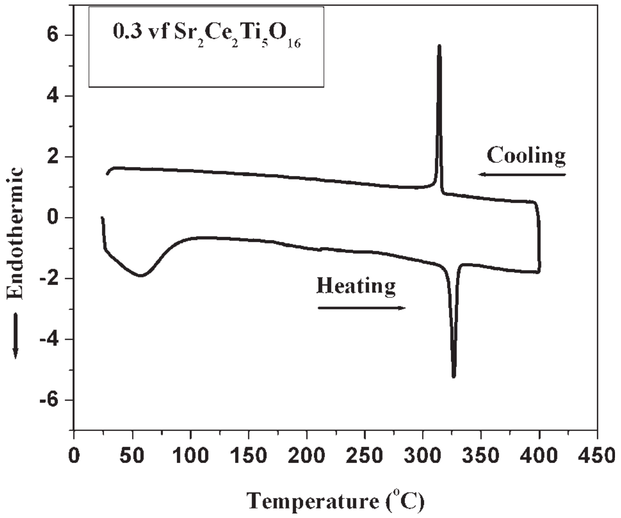

Figure 3 Heating and cooling DSC curves of a 0.3-vf $Sr_2Ce_2Ti_5O_{16}$ reinforced PTFE composite.

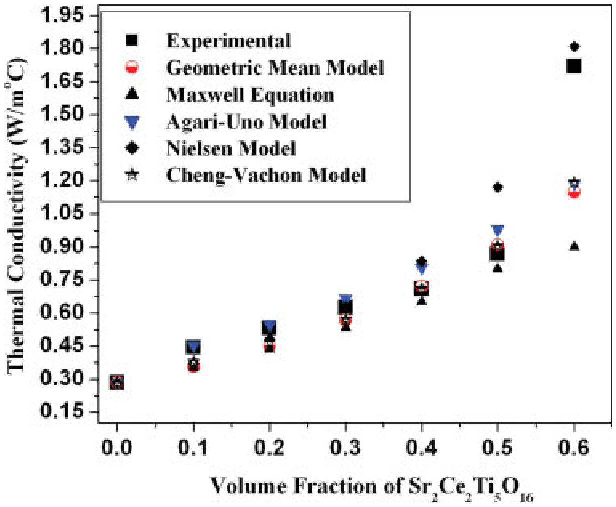

Figure 4 Comparison of the experimental and theoretical thermal conductivities of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

et al.[28] in AlN/epoxy composites for 60 vol % AlN. The thermal conductivity of the PTFE was improved from 0.283 to 1.7 W/m °C (standard deviation = ±0.03 W m^{-1} °C^{-1}) for the PTFE/0.6-vf $Sr_2Ce_2Ti_5O_{16}$ composite.

The effective thermal conductivity of a composite is strongly affected by its composition, structure, intrinsic thermal conductivities, filler particle size, shape, and interfacial thermal resistance. The interfacial thermal resistance has a significant effect on the thermal conductivity of a composite.[29,30] It arises from the combination of poor mechanical or chemical adherence at the interface and a mismatch in CTE.[30] However, no experimental method seems to be available for the direct measurement of interfacial thermal resistance.[29] A single equation for the prediction of thermal conductivity applicable to all systems is not possible. However, to predict the effective thermal conductivity of composites, researchers have developed a number of equations and theoretical models. In this study, the following equations were used to calculate the thermal conductivity theoretically:

Geometric mean model:[15]

$$k_c = k_f^{\phi} k_m^{1-\phi} \tag{2}$$

Maxwell equation:[15]

$$k_c = k_m \left[\frac{k_f + 2k_m + 2\phi(k_f - k_m)}{k_f + 2k_m - \phi(k_f - k_m)} \right] \tag{3}$$

Agari equation:[31]

$$\log k_c = \phi C_2 \log k_f + (1 - \phi) \log C_1 k_m \tag{4}$$

Nielsen equation:[15]

$$k_c = k_m \left[\frac{1 + AB\phi}{1 - B\phi\psi} \right] \tag{5}$$

Cheng–Vachon equation:[15]

$$\frac{1}{k_c} = \frac{1}{\sqrt{C(k_m - k_f)(k_m + D(k_f - k_m))}} \times \ln \frac{\sqrt{k_m + D(k_f - k_m)} + D/2\sqrt{C(k_m - k_f)}}{\sqrt{k_m + D(k_f - k_m)} - D/2\sqrt{C(k_m - k_f)}} + \frac{1 - D}{K_m} \tag{6}$$

$$B = \frac{(k_f/k_m) - 1}{(k_f/k_m) + A}$$

where A(-3) is a function of geometry of the filler particles and ϕ_m is the maximum filler content.

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi$$

$$D = \sqrt{3\phi/2}$$

$$C = -4\sqrt{2/3\phi}$$

where k_c, k_m, and k_f are the thermal conductivities of the composite, matrix, and filler, respectively, and ϕ is the volume fraction of the filler.

The geometrical mean model and Maxwell equation predicted a thermal conductivity less than that of the experimental values. Agari and Uno[31] developed a logarithmic relation involving two constants, C_1 and C_2, for the prediction of thermal conductivity. C_1 is the measure of the effect of particles on the secondary structure of the polymer, and C_2 measures the ease of particles to form conductive chains. The values of the constants C_1 and C_2 were found from data fitting. Table I shows values of the constants C_1 and C_2 in the Agari equation for some of the ceramic polymer composites reported in the literature and

TABLE I
Values of the C_1 and C_2 Constants in the Agari Equation for Some of the Ceramic Polymer Composites Reported in the Literature and in This Article

Composite	C_1	C_2	Reference
CuO/epoxy	0.930	1.447	18
Polystyrene/SiO_2	1	1.11	31
Polyethylene/SiO_2	1	1.11	31
Polyethylene/Al_2O_3	1.03	1.53	31
Polystyrene/AlN	1.078	1.026	30
PTFE/$Sr_2Ce_2Ti_5O_{16}$	1.3173	0.9613	This article

also in this article. The values of the constants C_1 and C_2 should be in the range of unity.[18,32,33] In the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites, C_1 and C_2 had nearly the same values as reported in earlier investigations. The previous equation predicted the effective thermal conductivity accurately below 0.4 vf of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. However, for higher vf's of the ceramics, the equation was not accurate. In the Nielsen equation, the A factor is a function of the geometry of the filling particles, and ϕ_m is the maximum filler content possible while the continuous matrix phase is maintained. The values of A (3) and ϕ_m (0.64) were chosen for irregularly shaped particles.[18] The shape of the particles was confirmed by SEM pictures (see Fig. 2). The equation by Nielsen was very accurate in predicting the thermal conductivity for the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites except for 0.5 vf. The Cheng–Vachon model predicted the effective thermal conductivity with the assumption of a parabolic distribution for the filler materials. This model failed to predict the effective thermal conductivity accurately. Among the five models that we tried, good fitting was obtained for the Nielsen model, which included the shape parameters of the fillers.

Figure 5 shows the variations in the specific heat capacity and thermal diffusivity of PTFE/$Sr_2Ce_2Ti_5O_{16}$. γ of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites depended on the vf of the ceramic in the composites. It increased with increasing filler content. A similar observation was also made by Aravind et al.[34] in lead titanate/polyvinylidene fluoride. The specific heat capacity of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites decreased with increasing ceramic content. This was due to the low specific heat capacity of the ceramic filler (1.67×10^{-2} J kg^{-1} °C^{-1}).

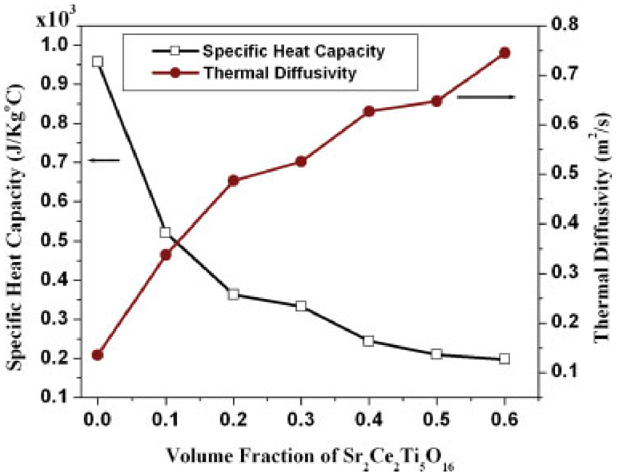

Figure 5 Variation in the specific heat capacity and γ of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

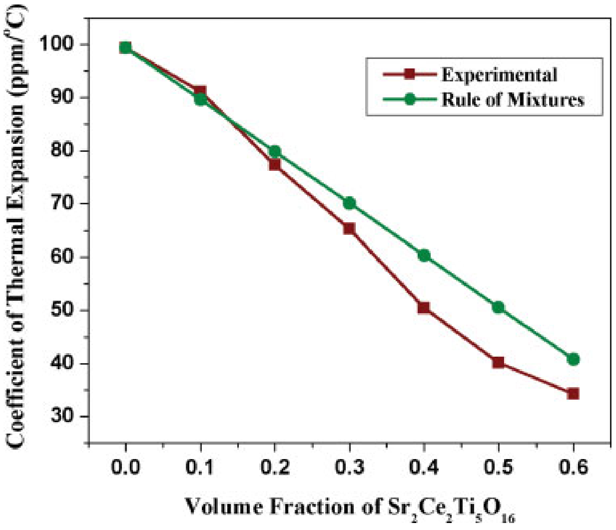

Figure 6 Comparison of the experimental and theoretical CTEs of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The variation in CTE of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites is shown in Figure 6. $Sr_2Ce_2Ti_5O_{16}$ had a CTE of 1.72 ppm/°C (standard deviation = 0.1 ppm/°C) in the temperature range 25–270°C. If a composite is heated, the polymer matrix will expand more than the ceramic fillers. However, if the interphases are capable of transmitting stresses, the expansion of the matrix will be reduced.[35] The CTE showed a gradual decrease with increasing filler content. A dramatic improvement in the CTE of PTFE was observed (34 ppm/°C from 99.3 ppm/°C) for a 0.6-vf loading of the filler ceramic. The most common equation for the prediction of the CTE of composites is the rule of mixtures:

$$\alpha_c = \phi\alpha_f + (1 - \phi)\alpha_m \tag{7}$$

where α_c, α_m, and α_f are the coefficients of thermal expansion of the composite, matrix, and filler, respectively, and ϕ is the volume fraction of the filler. The rule of mixtures can be used for the prediction of the CTE of composites. The calculated values were slightly higher than the experimental ones. This may be due to differences in the microstructure, bulk modulus, and thermal softening of the components in the composites, which were not accounted for in this relation.

CONCLUSIONS

PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites were prepared by a powder processing method. The structures and microstructures of the compounds were investigated with XRD and SEM techniques. The DSC analysis showed that the addition of ceramic fillers did not alter the melting point of the PTFE matrix. The thermal conductivities and thermal expansion of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites were improved to 1.7 W m^{-1} $^{\circ}C^{-1}$ and 34 ppm/°C, respectively. The thermal conductivity predicted by the Nielsen model fit accurately with the experimental data. The specific heat capacity of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites decreased with ceramic content. However, thermal diffusivity of the composites increased with the addition of $Sr_2Ce_2Ti_5O_{16}$. PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites with improved thermal and dielectric properties can be considered for practical applications.

References

1. Pecht, M. G.; Agarwal, R.; McCluskey, P.; Dishongh, T.; Javadpour, S.; Mahajan, R. Electronic Packaging Materials and Their Properties; CRC: London, 1999; Chapter 1.
2. Chung, D. D. L. Materials for Electronic Packaging; Butterworth-Heinemann: Washington, DC, 1995; Chapter 1.
3. Tummala, R. R. J Am Ceram Soc 1991, 74, 895.
4. Bolt, J. D.; Button, D. D.; Yost, B. A. Mater Sci Eng A 1989, 109, 207.
5. Chung, D. D. L. Appl Therm Eng 2001, 21, 1593.
6. Wong, C. P.; Raja, S. B. J Appl Polym Sci 1999, 74, 3396.
7. Hill, R. F.; Supancic, P. H. J Am Ceram Soc 2002, 85, 851.
8. Yoshido, K.; Morigami, H. Microelectron Reliability 2004, 44, 303.
9. Ohashi, M.; Kawakami, S.; Yokogawa, Y. J Am Ceram Soc 2005, 88, 2615.
10. Xiang, F.; Wang, H.; Yao, X. J Eur Ceram Soc 2006, 26, 1999.
11. Bur, J. A. Polymer 1985, 26, 963.
12. Price, D. M.; Jarralt, M. Thermochim Acta 2002, 392, 231.
13. Chen, C. Y.; Lin, C, H.; Lee, D. Y. J Polym Res 2003, 10, 247.
14. Subodh, G.; Pavithran, C.; Mohan, P.; Sebastian, M. T. J Eur Ceram Soc 2007, 27, 3039.
15. Progelnof, R. C.; Throne, J. L.; Ruetsch, R. R. Polym Eng Sci 1976, 16, 615.
16. Agari, Y.; Ueda, A.; Nagai, S. J Appl Polym Sci 1993, 49, 1625.
17. Erukhimovich, I. L.; Rivkin, M. S. AIChE J 1991, 37, 1739.
18. Lin, F.; Bhatia, G. S.; Ford, J. D. J Appl Polym Sci 1993, 49, 1901.
19. Ragahva, R. S. Polym Compos 1988, 9, 1.
20. Feng, J.; Carson, J. K.; North, M. F.; Cleland, D. J. Int J Heat Mass Transfer 2006, 49, 3075.
21. Lim, T. C. Mater Lett 2002, 54, 152.
22. Kumlutas, D.; Tavman, I. H.; Coban, M. T. Compos Sci Technol 2003, 63, 113.
23. Vo, H. V.; Todd, M.; Shi, F. G.; Shaprio, A. A.; Edwards, M. Microelectron J 2001, 31, 331.
24. Menon, C. P.; Philip, J. Meas Sci Technol 2000, 11, 1744.
25. Marinelli, M.; Murtas, F.; Mecozzi, M. G.; Martellucci, S. Appl Phys A 1990, 51, 387.
26. Sebastian, M. T.; Menon, C. P.; Philip, J.; Schwartz, R. W. J Appl Phys 2003, 94, 3206.
27. Rae, P. J.; Datebaum, B. M. Polymer 2004, 45, 7615.
28. Kim, W.; Bae, J. W.; Choi, D.; Yong, S. K. Polym Eng Sci 1999, 39, 756.
29. Nan, C. W.; Li, X. P.; Birringer, R. J Am Ceram Soc 2000, 83, 848.
30. Hasselman, D. P. H.; Johnson, L. F. J Compos Mater 1987, 21, 508.
31. Agari, Y.; Uno, T. J Appl Polym Sci 1986, 32, 5705.
32. Yu, S.; Hing, P.; Hu, X. Compos A 2002, 33, 289.
33. Agari, Y.; Ueda, A.; Tanaka, M.; Nagai, S. J Appl Polym Sci 1990, 40, 929.
34. Aravind, M.; Ong, C. W.; Chan, H. L. W. Polym Compos 2002, 23, 925.
35. Holliday, L.; Robinson, L. J Mater Sci 1973, 8, 301.