Preparation and the Properties of PMR-Type Polyimide Composites with Aluminum Nitride

Jiajun Wang,[1,3] **Xiao-Su Yi** [2,3]

[1]*College of Materials and Textiles, Zhejiang Institute of Science and Technology, CN 310033 Hangzhou, China*
[2]*National Key Laboratory of Advanced Composites (LAC/BIAM), CN 100095 Beijing, P. O. Box 81-3, China*
[3]*Institute of Polymers & Processing, Zhejiang University, CN 310027 Hangzhou, China*

Received 15 July 2002; accepted 6 January 2003

ABSTRACT: A new polyimide composite was developed relying on the concept of *in situ* polymerization of monomer reactants polyimide. High thermal conductive, low dielectric constant and dielectric loss, and thermal-stable composites were successfully demonstrated by incorporating aluminum nitride powder into the polyimide. The weight percent of aluminum nitride was up to 80%. The thermal and dielectric properties follow the classic composite theories. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3913–3917, 2003

Key words: polymerization of monomer reactant type polyimide; aluminum nitride; thermal conductivity; dielectric properties

INTRODUCTION

Polyimides (PIs) have widely been used as a standard electronic material for making circuit boards.[1,2] However, they exhibit intrinsic low thermal conductivities and fairly high thermal expansion coefficients, which can cause problems in heat dissipation and thermal fatigue failure in the electronic systems.[3] Aluminum nitride (AlN) is a nonoxidative ceramic with many attractive properties, including high thermal conductivity, low thermal expansion, and excellent dielectric properties.[4–7] Therefore, AlN/polyimide composites are expected to compensate to each other.[3,8,9]

Polyimide films and coatings are typically prepared in a two-step process. For the powder-filled composites, however, it is difficult to completely remove the residual solvent and by-products, which often results in high void content and defects. The *in situ* polymerization of monomer reactants (PMR) concept utilizes the polymerization directly on the reinforcements during the composite consolidation.[10–14] In a typical PMR approach,[15] reinforcements are impregnated with a methanol solution containing an aromatic diamine, an aromatic diester diacid, and a monoalkyl ester of 5-norbornene-2,3-dicarbonylic acid which is used as an endcapper. The monomers undergo cyclodehydration to form a norbornene-endcapped, low molecular weight imide prepolymer in the temperature range of 100–250°C. Volatile by-products produced at this stage are easy to be removed. Additional polymerization of the norbonene endcaps occurs at high temperatures without volatile reaction by-products. Composites with void contents less than 1% can be prepared.

This article reports the preparation of PMR-type polyimide composites with AlN powder as filler. The resulting thermal and dielectric properties were also studied.

EXPERIMENTAL

Preparation

The monomers of PMR-type polyimide used in this study were provided by the Institute of Chemistry, Chinese Academy of Science. They were 4,4′-methylene dianiline (MDA), diethyl ester of 3,3′,4,4′-benzophenone tetracarboxylic acid (BTDE), and monoethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), as shown in Figure 1.

The mixture of the three monomers was first treated under vacuum in sequence at 120–140°C for 120 min, 200–210°C for 60 min, and 220–250°C for 60 min to form imide prepolymer, following the chemical reactions shown in Figure 2.

Secondly, AlN powders were mixed with the imide prepolymer by mechanical milling. The AlN power used in this study was provided by The 43rd Institute, Ministry of Information Industry (Hefei, China). The average particle size of the AlN powder is 2.0 μm. The thermal conductivity and the thermal expansion of the AlN powder are 200 W/(m K) and 4×10^{-6}/°C, respectively.

Finally, composite discs were molded by hot compression at 180 MPa and 320°C for 60 min, resulting in AlN/PI composite specimens. Additional polymerization of the norbonene endcaps in molding is shown in Figure 3.

Correspondence to: X.-S. Yi (xiaosu.yi@biam.ac.cn).

Journal of Applied Polymer Science, Vol. 89, 3913–3917 (2003)

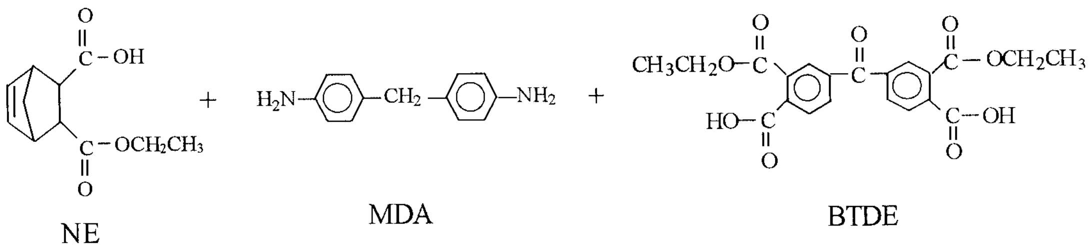


Figure 1 The monomers of PMR-type PI.

Measurements

The thermal conductivity was measured by C-MATIC, Thermal Conductance Test, model TCHM-LT, according to the steady heat flow meter method. Specimens for the measurement were in the form of a disk with diameter of 50 mm and a thickness of about 3 mm.

The dielectric properties were measured by a PL-DETA Dielectric Thermal Analyzer, which can measure the dielectric constant and the dielectric loss with increasing temperature in different frequencies. Specimens for the dielectric property measurement were also a disk with diameter of 30 mm and a thickness of about 1 mm.

RESULTS AND DISCUSSION

It was experimentally found that the PMR impregnation route was not perfect for preparing polyimide composite with high solid filler concentrations. The high AlN powder concentration often interferes with the chemical reaction of monomers and the release of solvent and volatile by-products. Therefore, carefully preparation and experimental skill were crucial.

Figure 4 shows the SEM micrographs of AlN/PI composites prepared by the PMR route, with respect to different AlN weight percents. As shown in the micrographs, all the specimens look void free and fully dense. The AlN powders are well dispersed in the polyimide matrix. The weight percent was as high as 80 wt % AlN. This indicates that the experimental preparation was successful.

The thermal conductivity of AlN/PI composites increases dramatically with the AlN volume fraction, shown in Figure 5. The highest conductivity of about 4.38 W/(m K) in the range of the experiment was obtained, which is more then ten magnitudes higher than that of the original polymer, suggesting that AlN is an effective component for increasing the composite thermal conductivity.

Many theoretical and empirical models have been developed to describe the mixing role of two-phase composite systems.[16–22] However, an accurate calcu-

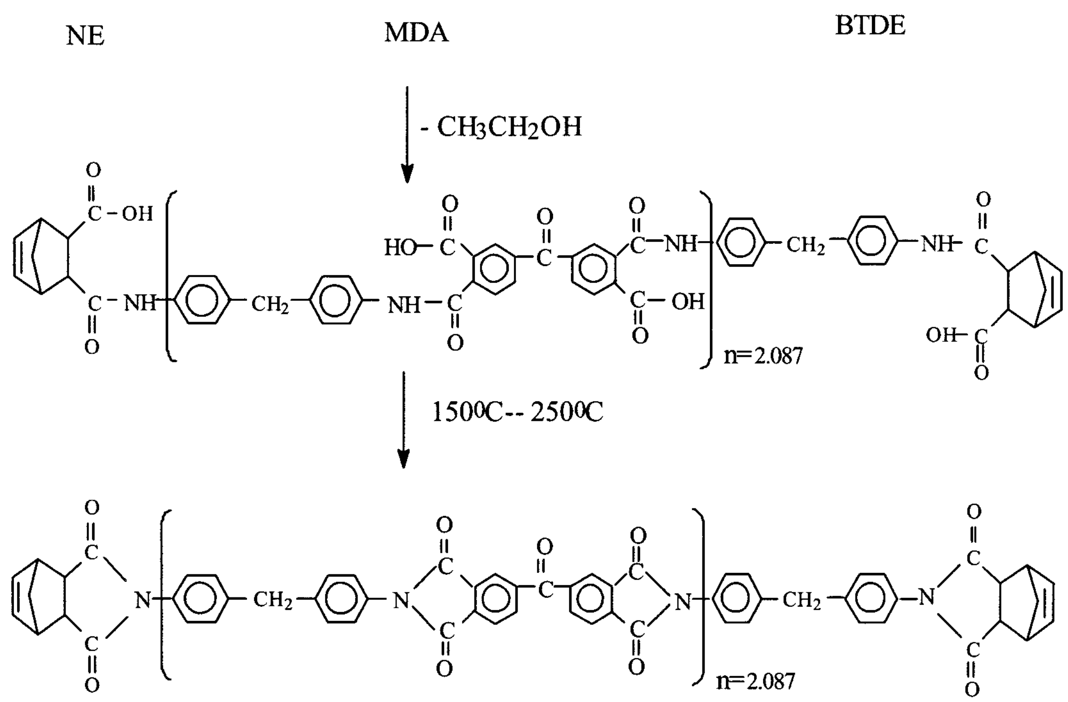


Figure 2 The sequence of chemical reactions of the PMR-type prepolymer.

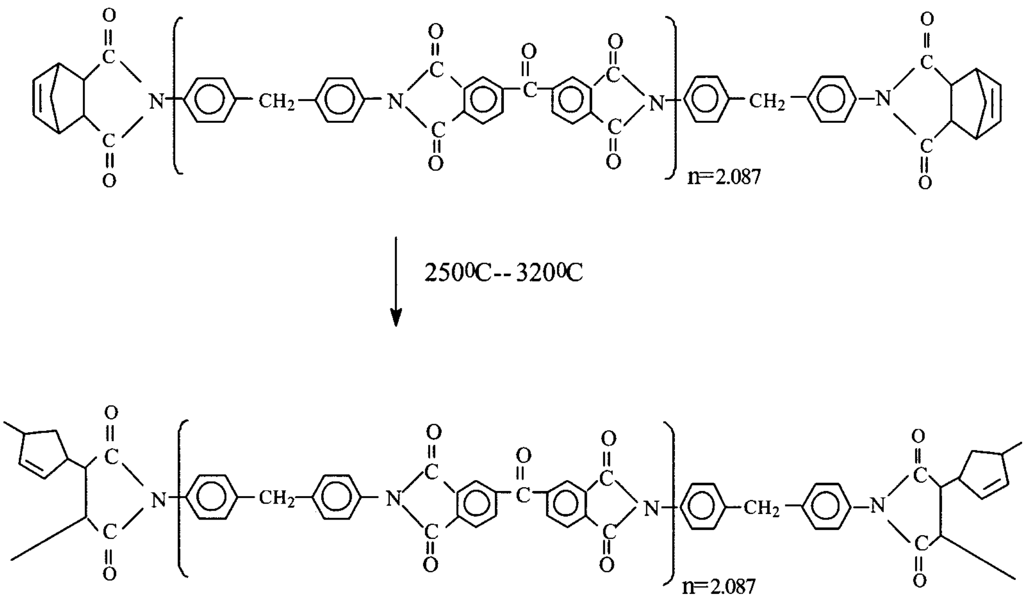


Figure 3 Additional polymerization of the norbonene endcaps.

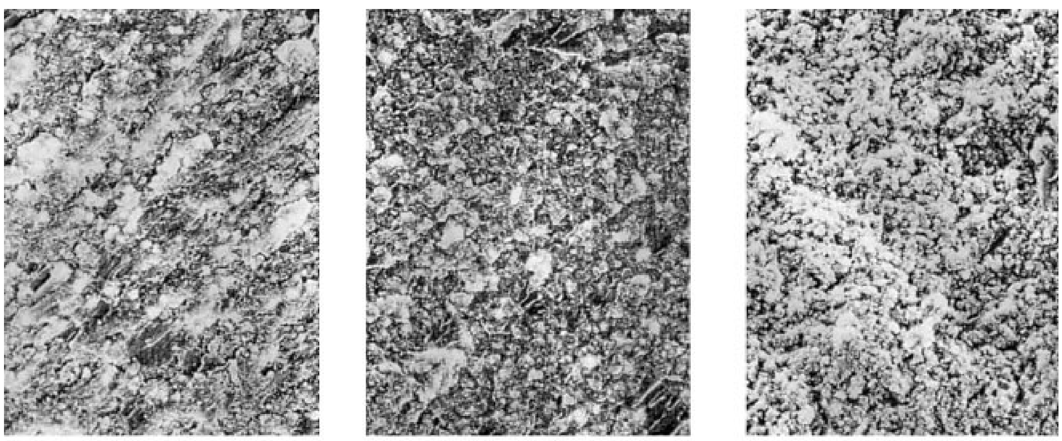
lation of the thermal conductivity of composites with high concentrations seems at the moment impossible, because it needs extensive information such as the position of the particles and the relationship between the particles. The most common for predicting the thermal conductivity are Maxwell's equation and Bruggeman's equation:

$$\lambda_c = \lambda_1 \frac{\lambda_2 + 2\lambda_1 - 2V_2\,(\lambda_1 - \lambda_2)}{\lambda_2 + 2\lambda_1 + V_2\,(\lambda_1 - \lambda_2)} \tag{1}$$

$$1 - V_2 = \frac{\lambda_2 - \lambda_c}{\lambda_2 - \lambda_1}\left(\frac{\lambda_1}{\lambda_c}\right)^{1/3} \tag{2}$$

where λ_c, λ_1, and λ_2 stand for the effective thermal conductivity of the composites, matrix and filler particles, respectively. V_2 is the volume fraction of filler.

Maxwell's equation is an exact solution for the effective conductivity of randomly distributed and non-interacting spheres in a continuous medium. However, it does not take into account the mutual interaction of the particles[20,21]; thus it is not a satisfactory treatment for our composites in high volume fraction range. Figure 5 shows that the experimental data hold well with Maxwell's equation only if the AlN volume fraction is less than 20%.



A 20 wt % AlN **B** 50 wt % AlN **C** 80 wt % AlN

Figure 4 SEM micrographs of AlN/PI composite materials (×1k)

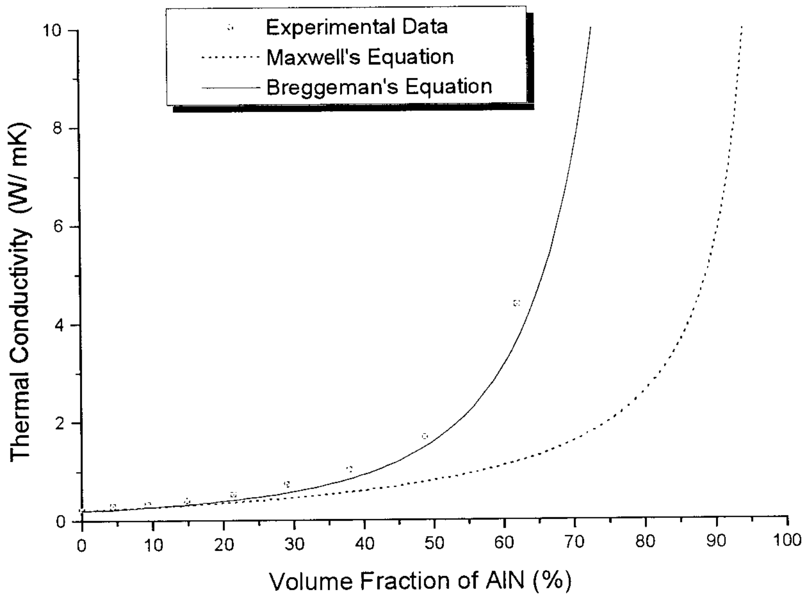


Figure 5 Theoretical curves and experimental data of AlN/PI composites in comparison.

Bruggeman's equation is derived by consideration of neighboring particles as the incremental dispersed particles and existing composite as the surrounding medium at each stage, and then integration of thermal conductivity.[20,22] It can be also found in Figure 5 that Bruggeman's equation fits better with the experimental data in all ranges of the AlN volume fraction, compared with Maxwell's equation.

The dielectric properties of AlN/PI composites were also varied with AlN volume fraction (Fig. 6). They were measured in room temperature with 50 Hz, 1 kHz, and 0.1 MHz, respectively. The dielectric constant varies from 2 to 4 for the AlN volume fraction from 0 to 62%, and it is obviously lower than that of AlN itself of about 8.

A theoretical model to describe the dielectric constant of composites is reported[23] as

$$\varepsilon = \varepsilon_1\left[1 + \frac{3V_f\,(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + 2\varepsilon_1 - V_f(\varepsilon_2 - \varepsilon_1)}\right] \tag{3}$$

where ε stands for the dielectric constant of composites, ε_1 and ε_2 for matrix and dispersed particles, respectively. V_f is again the volume fraction of the particles. The theoretical curve according to eq. (3) is compared in Figure 6 with the experimental data. There is a good agreement. The dielectric loss of the composites is shown in Figure 6(B). They are all below 0.003, with a big data scatter.

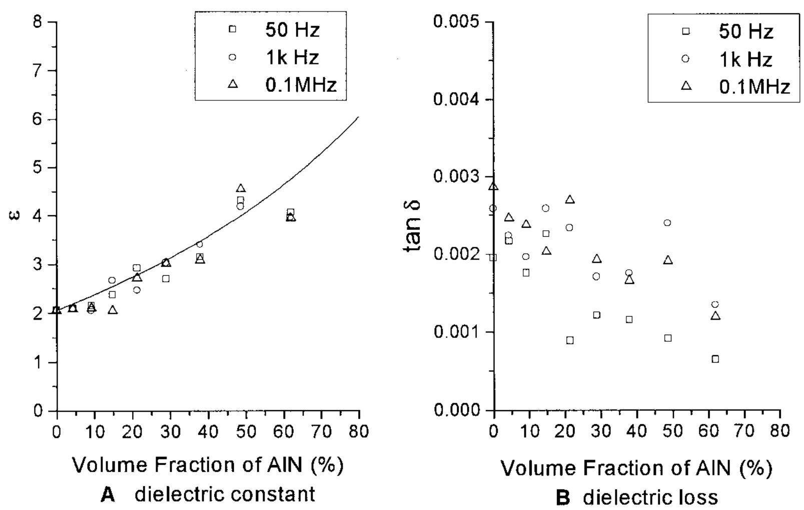


Figure 6 The dielectric properties of AlN/PI composites as function of AlN volume fraction.

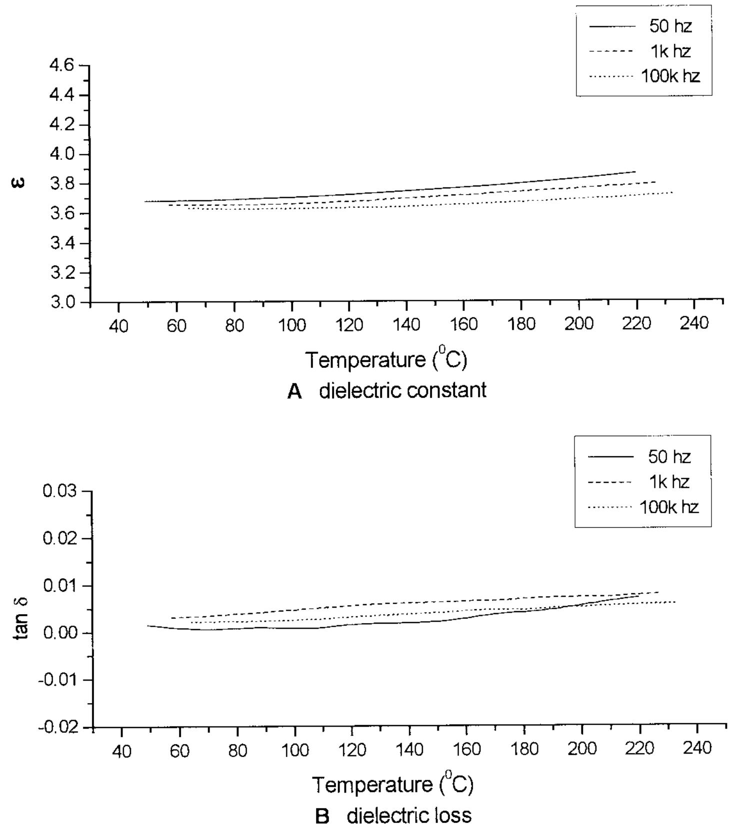


Figure 7 Plot of the dielectric properties of AlN/PI composites against temperature.

PI is a high-temperature resistant polymer. The temperature-dependent dielectric properties of our AlN/PI composites are shown in Figure 7. The volume fraction of AlN was constant of 62% for all the specimens. Both the dielectric constant and dielectric loss are generally stable with temperatures up to 220°C. The thermal stability is an important factor for electronic systems.

CONCLUSION

1. PMR-type PI composite specimens were successfully prepared with a wide range of AlN concentrations, up to 80 wt %. The composite specimens made were fully dense.
2. High thermal conductive PI/AlN composites were obtained. The thermal conductivity of the composites obeys the Bruggeman's equation more obviously than the Maxwell's equation in all ranges of AlN volume fraction studied.
3. The dielectric constant of PI/AlN composites varies from 2 to 4 for AlN volumes fraction from 0 to 62%. The dielectric loss is lower than 0.003. Both of them were found stable with temperature.

References

1. Sroog, C. E. Prog Polym Sci 1991, 16, 561.
2. Mittal, K. L. Polyimides Synthesis, Characterization and Application; Plenum Press: New York, 1984.
3. Li, L.; et al. J Electronic Mater 1994, 23(6), 557.
4. Mroz, T. J. Ceramic Bull 1992, 71(5), 782.
5. Sheppard, L. M. Ceramic Bull 1990, 69(11), 1801.
6. Mroz, T. J. Am Ceram Soc Bull 1996, 75(6).
7. Hirano, M.; et al. J Mater Sci 1993, 28, 5737.
8. Chen, X.; et al. Adv Mater 1994, 6(6), 481.
9. Chen, X.; et al. J Mater Res 1997, 12(5), 1274.
10. Delvigs, P.; et al. J Polym Sci B 1970, 8, 29.
11. Serafini, T. T.; et al. J Appl Polym Sci 1972, 16, 905.
12. Dynes, P. J.; et al. J Appl Polym Sci 1980, 25, 1059.
13. Gareia, D.; et al. J Polym Sci B 1987, 25, 2275.
14. Wilson, D. Br Polym J 1988, 20, 405.
15. Kantz, M. Plastics Eng 1990, (1), 27.
16. Kingery, W. D. J. Am Ceram Soc 1959, 42, 617.
17. Godbee, H. W.; et al. J Appl Phys 1966, 37, 56.
18. Qi, T. G. Thermal Properties of Inorganic Materials (in Chinese); Shanghai Science and Technology Press: Shanghai, 1981.
19. Lichtenecker, K. Physik Z 1926, 27, 115.
20. Sundstrom, D. W.; et al. J Appl Polym Sci 1972, 16, 3159.
21. Garret, K. W.; et al. J Phys D: Appl Phys 1974, 7, 1247.
22. Bruggemman, D. A. G. Ann Phys 1935, 24, 636.
23. Tonkin, B. A.; et al. J Mater Sci Lett 1996, 15, 2030.