

Dynamic Mechanical Properties of Polystyrene–Aluminum Nitride Composite

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ABSTRACT: A composite of aluminum nitride (AlN) particles dispersed around polystyrene matrix particles was synthesized in this study. The purpose of using this microstructure is to improve the thermal properties of a polymer at a low filler content with a minimal increase in the dielectric constant of the polymer composite to meet the material requirements for electronic packaging. The dynamic mechanical properties of this type of polystyrene–AlN composite were investigated here. The experimental results indicate that the dynamic mechanical property of the polystyrene–AlN composite is a function of the polystyrene particle size, AlN filler concentration, and temperature under this dispersion state. The addition of an AlN concentration into polystyrene increases both the storage modulus and the α -transition temperature. The smaller polystyrene particle size gives a higher storage modulus and damping peak. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1348–1353, 2000

Key words: aluminum nitride; polymer composite; dynamic mechanical thermal analysis; electronic packaging

INTRODUCTION

For polymer composites to be used in electronic packaging, the materials must have high thermal conductivity for dissipating the heat generated in the devices, matched coefficients of thermal expansion to that of silicon chips to reduce thermal failure, and a low dielectric constant to increase the operating speed of circuits.¹ Ceramic powder-reinforced polymer materials have been extensively used as a packaging substrate.^{2,3} The purpose of adding ceramic powder is to improve the thermal properties of polymers, which usually have low thermal conductivity and an extremely high coefficient of thermal expansion. Polystyrene composites filled with aluminum nitride (AlN) were prepared in this study. A special dispersion state of the filler is achieved in these composites

by surrounding the polystyrene particles with AlN powder. There are some advantages of this microstructure: (1) a thermal conductivity chain can be formed in the composite; (2) the thermal expansion of polymer particles can be restrained effectively by the surrounding filler particles; and (3) because it is possible to improve the thermal properties of a polymer at low filler content, so the adverse effect of a filler on the dielectric properties of a polymer could be minimized. A detailed discussion of the thermal properties of a polystyrene–AlN composite were published elsewhere.⁴

Besides the thermal and electric properties, the mechanical properties of materials are always very important. Perhaps the most characteristic feature of the mechanical response of polymeric materials is the frequency and temperature dependence. This is due to the viscoelastic essentials of polymer materials. Actually, the viscoelastic response is the direct reflection of the polymer structure, so it is usually used to study the structure of a polymer and the interaction between

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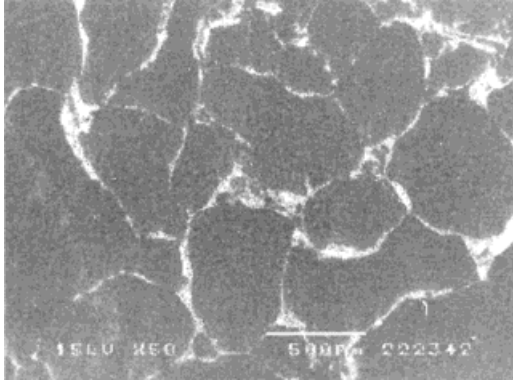


Figure 1 SEM of composite (AlN vol % = 6; polystyrene particle size, 0.15 μm).

constituents of polymer composites. For a common dispersion composite, filler mixes into a melted polymer matrix, there already have been many publications in this field.⁵⁻⁸ However, there are few discussions on other types of dispersions.

The purpose of this article was to study the dynamic mechanical properties of polystyrene-AlN composites under the special dispersion state used here. The relaxation properties of polystyrene composites are presented as a function of the AlN filler concentration and polystyrene matrix particle size. The important glass transition temperature of the polystyrene phase in the composite will also be discussed in detail.

EXPERIMENTAL

Materials

AlN with a diameter less than 10 μm supplied by the Aldrich Chemical Co. (U.S.) was used as a filler. Commercial polystyrene manufactured at Dow Chemical Pacific Ltd. (Hong Kong) was used as a material for the matrix. The glass transition temperature of polystyrene was determined by a differential scanning calorimeter (DSC) and was found to be about 100.9°C (DSC 2010, heating rate 5°C/min). To investigate the effect of the particle size of polystyrene on the dielectric properties of the composites, polystyrene particles with different sizes were prepared by grinding coarse polystyrene and adjusting the average particle size of the particulate by classification.

Preparation of Testing Specimens

Polystyrene and AlN were mixed at room temperature until the AlN powder surrounded the poly-

styrene particles; then, the mixture was put into a circular cylinder made of stainless steel and was hot-pressed at 180°C.

Measurement of Dynamic Mechanical Properties of Composites

Dynamic mechanical analysis (DMA) is useful for the evaluation of viscoelastic properties of a polymer. When an oscillating sinusoidal load is applied to a specimen at a particular frequency, the strain will lag somewhat behind the stress because of the viscoelastic nature. The data of the storage modulus, loss modulus, and loss tangent are obtained through DMA.

A DMA 2980 was used in this research. The mode chosen here was single cantilever; the sample size was about 25 \times 5 \times 1 mm. Testing samples were cut from the compacted materials using a diamond saw. Measurement was performed from 25 to about 200°C; the heating rate was 3°C/min. The testing frequency was set at 1 Hz. DMA standard data analysis software was used to evaluate viscoelastic properties of the composites. Samples were dried at least 2 days in a desiccator before measurements were carried out.

RESULTS AND DISCUSSION

Microstructure of the Composites

The dispersion state of the filler in the composites used in this study is one in which filler particles surround matrix particles. The overall morphology of the composite can be obtained by SEM.

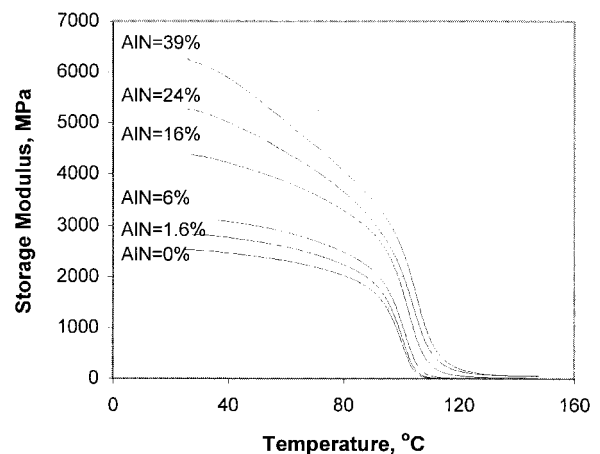


Figure 2 Storage modulus of the composite as a function of AlN content (polystyrene particle size, 0.15 μm).

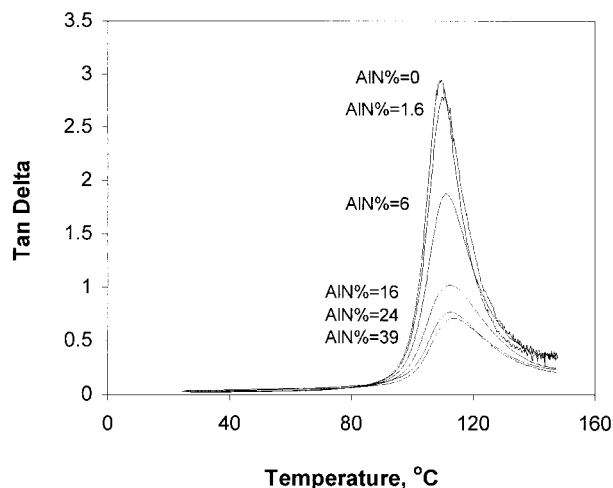


Figure 3 Loss tangent of the composite as a function of AlN content (polystyrene particle size, 0.15 mm).

Figure 1 shows a typical microstructure of the polystyrene–AlN composite. It can be seen that the polystyrene particles are surrounded by the AlN powder in the composite; however, polystyrene particles also exhibit some connectivity in some localized uncoated regions.

Effect of AlN Content on Dynamic Mechanical Properties of the Composite

A detailed discussion of the influence of the AlN fraction on the storage modulus appears below (Fig. 2). A change in the modulus indicates a change in rigidity and, hence, strength of the sample. It can be seen that the storage modulus of the filled composites increases with increasing AlN within the whole range of the testing temperature. The modulus of the composite with 24 vol % of AlN is almost double of that of polystyrene at a temperature below the α -transition. This means that the filled polystyrene will deform at a higher temperature than that of polystyrene, that is, the filled composite can resist a higher temperature than can the polystyrene matrix. Thus, the addition of a filler improves the useful temperature range of the polystyrene resin and the effective-

ness of this improvement increases with the AlN volume fraction.

Figure 3 depicts the influence of the AlN volume fraction on the loss tangent. Energy damping in viscoelastic polymers results from inelastic movement of molecular chain segments in the amorphous regions, whereby the applied elastic energy is dissipated as heat. In the transition region where the free volume reaches a critical level, the damping energy achieves a high value due to the initiation of molecular motion.

Three pieces of useful information can be drawn from the above experimental data: First, the loss tangent factor reflects the rigidity of the material. In Figure 3, the values of the loss tangent of the composites decreasing with AlN loading demonstrate the increasing trend of composite rigidity. This is in accordance with the curve of the storage modulus against the temperature in Figure 2. Second, the damping measurements also give practical information on glass transitions. The glass transition temperatures shift to the high-temperature area with increasing filler concentration. Table I gives the values of the transition temperature, T_g , of the composites estimated by the DMA software under different AlN volume fraction conditions.

The transition temperature, T_g , is not very much influenced by the volume fraction of AlN, so the interaction between AlN and polystyrene molecules does not seem very strong. Nevertheless, the transition temperature of the composite indeed shifts to higher temperature with increasing filler concentration, which indicates the enhanced interface interaction between the filler and the matrix.

From the view of the molecular structure of the materials, the magnitude of the damping peak and the transition temperature indicate the viscoelastic nature of the materials. Therefore, their characteristics are expected to reflect the presence of the filler. The increasing of T_g and the lowering of the damping energy suggest the restraint effect of the filler on the polymer segment

Table I Transition Temperature of Composites at Different AlN Contents

Parameter	Volume Fraction of AlN (%)					
	0	1.6	6	16	24	39
Transition temperature T_g , (°C)	109.58	110.04	110.77	112.83	112.31	113.92

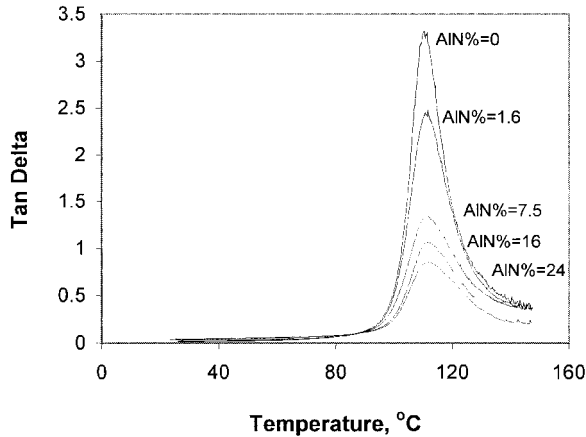


Figure 4 Loss tangent of composite as a function of AlN content (polystyrene particle size, 2 mm).

mobility, and this restriction is enhanced with an increasing filler fraction.

Finally, we can also see from Figure 3 that the damping peak becomes broader with increasing AlN reinforcement. This suggests that the AlN introduces many kinds of relaxation modes of the polystyrene chains. The above phenomena are very similar to other powder-filled polymer composites in which powder is dispersed in the melted polymer.^{9,10}

The same trend of the damping curve versus temperature appears in the composites when the polystyrene particle size is 2 mm. Figure 4 shows the results. However, the strength of the composites composed of 2-mm polystyrene particles and the AlN filler does not show a higher magnitude of the storage modulus at a higher AlN volume fraction (Fig. 5).

The storage modulus of the composites increases with the loading of AlN from 0 to 16 vol %;

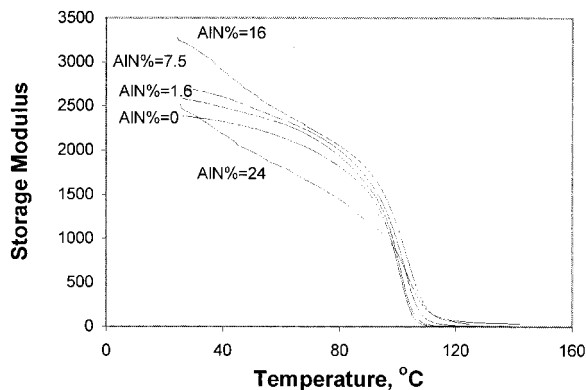


Figure 5 Storage modulus of the composite as a function of AlN content (polystyrene particle size, 2 mm).

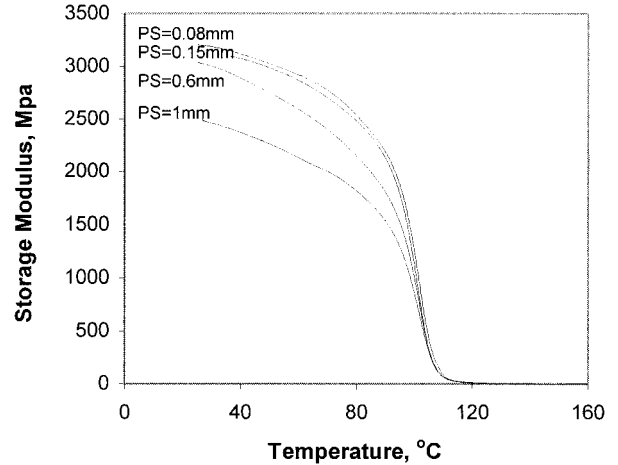


Figure 6 Storage modulus of composite as a function of polystyrene particle size (AlN vol % = 6).

then, the further addition of AlN results in decrease of the storage modulus of the composites, even lower than that of pure resin at 24 vol % of AlN. This result implies that the storage modulus is not proportional to the AlN content; there may be a critical threshold value of the AlN volume fraction. Further addition of AlN would decrease the storage modulus of the composite above this critical value.

There may exist a critical threshold value of the filler fraction in the composite with the structure used here. The storage modulus of the composite will decrease when the filler content is higher than is the critical threshold value. The morphology of the composite (Fig. 3) shows that the polystyrene particles are surrounded by AlN powder in the composite; however, polystyrene particles also exhibit some connectivity in some localized regions. So, the strength of the sample may result mainly from the contact of the polystyrene particles. The dispersed AlN powder around the polystyrene particles may not affect this bond unless there are too many AlN particles separated between the polystyrene particles. Under that situation, there could be a layer of an AlN barrier to block polystyrene particles from sticking together, which decreases the rigidity of the sample.

Effect of Polystyrene Particle Size on Dynamic Mechanical Properties of the Composite

Figures 6 and 7 display the effect of the polystyrene particle size on the storage modulus of the composites with different AlN volume fractions.

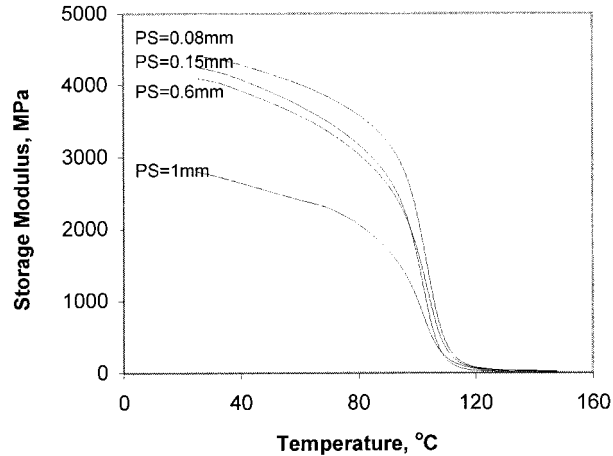


Figure 7 Storage modulus of the composite as a function of polystyrene particle size (AlN vol % = 20).

Analyzing the above curves, we can find that the storage modulus decreases with the polystyrene particle size at the same AlN concentration. Figures 8 and 9 show the influence of the polystyrene particle size on the loss tangent of the composites with different AlN volume fractions. The glass transition temperature of the composites does not change very much with the polystyrene particle size at 6 vol % AlN, but it shifts a little to a lower temperature with an increasing polystyrene particle size at 20 vol % AlN. At the same time, the damping peak decreases with the increasing polystyrene particle size. Different polystyrene particle sizes will give different amounts of the interfacial area under the same AlN fraction. The smaller the polystyrene particles size, the more

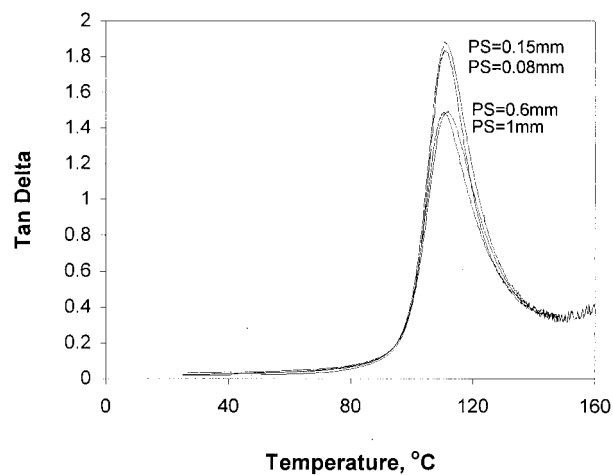


Figure 8 Loss tangent of the composite as a function of polystyrene particle size (AlN vol % = 6).

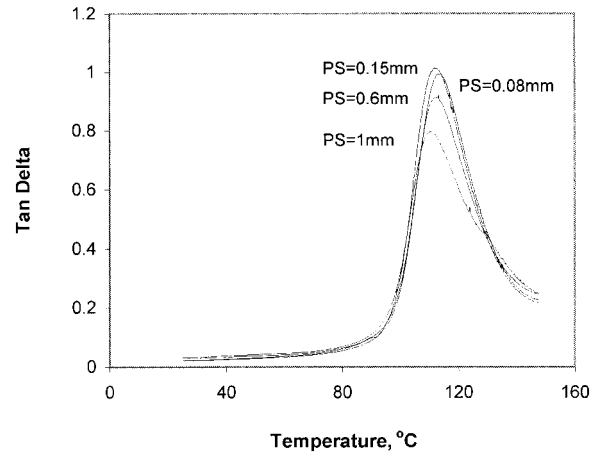


Figure 9 Loss tangent of the composite as a function of polystyrene particle size (AlN vol % = 20).

interfaces between polystyrene and AlN at the same AlN content, so the reinforcement effect of a filler on polymer rigidity is more obvious. However, the less sensitive glass transition temperature and the lower trends of the damping peak with increasing polystyrene particle size, especially at lower AlN content, reveal the fewer interactions between AlN and polystyrene. This may be because that the concentration of AlN at the interface decreases with an increasing amount of the interface under the same AlN concentration.

CONCLUSIONS

1. The dynamic mechanical properties of the polystyrene–AlN composite under a special dispersion state were studied. The storage modulus of the composite increases with increasing AlN concentration under a limit range of the AlN volume fraction. Beyond a certain value of AlN content, AlN might cause a decrease in the storage modulus of the composites.
2. The damping peak decreases and the curve of damping also becomes broader with the increasing fraction of AlN. At the same time, the glass transition temperature shifts to a higher temperature, although the increment is not very significant.
3. The size of the polystyrene particles influences the dynamic properties of the composites under the dispersion state used here. The bigger size of the polystyrene particle gives a lower storage modulus of

the composite. The damping peak also decreased with an increasing polystyrene particle size, but the transition temperature obviously does not seem to be affected.

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