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A study of the internal friction and modulus of epoxy-resin-dispersed nanometre-sized alumina particles

Zhang Lide, Xie Cunyi and Zhu Xianfang
Institute of Solid State Physics, Academia Sinica, Hefei 230031 (China)

Abstract

A systematic study of the internal friction (IF) of an epoxy–diaminodiphenylmethane (DDM) blend polymer containing nanometre-sized Al_2O_3 (n-Al_2O_3) particles with various filling factors F_f was carried out. It was found that the β-IF peak and the modulus of the composite materials depended strongly on F_f. The height of the β peak first increases and then decreases gradually with increasing F_f. When $F_f > 0.05$, the β peak drops substantially. However, the modulus of the composite materials first decreases with increasing F_f. When $F_f > 0.05$, the modulus increases dramatically. The experimental results show that the added amount of n-Al_2O_3 particles strongly affects the mechanical properties of the composites. A detailed discussion and explanation of the influence of n-Al_2O_3 particles on the behaviour of the β peak and modulus of the composites are presented in this paper.

1. Introduction

Epoxy resins belong to the class of thermosetting polymers which are widely employed as matrices for composite materials and as structural adhesives [1–4]. They are amorphous, highly cross-linked polymers and this structure results in these materials possessing a high modulus and fracture strength, low creep and good performance at elevated temperatures. Recently a higher dielectric constant for these kinds of composite materials has been observed [5]. In order to understand the effects of nanometre-sized Al_2O_3 (n-Al_2O_3) particles on structures of epoxy resin–diaminodiphenylmethane (DDM), internal friction (IF) measurements were carried out on such composite materials.

2. Sample preparation and experimental methods

n-Al_2O_3 particles with an average diameter of about 8 nm were mixed with hardener (DDM) and the mixture was uniformly dispersed in epoxy resin (E-51, 168) at 90 °C. The resulting composite liquid was then exhausted in vacuum. Finally, composite liquids with various filling factors F_f of n-Al_2O_3 (0, 0.001, 0.01, 0.05, 0.1) were poured into moulds and solidified for 3 h at 125 °C. The size of the composite samples was $50 \times 4 \times 1$ mm^3.

IF measurements were carried out in an automatic polyfunctional inverse torsion pendulum apparatus with a measurement frequency range from 10^{-5} to 10 Hz. The vibration amplitude was 2.5×10^{-5}. The measurement temperature range was from −120 to 180 °C. The measurement procedure was as follows: the sample was first heated to 170 °C, kept at that temperature for 15 min and then cooled to −130 °C. The IF was measured at a heating rate of 3 °C min^{-1}.

3. Experimental results

The IF spectrum for the epoxy–DDM blend polymer without n-Al_2O_3 particles is shown in Fig. 1. It can be seen that two IF peaks (α and β) appear in the temperature range from −120 to 180 °C. The α peak is located at about 175 °C and the β peak at about −40 °C. The α peak corresponds to the T_g transition and the β peak is caused by the movement of small

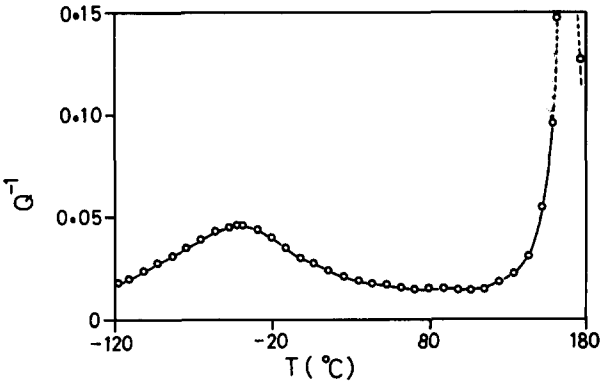

Fig. 1. IF spectrum *vs.* temperature for epoxy–DDM blend polymer.

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units or the rotation of side radicals, *i.e.* β relaxation. The results show that the epoxy–DDM blend polymer used in our experiments is a single-phase structure.

Figure 2 shows a series of IF curves corresponding to various filling factors of n-Al_2O_3 particles from 0.001 to 0.1. Clearly, in comparison with the IF curve for the sample without n-Al_2O_3 particles, with increasing F_f, the IF first increases (0, 0.001) and then decreases gradually (0.01, 0.05). It should be noted that the IF decreases dramatically when F_f reaches 0.1.

IF measurements *vs.* frequency show that with increasing measurement frequency the position of the β peak shifts to higher temperature, while the height of the peak increases slightly (Fig. 3). The activation energies of epoxy–DDM blend polymer composite materials (EDBPCMs) corresponding to various F_f values are given in Table 1.

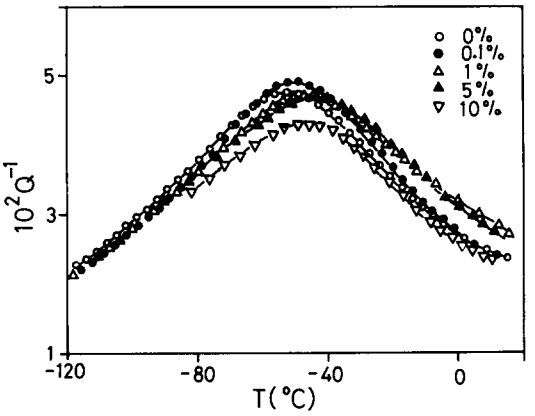

Fig. 2. IF curves *vs.* temperature for EDBPCMs with various F_f values.

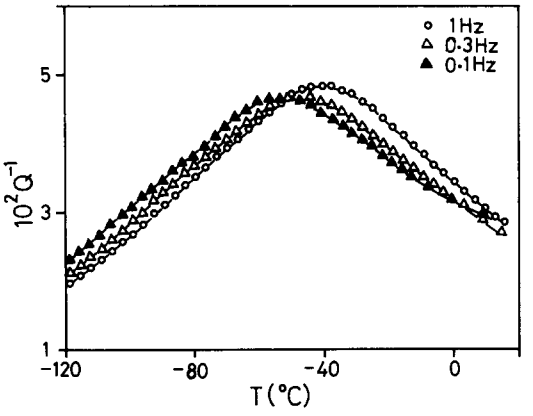

Fig. 3. IF curves *vs.* temperature at various measurement frequencies.

TABLE 1. Activation energies of EDBPCMs for various F_f values

F_f	0	0.001	0.01	0.05	0.1
H (ev)	0.61	0.75	0.72	0.87	0.99

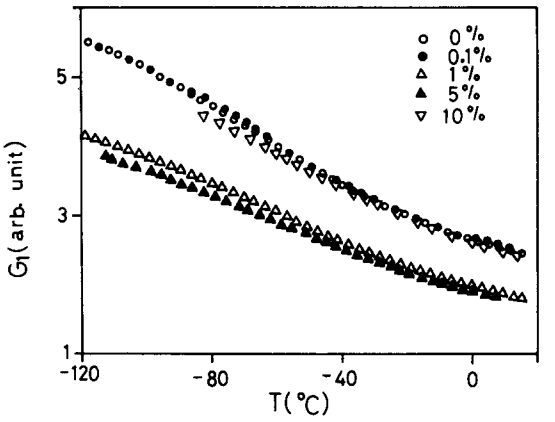

Fig. 4. Modulus curves *vs.* temperature for EDBPCMs with various F_f values.

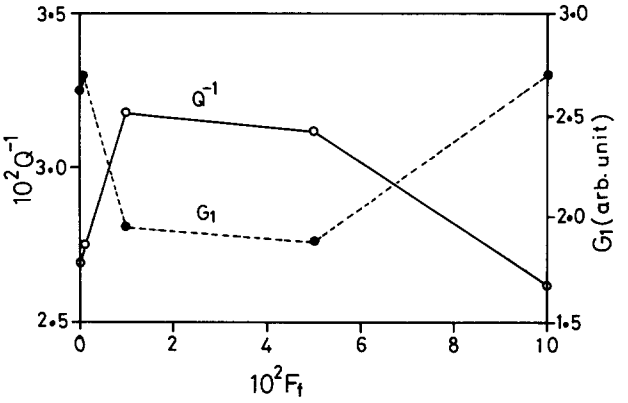

Fig. 5. IF and modulus curves *vs.* F_f for EDBPCMs at 0 °C.

Figure 4 shows the shear modulus *vs.* temperature curves corresponding to F_f values of 0, 0.001, 0.01, 0.05 and 0.1. It is clear that with increasing F_f the modulus first decreases substantially (0.01, 0.05) and then recovers to its original value (0.1).

Figure 5 shows the IF and modulus *vs.* F_f curves at 0 °C. With increasing F_f, the IF first increases (0, 0.01) and then decreases gradually (0.05, 0.1). The changing behaviour of the modulus with increasing F_f can be divided into three steps: firstly the modulus increases for $F_f < 0.001$, then decreases dramatically in the range $0.001 < F_f < 0.05$ and finally increases substantially for $F_f > 0.05$.

4. Discussion

The results presented here indicate that the EDBPCM containing n-Al_2O_3 particles with a filling factor of 0.001 shows an increase in the height of the β peak, while the shear modulus practically does not change. On further increasing F_f, both the β peak height and the modulus decrease. When $F_f > 0.05$, the β peak height is reduced but the modulus is restored to the value

for the epoxy–DDM blend polymer without n-Al_2O_3 particles. In order to explain the difference in IF and modulus behaviours of EDBPCMs with various filling factors, we first analyse the molecular structures of the epoxy resin, DDM and their blends and then discuss the effect of the addition of n-Al_2O_3 particles on the cross-linked networks. The repeat units of the epoxy resin and DDM are shown in Figs. 6(a) and 6(b) respectively. After thermosetting blending at a temperature of 125 °C, cross-linked networks of epoxy resin containing DDM are formed, the repeat unit of which is shown in Fig. 6(c). It can be seen from Figs. 6(a)–6(c) that the interaction between oxygen atoms in the epoxy resin and the NH_2 chain in DDM is responsible for the formation of the cross-linked networks. With the addition of n-Al_2O_3 particles a slight structural change of the cross-linked networks occurs. Generally the n-Al_2O_3 particles occupy two kinds of positions: (1) segregating to cross-linked nodes; (2) filling in the interstices in the cross-linked networks. Because the n-Al_2O_3 particles lack oxygen, preferential segregation near the cross-linked nodes probably leads to a "weak area" being formed easily, even at a very low content of n-Al_2O_3 particles. Thus in the former case the appearance of the weak area near the cross-linked nodes due to n-Al_2O_3 particles causes the IF of the β peak to increase. However, in the latter case the n-Al_2O_3 particles filling the interstices of the cross-linked networks can weaken the mobility of the small molecular units. Therefore the IF of the EDBPCM decreases and the modulus increases. It should be pointed out that the "weak area" due to segregation of n-Al_2O_3 particles is more sensitive to IF than to the modulus. As a result, a small content of n-Al_2O_3 particles ($F_f = 0.001$) can give rise to an increase in IF, but the modulus does not change noticeably. Upon increasing F_f (0.01, 0.05), some of the n-Al_2O_3 particles occupy the interstices in the EDBPCM and the increase in IF due to the n-Al_2O_3 particles near the cross-linked nodes is compensated by the decrease in IF caused by the n-Al_2O_3 particles filling in the interstices. Thus no change in IF is noticeable. However, the "weight" of the modulus decrease caused by the preferential segregation of n-Al_2O_3 particles near the cross-linked nodes is larger than that of the modulus increase due to the filling of n-Al_2O_3 particles in the interstices of the cross-linked networks. Because of the preferential segregation at the cross-linked nodes, the modulus of the composite materials with filling factors from 0.01 to 0.05 thus decreases. For the case of $F_f = 0.1$, besides the n-Al_2O_3 particles occupying the cross-linked nodes, most of the n-Al_2O_3 particles fill in the interstices. The movement of the small units is strongly hindered by the n-Al_2O_3 particles. As a result, the modulus of the EDBPCM with $F_f = 0.1$ increases again and almost recovers to the original value for the epoxy–DDM polymer.

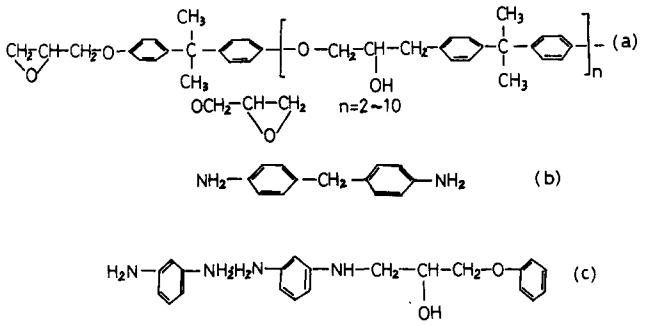

Fig. 6. Repeat units corresponding to (a) epoxy resin, (b) DDM and (c) EDBPCM.

For the case of $F_f = 0.01$ the IF peak shifts to higher temperature with increasing frequency. This phenomenon can be attributed to the increase in activation energy owing to the enhanced interaction of n-Al_2O_3 particles near the cross-linked nodes with oxygen atoms in the epoxy resin.

5. Conclusions

The addition of n-Al_2O_3 particles affects the behaviour of the β-IF peak and modulus of the EDBPCMs. A small addition of n-Al_2O_3 particles ($F_f = 0.001$) causes the β-IF peak to increase, whereas the modulus practically does not change. On increasing F_f (0.01, 0.05), the β peak height decreases slightly and the modulus drops substantially. However, when F_f reaches 0.1, the β-IF peak decreases noticeably and the modulus recovers to the original value for the epoxy–DDM blend polymer without n-Al_2O_3 particles. The influence of n-Al_2O_3 particles on the behaviour of the IF and modulus is of great importance.

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