

Rubber-modified epoxy resins:

3. Influence of filler on the dielectric relaxation properties

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Dielectric measurements are reported on the effect of addition of glass (wool and beads) to a rubber modified epoxy resin. A parallel study of the influence of the addition of polydimethylsiloxane is also reported. It is found that there are significant shifts in the position of the dielectric relaxation associated with the acrylonitrile/butadiene phase. Analysis of the data indicates that the activation energy of the relaxation is little affected by the additives and the observed effects can be explained by the change in internal field brought about by the addition of filler through its effect on the permittivity of the material.

Keywords Rubber modified epoxy resins; dielectric relaxation; filler interactions; glass filled

INTRODUCTION

Rubber modified epoxy resins are often used as adhesives and as such are applied to substrates with added filler. In particular, glass beads are used to obtain uniform thickness of the adhesive layer in certain airframe structure applications. In this study the effects of addition of various fillers on the dielectric properties of the rubber modified epoxy resins are reported. In a previous paper¹, the analysis of the dielectric and mechanical properties of epoxy resins modified by the addition of an acrylonitrile-butadiene copolymer were reported. It was observed that a dielectric loss in the kilohertz region at 233–253K can be associated with the motion of the copolymer. The influence of various types of fillers on the mechanical properties of polymers has been extensively studied by Lewis and Nielson², and Shreiner³. Epoxy resins loaded with titanium dioxide or zinc oxide exhibited increases in their mechanical strengths. Glass filled rubber and epoxy systems show quite significant changes in their stress-strain behaviour whereas there appears to be little effect on the dynamic mechanical properties. For instance, Landel⁴ has shown that the addition of silica increases the equilibrium modulus and low frequency dynamic mechanical modulus. However, the high frequency modulus is virtually unaffected. In an attempt to characterize the effects of the filler on these rubber modified epoxy resins the following study was undertaken.

EXPERIMENTAL

The structure and properties of the epoxy resins used have been discussed in an earlier paper¹. The present studies were performed with a 12½% by weight rubber modified epoxy and were cured with triethylenetetramine (TETA). Three additives were used: glass wool, glass beads and

polydimethylsiloxane. The PDMS had a viscosity of 100cS and an M_n of 6.2×10^3 . This material was used as received. The glass materials were cleaned by refluxing in methylene chloride for six hours and dried in a vacuum oven. The glass beads were of two different sizes, viz. 1.15 mm and 0.212 mm respectively. Samples of the smaller diameter beads were given further treatment. One was treated with concentrated nitric acid and the other was refluxed with hexamethyldisilazane for eight hours to remove surface OH groups. In all cases the samples were cast as flat discs. The dielectric measurements were carried out as indicated previously¹.

RESULTS

For each of the systems studied the dielectric permittivity (ϵ') and loss (ϵ'') were measured as a function of frequency over a range from 100 Hz to 100 kHz, from 230 to 263 K. Analysis of the data yields the value of the maximum loss, ϵ''_{\max} , and the characteristic frequency, f_c . Data obtained as a function of temperature allowed the activation energy plots to be drawn and these are presented in *Figures 1–4*. Also, the variations of ϵ''_{\max} as a function of filler concentration are summarized in *Figures 5 and 6*.

DISCUSSION

Glass beads as filler

The addition of glass beads shifts the relaxation to lower frequency. However, the variation with change in concentration is far from clear (*Figure 2*). This implies that the factors causing the shift do not exhibit a simple correlation with the volume of beads present. Comparison of the shifts observed with a similar concentration of smaller diameter beads (*Figure 4*) indicates that there is no apparent correlation of the observed behaviour with the surface area of filler. There is,

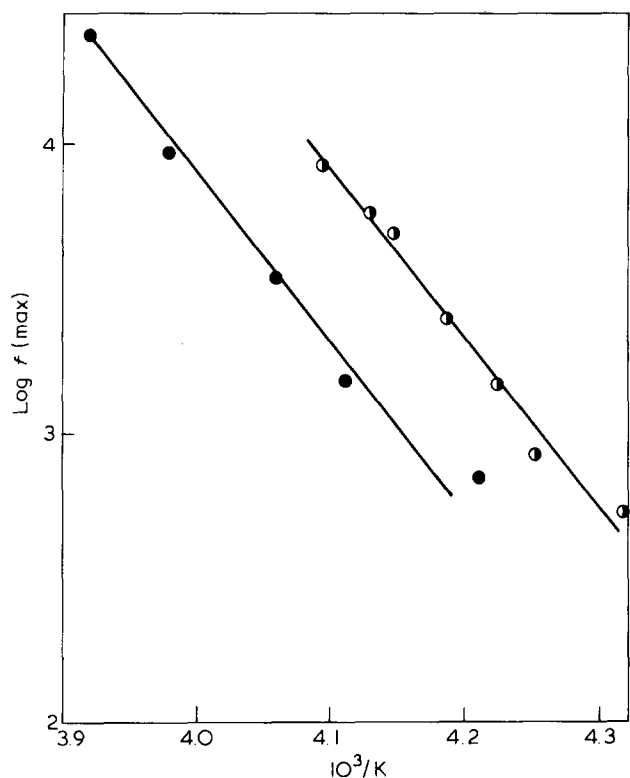


Figure 1 $\text{Log } f_{\text{max}}$ as a function of reciprocal temperature for glass wool filled systems. \circ , Unfilled; \bullet , with glass wool

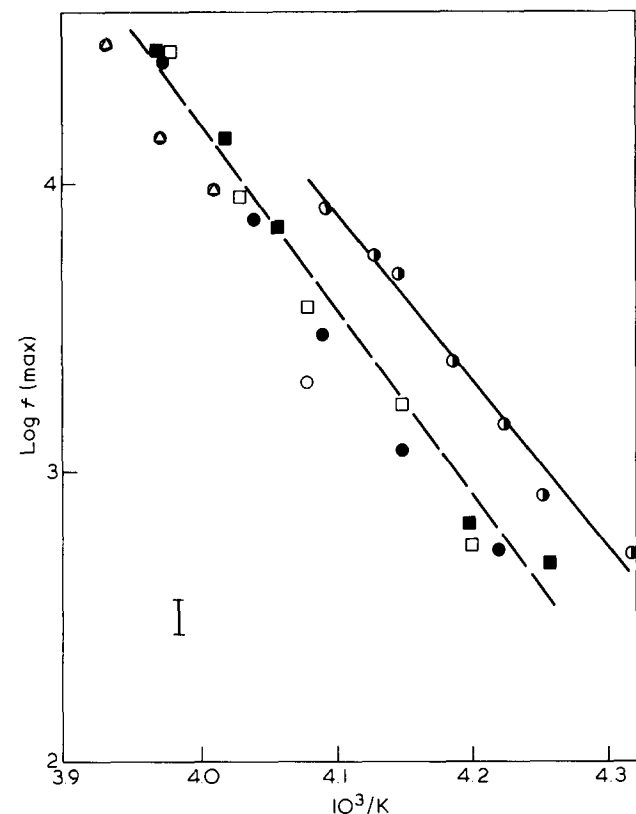


Figure 2 $\text{Log } f_{\text{max}}$ as a function of reciprocal temperature for glass beads (diameter 1.15 mm) filled systems. \circ , Unfilled; \bullet , 1.10 g, \blacksquare , 0.5 g, \triangle , 6.55 g, \square , 10.63 g glass beads

therefore, no simple relationship between the shifts produced and the absorption of polymer onto the bead surface. This factor is further exemplified by noting the insensitivity of the shift to glass type and surface treatment (Figure 1 and Figure 4).

Influence of polydimethylsiloxane

The shift of the dielectric loss with varying amounts of PDMS is complex and the data exhibited a high degree of scatter (Figure 3). It appears that as in the case of the glass beads, the addition of the PDMS causes an initially large shift to low frequency which is then subsequently counteracted by a plasticization effect associated with the further addition of PDMS.

It is clear that the observed effects are not associated with the formation of an adsorbed surface layer onto the filler. The results obtained with beads of differing surface area and treatment corroborates this observation. Therefore, an alternative explanation must be sought. The motion of a dipole will depend on the dielectric properties of the environment in which it resides. The effect of introducing a filler of different dielectric properties from that of the matrix might be expected to lead to a change in the effective local permittivity, and hence on the motion of the dipole. In order to examine the effect of a change in dielectric amplitudes we have used the relationship of Powles⁵:

$$\tau^* = [(2\epsilon_0 + \epsilon_\infty)/3\epsilon_0]\tau \quad (1)$$

where $\epsilon_0, \epsilon_\infty$ are the zero and infinite frequency values of the permittivity, τ is the experimentally observed effective relaxation time, and τ^* is the time constant for the immediate molecular dipole relaxation. If the dielectric effect is dominant then the ratio of τ^*/τ will remain independent of the system and will be approximately equal to unity. Data for the above systems are summarized in Table 1.

It can be seen that the shifts are simply described by the

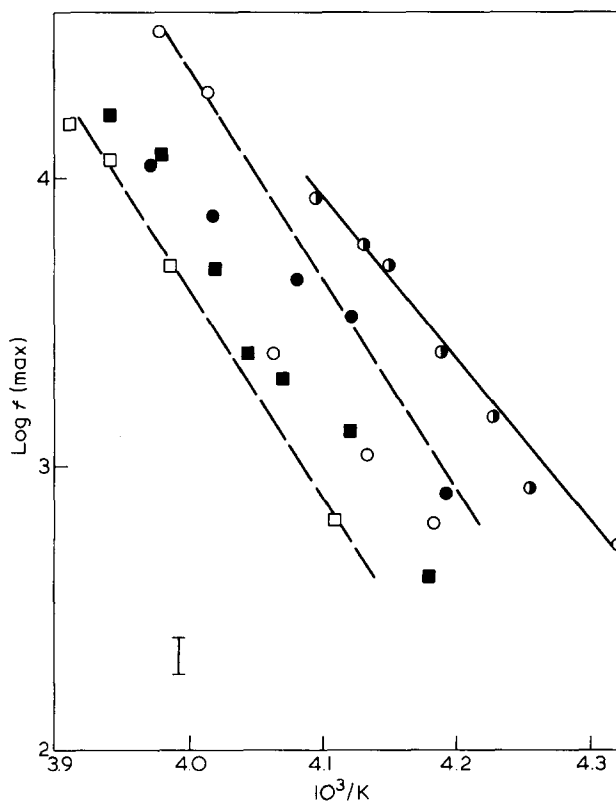


Figure 3 $\text{Log } f_{\text{max}}$ as a function of reciprocal temperature for PDMS filled systems. \circ , Unfilled; \square , 0.5%, \blacksquare , 2%, \circ 1%, \bullet 10% PDMS

change in the bulk permittivity of the sample and we do not need to invoke any specific interaction effects. The scatter in the case of the PDMS samples probably reflects the incompatibility of the various polymer components involved.

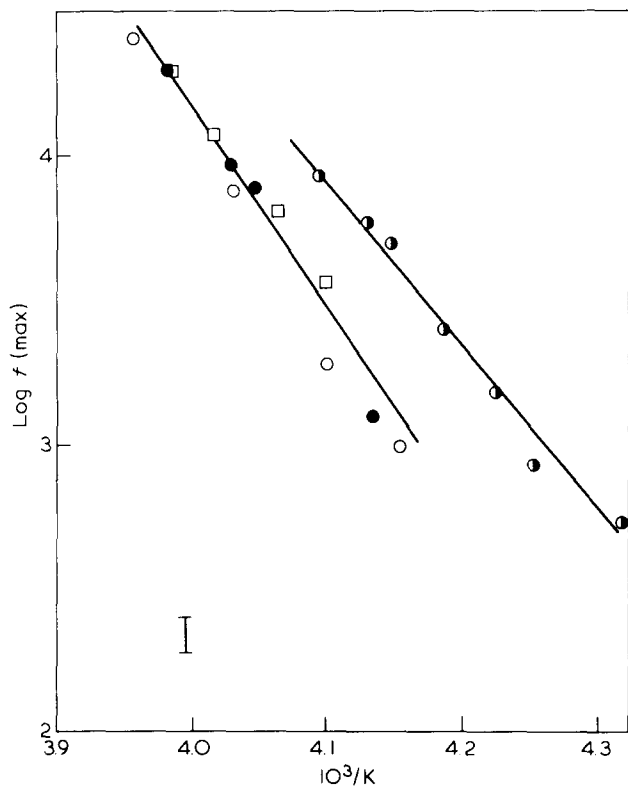


Figure 4 Log f_{max} as a function of reciprocal temperature for treated glass beads (diameter 0.212 mm) filled systems, ●, Unfilled; ○ + untreated beads; ● + treated with silazane; □ + treated with HNO_3

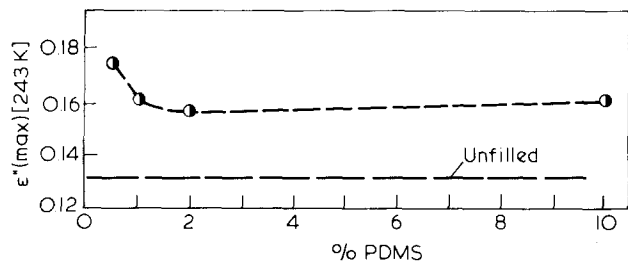


Figure 5 Amplitude of ϵ'' (max) as a function of PDMS concentration

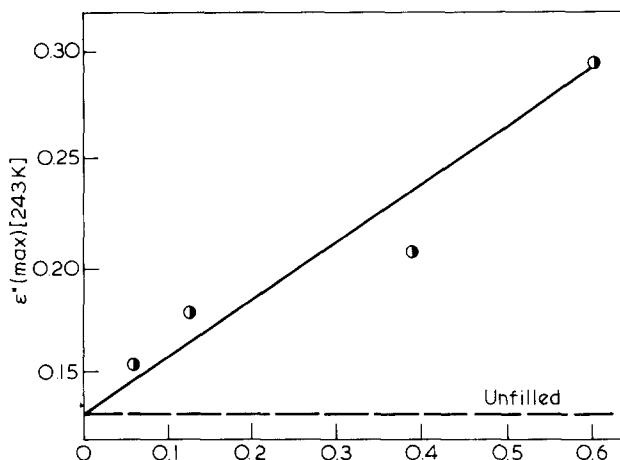


Figure 6 Amplitude of ϵ'' (max) as a function of concentration of glass beads (diameter 1.15 mm)

Table 1 Summary of Powles Factors for 12% + TETA systems

Filler	$r^*/r(2\epsilon_0 + \epsilon_\infty)/3\epsilon_0$
Unfilled	0.97
0.5% PDMS	0.97
1.0% PDMS	0.97
2.0% PDMS	0.97
10.0% PDMS	0.97
Glass wool	0.97
0.516 g Glass beads (1.15 mm dia.)	0.97
1.10 g	0.97
6.55 g	0.97
10.63 g	0.98

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