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Temperature variation of dielectric loss of silver-thermosetting polyester composites at audio frequencies

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Dielectric loss of a metallopolymer system consisting of silver-coated glass spheres dispersed in unsaturated polyester is investigated at audio frequencies in the temperature range −180 to 45° C. The effect of the conductive filler is generally an enhancement of the dielectric loss due to the polymr matrix and no new loss peak is observed, and the activation energy for the β-relaxation remains unaffected. It has also been found that dielectric dispersions corresponding to various filler concentrations appear to possess identical shapes in a pseudo Cole–Cole plot and that the loss maxima are collinear.

1. Introduction

The d.c. electrical conductivity and dielectric constant of composites consisting of silver-coated glass spheres (SCGS) dispersed in unsaturated polyester has been studied in two previous papers [1, 2]. This present work deals with dielectric loss measurements at audio frequencies of such composite systems in the temperature range −180 to 45° C.

Dielectric loss in heterogeneous systems composing of a mildly conducting filler in a dielectric medium of low loss have been studied by many authors [e.g. 3–5], affirming the existence of Maxwell–Wagner loss. Our system differs from theirs in that our filler may be regarded as very conducting and that the polyester matrix has noticeable dielectric dispersion when measured over a sufficiently wide range of temperatures. No anomalous Maxwell–Wagner peak is discernible from our measurements and the effect of the addition of silver-coated glass spheres to the polyester has been to displace the temperature response curves upwards in log ε'' against $1/T$ plots.

An interesting experimental finding arising from this work is that the temperature response curves of samples having various filler concentrations, when plotted in a pseudo Cole–Cole plot, all possess approximately identical shapes around their respective relaxation peaks and that the latter are collinear. It is suspected that this is a characteristic feature also for other metallopolymer systems.

2. Experimental procedure

The method of sample preparation has followed the procedures as set out in [1], with the following modifications. The setting of the unsaturated polyester was accelerated by cobalt naphthalene and curing was achieved at room temperature with 0.5% hardener. Sample dimensions are 54 mm diameter and 2 mm thickness, and silver epoxy coating as electrode is not necessary for the present study.

The dielectric response was measured by a General Radio 1615-A Capacitance Bridge at audio frequencies and from −180 to 45° C for composite samples with 0 to 35 vol % of filler. Temperature control has an accuracy of 1° C.

3. Results

Because of our narrow frequency range, no prominent relaxation peak is observed in dielectric loss against log (frequency) plots for all samples studied, with or without silver-coated glass spheres filler. Much information is revealed, however, when plotted against inverse temperature.

3.1. Temperature response of the polyester matrix

Fig. 1 depicts log ε'' against $1/T$ for a typical sample of 0% SCGS filler. Relaxation peaks for the various

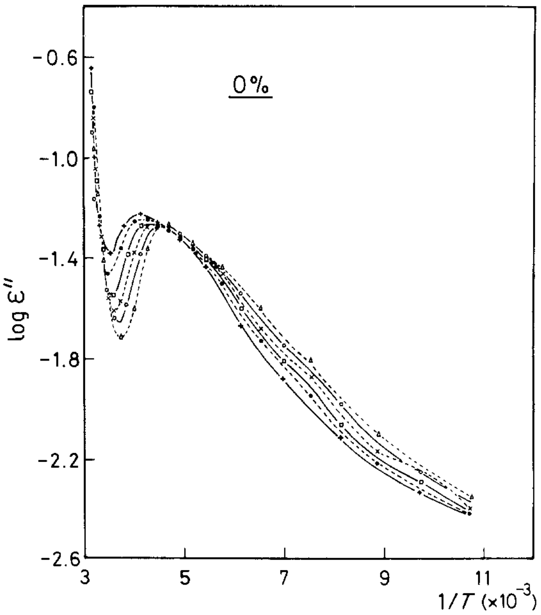

Figure 1 Log ε'' against $1/T$ for the polyester matrix. Temperature range: −180 to 45° C; frequency range: 200 Hz to 10 kHz. (△) 200 Hz, (○) 500 Hz, (×) 1 kHz, (□) 2 kHz, (●) 5 kHz, (+) 10 kHz.

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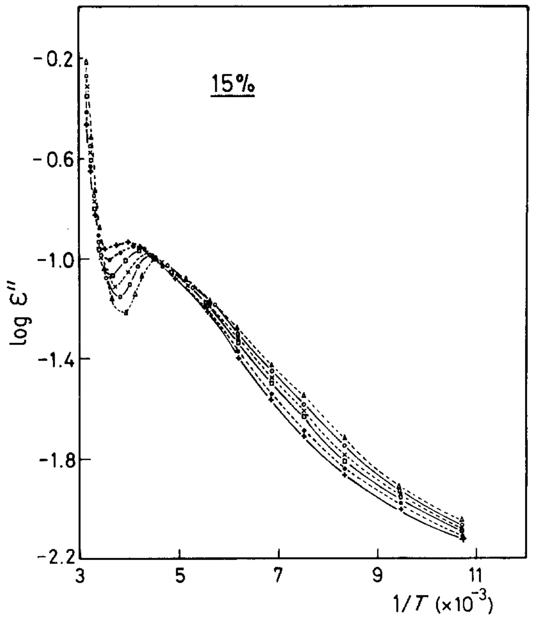

Figure 2 Log ε'' against ln $\omega\tau/\tau_0$ for the polyester matrix. Here $\tau/\tau_0 = \exp(7000/T)$. (△) 200 Hz, (○) 500 Hz, (×) 1 kHz, (□) 2 kHz, (●) 5 kHz, (+) 10 kHz.

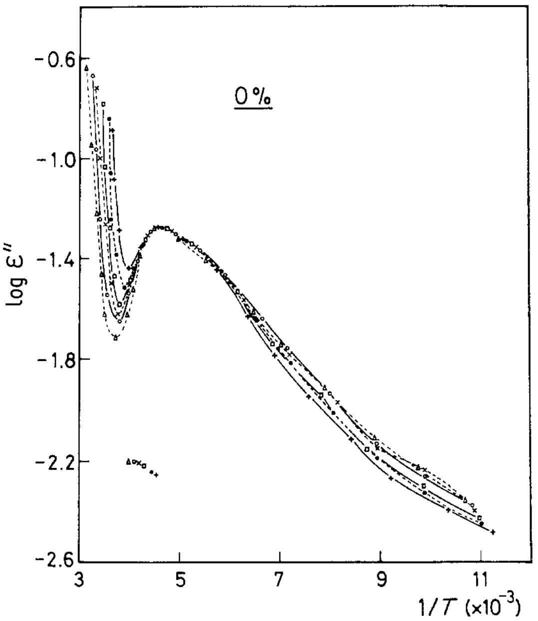

Figure 3 Log ε'' against $1/T$ for the polyester matrix "normalized" to 200 Hz (see text). (△) 200 Hz, (○) 500 Hz, (×) 1 kHz, (□) 2 kHz, (●) 5 kHz, (+) 10 kHz.

frequencies are found to be temperature activated with 58 kJ mol^{-1} activation energy and $\tau = \tau_0 \exp(7000/T)$. The log ε'' against ln $\omega\tau$ plot of Fig. 2 gives excellent overlap of the frequency curves, supporting the above activation. Fig. 3 is a log ε'' against $1/T$ plot normalized by the technique of Jonscher [6], in which shift along the ordinate-axis is also effected; the frequency trace is shown in the lower part of the diagram. Concurrence at the low temperature end is good, but not at and around the high temperature tail which is manifested by another relaxation together with conductivity. This is evidenced in Fig. 4 where the "tail" is further tracked down by measurement at higher temperatures. While the general trend for all the frequency curves in Fig. 4a is to increase with temperature, a marked turn is exhibited in high frequency curves at 75° C, ($1/T = 2.87 \times 10^{-3}$) reminiscent of an α-relaxation of the polyester; the low frequency curves continue to go up, allegedly because of the more pronounced effect of conductivity at lower frequencies.

From the above discussion it is clear that the region above $-10°$ C ($1/T = 3.80 \times 10^{-3}$) in Fig. 1 represents a complicated superposition of (i) the tail of

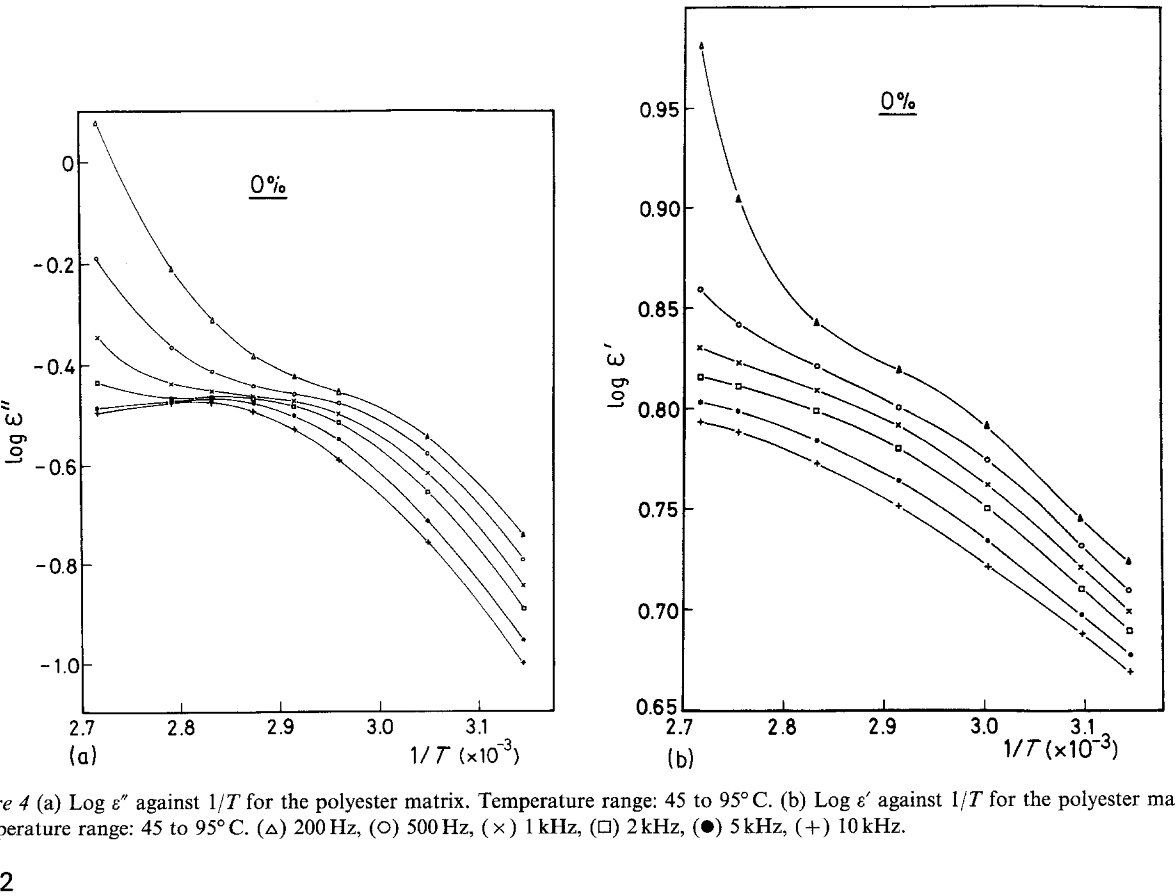

Figure 4 (a) Log ε'' against $1/T$ for the polyester matrix. Temperature range: 45 to 95° C. (b) Log ε' against $1/T$ for the polyester matrix. Temperature range: 45 to 95° C. (△) 200 Hz, (○) 500 Hz, (×) 1 kHz, (□) 2 kHz, (●) 5 kHz, (+) 10 kHz.

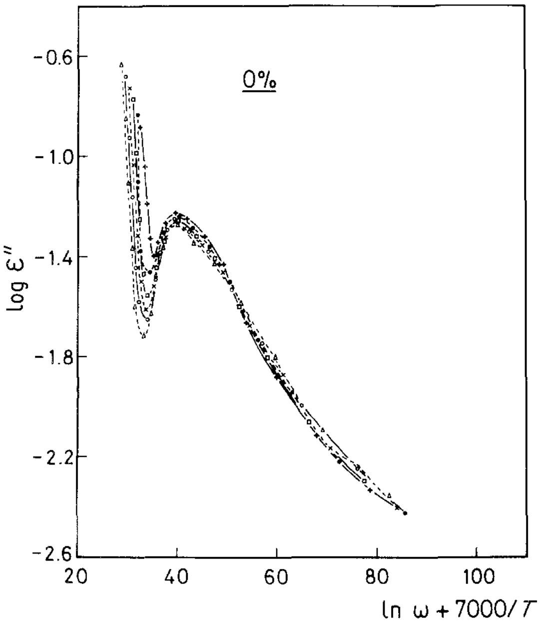

Figure 5 Log ε'' against $1/T$ for a sample with 15 vol % SCGS filler. (△) 200 Hz, (○) 500 Hz, (×) 1 kHz, (□) 2 kHz, (●) 5 kHz, (+) 10 kHz.

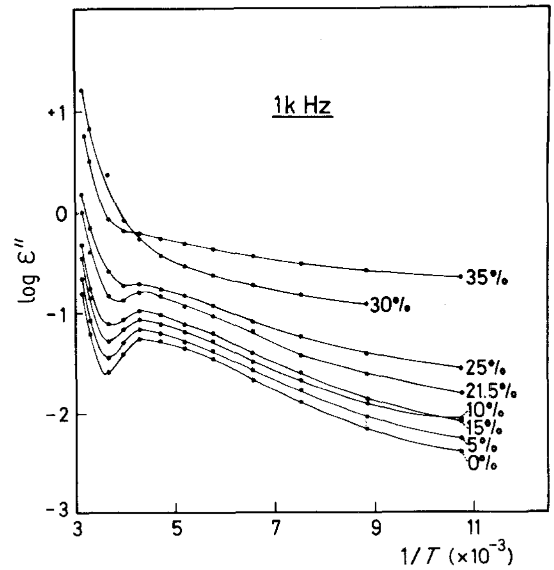

Figure 6 Log ε'' against $1/T$ at 1 kHz. Filler concentrations are as indicated.

β-relaxation, (ii) the rising edge of an α-relaxation together with (iii) conductivity. We therefore in this paper confine our attention to the effect of the addition of conducting particles to the polyester on the rising edge of β-relaxation up to and around the β-peak, i.e. from -180 to about $-20°$C ($1/T \sim 11 \times 10^{-3}$ to 4×10^{-3}), although the dielectric response up to 45°C ($1/T \sim 3 \times 10^{-3}$) is also shown in the $1/T$ plots.

3.2. Samples with SCGS

For volume concentrations of SCGS filler of less than 25%, log ε'' against $1/T$ plots have the general shape of Fig. 1. The peaks are also thermally activated by the same activation energy and the location (on the $1/T$-axes) of the peaks for a given frequency appears to be independent of filler concentration. As an example to illustrate the above observations, Fig. 5 shows the response for a 15 vol % sample.

No peaks are observed for concentrations of 30 vol % and beyond. This circumstance is clearly illustrated in Fig. 6 in which the 1 kHz response is shown. The prominence of the β-relaxation peak is seen to diminish with filler concentration and finally disappears in the 30 and 35 vol % curves.

3.3. Effect of filler

Fig. 6 lends itself readily to analysis of the effect of filler. The temperature peaks for samples with less than 25 vol % filler are all located at $-45°$C ($1/T = 4.39 \times 10^{-3}$) while the peak values increase with concentration. The slopes of the curves in the region just to the right of the peaks, e.g. from -73 to $-130°$C ($1/T = 5 \times 10^{-3}$ to 7×10^{-3}) are markedly similar whereas a tendency to flatten thereafter with increase in filler concentration is quite apparent. Fig. 7 shows the variation of log peak values with log (1-filler concentrations) and gives a straight line fit with slope ~ -4.6.

A variant of the pseudo Cole–Cole plot technique, c.f. [7], in which log ε'' is plotted against log ε' for a given frequency with varying temperature has been found useful for the description of the effect of conducting filler. Fig. 8 is such a plot for 1 kHz. The curves corresponding to the various concentrations of SCGS filler are found to possess the same shape and further, the points (log $\varepsilon'_{\mathrm{m}}$, log $\varepsilon''_{\mathrm{m}}$) corresponding to the loss maxima all lie on a straight line, giving $\varepsilon'' = 0.0125\varepsilon'^{1.17}$.

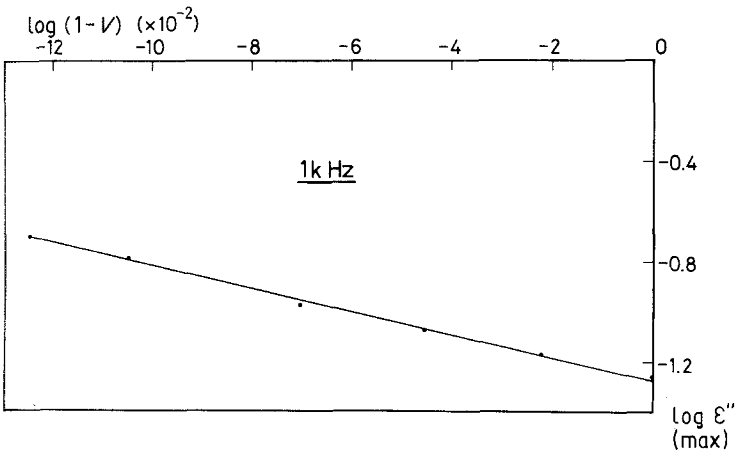

Figure 7 Log ε'' (max) against log $(1 - V)$ for 1 kHz.

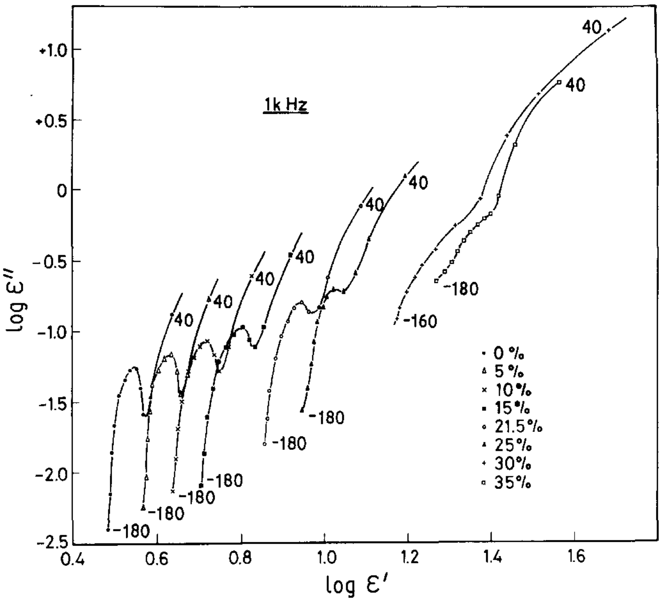

Figure 8 Log ε″ against log ε′ at 1 kHz. Temperatures (° C) are spaced at 20° C intervals. Solid lines are drawn from more data points than as depicted. (●) 0%, (△) 5%, (×) 10%, (■) 15%, (○) 21.5%, (▲) 25%, (+) 30%, (□) 35%.

4. Conclusion

The dielectric loss in SCGS–polyester composites at audio frequencies in the temperature range − 180 to 45° C has been investigated in this paper. No new relaxation peak due to the introduction of the conducting filler is observed in the temperature and frequency range investigated. This is reasonable because it is expected that Maxwell–Wagner peaks would not arise when the filler has infinite dielectric constant.

Our main analysis has been based on the rising edge of the β-relaxation up to and around the β-peak, the reason being that the part thereafter is complicated by α-relaxation and conductivity. It was found in $1/T$ plots that the loss induced by the conducting filler is an enhancement of the peaks by $(1 - V)^{-4.6}$ for a given frequency, and that the peaks are activated by an energy of 58 kJ mol^{-1} for a given concentration V.

While this is a continuation of the work in [2], the effect of conducting filler on the dielectric response of a matrix deserves attention by its own right. Although ideally one would like to work with a matrix having a single relaxation peak or at least having well separated peaks, results of our work are already suggestive of the generality of the experimental result that curves corresponding to different concentrations of conducting filler have identical shapes in pseudo Cole–Cole plots of log ε″ against log ε′ for a given frequency, and that the points of maximum loss are collinear. Whether this result is indeed upheld in other metallopolymer systems deserves further investigation.

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