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Dielectric Relaxations of Shellac/Amino Resin Blends

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Synopsis

The dielectric constant (ϵ') and loss (ϵ'') of shellac/melamine resin blends have been determined at temperatures between 20° and 120°C and frequencies between 0.1 and 100 kHz. ϵ' decreases with increase in the percentage of melamine resin in the blend. Two relaxations have been observed, of ΔH = 4.99 kcal/mole and 11.1 kcal/mole. The glass transition is observed between 60° and 70°C. The cole-cole parameter increases with temperature and becomes constant above T_g.

INTRODUCTION

The cure of synthetic resin systems and polymers has been studied using dielectric constant (ϵ') and loss (ϵ'') as cure parameters.[1–3] Learmonth et al.[1] has reported that ϵ''/ϵ' in unsaturated polyester resins is normally high in the early stages of cure because of ionic conductance arising from impurities. ϵ'' then falls and later exhibits a peak. ϵ' falls during cure because of the gradual immobilization of the polar groups. Dasgupta et al.[2] have found that, below 1 kHz, the loss of an unmodified epoxy resin and a pure hardener were high; and when the two were mixed together to obtain a cured product, the loss was minimum when the resin precentage was 10. Van Beek[3] has also studied the cure of phenolic resins using ϵ'' as the cure parameter.

In other papers,[6,7] the dielectric strength and related properties of shellac and butylated melamine formaldehyde resin blends as insulating varnishes have been described. In this paper, the dielectric constant and loss of molded precipitates of these varnishes are reported in order to get an insight into the curing mechanism and relaxation behavior of the modified lac.

MATERIALS AND METHODS

Preparation of Specimens. Varnishes (25% solid content in methylated spirit) of different proportions of dewaxed "lemon" shellac and butylated melamine formaldehyde resin (Biomine 1651) obtained from Hardcastle Waud & Co., Bombay, were prepared[6] (Table I). The shellac amino resin

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TABLE I
Sample Characterization

Sample	Shellac content, wt %	Malamine resin content, wt %
SMF 91	90	10
SMF 82	80	20
SMF 73	70	30
SMF 64	60	40
SMF 55	50	50

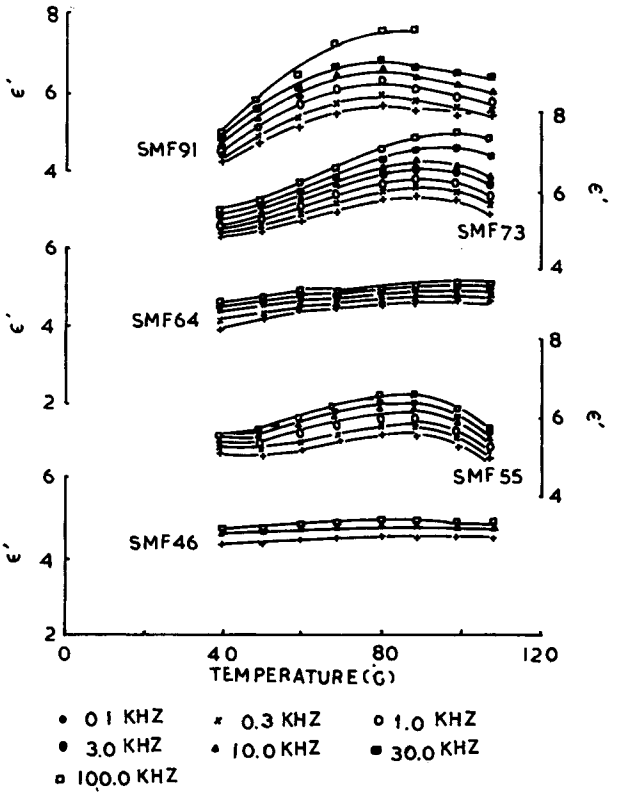

Fig. 1. Variation of dielectric constant of SMF compositions with temperature at different frequencies.

varnish blends, when allowed to air dry at room temperature, become polymerized and hence are of no use for molding purposes. In the course of these experiments, the varnishes were poured into water and the precipitates were dried in air at room temperature for one week before they were powdered. Discs of 10 cm in diameter and 150 mil thick were molded at 120°C and 10,000 lb/sq in. pressure for 10 min and ejected at the same temperature after the prescribed time.

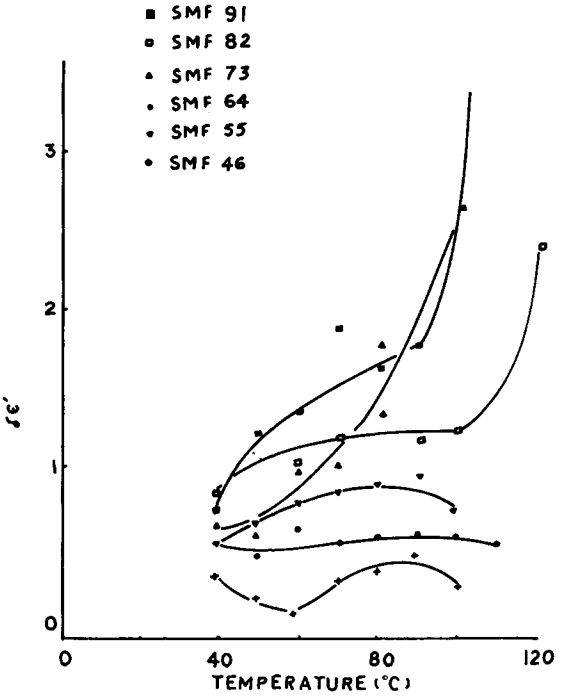

Fig. 2. Dependence of dielectric constant decrement on temperature for SMF compositions.

Electrodes. Tin foil electrodes were used by fixing them on to the surface of the specimen with a thin coat of petroleum jelly.

Conditioning of the Specimens. The specimens were conditioned in an atmosphere of 0% relative humidity for 72 hrs before testing.

Measurement of Thickness. The thickness of the discs was measured using a calibrated micrometer dial gauge capable of measurement precision up to ±0.5 mils.

RESULTS

The ϵ' value of shellac increases with temperature. Similarly, ϵ' of SMF compositions (Table I) also increase with temperature (Fig. 1). On close scrutiny of Figure 1, one finds that the increase in ϵ' for SMF 91 is greater than that of SMF 82, and that of SMF 82 is greater than that of SMF 73, etc., in the temperature range of 40–80°C. Above 80°C, the curves tend to drop to lower values. The dielectric constant decrement between the observable frequency limits as plotted in Figure 2 against temperature reaches a maximum value between 70° and 90°C depending on the composition.

ϵ' decreases with increasing frequency (Fig. 3). The decrement is greater the larger the shellac content of the sample. The decrease is also higher at higher temperatures.

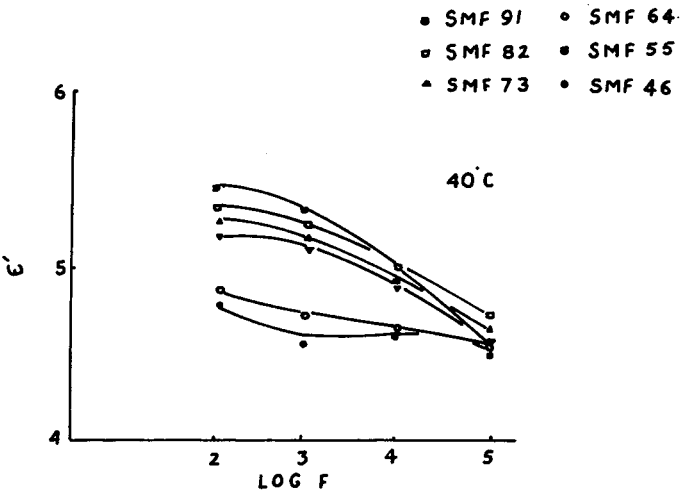

Fig. 3. Dielectric constant–log frequency relation for SMF compositions at 40°C.

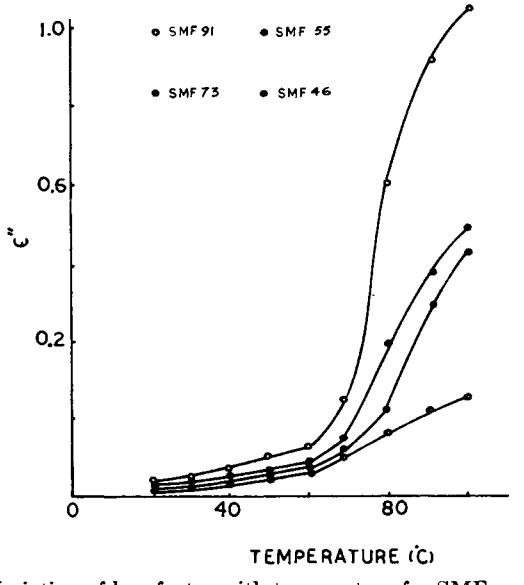

Fig. 4. Variation of loss factor with temperature for SMF compositions.

ϵ'' is plotted against temperature and frequency in Figures 4–7. In ϵ''–log f curves, two relaxations are observable, one in the low-temperature, high-frequency range and the other, in the high-temperature, low-frequency region. Since the relaxations overlap, the picture is complicated. Repeated experiments confirm this behavior.

ϵ' and ϵ'' have been plotted against percentage of shellac in the cured blend in Figures 8 and 9. When the amount of melamine resin in the blend

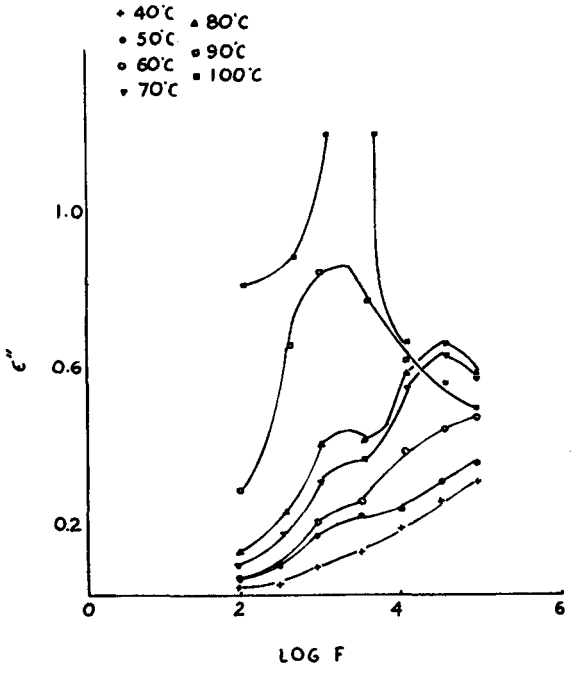

Fig. 5. Variation of loss factor with frequency for SMF 91.

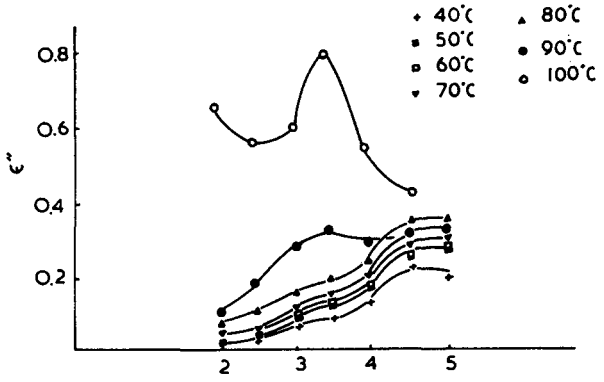

Fig. 6. Variation of loss factor with frequency for SMF 55.

increases, ϵ' and ϵ'' decrease reaching a minimum value for SMF 64, then slightly increasing for SMF 55 and then again decreasing for SMF 46.

DISCUSSION

The rise in ϵ' of shellac with temperature has been ascribed by Bhattacharya[4] to the polar nature of the molecules. That the net rise in ϵ' with temperature decreases when melamine resin is added indicates that the movement of the polar groups is restricted owing to the cure reaction. It

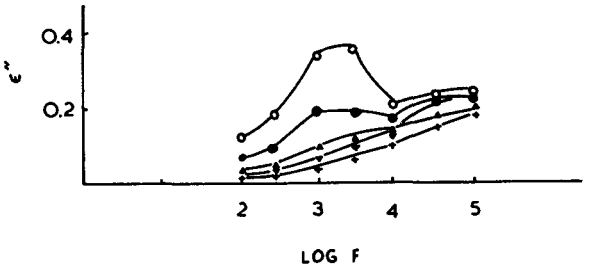

Fig. 7. Variation of loss factor with frequency for SMF 46.

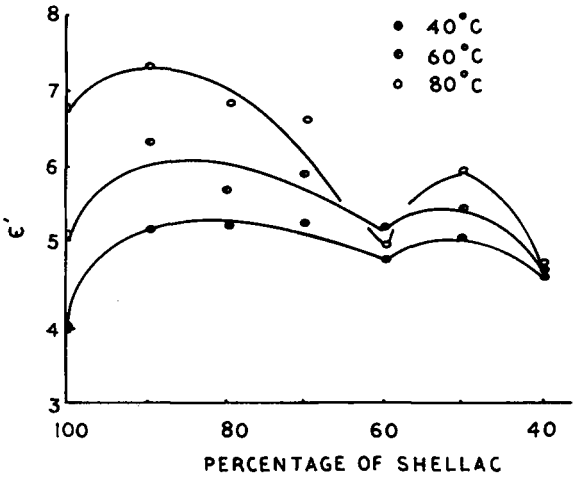

Fig. 8. Dependence of dielectric constant on the percentage of shellac in the blend.

is also evident that the crosslinking increases with the amount of melamine resin in the blend. At low frequencies and at temperatures above 70°C, there is a relaxation observable around 5 kHz. Similarly, at lower temperatures a relaxation is observable around 50 kHz. The loss factor maximum for these relaxations decreases with increasing melamine resin content. It seems that the crosslinking forces weaken, thus resulting in the increase in ϵ' above 70°C.

Bhattacharya[5] suggests that the shellac molecule with the interposition of formaldehyde, urea, or melamine increases so much in size that it becomes less and less probable for it to orient in response to the applied field, owing to the large time of relaxation. There is one more possibility. If we ascribed the rise in ϵ' and ϵ'' to the polar groups, viz., the carboxyl, carbonyl, and hydroxyl groups, then these groups are bound up in such a way that their freedom of movement is very much restricted. With the decrease in the frequency of the applied field, more and more groups can contribute toward the increase of the dielectric constant by aligning themselves as far as possible along the field. It has been postulated that all the groups need not be involved in the cure reaction. Hence, it is always

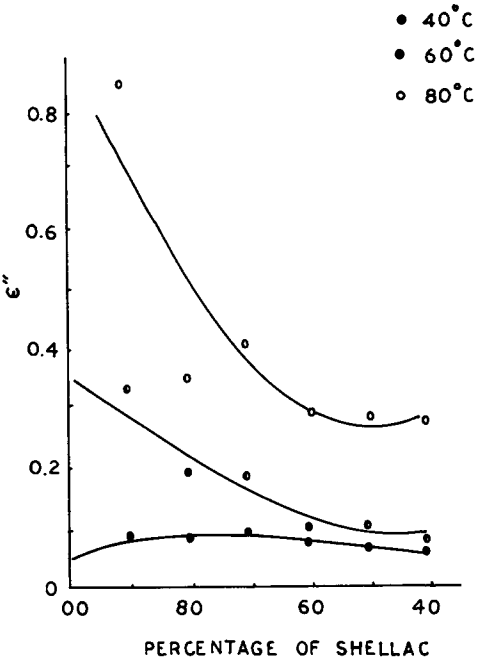

Fig. 9. Dependence of loss factor on the percentage of shellac in the blend.

possible that some groups do remain without involving themselves in crosslinking or mutual curing. These may be contributing to the increase in ϵ' and ϵ'' with temperature and frequency. From the nature of the relaxations, it seems that the relaxation forces are quite weak. The activation energies (Fig. 10) computed for the two processes from the $\log f_m$–$1/T$ curves on the basis of the Arrhenius equation[8]

$$\Delta H \pm = 2.303R \frac{\mathrm{d}\ (\log f_m)}{\mathrm{d}\ 1/T}$$

are only 4.99 kcal/mole for the low-temperature relaxation and 11.1 kcal/mole for the high temperature relaxation. Sasabe et al.[9] have found similar overlapping of relaxation in the case of poly(vinylidene fluoride) at very low temperatures. The calculation of activation energies for the two relaxations in SMF blends has been made difficult owing to the overlapping; and since all the SMF compositions possess nearly the same activation energy, it seems that the energy is not related to the rate of curing.

The plot in Figure 4 shows that the SMF blends exhibit patterns similar to that of an amorphous polymer without flexible side groups,[10–12] with the ϵ'' curve steeply rising from 70°C and practically falling at lower temperatures. We have indicated earlier that crosslinking has bound the main chains in such a way that at temperatures below the glass transition, the loss is low. At glass transition, there is a clear break in the relaxational behavior of the resin. At higher temperatures, ionic conduction also con-

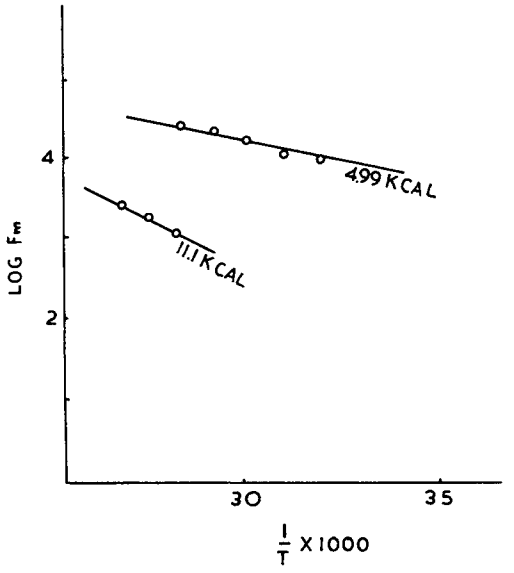

Fig. 10. Log f_m–$1/T$ relation for SMF 64 compositions.

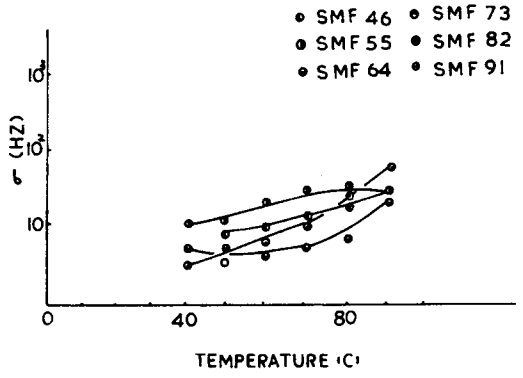

Fig. 11. Variation of frequency half-width of relaxation with temperature for SMF compositions.

tributes to the loss, its share of the total loss increasing with increasing temperatures. The conduction losses decrease with increasing amounts of melamine resin in the blend. The plot in Figures 5–7 show that the loss maxima due to the α and β relaxations decrease with increase in amount of shellac in the blend. This, along with the observation that ϵ'–temperature curves flatten with increasing amount of melamine resin, indicates that the degree of crosslinking increases.

The high-temperature relaxation has been termed β_1 relaxation in the case of polar amorphous polymers, and the low temperature relaxation has been termed β_2. The frequency half-widths for the β_1 relaxation are plotted in Figure 11. The curve shows an inflection point at 65°C. It

TABLE II
Cole-Cole Parameters of Some SMF Compositions

Specimen	Temperature, °C	ϵ_0'	ϵ_∞'	$\epsilon_0' - \epsilon_\infty'$	ϵ_m''	β
SMF 91	40	5.33	3.87	1.46	0.30	0.41
	50	6.35	3.90	2.45	0.36	0.29
	60	6.65	3.80	2.85	0.48	0.34
	70	7.60	3.80	3.80	0.58	0.30
	80	7.90	3.90	4.00	0.56	0.28
	90	8.10	4.70	3.40	0.65	0.38
SMF 82	24	4.72	3.94	0.78	0.18	0.46
	34	5.04	3.94	1.10	0.18	0.33
	40	5.38	3.94	1.44	0.18	0.25
	50	5.40	3.94	1.46	0.22	0.30
	60	6.00	3.80	2.20	0.22	0.20
	70	6.55	3.85	2.70	0.34	0.25
	80	7.60	3.70	3.90	0.35	0.18
	90	7.90	4.50	2.40	0.50	0.41
SMF 73	40	5.45	4.35	1.10	0.25	0.45
	50	5.85	4.35	1.20	0.25	0.42
	60	6.20	4.35	1.85	0.33	0.36
	70	6.65	4.34	2.30	0.40	0.35
	80	7.00	4.35	2.65	0.50	0.37
	90	7.35	4.35	3.00	0.50	0.33
	100	7.60	4.35	3.25	0.60	0.36
SMF 55	40	5.20	4.25	0.95	0.20	0.44
	50	5.35	4.25	1.10	0.23	0.42
	60	5.38	4.25	1.43	0.27	0.38
	70	5.95	4.25	1.70	0.30	0.35
	80	6.20	4.25	1.95	0.33	0.34
	90	6.33	4.25	2.08	0.35	0.34

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becomes evident that some sort of transition is attached with the break in the curve. In this connection, it is of importance to note that there is a sudden shift in the prominence from the β_2 to the β_1 relaxation above 65°C.

The cole-cole[14] parameters for the different blends are as shown in Table II. While there is little difference in the value of ϵ_∞, there is a shift to the right in the case of ϵ_0 with increasing temperature, indicating that the distribution becomes broader and broader as temperature increases. Since, however, there is an increase in ϵ'' correspondingly, there is not much variation in the value of β, as shown in Table II. A plot of β versus T is given in Figure 12. From Table II, one more fact is evident. The average value of β increases with increase in the amount of melamine resin in the blend, indicating that there is a tendency for the concentration of the relaxational forces as the curing increases. It is also found that the

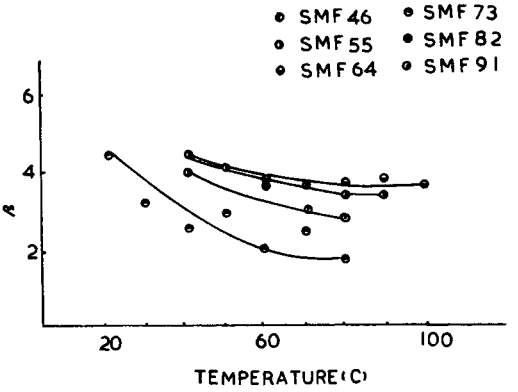

Fig. 12. Variation of dispersion parameter with temperature for SMF compositions.

value of β becomes constant above T_g as in Figure 12. There are instances in the literature[15] wherein the cole-cole distribution parameter has been found to vary with temperature. The anomaly in the value of β above 80°C for SMF 82 can be attributed to direct-current conductivity. Figure 11 shows that the frequency half-width (σ) of the relaxations increase with increase in temperature.

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