Vinyl Ester Resins. II. Effect of Styrene on Electrical Properties

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Synopsis

Bisglycidyl methacrylate of bisphenol A (vinyl ester resin) having systematically varying styrene content was cured by using benzoyl peroxide as a initiator. Thermally stimulated discharge current (TSDC) and ac dielectric measurements of the cured resins were carried out. The polarization of these resins depended on the presence of polar groups and space charge. The lowest dielectric constant was observed with the resin having 30% styrene.

INTRODUCTION

Bisglycidyl methacrylates of bisphenol A (vinyl ester resin) can be used in neat form or it can contain a reactive diluent, such as styrene. Several resin formulations containing different weight fractions of styrene monomer are commercially available. In terms of electrical properties, these resins are medium frequency dielectrics and the dielectric constant ϵ of styrenated resin is reported to range between 3.16 and 3.5.[1] The specific volume resistance is above $10^{16}\ \Omega \cdot$ cm at room temperature and the tangent of the dielectric loss angle, tan δ, is approximately equal to $0.9–2 \times 10^3$. The dielectric losses in these resins are apparently caused by the polar (π) groups of the ester linkage.

The dielectric losses in styrenated vinyl ester resins may be influenced by the weight fraction of styrene. No systematic investigations have been reported in the literature regarding effects of styrene concentration on the electrical properties of cured vinyl ester resins. These studies are relevant for extending the use of such resins in electrical applications. In fact, dielectric constant and loss measurements are important tools to study the dielectric dispersion in a medium. These parameters depend on the molecular structure of δ materials and different dielectric relaxations manifest at different frequencies.[2] At the same time thermally stimulated discharge current (TSDC) measurements are extensively used to study the relaxation properties in the solid state, especially due to their rather exceptional ability for resolving multicomponent or distributed relaxations.[3] Thermally stimulated discharge current (TSDC) and ac dielectric measurements were carried out on vinyl ester films containing a different percentage of polystyrene, and the results are being reported in this paper.

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EXPERIMENTAL

Vinyl ester resin was prepared according to the procedure reported elsewhere.[4] The resin was diluted with styrene so as to get samples having 20%, 30%, 40%, 50%, and 60% of styrene (w/w). Curing of resin containing benzoyl peroxide as catalyst was done at 100°C between glass plates provided with a teflon spacer. Sheets of thickness 0.04–0.05 cm were polarized by subjecting them to a field-temperature treatment. TSDC was measured at a linear heating rate of 4°C/min with a Keithley Model 610C Electrometer. Permittivity and loss tangent was measured as a function of temperature (20–200°C) and frequency (5–100 kHz) by a 1615 Model GEC bridge.

RESULTS AND DISCUSSION

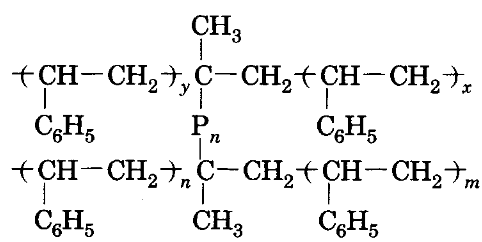
Measurement of thermally stimulated discharge current (TSDC), dielectric constant, and dielectric loss was carried out for various vinyl ester resins containing systematically varying styrene content.

TSDC Measurements

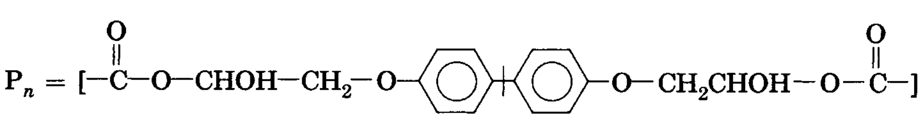
Some of the factors which influence TSDC are (i) backbone structure of the polymer, (ii) field, and (iii) temperature of polarization.[5,6] The effects of these parameters of vinyl ester resins were investigated.

Effect of Structure

Styrenated vinyl ester resin films containing different wt % of styrene were polarized at a fixed temperature (100°C) and field (20 kV/cm) and depolarization current was measured (Fig. 1). A single peak was observed in all the samples. It is obvious that on increasing the styrene content TSDC increases in all these cases except in the sample having 30% styrene. The increase in styrene in cured resins results in a shift in the peak position to higher temperatures in all samples. The crosslink density of vinyl ester resins is reduced by increasing the styrene content (structure I). The flexibility of the backbone is thus increased by incorporation of styrene:



where



(Structure 1)

Crosslinked vinyl ester resin contains polar groups like hydroxyl, carbonyl, and ether. Copolymerization with a nonpolar monomer (styrene) results in

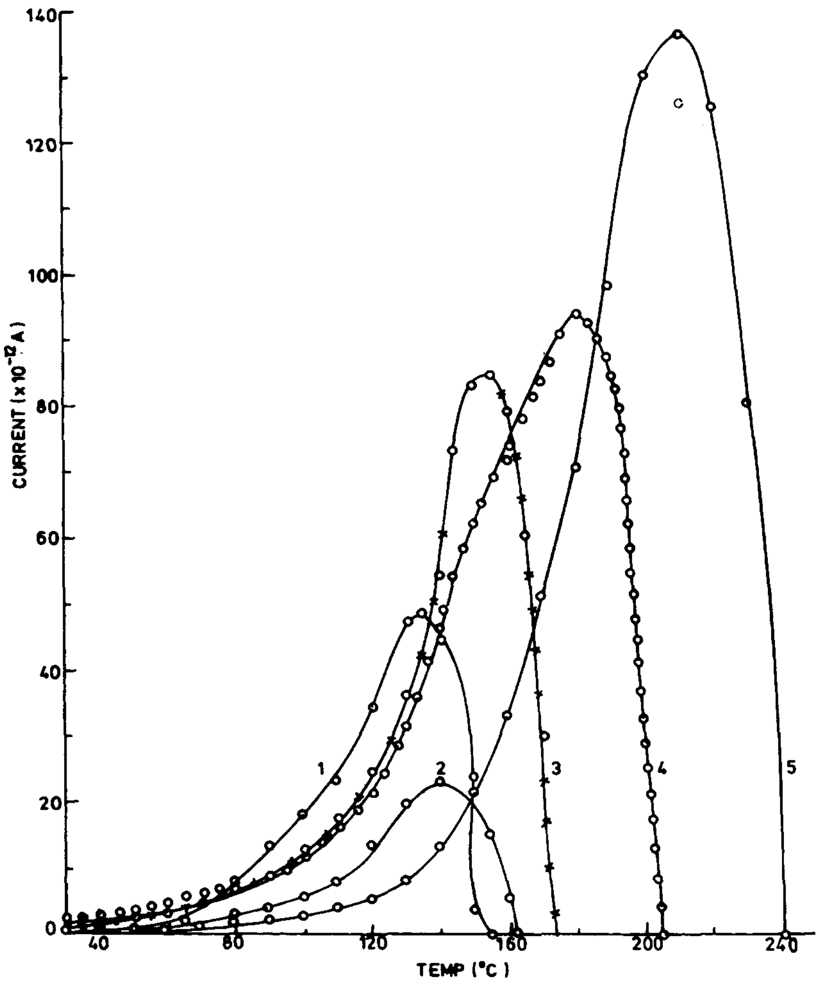


Fig. 1. Plot of depolarization current vs. temperature of vinyl ester resin films containing different percentage of polystyrene: (1) 20% PS; (2) 30% PS; (3) 40% PS; (4) 50% PS; (5) 60% PS.

a decrease in the polarity of the system. An increase in styrene content in vinyl ester resins thus leads to increased flexibility and reduced polarity.

Effect of Temperature

A vinyl ester resin film containing 20% styrene was polarized at 100°C, 120°C, and 140°C by using 20 kV/cm as polarizing field (Fig. 2). Corona charging current has also been observed for the same field and is shown in the same figure. Peak temperature was same for both the cases and was observed at 130°C.

Effect of Field

To study the field effect on the polymer film, it has been polarized at fixed temperature (100°C) by applying 20 kV/cm, 30 kV/cm, and 40 kV/cm field (Fig. 3). No shift has been observed in peak temperature (130°C).

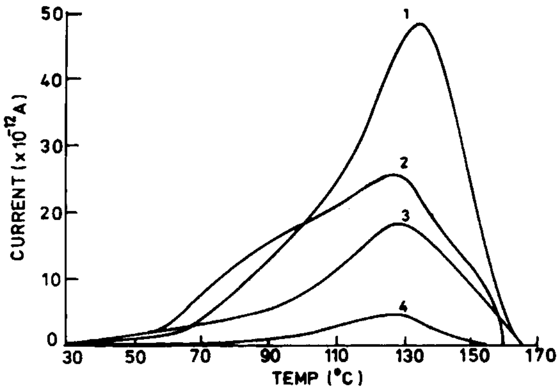


Fig. 2. Plot of depolarization current vs. temperature of vinyl ester resin containing 20% PS at different polarizing temperatures and fixed field 20 kV/cm: (1) 140°C; (2) 120°C; (3) 100°C; (4) Corona charging current.

This peak is, therefore, only due to space charge.

Dielectric Constant and Loss

Tan δ and dielectric constant measurements were done for samples containing different percentage of styrene as a function of frequency and temperature. Typical plots for samples containing 30% styrene are given in Figures 4–6.

It is very clear from Figure 4 that dielectric constant is increasing with decreasing frequency. This shows nonpolarity of the sample. In Figure 5 the maxima which is observed with increasing temperature is because the chaotic thermal oscillations of molecules are intensified and the degree of orderliness of their orientation is diminished.

This causes the curve to pass through maxima and then drop.[7] The molecular flexibility of the chains is perhaps responsible for the peculiar nature of the curve (Fig. 6). The variation of dielectric constant with different

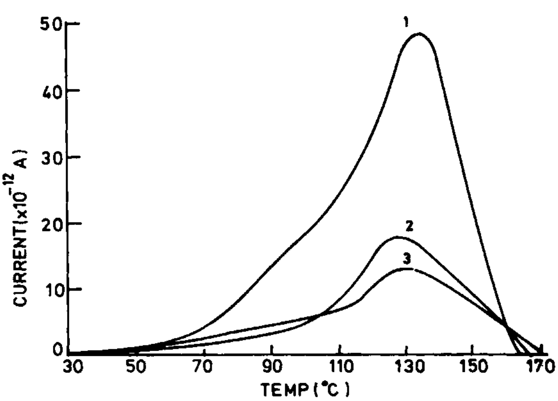


Fig. 3. Plot of depolarization current vs. temperature of VE resin film containing 20% PS at fixed polarizing temperature 100°C and different fields (kV/cm): (1) 40; (2) 30; (3) 20.

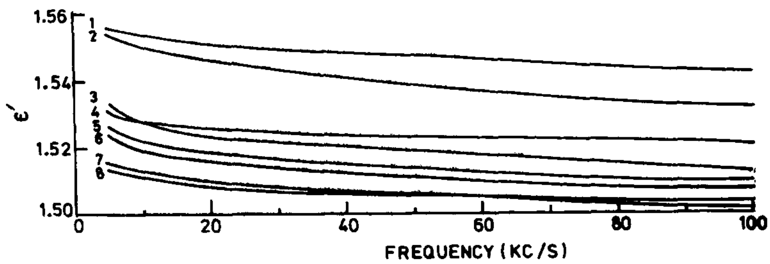


Fig. 4. Plot of dielectric constant vs. frequency at different temperatures of VE resin film containing 30% PS: (1) 40, (2) 20, (3) 160, (4) 60, (5) 140, (6) 120, (7) 100, (8) 80°C.

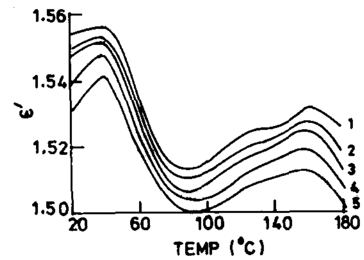


Fig. 5. Plot of dielectric constant vs. temperature at different fixed frequencies (kHz): (1) 5; (2) 10; (3) 20; (4) 50; (5) 100 of VE resin film containing 30% PS.

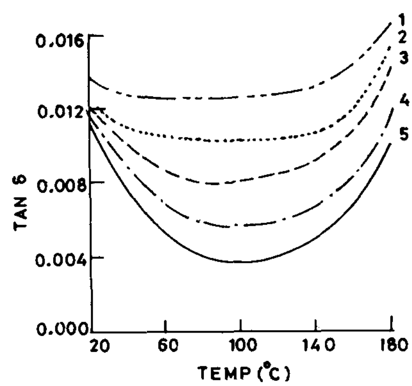


Fig. 6. Plot of tan δ vs. temperature of VE resin film containing 30% PS at different frequencies (kHz): (1) 5; (2) 10; (3) 20; (4) 50; (5) 100. The scale on the *Y*-axis has been shifted to avoid superimposition of points.

percentage of polystyrene at fixed frequencies and temperatures is shown in Figure 7. As is evident from this figure, the dielectric constant increases with percentage of polystyrene except for 30% polystyrene sample in which polarization is minimum. Maximum value of dielectric constant was observed for samples having 50% styrene. Further increase in styrene content had only a marginal effect on dielectric constant. Similar trend was observed in tan δ vs. temperature plots where the value of dielectric loss for 30% styrene was lowest (Fig. 8).

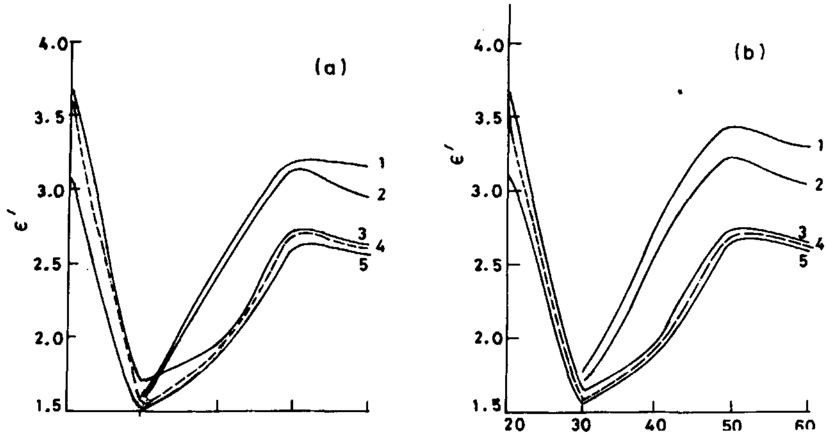


Fig. 7. Plot of dielectric constant vs. different percentage of polystyrene at 5 kHz and 100 kHz: (1), (2), (3), (4), (5) is for different temperatures, i.e., 180°C, 140°C, 100°C, 60°C and 40°C.

CONCLUSION

On the basis of these investigations, it can be concluded that the polarization of vinyl ester resin containing styrene depends on two factors: (a) presence of polar groups and (b) space charge.

At lower styrene content the contribution by the polar groups is significant while at higher styrene content the space charge contribution becomes important.

The lowest dielectric constant was observed with vinyl ester resin having 30% styrene. This formulation, therefore, seems most appropriate for insulation purposes.

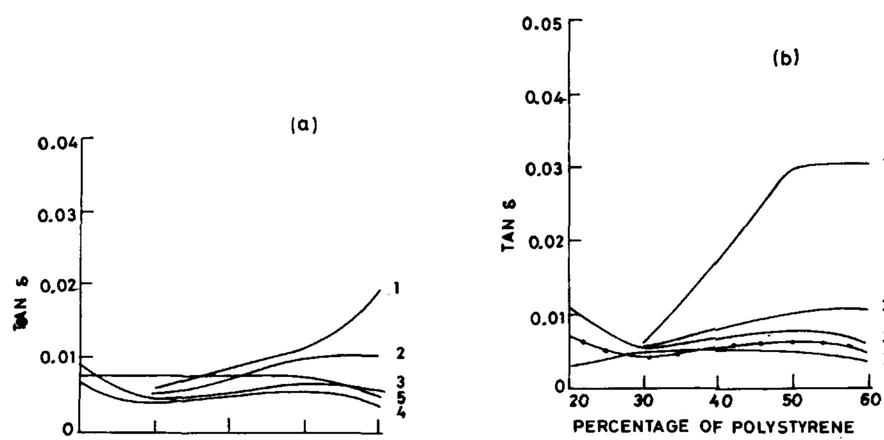


Fig. 8. Plot of tan δ vs. percentage of polystyrene at 5 kHz and 100 kHz: (1), (2), (3), (4), (5) is for different temperatures, i.e., 160°C, 140°C, 120°C, 100°C, and 40°C.

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