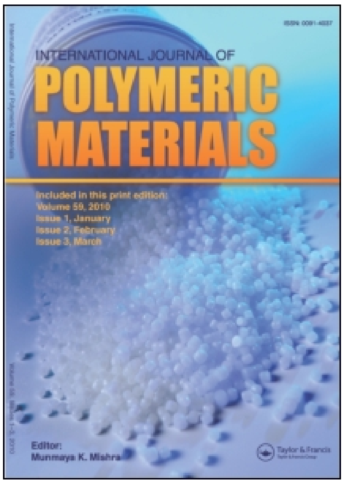

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Dielectric Properties of Polystyrene and Some Related Polymers

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Dielectric Properties of Polystyrene and Some Related Polymers

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Dielectric parameters such as permittivity and loss tangent have been determined for polystyrene, polystyrene-chloranil complex, poly (styrene-chloranil) copolymer, and poly (styrene-allyl alcohol) copolymer. Measurements have been made by a.c. bridge method as a function of temperature, and frequency. The effect of changes in molecular structure of polystyrene by formation of donor-acceptor complex and/or copolymer on dielectric properties have been discussed. The results have been found to be in good agreement with the TSD results obtained previously.

1. INTRODUCTION

Dielectric behavior of a polymer is determined by the charge distribution in its molecules and thermal motion of the polar groups. In a polymeric system, the molecular relaxations correspond to various transitions of the polymer. The main transition exhibited by all the polymers is the second order phase transition, involving transformation from glassy phase to the rubbery region (glass transition). The relaxation at this temperature is a low frequency process (α) and is due to cooperative micro-Brownian motion of the polymer chain or main chain segmental motion. The transitions in the glassy state of the polymers involve local mode molecular motion and are labelled β, γ, δ etc. in order of decreasing temperature (and increasing frequency). Dielectric properties of polymers, investigated as a function of temperature, therefore, undergo a sharp change at the polymeric transitions.

Relaxations in polystyrene and related polymers have been investigated by a number of researchers by different dielectric methods.[1–24] The present paper deals with a.c. dielectric measurements on polystyrene, polystyrene-chloranil donor–acceptor complex, poly (styrene-chloranil) copolymer, and poly (styrene-allyl alcohol) copolymer. Permittivity and loss tangent have been determined as a function of frequency and temperature. The effect of changes in molecular structure on these dielectric parameters has been discussed.

2. EXPERIMENTAL DETAILS

All the samples, except poly (styrene-chloranil) copolymer, were in the form of films with vacuum evaporated aluminium electrodes on both sides. The latter was in the form of a pellet. The details of the materials used and sample preparation are as follows:

Material	Source
Polystyrene (PS)	Shri Ram Institute for Industrial Research, Delhi, India
Choranil (CA)	Merck, Germany
Poly (styrene-allyl alcohol) (PSA)	Polysciences Inc., U.S.A.

Films were cast from solution of polymer in benzene. PS–CA complex[23] was formed by adding 1% (by weight) CA in the benzene solution of PS. PSCA copolymer[25] was prepared in the laboratory by bulk polymerization of styrene and chloranil at 60°C using benzoyl peroxide as initiator. Complex formation and copolymerization were confirmed by absorption studies in the ultra-violet and infra-red ranges respectively.

Capacitance and loss tangent were measured by an L.C.R. bridge (Systronics), which is essentially a Schering type bridge. Measurements were done in the frequency range 310 to 9600 Hz. Temperature region scanned was from room temperature to a highest temperature possible for each material, such that, its thermal history was preserved. Highest temperature investigated for different materials are as follows:

PS:150°C; PS–CA complex:150°C; PSCA copolymer:90°C, and PSA copolymer:70°C.

Voltage applied to the samples in the experiments was 20V r.m.s.

3. RESULTS

Figure 1 is a plot of permittivity and loss tangent, as a function of temperature at fixed frequencies for a PS sample. Permittivity was found to be independent of frequency within the range of investigations. With temperature, its value was observed to diminish. Loss tangent vs. temperature curves show a peak, which shifts to higher temperatures with increase in frequency.

Variation in permittivity and loss tangent with temperature are shown in Figure 2 for PS–CA complex. Permittivity is again independent of frequency and decreases with temperature. Its value is higher than the pure polymer at all temperatures. Magnitude of loss tangent is also higher. The loss peaks have shifted to lower temperatures along with increase in peak width. For example, the loss peak was observed at 137°C for pure PS, whereas for the complex it has come down to 108°C at 310 Hz.

Figure 3 shows the effect of copolymerization of PS with CA on its dielectric parameters. Permittivity is still independent of frequency, but with temperature it increases. Its magnitude at room temperature is lower than pure PS as shown in Figure 1. But it is not so, because, for PS polymerized from

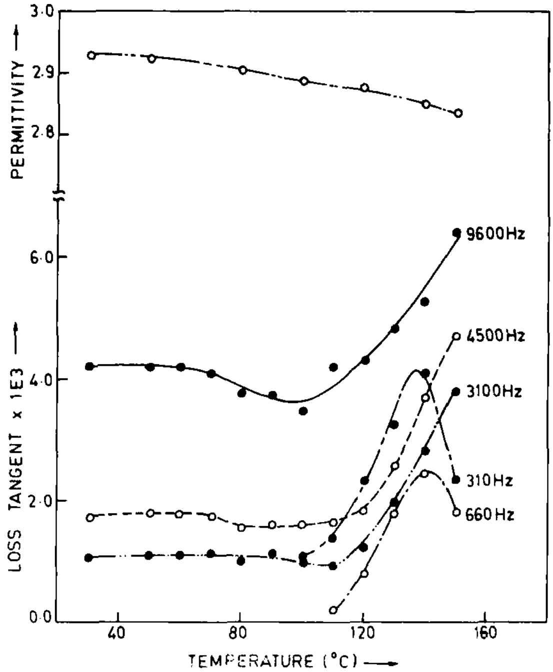

FIGURE 1 Permittivity and loss tangent of polystyrene as a function of temperature.

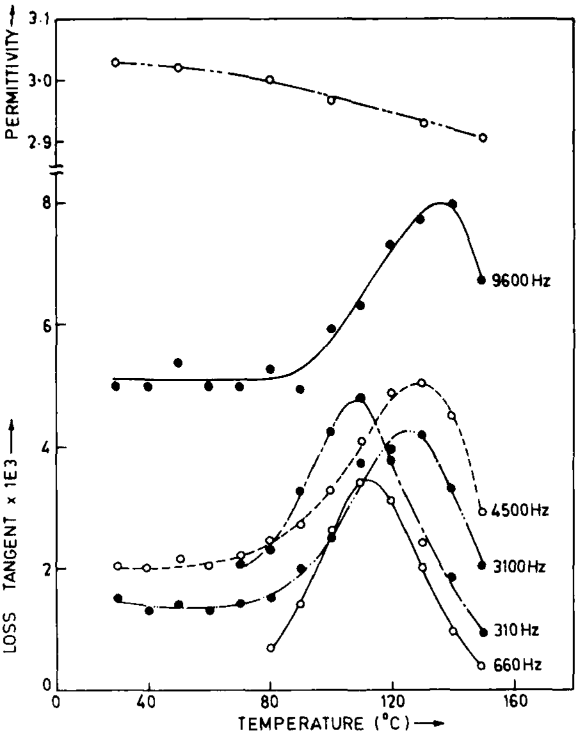

FIGURE 2 Permittivity and loss tangent of polystyrene-chloranil complex as a function of temperature.

same styrene as used in polymerization of PSCA copolymer, the room temperature value is 2.71, where as for the copolymer it is 2.86. Loss tangent is seen to increase with both temperature and frequency and its magnitude is higher by one order. No loss peak is observed up to 90°C.

The results of permittivity and loss tangent measurement for PSA copolymer are shown in Figures 4 and 5. Permittivity for this copolymer is temperature as well as frequency dependent. Increase in frequency lowers the values of permittivity and loss tangent, whereas the effect of temperature rise is to increase them.

4. DISCUSSION

Polystyrene is a high resistivity and weakly polar material with a very small dipole moment of 0.2 Debye associated with its phenyl groups.[1] Therefore, dielectric loss in this material is expected to be very small. Frequency inde-

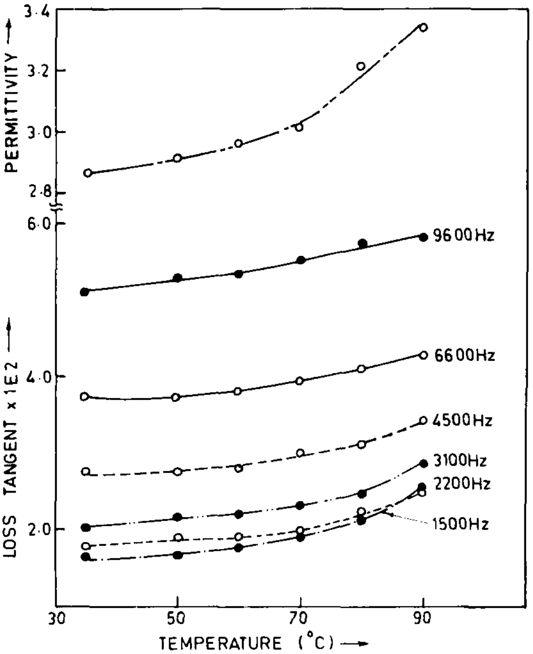

FIGURE 3 Permittivity and loss tangent of poly (styrene-chloranil) copolymer as a function of temperature.

pendence and decrease with temperature of permittivity is in accordance with dielectric behavior of non polar materials.[26] The difference in magnitudes of permittivity for samples from two different sources can be due to presence of trace impurities. Dielectric losses under alternating voltage arise due to absorption of energy coupled with polarization in the medium and Joule loss due to conduction current. Losses due to dipolar polarization reach maximum at relaxation temperatures (which depend on material, and applied frequency) and then fall. On the other hand, conduction losses grow with increase in temperature. The loss peak observed in the plot of loss tangent vs. temperature (Figure 1) corresponds to the α relaxation process of PS.[23] The frequency dependence of relaxation temperature is a characteristic of temperature activitated processes. Conduction losses are observed clearly after the α loss peak. In PS, these losses would be observed at temperatures above 150°C.

On formation of a donor–acceptor complex with CA, the permittivity and loss tangent of PS are increased (Figure 2). The complex formation is accompanied by increase in dipole moment, and conductivity of the polymer and thus causing the above changes in dielectric parameters. The increase is small as the PS–CA complex is a weak π:π complex.[27] On the other hand the

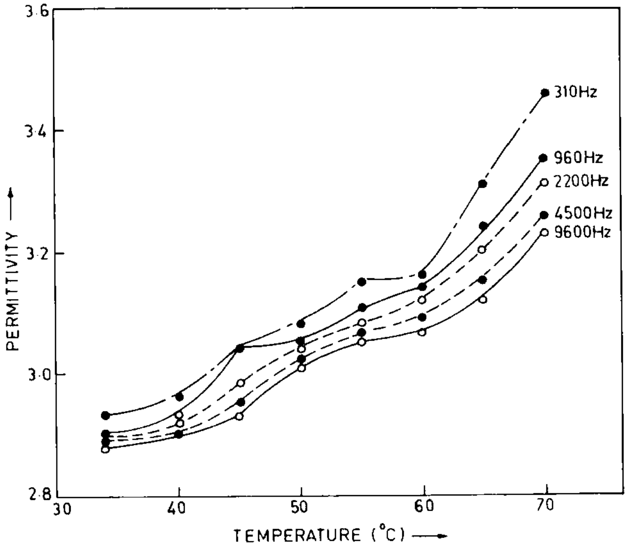

FIGURE 4 Variation in permittivity of poly (styrene-allyl alcohol) with temperature.

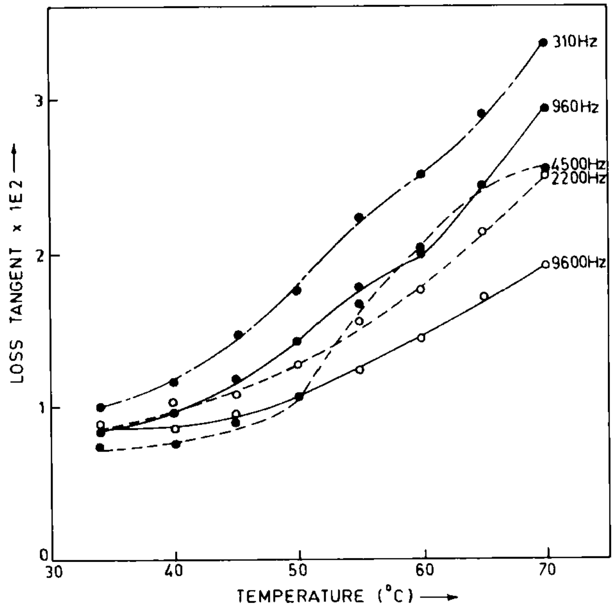

FIGURE 5 Variation in loss tangent of poly (styrene-allyl alcohol) with temperature.

lowering of loss peak temperatures is quite appreciable and is linked with increase in free volume of the polymer due to addition of low molecular weight dopant.[28] Variation of permittivity with frequency, and temperature is same as that of non polar dielectrics. Increase in peak width suggests increase in distribution of the α relaxation, again a consequence of doping with low molecular weight material. The TSD results of PS, and PS–CA complex have been compared with a.c. dielectric measurements in an earlier paper.[23]

On copolymerization with CA, there is increase in polarization of PS, as indicated by the dielectric behavior of PSCA copolymer (Figure 3). This is reflected in rise of permittivity with temperature and increase in loss tangent by an order of magnitude. The increase in dipole moment of PS on formation a complex with CA is due to the donor–acceptor interaction between the phenyl rings of PS and the CA molecules. In PSCA copolymer there is no such interaction as the CA molecules are now in the main chain. CA molecule has symmetric structure and therefore, theoretically should have zero dipole moment. Thus for PSCA copolymer also dipole moment should be zero except for small non zero moment associated with the phenyl groups. However, experimental results speak against this. For *p*-benzoquinone, which has similar symmetrical structure as CA, dipolar polarization has been observed.[29] TSD analysis of CA pellets[30] have also revealed dipolar dipolarization. Polarization in electrets of PSCA copolymer[31] also was partly due to dipoles rest being ascribed to space charge polarization. Space charge polarization in the copolymer is expected to be quite large compared to pure PS. This being due to increase in conductivity of the copolymer (as CA has higher conductivity than PS) and hence greater accumulation of space charges.

Dependence of permittivity on frequency (dielectric dispersion), and temperature shown by PSA copolymer is characteristic of polarization in the medium. This polarization may be dipolar and/or due to space charges. When the frequency of the applied voltage is increased, at a certain characteristic frequency (which is a function of temperature) the polarization fails to keep up and permittivity begins to fall. Dispersion regions of space charge, and dipolar polarization are different. The former is at lower frequencies than the latter. TSD results for PSA electrets[32] give evidence for both type of polarization. As only one dispersion region has been observed, it may be associated with dipolar polarization. The other dispersion region would be observed at frequencies lower than the investigated range. Increase in temperature facilitates the orientation of dipoles and increases the number and mobility of charge carriers, thus increasing polarization of the medium. This explains the increase in permittivity with temperature. Dipolar polarization in PSA is due to the presence of polar OH groups (dipole moment ~ 1.50 Debye).[26] Space charge polarization was observed to be due to trapping of charge carriers at various molecular sites and crystalline-amorphus interfaces.[32]

Dielectric loss peaks are observed only for certain combinations of frequency and temperature. For PSA (and also PSCA copolymer), the dipolar loss peaks would be observed at higher temperatures in the investigated range of frequency or at lower frequencies in the experimental temperature range. This was indicated by TSD analysis also. For example, for PSA electrets[32] relaxation time of dipoles at room temperature was about 1.5E3 sec which would correspond to a frequency of the order of E–4 Hz.

5. CONCLUSIONS

Dielectric properties of polystyrene are transformed to various extents by doping and copolymerization. On doping with chloranil, changes in dielectric properties are small as the complex formed is not very strong. Introduction of chloranil in the polymer main chain (i.e. copolymerization of styrene and chloranil), brings a much larger transformation in the dielectric properties. Poly (styrene-allyl alcohol) on the other hand was observed to have the typical character of polar materials.

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