JOURNAL OF MATERIALS SCIENCE 14 (1979) 2791–2796

The effects of plasticizer on the electric strength of polystyrene

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Measurements made on polystyrene samples indicate that a marked reduction in electric strength occurs at a critical temperature which is indistinguishable from the glass transition temperature determined by differential thermal analysis. Both the electric strength and the critical temperature are shown to be dependent on the presence of plasticizing agent in the polymer. X-ray analysis of both plasticized and unplasticized materials over a range of temperature indicates changes of inter-molecular distance supporting the hypothesis that the action of the plasticizer is to influence the free volume exhibited. The experimental results are discussed and analysed on the basis of a free volume approach.

1. Introduction

In a previous paper [1] the study of a range of co-polymers provided good evidence that the electric strength of polymeric materials was intimately associated with molecular structure and movement. Specifically, the temperature, T_c, at which a marked reduction in strength is observed was found to be indistinguishable from the glass transition temperature, T_g, of the materials. Furthermore, it was suggested that the free volume exhibited by a polymer was responsible for the behaviour observed. On this basis, the use of plasticizers to modify the mechanical properties of polymers may be expected to affect their electrical properties, although the idea has not attracted much previous attention. In this respect, the interpretation of plasticizer effects is still lagging behind technical developments in the cable industry.

The material chosen for study is atactic polystyrene, being an amorphous non-polar polymer uncomplicated by any partial crystallinity.

2. Characterization of the atactic polystyrene

The important characteristics of the two polystyrene materials investigated are listed in Table I. The effect of the plasticizer present in PS(B) is seen to change both the melt flow index and Young's modulus. The materials were moulded at 135° C by subjecting them to a pressure of 6.4 MN m^{-2} between Melinex foils.

2.1. Plasticizer content

The presence of plasticizer in PS(B) has been confirmed by a comparison of the infra-red spectra of the two materials. The absorbtion bands show characteristic differences at 5.78, 7.81 and 8.93 μm. The intensity of the first band is likely to be attributed to stretching vibrations of C=O groups and the other two to C—O groups [2] suggesting the plasticizer is of ester type. A chemical analysis carried out by an extraction and recovery process provided an estimate of 2.7% by weight as the amount of plasticizer present. Subsequent infra-red analysis of the extract would indicate that the plasticizer present is probably dibutylphthalate C_6H_4 $(COOC_4H_9)_2$. On this assumption, the amount of plasticizer present was also determined by gel-permeation chromatography and found to be of the same order.

2.2. Molecular weight determination

The molecular weights of the two materials have also been estimated by gel-permeation chromatography. The number-average $\bar{M}_n$, and weight-

0022–2461/79/122791–06$02.60/0

TABLE I Characteristic properties of unplasticized, PS(A), and plasticized, PS(B), polystyrene samples

Property	PS(A)	PS(B)
Density (g cm^{-3})	1.05	1.05
Melt flow index (g/10 min)	1.1	9.0
Young's modulus (N mm^{-2})	3500	3400
Dissipation factor at 10^6 Hz	1.4×10^{-4}	1.4×10^{-4}
Dielectric constant at 10^6 Hz	2.5	2.5
$\bar{M}_n \times 10^5$	1.614	1.150
$\bar{M}_w \times 10^5$	3.341	2.890
$\bar{M}_w/\bar{M}_n$	2.07	2.51

average molcular weight. $\bar{M}_w$, are given in Table I. However, it may be inferred from the fact that $\bar{M}_w/\bar{M}_n > 2$ that these materials are polydisperse [3].

2.3. Differential thermal analysis (DTA)

Since structural parameters such as cohesive energy density, free volume and related molecular motion are believed to play a dominant role in the temperature dependence of electric strength [4], it is essential to determine the glass–rubber transitions for both the unplasticized and plasticized polystyrene. This was accomplished by detecting the differential endothermic changes with respect to an inert reference using a duPont-900 thermal analyser. The DTA thermograms are shown in Fig. 1 and result from measurements carried out on 6 mg samples with a temperature rate of rise of 5° C min^{-1}. The constructions shown by broken lines indicate the position of the glass transition temperatures, T_g, which are reproducible to ± 1° C.

3. Electric strength measurements

Direct voltage electric strength measurements were undertaken on PS(A) and PS(B) at discrete temperatures chosen to lie near, above and below the glass transition region determined from Fig. 1. Below T_g, the electric strength of polystyrene is known to be substantially independent of temperature [5] and for PS(B) measurements above 90° C are limited by the softening of the polymer. The meticulous sample preparation of the recessed specimens used and the experimental procedure were as previously described [1]. The results obtained from these measurements are summarized in Table II. A linear gap dependence at room temperature for both materials is depicted in Fig. 2 and justifies confidence in the techniques adopted.

It is considered that the marked drop in electric strength evident at elevated temperatures for both these low-loss materials cannot be explained by the onset of thermal breakdown. The critical temperature at which the characteristic drop in strength is observed changes in a predictable way for styrene/butadiene co-polymers as the percentage of bound styrene is altered [1]. Since there is no deviation between the experimental critical temperatures and those predicted from −93° C (polybutadiene) to + 85° C (polystyrene) it is extremely unlikely that thermal breakdown can intervene for the higher temperature measurements.

Introduction of a polar plasticizer will undoubt-

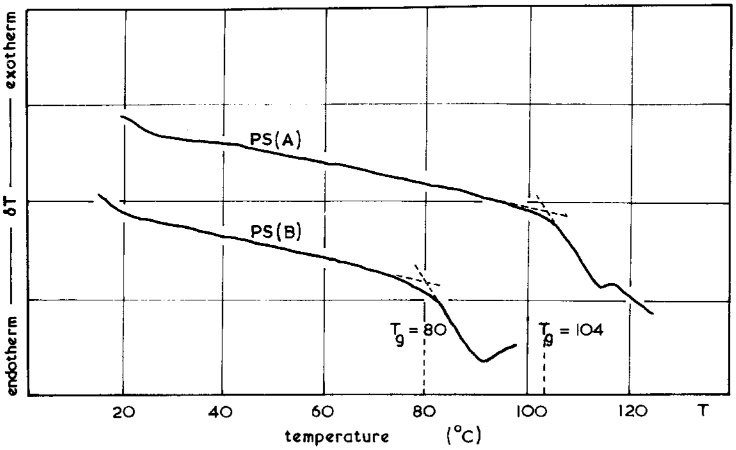

Figure 1 Data thermograms for PS(A) and PS(B). Heating rate 5° C min^{-1}.

TABLE II Electric strength data for samples of PS(A) and PS(B)

Polymer	Temperature (0° C)	Electric strength (MV cm^{-1})			No. of samples	Standard deviation
		Min	Mean	Max		
PS(A)	21	6.35	6.79	7.42	15	0.3 (5%)
	90	5.47	6.73	7.57	10	0.6 (8%)
	100	5.78	6.39	7.05	8	0.4 (6%)
	110	2.58	2.93	3.14	7	0.2 (6%)
PS(B)	22	4.79	5.71	6.56	13	0.5 (8%)
	80	5.50	6.02	6.44	8	0.3 (6%)
	90	3.39	4.03	4.59	10	0.3 (8%)

edly increase the dielectric loss. Fuoss [6] has shown that the presence of a polar solute in a polystyrene matrix increases the magnitude of the high-frequency absorption peak due to the relaxation of solute molecules. At low frequencies this effect is much reduced, although the plasticizer might perhaps be expected to show an additional small loss due to interfacial polarization. For the d.c. conditions used in this work, however, conduction losses will predominate since they are sensitive to impurities. Although the attendant lowering of the d.c. volume resistivity increases the loss, previous studies [7] show this has little significant effect on electric strength. Furthermore, similar measurements taken on polymers with substantially greater losses than polystyrene reveal the existence of a quasi constant plateau above the critical temperature which cannot be explained by a thermal instability [5].

4. X-ray study

The X-ray diffractions of a perfect crystal display sharp and distinct patterns from which the interplanar distances can be deduced on the basis of Bragg's law. Completely amorphous polymers on the other hand reveal X-ray patterns which consist of one or more broad diffuse haloes (maxima) indicating a lack of long-range molecular order [8]. However, these haloes may be interpreted as corresponding to distances frequently occurring between molecules, atoms or ions. Amorphous polystyrene patterns at room temperature invariably display two broad haloes. The innermost one is less intense and corresponds to the average interchain distance, while the other halo is usually related to distances between the phenyl groups.

4.1. Experimental procedure and results

The diffraction diagrams were obtained using a Philips PW 1010 X-ray generator with a vertical goniometer allowing angular adjustment to within 0.05°. The nickel-filtered Cu$K\alpha$-radiation used had a wavelength, $\lambda = 1.54$ Å and an intensity constant to within ± 1%.

A special heated radiation-proof sample holder was designed to allow a 200 mg powdered sample to be irradiated at temperatures up to 135° C. No internal standard was used. Temperature control to within ±0.5° C was achieved by an embedded

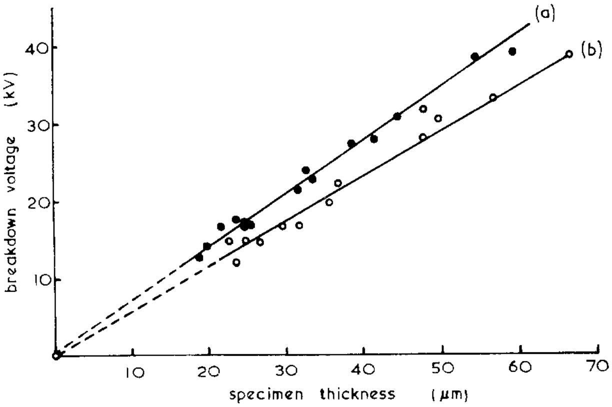

Figure 2 Breakdown voltage as a function of specimen thickness at room temperature (a) PS(A); (b) PS(B).

thermocouple. The powdered samples were scanned through scattering angles between 5° and 14° where only the inner peak appears. A low scanning speed ($\frac{1}{4}$ deg min^{-1}) was chosen to attain a high resolution and the broad peaks pinpointed by additional 10 sec counts. Typical peak-to-background count ratios were of the order of 2.75 and in every case the peaks were over 8 standard deviations above the background count level. The average interchain distance d_a for both PS(A) and PS(B) has been determined from the location of the peak scattering angles, θ_{max} on the basis of the relationship due to Guinier [9].

$$d_a = 1.22\,\lambda/2\sin\theta_{max}. \qquad (1)$$

The reciprocal values, d_a^{-1}, have been plotted at a function of temperature in Fig. 3, together with mean electric strength figures from Table II.

5. Interpretation

The results of Section 3 imply that the addition of plasticizer into the pure polystyrene affects the electric strength in two ways:

(a) there is a considerable shift in critical temperature towards a lower value;

(b) there is a reduction in electric strength over the entire temperature range.

The change in glass transition temperature brought about by increasing the percentage of bound styrene in a styrene/butadiene co-polymer referred to in Section 3, is mirrored by a shift in the critical temperature marking the onset of an abrupt change in electric strength. It is considered in this case that the plasticizer is having a similar effect and it is no coincidence that the transition temperatures obtained by thermal, X-ray and electric strength measurements are almost identical for both PS(A) (~ 100° C) and PS(B) (~ 80° C).

It is clear from Table I that one effect of the plasticizer is to reduce the molecular weight of the material. According to Fox and Flory [10], the value of $T_g(m)$ for a polymer of finite number average molecular weight $\bar{M}_n$ may be estimated from

$$T_g(m) = T_g^{\infty} - A/\bar{M}_n \qquad (2)$$

where T_g^{∞} is the glass transition temperature of a polymer of "infinite" molecular weight. Most commercially available high polymers ($\bar{M}_n > 80\,000$) attain their T_g^{∞} provided they are unplasticized. Although it is clear that Equation 2 is intended to provide a basis for estimating T_g for large changes in $\bar{M}_n$, it is instructive to apply it to the present case. Using available constants for polystyrene ($T_g^{\infty} = 100 \pm 2°$ C; $A = 1.7 \times 10^5$) it would appear that the change in molecular weight *per se* is not sufficient to explain the experimentally observed shift in critical temperature for the plasticized material and an alternative explanation must be sought.

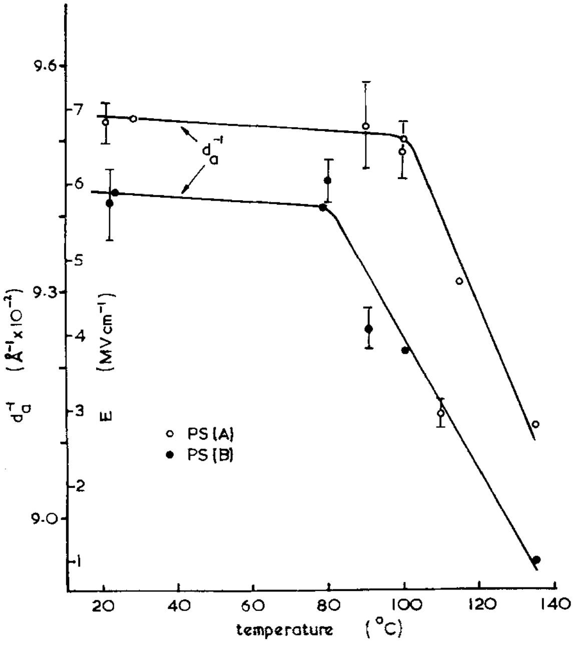

Figure 3 Reciprocal values of the average interchain distance, d_a, as a function of temperature. (Electric strength data from Table II superimposed.)

The X-ray results make it clear that the average spacing, d_a, of PS(B) is always larger than that of the pure PS(A) sample. In this context one may speculate that the infiltered plasticizer molecules between the macromolecules tend to neutralize some of the intermolecular cohesive energy of the original polymer. This would automatically create an increase in interchain distance since the intermolecular energy $U(d_a) \sim d_a^{-6}$. Furthermore, the consequent loosening of the structure would reasonably allow more freedom for segmental mobility at a still lower temperature and thus explain the reduction in T_g.

This action of the plasticizer may be visualized as the creation of additional free volume in the system. Utilizing the approach of Kelley and Bueche [11] for predicting the glass transition temperature of polymer-diluent systems:

$$T_g = \frac{[v \cdot \Delta\alpha_u \cdot T_{gu} + (1-v)\Delta\alpha_d T_{gd}]}{[v \cdot \Delta\alpha_u + (1-v)\Delta\alpha_d]} \quad (3)$$

where v is the volume fraction of the polymer, $\Delta\alpha_d$, T_{gd} and $\Delta\alpha_u$, T_{gu} are the differential thermal coefficient of expansion and glass transition temperatures of plasticizer and pure polymer respectively. Substituting appropriate values for polystyrene with dibutylphthalate as plasticizer [12, 13], the transition temperature of the plasticized material is found to be ~87° C. The difference between the calculated and measured values is likely to result from both the empirical method and difficulties is accurately estimating the proportion of plasticizer present.

For temperatures below the transition region, the electric strength is determined by the energy exchange between the accelerated conduction electrons and the polymer structure. The increase of free volume in the PS(B) material would inevitably increase the electron mean free path and provide more suitable conditions for the attainment of the higher energies required for breakdown. Not only would a lower electric strength be expected on this basis for the plasticized material, but, since neither the amount nor the distribution of free volume is temperature dependent below T_g, the observed constancy of strength is also explained.

Above the respective critical temperatures, the fractional free volume is increased and redistributed. This may be expected to cause the marked reduction in electric strength evident from Table II in a way determined by the variation of free volume and the molecular relaxation time. On the basis of a free volume theory, Artbauer [5] has ascribed the electric strength, E, of a non-polar, amorphous polymer as

$$E = \Delta w/e \cdot l_x \quad (4)$$

where Δw is the energy increment of the conduction electrons after passing through a free volume whose average field directed length is l_x. The characteristic length l_x is related to the specific

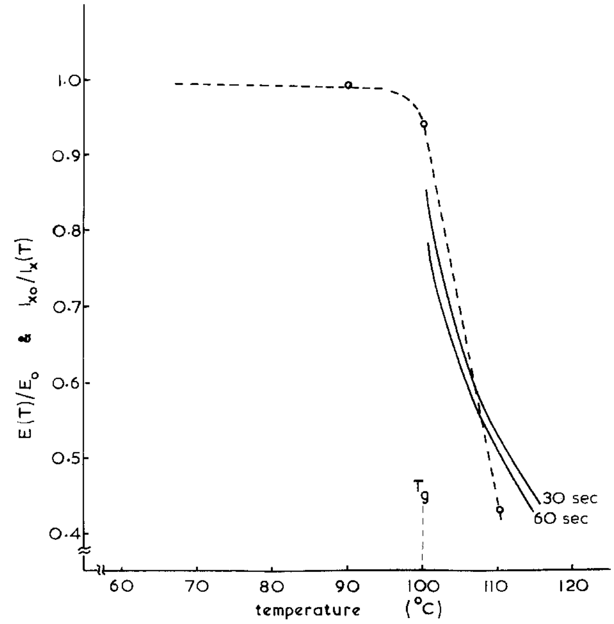

Figure 4 Comparison between the theoretical value of $l_{x0}/l_x(T)$ and the experimental electric strength ratio $E(T)/E_0$ for polystyrene PS(A). Broken lines: experimental; solid lines: theoretical.

free volume f as follows:

$$l_{x0} = k.d. \quad 1 - \frac{\log (a \cdot f_0)}{\log [1-(1-f_0)^6]} \quad T < T_g \tag{5}$$

$$l_x(T) = k.d. \quad 1 - \frac{\log (af^2(T) \cdot t/\tau(T))}{\log [1-(1-f(T))^6]} \quad T > T_g \tag{6}$$

where d is the diameter of an individual hypothetical spherical void, t the stressing time, τ the molecular relaxation time and k and a are constants. The variation of f and τ with temperature above T_g may be predicted on the basis WLF theory (Williams, Landel and Ferry) [14]. The free volume, f, exhibited for $T > T_g$ is dependent on the difference between the expansion coefficients above and below T_g thus making the free volume approach entirely consistent with known changes of density with temperature [15]. Equations 5 and 6 may then be used with Equation 4 to predict the temperature-dependent change in electric strength $E(T)$ relative to a value E_0 below T_g. Using the appropriate available constants for unplasticized polystyrene [12], such a prediction has been made in Fig. 4 for PS(A) for typical stressing times of 30 and 60 sec. Comparison of this rudimentary theory with the experimental results adds evidence to the idea that free volume is exercising an overriding effect on the breakdown of the polymer.

Acknowledgements

The authors are indebted to the University of Damascus for the provision of a study grant (H.S.).

Thanks are also due to the Rubber and Plastics Research Association for help in the determination of molecular weights. Help from the Departments of Geology and Materials at Queen Mary College is also gratefully acknowledged.

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Received 6 February and accepted 19 April 1979.