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Thermally stimulated discharge in polymer electrets: Compatibility and impurity effects

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Polymer electrets have been prepared and studied by measuring thermally stimulated discharge currents. Two current maxima have been observed for samples of polystyrene, poly(*p*-chlorostyrene), and a random copolymer of styrene and *p*-chlorostyrene. These maxima are attributed to dipole reorientation accompanying the glass transition and to real charge drifts. Poly(2,6 dimethyl-1,4-phenylene oxide) and blends of this polymer with the three aforementioned polymers were also studied. In these systems unresolved and nonreproducible peaks were obtained, and these difficulties have been attributed to impurities present.

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INTRODUCTION

Permanent polarization may be induced in polymeric dielectrics, such materials being then referred to as electrets. This charging can be accomplished by a variety of treatments, including electron bombardment or exposure of the dielectric to a strong dc field at high temperatures followed by cooling in the presence of the field. The mechanisms of charge storage are manifold. Charge may be injected from the electrodes into the dielectric—this process being referred to as a homo-charge. The resulting electret has the same polarity as the adjacent forming electrode. Conversely, a hetero-charge results from the alignment of dipoles or from the drift of real charge leading to a space-charge polarization. With heterogeneous systems interfacial polarization contributes to the total effect.

The thermally stimulated discharge (TSD) technique for the investigation of the properties of polymer electrets has been described in the literature.¹⁻⁴ The electret film is short circuited through a sensitive ammeter, and the temperature of the film is increased at a constant rate. The areas under the resulting time- or temperature-vs-current plots can be integrated to determine the total charge released. Depending on the decay process and its efficiency in releasing charge, the current passing through the ammeter will be equal to or less than the net polarization of the electret film. In most cases, a number of maxima attributable to different depolarization processes will be observed. Such peaks may in some cases be resolvable and can be correlated with a known relaxation process. In favorable cases, other parameters including the apparent activation energy for a given relaxation process can be calculated.⁵

In this study, primary emphasis has been on TSD current maxima associated with the randomization of dipoles oriented during polarization. For this relaxation, the efficiency of short-circuit charge release is 100%⁴; the image charge that flows through the ammeter is equal to the heterocharge polarization due to dipole alignment. The temperature at which these peaks are observed is associated with the glass transition temperature of the given polymer. Dipole reorientation may be compared to the current arising from the drift of real charge. In the latter process the polarization is dissipated by Ohmic conduction in the polymer and other

charge recombination events. The highly temperature-dependent conductivity of the polymer now becomes important, hence the nature of impurities present and sample dimensions may play a role.

The system investigated using the TSD technique were the individual species and blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polystyrene (PS), poly(*p*-chlorostyrene) (PpClS), and a random copolymer of styrene and parachlorostyrene (pClS-coS). The blends of PS and PPO have previously been found to be completely compatible throughout the entire composition range.⁶⁻⁸ In contrast, PPO and PpClS are immiscible.⁹ The compatibility of the pClS-co-S copolymers with PPO depends on the fraction of styrene in the copolymer. An abrupt transition from a miscibility to immiscibility regime occurs when the *p*-chlorostyrene content exceeds about 65 mole%.⁹ It was therefore the primary purpose of this study to determine the information that the TSD technique can yield on the compatibility of these polyblend systems.

EXPERIMENTAL

The equipment used for this study was the Electret Thermal Analyzer, manufactured by Toyo Seiki Seisaku-Sho, Ltd. It was made available for our use by Atlas Electric Devices Co., Chicago, Ill. It consists largely of a vacuum chamber containing a heating element, thermocouples, and the sample cell with gold-plated electrodes. Discharge currents are measured using a Keithly model 410A picoammeter; other ancillary components include a temperature programmer, dc power supply, and a dual-channel strip-chart recorder.

PPO was supplied by the General Electric Co. through the courtesy of Dr. A. Katchman. The PS used was Monsanto HH101 resin. The (pClS-co-S) copolymer was prepared in these laboratories using free-radical initiation with AIBN. Its *p*-chlorostyrene content, determined by elemental analysis for chlorine, was 50.1 mole%; this polymer thus lies within the range of compatibility with PPO.

All polymers were first purified by dissolution in toluene and reprecipitation into methanol. The blends were prepared by a second dissolution of the respective constituents in toluene, with subsequent coprecipitation

FIG. 1. TSD of PS: $T_p = 134^\circ\text{C}$, $E_p = 25\text{ kV/cm}$.

into methanol. After vacuum drying for 48 h at 110°C , films 0.005-in. thick were prepared by compression molding of the appropriate polymers or blends above their T_g 's. Some specimens received gold-evaporated electrodes.

Samples were heated in the chamber to the desired polarization temperature T_p . A dc field of strength E_p was then applied. After $\frac{1}{2}$ h the power to the heater was withdrawn, and the sample and cell were allowed to cool to ambient temperature. The field was then removed, and a programmed heating at 2°C/min was immediately begun. The sample was enclosed in a nitrogen atmosphere at ambient pressure during the entire measurement cycle.

FIG. 2. TSD of PpClS: $T_p = 150^\circ\text{C}$, $E_p = 25\text{ kV/cm}$.

TABLE I. Charge released, $E_p = 25\text{ kV/cm}$.

Sample	Charge (C/m ²)	Comment
PS	1.3×10^{-6}	T_g peak
P(pClS-co-S)	2.8×10^{-5}	T_g peak
PpClS	6.2×10^{-5}	T_g peak
PPO	2.2×10^{-3}	Variable
50-50 PPO-PS	3.0×10^{-4}	Two peaks
50-50 PPO-P(pClS-co-S)	5.7×10^{-4}	Two peaks
50-50 PPO-PpClS	2.5×10^{-4}	Two peaks

Glass transition temperatures of the samples were determined in ancillary experiments using a Perkin-Elmer DSC-2 at 20°C/min heating rate.

RESULTS AND DISCUSSION

The TSD spectrum of atactic PS is shown in Fig. 1. Three features are apparent: two peaks with maxima at 103 and 148°C and an increasing current of opposite polarity at higher temperatures. The first peak may be attributed to the relaxation of oriented dipoles at the glass transition. The glass transition temperature obtained by differential scanning calorimetry (DSC) is 105°C for PS. Peak areas of the TSD spectrum for this polymer were reproducible to within 10% and linearly dependent on field strength E_p . Varying the formation conditions, T_p and E_p , did not change the temperature at which the current maximum was observed. Polarization below T_g , at 77°C for example, still produced a maximum though of reduced magnitude.

The second PS current maximum can be attributed to the drift of space charge. This feature was only observed when T_p was above T_g . Both the temperature of the peak maximum and the peak area were variable. Repeated cycling of the sample through the polarization-cooling-

FIG. 3. TSD of PPO: $T_p = 170^\circ\text{C}$, $E_p = 25\text{ kV/cm}$.

FIG. 4. TSD of 50-50 PPO-P(*p*ClS-co-S): $T_p = 176^\circ\text{C}$, $E_p = 25\text{ kV/cm}$.

TSD sequence produces a large increase in peak area, as is illustrated in Fig. 2 for the similar case of *Pp*ClS. This phenomenon was observed with PS, *Pp*ClS, and *p*ClS-co-S copolymer samples and is attributed to the presence of impurities of an ionic nature during polarization.

The third feature is the steadily increasing current of opposite polarity to the heterocharge peaks. van Turnhout¹ attributes these "parasitic" currents to the increasing Ohmic conductivity of the polymer at higher temperatures, coupled with an electrochemical potential difference. This effect was also observed with TSD measurements for an unpolarized sample.

Identical results were obtained for PS samples with and without evaporated gold electrodes, provided that the unmetallized sample had first been intimately coupled to the gold electrodes of the sample cell by heating the latter above T_g . A homocharge peak of opposite polarity to the 103°C T_g peak appeared at 111°C if a nonmetallized sample was polarized below T_g without prior "fusion" to the electrodes.

*Pp*ClS and *p*ClS-co-S copolymer TSD spectra also exhibited the same three features: two current maxima and a parasitic discharge current. Calorimetric glass transition temperatures of these samples were 132°C and 121°C , respectively, and the current maxima were observed at 131°C and 119°C , respectively. Table I lists the quantity of charge released at the T_g peaks. It may be noted that for gas-phase dipolar molecules, polarization P is described by Eq. (1).

$$P = N\mu^2 E_p / 3kT_p, \quad (1)$$

where P is the polarization, μ is the dipole moment, E_p is the dc field strength, T_p is the polarization temperature, N is the dipolar concentration, and k is Boltzmann's constant. This expression greatly underestimates the observed polarization for PS and *Pp*ClS; this is to be expected because of the importance of the internal field effect in condensed phases. However, using for the dipole moment μ the appropriate values for *p*-chlorotoluene and toluene as representing those of the segments of *Pp*ClS and PS, the ratio of the dipole moments squared suggests that the polarization of *Pp*ClS should be 38 times that of PS. The observed ratio of areas under the T_g peaks was found to be 46.

The TSD spectra of PPO is shown in Fig. 3. The charge observed in this polymer is more than two orders of magnitude greater than that found in PS, and proved to be largely irreproducible. The temperature of the current maximum also varied nonsystematically. The calorimetric glass transition of PPO is 216°C ; polarization above or below this temperature yields qualitatively the same result, namely, a substantial peak below T_g . PPO synthesis involves a copper salt-amine catalyst system and the TSD study provides some insight into the difficulty of freeing the polymer from catalyst-related impurities. Reed¹⁰ has observed low-frequency dielectric losses in PPO above 100°C and he attributes these to amine salts. He further suggests that these salts may be present in a free state or may be incorporated into the polymer backbone. Rigorous purification of the PPO was only partially effective in reducing the observed loss peaks.

Figure 4 is representative of the several compatible blends studied. In each case two partially superimposed peaks were observed. For the 90/10 and 60/40 (wt. %) PS/PPO blends, the temperature of the first current maximum was within two degrees of T_g . However, with the 50/50 PS/PPO and *p*ClS-co-S/PPO blends, peak temperatures did not correspond to calorimeter T_g 's.

FIG. 5. TSD of 50-50 PPO-*Pp*ClS: $T_p = 160^\circ\text{C}$, $E_p = 25\text{ kV/cm}$.

Again the charges observed were not reproducible; this proved to be the case for all samples containing PPO. Repeated thermal and polarization cycling led to the merging of the two maxima into one larger peak.

Figure 5 is the TSD spectra of a 50/50 PpCIS/PPO incompatible blend. Two distinct peaks are seen at 144 and 222°C which are reasonably close to the 132 and 216°C calorimetrically determined T_g 's of the individual components. However, the impurities present in the PPO and the multiple peaks observed for unblended components yielded the conclusion that TSD measurements cannot be used unequivocally to infer polymer-polymer compatibility for this system.

CONCLUSION

For pure polymers the TSD method in this study has provided corroborative evidence with regard to phenomena such as the glass transition, TSD currents are, as expected, highly sensitive to the presence of impurities, and therefore to any thermal history of samples used, that may be involved in producing such impurities. Blending of polymers in this study led to nondefinitive results.

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