

Space Charge in Polyethylene/Ionomer Blends

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ABSTRACT

Measurements of thermally stimulated currents were made on ionomer/polyethylene blends. The objective of this work was to study space charge formation in these materials. Two ionomers were compared; both ionomers contained methacrylic acid, neutralized by zinc in one and by sodium in the other. A large current peak centered near 60°C was observed in all blends and associated with the motion of space charges injected into the blends during poling. All blends accumulated large negative space charge concentrations. The approach to the equilibrium space charge distribution (negative and spatially uniform in all blends) is much more rapid in the blends containing the sodium ionomer than in the blends containing the zinc ionomer.

1. INTRODUCTION

FUKUGAWA and Nitta reported that ionomer/polyethylene blends exhibit a high dielectric strength to dc voltages [1]. They suggested that these polymer blends diminished the possibilities of space charge formation and so improved the breakdown strength.

An ionomer is a copolymer containing a monomer which is nonpolar and a monomer with a functional group capable of being converted to an ionic salt. Fukugawa and Nitta did not specify the ionomer used in their work. This study used the well characterized ionomer, SurlynTM. Surlyn is a polymer consisting mostly of ethylene monomers with the presence of occasional methacrylic acid monomers. Thus the structure is mostly like that of polyethylene with an occasional methacrylic acid group inserted into the chain. The carboxylic acid part of methacrylic acid is then converted into a metal salt. The ionic metal carboxylates are found to form multiplets or clusters, a phenomenon which is not surprising for polar ionic species in a nonpolar environment. Two of the commercial ionomers produced by DuPont are the sodium ion and zinc ion carboxylates.

The object of this study was to examine the physics and chemistry of the polyethylene/ionomer blends in re-

lation to space charge formation. Because the Fukugawa paper [1] did not discuss the space charge characteristics as a function of ionomer concentration, this needed to be determined. The other variables which might affect the space charge such as ionomer type, thermal annealing, and poling field were studied. For this purpose, the thermally stimulated current (TSC) technique was used.

The thermally stimulated current measurement involves the determination of the currents which are released from a poled sample as a function of temperature. Poling is accomplished by placing the sample under a high dc stress and then cooling with liquid nitrogen. Cooling freezes the molecular motion of the polymer and immobilizes the charges injected by the poling process. On slowly warming the sample, the trapped charges are released. By measuring the amount of charge released and noting the characteristic temperature at which these charge releases occur, inferences can be made on the space charges which form in the polymer.

This work was supported by the Electric Power Research Institute (EPRI). Complete results may be found in EPRI Report EL-6977 [2]. Simultaneous with the Connecticut work EPRI supported a project at the National Institute of Standards and Technology (NIST). The

NIST results are described in EPRI Report EL-7301 [3]. In this paper no attempt will be made to give a complete account of the results described in [2]. The results which appear to be the most important to the possible use of polyethylene/ionomer blends are the subject of this paper. These are:

1. the variation of the electrical properties with ionomer concentration
2. the different effects of zinc and sodium counter ions,
3. the effect of annealing on the electrical properties of the blends.

2. EXPERIMENTAL PROCEDURES

2.1. MATERIALS

The polyethylene used in these studies was low density polyethylene (LDPE), Union Carbide PE 6201, and the ionomers were DuPont's Surlyn 1601 (a sodium ionomer) and Surlyn 1652 (a zinc ionomer). The nominal mole percent of methacrylic acid in the zinc ionomer is 8.7% which is approximately 18% neutralized with zinc. The nominal mole percent of methacrylic acid in the sodium ionomer is 10.0% which is approximately 53% neutralized with sodium.

2.2. BLENDS OF POLYETHYLENE AND SURLYN IONOMERS

Blends of polyethylene and the ionomers were made by a plasticizing extruder with a single screw made by Wayne Machine & Die Co. Temperatures for screw and die were set so that 180°C was continuously maintained. The screw speed was 20 rpm, and, with that speed, the pressure was recorded between 6.8 to 7.5 MPa. The melt temperature was measured by inserting a needle-tipped pyrometer through the die.

The blend ratios were typically 5, 10, 20, 50, and 80% by weight of ionomer with the balance consisting of polyethylene for both sodium ionomer/PE and zinc ionomer/PE blends. The thick tapes of the blend obtained from the extruder were stored in a desiccator. Films were made using a hot press maintained at 180°C for 10 min. A small amount of sample was placed between the metal plates lined with Mylar film. The metal plate in contact with the Mylar film was a chrome plated one designed for photographic purposes; it was backed by a 1 cm thick stainless steel plate. An appropriate shim was used to make the 127 μm thick films, but no shims were used in pressing the 25.4 μm thick films.

Most of the films used for the thermally stimulated current (TSC) measurements were $\sim 25 \mu\text{m}$ thick. All of the data shown in this paper were measured on such samples. Considerable difficulties in preparing these films

were encountered. Many pressings were made and the samples closest to 25 μm were selected. Small variations in thickness were compensated by adjusting the poling voltage so that the same poling fields could be impressed on all samples. The Keithley model 247 HV power supply used in this work permits precise settings of the poling voltage.

2.3. CRYOFRACTURE FOR MICROSCOPY

In order to study the morphological changes upon multistressing, bars of $\sim 2 \text{ mm}$ thickness were hot pressed. These bars were physically broken after being immersed in liquid nitrogen for $\sim 20 \text{ min}$.

2.4. VACUUM EVAPORATION OF THE ELECTRODE

Gold was vacuum deposited on both sides of the sample. The guard ring and measuring electrode were evaporated on one side and the counter electrode on the other side. Care was taken to maintain a high vacuum $2.66 \times 10^{-3} \text{ Pa}$ during deposition. Tests were conducted to insure that the heat from the electrode evaporation did not cause morphological changes in the polymer film.

2.5. DSC AND DMA

The differential scanning calorimetry (DSC) was carried out on 4 to 8 mg samples under nitrogen in an Omnitherm Corporation instrument. The heating rate was 10°C/min.

The differential mechanical analysis (DMA) was determined on a DuPont 990 DMA instrument in the temperature range -140 to 100°C at a heating rate of 5°C/min.

2.6. THERMALLY STIMULATED CURRENTS

The TSC apparatus, constructed in our laboratories, was described in a previous publication [4,5]. Typically, the sample was poled at 70°C for 20 min at a field of 8 kV/mm. The temperature was dropped to -50°C with the field applied. At this point the field was removed, the electrodes short circuited and the temperature held at -50°C for 30 min. After this period, the temperature was allowed to rise 5°C/min. In our first measurements the TSC data was recorded on a strip chart recorder. An improved apparatus using a MacIntosh computer and LabView software has been described in a recent publication [6].

3. THEORETICAL BACKGROUND

Although a number of experimental variations are possible, measurements of TSC are used most often to ascertain the state of charge of a dielectric produced by an applied electric field. The sample is placed between two metal electrodes and then polarized with a large electric field. As a result, image or compensating charges accumulate on the electrodes. It is the subsequent release of the charges on the electrodes when the sample is heated that creates the measured currents. It is possible to discharge the sample by shorting the electrodes with an electrometer with a small bias or collecting voltage across the sample. The effect of this bias voltage can be used to distinguish between dipole and injected charge polarizations. The principal concern of a TSC measurement is the study of the charge decay as a function of temperature. A current peak may be observed at a temperature where dipole orientation, ion migration or electron/hole release from traps is activated. In the case of polymers, the release of charge may result from the activation of the various motions of the polymer chain. Thus TSC measurements often yield results similar to those obtained from mechanical and dielectric loss measurements [7].

The results presented below exhibit an unusual dependence of the charge released upon the poling field strength in isochronal poling. The very complicated morphology of these materials (see Section 4.1) involving two crystallites, amorphous polyethylene, and amorphous ionic clusters might suggest that interfacial polarizations contribute to the measured TSC. However, this type of polarization is usually only important if the material consists of a relatively highly conducting phase dispersed in an insulating phase. In this case all 'phases' are highly insulating. The ionic clusters are composed of negative ions bound to the polymer chains and are thus incapable of translational motion in the solid state. Similarly the positive ions will not contribute to a dc conductivity. The apparatus used for these measurements is not well suited to the measurement of dc conductivity (it was designed to provide an accurate linear temperature ramp, not a stable temperature over the 30 to 60 min periods needed to make good measurements of the dc conductivity). Nevertheless, a few measurements were made which showed negligible differences between the conductivities of the pure polyethylene and 80/20 blends of polyethylene with both β and γ types of Surlyn.

Independent evidence, to be discussed below, shows that excess charges are injected into these samples during poling. The measured TSC result from the thermally stimulated motion of these charges. It is very difficult to derive equations that will describe such motions in any generality. In contrast to dipole relaxations, some charge

will cross the polymer-metal interface and therefore the results will depend on the character of the interfaces as well as on the space charge distribution and the mobility of the carriers. It will be assumed that the contacts are ohmic and that any effect of the intrinsic conductivity is negligible. These are reasonable assumptions although they have not been conclusively established. As mentioned above, all samples, even those with high concentrations of ionomers have a very low conductivity. The poling currents show that the electrodes are certainly not blocking although it cannot be asserted that there are no barriers at the contacts and that the two contacts are identical.

Gross and Perlman [8] have derived an equation for the external current resulting from the motion of charges in a charged dielectric slab with metalized short-circuited electrodes. This is

$$J(t) = - \frac{A\rho(x_o, t)dx_o}{dt} \quad (1)$$

where $\rho(x_o, t)$ is the charge density at the zero-field plane located at x_o at time t , and A is the area of the sample. As will be discussed, the results of this investigation, to an excellent first approximation, involve only negative charges, and therefore there will be only one zero-field plane in the sample. From this equation one sees that if the initial distribution of excess charge were to be symmetrically distributed about the center of the sample then the zero field plane would be located at this point and it would not move if the two contacts were to be identical. No external current would be observed, no matter how large the excess charge might be.

Now dx_o/dt will be proportional both to the carrier mobility and to the field experienced by the injected charge which in turn depends on the injected charge density. Therefore, Equation (1) shows that the magnitude of the TSC will increase with the square of the magnitude of the injected charge and thus faster than linearly with the poling field strength, unlike the TSC resulting from dipole relaxation which is linear in the poling field. If the carrier mobility is thermally activated, the TSC curves will otherwise be very similar in shape to those resulting from dipole depolarization with an Arrhenius relaxation time. Indeed, work by van Turnhout [9] yielded equations for the TSC proportional both to the carrier mobility and to the square of the injected charge.

Two recent review articles [10, 11] describe the use of TSC measurements to characterize insulating polymers. An account of the theory of the discharge of electrets has been given by van Turnhout [7]. Chen and Kirsch [12] have published a comprehensive description of thermally stimulated processes.

4. RESULTS

4.1. MATERIALS CHARACTERIZATION

The question of how well the ionomer and polyethylene were blended by the techniques used for the sample preparation, i.e. by screw extrusion and hot pressing the extruded material to form a film, is especially important. Whether there was or was not a phase segregation in the as-pressed sample and what happens with aging or thermal annealing were studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and microscopy.

Both the zinc ionomer/polyethylene blend and the sodium ionomer/polyethylene blend are mixtures rather than polymer solutions. Although low magnification examination indicates a homogeneous material, the DSC thermogram shows, as expected for a blend of two semicrystalline polymers, two melting peaks, one for each of the two blend components. The crystalline melting temperature of the two components were found not to be shifted appreciably, the observed changes being within 2°C. In addition, the heat of fusion was found to obey the 'additive rule' for incompatible blends. This rule assumes that for non-compatible polymers the heat of fusion of the blend is composed of two components, that of the heat of fusion of polyethylene and that of the heat of fusion of the ionomer. The contribution of each is proportional to the weight fraction of each component present. The melting points and heat of fusion indicate that crystalline domains of the ionomer and polyethylene remain independent and that a true solution does not form.

The DMA data also change with the blend ratio. The mechanical $\tan\delta$ as a function of temperature was measured for the different blend ratios. The α peak for each composition showed a distinct temperature shift. As the ionomer component increases, the peaks shift to lower temperatures. Although these data are consistent with two phases, they do not indicate definitively that there are two phases. The DMA data shows that the γ transition temperature is the same for polyethylene, ionomer, and the blends. This is not surprising in that both polyethylene and ionomer have similar structures. Even though the ionomer is a copolymer of ethylene and methacrylic acid, the percent of methacrylic acid is low and randomly distributed. The constancy of the γ transition temperature confirms that the short segments of ethylene chain were not influenced by blending and the small amount of the methacrylic acid does not create enough change in the ethylene backbone to alter the $-\text{CH}_2-$ relaxation observed for the amorphous regions.

Since the evidence indicates discrete phases in the film as pressed, the extent of phase domain growth on aging or annealing was examined. The DSC thermograms on an

80% polyethylene/20% zinc ionomer blend thermally annealed at 80°C showed changes taking place for 14 days. Between 14 and 29 days at 80°C the DSC was found to show similar peak positions and peak shapes. The $\tan\delta$ vs. temperature for the zinc ionomer changes somewhat from the initial point to 14 days but vary little from 14 days to 29 days. The small changes observed in the DSC, the heat of fusion, and DMA between 14 and 29 days of annealing are similar. The small change in the $\tan\delta$ vs. temperature for samples annealed for 14 and 29 days indicates that extensive oxidation or degradation does not occur between the second week and fourth week of thermal annealing. The γ transition temperatures for all of the samples remain unchanged after the month-long oven annealing.

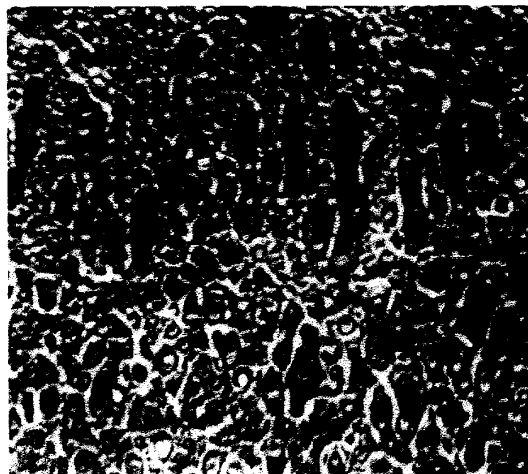


Figure 1.

Cryofractured surface. The cryofractured surface of two-week annealed PE/Surlyn (80/20) blend: Annealing condition: 80°C, 2 week, air convection oven. Cryofractured cross section. The length bar shows a distance of 2 μm .

In summary, the DSC data shows the clear separation of the two crystalline phases of polyethylene and ionomer whereas the DMA data only exhibit a single peak and do not establish the existence of two crystalline phases. In order to confirm the phase separation in the blend, SEM images on the cryofractured cross section were obtained on an 80% polyethylene/20% zinc ionomer blend in as-pressed and annealed conditions. The photomicrograph of the as-pressed sample is shown in Figure 1. The white areas were characterized as domains of ionomer rich materials surrounded by a polyethylene matrix based on the corresponding patterns obtained by elemental mapping by SEM/EDX. It is clear that the two phases exist in small domains which are evenly patterned through the sample. The pictures of the samples annealed at 80°C

for one and two weeks using an air convection oven and the samples subjected to an electric field (dc, 2 kV/mm) at 80°C for one and two weeks in an aging oven indicated that the domain size increased as a function of the annealing or multistressing time as shown by the increase in size of the white areas indicative of ionomer rich domains. The domain size of the thermal annealed sample and the multistressed sample after two weeks were similar. This fact indicated that the thermal effect is the dominant factor in determining the phase agglomeration.

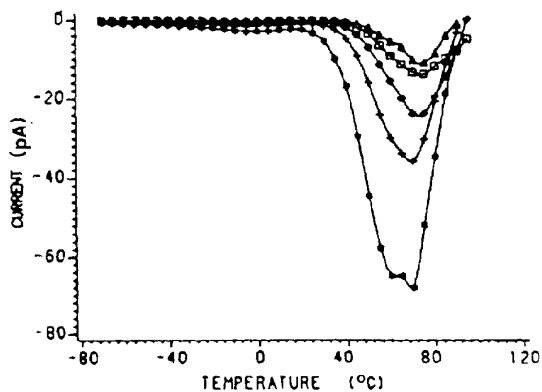


Figure 2.

TSC Zinc ionomer 80/20 with E_p . TSC of as-pressed PE/zinc ionomer (80/20) blend. Poling condition: 70°C, 20 min, +4.8 kV/mm (Δ), +8 kV/mm (\square), +12 kV/mm (\diamond), +16 kV/mm (+), +28 kV/mm (*), As-pressed. Au electrode.

4.2. TSC RESULTS

TSC measurements yield pairs of current, temperature values which are conveniently displayed on linear plots of current vs. temperature. A typical result is shown in Figure 2 for a 80/20 blend of polyethylene/zinc ionomer. This sample was measured after being pressed into a sheet ~ 0.15 mm thick, without additional annealing. Such samples are referred to as 'as-pressed'. The variables under the control of the experimenter are the poling temperature T_p , the poling time t_p , and the poling voltage V_p , or poling field $E_p = V_p/\text{sample thickness}$. The heating rate is kept constant and monitored continuously.

The measurements shown in Figure 2 were made on a single sample. All poling was done at 70°C for 20 min. A sequence of values of E_p were used with the sample repoled for each poling voltage. Checks were made on fresh samples to make sure that the repoling was not giving results which were dependent on the history of poling. With increasing E_p , the large high temperature peak (α peak) increases in magnitude and the temperature of the maximum shifts to lower temperatures. The

results obtained with the highest poling voltage clearly show that the α peak is a doublet. Comparable structure is seen in the TSC measured with smaller poling voltages. Near -10°C a much smaller peak (β peak) is regularly observed. For 20 min poling, the α peak does not appear for poling temperatures much below 70°C. Results also show that even at 70°C, poling has not produced a steady state polarization.

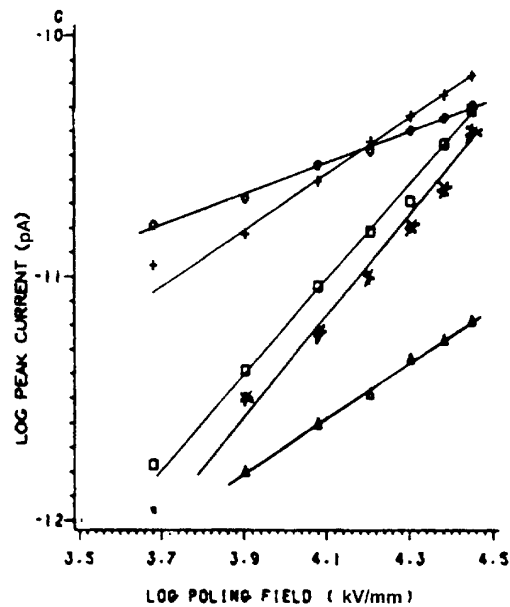


Figure 3.

TSC Sodium ionomer 80/20 with E_p . TSC of as-pressed PE/sodium ionomer (80/20) blend: Poling condition: 70°C, 20 min, +8 kV/mm (Δ), +12 kV/mm (\square), +16 kV/mm (\diamond), +28 kV/mm (+), +37 kV/mm (*) As-pressed. Au electrode.

Results for an 80/20 blend of polyethylene and sodium ionomer are shown in Figure 4. This Figure shows that with increasing E_p the TSC peak first increases and then decreases. Similarly at constant E_p , the TSC peak first increases and then decreases with increasing poling time. Again there is an indication of a double peak. Comparison of Figures 2 and 4 shows that for the same values of E_p , T_p , and t_p the polarization of the 80/20 blend with zinc ionomer is very different from that of the 80/20 blend with sodium ionomer.

Measurements have also been made on the pure polymers: polyethylene, zinc ionomer and sodium ionomer. The results show that both the α and β peaks are associated with the presence of the ionomers. The variation of peak heights with poling fields for the pure ionomers is the same as for the 80/20 blends shown in Figures 2 and 4.

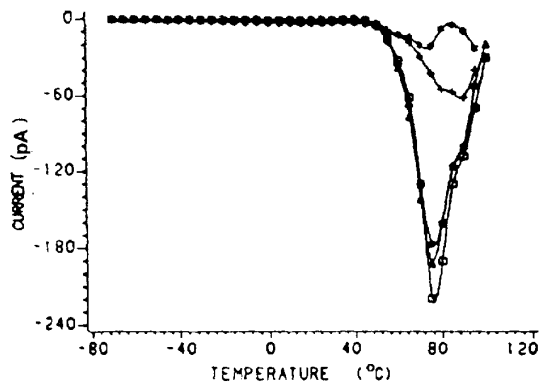


Figure 4.

i_m vs. E_p Zinc ionomer blends. Effect of poling field on the α peak current for as pressed PE/zinc ionomer blends: % wt of PE/zinc ionomer: 100/0 (Δ), 95/5 (\square), 90/10 (\diamond), 80/20 (+), 50/50 (*).

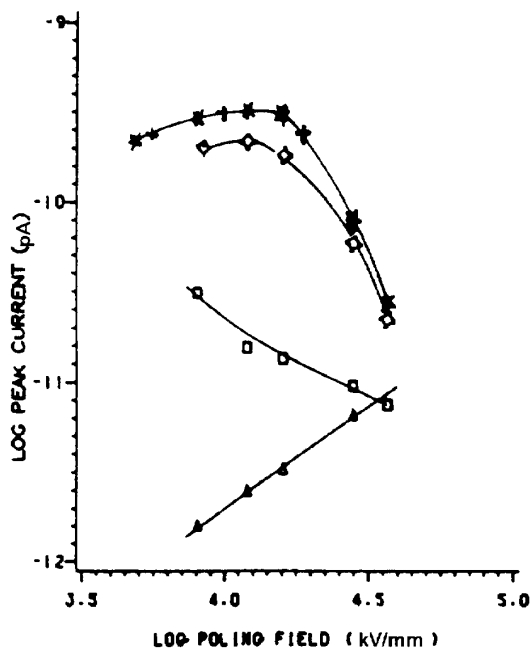


Figure 5.

i_m vs. E_p Sodium ionomer blends. Effect of poling field on the α peak current for as pressed PE/sodium ionomer blends: % wt of PE/sodium ionomer: 100/0 (Δ), 95/5 (\square), 80/20 (\diamond), 50/50 (+), 0/100 (*).

Samples with PE/Surlyn ratios of 100/0, 95/5, 80/20, 50/50, and 0/100 were measured. The next few Figures compare the various blends. The peak current i_m (T_m) and the peak temperature may be used to characterize and compare the blends. Figures 3 and 5 show the variation of the peak current with poling fields. For the blends

with zinc ionomer, the peak current increases uniformly with poling field. For these blends, the increase is faster than linearly in the field strength and, in two cases, about quadratically in the field strength. As shown in Figure 5, the decrease in the height of the TSC peak at high poling fields was observed in all blends containing the sodium ionomer.

The TSC curves for the 80/20 blends have been integrated in order to find the charge released, i.e., the total charge that passed through the electrometer during the TSC run. Table 1 lists these results: Q is the charge released, Q/i_m is the ratio of the charge released to the peak TSC current and Q_e is the charge on the electrodes during poling assuming a space charge free dielectric of static permittivity 2.6.

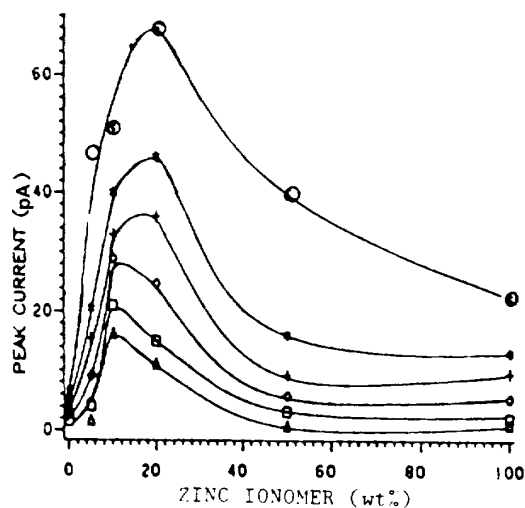


Figure 6.

i_m vs. Zinc ionomer concentration. Effect of ionomer concentration on the α peak current for as-pressed PE/zinc ionomer blends: Poling fields: +4.8 kV/mm (Δ), +8 kV/mm (\square), +12 kV/mm (\diamond), +16 kV/mm (+), +24 kV/mm (*), +28 kV/mm (O). As-pressed. Au electrode.

One would certainly expect $Q < Q_e$ and most often $Q \ll Q_e$. The values of Q for the sodium ionomer blend with a poling field of 12 kV/mm is surprisingly large. Figures 6 and 7 show the variation of the height of the α peak with ionomer concentration. Again the two ionomers show very different behaviors.

The β peak heights as functions of ionomer concentration and poling field strength are shown in Figures 8(a) and (b).

The data presented above are the results of measurements made on as-pressed samples. A few samples have

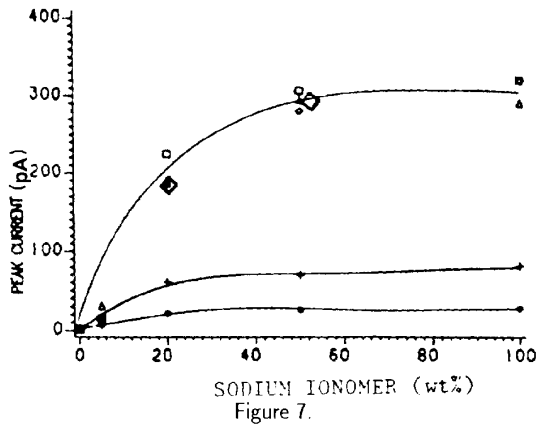


Figure 7. i_m vs. Sodium ionomer concentration. Effect of ionomer concentration on the α peak current for as-pressed PE/sodium ionomer blends: Poling fields: +8 kV/mm (Δ), +12 kV/mm (\square), +16 kV/mm (\diamond), +28 kV/mm (+), +37 kV/mm (*). As-pressed. Au electrode.

Table 1.

Charge released, calculated by integrating the TSC curves for the 80/20 polyethylene/Surllyn blends.

E kV/mm	Q_e nC	Zn ionomer 80/20 blend		Na ionomer 80/20 blend	
		Q nC	Q/i_m s	Q nC	Q/i_m s
4.8	33	3.6	365	-	-
8.0	57	6.1	430	42	221
12.0	83	9.6	398	52	208
16.0	120	13.7	381	46	210
28.0	190	28.5	419	17	246
37.0	250	-	-	5	210

been measured after thermal annealing, thermal annealing with the sample subjected to an applied electric field, and crosslinking with 2 wt% dicumyl peroxide.

In general these results show small but very complicated changes in the shapes of the TSC curves. The present results do not provide a comprehensive description of these changes; nevertheless, a few features which appear to be general may be noted.

Figure 9 shows the TSC for an 80/20 blend of PE and zinc ionomer after annealing at 80°C for 2 weeks in an air convection oven. These results should be compared to those of Figure 2, the poling time and temperature are identical. For the same value of the poling field the α peak heights are reduced by the annealing and there are some changes in the shape of the curves. However, the principal features of the TSC curves are the same. The β peaks are nearly identical. Some caution must be

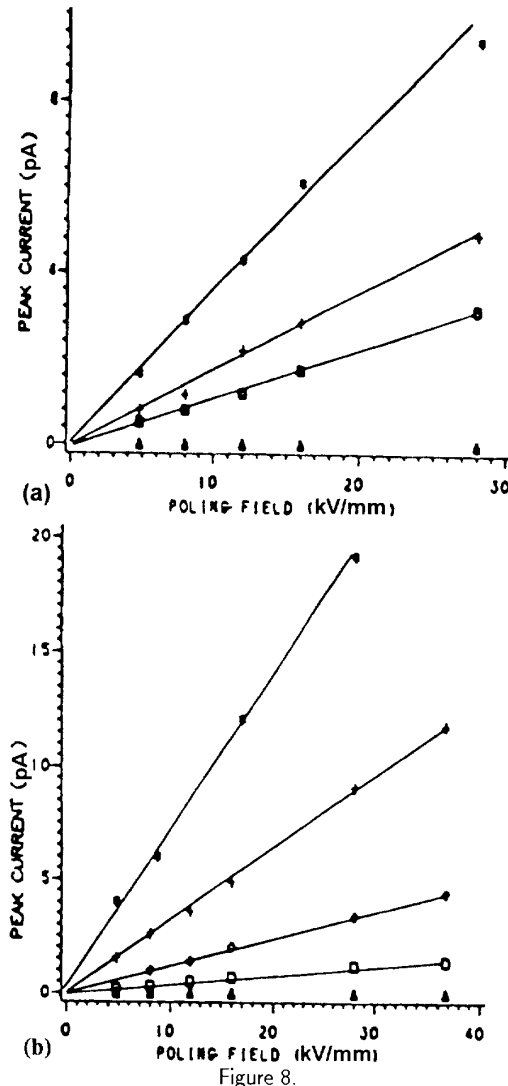


Figure 8. Effect of poling field on the β peak current of as-pressed PE/Zinc ionomer blends: % wt of PE/zinc ionomer: 100/0 (Δ), 90/10 (\square), 80/20 (\diamond), 50/50 (+), 0/100 (*). As-pressed. (a) PE/Zn, (b) PE/Na.

exercised before attempting a detailed comparison; remember that the annealing was carried out in air and therefore, despite the presence of antioxidants, there will be some oxidation of the annealed sample. Figure 10 shows the results for several samples of the 80/20 blend with zinc ionomer annealed in the presence of an electric field. In all cases the samples were poled at 70°C for 20 min in a field of 16 kV/mm. The annealing was carried out at 80°C in a field of 20 kV/mm. The annealing times were 1.2, 5, 10 and 100 h. Again the peak cur-

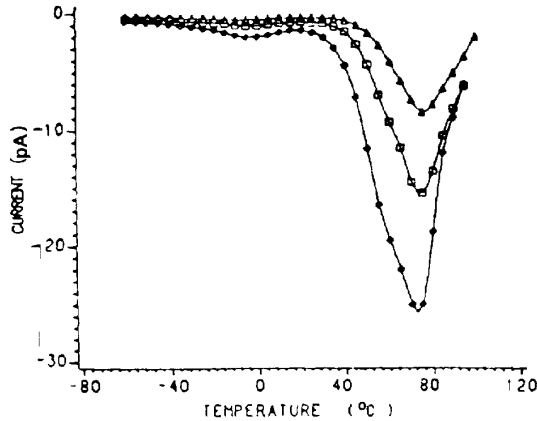


Figure 9.

Thermal Stress on zinc ionomer (80/20). TSC of annealed PE/zinc ionomer (80/20) blend: Annealing condition: 80°C, 2 week, air convection oven. Poling condition: 70°C, 20 min, +8 kV/mm (Δ), +16 kV/mm (\square), +28 kV/mm (\diamond).

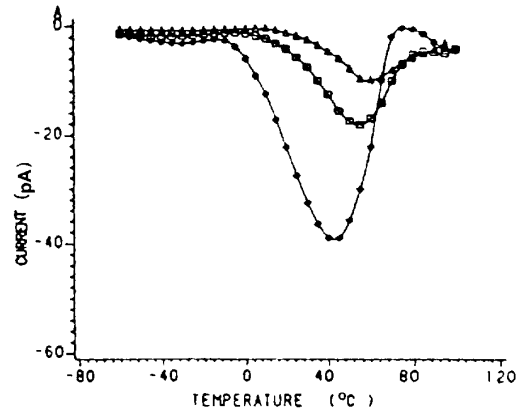


Figure 11.

TSC of crosslinked blends. TSC of crosslinked PE/zinc ionomer (80/20) blend: Poling condition: 70°C, 20 min, +8 kV/mm (Δ), +16 kV/mm (\square), +28 kV/mm (\diamond). All samples were heated at 90°C for 3 h in a vacuum oven.

5. DISCUSSION

The evidence indicates that the polyethylene/ionomer blends are phase segregated and that the phase domains grow in the first 14 days of annealing. After that, the system is relatively stable. Change is not noticeable at room temperatures for periods of weeks, but the change observed at annealing temperatures of 80°C suggest that domain growth might be expected in time at room temperatures.

Broadhurst and DeReggi [3] used thermal pulses to measure the distribution of space charges in these polyethylene/ionomer blends. With short time poling they found extremely variable results and so, in order to characterize the steady state, carried out most of their poling at 60°C for ~ 5 h. With this poling their results showed that all samples, pure polyethylene, pure ionomers and the various blends accumulated a nearly uniform distribution of negative space charge. The total accumulated space charge was large in all samples, being a significant fraction of the charge on the poling electrodes (Q_e of Table 1). The concentration of space charge was larger in the blends than in the samples of pure polyethylene. In no case did they see any evidence for the conjecture [1] that space charge accumulation is reduced in the blends. They reported some small differences between the space charge distributions in the blends containing the sodium ionomer from those containing the zinc ionomer, but for the most part all materials yielded nearly identical results. They further showed that their results were consistent with a simple model of unipolar or bipolar charge injection. A few measurements of transient conditions

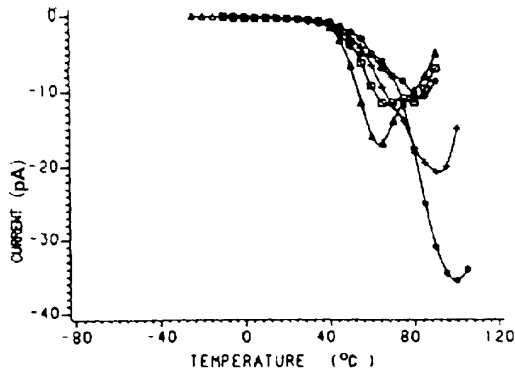


Figure 10.

Multistress on zinc ionomer 80/20. TSC of multistressed PE/zinc ionomer (80/20) blend: Poling condition: 70°C, +16 kV/mm, 20 min. Multistressing condition: 80°C, +20 kV/mm, 1 h (Δ), 2 h (\square), 5 h (\diamond), 10 h (+), 100 h (*).

rents are somewhat reduced from those measured on as-pressed samples. This annealing makes rather complicated changes in the shape of the curves. Finally Figure 11 shows the results of an 80/20, PE/zinc ionomer blend after crosslinking with dicumyl peroxide. Note again the β peaks are nearly identical with those measured on the as-pressed samples. The α peak is now slightly larger than that observed for the as-pressed sample. The shift of the temperature of the α peak to lower temperatures with increasing poling field strength is much larger than it was for the as-pressed sample.

showed that the initial injected space charge was homocharge at both electrodes, but over the course of a few hours evolved into the distribution of uniform negative space charge.

Typically poling for the TSC measurements was done for only 20 min. The charge distribution so produced cannot be expected to have reached a steady state. The charge state resulting from the 20 minute poling depends sensitively on the poling temperature and field. The poling temperature is not precisely reproducible and this undoubtedly contributes to the scatter of the TSC data. The measurements provide information about the processes that lead to the establishment of the space charge distributions. Uniform distribution of space charge in a sample with identical electrodes will discharge without the appearance of any TSC.

Considering the dependence of the height of the α peak on poling voltage (Figures 3 and 5), poling time and poling temperature, one concludes that the α peak results from the discharge of the injected space charge. Many of the TSC curves show two distinct α peaks. The blends, as noted above, are mixtures and DSC measurements always yield two melting temperatures. This suggests the TSC α peaks are associated with the onset of crystallite melting, or simply the motion of large segments of the polymer chain, and that the space charge is the result of trapping injected electrons at interfacial sites. The nature and concentration of these sites must also depend on the presence of the ionomer. It is generally accepted that the ionic centers in ionomers are clustered [13]. Various models have been suggested for the clusters, but there is no general agreement as to the details of the cluster structure. Experimental evidence [13] indicates that ionic clusters exist in ionomers from the time they are formed. Blending with polyethylene dilutes the clusters. Thus the blends have an extremely complicated microstructure being composed of two crystallites, ionic clusters (noncrystalline) and nonpolar amorphous random coils. Injected electrons are trapped at interfacial sites whose formation may involve both the crystallites and the ionic clusters. Annealing with and without electric field and crosslinking all cause major changes in this microstructure and so produce the changes seen in the measurements.

Van Turnhout has discussed the problem of injected charge motion [7], but the theory does not yield equations that can be applied to every experimental situation. A simple equation (Equation 3.42 of [7]), valid for the initial portion of the discharge shows that the TSC should be thermally activated if the hopping mobility is thermally activated. Semilog plots of the initial current plotted against reciprocal temperature did yield straight

lines and the activation energies listed in Table 2 were calculated from these plots. The currents ranged from ~ 0.5 to 15% of the peak current and typically spanned a temperature range from about 40 to 60°C. The values listed in the table have been specified to two decimal places. It is unlikely that the error figure for these values is $< 20\%$, but all plots have been done in exactly the same way and it is hoped that some comparisons can be made. It appears that the activation energies for the blends containing sodium ionomer are larger than those for the blends containing zinc ionomer. It is unlikely that the variation of the activation energy listed for the 50/50 blend of PE/sodium ionomer is real. The value of 2.14 eV seems unrealistically high. Activation energies for conduction in polyethylene samples found in a large number of investigations [14] range from 0.75 to 1.5 eV. The absence of systematic results probably reflects the absence of peak cleaning i.e., the measured activation energies represent some combination of several processes. For thermally activated hopping, one might expect the applied field to effect some barrier lowering; this appears to be the case in about half the results shown in Table 2.

Table 2.

Activation energies in electron volts for the alpha peaks of the ionomer blends. The tabulated values were obtained from the initial rise of the stimulated currents.

	Poling field, kV/mm					
	4.8	8	12	16	28	37
Zn ionomer blends PE/Zn						
95/5	—	0.95	1.07	1.01	—	—
90/10	1.16	0.81	0.80	0.97	0.95	—
80/20	1.07	1.08	0.98	1.07	0.93	—
50/50	0.49	0.49	0.54	0.62	0.69	—
Na ionomer blends PE/Na						
95/5	—	1.32	1.05	—	—	—
80/20	—	1.66	1.52	1.27	0.75	0.66
50/50	1.6	1.94	2.14	2.11	1.37	0.85
0/100	1.42	1.98	2.01	2.11	1.68	—

Certainly the most interesting feature of these TSC measurements is the difference between the results for the blends with the sodium ionomer and those with the zinc ionomer shown for the 80/20 blends in Figures 2 and 4. Considering the results of Broadhurst and DeReggi, one knows that the small TSC observed for the blends containing sodium ionomer at high poling fields and long poling times is not due to an absence of space charge in these materials. Instead it must be due to the distribution of this charge. In equilibrium one expects a uniform distribution of negative charge (with no TSC) and one can only conclude that the equilibrium distribution of

space charge approaches equilibrium much more rapidly in the blends containing the sodium ionomer than it does in the blends containing the zinc ionomer.

It is not easy to single out a correct explanation of the more rapid approach to the equilibrium space charge distribution in the blends containing the sodium ionomer. Different mobilities, different trapping rates or a different mix of multiple polarization mechanisms might play a role. The structure of the clusters may be different for the two ionomers since the percent neutralization is quite different for the sodium and zinc ionomers and the two ions are, in addition, monovalent and divalent. Until one can identify the measured activation energy, it will be very difficult to discuss these possibilities. In the simplest situations, the activation energy would be that of the hopping mobility. If this were to be the case, then the results would seem to rule out a consistently (*i.e.* at all temperatures) higher mobility for the blends containing the sodium ionomer since these materials exhibit a larger activation energy. Another mechanism involves the motion of the positive ions. Now the negative ions are attached to the polymer backbone and one certainly cannot expect any transport of ions over large distances. However, ion motion over short distances, say of the order of a nanometer, should be quite possible and might be quite different in the two ionomers. Sodium ions will prefer a six-fold coordination—the bonding is purely electrostatic and some displacement of the sodium ion with respect to its negatively charged companions should be quite possible. Zinc ion being double positive must bond with two negative ions. Moreover, zinc is often found in covalent structures (ZnS). It seems possible that the zinc ions might be much more strongly bound to the polymer chains than the sodium ion. During the polarization process, DeReggi and Broadhurst have shown that homocharge first appears at the injecting electrodes. One pictures the positive sodium ions responding to this charge much more effectively than the zinc ions. Then in the blends containing the sodium ionomer, space charge effects should be reduced and the charging currents would remain larger than those in the blends containing the zinc ionomer. Present results cannot decide between these possibilities. Future work will attempt to examine them.

The β peak is much too broad to be a simple dipole peak. For all poling fields and all ionomer concentrations, the widths of the peaks at the base line are nearly identical. The peak height (Figures 8(a) and (b)) then provide a measure of the charge released in a TSC measurement. As directly shown in Figure 8, the peak height increases linearly with poling field. Indirectly, Figure 8 also shows that the peak height is very nearly directly proportional to ionomer concentration. The beta peak is therefore associated with the relaxation of $[n(\text{COO}^-)$,

(metal ionⁿ⁺)] dipoles. The peak temperature is somewhat higher than that of the beta peak in the mechanical loss spectrum of polyolefins which is usually associated with the motion of side chains or small segments of the main chain. The width of the TSC beta peak and the higher temperature of the maximum current would then result from the interactions among the clustered dipoles. Figure 8 also shows that for given ionomer concentrations and poling field the peak current observed in the samples containing the sodium ionomer is roughly twice that observed in samples containing the zinc ionomer. This, at least in part, may be traced to the differences between the two ionomers. The zinc ionomer contains a nominal concentration of 8.7% methacrylic acid, the sodium ionomer 10%. However, the zinc ionomer is only 18% neutralized whereas the sodium ionomer is 53% neutralized. Were the dipoles formed in the zinc ionomer to have twice the dipole moment of the dipoles formed in the sodium ionomer and were the dipole moment of the methacrylic acid to be negligible, then one might expect the peak height for a sodium ionomer blend to be 1.7 \times that of the same blend of the zinc ionomer. Without any knowledge of the structure of the clusters one does not know how to compare dipoles in the two ionomers. The calculated factor, 1.7, does agree (possibly accidentally) quite well with the experimental result.

The electrical properties of the ionomer/polyethylene blend may well depend on the dispersion of the mixture. The stability of such blends is, therefore, a concern in a real world application which will be always involve aging. Because the ionomer and polyethylene do not form a true solution, there is the possibility of phase segregation with aging. If ionomers stabilize space charges in some way, there are possible ways to stabilize the distribution of the ionic centers. One is to crosslink the polymer. The other is to tailor make a polyethylene copolymerized with a low level of methacrylic acid rather than the relatively higher levels found in the ionomer.

6. CONCLUSION

THE as-pressed samples of the polyethylene/ionomer blend are a two phase system even though the ionomer is mostly polyethylene and might be expected to blend with polyethylene. On thermal aging or thermal and voltage aging, a rapid change occurs in which the phase segregation becomes more pronounced. The segregation process seems to level out after about two weeks.

All of the blends studied, which included the zinc ionomer/polyethylene and sodium ionomer/polyethylene in a variety of ratios, showed negative space charges. The presence of the ionomer did not reduce the space charge over that for pure polyethylene. If in fact these blends do have a higher dielectric strength the increased breakdown

strength is not due to a reduction in the space charge concentrations, but due to a stabilization of the space charge or a modification of the distribution of the space charge in some way.

The TSC peaks result from a discharge of injected space charge. Evidence indicates that the injected charges are electrons at the interfacial sites. These data show significant differences between the zinc ionomer/polyethylene and sodium ionomer/polyethylene blends. Yet measurements made at NIST [3] show very little difference between the two ionomers with regard to the distributions of injected space charge after long poling times (~ 5 h). The differences observed in the TSC must, therefore, be due to differences in the motion of the charges during poling. The sodium ionomer decreases in peak current with field. The activation energy for the motion of injected charge is larger for the sodium ionomer than for the zinc ionomer.

Many of the TSC curves show two peaks near 70°C. This is probably another result of the two phase nature of these samples, i.e., parallel currents in two continuous phases. If the electron hopping probability is the rate limiting parameter, then this result suggests different mobilities due to different activation energies in the two phases.

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