New Polyisobutylene-Based Model Elastomeric Ionomers. VI. The Effect of Excess Neutralizing Agents on Solid-State Mechanical Properties

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Synopsis

The role of excess neutralizing agents on the mechanical properties of three-arm star polyisobutylene-based model ionomers is discussed. The stress level, particularly at high elongations, is significantly affected by the presence of excess neutralizing agents, and these effects are observed with different cations such as potassium, calcium, and zinc. A morphological model is proposed that can account for the observed mechanical behavior.

INTRODUCTION

In recent years considerable research has focused on the bulk properties of low-level ion containing polymers (ionomers).[1-5] Some work on the solution behavior of these systems has also been reported.[6,7] Intra- and interchain association of the ionizable groups, neutralized by metal cations, leads to a unique set of properties. For example, in the presence of a small percentage of ionic groups in the rubbery matrix of sulfonated EPDM, this material has been reported to behave as a thermoplastic elastomer.[1] The ionic groups, which develop strong coulombic interactions, function as thermally reversible physical crosslinks. The production of ionomers usually involves neutralization of ionizable groups, such as carboxylic or sulfonic acids. Although some effort has been made to study the effect of partial neutralization of acid groups on the ionomers properties,[4,5] the effect of excess neutralizing agent has not been investigated in any detail. The importance of excess neutralizing agent has been realized, however, in at least two reports. Makowski et al.[8] have noted that during neutralization of sulfonated EPDM by zinc acetate, the excess reagent was absorbed and retained in the matrix and affected the melt rheological behavior of the ionomer. Specifically, it was observed that essentially all the zinc acetate that was added to the polymeric free acid was retained by the polymer. Recently, Pecsi et al.[9] have studied the crystallization behavior of the magnesium salt of a polyester containing terminal carboxylic acid groups, and have reported that above the stoichiometrically equivalent Mg content, abrupt changes in the percent crystallinity and the bulk morphology occur.

Earlier we have reported preliminary mechanical studies on a series of novel three-arm polyisobutylene-based ionomers carrying exclusively terminal sulfonic groups.[10-13] It was observed that the addition of a stoichiometric excess of

neutralizing agent greatly affects the mechanical properties of the polymers. Indeed, in some instances this effect overshadowed the effect of other variables such as the identity of the cation.

The objective of this report is twofold: First, to show that excess over neutralization effects are common in our system for various types of neutralizing agents. Second, to forewarn those who commonly treat polymeric acids with excess neutralizing agent and assume that conventional purification (i. e., precipitation or washing with water) removes the excess neutralizing agent. Our experience has been that excess neutralizing agent is retained in the ionomer (depending on the number of precipitations, etc.) and significantly influences the bulk behavior of the polymer.

EXPERIMENTAL

Materials: The synthesis, purification, and sulfonation of the parent three-arm star polyisobutylene (PIB) triolefins have been described by Kennedy et al.[10,14-16] The chemical structure of the acid terminated polymer is:
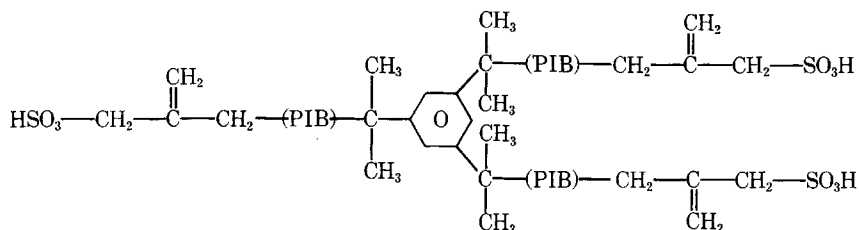
The polymer is designated by indicating its functionality (T for trifunctionality in this case) followed by the molecular weight of the polymer and then the type of functional groups. Two polymeric acids of varying molecular weight were used: T-14–SO_3H and T-21–SO_3H, i. e., trifunctional polymers with overall molecular weights ($\overline{M}_n$) of 14×10^3 and 21×10^3 carrying —SO_3H end groups. The polymeric acids were neutralized to different extents with various salts; for example, T-14–Ca–0 indicates that the polymer of 14,000 molecular weight was neutralized with $Ca(OH)_2$ to the exact equivalence point. The zero indicates that 0% excess of $Ca(OH)_2$ was used. T-14–K–(−10) represents the same polymer acid in which 90% of the SO_3H groups were neutralized with KOH (i. e., 90% of the amount required for neutralization). T-21–ZnAc–100 indicates a trifunctional polymer acid of 21,000 molecular weight neutralized with 100% excess of zinc acetate (i. e., the number of equivalents of zinc is twice the number of equivalents of SO_3H).

NEUTRALIZATION

Since the procedures for neutralization with KOH, $Ca(OH)_2$, and zinc acetate ($ZnAc_2$) differed, the details are described separately.

Potassium Hydroxide: The polymer T-14–SO_3H was partially dried at room temperature for 40 min in a vacuum oven and approximately 2.0 wt % was then dissolved in a mixture of hexane–ethanol (95/5 v/v). After the addition of a few

drops of alizarin and thymolphthalein indicator solution (in ethanol), it was titrated with an ethanolic KOH solution (0.1M) to a faint pink color. To prepare ionomers with excess neutralizing agent, the following procedure was used. After attainment of the end point, the desired volume of excess KOH was added to the polymer solution. Upon addition of excess KOH, the color changed from pink to purple and finally to blue, and concurrently polymer precipitation occurred due to the presence of excess ethanol. The average volume of KOH needed to neutralize a unit weight of polymeric acid was calculated from about four titrations, and, using this value, the partially neutralized sample T-14–K–(−10) was prepared by addition of 0.9 mol KOH/mol acid. The ionomer solutions were dried under nitrogen and then redissolved in a mixture of hexane–ethanol (95/5 v/v) to yield a 2 wt % polymer solution. After dissolution, 0.2 wt % of antioxidant (Irganox 1010) was added. Then the polymer was "steam-stripped" by pouring the solution in a thin stream into boiling water (using about 1 L of boiling distilled water for each 50 mL of solution). To check whether further washing would eliminate excess KOH, the precipitated polymer was agitated in 1 L of boiling distilled water for 0.5 h, the water was drained off, and the washing cycle was repeated two more times with fresh boiling distilled water. The polymer crumbs were filtered and dried in a vacuum oven at 80°C for at least 24 h.

Calcium Hydroxide: The procedure employed was similar to that described above, with the following exceptions. Tetrahydrofuran (THF) was employed for dissolution of the polymer acid because this solvent is miscible with water which is present in the reagent. A saturated aqueous 0.04N Ca(OH)$_2$ solution was rapidly added with good agitation to the polymer solution (about 0.5–1 wt % polymer) using the same mixture of indicators. After addition of portions of the calcium hydroxide solution, precipitation of the ionomer occurred due to addition of the large volume of water. However, phase separation did not affect the neutralization end point if the reagent addition was fast and coagulation of the polymer in the form of large aggregates did not occur. Even in such instances, the addition of more THF and strong agitation resulted in dispersion of the precipitate, and neutralization values were essentially the same as those obtained in titrations in homogenous solutions (for example, against alcoholic KOH). After Ca(OH)$_2$ addition, the solvent and water were removed in a vacuum oven, and the precipitate was dissolved in a hexane–ethanol mixture (approximately 2 wt %). The resulting solution was cast in a Teflon mold, and the films were dried in a vacuum oven for at least 24 h at 80°C before compression molding.

Zinc Acetate: Since this reagent is not a strong base, direct titration cannot be carried out. Thus the required volume of 0.1N aqueous zinc acetate solution was calculated from titrations against a standard KOH solution. The concentration of the zinc acetate solution was determined quantitatively by titration against a standard 0.1N EDTA solution using Erio Chrome Black T as indicator. The zinc acetate ionomers were prepared as follows: sample T-21–SO$_3$H was dissolved in THF (1.0 wt %), and the solution was divided into eight equal charges. The first three charges were titrated against a standard KOH solution, as described above, and from these data the number of equivalents of acid per unit weight of solution was obtained. This value and the weight of polymer solution in each charge yielded the required number of equivalents of zinc acetate solution to be added to the remaining five charges. After addition of the required volume of zinc acetate to the polymer solution, the solvents were evaporated,
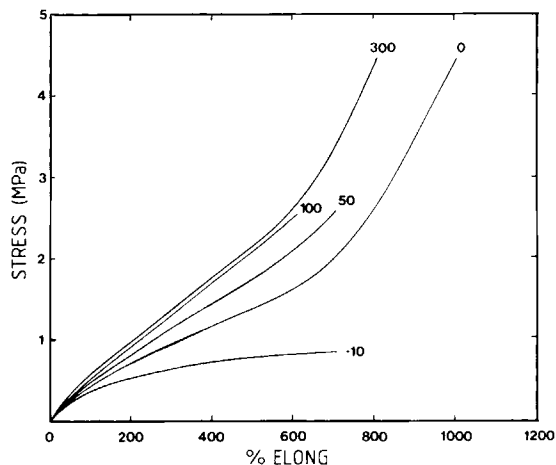
Fig. 1. Stress vs. percent elongation for the T-14–K–X material, where X represents the percent excess neutralizing agent.

% excess	E (MPa)
−10	0.50
0	0.80
50	0.84
100	0.89
300	0.95

the polymer was redissolved in hexane–ethanol mixture, antioxidant was added, and films were cast in Teflon molds. The films were dried in a vacuum oven at 80°C for at least 24 h before compression molding.

Film Preparation: Films for stress–strain studies were prepared by compression molding at 150°C between Teflon sheets at about 1000 psi for 15 min and rapidly quenching to room temperature on a metal sheet. The polymers were stored in a vacuum dessicator.

Mechanical Properties: The stress–strain behavior was determined on an Instron (Model 1122) at room temperature at a constant elongation ratio of 100% min^{-1} based on the initial length of the sample. Dog-bone samples of 1.0-cm length, 0.28-cm width, and about 10-mil thickness were used.

RESULTS AND DISCUSSION

Figure 1 shows the stress–strain behavior of a series of trifunctional ionomers of 14,000 molecular weight as a function of the extent of neutralization with KOH. Evidently, to obtain a good elastomer, it is essential that the neutralization be carried out at least close to the equivalence point; the polymer neutralized to 90% of the end point displayed poor elongation and low recovery. This is expected since un-ionized functional groups are at best weakly interacting and do not participate in the formation of strong multiplet junction points. Moreover, unreacted acid groups may thermally degrade during compression molding at 150°C.[6] Ionomers obtained by titration to or above the equivalence point are good elastomers. The modulus of the polymer not totally neutralized, sample

T-14–K–(−10), is significantly lower (0.5 MPa) than those neutralized to the end point or higher (moduli 0.8–0.9 MPa). Additional data, corroborating the effect of excess neutralizing agent on the properties of PIB ionomers, are available.

Above the equivalence point, the addition of excess KOH does not greatly change Young's modulus. Apparently, excess neutralizing agent does not significantly increase the number of junction points and the molecular weight between "crosslinks," $\overline{M}_c$, remains relatively constant. However, the ultimate properties, e. g., stress at higher elongations, are greatly dependent on the amount of excess KOH added (compare, for example, stresses at 600% elongation). Rheological, thermomechanical, and solution properties, to be dealt with in later publications, are also strongly influenced by the presence of excess neutralizing agent. It is postulated that excess neutralizing agent does not greatly affect the number of ionic aggregates, but it does greatly increase the strength of the associated ionic domains or multiplets. The decrease in the crystallinity of semicrystalline polyesters carrying carboxylate terminal groups upon the addition of Mg salt has also been attributed to the enhanced strength of ionic associations[9] and substantiates our postulate. It may be stated here that Makowski and Lundberg[17] have also noted that the addition of zinc stearate not only markedly facilitates the melt flow of metal sulfonate ionomers at processing temperatures, but also simultaneously influences the mechanical properties of the resultant system. They have explained this behavior in terms of selective plasticization of the ion domains above 120°C by "melted" zinc stearate. Specifically, the zinc stearate is believed to migrate preferentially to the ion domains rather than become uniformly distributed throughout the matrix.[18] Through competitive forces, the zinc stearate "solubilizes" or plasticizes the ion multiplets and/or clusters, thereby facilitating flow. Upon cooling, the zinc stearate separates out within the matrix and recrystallizes, thereby serving as a hard filler, which in turn influences the mechanical properties.

As will be reported in a future publication, neutralization beyond the equivalence point might be construed to affect properties by the removal of associated water from the ion pair multiplets. Information obtained from infrared spectroscopy in conjunction with thermal cycling and mechanical studies indicates that this speculation would not explain our data.

It is important to emphasize that after addition of the neutralizing agent, the ionomers were washed and extracted with hot water, under severe conditions (see Experimental) and, in fact, these conditions are more severe than what is typically reported in the literature. However, apparently not even our treatment eliminated completely the water-soluble KOH from the polymer matrix. Retention of the excess base by the ionomer may be due to kinetic and/or thermodynamic factors and more rigorous washing and/or longer contact with water may reduce or eliminate excess ions. In any event, the influence of excess neutralizing agent on the properties of these polymers is significant. Therefore, when a series of ionomers is compared, consideration of the extent of excess over neutralization should be made. The effect of extra KOH cannot be due to a "filler effect" because, even at the highest concentrations, the volume fraction of KOH in the ionomer would be below 3%.

The effect of excess KOH is not unique; the effect of excess $Ca(OH)_2$ on the stress–strain properties is shown in Figure 2. As before, the excess base added
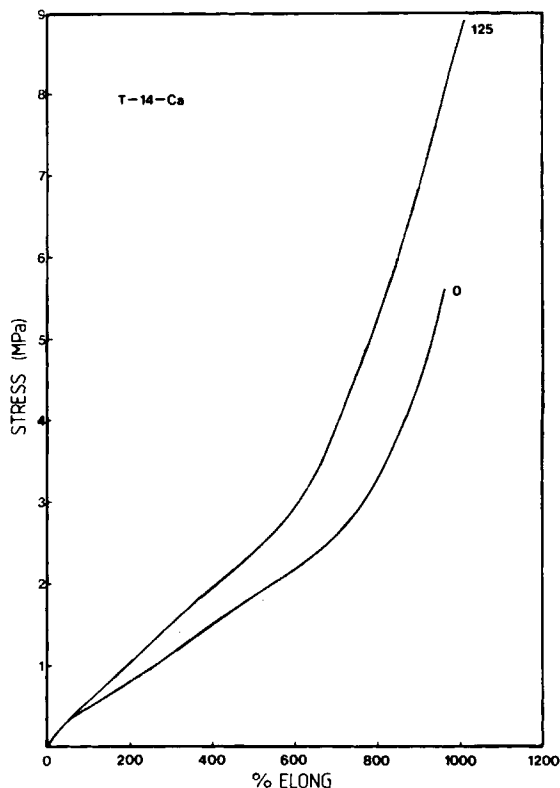
Fig. 2. Stress vs. percent elongation for T-14–Ca-0 and T-14–Ca-125.

beyond the equivalence point influences the ultimate properties much more than it affects the modulus. A comparison of Figures 1 and 2 shows that for polymers of the same molecular weight, neutralized to the equivalence end point, the calcium ionomer is stronger at higher elongations than the potassium ionomer perhaps because the former contains a divalent cation which is better capable of bridging —SO$_3$ groups than the latter, which contains monovalent ions. However, when enough excess base is added to the potassium ionomer, it becomes stronger at an equivalent elongation above 200% than the end point neutralized calcium ionomers (compare for example T-14–K-300 with T-14–Ca-0). Thus precautions must be taken to avoid the effect of excess base and the reaching of erroneous conclusions.

The neutralization with zinc acetate was carried out on a polymer acid of 21,000 molecular weight. However, the effect of excess neutralizing agent is common to all members of our ionomer series. The behavior of zinc ionomers is similar to that of previously discussed ionomers, except for one difference in regard to the stress–strain behavior, i. e., in the zinc ionomers more than an equivalent amount of zinc must be added before the polymer begins to exhibit as a pseudocrosslinked elastomer behavior. According to the results shown in Figure 3, polymer T-21–ZnAc-0 does not behave as a good thermoplastic elastomer. Most likely, neutralization of the sulfonic acid with strong bases [KOH, Ca(OH)$_2$] is essentially complete at the equivalence end point; however, in the case of titration with a weaker base, such as zinc acetate, a higher volume of reagent is required to reach complete ionization of the sulfonic groups. At and above 10% excess
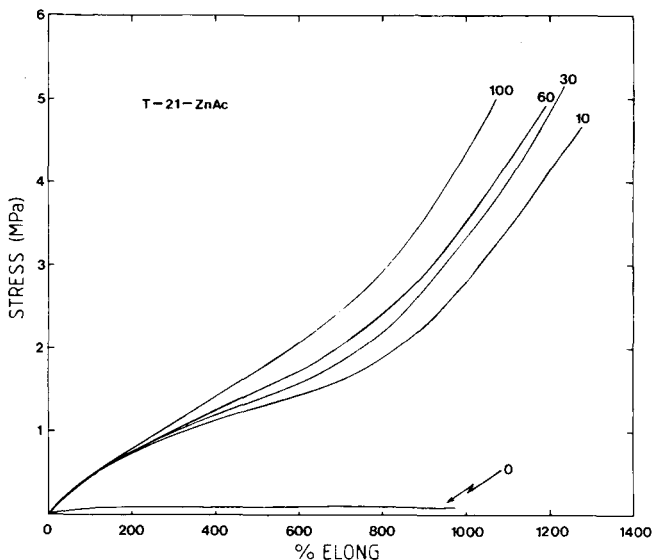
Fig. 3. Stress vs. percent elongation for T-21–ZnAc–X, where X represents the percent excess neutralizing agent.

zinc acetate, the ionomers are good elastomers. The Young's modulus of these elastomers is essentially the same as those of the potassium or calcium systems provided "complete network" formation occurs. In addition, the stress at high elongation (e. g., 800%) also increases with a rise in the salt content for the zinc ionomers.

The last topic to be addressed is whether there is any limit to the excess neutralizing agent with respect to its influence on properties. Above a given quantity of excess for any neutralizing agent, depending on the ionomer and the salt system, phase separation will undoubtedly occur and inorganic material will crystallize out. In this instance the inorganic components will act as filler. However, at the level of excess ions utilized (which is not even close to 5 vol % even at the highest concentration) the filler effect would be negligible compared to what we have observed in our ionomer systems. Thus the effect is due to the interaction of the neutralizing agents with the ionic aggregates or multiplets as might be suggested by the simple model given by Figure 4. According to the results shown in Figure 1 the effect of excess neutralizing agent is nearly negligible above 100%. Possibly above 100%, added neutralizing agent starts to crystallize out and possibly acts as a filler. Since this ionomer was well "washed out," it is expected that the *phase-separated KOH* may be removed more readily. The
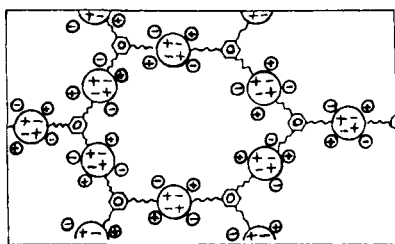

Fig. 4. Simple schematic model used to account for the observed solid state mechanical behavior of those ionomers having an excess of neutralizing agent. Small circles represent ions of the excess salt.

same phenomenon has also been observed with calcium salts (not shown in Fig. 2), where the limit of solubility is reached very early and further addition of $Ca(OH)_2$ produces a precipitate. With zinc acetate, however, the salt is more soluble in an organic matrix, and the addition of excess salt above 100% continues to toughen the polymer further, and, even at levels as high as 400%, excess precipitation does not occur (not shown in Fig. 3).

CONCLUSIONS

Addition of excess neutralizing agents to ionomers results in the absorption of the inorganic component in the polymer matrix. It is speculated that the retained excess salt increases the strength of the ionic association but has little influence on the number of ionic domains. Excess neutralization significantly influences bulk behavior, particularly at high elongations. The effect of the excess neutralizing agents on other properties, such as rheological, thermomechanical, and solution behavior, is significant and is the subject of current investigations.

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