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Influence of plasticizers on poly(methyl methacrylate) ionomers

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The influence of a polar plasticizer glycerol, and a nonpolar plasticizer, dioctylphthalate (DOP), on the microstructure and relaxation properties of poly(methyl methacrylate) ionomers has been investigated by dynamic mechanical thermal analysis. The test results indicate that glycerol strongly interacts with and weakens the ionic cluster 'phase', and also significantly increases the mobility of backbone hydrocarbon chains in the multiplet-containing matrix phase. In contrast, the nonpolar plasticizer DOP is more selective in that it appreciably reduces the glass transition temperature of the hydrocarbon-rich matrix phase, but has a much smaller effect than glycerol on the glass transition temperature of the ion-rich cluster 'phase'. The present results are compared and contrasted with the effects of the same two plasticizers on polystyrene ionomers. © 1997 Elsevier Science Ltd.

(Keywords: PMMA ionomer; plasticizers (DOP and glycerol))

INTRODUCTION

As a result of studies by many investigators using various experimental techniques, such as dynamic mechanical thermal analysis (d.m.t.a.) and small-angle X-ray and neutron scattering, it is now generally accepted that ionomers contain two types of aggregates[1–8]. These are nano-sized multiplets, consisting of a small number of interacting ion pairs, and larger aggregates or clusters, which are ion-rich regions that have their own glass transition that occurs at a higher temperature than that of the multiplet-containing matrix phase. A modification of the classical multiplet-cluster model of ionomers is able to account for a wide range of experimental data on ionomers[9]. According to this model, known as the EHM model, a region of restricted chain mobility, whose thickness depends on the backbone chain mobility and is comparable in size to the persistence length of the polymer, surrounds each multiplet. As ion content rises, these restricted regions begin to overlap to form the ion-rich cluster 'phase'.

In the dynamic mechanical testing of ionomers, the two phases give rise to two separate mechanical loss, tan δ, peaks. The lower temperature peak is associated with the glass transition, T_{g1}, of the hydrocarbon-rich matrix phase and the higher temperature peak is a result of the glass transition, T_{g2}, of the ion-rich cluster 'phase'. With increase of ion content, there is a decrease in the intensity of the matrix peak and an increase in intensity of the cluster peak. Hence, there exists a critical ion content where the two loss peaks have comparable intensity. For polystyrene-based ionomers, the critical ion content is about 6 mol% and, at higher ion contents, the cluster 'phase' becomes dominant[10,11]. Also, as ion content rises, the storage modulus, particularly at temperatures above T_{g1}, increases in value due to increasing intermolecular interactions. As a result, ionic polymers tend to have high melt viscosity, and processing of them into useful products is difficult.

In view of the above, studies of the influence of plasticizers on ionomers are of particular interest. Such studies provide information as to how the viscoelastic properties of the ionomer, and its two-phase microstructure, can be modified so as to obtain the best balance of physical properties and processability.

The two-phase morphology of ionomers, and the resulting differences in polarity of the two phases, provide possibilities of preferential solvation by different plasticizers. This is evident from results of early studies by Lundberg *et al.*[12] on lightly-sulfonated polystyrene (SPS) ionomers containing a nonpolar plasticizer, such as dioctyl phthalate (DOP) or dibutyl phthalate (DBP), or a polar plasticizer, such as glycerol. Glycerol was found to be effective in plasticizing the ionic domains and in reducing melt viscosity, but had little effect on the mobility of the matrix phase. In contrast, the nonpolar plasticizers preferentially plasticized the backbone hydrocarbon chains but had less of an effect on the cluster 'phase'. Additional studies on PS-based ionomers, containing either sulfonate or carboxylate ions, have been reported[13,14]. When these ionomers were plasticized with nonpolar diethylbenzene (DEB), both glass transition temperatures were shifted to lower temperatures; but, for the sulfonate ionomer, the shift of the ionic peak was less than for the carboxylate ionomer. A more recent study of plasticization effects in a lightly sulfonated PS ionomer indicated that nonpolar DOP primarily affected the T_g transition, and that glycerol had a greater effect on the cluster 'phase'

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transition[15]. A more complete discussion of these investigations and of plasticization studies on other types of ionomers is available[16,17].

The principal purpose of the present paper is to investigate the effects of both polar and nonpolar plasticizers on the microstructure and viscoelastic properties of a newly-introduced amorphous ionomer, based on poly(methyl methacrylate) (PMMA). Samples of this ionomer having various ion contents have been prepared in our laboratory. Their dynamic mechanical properties as a function of ion content have been reported[18,19] and a discussion has been given of their deformation modes under tension[20]. In d.m.t.a. tests, these PMMA-based ionomers show two distinct mechanical loss peaks, one associated with the glass transition of the multiplet-containing matrix phase and the other with the glass transition of the ion-rich cluster 'phase'. To assess the effects of plasticizer on each of these two phases, we have selected for study a PMMA-based ionomer having an ion content of 12.4 mol%; as, at this value, both the matrix phase and the cluster 'phase' are essentially comparable in size[18,19].

The second purpose of the paper is to compare the results obtained on PMMA ionomers with those obtained, under the same experimental conditions, on PS-based ionomers. The two homopolymers, though having T_gs at about the same value, differ in other respects such as dielectric constant, polarity and persistence length. Also, the critical ion content at which the cluster 'phase' begins to dominate over the matrix phase is different for the two ionomers, viz. about 12 mol% for PMMA ionomers and about 6 mol% for the PS ionomers. As a result, some changes in the influence of plasticizers on the two ionomers may be anticipated. Result of both aspects of our studies will be discussed in terms of the multiplet-cluster, EHM model of ionomer microstructure[9].

EXPERIMENTAL

Ionomer samples

The PMMA ionomer selected for use in this study, having an ion content of 12.4 mol%, is the same as that used previously for d.m.t.a. studies[18,19] and for deformation/fracture studies[20]. The PMMA-based ionomer was made by neutralization of a random copolymer of methyl methacrylate and methacrylic acid with methanolic sodium hydroxide solution. The ion content was determined by titration of the acid copolymer in benzene/methanol (90/10, v/v) with methanolic hydroxide solution. Ionomer samples were obtained as a powder form by freeze drying and subsequent vacuum drying for 1 week. Details concerning the preparation of the PMMA ionomers are described elsewhere[18,19].

Lightly sulfonated PS were made by sulfonation of PS according to the method reported by Makowski *et al.*[21]. The ionomer synthesized by this method has a random distribution of ionic groups and no significant side reactions (e.g. crosslinking or degradation)[22]. The polystyrene (purchased from Polyscience) has a molecular weight in the range 125,000–250,000. The sulfonation reaction was carried out in dichloroethane (DCE) at 50°C for 1 h. By controlling the amount of sulfonating agent, the degree of sulfonation, i.e. the ion content, was controlled. The reaction was terminated by adding methanol into the reaction mixture. The partially sulfonated PS was completely neutralized with an appropriate amount of methanolic sodium hydroxide. The SPS ionomers were recovered by steam stripping in boiling water, and then pulverized in a blender. The resulting powder sample was washed three times with deionized water and once with methanol. The polymer was redissolved in benzene/methanol (90/10, v/v), freeze dried and vacuum dried for 1 week. Other details of the preparation of SPS ionomers are given elsewhere[23].

Table 1 Compression moulding temperatures of d.m.t.a. specimens

Sample	Moulding temperature (°C)	Releasing temperature (°C)
PMMA	200	80
PMMA ionomer (12.4 mol%)	240	100
+9.2% Glycerol	200	70
+19.4% Glycerol	200	70
+22.4% DOP	200	65
+40.2% DOP	200	65
PS	160	80
SPS ionomer (5.5 mol%)	220	85
+11.7% Glycerol	200	70
+9.5% DOP	200	75

Plasticized samples

Two plasticizers were used in this study: glycerol that served as a polar plasticizer ($\epsilon = 42.5$) and nonpolar dioctylphthalate (DOP, $\epsilon = 6.4$); here ϵ is the dielectric constant of the solvent. Various amounts of plasticizer were added to the ionomer sample contained in a piece of aluminium foil, followed by mixing. Care was exercised so that no ionomer powder was lost during mixing. The plasticized samples were kept in a desiccator with an open bottle of the same plasticizer for more than 72 h. The samples were then transferred into a preheated mould after final mixing. The plasticizer content was determined from the difference in weights between the final moulded product and the original ionomer sample. Molding temperatures for all polymer–plasticizer systems are listed in *Table 1*. An applied pressure was increased step by step. After maintaining the pressure at 3000 psi for 10 min, the mould was cooled down with cooling water under pressure. The pressure was released at the releasing temperatures listed in *Table 1*.

Dynamic mechanical thermal analysis

Moulded samples were cut into dynamic mechanical thermal analysis (d.m.t.a.) specimens (0.5 mm ×2.5 mm × 12 mm) and polished with emery papers. A piezotron (Rheolograph Solid: Toyoseiki, Japan) was used to conduct the d.m.t.a. The test frequency was 1 Hz and the heating rate was 4°C min^{-1}. Details of the measurements, including specimen preparation and analysis, have been reported[11,24].

RESULTS

PMMA-based ionomers

Figure 1 shows the effects of glycerol on the storage modulus of the PMMA ionomer having an ion content of 12.4 mol%, plasticized with 9.2 and 19.4 wt% glycerol.

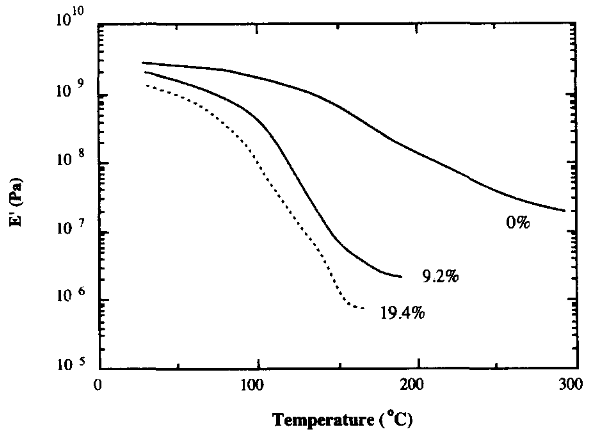

Figure 1 Storage modulus vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol

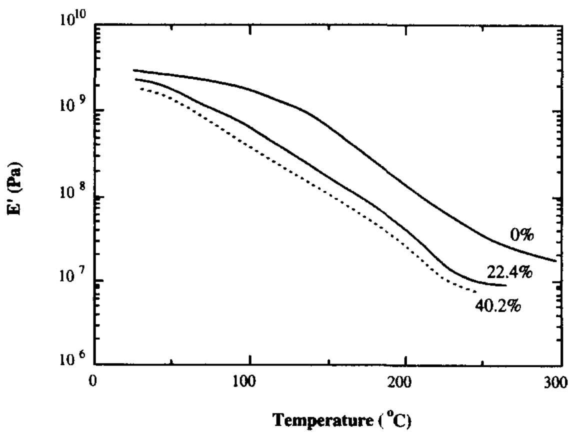

Figure 3 Storage modulus vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with DOP

Table 2 Data on plasticized PMMA ionomers with 12.4 mol% ion content

Sample	E' (at 30°C, GPa)	T_{g1} (°C)	T_{g2} (°C)
PMMA ionomer	2.79	183	254
+ 9.2% glycerol	1.92	140	180
+ 19.4% glycerol	1.31	117	145
+ 22.4% DOP	2.25	121	225
+ 40.2% DOP	1.80	121	219

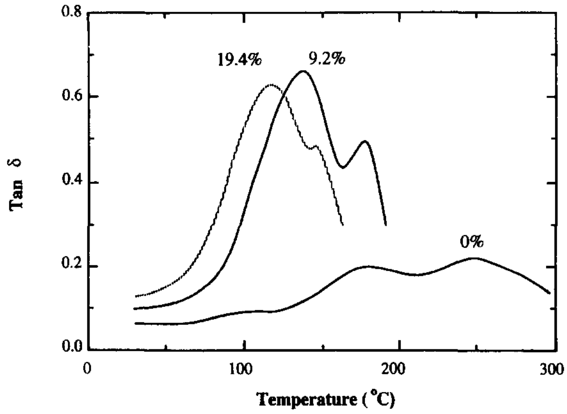

Figure 2 Loss tangent vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol

The unplasticized ionomer shows a rather broad transition with a modulus drop in the high temperature region of only two orders of magnitude, due to the ionic crosslinking effect of the ionic aggregates and a reinforcing effect of a phase-separated cluster domain[18,19]. Upon addition of 9.2 wt% glycerol, the modulus values decrease over the entire temperature range studied. The modulus in the glassy state (chosen as the value of the modulus at 30°C and listed in *Table 2*) decrease moderately while the drop in modulus at temperatures above 100°C is dramatic. With further addition of glycerol, the entire modulus–temperature curve shifts downward and to the left.

Figure 2 is a plot of loss tangent as a function of temperature for the PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol. The unplasticized ionomer shows two primary relaxation peaks, at 183°C and 254°C. The 183°C mechanical loss peak is associated with the glass transition temperature, T_{g1}, of the multiplet-containing matrix phase and the higher temperature mechanical loss peak at 254°C is associated with the glass transition, T_{g2}, of the ion-rich cluster 'phase'. The peak height of each of these mechanical loss peaks is almost the same, indicating that the ionic cluster phase only begins to dominate over the multiplet-containing matrix phase at around 12 mol%, the critical ion content of the PMMA ionomer. This assessment of the d.m.t.a. results is based on the assumption that the tan δ peak height (more rigorously the peak area) reflects the amount of materials in each phase, as typically seen in polymer blends. Although rigorous (quantitative) estimate of the materials may be difficult because of the lack of a detailed knowledge of the morphology, approximate (qualitative) estimate of the ratio of each phase can still be valid, as described in detail by Eisenberg and coworkers[9,10]. In addition to the two primary relaxation peaks, this PMMA ionomer also exhibits, at lower temperatures, two secondary relaxation peaks, designated $T_{\beta 1}$ and $T_{\beta 2}$, reflecting side chain motion of the methoxy-carbonyl groups situated respectively in the ion-poor matrix phase and the ion-rich cluster phase[18,19]. However, only the higher temperature secondary relaxation, $T_{\beta 2}$ associated with the ion-rich cluster 'phase', is visible in *Figure 2* near 100°C.

Upon addition of 9.2 wt% glycerol, both of the primary mechanical loss peaks shift significantly to lower temperatures but the shift of the cluster T_{g2} peak is greater. In addition, the intensity of, or the area under the lower temperature T_{g1} becomes much larger than that of the higher temperature T_{g2} peak. This is an indication that the ionomer microstructure has been altered: the volume fraction of the cluster 'phase' has been reduced, and that of the matrix phase has been increased, by presence of the glycerol. Upon further addition of glycerol to 19.4 wt%, the two primary relaxation peaks further shift to lower temperatures and the intensity of the cluster peak is reduced. The relaxation temperatures, taken as the temperature of maxima in the tan δ data, are listed in *Table 2*. The small secondary, $T_{\beta 2}$, peak near 100°C in the PMMA ionomer, seems to disappear (or to become negligibly small) upon glycerol addition. This also is a consequence of the solvation of the ionic clusters by glycerol.

Figure 3 shows the effects of DOP on the storage modulus of the PMMA ionomer having an ion content of 12.4 mol%. Upon addition of DOP, the modulus

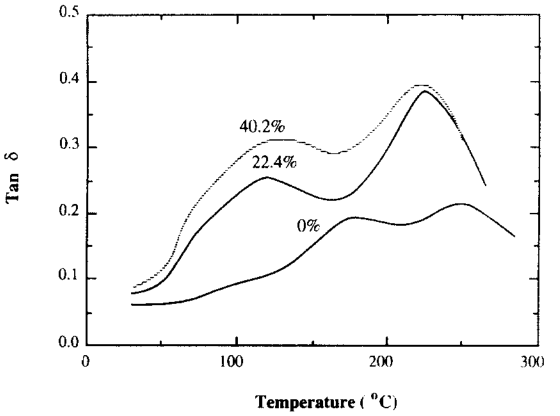

Figure 4 Loss tangent vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with DOP

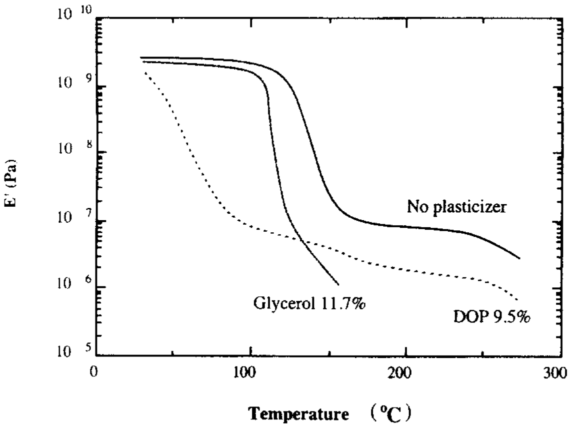

Figure 5 Storage modulus vs temperature for SPS ionomer having an ion content of 5.5 mol%, plasticized with glycerol and DOP

decreases over the entire temperature range, but the drop in modulus at temperature above 100°C is much less than for glycerol. The effects of the DOP plasticizer on the values of the glassy modulus at 30°C are shown in *Table 2*.

Figure 4 shows loss tangent vs temperature curves for the 12.4 mol% PMMA ionomer plasticized with nonpolar DOP. The two primary relaxation peaks are shifted to lower temperatures. For the 22.4 wt% DOP-plasticized system, the 183°C peak, associated with the hydrocarbon-rich matrix phase, is shifted about 60°C to lower temperatures, a value comparable to that caused by 19.4 mol% glycerol. The high temperature peak, associated with the cluster 'phase', is also shifted downwards by DOP but the amount of the shift, about 30°C, is much smaller than that of the matrix phase. The downward shifts of the two primary relaxations appear to level off with further addition of DOP. This is believed to arise from phase separation (due to saturation) of DOP from the ionomer at high DOP content. A loss peak due to a separate DOP phase does not appear in our results as the T_g of DOP is well below room temperature (*ca* -85°C). In the DOP plasticized samples, the small shoulder on the low temperature side of the matrix peak is an indication that the secondary $T_{\beta 2}$ relaxation is still present, in contrast to its disappearance in the glycerol-plasticized samples. The shift to lower temperatures, on addition of DOP, of both the cluster T_{g2} relaxation, and of the secondary $T_{\beta 2}$ relaxation, are indications that the nonpolar DOP does act, to some extent, as a plasticizer for the ionic cluster 'phase'. This finding is in accord with the EHM model of ionomer microstructure as the cluster 'phase', though containing a higher density of ionic groups, also contains many hydrocarbon chain segments between the ionic aggregates[9].

PS-based ionomers

To investigate the influence of backbone chain composition on plasticization effects, we have carried out a d.m.t.a. test, using the same two plasticizers and the same facilities and test conditions, on sulfonated PS ionomers. These tests were made on samples having an ion content of 5.5 mol%. This value is close to the critical ion content of 6 mol%, where the two primary mechanical loss peaks, arising respectively from onset of mobility in the ion-poor matrix phase and in the ion-rich cluster 'phase', have comparable intensities. Another reason for choosing an ion content of 5.5 mol% for the SPS ionomer is that, for this ionomer, data on the effects of both glycerol and DOP on tensile properties are already available[25]; hence the relaxation measurements may provide a basis for achieving a better understanding of the relation between the mechanical properties and morphology.

Figure 5 gives plots of tensile modulus vs temperature for this SPS ionomer and for the ionomer plasticized with about the same amounts (~ 10 wt%) of glycerol and DOP. An interesting feature is that the glassy modulus at 30°C of the DOP-plasticized ionomer is lower than that of the glycerol-plasticized ionomer, while in the high temperature range the reverse is true. In fact, for the glycerol-plasticized samples, measurements could not be made above 150°C, because the samples became too soft. These results, indicating that glycerol preferentially plasticizes the cluster 'phase', while nonpolar DOP preferentially plasticizes the multiplet-containing matrix phase, are in general accord with prior studies on SPS ionomers[12–15]. However, in our samples with ion content of 5.5 mol%, we find that DOP somewhat lowers the value of the high temperature plateau modulus but does not limit its extension. In contrast, for a lightly sulfonated PS (2.59 mol%) ionomer plasticized with about the same amount of DOP, it was noted that the level of the plateau modulus was unaffected, but its extension to higher temperatures was reduced[15]. Our results are more in harmony with test results obtained on a DEB-plasticized SPS ionomer (5.1 mol%)[13]. *Figure 5* also indicates that glycerol increases the sharpness of the matrix transition while DOP reduces the sharpness. These findings are consistent with results obtained on poly(styrene-*co*-sodium methacrylate) ionomer plasticized with glycerol or DEB[13] but they are not evident from the data obtained on the plasticized lightly sulfonated SPS ionomer[14,15].

Figure 6 shows loss tangent data as a function of temperature for 5.5 mol% SPS ionomer and its plasticized systems. For the glycerol-plasticized SPS, the cluster peak is not evident on this graph; however, a plot of loss modulus (not shown) vs temperature shows a very small cluster loss peak at 150°C. For the DOP-plasticized ionomer, there is a much greater shift to lower temperatures of the ion-poor matrix phase than that of the ion-rich cluster 'phase', an indication that the nonpolar plasticizer preferentially plasticizes nonpolar backbone chains of the ionomer. In contrast, glycerol shifts the relaxation peak of the ion-poor matrix phase

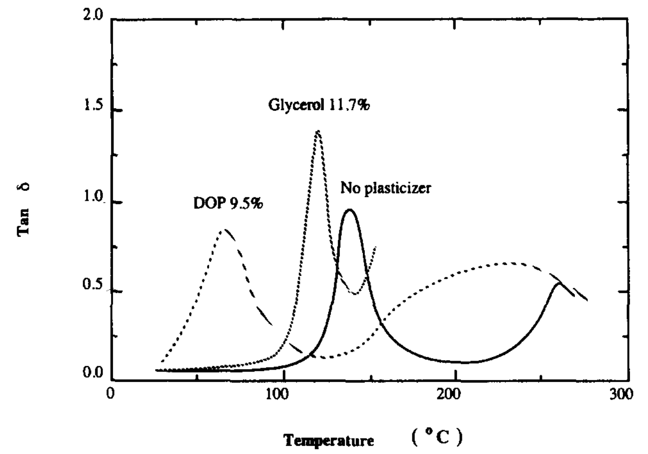

Figure 6 Loss tangent vs temperature for SPS ionomer having an ion content of 5.5 mol%, plasticized with glycerol and DOP

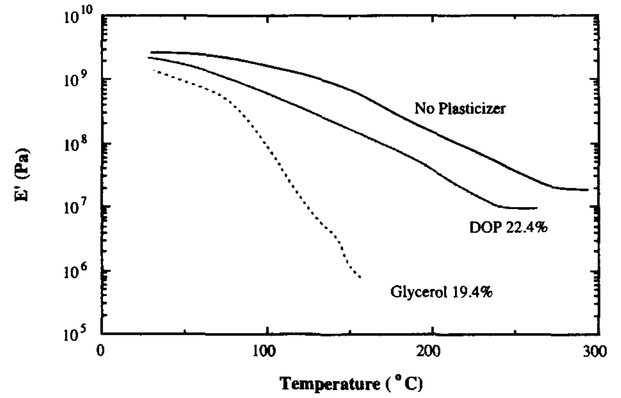

Figure 7 Storage modulus vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol and DOP

only a small amount ($\sim$ 17°C), while the ion-rich 'phase' is essentially eliminated.

DISCUSSION

First we discuss the comparative effects of the two plasticizers on the PMMA ionomer samples. It is evident from the T_gs listed in *Table 2* that glycerol interacts much more strongly with the ion-rich 'phase' than does the nonpolar DOP, and this behaviour is in accord with the greater polarity and higher dielectric constant of glycerol. What is perhaps surprising is that the polar glycerol appears to be at least as effective a plasticizer as nonpolar DOP for the hydrocarbon-rich matrix phase. For example, for comparable concentrations of about 20 wt%, the matrix T_{g1} temperature is actually lowered a slightly greater amount by glycerol than by DOP. Based on solubility parameter values of respectively 16.5, 7.9 and 9.3 (cal cm^{-3}) for glycerol, DOP and PMMA, this would not be expected. However, the high ion content, 12.4 mol%, of the PMMA ionomer gives it a much greater degree of compatibility with the polar glycerol than would be achieved by the PMMA homopolymer.

The comparative effects of glycerol and DOP, at concentrations of close to 20 wt%, on the storage modulus are shown in *Figure 7*. In the high temperature range glycerol has a much stronger effect than DOP. For example, at 150°C, as a result of the interaction of the polar plasticizer with the ionic cluster 'phase', the modulus is several decades below that of the DOP-plasticized ionomer. Even at lower temperatures in the glassy state, the polar glycerol exerts a stronger influence. This is evident from *Figure 8* where the modulus, determined at 30°C, is plotted against concentration of the plasticizer. Values decrease linearly with plasticizer content, but the rate of decrease is 7.7% per wt% glycerol vs 2.5% per wt% of DOP. Clearly, by control of plasticizer type and content, processability can be improved and a wide range of properties achieved in PMMA-based ionomers.

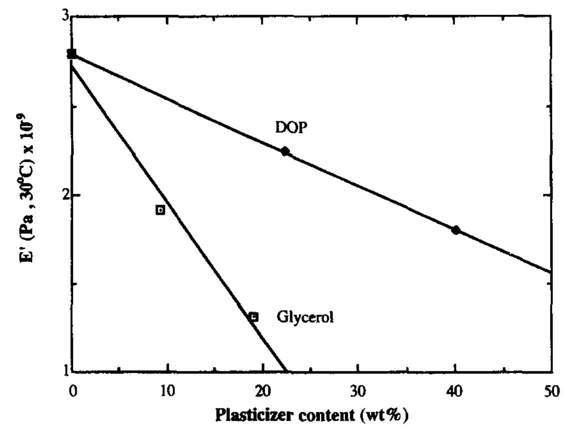

Figure 8 Glassy moduli (at 30°C) vs plasticizer content for PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol and DOP

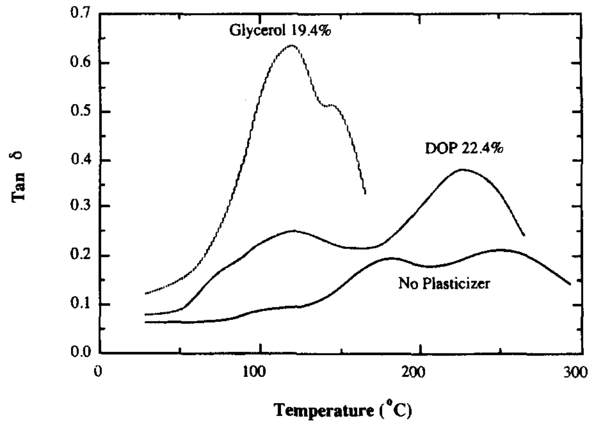

Figure 9 Loss tangent vs temperature for PMMA ionomer having an ion content of 12.4 mol%, plasticized with glycerol and DOP

Figure 9 gives comparative plots of the mechanical loss, $\tan\delta$, vs temperature for the PMMA ionomer and for the ionomer plasticized with approximately equal amounts of DOP and glycerol. Here too we see that glycerol interacts much more strongly than DOP with the ion-rich cluster 'phase', shifting the cluster loss peak to lower temperatures by over 100°C and considerably reducing its intensity. As a result, the intensity of the multiplet-containing matrix phase is increased at the expense of the cluster 'phase'. It may be concluded that the nonpolar DOP preferentially plasticizes the hydrocarbon-rich matrix phase but does interact, to some extent, with the cluster 'phase' as that phase, though ion-rich, also contains hydrocarbon chains: and that glycerol effectively serves as a dual plasticizer for PMMA ionomers, as it has a comparable effect to nonpolar DOP on the multiplet-containing matrix phase and a very strong effect on the ion-rich cluster 'phase'.

We next compare results obtained on plasticized SPS ionomers with those obtained on the plasticized PMMA ionomers. In our study of plasticized SPS ionomers, experimental conditions as to specimen size and shape, frequency, heating rate and types of plasticizers, were maintained the same as for the PMMA ionomer studies; hence, a reasonable comparison of the results can be made. In general, both from our studies on SPS ionomers, and from literature reports concerned with both SPS ionomers and poly(styrene-*co*-metal methacrylate) ionomers, it has been found that nonpolar plasticizers, such as DOP or DEB, preferentially plasticize nonpolar backbone chains and that polar plasticizers, such as glycerol, preferentially interact with ionic domains and tend to destroy them.

Our data on the 5.5 mol% SPS ionomer show that, for approximately 10 wt% of plasticizer, polar glycerol shifts the cluster peak about 100°C to lower temperatures and greatly weakens the clusters. Somewhat similar effects, with a shift of about 75°C to lower temperatures, was observed for the glycerol-plasticized PMMA ionomer. However, marked differences arise between the two ionomers in the effects of polar glycerol on the hydrocarbon-rich matrix phase. For the SPS ionomer, as *Figure 6* shows, 11.7 wt% glycerol shifts the matrix peak to lower temperatures by only 17°C while, as *Table 2* indicates, the shift is 43°C for the 9.2 wt% glycerol-plasticized PMMA ionomer. This latter value is even greater than the shift anticipated from a comparable concentration of DOP in the PMMA ionomer, as may be inferred from the data of *Figure 4* and *Table 2*. Thus, while polar glycerol preferentially plasticizes the ionic clusters in SPS ionomers, in the PMMA ionomer it clearly acts as a dual plasticizer for both the multiplet-containing matrix phase and for the ionic-rich cluster 'phase'.

A dual plasticization effect by a single plasticizer, as observed herein for glycerol in PMMA ionomer, has also been noted in the PS ionomer/dimethylformamide (DMF) system[24]. In that study, an SPS ionomer (8.5 mol%) having 10.8 wt% DMF was investigated by d.m.t.a. It was found that DMF almost completely eliminated the high temperature peak (cluster 'phase') and also shifted the low temperature peak (ion-poor matrix phase) to temperatures below the T_g of PS. The low temperature transition was also much broader than that of PS, indicating a typical backbone plasticizer effect. Thus, DMF works not only as an ionic domain plasticizer, weakening ionic interactions in the ion-rich 'phase', but also as a backbone plasticizer. This behaviour is attributed to the fact that DMF is known to be a good solvent for PS[26]. For example, the second virial coefficient, A_2, of the PS solution in DMF is 2.0×10^4, comparable to the A_2 value of the PS solution in toluene, a well-known good solvent for PS[27]. In addition, it is known that DMF completely destroys ionic aggregates in dilute solution and even causes polyelectrolyte behaviour[28].

In a similar fashion, glycerol works as an effective dual plasticizer for PMMA ionomers. Possible reasons why glycerol functions as an effective dual plasticizer for the PMMA ionomer, but not for the PS ionomer, are as follows. First, polar glycerol ($\epsilon = 42.5$) can interact with ionic groups in the ion-rich 'phase', as is the case of DMF ($\epsilon = 36.7$), and thereby weaken ionic associations. Secondly, glycerol may have better compatibility with PMMA than with PS, because PMMA ($\epsilon = 3.0$) is more polar than PS ($\epsilon = 2.5$)[27]. In addition, ester groups in the repeating unit of PMMA may form hydrogen bonds with the hydroxyl groups in glycerol, thereby increasing interaction between glycerol and the matrix phase of the PMMA ionomer.

With regard to the effects of nonpolar DOP on the two ionomers, the influence appears to be greater for the less polar SPS ionomer. For example, for 9.5 wt% concentration of DOP in the SPS ionomer, the plasticizer, as *Figure 6* shows, shifts the matrix T_{g1} peak to a lower temperature by about 75°C, while the cluster peak is shifted about 30°C; but for a much higher concentration (22.4 wt%) of DOP in the PMMA ionomer, the temperature shift, as *Table 2* indicates, is 62°C for the matrix peak and 29°C for the cluster peak. In both ionomers, the nonpolar DOP interacts more strongly with the less polar matrix than with the more polar cluster 'phase', but the effects are greater, for comparable plasticizer concentration, in the SPS ionomer than in the more polar PMMA ionomer.

CONCLUSIONS

1. Glycerol acts as a dual plasticizer for PMMA ionomers, significantly affecting both the ion-rich cluster 'phase' and the hydrocarbon-rich matrix phase.
2. In the glassy state at 30°C, the modulus of the PMMA ionomer decreases linearly with plasticizer content for both glycerol and DOP but the rate of decrease is three times greater for glycerol.
3. Nonpolar DOP preferentially plasticizes the matrix phase of both PMMA and PS ionomers but the effects are greater for the less polar SPS ionomer.
4. By control of plasticizer type and concentration, processability of PMMA and PS ionomers can be improved and a wide range of properties can be achieved.

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