Tangible Plasticization/Filler Effects of Sodium Salts of Dimer Acids on the Mechanical Properties of Styrene Ionomers

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ABSTRACT: The effects of the presence of dimer acid (DA) molecules in Na-sulfonated polystyrene (PSSNa) and poly(styrene-co Na-methacrylate) (PSMANa) ionomers on the ionomer properties were investigated using a dynamic mechanical analysis technique. The DA decreased the matrix and cluster T_gs of PSSNa ionomer without changing the ionic modulus, suggesting that the DA resided both in the matrix and cluster regions of PSSNa ionomer and acted mainly as a plasticizer. On the other hand, the DA decreased the cluster T_g of PSMANa ionomer, without changing the matrix T_g, and also increased the ionic modulus, implying that the DA behaved like plasticizer only for the cluster regions. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2443–2450, 2013

INTRODUCTION

Ionomers are polymeric materials containing a relatively small amount of ionic groups (<15 mol %) embedded in a polymer matrix of low dielectric constant.[1] The presence of the ionic groups in the polymer matrix generally causes ion aggregation. The ionic aggregates (so-called multiplets) induce the restriction of the mobility of the polymer chains emanating from the multiplet and in the vicinity of the multiplets.[2] When the concentration of ionic groups of an ionomer is very low, the number of the multiplets is relatively small so that the restricted mobility regions of the polymer chains do not overlap, and the ionomer shows only the glass transition (T_g) of non-ionic polymer matrix (i.e. matrix T_g). On the other hand, with increasing ion content, the number of the multiplets increases and the restricted mobility regions start overlapping. When the size of the restricted mobility regions becomes large enough to have their own T_g (i.e. cluster T_g), the regions are called clustered regions. At this stage, the ionomer shows two T_gs; the matrix T_g is seen at low temperatures, and the cluster T_g occurs at high temperatures. In addition, the ionomer exhibits an "ionic" plateau in the plots of log(storage modulus) vs. temperature, which is shown in the temperature range between the matrix and cluster T_gs.[3,4] The height and width of ionic plateau are mainly related with the amounts of clustered regions and the strength of interactions between ionic groups in the multiplets, respectively.[1]

Only a few studies have been performed on the effects of the aliphatic dicarboxylic acid salts on the properties of amorphous polystyrene (PS)-based random ionomers.[5,6] It was suggested that the di-functional organic salts became phase-separated and acted mainly as filler particles in poly(styrene-co Na-methacrylate) (PSMANa) ionomers.[5] It was also found that when a large amount of sodium hexadecanedioate was added to the poly (styrene-co-sodium styrenesulfonate) (PSSNa) ionomer, the organic salt acted both as a reinforcing filler and as preferential plasticizer for the clustered region of PSSNa ionomers.[6] On comparing these results with those of other systems, it was proposed that the amount of the additives was responsible for the increasing ionic modulus.

These days, the environmental regulations on industrial consumption have been tightened up, and there is an urgent need for the development of new eco-friendly materials. Thus, natural products (e.g. vegetable oil), non-toxic, and environmental-friendly products have gained much attention in regard to the development of "green chemicals". Recently, we have conducted a research on the preparation and modification of bio-based monomers. In course of the research, various "dimer acids" (DA), e.g. monocyclic, bicyclic, acyclic DA (Scheme 1), have been prepared from waste fatty acid cooking oils (vegetable and animal oils) as raw materials; the detailed compositions of the DAs are not known at present, but it is known that the reaction
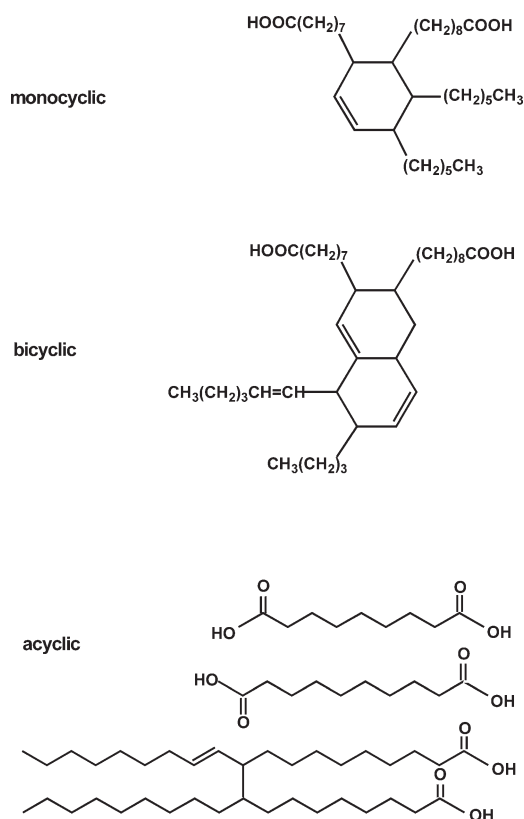
Scheme 1. Chemical structures of dimer acids obtained from waste fatty acid vegetable oils.

condition could control the compositions. From our previous studies,[5,6] we have known that the DA obtained from the waste cooking oil, being eco-friendly additives, can also be utilized as filler/plasticizer for the PS-based ionomers. Thus, in this study, we attempted to investigate the effects of the addition of sodium salts of DA compounds to the PS-based ionomers on the mechanical properties and morphology of the ionomers.

EXPERIMENTAL

Sample Preparations

The preparation method of DA using the fatty acids of soybean oil, modified from the work by Paschke et al.[7] and Wheeler and White,[8] is described briefly below: Fatty acid, catalyst, hypophosphoric acid, and deionized water were placed in a high-pressure stainless-steel reactor that was equipped with a mechanical stirrer and a cooling water line equipped with a temperature controller. The reactor was sealed and purged with N_2 gas four times to remove O_2, and then N_2 gas was released. The reactor was heated to 250°C, and kept at that temperature for 6 hr. When the reaction was complete, the products were taken out from the reactor, and the hypophosphoric acid was added to the products for the neutralization, which was then stirred at 80°C for 1 hr. Subsequently, diatom earth was added to the products: the solution was stirred sufficiently and, then, filtered. Finally, the DAs were separated from the monomer fatty acids by using a distillation process at 270°C. To prepare the ionomers, polystyrene (PS) homopolymer (MW = ca.

300,000) and poly(styrene-co-methacrylic acid) PSMAA copolymer (MW = ca. 300,000) containing 7.0 mol% of methacrylic acid units were synthesized by the method described elsewhere.[4] Poly(styrene-co-styrenesulfonic acid) copolymer was prepared by the sulfonation of the PS using the method reported by Makowski et al.[9]; the content of the styrenesulfonic acid units was 7.7 mol%. To prepare the ionomer samples containing varying amounts of DA, the DA and copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture, and the acid groups of the DA and copolymers were fully neutralized with methanolic NaOH solution. Then, the samples were freeze-dried and dried further in a vacuum oven at ca. 150°C for 24 hr. For the dynamic mechanical property measurements, the samples were compression-molded when the mold temperatures reached ca. 190 and 230°C for the methacrylate and sulfonated ionomers, respectively, at a pressure of ca. 25 MPa. The molded samples were annealed under a vacuum at 150°C for 12 hr. The sample denotation used in the present work is PSSNa-x and PSMANa-x, where PSSNa and PSMANa are Na-neutralized sulfonated polystyrene and poly(styrene-co-sodium methacrylate) ionomers, respectively, and x indicates the weight % of Na-neutralized DA. To compare the results obtained from the DA-containing ionomers with those obtained from the ionomers containing only one type of sodium salt of aliphatic diacids, we also prepared PSSNa and PSMANa ionomers containing varying amounts of sodium salt of aliphatic diacid, i.e. sodium hexadecanedioate (HD). An ASPECT 1000 Fourier transform infrared spectrometer (Bruker AXS, Madison, WI) was used to check the neutralization of PSSNa-x ionomers. The samples were pelletized with KBr and scanned 64 times, and the scanning range was from 4000 to 400 cm^{-1}. It was found that in the wavenumber range of 900–1300 cm^{-1} the IR spectrum of pure PSSNa ionomer was similar to those obtained by other researchers10–19 and was also similar to those of DA-containing ionomers (spectra are not shown here), indicating that the ionomers were fully neutralized. At this point, it should be mentioned that the PSMANa and PSSNa ionomers are known to be thermally stable well above 300°C,[20] but the thermal stability of Na-neutralized DA is not known yet. Thus, a TA instrument 2050 thermogravimetric analyzer (TGA) was utilized to study the thermal stability of the Na-neutralized DA in the ionomers. The experiments were carried out as a function of temperature, over the range of 50–500°C, at a heating rate of 10°C min^{-1} under nitrogen and at a N_2 flow rate of 30 mL min^{-1}. For a thermal property study, a TA DSC 2010 differential scanning calorimeter (TA Instruments, New Castle, DE) was used. The samples were scanned using the DSC from 30°C to 300°C, with a heating rate of 10°C min^{-1}.

Dynamic Mechanical Property Measurements

The storage modulus (E') and loss tangent (tan δ) of each sample were measured as a function of temperature using a TA Instruments Q 800 dynamic mechanical analyzer in a dual cantilever-bending mode. The samples were heated at a heating rate of 1°C min^{-1}. The detailed data analysis was performed using the data obtained at 1 Hz. When deconvolutions on the loss tangent data were necessary, we performed the curve deconvolutions using PeakFit program (Jandel). The best fits were
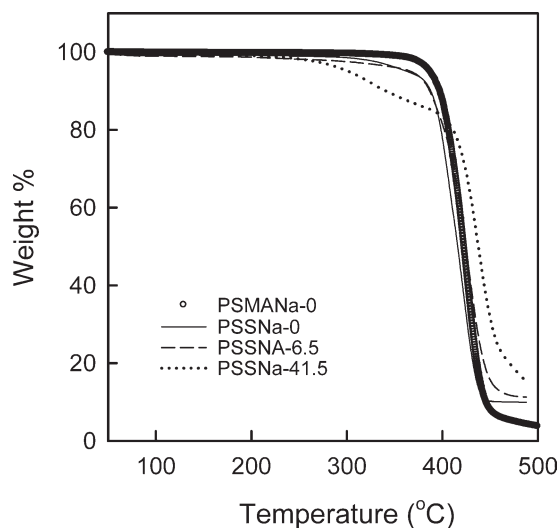
Figure 1. TGA thermograms of PSMANa-0, PSSNa-0, PSSNa-6.5, and PSSNa-41.5 ionomers.

achieved by assuming an exponential background and fitting the matrix and cluster peaks with Gaussian Area peaks.

Small Angle X-ray Scattering Experiments

The small angle X-ray scattering (SAXS) experiments were conducted at Station 3 C of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The sample-to-detector distance was 1 m, which allowed SAXS data to be obtained in the q (scattering vector) ranging from ca. 0.2 to 4.2 nm^{-1}, where $q = 4\pi \sin\theta/\lambda$; θ is half the scattering angle, and λ is the X-ray wavelength ($\lambda = 0.1608$ nm).

RESULTS AND DISCUSSION

Figure 1 shows the weight loss of PSMANa-0 and PSSNa-x ionomers as a function of temperature. At this point, it should be mentioned that we chose only one ionomer system that contains Na-neutralized DA, i.e. PSSNa-x ionomers, because the purpose of this TGA study was to investigate the thermal stability of the Na-neutralized DA, not those of the ionomers. The PSMANa-0 and PSSNa-0 ionomers are shown to be thermally stable well above 300°C.[20] The temperatures of 2% and 5% weight loss for the PSSNa-0 ionomer are ca. 320 and 370°C, respectively, while those for the PSSNa-6.1 ionomer are ca. 270 and 370°C. On the other hand, the temperatures of 2% and 5% weight loss for the PSSNa-41.5 ionomer are ca. 260 and 310°C, respectively. Thus, in the present work, the mold temperatures of 190 and 230°C for the methacrylate and sulfonate ionomers are suitable for the sample preparation and for the measurement of dynamic mechanical properties of these ionomers, since residence times are short.

The loss tangents of PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 2 as a function of temperature. First of all, as expected, two loss tangent peaks are seen in the figure; the matrix peak at low temperatures and the cluster peak at high temperatures. The presence of well-developed two loss tangent peaks indicates that these ionomers are well clustered ionomers.[1] Secondly, it is observed that the

positions of the matrix and cluster peaks of the PSSNa ionomers shift to lower temperatures with increasing amounts of DA. In addition, the intensity of the matrix peak decreases gradually with increasing DA amounts, but that of the cluster peak seems to increase slightly. In the case of PSMANa ionomers, only the cluster peak position shifts to lower temperatures, but the matrix peak position seems to remain constant. The intensities of the matrix and cluster peaks of the PSMANa ionomers change in a similar way found in the PSSNa ionomers. In the case of the loss tangent and storage modulus curves of the PSSNa and PSMANa ionomers containing HD, even though we obtained them by using the samples that we prepared in the present work, we do not show them here because similar results had already been shown elsewhere.[5,6] We only use the T_gs and ionic moduli of HD-containing ionomers to compare them with those of the ionomers containing DA.

Figure 3 shows, as a function of the amounts of DA or HD, the T_gs of the PSSNa and PSMANa ionomers obtained from the positions of the loss tangent peaks.

The data can be fitted to linear functions and the intercepts and slopes of the fitted lines for the T_gs of PSSNa and PSMANa ionomers containing either DA or HD are listed in Table 1.

The matrix and cluster T_gs of the PSSNa ionomers decrease in similar rates with increasing amounts of DA. This suggests that the DA might act as plasticizer, at least to some extent, in the PSSNa ionomer. In addition, the decreasing rates of T_gs (i.e., ca. 1°C/wt%) imply that the DA might be very effective plasticizer, which is one of very important factors for polymer processing.
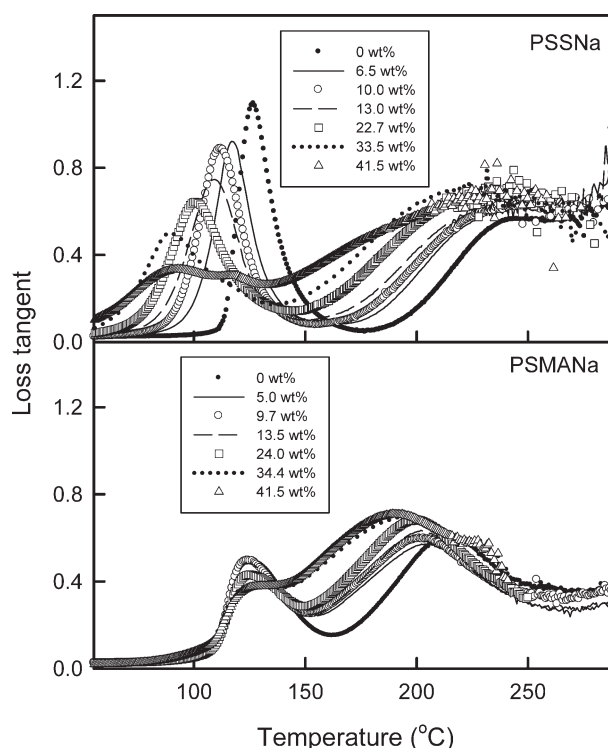

Figure 2. Loss tangents of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.
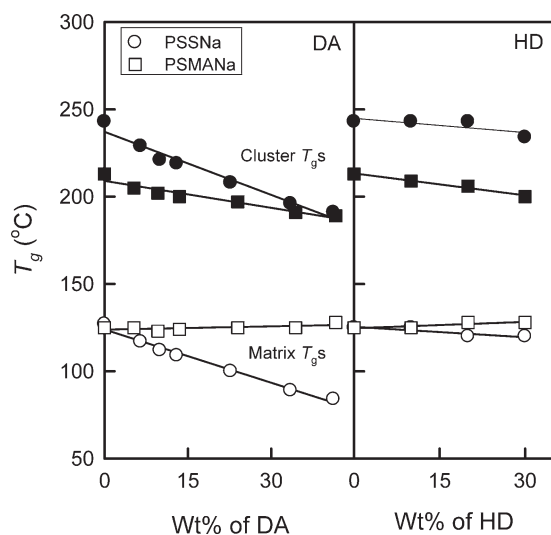
Figure 3. Matrix and cluster T_gs of PSSNa and PSMANa ionomers containing DA (left) or HD (right) obtained from the loss tangent peak positions (at 1 Hz) as a function of wt% of DA or HD.
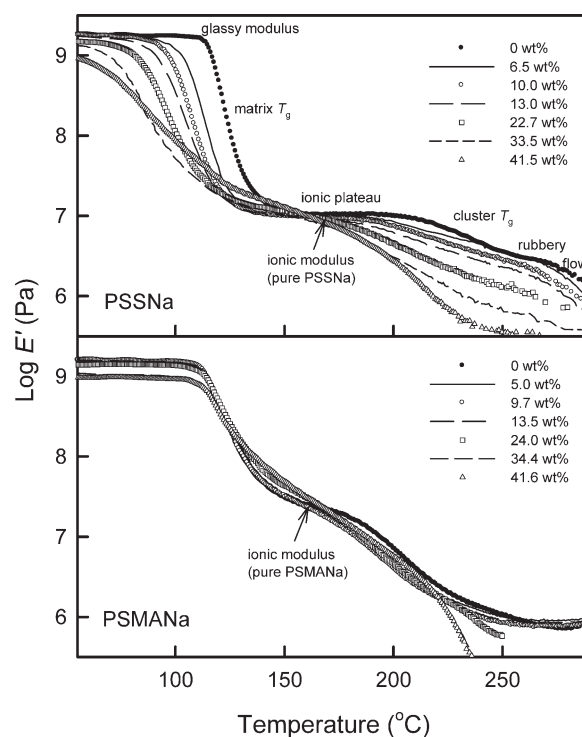

Figure 4. Storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.

In the case of PSMANa ionomer, the cluster T_g also decreases but slowly. On the other hand, the matrix T_g seems to remain constant at 125°C. The results mentioned above imply that the roles of DA in the PSSNA and PSMANa ionomers are not the same; the DA in the PSMANa ionomers might behave like plasticizer only for the cluster regions. In the cases of the ionomers containing HD, the decreasing rates of the matrix and cluster T_gs are lower than those of the PS ionomers containing DA. These results clearly indicate that the effect of the presence of the DA on the T_gs of PSSNa ionomers is stronger than that of the HD.

The storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 4 as a function of temperature.

In the case of PSSNa-0 ionomer, it is seen that the modulus curve changes from a glassy modulus, a sharp modulus drop due to the glass transition of matrix regions, a relatively long and horizontal "ionic" plateau (the segment of the modulus curve between the matrix and cluster T_gs), a second modulus drop due to the glass transition of the cluster regions, a slight downward slope related to a rubbery modulus and the last modulus drop related to sample flow. It is observed that, with increasing amounts of DA, the slopes of the modulus curve for

the matrix T_g and cluster T_g become less steep. This indicates that, with increasing amounts of DA, the glass transitions take place in a relatively wider temperature range. The onset points of the modulus drops for the matrix and cluster T_gs of the PSSNa ionomer shift to lower temperatures with increasing DA contents. It is also observed that the slope of ionic plateau becomes slightly steeper with increasing DA amounts. In the case of the PSMANa ionomers, it is seen that the changes of modulus curves with the amounts of DA are different from those found in the PSSNa ionomers. Especially, with increasing amounts of DA, the onset points of the modulus drop for the matrix glass transition of the PSMANa ionomers seems to remain at similar positions. The slope of ionic plateau of the PSMANa ionomers becomes also steeper with increasing amounts of DA.

The presence of ionic plateau is the unique characteristics of PS-based ionomers. Thus, it is useful to analyze the ionic plateau in more detail to gain an insight into the roles of DA in the ionomers. Before we start to discuss the ionic plateau of the ionomer containing DA, let us review the ionic plateaus of pure PSSNa and PSMANa ionomers. Since some of amorphous ionomers show the ionic plateau between the matrix and cluster T_gs, it can be thought that the cluster regions including multiplets act as cross-links as well as reinforcing filler particles.[3,21–24] If the multiplets remained intact in the temperature range between the matrix and cluster T_gs, the ionomer would show a modulus plateau (i.e. ionic plateau), higher than the rubbery plateau, due to the filler effect of the clusters. The height and width of ionic plateau are related to the degree of clustering and the strength of the interactions between the ion pairs in the

Table I. The Intercepts and Slopes of the Lines Fitted to the T_gs of PSSNa and PSMANa Ionomers Containing Either DA or HD

Ionomers	Cluster (T_g)		Matrix (T_g)	
	Intercept	Slope	Intercept	Slope
PSSNa-DA	237	−1.2	124	−1.0
PSMANa-DA	209	−0.5	125	0
PSSNa-HD	245	−0.3	126	−0.2
PSMANa-HD	213	−0.4	127	0

multiplets, respectively.[1,3,20] As can be seen in Figure 4, the ionic plateau of the PSSNa ionomer is lower but wider than that of the PSMANa ionomer of the same ion content. This is due to the differences in the position of ionic groups and the strength of interactions between the ion pairs in the multiplets. Firstly, the sulfonate anionic group of the PSSNa ionomer and the carboxylate anionic group of the PSMANa ionomer are attached to the *para* position of the benzene ring of a styrene unit and the main chain of the ionomer, respectively. Thus, the distance between the anionic group and the main chain is longer for the PSSNa ionomer, compared to the PSMANa ionomer. This implies that the ion pairs of the PSSNa ionomer can form larger multiplets, compared to the PSMANa ionomer,[3] because of less steric hindrance. Secondly, the interactions between the Na-sulfonate ion pairs are stronger than those between the Na-carboxylate ion pairs.[3,25] This leads to more ion pairs per multiplet of the PSSNa ionomer, compared to those of PSMANa ionomer of the same ion content. At this point, it should be mentioned that the ion-hopping is related to the strength of interactions between ion pairs in the multiplets and is one of the cluster glass transition mechanisms:[3,4,26–33] When the ion-hopping occurs, the storage modulus of the ionomer starts decreasing. Naturally, the more ion pairs per multiplet and the stronger interactions between ion pairs in the multiplets of the PSSNa ionomer make the ion-hopping occur at higher temperatures (i.e. higher cluster T_g), compared to the PSMANa ionomer. This higher cluster T_g causes a wider ionic plateau for the PSSNa ionomer. Now, let us talk about the height of ionic plateau in the modulus–temperature plots, which, again, is not directly related with the cluster T_g that is mainly related with the strength of interactions between ion pairs. It is known that with increasing ion contents, the ionic plateau shifts to higher positions,[4] indicating that the ionic plateau position is associated with the degree of clustering. Since the PSSNa ionomer has more ion pairs per multiplet than the PSMANa ionomer, there must be fewer multiplets for the PSSNa ionomer, at the same ion content. If the thickness of reduced mobility regions surrounding the multiplets were constant, the size of the restricted mobility regions would be smaller for the ionomer having fewer multiplets. Thus, at the same ion content, the degree of clustering (i.e. the size of reduced mobility regions) of the PSSNa ionomer is lower than that of the PSMANa ionomer. As a result, the ionic plateau of the PSSNa ionomer is lower than that of the PSMANa ionomer, even though the cluster T_g of the PSSNa ionomer is higher than that of the PSMANa ionomer.[3] One should keep these aspects in mind when one interprets the modulus data of polystyrene ionomers.

To evaluate the position of ionic plateau, we obtained the ionic moduli (E'_{ionic}) of the ionomers. The ionic modulus is a modulus at the point of a minimum slope in the ionic plateau region. Figure 5 shows the ionic moduli of the PSSNa and PSMANa ionomers containing various amounts of DA as a function of wt% of DA. This figure also includes the ionic moduli of styrene ionomers containing HD. It is seen that, with increasing DA amounts, the $\log E'_{ionic}$ (Pa) of the PSSNa seems to remain constant at 7.0 ± 0.008, but that of the PSMANa increases linearly. Figure 4 also shows that the ionic moduli of PSSNa and PSMANa ionomers containing HD also increase not
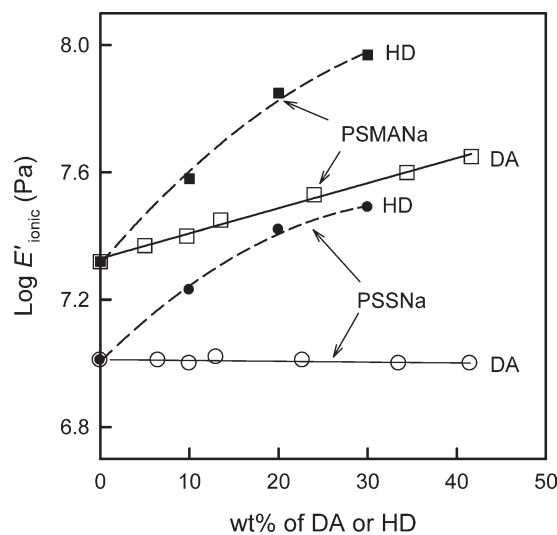

Figure 5. Ionic moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA or HD as a function of wt% of DA or HD, measured at 1 Hz.

linearly but rather quadratically, with increasing HD amounts. It is clear that the increasing rates of log E'_{ionic} of the ionomers containing HD are higher than those of the ionomers containing DA. At this point, it should be mentioned that the increasing ionic modulus of the PSSNa-HD or PSMANa-DA or PSMANa-HD ionomers might be due to the fact that the DA or HD in the ionomer might act as filler particles (the endothermic DSC peak for the T_m of Na-neutralized HD and DA is seen at 222 and 228°C, respectively). In addition, the filler effect of the HD in the PSMANa ionomer is stronger than that of DA in the PSSNa and PSMANa ionomers on the increasing ionic moduli of the ionomers.

Shown in Figure 6 are the SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of either DA or HD. First of all, small-angle upturn is seen for all the ionomers. This upturn might be due to the compositional heterogeneity or the large-scale density fluctuations of scattering centers of the ionomers.[34–40] In the case of PSSNa ionomer, a well-developed SAXS peak is seen at q (scattering vector) = ca. 1.5 nm^{-1}, and the peak position shifts to slightly higher q (indicating that the Bragg distance between scattering centers becomes slightly shorter and the peak intensity increases, with increasing DA amounts. In addition, the width of the SAXS peak becomes narrower with increasing DA amounts. This implies that the DA molecules in the PSSNa ionomer act as plasticizer, which makes the T_gs of the matrix and cluster regions of the PSSNa ionomer lower, to some extent. This makes the formation of multiplets at relatively regular distances easier, which leads to the appearance of a narrower SAXS peak at higher q values. In the case of PSMANa ionomer, there is no well developed SAXS peak in the q range of 0.5–4 nm^{-1}. However, upon the addition of DA, a peak is seen at q = ca. 2.0 nm^{-1}, and the peak intensity increases progressively with increasing DA amounts, without changing the peak position and width, suggesting that the DA acts as plasticizer. In addition, a shoulder is seen at q = ca. 1.2
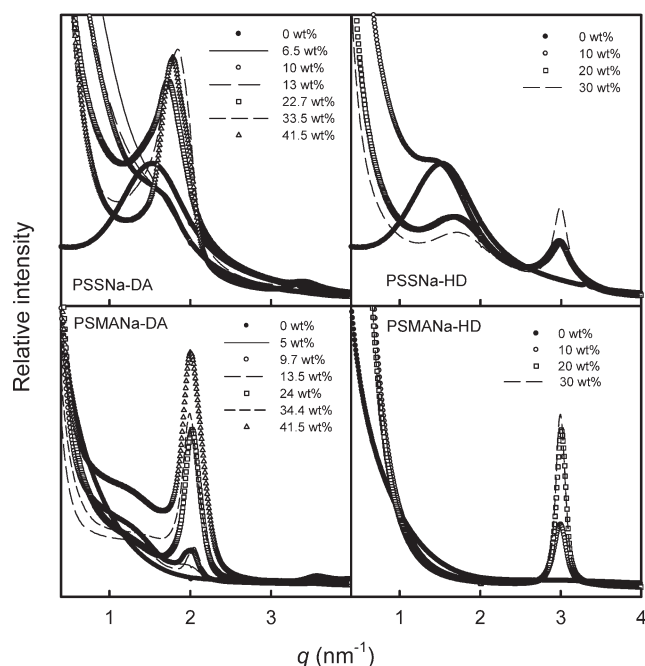
Figure 6. SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of DA or HD.

Figure 8. DSC thermograms of DA, PSSNa, and PSMANa ionomers containing varying amounts of DA.

nm^{-1} upon the addition of DA and becomes more visible with increasing DA amounts. This suggests that the shoulder is related to the formation of phase-separated DA molecules. In the case of PSSNa-HD ionomers, the SAXS peak at q = ca. 1.5 nm^{-1}, shifts to slightly higher q, but its intensity decreases strongly, with increasing HD contents. In addition, a new peak is seen at q = ca. 3.0 nm^{-1}, and the peak intensity increases noticeably as the HD content increases. For the PSMANa, usually showing a very weak shoulder at q = ca. 3.0 nm^{-1}, a new peak is also seen at the same position, with increasing its intensity, as the HD content increases. The above results imply that the appearance of the peak at q = ca. 3.0 nm^{-1} is related with the presence of phase-separated HD that acts as filler particles and increases ionic modulus.
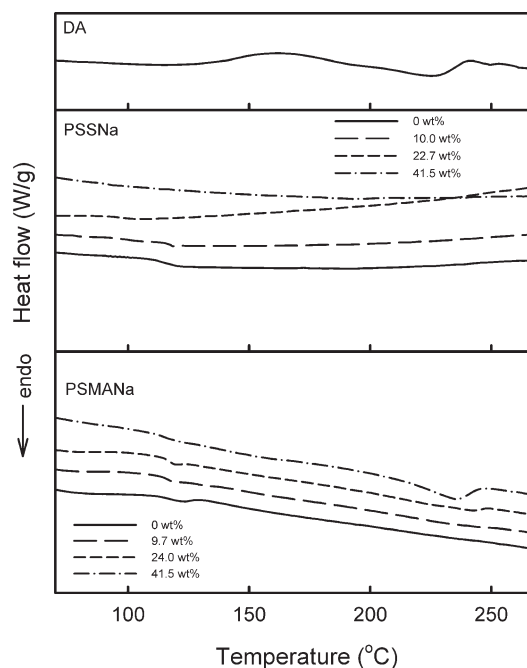
The IR spectra of Na-neutralized DA, PSSNa and PSMANa ionomers in the wavenumber range of 900−2000 cm^{-1} are seen in Figure 7. We assigned IR bands with reference to others' interpretation.[41,42] In the case of PSSNa ionomers, the intensity of IR bands at ca. 1740 cm^{-1} increases with increasing DA contents, but the intensities of the rest of IR bands decrease systematically. At this point, it should be noted that the IR band at ca. 1680 cm^{-1} decreases drastically for the PSSNa-41.5 ionomer; we do not have clear explanation for this finding, yet. For the PSMANa ionomers, the IR spectra do not show any new IR band upon the addition of DA compound. Only the relatively intensities of the IR bands decrease with increasing DA contents. This different trend in IR band intensities also supports the idea that the roles of DA in PSMANa and PSSNa ionomers are not the same.
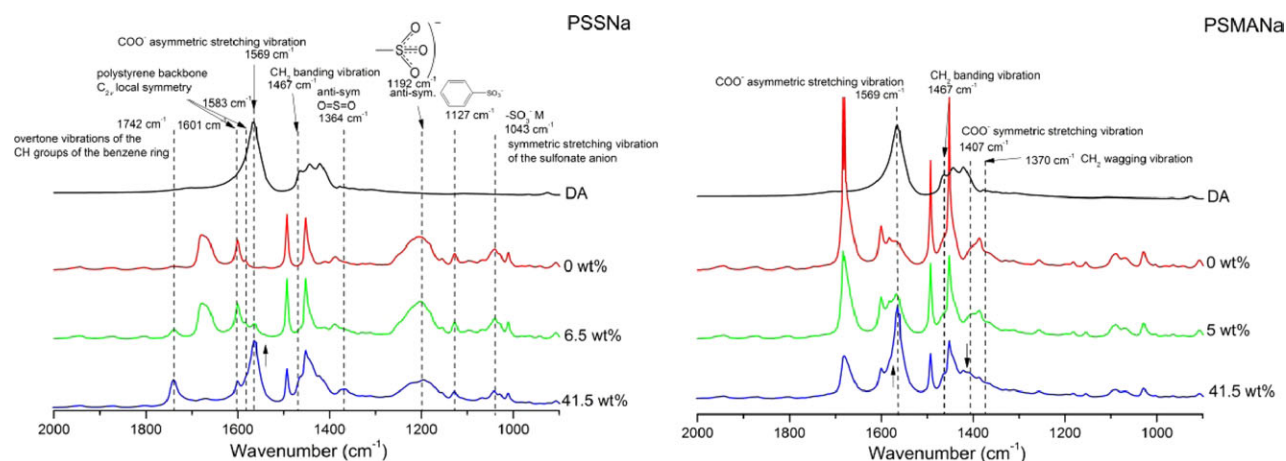

Figure 7. IR spectra of DA, PSSNa, and PSMANa ionomers containing varying amounts of DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The DSC thermograms of Na-neutralized DA itself, PSSNa and PSMANa ionomers are shown in Figure 8. It is seen that the DA shows a broad endothermic peak at 228°C, which is related to the melting of crystalized DA compounds. For the PSSNa ionomers, only the glass transitions of the matrix regions of the ionomers are seen at ca. 120°C. In the case of the PSMANa ionomers of low DA contents, they also exhibit only the matrix glass transition. In addition to the matrix glass transition, PSMANa-24.0 and PSMANa-41.5 ionomers show a small shoulder at ca. 245°C and a small, broad endothermic peak at ca. 240°C, respectively. This endothermic peak is probably related to the phase-separated Na-neutralized DA. These DSC results are in agreement with the findings in DMA results discussed earlier.

Now, let us talk about the roles of DA molecules in the PSSNa and PSMANa ionomers in more detail. The fact that the matrix and cluster T_gs of PSSNa ionomers decrease significantly in a similar way with increasing DA amounts suggests that the DA molecules may reside in both the matrix and cluster regions of PSSNa ionomer relatively evenly and act as effective plasticizer for both the matrix and cluster regions, which lowers the matrix and cluster T_gs. Naturally, some of Na-carboxylate ion pairs of the DA may participate in the formation of multiplets with Na-sulfonate ion pairs of the PSSNa ionomer. If this were the case, the interactions between ion pairs in the multiplets might become weaker due to the heterogeneous compositions of ion pairs in the multiplets, at least to some extent. Thus, the ion-hopping would occur at relatively lower temperatures, leading to a lower cluster T_g. In the case of ionic modulus, since the DA molecules in the PSSNa act mainly as plasticizer, the ionic modulus would not be expected to change; this is what we observed here. According to the dynamic mechanical data of the PSMANa ionomer containing DA, the presence of the DA does not change the matrix T_gs, but it decreases the cluster T_g, and it increases the ionic modulus strongly. This is due to the phase-separation of DA molecules. It should be recalled that the DA molecules in the present work are mixtures that consist of monocyclic, bicyclic and acyclic compounds, but the HD molecules have linear alkyl chains having Na-carboxylate ion pairs at both ends of the chain. Since aliphatic dicarboxylate can form the filler particles more easily, the filler effect of HD would be stronger than that of DA.[5,6] In addition, as expected, the plasticization effect of DA is more profound than that of HD because of the nature of DA, i.e. mixture of various DAs.

CONCLUSIONS

The DA molecules resided in the hydrocarbon matrix and cluster regions of PSSNa ionomers, and acted mainly as plasticizer to decrease the matrix and cluster T_gs without changing the ionic modulus. In the case of PSMANa ionomer, the monocyclic and bicyclic DA molecules in the PSMANa ionomer also acted as plasticizer, but the acyclic DA molecules were phase-separated to form filler particles that increased the ionic modulus of the PSMANa ionomer. The above findings suggested that the monocyclic and bicyclic DA molecules could be used as very effective plasticizer.

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