

Dynamic Mechanical Analysis of Sulfonated Polyurethane Ionomers

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SYNOPSIS

Dynamic mechanical analysis, using a flat-spring to support the sample, was conducted to study the properties of polyurethane ionomers prepared from poly (epoxy chloropropane) as polyol. The effects of the soft segment length and ionization level on the properties were studied. For the unionized polyurethane, the soft and hard segments had good compatibility and little phase separation was found due to the high polarity of the polyol. For the shorter hard segment ionomers, as the ionization level increased, the matrix T_g rose due to the increase in the compatibility of hard and soft segments. For the longer ionized hard segment ionomers, the aggregating tendency of ion pairs enhanced phase separation. Quenching or annealing the samples showed that clusters existing in bulk materials did not dissociate below the degradation temperature and multiplets can dissociate or transform to clusters below 150°C.

INTRODUCTION

The method of introducing small amounts of ionic groups into polymer chains is becoming increasingly useful for modifying the properties of polymers.^{1,2} These ionic polymers are termed ionomers. Because of interionic electrostatic forces, as well as the high degree of thermodynamic incompatibility between the ionic groups and the polymer matrix (typically nonpolar hydrocarbon), these ionic groups tend to aggregate in the bulk material. It is now well established that profound changes in various physical properties of these ionomers are due to the aggregation of ion pairs in a medium of low dielectric constant. Eisenberg³ postulated the existence of two types of ionic aggregates, termed multiplets and clusters. A multiplet is a group of a few tightly-bound ion pairs, and substantially excludes chain backbone material, which primarily works as a physical cross-link. A cluster, formed at higher ion content, is a domain, consisting not only of several multiplets, but also of a significant number of hydrocarbon chains. A cluster bears many characteristics of microphase separation.

The persistence of the ionic aggregates at high temperature leads to a melt viscosity of an order of magnitude greater than the analogous nonionic polymers.⁴ Dissociation is highly desired in processing. Because the process of ionic aggregation is presumably enthalpically favorable and entropically unfavorable, it has been suggested that at sufficiently high temperature the ionic aggregates should dissociate.³ However, such dissociation has never been observed,⁵⁻⁸ perhaps because the ionic aggregates present in the low dielectric medium are incompatible with the polymer matrix. The ionic aggregates only break up when deformed.⁹ So, improving the ion-matrix compatibility may cause the ionic aggregates to dissociate at the processing temperature.⁵

In order to investigate ionic aggregate structures and their characteristics, various methods have been used. One of the most widely used techniques is dynamic mechanical measurement. Systematic studies have been conducted for some ionomers, such as polyethylene ionomers, polystyrene ionomers, and polyurethane ionomers.^{1,10-12} However, more detailed studies with this technique for most ionomers were difficult to conduct, due to the low modulus and dramatic elongation of the samples at high temperature. In our previous work,¹³ a technique in which the sample was supported with a flat-spring was successful in studying the dynamic mechanical prop-

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erties of polymer at high or low modulus. The technique can be used to measure a sample from glassy state up to the degradation temperature.

In this work, we introduced poly(epoxy chloropropane) into the backbone of sulfonated polyurethane ionomers to increase the matrix polarity. Dynamic mechanical measurements were performed with the flat-spring supporting technique to examine the effects of ionization level, polyol molecular weight, and thermal history on the properties of these polyurethane ionomers.

EXPERIMENTAL

Sample Preparation

The synthetic method, used to prepare the polyurethane ionomers based on poly(epoxy chloropropane) (PECH), was described in another article.¹⁰ The PECH 1000 ($M_n = 1100$) and PECH 2000 ($M_n = 2000$) was synthesized from epoxy chloropropane by the method of cationic ring-opening polymerization.¹⁵ The ionic chain extender, sodium-S-1,2-dihydroxypropyl sulphonate (SDPS), was synthesized by the method described by Chui et al.^{16,17} These polyols were reacted with methylene bis(*p*-phenyl isocyanate) (MDI) to form oligomers, then the chains were extended with SDPS to form ionomers.

Different ionic contents can be obtained by substituting SDPS with butane-1,4-diol (BD). The samples are listed in Table I. In this table, the first letter, E, of a sample name represents PECH. The first number is the molecular weight of polyol in thousands, the next number following a bar is the mol percentage of SDPS in chain extenders (SDPS and BD), and the numbers in brackets represent the mol ratio of PECH to MDI. $W_{1/2}$ is the full width at half maximum of the glass transition peak of matrix. E_a is the active energy of the glass transition of matrix.

Dynamic Mechanical Analysis

To sustain the dynamic mechanical measurement up to high temperatures, we used a flat-spring to support the sample. This method was described in our previous article.¹³ The ionomer-spring composites were prepared by casting the ionomer solutions in DMF onto the springs, then the samples were dried in vacuum at 60°C for 2 days. The size of the composite samples was about 0.15 mm thick, 2.0 mm wide, and 25 mm long. The measurements were done by using a Rheovibron DDV-II-EA dynamic viscoelastometer with a pair of common sample clamps in the tensile test mode. Samples were analyzed in nitrogen atmosphere from -50°C to 200°C at a heating rate of 1°C/min with four test frequencies of 3.5, 11, 35, and 110 Hz simultaneously. The correction for instrument compliance¹⁸ was performed automatically by the Rheovibron itself.

The dynamic mechanical behavior of the two-component system of the spring and polymer can be described by a parallel model.¹⁹ The storage modulus of polymer in the composite can be obtained from the following expression.¹³

$$E'_p = (1 - \phi_s)(E'_c - E'_s) \quad (1)$$

where ϕ_s is the volume fraction of spring in the composite, subscripts *p*, *c*, and *s* represent polymer, composite, and spring, respectively. Our previous work¹³ shows that the loss tangent values of polymer equal those of the composite.

RESULTS AND DISCUSSION

The Compatibility of Soft and Hard Segments

In the dynamic mechanical analysis, the storage modulus and loss tangent of each sample were obtained as a function of temperature at four different frequencies. Because of the similar behavior for each

Table I Sample Designation, Compositions, and Mechanical Properties

Sample	Wt % Polyol	Wt % Na ⁺	Matrix T_g °C (Tan δ Peak)	Cluster T_g °C (Tan δ Peak)	$W_{1/2}$	E_a Kj/mol
E1-000(1 : 2)	65.4	0.0	32.0	105	30	224
E1-025(1 : 2)	64.5	0.3	37.5	110	48	228
E1-050(1 : 2)	63.6	0.7	43.0	130	53	230
E1-100(1 : 2)	61.9	1.3	47.0	148	62	247
E1-100(1 : 3)	48.9	2.0	39.2	160		275
E2-100(1 : 3)	56.4	1.8	29.5	154	65	217

series, only representative results at the frequency of 110 Hz will be given here in graphical form. Figures 1 and 2 show the typical dynamic mechanical responses of these samples. In these figures, two relaxation peaks are seen. The first loss tangent peak (at lower temperature) corresponds to the glass transition of matrix materials with small ionic aggregates (i.e., multiplets), and the second peak corresponds to the relaxation of large ionic aggregates (i.e., clusters).

For the PECH-based polyurethane, the soft segments have greater polarity than other polyols. Its polarity may be near that of the hard segment, which contains polar groups, so that the soft and hard segments have good compatibility. The dynamic mechanical analysis (Fig. 1) shows that the glass transition temperature of the matrix, which corresponds to soft segments, is 32°C, much higher than that of pure PECH. This indicates that a large amount of hard segment is dissolved in the soft matrix. However, further examination shows that the soft segments and hard segments are not totally compatible, even though they all have similar polarity. The mechanical loss curve has a shoulder peak at 105°C, which is due to the glass transition of hard domains. The height and position of this peak are much lower than those of other polyol-based polyurethanes. This indicates that the sample has better compatibility of soft and hard segments and that only minor mi-

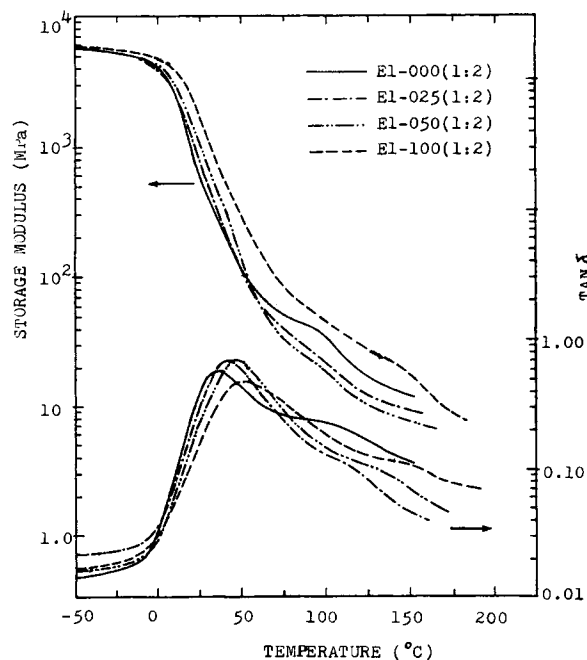


Figure 1 Storage modulus and loss tangent for E1 series with different ion contents.

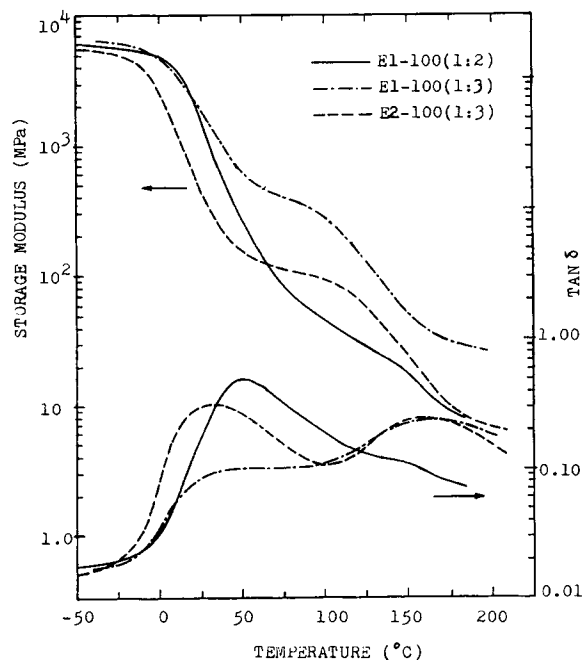


Figure 2 Storage modulus and loss tangent for 100% ion content ionomers.

crophase separation has occurred in the bulk material.

When the ionic chain extender was incorporated into the backbone, the polarity of the hard segments increased dramatically with the rising ionization level. In the nonpolar matrix ionomers, the ion pairs, which attached to the hard segment, tend to aggregate to form large ionic domains (clusters).^{11,12} But, in the PECH-based polyurethane ionomer, the matrix polarity was great, the ionic extender incorporating into the main chain enhanced the interaction of the soft and hard segment when the ionization level was below a certain value, and caused an increase in the segments' compatibility. So, Figure 1 shows the height of the second loss tangent peak (clusters) decreasing in favor of the first peak (matrix) and the first peak position shifting to higher temperature with an increasing degree of ionization (from 32°C for a nonionic sample to 47°C 100% ionization ionomer). This feature is attributed to the increasing amount of hard segments that dissolve in the matrix with increasing ion content, which also causes the activation energy of the matrix glass transition (listed in Table I) to increase slightly with the ion content increase.

Figure 2 shows the dynamic mechanical responses of the totally ionized ionomers. As the hard segment content increased, the mol ratio of MDI to polyol from 2 : 1 for Sample E1-100 (1 : 2) changed to 3 :

1 for Sample E1-100 (1 : 3), or, the number of ion pairs in each hard segment increased from 1 to 2. Also, the ion density became much higher and the ion pairs tended to aggregate to form clusters. So, the intensity of the high-temperature peak was enhanced and its position shifted to higher temperature, whereas the temperature of the first peak decreased, indicating a lesser amount of hard segments dissolved in matrix. For the longer, soft segment sample [E2-100 (1 : 3)], similar behavior was found.

Figure 2 also shows a well-developed, rubbery plateau region, attributed to the presence of ionic crosslinks. The longer the length of the polyol, the wider the rubbery plateau region. The higher the content of hard segment, the greater the rubbery modulus. This indicates that longer soft segments and higher ion content favor ion pair aggregation. The effect of the hard segment content on rubbery plateau modulus can be ascribed to two mechanisms: one is the increase of ion crosslinks, which are formed by ionic aggregation, the other is the increase of the hard domains, which have much higher modulus than the matrix. These factors both cause an increase in rubbery plateau modulus.^{20,21}

Effects of Aging on the Morphology

Figures 3 and 4 show the effects of heating on the dynamic mechanical behavior of Sample E2-100

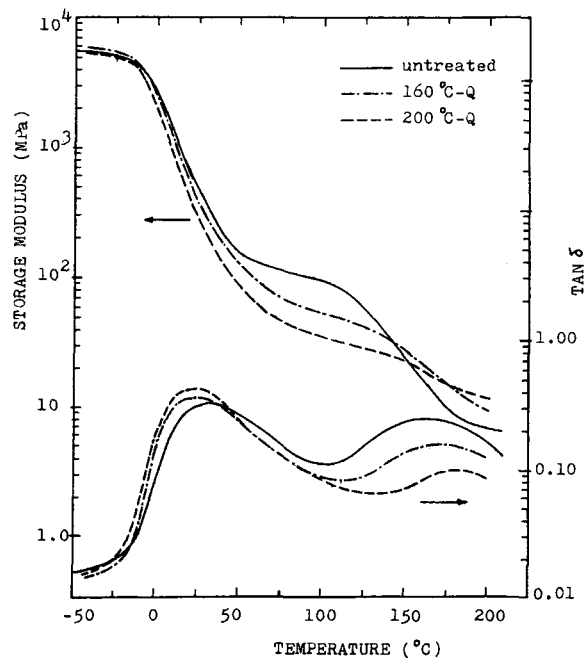


Figure 3 Storage modulus and loss tangent for E2-100 (1 : 3), which was quenched at ambient (—), 160°C (---), and 200°C (-·-·-).

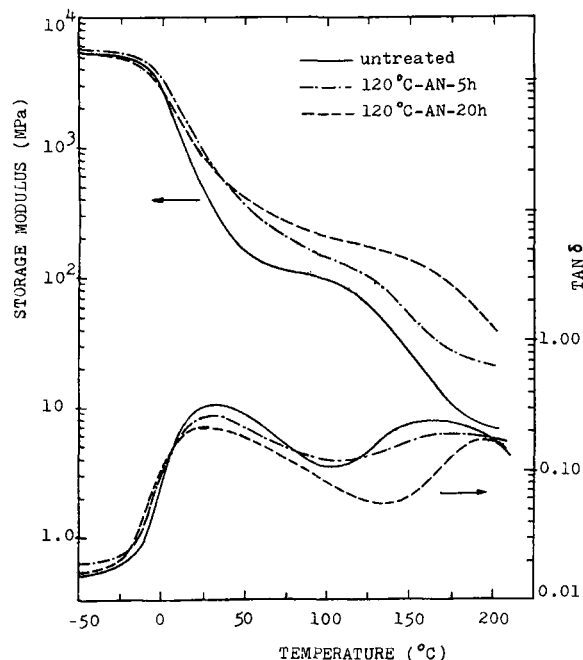


Figure 4 Storage modulus and loss tangent for E2-100 (1 : 3), which was annealed at 120°C for 0 h (—), 5 h (-·-·-), and 20 h (---).

(1 : 3). Table II lists the values of the T_g of matrix and clusters, the peak width at half-height ($W_{1/2}$) of matrix, and the values of rubbery modulus (E'_{in}) and temperature (T'_{in}) at the inflection point on the storage modulus curves. The treating condition, Q or AN, means quenched or annealed samples. Annealing and quenching the sample at high temperature make both the first peak in loss tangent curves shift to lower temperature and the second peak shift to higher temperature. This indicates that thermal treatment at high temperature develops microphase separation. It is imperative to point out that the high-temperature peak does not disappear or deaden when the sample is quenched at 200°C, which is much higher than the position of second peak. The peak only shifts to higher temperature, indicating that the clusters exist in the bulk material and aggregate much more tightly at 200°C. More aggregated clusters cause the movement of hard segments to become more difficult, and make T_g of the hard domains shift to higher temperature. Therefore, the high-temperature peak is not due to the "breakup" of the clusters, it is caused by the glass transition of the hard domains. On the other hand, the mobility of hard segments affects the characteristic of ionic aggregation. At low temperature, the hard segment conformation is difficult to change, only loose clusters could be formed. When

Table II Effects of Thermal History on the Mechanical Properties

Condition	Matrix T_g ($^{\circ}\text{C}$)		$W_{1/2}$	Cluster T_g ($^{\circ}\text{C}$)	E'_{in} N/m^2	T_{in} ($^{\circ}\text{C}$)
	E'' Peak	Tan δ Peak				
Sample E2-100 (1 : 3)						
Untreated	7.5	29.5	65	154.3	1.1 E8	86
160 $^{\circ}\text{C}$ -Q	3.4	23.5	60	170.5	5.0 E7	100
200 $^{\circ}\text{C}$ -Q	1.0	20.5	60	183.0	2.8 E7	122
120 $^{\circ}\text{C}$ -AN-5 h	6.5	27.8	55	175.0	1.3 E8	105
120 $^{\circ}\text{C}$ -AN-20 h	3.1	23.1	85	191.2	1.6 E8	122
Sample E1-100 (1 : 3)						
Untreated	20.9	47.0	62			
120 $^{\circ}\text{C}$ -Q	23.7	49.8	60			
150 $^{\circ}\text{C}$ -Q	19.9	48.8	83			
180 $^{\circ}\text{C}$ -Q	16.2	51.2	100			
200 $^{\circ}\text{C}$ -Q	9.9	59.8	142			

the temperature is higher than the T_g of the hard domain, the movement of the hard segment causes the clusters' rearrangement to form tighter ion aggregation domains. At this point, the high-temperature peak may also be recognized as a rearrangement relaxation peak of clusters.

Figures 3 and 4 also show that quenching the sample at high temperature causes the width of the glass transition peak of the matrix to decrease, whereas annealing the sample at 120 $^{\circ}\text{C}$ causes the peak width to increase. The rubbery plateau modulus decreases with increasing quenching temperature, whereas it increases with increasing annealing time at 120 $^{\circ}\text{C}$. This feature perhaps corresponds to the properties of multiplets present in the matrix. In the ECH-based PU ionomers, the polarity of the matrix enhances the compatibility of ion-matrix, and causes the ion content of matrix to increase. These ions disperse in the matrix in two forms, ion pair and multiplet. The latter can act as a crosslinking point. The sample with a higher multiplet content will display a higher matrix T_g and greater rubbery modulus.

Because a multiplet is much smaller than a cluster, it may dissociate at a lower temperature. So, though quenching the samples at high temperature (above 150 $^{\circ}\text{C}$) does not make clusters break up, it will make the multiplets dissociate, resulting in the samples' having less ion crosslinks and showing lower matrix T_g and smaller rubbery modulus.

When the sample was annealed at 120 $^{\circ}\text{C}$, although the chains have more mobility to enhance the microphase separation and cause the clusters to aggregate more tightly, they have insufficient energy to make the multiplets dissociate. Whereas the ac-

tive chains lead more ion pairs to transform to multiplets and clusters, and more ion crosslinks are formed. So, as the annealing time increases, the sample has lower matrix T_g , corresponding to a larger scale phase separation, and it also has higher rubbery modulus, attributed to more ion crosslinks.

Figure 5 shows the dynamic mechanical behavior of Sample E1-100 (1 : 2), which was quenched at high temperature. On its loss tangent curves, only

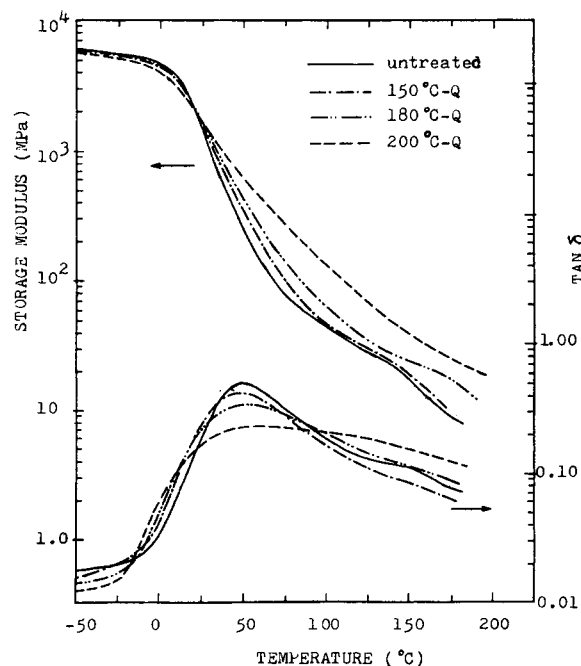


Figure 5 Storage modulus and loss tangent for E1-100 (1 : 2) quenched at ambient (—), 150 $^{\circ}\text{C}$ (---), 180 $^{\circ}\text{C}$ (- · - · -), and 200 $^{\circ}\text{C}$ (····).

a very weak high-temperature peak was found, indicating difficulty in forming clusters even at high temperature. This is due to the fact that the ion content in the hard segment is lower and that the soft and hard segments have good compatibility. When the sample was quenched at 120°C, its dynamic mechanical response (not shown) was similar to that of the untreated sample, except that its matrix T_g was 2°C higher, indicating the number of multiplets increased slightly. If the sample was quenched at above 150°C, the matrix T_g (from E'' peak listed in Table II) decreased and its loss tangent peak broadened. This behavior means that the multiplets with larger volume tend to aggregate to form clusters and the smaller multiplets will dissociate at high temperature.

CONCLUSIONS

1. In the MDI-based polyurethane with poly(epoxy chloropropane) as polyol, the high polarity of the soft segment gives soft and hard segments good compatibility, which leads to a high matrix T_g and a very weak loss peak for the hard domains with a low peak temperature, indicating a large amount of hard segments dissolved in the matrix.
2. When ion chain extender was incorporated into the backbone under a certain ionization level, as the ion content increased, the polarity of hard segments was increased, as did the compatibility of soft and hard segments. This makes the matrix T_g increase and the height of the peak due to hard domains decrease.
3. If the ion content of a hard segment is further increased (the mol ratio of MDI to polyol is increased from 2 : 1 to 3 : 1), the polarity of hard segments is too high to provide compatibility of soft and hard segments. A larger loss tangent peak at high temperature, corresponding to clusters, is found, and a well-developed rubbery plateau region is formed.
4. Two types of ionic aggregates, multiplets and clusters, both exist in the PECH-based PU

ionomers. The dissociation of clusters was not found in the region from ambient to 200°C, whereas the multiplets could dissociate or transform to clusters when temperature was above 150°C.

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