The Influence of the Degree of Neutralization, the Ionic Moiety, and the Counterion on Water-Dispersible Polyurethanes

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ABSTRACT: A number of polyurethane anionomers based on isophorone diisocyanate, polytetrahydrofuran, and cyclohexane dimethanol were prepared as aqueous dispersions. The dispersions were stabilized by the use of an internal emulsifier. The principal ionic moiety used was dimethylol propanoic acid, but dimethylol butanoic acid and an experimental suphonate diol sodium salt were also used. The consequence of the neutralization step, the degree of neutralization, the type of ionic component, and the type of counterion were investigated for their effect on the mechanical and colloidal properties of the polyurethanes. Dynamic mechanical thermal analysis, tensiometry, solvent spot testing, and swelling studies were used for the characterization of the materials. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 556–566, 1999

Key words: ionomers; polyurethane; water dispersibility; structure-property relations

INTRODUCTION

Polyurethanes (PUs) represent a well-established area of polymer science, and their versatility has resulted in much research¹⁻³ into developing an understanding of their structure-property relations. It is well documented that PUs obtain their unique properties from microphase separation⁴ of the incompatible soft (flexible) polyol and hard (much less flexible) urethane sequences. Many studies have been performed to determine the driving force for microphase separation⁵ and the factors that affect it. The symmetry and type of diisocyanate,⁶ the molecular weight, and symmetry of the soft segment polyol⁷ and the chain extender⁸ have all been discovered to affect microphase separation and properties. Since at least the late 1960s, the introduction of ionic groups into the PU backbone has led to the development of a new class of PU, the PU ionomers.

Structure-property relations of ionomers containing a small fraction of ionic repeat units have been the subject of numerous articles and reviews.^{9–11} The area of PU ionomers has grown rapidly in recent years. These ionomers usually contain pendant acid groups or tertiary amine groups. Water dispersibility is obtained on neutralization of the acid groups to form internal salts. The advantages and disadvantages of ionic PUs are well documented¹² in the literature. The presence of the ionic species has a considerable effect on the physical properties,¹³ and it is rea-

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		Chain			
	Prepolymer	Extension	Ionic Moiety	Neutralization	Solids
	NCO/OH	(%)	(wt %)	(%)	(%)
Series A ^a					
Na40	1.6	98	10	40	25
Na60	1.6	98	10	60	25
Na80	1.6	98	10	80	25
Na100	1.6	98	10	100	25
Series B ^b					
$AQ1^{c}$	2	98	4.9	100	35
$AQ2^{d}$	2	98	4.9	100	35
Series C ^e					
DMPA	2	98	4.9	100	35
DMBA	2	98	5.4	100	35
SDA	2	98	15.5	100	35
Series D ^f					
ORG1	2	98	4.9	100	35
(Et_3NH^+)					
ORG2	2	98	4.9	100	35
$(\mathrm{NH_4^+})$					
INORG1	2	98	4.9	100	35
(Na^+)					
INORG2 (K ⁺)	2	98	4.9	100	35

Table I Formulation Details for the Polyurethane Synthesis

^a Contains DMPA neutralized with NaOH.

^b Contains DMPA neutralized with TEA.

^c The sample was neutralized before dispersion with TEA (preneutralized).

^d The sample was neutralized with TEA in the aqueous phase during dispersion and chain extension (postneutralized).

^e Contains DMPA, DMBA, or SDA, as indicated, neutralized with NaOH.

^f Contains DMPA neutralized, as indicated, with TEA, ammonium hydroxide, NaOH, or KOH.

sonable to suppose that the interactions between ions and their counterions are responsible for these effects.^{14–16} It has been discovered that the degree of neutralization,¹⁰ the type of ionic component,¹⁷ and the counterion¹⁸ used all contribute significantly to the properties of PU ionomers. Aqueous dispersions of PU ionomers are now one of the most rapidly developing and active branches of PU chemistry.

This article addresses the effects of the degree of neutralization by NaOH, the type of ionic moiety, and the type of counterion have on certain colloidal and mechanical properties. In addition, the influence of the neutralization stage is highlighted from a comparison of preneutralized and postneutralized samples.

EXPERIMENTAL

Materials

Polytetrahydrofuran (PTHF) ($M_n = 1000$) (Aldrich Chemical Co., UK) was dried at 0.1 mmHg

and 80°C for 3 h before use. Dimethylol propanoic acid (DMPA) (Aldrich), dimethylol butanoic acid (DMBA) (Nagase, Japan), SDA, an experimental sulphonate diol (sodium salt) (Zeneca Pharmaceuticals, Macclesfield, UK), triethylamine (TEA) (Aldrich), ammonium hydroxide (BDH), sodium hydroxide (Aldrich), potassium hydroxide (Aldrich), *N*-methyl-2-pyrrolidone (NMP) (Aldrich), and cyclohexane dimethanol (CHDM) (Aldrich) were used without further purification. The IPDI (Aldrich) had a purity of 98%. Dibutyl tin dilaurate (DBTDL) (Aldrich), used to catalyse the reaction, and the chain extender, hydrazine monohydrate (Aldrich) were also used as received.

General Procedure

The formulations of the samples are presented in Table I. Any variations to this method will be stated when such samples are discussed. The prepolymer reaction apparatus consisted of a 250-ml flange flask and lid fitted with a nitrogen bubbler inlet, a thermometer, and a stirrer paddle. The reaction temperature was controlled using a constant temperature oil bath. The CHDM, PTHF, and the ionic component (DMPA, DMBA, or SDA) as a solution in NMP were weighed out into a clean, dry flask. The contents were then heated to 50°C with stirring to homogenize. At 50°C, the IPDI and the first portion of catalyst, DBTDL, were added. The reaction temperature was increased to 95°C, where it was maintained for 1 h. A further portion of catalyst was then added and the reaction continued at 95°C for a further hour. The temperature was then lowered to 70°C and the isocyanate number was determined using the standard dibutylamine back titration method.¹⁹

The isocyanate groups of IPDI preferentially react with the hydroxy functionality of the polyol and diols. No reaction takes place between the NCO and carboxylic acid groups of the ionic material. The methyl and butyl groups in DMPA and DMBA, respectively, provide protection for the carboxylic acid groups by making the reaction with IPDI sterically unfavorable. Similarly, esterification reactions do not take place because these require strong catalysts and high temperatures (160°C). These reactions only become significant at temperatures exceeding 100°C and result in a depleted number of stabilizing groups and a stoichiometric imbalance.

On achieving the theoretical NCO value, neutralization of the carboxylic acid groups was performed in one of two ways. The first route and the most common was preneutralization. The carboxylic acid groups on the prepolymer chain were neutralized by adding TEA to the molten prepolymer at 70°C before dispersion. After 30 min, the neutralized prepolymer was then added via a funnel to a three-necked round-bottomed flask containing the water and the chain extender, hydrazine monohydrate. The flask was fitted with a stirrer and a condenser. Preneutralization was not performed using the inorganic bases. Alternatively, postneutralization was performed. The neutralizing agent was added to the aqueous phase with the chain extender. The molten prepolymer at 70°C was then added so that dispersion and neutralization took place simultaneously. This was performed with TEA, NH₃, NaOH, and KOH where stated to postneutralize the samples. In each case, dispersion was performed over a 40-min interval to ensure that the dispersion temperature did not exceed 40°C. The dispersion was then allowed to stir for a further 30 min. All the dispersions were prepared at 35 wt % solids. The experimental SDA diol was always used as its sodium salt without further modification.

Films were prepared by pouring the dispersions into an aluminum mould. The films (typically about 0.5-mm thick) were allowed to dry at room temperature for 2 days. The residual water was removed by placing the films overnight into a vacuum oven at 25°C. These films were then used for DMTA, DSC, swelling, tensile testing, and wide-angle X-ray diffraction experiments.

Characterization

Photon Correlation Spectroscopy

Particle sizes of the dispersions were determined by light scattering using a Malvern Autosizer model (Iic). The sample was diluted to the required concentration with distilled water before measurement.

Rheometry

Viscosity measurements on the dispersions was performed using a Haake DC3 over a range of shear rates (0 to $100s^{-1}$) at 25°C. A 'cup and bob' set-up was used for these investigations and the viscosity at $100s^{-1}$ was taken as being the viscosity of each dispersion. This technique was also used to determine the viscosity and flow activation energy of prepolymers prepared with different ionic moieties.

Tensile Testing

Tensile properties were measured at room temperature using a J. J. Lloyd (UK) tensometer following the ASTM D-412 specifications. A crosshead speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all the samples. The values quoted are the average of four or five tests.

Dynamic Mechanical Thermal Analysis

DMTA was undertaken over the temperature range -100 to 150° C using a Polymer Laboratories DMTA (Mark II) (UK) at a frequency of 10 Hz, a strain amplitude setting of $\times 4$, and a heating rate of 4°C/min. A single cantilever clamping system was used. Plots of loss modulus (E") vs. temperature were obtained and the T_{gs} of the samples were determined from the E" peaks.

Swelling Studies

To measure swelling in water, 2-butanone, 2-propanol (IPA), dimethylformamide (DMF), and xy-

	40%	60% NaOH	80%	100% NaOH
Characterization	NaOH		NaOH	
Particle size (nm)	132	104	76	63
Latex viscosity (mPas)	7.2	8.5	12.7	15.3
pH	7.2	7.8	8.1	8.3
Tensile strength (MPa)	$12 (44)^{a}$	$11 \ (46)^{a}$	$18 \ (49)^{a}$	$23 \ (50)^{\rm a}$
Elongation (%)	$240 \ (243)^{\rm b}$	$278\ (271)^{\rm b}$	$233 \ (317)^{\rm b}$	$305 (294)^{b}$
$T_{\rho s}$ (°C)	-40	-40	-41	-43
Water absorption (%)	187	291	372	405
Overall solvent spot	18	22	27	31
Swelling (%)				
2-Butanone	117	108	98	139
IPA	154	166	291	180
DMF	D	D	D	D
Xylene	80	96	109	125

 Table II
 Colloidal and Mechanical Properties of Materials with Increasing Degrees of Neutralization

 by NaOH (Series A)

^a Tensile strengths of the films after being heated at 80°C for 1 week under vacuum.

^b Elongation at break of the films after being heated at 80°C for 1 week under vacuum.

lene, films were immersed in each liquid for 24 h at room temperature and the percentage of swelling was determined by measuring the weight increase:

$$%$$
Swelling = 100($W - W_{o}$)/ W_{o}

Wo is the initial dry weight and *W* is the weight of the film at equilibrium swelling.

Solvent Spot Testing

The solvent resistance of the films was determined by exposing the film to a liquid droplet (≈ 1 cm in diameter) for 1 h. The remaining solvent was then removed and the film reexamined for deterioration. A grading system of 0–10 was used, where 0 indicates total dissolution of the film and 10 represents total solvent resistance. The test liquids used were acetone, toluene, tetrahydrofuran, methanol, dichloromethane, water, and isopropanol. A film unaffected by these test liquids would score a maximum of 70.

RESULTS AND DISCUSSION

Series A: The Effect of Increasing Neutralization of the Ionic Moiety

The synthesis details and the polymer properties of the samples with increasing NaOH neutralization are shown in Tables I and II. The particle size decreased significantly with increasing neutralization of the carboxylic acid groups of the ionic chain extender. This decrease is the consequence of the increasing number of carboxylate anions present, which result in the ability to stabilize a greater total particle surface area. Increasing neutralization and its effect on particle size was observed visually as a transition from a white dispersion of particles at 40% NaOH to an almost translucent solution at high degrees of ionization. Lorenz et al.²⁰ have shown that in carboxylate anionomers the COOH and COO⁻ are located substantially at the particle surfaces.

The viscosity increases with decreasing particle size as is common for colloidal dispersions. The effect of the degree of neutralization on particle size, viscosity, and pH is shown in Figure 1.

The mechanical properties of these samples are outlined in Table II and Figure 2. The tensile strength increased from 12 MPa at 40% neutralization to 23 MPa at complete ionization. The ionic sites augment the interchain interactions between ionic centers and the counterions. However, because the ionic component contributes to the hard segments, interchain interactions mainly occur between hard domains.²¹ The films did tend to be transparent, but hazy, and when they were heated in a vacuum oven at 80°C for 7 days, they exhibited higher tensiles strengths (values in brackets in Table II), but they still remained the same.



Figure 1 Colloidal properties of the materials of increasing extent of NaOH neutralization. Series A.

The viscoelastic properties of the samples were examined by DMTA (Fig. 3). A slight increase in microphase separation with increasing neutralization was probably due to an increasing number of hard-segment interactions. This was observed as a slight decrease in T_{gs} , the soft segment T_g . Kim and Lee¹⁰ conducted a similar study using TEA as the ionizing moiety. They observed increasing tensile strength and microphase separation at the expense of elongation as they increased the degree of neutralization from 0–100%. However, they conducted their studies in DMF and, hence, as well as being able to study the unneutralized sample, they were also able to overcome solvent retention because of their lower DMPA levels. However, in our study, the DMPA

level had to be high to maintain a high number of ionic species to provide stabilization even at low neutralization levels. Low levels of DMPA less than 10 wt % result in instability of the resulting dispersion at 40% neutralization. It is this high DMPA content that is responsible for the difficulty in removing plasticizing water in this series of polymers.

The values for water absorption are shown in Table II. Water absorption was seen to increase with the increasing degree of neutralization of the films. The ionic stabilizing moiety also generally resulted in poorer overall organic solvent resistance as the neutralization of the carboxylate anion concentration was increased from 40-100%.



Figure 2 Mechanical properties of the materials with increasing extent of NaOH neutralization. Series A.



Figure 3 Loss modulus vs. temperature plots for the Na40 (*), Na60 (+), Na80 (0), and Na100 (X) series A materials.

Series B: The Effect of the Neutralization Step

To investigate the effect of the staging of the neutralization process, two samples of identical structure were prepared. The specifications for the two samples (series B) are shown in Table I. The results from the examination of these are shown in Table III. The first sample, AQ1, was preneutralized with TEA before dispersion. The second sample, AQ2, was postneutralized, as outlined previously. In each case, the chain extension was carried out in the aqueous phase during prepolymer dispersion.

The particle size of the samples was clearly different with AQ2 having a significantly higher particle size. This suggests that the stage at which neutralization is performed is important in controlling the colloidal properties of the samples. A number of factors have to be considered in explaining this result. One factor is that in the case of preneutralization all the carboxylic acid groups are ionized before the dispersion step, resulting in effective and homogeneous emulsification of the prepolymer in water, without the problem of accessibility of the unreacted carboxylic acid groups to the TEA experienced in the postneutralization process. Another factor is that in the postneutralization process there is the possibility that some of the hydrazine will compete with the TEA in neutralizing the carboxylic acid groups, and hence be unavailable for chain extension. It has been shown²² in a yet unpublished

Table III	The Colloidal and Mechanical
Properties	s of the Pre- and Postneutralized
Samples (S	Series B)

Characterization	Preneutralized AQ1	Postneutralized AQ2
Particle size (nm)	57	171
Latex viscosity (Pas)	0.38	0.37
Tensile strength (MPa)	50	35
Elongation (%)	314	369
T_{as} (°C)	-52	-40
$T_{\sigma h}^{gs}$ (°C)	78	40
Solvent spot	33	30
Swelling (%)		
2-Butanone	133	193
IPA	231	120
DMF	D	D
Water	56	34
Xylene	84	96



Figure 4 Loss modulus vs. temperature plots for the AQ1 (+) and AQ2 (X) series B materials.

article that the effect of reducing the concentration of hydrazine relative to that of the NCO groups is to reduce the polymer molecular weight and increase the particle size. The reason for this is thought to be that as the polymer molecular weight increases then the concentration of DMPA units per chain increases, thus increasing the effect on colloidal stabilization of the carboxylate anions with a consequent decrease in particle size. However, it is also important to consider the reaction of the NCO end groups with water. The presence of the tertiary amine catalyzes this reaction and facilitates the formation of amine end groups. These subsequently react with other NCO groups to form urea groups. This, again, can affect the mechanical properties and the morphology of the polyurethane. All these points must be considered when explaining the differences in the physical properties of the AQ1 and AQ2 samples.

The preneutralized sample exhibited (Table III) a significantly higher tensile strength, but somewhat lower elongation at break compared with that of the postneutralized sample. The DMTA traces of both samples are shown in Figure 4 and the values T_{gs} and T_{gh} , corresponding to relaxations of the soft and hard segments, respectively, are shown in Table III. These highlight the

greater degree of segregation in the preneutralized sample AQ1. The T_{gs} value for AQ1 (-52°C) is significantly lower than for AQ2 (-40°C). This suggests that preneutralization facilitates a

Table IVColloidal and Mechanical Propertiesof Samples Containing Different IonicMoieties (Series C)

Characterization	DMPA	DMBA	SDA
Particle size (nm)	57	36	55
Latex viscosity (Pas)	0.34	0.31	0.41
Tensile strength (MPa)	50	41	22
Elongation (%)	314	407	471
T_{gs} (°C)	-52	-45	-40
T_{gh}^{so} (°C)	78	75	30
Solvent spot	33	30	24
Swelling (%)			
2-Butanone	133	387	214
IPA	231	190	181
DMF	D	D	D
Water	56	36	114
Xylene	84	90	161



Figure 5 Loss modulus vs. temperature plots for the DMPA (+), DMBA (0), and SDA (X) series C materials.

higher degree of segregation of the hard and soft domains. This results in an improvement in the strength of the film although the elongation at break decreases somewhat. Similarly, the high temperature transition, T_{gh} , decreases in AQ2, which is indicative of hard/soft domain mixing and lower cohesion in the hard domains. This decrease in strength is possibly the result of poorer chain extension as a consequence of competition between hydrazine monohydrate and triethylamine, the chain extender and neutralizing cation, in addition to the influence of the NCO– water reaction. Results from an earlier study²² seem to support this.

However, the solvent resistance of the two films was reasonably good with little difference between the samples. AQ2 showed an increased resistance to swelling in IPA and water.

Series C: The Effect of the Stabilizing Species

In this series, all the samples had the same molar concentration of the stabilizing species and were fully neutralized as the sodium salt. The specifications of the three samples are outlined as series C in Table I. It has been reported²³ that DMBA has excellent solubility in solvents such as ace-

tone and 2-butanone compared with DMPA and so makes it easier to use for polyurethane prepolymer dispersion.

Table IV shows that the DMBA-derived sample gave a smaller particle size than the corresponding DMPA sample. This observation may be due to the better solubility of DMBA in the prepolymer, which would be expected to give rise to a more uniform distribution of ionic groups, and hence based on published work²⁴ give better colloid stabilization.

There was little difference in the particle sizes of the DMPA and SDA-containing samples.

The mechanical properties of the three samples are given in Table IV. The DMBA and DMPA samples clearly exhibited greater strength than the SDA sample.

The level of CHDM also plays a significant role in explaining mechanical property difference. Because DMPA and DMBA have similar molecular weights, 134 and 148, respectively, the level of CHDM remains almost constant in both polymers. However, because of the higher molecular weight of the experimental SDA, then the polymer contains a higher wt % of SDA (15.5 compared with 4.9 for DMPA and 5.4 for DMBA) and thus a lower wt % of CHDM. This lower CHDM



Figure 6 Log (viscosity) vs. 1/T for the prepolymers containing DMPA, DMBA, and SDA. Series C materials.

content is, in part, responsible for the lower strength of the SDA-containing polymer. Additionally, the DMPA and DMBA components augment the hard domains. However, the relatively flexible SDA moiety may tend to augment the soft domains and the resultant films thus tend to possess lower strength and quite high extensibility. The extent to which this occurs is shown clearly in the DMTA traces in Figure 5. The SDA-containing polymer is significantly different from those of the other two samples. Two important points should be noted. First, only one major transition is observed for the SDA sample. This transition, corresponding to the soft domains, appeared at -39°C and was significantly higher than for the other samples. Hence, the SDA-derived PU has a greater degree of segment mixing. Second, there was no significant high-temperature transition corresponding to the hard component, which is clearly seen in the DMPA and DMBA samples. Instead, a broad shoulder adjacent to the main transition is seen starting at approximately 25°C.

The viscosities of the three prepolymers were also determined as a function of temperature before dispersion to establish the influence of the different ionic components. The data were treated according to the Arrhenius equation²⁵:

$$\eta = k e^{Ea/RT}$$

where η is the viscosity of the prepolymer, k is a constant, Ea is the flow activation energy, R is the molar gas constant and T is absolute temperature. The values of Ea (see Fig. 6 and Table V) can be placed in increasing order of SDA < DMPA

< DMBA, which is a consequence of their relative polar nature. 26

Series D: The Effect of the Neutralizing Cation

The specifications for these samples are outlined as series D in Table I. Table VI shows the particle size of the samples ionized with Na⁺, K⁺, R₃N⁺, and NH₃⁺. The particle sizes can be placed in increasing order Na⁺ < K⁺ < NH₃⁺ < Et₃NH⁺.

The tensile properties of the samples are also included in Table VI. The ionic potential ϕ has been empirically defined by Cartledge²⁷ using the following expression:

 ϕ = cation charge (q)/cation radius (r)

Increasing ionic potential on going from Et_3NH^+ to NH_4^+ contributes to a higher tensile strength, but lower elongation. This is probably due to enhancement of the coulombic forces which improved the mechanical properties. This is also consistent for the alkali metal ions as the ionic

Table V	The Activation Energies (Ea) of
Viscous 1	Flow for the SDA, DMPA, and
DMBA S	tabilized Prepolymers

Sample	Ea (kJ mol ⁻¹)
DMPA	61.2
DMBA	67.3
SDA	23.2

Characterization	$\frac{\rm INORG1}{\rm Na^+}$	$\frac{\rm INORG2}{\rm K^+}$	$\begin{array}{c} \text{ORG1} \\ \text{Et}_3\text{NH}^+ \end{array}$	$\begin{array}{c} \text{ORG2} \\ \text{NH}_4^+ \end{array}$
Particle size (nm)	101	123	171	156
Latex viscosity (Pas)	0.26	0.41	0.37	0.02
Tensile strength (MPa)	37	32	35	42
Elongation (%)	275	352	369	300
Tgs (°C)	-45	-44	-40	-46
Tgh (°C)	35	35	40	63

Table VIColloidal and Mechanical Properties of Samples FullyNeutralized with Different Cations (Series D)

potential increases from K^+ to Na^+ , when again the tensile strength increased and the elongation at break decreased This is consistent with work by Xiao et al.²⁸ who studied the mechanical properties of anionomers neutralized with a number of metal cations.

The DMTA traces for all the four series D samples are shown in Figure 7. The NH_4^+ clearly exhibited a more phase segregated structure than the Et_3NH^+ sample and exhibited a higher tensile strength. However, there seemed to be little difference in the morphologies of Na^+ and K^+ samples.

The swelling and solvent spot studies show the samples to be fairly similar (Table VII). However, there was a very large difference in the aqueous resistance with the samples containing Na^+ and K^+ , both being very inferior to the volatile organic cation situation. This result is probably due to the presence of the Na^+ and K^+ ions in the film which encourages the ingress of water. The organic cations are lost during the film drying process.

CONCLUSIONS

This study has highlighted the differences in properties that may be achieved by modifying the ionic moiety or counterion. The microphase separation was the primary factor in the development of good mechanical properties. This was discovered to depend on the neutralization process, the



Figure 7 Loss modulus vs. temperature plots for the INORG1 (NaOH) (+), INORG2 (KOH) (X), ORG1 (TEA) (0), and ORG2 (NH₄OH) (*) series D materials.

Characterization	INORG1 Na ⁺	INORG2 K ⁺	$\begin{array}{c} \text{ORG1} \\ \text{Et}_3\text{NH}^+ \end{array}$	$\begin{array}{c} \text{ORG2} \\ \text{NH}_4^+ \end{array}$
Solvent spot				
Acetone	5	6	5	3
Toluene	10	9	10	10
THF	0	0	0	0
IPA	1	1	0	1
MeOH	0	0	1	0
CH_2Cl_2	5	5	4	2
Water	1	1	10	10
Swelling (%)				
2-Butanone	D	D	193	305
IPA	78	D	120	178
DMF	D	D	D	D
Water	276	15	34	38
Xylene	168	141	96	115

Table VIIDetermination of the Solvent Susceptibility of the SamplesNeutralized with Different Cations (Series D)

degree of ionization, the counterion, and the type of ionic component used. Increasingly, phase segregated morphologies and improving mechanical properties were achieved with increasing neutralization and with preneutralization of the pendant carboxylic acid groups. Carboxylate ionomers exhibited a higher strength than the experimental sulphonate ionomer examined.

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