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Elastometric Ionomers

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One Short Review is on the pages which follow.

ELASTOMERIC IONOMERS

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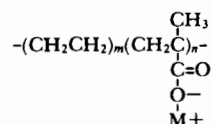LINDEN, NEW JERSEY 07036

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I. INTRODUCTION

Ionomers are a class of materials which are emerging as important commercial polymers but yet have many intriguing scientific characteristics. Typically, ionomers consist of a low level of inorganic salt groups pendent to a polymer chain. For this article, we will consider ionomers to possess a maximum level of about 10 mol% ionic groups pendent to a hydrocarbon polymer chain. While this definition is somewhat arbitrary, it is one generally accepted[1] in the polymer field.

Unlike homogeneous polymer systems, the pendent ionic groups can interact to form ion-rich aggregates contained in the nonpolar polymer matrix. The resulting ionic interactions can have a major influence on polymer properties and applications which have made this area an extremely fertile one for research and development. A typical ionomer structure can be approximated as follows:

$$-(CH_2CH_2)_m(CH_2\underset{\underset{\underset{\underset{M+}{O-}}{C=O}}{|}}{\overset{\overset{CH_3}{|}}{C}})_n-$$

Typically, the ratio m/n would be on the order of 10 to 100, reflecting a low level of ionic groups present in the overall copolymer. The presence of this level of salt groups chemically combined with a nonpolar polymer backbone can have a dramatic influence on polymer properties not observed with conventional homopolymers or with copolymers based on nonionic species. It is generally accepted that the ionic groups interact or associate to form regions rich in ions in the polymer matrix as illustrated schematically in Figure 1. The specific details of structure of the ionic aggregate have been the subject of numerous experimental and theoretical papers and are still the subject of considerable research activity.

In this class of polymers, the ionic interactions and resultant polymer properties are dependent on the following variables:
- Type of polymer backbone (plastic or elastomer)
- Level of ionic functionality (ionic content), 0 to 10%
- Type of ionic moiety (carboxylate, sulfonate, phosphonate)
- Degree of neutralization (0 to 100%)
- Type of cation (amine, metal, monovalent, or multivalent)

The influence of ionic level, degree of neutralization, and type of cation are factors which can dominate the properties of the resultant polymer system. With this range of experimental variables, the spectrum of polymer properties available within the ionomer family is extremely broad. In this paper, we shall examine mainly elastomeric ionomers with brief mention of the other classes. Several recent review articles[1,2] and three books[4-6] have been published on ionomers. These references offer greater detail on specific topics.
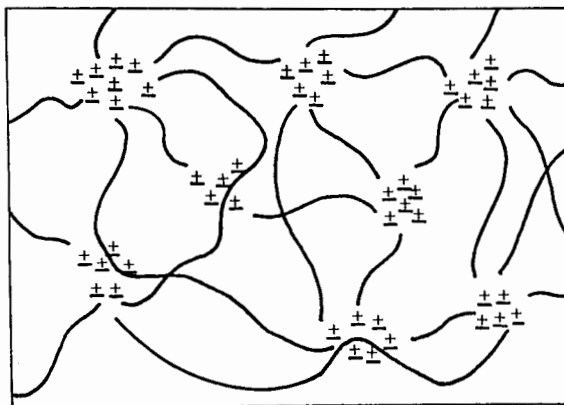
FIG. 1.—Model for ionic aggregates. Metal ions +; sulfonate ions on the polymer —.
Lines are hydrocarbon polymer chains.

II. HISTORICAL BACKGROUND

One of the first elastomers which was based on ionic interactions, a butadiene-acrylonitrile-acrylic acid terpolymer, was introduced by Goodrich in the early 1950's. Brown[7] described how these materials could be suitably neutralized with zinc oxide or other zinc salts and plasticized to break up ionic association at elevated temperature. These ionic elastomers provided enhanced tensile properties and improved adhesion compared to conventional copolymers.

A second family of elastomers which possesses a substantial level of ionic interactions was also introduced during the early 1950's by Du Pont; it was based on the sulfonated structures obtainable from chlorinated polyethylene[8]. These materials, suitably cured with various metal oxides, gave rise to a combination of ionic and covalent crosslinks and were commercially available under the trade name "Hypalon." Because these polymers possess both covalent and ionic interactions, we will not consider them as part of the ionomer family for this article.

A major breakthrough in ionomers occurred in the mid 1960's when Du Pont introduced their ethylene-methacrylic acid polymers which were partially neutralized with sodium and zinc cations under the trade name "Surlyn." These modified polyethylenes possessed remarkably enhanced clarity and tensile properties over conventional polyethylene. The Surlyn systems emphasized the versatility of the ionomer structure and the unique properties available by modification of a polyethylene backbone. In several of their early papers, Rees and Vaughn[9,10] described the structure, morphology, and physical properties of this family of materials. In the 1960's and early 1970's, a number of investigators explored the structure and properties of these ionomers. Specifically, MacKnight[1,11], Otocka[12-14], Cooper[15], and Eisenberg[16-19] were among those who postulated various structures for ionic crosslinks and the resultant morphology. In 1970, Eisenberg undertook the first comprehensive theoretical attempt to understand the arrangement of salt groups in ionomers. In subsequent studies, Eisenberg and coworkers have explored various classes of ionomers, styrene-acrylic acid copolymers among others, and have interpreted morphology and properties of these systems in the light of different degrees of interaction of the ionic groups.

More recently, new families of ionomers have emerged which possess a wide variety of properties leading to different applications. Specifically, Du Pont introduced the "Nafion" class of perfluorinated sulfonated ionomers[20,21], Exxon described their work on sulfonated ethylene–propylene terpolymer[22,23], a new family of thermoplastic elastomers, and Asahi Glass Company introduced their perfluorinated carboxylate ionomers known as "Flemion"[24]. In addition, there has been a dramatic increase in research in this area on a number of other polymer systems that are still in the laboratory stage[25].

III.   MANUFACTURE/SYNTHESIS

A. GENERAL

The preparation of ionomers of practical interest is readily achieved by one of two techniques: (a) copolymerization of a low level of functionalized monomer with an olefinically unsaturated monomer or (b) direct functionalization of a preformed polymer. Typically carboxyl-containing ionomers are obtained by direct copolymerization of acrylic or methacrylic acid with ethylene, styrene, and similar comonomers by free-radical copolymerization. Rees has described the preparation of a number of such copolymers[26]. The resulting copolymer is generally available as the free acid, which can be neutralized to the degree desired with metal hydroxides, acetates, and similar salts.

The second route to ionomers involves modification of a preformed polymer. Sulfonation of ethylene–propylene diene monomer (EPDM), for example, permits the preparation of sulfonated EPDM with a level of sulfonic acid groups in proportion to the amount of sulfonating agent[25]. Typically, these reactions are conducted in homogeneous solutions, permitting the direct neutralization of the acid functionality to the desired level. Isolation of the neutralized ionomer is then effected by conventional polymer isolation techniques (e.g., coagulation in a nonsolvent, solvent flashing, etc.). These procedures are detailed in several patents or publications[23a,23b,27].

A listing of representative commercial and experimental ionomers is described in Table I. These systems are obtained either by direct copolymerization of a carboxylate or sulfonate ionomer or by direct functionalization of a preformed polymer. The ionomers described are generally based on either carboxylic acids or sulfonic acid systems. The carboxylic acid copolymers are generally prepared by copolymerization of acrylic or methacrylic acid while, for the most part, the sulfonated polymers are obtained by direct sulfonation of an unsaturated or aromatic containing preformed polymer. MacKnight and coworkers[1] have described the preparation of other types of ionomers based on phosphonates, but generally commercial and experimental activity has been directed at ionomers based on either carboxylate or sulfonate species.

B. CARBOXYLATED ELASTOMERS

1. *General.*—The incorporation of acrylic and methacrylic acid groups into synthetic elastomers by free radical copolymerization has been commercially practiced for over 30 years. Typical examples of such systems include styrene–butadiene–acrylic acid, butadiene–acrylonitrile–acrylic acid, and butadiene–acrylic acid polymers. Typically less than 6% of carboxylic monomer is employed in order to preserve the elastomeric properties inherent in these sys-

TABLE I

EXAMPLES OF COMMERCIAL AND EXPERIMENTAL IONOMERS

Polymer system	Trade name	Comment
Commercial systems		
Ethylene–methacrylic		
acid copolymer	Surlyn (Du Pont)	Modified thermoplastic
Butadiene–acrylic acid	Hycar (Goodrich)	High green strength elastomer
Perfluorosulfonate		
ionomers	Nafion (Du Pont)	Multiple membrane users
Perfluorocarboxylate		
ionomers	Flemion (Asahi Glass)	Chloralkali membrane
Telechelic		
polybutadiene	Hycar (Goodrich)	Specialty uses
Sulfonated ethylene–	Ionic Elastomer[a]	
propylene terpolymer	(Uniroyal)	Thermoplastic elastomer
Experimental systems		
Styrene–acrylic		
acid copolymer	Experimental	Model ionomer system
Sulfonated polystyrene	Experimental	Model ionomer system
Sulfonated butyl		
elastomer	Experimental	High green strength elastomer
Sulfonated		
polypentenamer	Experimental	Model ionomer system

[a] Development stage.

tems. Currently, worldwide production of such systems is estimated to be in excess of 0.5 million tons/year[28]. The manufacture of these systems is discussed below.

A second class of carboxyl-containing elastomers has emerged in recent years; these are often termed "telechelic" polymers. In these systems the carboxyl functionality terminates both ends of the polymer chain. Such polymers range in molecular weight from 1500 to about 6000 and represent a specialty class of elastomers. These systems are also described below.
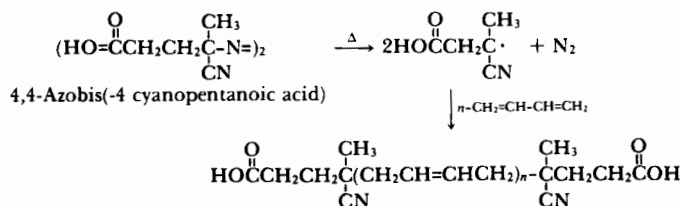
2. *Conventional carboxylated elastomers.*—The vast majority of commercially available carboxylated elastomers are prepared by emulsion polymerization. Typically[28], the polymerizations are conducted in acidic emulsion formulations, because the free acid copolymerizes much more readily than the neutralized salt. The lack of solubility of the salt form of these monomers in the hydrocarbon phase precludes significant monomer incorporation. A typical procedure for the preparation of a carboxylate elastomer would be the following: 100 parts butadiene (or combination with other monomers), 100 parts water (deionized), 5 parts methacrylic acid, 1 part sodium alkyl aryl polyether sulfate, and 0.4 parts potassium persulfate.

The polymerization is conducted at 30–50°C and can be carried to high conversion. The resulting latex preferably should approach 45–50% solids.

Alternate techniques have been described for preparing such systems, including solution copolymerization and grafting procedures on preformed polymer. Due to the simplicity of the direct polymerization process, the ease of product control, and finally the economics of this process, it is much preferred as a route to elastomers containing random incorporation of carboxyl groups.
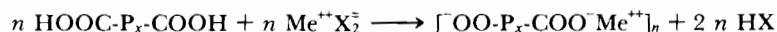
3. *Telechelic carboxyl elastomers.*—The synthesis of low molecular weight difunctional carboxyl-terminated butadiene-based polymers has been described

in several review articles[29,30]. These materials can be prepared by several synthetic routes involving anionic polymerization or free-radical-initiated polymerization processes. The first route offers polymers of relatively narrow molecular weight distribution; however, in the molecular weight ranges of interest (1500–6000) substantial levels of organometallic catalyst are required. The free-radically initiated process offers a route to carboxyl-terminated polymers of broader molecular weight distribution and one which is applicable to copolymers of butadiene and acrylonitrile. Free-radical initiators which contain carboxyl groups typically are used at reaction temperatures of 70–130°C.

$$(HO=\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{\underset{CN}{|}}{C}-N=)_2 \quad \xrightarrow{\Delta} \quad 2HO\overset{O}{\overset{\|}{C}}CH_2\underset{\underset{CN}{|}}{C}\cdot \quad + N_2$$

4,4-Azobis(-4 cyanopentanoic acid)

$$\Big\downarrow {}_{n\text{-}CH_2=CH\text{-}CH=CH_2}$$

$$HO\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}(CH_2CH=CHCH_2)_n\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$$

The selection of appropriate solvents is important to minimize chain transfer to solvent, which has an important effect on the final polymer functionality. Typically, t-butanol is employed, although tetrahydrofuran and acetone have also been used. The liquid polymers are recovered by solvent stripping to yield products of viscosities of 10–40 Pa·s.
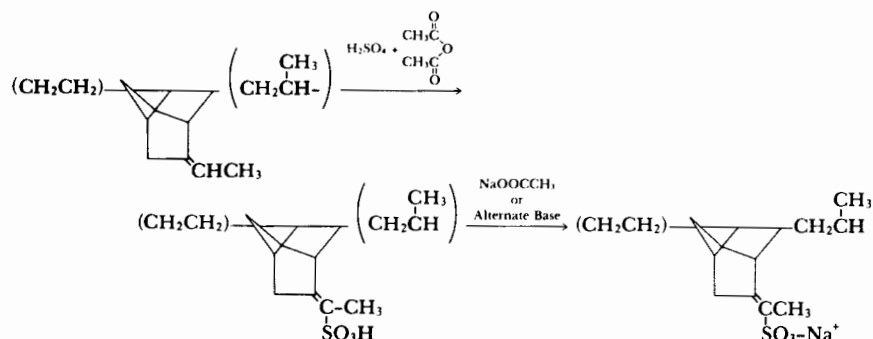
The neutralization of these carboxyl-terminated polymers by suitable metal alkoxides to yield halato-telechelic polymers has been described in articles by Broze, Jerome, and Teyssié[31]. The resulting high molecular weight products are obtained by neutralization in toluene and removal of the methanol by-product under vacuum.

$$n \ HOOC\text{-}P_x\text{-}COOH + n \ Me^{++}X_2^= \longrightarrow [^-OO\text{-}P_x\text{-}COO^-Me^{++}]_n + 2 \ n \ HX$$

C. SULFONATED ETHYLENE-PROPYLENE TERPOLYMER

The introduction of sulfonate groups into ethylene-propylene-diene polymers (EPDM) occurs by electrophilic attack of the sulfonation reagent on the polymer unsaturation. A number of different termonomers that can be copolymerized with ethylene and propylene are amenable to sulfonation. One of the preferred structures for this reaction is that based on 5-ethylidene-2-norbornene (ENB). A number of publications and patents have described the process[23a,23b]. Typically, EPDM based on ENB is dissolved in an aliphatic hydrocarbon, generally hexane, at a concentration of 50–100 g/l. A typical commercial EPDM, "Vistalon" 2504, can be used as received. The sulfonation agent which is preferred at ambient temperature is acetyl sulfate, generated by reaction of acetic anhydride and concentrated sulfuric acid. After 30 min reaction time, the sulfonation is terminated by addition of an alcohol, and the resultant polymer sulfonic acid is treated with a water–alcohol solution of metal acetate, agitated, and the metal sulfonated EPDM isolated by solvent flashing in boiling water. The sulfonation proceeds typically at 95% conversion of sulfuric acid to polymer-sulfonic acid based on titration of the final product.

The reaction proceeds as follows:

Compared to the metal-neutralized sulfo-EPDM, the polymer sulfonic acids are not highly associated. The free acids possess low strength and are less stable thermally. When treated with metallic bases, the bulk and solution properties of the neutralized products are changed markedly. In the absence of a polar cosolvent, such as methanol, the hydrocarbon solutions of the metal salts of sulfo-EPDM are solid gels at polymer levels above several per cent[27]. With 1–5% alcohol, the polymer solutions are quite fluid with solution viscosities of 1–5 Pa·s.

IV. IONOMER PROPERTIES

A. INTRODUCTION

The presence of relatively low levels of metal carboxylate or sulfonate groups pendent to a polymer chain clearly has profound effects on polymer properties. Specific properties, such as the polymer glass transition, the rubbery modulus above the glass transition, dynamic mechanical behavior[32], the melt rheology[33], the relaxation behavior, dielectric properties, and polymer solution behavior, are all modified by the presence of low levels of ionic groups. Several reviews[1,2] have discussed the influence of ionic functions on polymer properties in considerable detail. In this section, we will highlight the more significant features unique to ionomers. Specifically the influence of pendent ionic functions on elastomeric polymer backbones will be described.

B. ELASTOMERS

1. *Butadiene–methacrylic acid ionomers.*—The copolymerization of methacrylic acid with butadiene leads to an elastomer that is tougher and less elastic[2,28] than the base polybutadiene. This toughness is manifested as an increase in tensile strength with increasing methacrylic acid content. If the amount of acid incorporated in the polymer exceeds 40 wt%, the rubbery properties of the material are lost. While the acid form of such elastomers is useful in improving selected properties and in providing improved adhesion, very significant property changes are observed upon neutralization (or vulcanization) with suitable metal oxides. The incorporation of suitable divalent metal oxides provides rubbers of very high green strength as compared to sulfur-vulcanized butadiene-based elastomers. While such metal oxides neutralize the carboxylate groups and form sta-

ble neutral salts, COO–Zn–OOC, it now appears that the final product is a mixture of some free acid and some mixed salts. The resulting products exhibit poor compression set, high stress relaxation, and fluidity at elevated temperatures. Such behavior is consistent with a combination of chemically bonded crosslinks and with secondary bonding due to ionic aggregation.

Neutralization of these carboxylated rubbers with monovalent salts results in a weaker network than that obtained with divalent salts, and this weak network is substantially destroyed upon heating the system to about 100°C.

Evidence for this thermoplastic network has been obtained in butadiene-methacrylic acid copolymers of varying acid content neutralized with lithium[13]. The neutralization of the acid results in an increase in the glass transition and an enhancement of the rubbery modulus at elevated temperatures. However, above 75°C, viscous flow is evident. Therefore, the monovalent salts of these carboxylated rubbers exhibit a weak ionic association consistent with some degree of multiplet and cluster formation.

2. *Sulfonated ethylene-propylene terpolymer.*—Recent patents[23] and publications[22,34] have described a new type of sulfonated ionomer, that based on the sulfonation of ethylene-propylene-diene monomer (EPDM). EPDM is a commercially available elastomer which possesses excellent oxidation and weathering resistance due to a saturated polymer backbone. EPDM can be sulfonated in hydrocarbon diluents at low levels without substantial change in the EPDM molecular weight. The resulting polymer sulfonic acid is then neutralized with suitable bases, preferably metal acetates, to yield a fully neutralized metal sulfo-
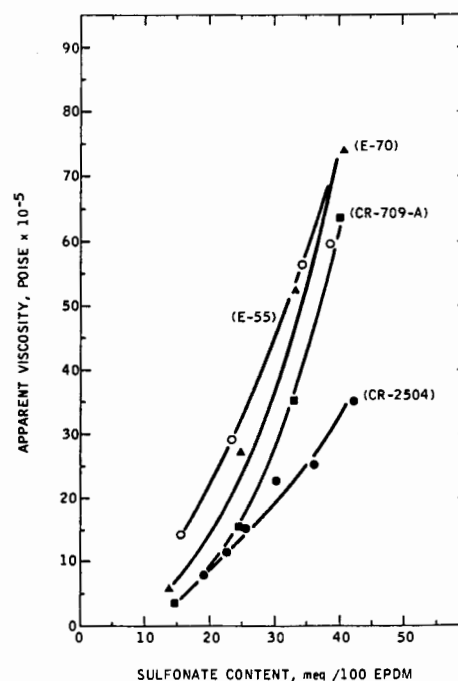

FIG. 2.—Dependence of melt viscosity at 200°C and 0.74 s^{-1} on sulfonate content for sulfo-EPDM's with zinc counterions. (Note: 10^5 poise $= 10^4$ Pa·s)

nated EPDM. The sulfonic acid intermediate is described as thermally unstable and, therefore, is normally not isolated.

The neutralized sulfo-EPDM polymers are thermally stable, strongly associating ionomers with properties approaching those of covalently crosslinked EPDM at very low levels of metal sulfonate groups[35]. Because the ionomer is obtained by direct modification of the base polymer, these systems offer an excellent opportunity to compare the ionomer properties with those of the base EPDM.

The effect of varying the sulfonate content with this family of polymers on melt viscosity is shown in Figure 2 for zinc as the metal cation. The four curves shown reflect EPDM elastomers of different ethylene/propylene composition and different sulfonate distribution. Even at zinc sulfonate levels as low as 20 meq/100 g polymer (or ~0.6 mol%), the melt viscosity is substantially enhanced over that of the base EPDM. Similarly, at sulfonate levels above about 0.5 mol%, the tensile strength increases markedly in those EPDM's which are noncrystalline (see Figure 3). For EPDM's having modest levels of crystallinity (samples designated E-55 and E-70), the tensile strengths approach 30-40 MPa (4000-6000 psi) at about 1 mol% ionic content.

From these and other data, it appears that the metal sulfonated EPDM ionomers offer an ionic network which is more persistent (*i.e.*, more temperature resistant) at lower levels of ionic functionality than that obtained with the carboxylated elastomers above. The effect of metal cation on the melt viscosities and
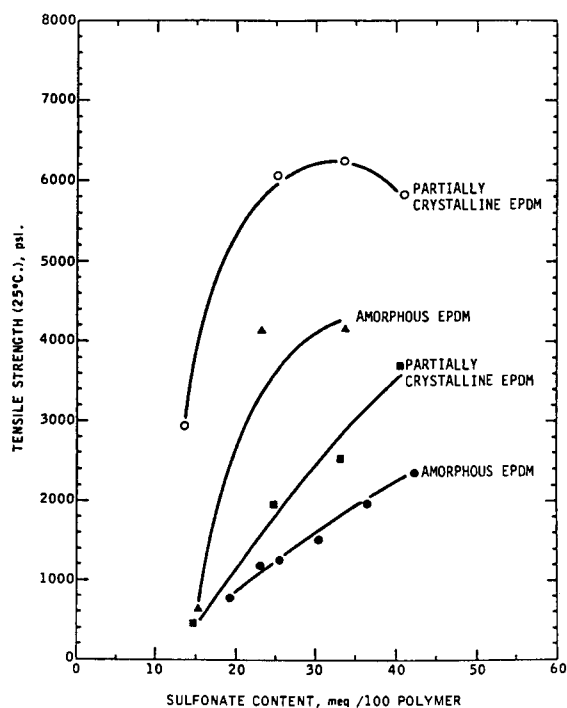

FIG. 3.—Dependence of tensile strength at 25°C on sulfonate content for the sulfo-EPDM's of Figure 2. (Note: 1000 psi = 6.9 MPa)

TABLE II

EFFECT OF CATION ON FLOW AND PHYSICAL PROPERTIES OF SULFO-EPDM[a]

Metal	Apparent viscosity[b], kPa·s	Melt fracture at shear rate, s^{-1}	Melt index[c], g/10 min	Tensile strength, MPa	Elongation, %
Hg	—	—	disintegrated	—	—
Mg	550	<0.88	0	2.2	70
Ca	532	<0.88	0	2.8	90
Co	523	<0.88	0	8.1	290
Li	515	<0.88	0	5.2	320
Ba	508	<0.88	0	2.3	70
Na	506	<0.88	0	6.6	350
Pb	328	88	0.1	11.6	480
Zn	120	147	0.75	10.2	400

[a] Base polymer, CR-2504, sulfonate content 31 meq/100 g EPDM. Dissolved 100 g of free acid in 1000 cm³ hexane–150 cm³ isopropanol; neutralized with 90 meq acetate in 25 cm³ water[22].
[b] At 200°C and 0.88 s⁻¹.
[c] At 190°C and 3.3 MPa (478 psi).

physical properties of sulfo-EPDM is shown in Table II[22]. It is apparent that only zinc and lead confer significant melt flow at 200°C, while the other cations, both mono- and divalent, result in very high melt viscosities. These data suggest that sulfonate ionomers based on EPDM exhibit an exceptional degree of ionic association, one that is very resistant to flow at modest ionic contents. Nevertheless, these polymers can be dissolved in suitable mixed solvents, demonstrating that they are not covalently crosslinked.

V. APPLICATIONS

A. SULFO-EPDM, IONIC ELASTOMER

"Ionic Elastomer"[36] is a metal sulfonated EPDM available in powdered form. It can be compounded with fillers, rubber processing oils, and selected polymers into a variety of elastomeric materials. Initially, two grades of ionic elastomers have been available. These materials can be formulated into a wide variety of compounds which are of interest in a number of rubber applications. These include adhesives, impact modifiers, footwear applications, such as unit soles, calendered sheet, garden hose, and similar rubber goods[37].
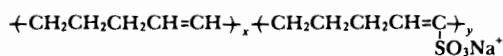
"Ionic Elastomer" differs from conventional vulcanized rubbers in that the presence of metal sulfonate groups provides strong physical crosslinks at ambient temperatures. However, when a suitable polar additive, termed an "Ionolyzer", (such as zinc stearate) is incorporated, the elastomer becomes thermoplastic at elevated temperature, permitting melt processing. Thus, by combining materials such as zinc stearate along with other ingredients, a wide variety of products is available based on several "Ionic Elastomer" gums. The addition of zinc stearate not only improves thermal processibility, but also improves tensile properties, so that very strong ionomers with properties approaching those of polyurethanes can be formulated. Typical ranges of physical properties available from "Ionic Elastomer" compounds are shown in Table III below.

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TABLE III

TYPICAL PROPERTY RANGE OF IONIC ELASTOMER COMPOUNDS

Property	Typical Range
Shore A hardness	45–90
100% Modulus, MPa	1.2–6.9
Tensile strength, MPa	3.4–17
Elongation, %	350–900
Tear strength, N·m	15–38
Specific gravity	0.95–1.95
Compression set (R.T.)	30–35
Brittle point, °C	−56–−46
Processing temperature, °C	150–260

VI. MISCELLANEOUS

MacKnight and Earnest[1] have described a family of new ionomers based on the starting elastomer, "polypentenamer." Phosphonate, sulfonate, and carboxylate derivatives have been prepared over a broad range of ionic contents. The chemical formula for one of these ionomers is as follows:

$$+CH_2CH_2CH_2CH=CH+_x+CH_2CH_2CH_2CH=C+_y$$
$$SO_3Na^+$$

Sodium Sulfonated Polypentanamer

Studies conducted on this class of materials provide substantial insight into the morphological behavior of ionomers in general. Through a variety of experimental techniques, evidence for a separate ionic phase in these systems has been accumulated.

Recent studies by Broze, Jerome, and Teyssié[31] have described the physical properties and solution behavior of "halato telechelic" polymers. These polymers typically are polybutadienes of low molecular weight, terminated by carboxyl groups and neutralized by various cations. A broad range of systematic modifications can be applied to these materials. A key discovery in the synthesis of these systems was the observation that very high apparent molecular weights could be achieved by complete removal of the water or alcohol evolved during preparation. Viscoelastic, small angle x-ray, and dynamic mechanical studies have been conducted on these polymers and are consistent with a phase-separated ionic morphology.

A rather novel approach to ionomers has been described[38] recently, involving the chemical modification of asphaltic bitumen. Reaction of maleic anhydride or sulfur trioxide–trimethylamine complexes with asphalt leads to a chemically modified product. These modified asphalts are subsequently reacted with suitable oxides or bases to yield asphalt ionomers. The resulting products produced composites when mixed with aggregate fillers that retained a very high fraction of their strength when wet. In contrast, unmodified asphalt lost most of its strength upon exposure to water. It has been suggested[38] that these asphalt ionomers would produce more durable road paving materials.

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