

Some electron microscopic observations of sulphonated EPDM polymers

P. K. Agarwal and E. B. Prestridge*

Corporate Research – Science Laboratories

*Analytical and Information Division, Exxon Research and Engineering Company, P.O.

Box 45, Linden, New Jersey 07036, USA

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The electron microscopy observations have been conducted with films cast from dilute solution based on sulpho EPDMs derived from various cations. Some very interesting morphological features are observed. Aggregated regions of sizes in the range of 500 to 1000 nm are found in the metal sulphonated polymers, while the absence of structure is observed in the base polymer and its acid derivative. This type of morphology has not been previously reported, and these aggregates appear about 100 times larger than typically expected for phase separated ionomers. Possible explanations of these morphologies are discussed.

Keywords Sulphonated ethylene-propylene diene monomer; ionomers; transmission electron microscopy; morphology; domains; structure; property

INTRODUCTION

During the last few years there has been a rapid growth in the research activities of ion-containing polymers, both from scientific and technological viewpoints. A number of publications regarding the nature and structure properties relationship of ion-containing polymers have appeared in the literature^{1,2}. The unique physical properties of ion-containing polymers has been ascribed to their multiphase nature. The introduction of a small amount of ionic crosslinks in the polymer hydrocarbon chain is presumed to form a domain structure due to their strong associative nature.

The presence of domains or a phase separated system in ionomers has been described on the basis of results of various kinds of experimental techniques. These techniques involve both direct and indirect observations of the structural features of ionomers. Indirect techniques include the study of viscoelastic^{3,4}, and dielectric properties⁵, n.m.r.⁶ and i.r.⁷ spectra, and X-ray diffraction⁸⁻¹⁰, etc. Direct observations of ionomer morphology have been achieved via electron microscopy¹¹⁻¹⁵. On the basis of these studies various kinds of models of the structure of ionomers have been proposed. However, none of these models have been widely accepted, which is not very surprising in view of the lack of direct application of any analytical tool. The interpretation of the phase contrast microscopy is difficult at best. The early electron microscopy investigations by Davis¹¹ *et al.* of the structure of the ethylene-methacrylic acid copolymers and their metal salts at intermediate magnifications revealed a granular structure of about 30 nm in size. At higher magnifications a fine structure of about 10 nm was observed, however, it could not be interpreted because the micrograph was taken with the image being out of focus. Attempts to observe the morphological features of butadiene-methacrylic acid copolymers at very high magnifications (160 000 ×) was undertaken by Marx¹³ *et al.* Their micrographs of

osmium tetroxide treated samples showed two different structures. Two different sizes of spherical unstained regions of diameters of ~1.5 and ~2.5 nm were observed. These spherical domains and the strings of overlapping spherical regions were found to be uniformly distributed throughout the matrix. The electron microscopy studies of polyethylene-phosphoric acid and its caesium salt by Phillips¹⁴ suggested the presence of two phase structure in these ionomers. In acids large regions of the size of about 50–80 nm indicative of hydrogen bonded domains were found, while in the fully neutralized ionomers smaller domains of about 5–8 nm were observed. In view of the rather large size of the hydrogen bonded domains observed compared to that expected on a simple molecular volume basis, it was suggested that a significant amount of hydrocarbon chains is trapped in these domains.

Here we report some of our preliminary morphological observations on sulphonated polymers using the transmission electron microscope.

EXPERIMENTAL

The sulphonated ethylene-propylene diene monomer (EPDM) polymers were supplied to us by courtesy of the late Dr. H. S. Markowski of our laboratories. They were prepared by procedures discussed in detail earlier^{16,17} by the reaction of EPDM containing 5-ethylidene-2-norbornene (ENB) with acetyl sulphate. All the sulphonated samples were prepared from the same base EPDM. The number average molecular weight of the base polymer was ~40 000 and its heterogeneity index $M_w/M_n = 2.1$. The ethylene and ENB content of this material were 55% and 5% by weight, respectively.

Three samples, two metal neutralized and one ammonium neutralized, were studied. The metal neutralized samples were the caesium and zinc salts of sulpho EPDM. Prior to full neutralization each was sulphonated to about 1 mole% based on polymer

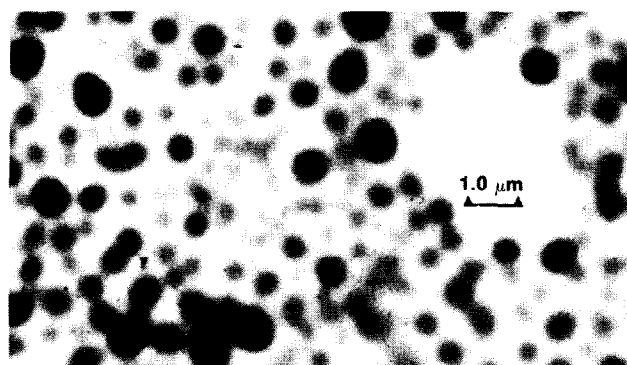


Figure 1 Electron micrograph of solution cast film of sulphonated EPDM caesium salt (sulphonation level ~20 meq). Magnification 10 000 x

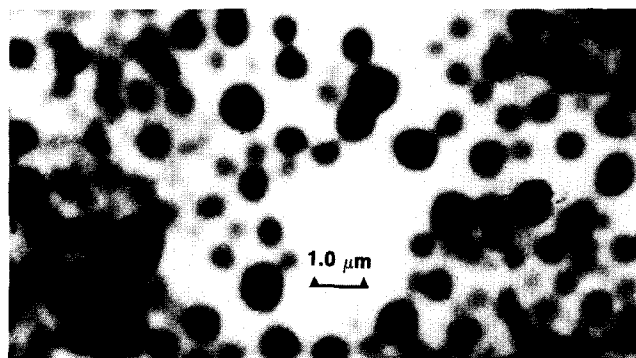


Figure 2 Electron micrograph of solution cast film of sulphonated EPDM zinc salt (sulphonation level ~20 meq). Magnification 10 000 x

backbone. The concentration of the caesium and zinc in these samples were about 4.5 and 2.5 wt%, respectively. The ammonium salt of sulpho EPDM had a sulphonate content of ~0.7 mole% and was fully neutralized. Upon analysis it was found to contain about 0.2 wt% of nitrogen.

Specimens for the electron microscopy were prepared as follows. Dilute solution of 0.1% (by weight) of the samples were made in a cosolvent* mixture of toluene and methanol (95/5 by volume) and the solutions were left overnight with stirring. After complete dissolution of the sample the solutions were further diluted. The films were then cast on carbon coated copper grids by placing a drop of the solution on them and drying the grid at room temperature. The samples were then observed under a Philips (EM 300) electron microscope operated at about 100 kV at various magnifications and typical micrographs were taken.

RESULTS AND DISCUSSION

Typical electron micrographs obtained on the sulphonated EPDM's are shown in Figures 1 and 2.

* It can be pointed out here that due to the rather strong associative nature of the metal sulphonate groups in the sulphonated EPDM polymers¹⁷, these materials are not soluble in typical non-polar organic solvent. In order to dissolve them it is necessary to use a polar cosolvent¹⁸.

Figure 1 shows the structure of the solution cast film of the caesium sulpho EPDM sample. A long range morphological feature of the sample is clearly seen. Dark spherical regions of about 500 to 1000 nm are seen. These regions are randomly distributed throughout the system. Similar features were observed in the film cast from the zinc sulphonated EPDM sample as shown in Figure 2.

The size of the dark regions seen in these Figures is rather large, however, all the cast films observed gave similar results. In view of these repeat observations we are led to conclude that these regions are representative of the morphology of these films. No such features were observed in films cast from solutions of either base EPDM polymer or its sulphonic acid. These dark regions of the micrographs could result from two different mechanisms: (1) the regions have a substantially increased thickness relative to the surrounding area, or (2) they contain a high concentration of atoms that have a large elastic scattering cross section.

To determine the thickness of the regions in question, the polymer films were 'shadowed' to show topographical features of the film. Shadowing is an electron microscope specimen preparation technique where a metal (uranium was used here) is deposited in a high vacuum evaporation onto a surface at an acute angle. In our study the angle was chosen so that the shadow created by the dark region would be five times as long as it was high. Figure 3 is a typical shadowed micrograph of a film cast from caesium sulpho EPDM. The shadow lengths indicate that the domains (dark regions) are only at most 30 nm above the remaining matrix. Lenz's²³ calculations on the elastic scattering cross section of various atoms for electrons of intermediate energies demonstrates that for atoms of low atomic number a 30 nm change in thickness will not produce the change in contrast we observe.

These dark regions therefore appear to represent the ion concentrated areas. The ionic concentration in these materials is low and just on a molar volume basis one would expect a significantly smaller domain than that which has been observed in the present studies. A possible argument which can help explain their large size is that these 'super domains' contain significant amounts of the hydrocarbon matrix. Similar viewpoints had been expressed earlier by Phillips¹⁴ to explain large irregular shaped domains of about 80 nm in the polyethylene-phosphonic acid ionomers as mentioned previously. Iron-rich aggregates up to 500 nm in size have also been observed by Pineri¹⁵ *et al.* during their ion clustering

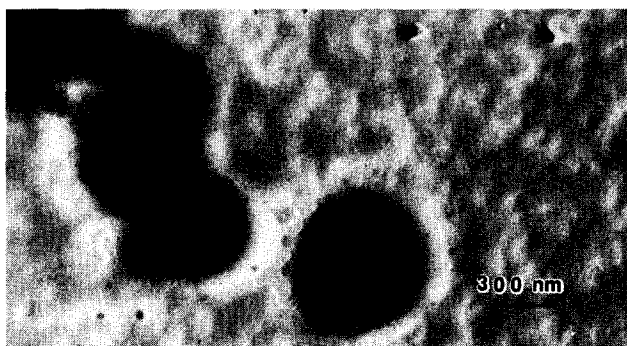


Figure 3 Uranium shadowed micrograph of film cast from Cs Sulpho-EPDM

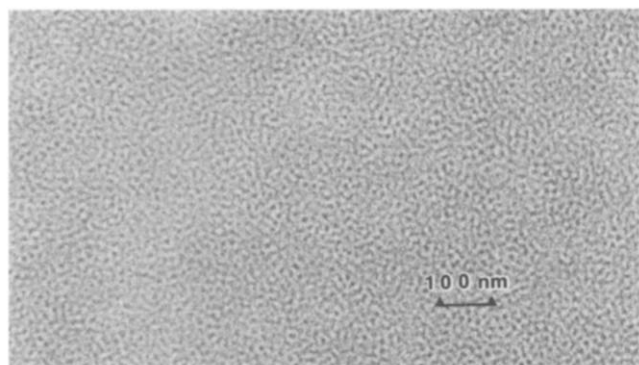


Figure 4 Electron micrograph of a typical styrene-butadiene-styrene block polymer film cast from toluene solution

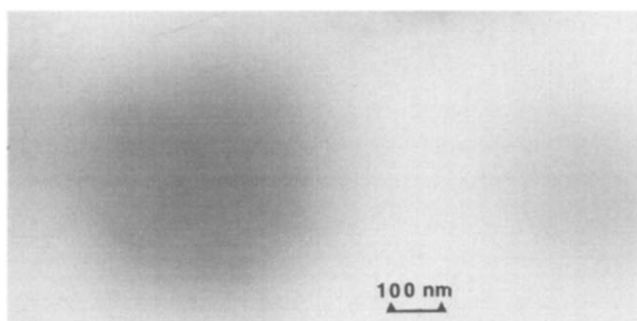


Figure 5 Electron micrograph of Cs Sulpho-EPDM film of Figure 1 at higher magnification 100 000 x

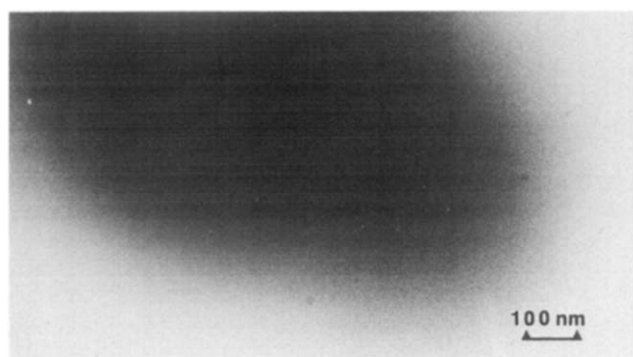


Figure 6 Electron micrograph of Zn sulpho-EPDM film of Figure 2 at higher magnification 100 000 x

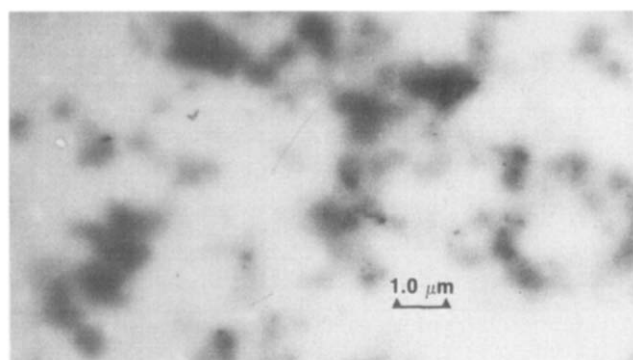


Figure 7 Electron micrograph of solution cast film of sulphonated EPDM ammonium salt (sulphonation level ~20 meq). Magnification 10 000 x

studies in poly(butadiene-styrene-4-vinyl pyridine) crosslinked by iron chloride. Typically, however, it should be pointed out that both in block copolymers and in ionomers domains much smaller in size are observed (Figure 4). In block copolymers their two phase morphology is known to depend upon the history of sample preparation and the domains can vary from 2.5 to 50 nm in size¹⁹. In ionomers fewer morphological studies have been done and domains of more or less constant size (about 5 nm) have typically been reported. Longworth and his coworkers^{11,12} had observed in films prepared from solutions of ethylene-methacrylic acid copolymers (E/MAA-90/10) cast on rubidium oxide, an ion rich granular structure of 5–10 nm in size. The films prepared by casting the E/MAA copolymer solution on hot water showed a spherulitic structure very similar to that obtained from films prepared by casting polyethylene spherulitic (in hot xylene solution) on hot water. These results suggested that the polyethylene structure is maintained in the copolymer acid but is destroyed upon neutralization with a metal cation. The base EPDM polymer used in the preparation of the sulphonated materials is amorphous and thus it is not surprising to observe a featureless structure when the polymer is converted to its sulphonic acid derivative.

In view of the relatively low magnifications of the micrographs shown in Figures 1 and 2, one could argue that the super domains observed in the metal salts of the sulphonated polymers are regions of possibly closely packed small size domains similar to those observed in carboxylate ionomers. Such a possibility is apparently ruled out on the basis of Figures 5 and 6 which show the micrographs of the caesium and zinc salts of sulpho EPDM, respectively, at higher magnifications. Here again large dark regions of about 800 nm are observed. Figure 7 shows the structure of the film prepared from the ammonium salt. Essentially all the structural features seen before in the caesium and zinc films are present in the ammonium as well. The dark regions are somewhat more diffuse, nevertheless, their dimensions are more or less similar. A similarity of structure between three different kinds of salts suggest that in these systems an aggregated state exists. The preparation techniques of these samples may play a significant role in determining the nature and extent of aggregate state. The samples were prepared using a cosolvent mixture, where the preferential evaporation of the particular solvent and/or selective precipitation of the polymer may exert an influence on the morphology of the films. However, in view of earlier morphological observations^{11,12} on carboxylate ionomers, it seems unlikely. In those studies a three component mixed solvent system was used in the preparation of the films. The morphological features observed in these films and that of their sectioned films gave very similar results. However, in the case of block copolymers such as Kratons, varying degrees and types of morphologies, depending on the preparation techniques, have been well documented in the literature¹⁹. It has been observed quite frequently that certain block and graft copolymers form micelles in selective solvent-nonsolvent systems²⁰. The micelle formation characteristic is due to the varying amphiphilic characteristics of various groups of such polymers. The individual groups or sequences of molecules of these polymers interact differently, not only with each other, but to varying extents with the particular

solvent-nonsolvent system. Such morphologies play an important role in determining the properties of the bulk systems.

In addition to the ions, the large domains observed in the solution cast films of sulphonated EPDM's obviously must contain mostly non-ionic polymer matrix and thus perhaps are a reflection of strong nature of the metal sulphonate interactions which tend to pull and pack the chains together. In the past a number of studies were done on the state of aggregation of low molecular weight sulphonates. For example Kaufman and Singleterry²¹, from their extensive studies on the state of aggregation of various cations including Zn, NH₄ and Cs salts of dinonylnaphthalene sulphonates had concluded that the aggregation state of sulphonates is micellar and in general the size of these micelles is independent of the type of cations. In view of the low ionic content and gross similarity in size of domains of various salts of the sulphonated EPDM's studied here, together with their strong associative nature a tendency of the micelle formation by these polymers in such solvent systems cannot be ruled out. Variations in the strength of the metal sulphonate groups by preferential plasticizers and degree of ionizations are possible¹⁷ and can be expected to play a crucial role in determining the state of aggregation in such ionomers. Significant effects of the morphology of sulphonated ionomers in various physical properties of the blends of such polymers with polyolefins have been the subject of a recent study²². Future investigations include possible correlations between the varying morphologies and the macroscopic properties of such varying systems.

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