MECHANO-OPTICAL BEHAVIORS OF Ionomers

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

Linkun Zhang

August, 2015
ABSTRACT

The ionomer, zinc neutralized sulfonated ethylene-propylene-diene monomer terpolymer (Zn-S-EPDM), was synthesized. The neutralization of the polymeric sulfonic acid to the metal sulfonate results in special ionic association which forms an effectively cross-linked structure, known as ionic domain. The sulfonation degree, a magnitude of the density of the ionic domains, was characterized qualitatively by using Fourier Transform Infrared Spectroscopy (FTIR) and quantitatively by combustion analysis.

The effect of the sulfonation degree was studied. The mechanical properties and mechano-optical properties of the materials were investigated by using the real time spectral birefringence stretching machine. The thermal transition behavior and thermal degradation processes were studied by Differential Scanning Calorimeter (DSC) and thermogravimetric analysis (TGA) respectively. Small-angle X-ray scattering (SAXS) was employed to give an insight into the microstructure of ionic domains.

The properties of the zinc stearate plasticized Zn-SEPDM system were also studied. Zinc stearate was found as a highly effective plasticizer which not only enhances the mechanical properties of the Zn-SEPDM but also reduces the viscosity of
the system during the manufacturing process at high temperatures. The effect of zinc stearate and its special association with the ionic domains were investigated with the same devices as mentioned in previous paragraph.
ACKNOWLEDGEMENTS

I sincerely appreciate my advisors Dr. Mukerrem Cakmak and Dr. Robert Weiss for their generous helps and constructive guidance. Special thanks to Dr. Robert Weiss for supplying the high-performance Zn-SEPDM rubber and to Dr. Mukerrem Cakmak for authorizing advanced real time spectral birefringence stretching system for my research.

I would like to show deeply appreciation to committee member Dr. Kevin Cavicchi for coming to my defense and providing valuable advice. It is a great honor.

I would like to appreciate Dr. Nicole Zacharia for support and instrument.

I would like to thank Greg Treich and Rui Ma from Dr. Scotz’s group for their kindly and gratis help.

I want to express great appreciation to Dr. Zhorro Nikolov for his kindly help and guidance on SAXS and also Surface and Optical Analysis (SOA) Facility of the University of Akron for instrument.

I thank my lab mates: Chongwen Huang, Zhiyang Zhao, Longhe Zhang, Jiawei Wu in Dr. Weiss group. Ido, Yuanhao Guo, Enmin Wang, Liyang Shen in Dr. Cakmak group.

I appreciate my family and my parents for encouraging.
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CHAPTER I

INTRODUCTION

Ionomers are polymers containing a relatively low level of ionic groups. The aggregation of these ionic groups leads to ionic domains which act as physical crosslinks. The association within the ionic aggregates is so strong that only a small amount of ionic groups can lead to a significant enhancement of the materials.

In the 1970s, metal-sulfonate groups had been introduced in ethylene-propylene-diene terpolymer (EPDM) to obtain high-performance ionic rubber. These metal-sulfonates containing EPDM possess excellent mechanical properties which are comparable to common chemical cross-linked rubbers due to the physical crosslinks formed by ionic aggregates. The superiority of these types of physical crosslinks is that they are reversible. With elevated temperatures, the physical crosslinks are weakened to provide melt flow for industrial processing, conversely, with declining temperature, the physical crosslinks will be reformed to provide desirable mechanical properties. Thus, the metal-sulfonate containing EPDMs were considered to be thermoplastic elastomers. In our studies, we focus on zinc neutralized sulfonated EPDM (Zn-S-EPDM) only.
One important controlling factor for Zn-S-EPDM is the sulfonation degree, which is the magnitude of the density of ionic aggregates. One can get the ideal processing conditions for Zn-S-EPDM with desirable properties by adjusting the sulfonaiton degree to an appropriate level. As the sulfonation degree has such profound effects on the bulk properties of the Zn-S-EPDM, it is important to have a fundamental understanding of the influence of sulfonation degree on the orientation behaviors and structure development of the materials. The real-time spectral birefringence stretching machine was employed to investigate the real time mechano-optical behaviors and real time mechanical responses for Zn-S-EPDM with varied sulfonation levels under uniaxial stretching. The influence of the sulfonation level on the thermal transition and thermal degradation behaviors were also studied by differential scanning calorimetry and thermogravimetric analysis. Lastly, the morphology of the ionic domains was studied by using small-angle X-ray scattering.

The association of metal sulfonate groups significantly enhances the mechanal properties of the Zn-S-EPDM, however, it also produces an undesiriable high melt viscosity which limits the processability of the material. Zinc stearate was reported to be an ideal polar plasticizer for Zn-SEPDM, which not only significantly reduces the melt viscosity at temperatures above its melting point, but also enhances the mechanical properties as a reinforcing filler at room temperature. The polar plasticizer can interact with the nanodomains, thereby reducing the density of physical crosslink junctions, which causes a reduction of viscosity. Processing and material variables
such as temperature, rate of stretching, and Zn(st)$_2$ concentration are likely to affect the extent of anisotropy achieved when these compounds are deformed. As the second part of this project, the real-time true stress-true strain birefringence measurement system was used to provide insight into the effect of processing variables and Zn(st)$_2$ crystals on the orientation behavior of plasticized Zn-S-EPDM composition.
CHAPTER II

BACKGROUND & LITERATURE REVIEW

2.1 Ionomer

Ionomers are polymers containing a relatively low level of ionic groups.\textsuperscript{1-5} The aggregation of these ionic groups leads to nanophase separation of ion-rich domains which act as physical cross-links. The distinction of ionomers and polyelectrolytes was pointed out by A. Eisenberg and M. Rinaudo which led to a more rigorous definition of ionomers.\textsuperscript{6} Thus, more scrupulously, the ionomers were defined as \textit{polymers in which the bulk properties are governed by ionic interactions in discrete regions of the material (the ionic aggregates)}.\textsuperscript{6} By this definition, materials with properties controlled by the ionic groups will be defined as ionomers.

Interest in ionomer is continuing and growing for its large potential in applications.\textsuperscript{2} One industrial interest is, because ionic interactions have a strong influence on the physical properties of the ionomer, even at relatively low concentration, which permits the control of the bulk properties of the product by making small changes in the ionic part.\textsuperscript{7} Another industrial interest comes from the strong electrostatic attraction within ionic aggregations which make it possible for using ionomers as additives to enhance or modify the mechanical and rheological
properties of composites. Next, electrolytes may be made by ionomers for the modification of conductivity of the materials by the ions without the ionomers.

In the research of ionomers, understanding the formation, structure, morphology of the ionic aggregates is of fundamental interest. The ionic association, known as multiplet, was formed by a small number of ion pairs which does not form a separate phase. The aggregation of multiple leads to cluster. The shape of the clusters varies from different ionomer systems. Both spherical and nonspherical structures of clusters were reported. One example of spherical clusters, as shown in figure 2-1, was the ionic domains of Zn$^{2+}$ and Ni$^{2+}$ neutralized SPS observed by Li, Register and Cooper, who employed High-voltage electron microscopy (HVEM) during the research.

![Figure 2-1 Ionic domains of Zn$^{2+}$ and Ni$^{2+}$ neutralized SPS from HVEM](From Li, Register and Cooper, Direct observation of ionic aggregates in sulphonated polystyrene ionomers 1989, *Polymer*, 30, 1227.).

The size of the ionic aggregates was determined by a series of factors. Increase the size of ion pairs and ion content usually leads to larger multiplets. One study from
Moore et al.\textsuperscript{9} shown that the radiuses of styrene-based ionomers increase linearly with the length of side chains of ion pairs, as shown in figure 2-2.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Aggregate radius vs the side-chain length. Alkyl (filled symbols) and ether (open symbols)(From Moore et al, Small-Angle X-ray Scattering Investigations of Ionomers with Variable-Length Side Chains \textbf{1991}, \textit{Macromolecules}, 24, 1376-1382)}
\end{figure}

On the other hand, the mutiplets’ size decrease with increase of the chain segment length contacted directly with the ionic aggregates and backbone flexibility.

2.2 Structure of ionomer

One powerful technique to study the morphology of the ionomers is small-angle X-ray scattering (SAXS). The SAXS peak observed at low angles in ionomers, known as ionic peak, is a strong evidence for the existence of the ionic domains. The ionic peak was first reported by Longworth et al. in 1968.\textsuperscript{10,11} After that, the origin of the ionic peak was widely discussed and further a series of models of the ionic domains
were proposed based on the SAXS data by different researchers. One major different
between these models is the interpretation for the origin of ionic peak to intraparticle
interference or to interparticle interference.

The first multiplet-cluster model was presented by Eisenberg,\textsuperscript{12} in 1970. In his
paper, the multiplets were described as noncrystalline, spherical liquid-drop like
aggregates contain only ions. The cluster was formed by the arrangement of
multiplets which, therefore, own a larger size and higher ion concentration.

Modified hard-sphere model was proposed by Yarusso and Cooper\textsuperscript{13} in 1983,
based on zinc-neutralized sulfonated polystyrene system, shown in figure 2-3. The
ionic domain is formed by a core, which is a dense aggregate of ionic groups, coated
with hydrocarbon layer whose electron density is much lower, and immersed in a
matrix of intermediate ion content. The closest distance of between the domains is
limited by the hydrocarbon layers thickness. The ionic peak was assigned as the
interparticle interference in this model.

![Figure 2-3 Schematic of modified hard-sphere model](image)

(From Yarusso and Cooper., Microstructure of ionomers: interpretation of
Core-shell Model was proposed by MacKnight et al.\textsuperscript{14} This model, shown in figure 2-4, assumes that a core formed by ion pairs is surrounded by a shell of material with lower electron density, which is, surrounded by another outermost shell with a higher electron density. The core is an aggregate of about 50 ion pairs with a radius of 8-10Å. The surrounding hydrocarbon cell is of an order of 20Å. The authors of this model suggested that it is the intraparticle interference which leads to the ionic peak.

Another model is the Eisenberg-Hird-Moore (EHM) model.\textsuperscript{15} The concept of restricted mobility region, shown in figure 2-5, was proposed in this model. The mobility of the chains directly attach to the multiplet is reduced because of the anchoring of the chains to the multiplets and the crowding of the chains. Multiplets were surrounded by these kind of restricted mobility region. The size of regions of reduced mobility become larger and larger as overlapping and may lead to special regions that are over the threshold size for independent phase behavior. These regions were defined as cluster by the authors.
As shown above, Researchers have provided a lot theoretical interpretation for the structure of the ionomers. A lot of models describing the morphology of the ionic domains were presented, and most which were in good agreement with experimental dates for corresponding ionomer systems.

2.3 Sulfonated EPDM

EPDMs contain low levels of olefinic functional groups which permit the vulcanization of commercial rubbers. One of the major diene monomers of EPDMs is 5-ethylidene-2-norbornene (ENB). For ENB, only one of the two olefinic sites will be consumed during polymerization. The residual unsaturation was available for future
modification such as sulfonation. Sulfonated ionomers were reported to have a stronger physical properties than corresponding carboxylate ionomers. The ionic interactions within sulfonated ionomers are so strong that even a relative low level of sulfonate groups will have large effect on the properties of the materials. The influence of the ionic interaction on the viscoelastical properties of ionomer is highly dependent on the ionic concentration.

The way to synthesize the metal sulfonate-containing EPDM was provided by Makowsk et al. The EPDM was, first, dissolved in hexane, then sulfonated by sulfonation reagent acetyl sulfate, and finally neutralized with metal acetate. The equation of the sulfonation was shown in figure 2-6. The reaction seems to be a simple substitution: the sulfonate substitutes the labilized hydrogen ion on the carbon double bond of olefin site of the ENB. However the real process of the sulfonation was complicated, as presented by Thaler. This paper investigated the chemistry of the sulfonation of EPDM and the structure of the intermediates by examining the chemistry of small molecule analogs of the olefinic sites of the third monomer. A sultone model was proposed based on NMR examination. Sultones are cyclic carboxylic acid esters, however, similar with open-chain sulfonate esters which can react with nucleophiles and open the ring. The results were shown in figure 2-7. This study provided some details in sulfonation process of EPDM which may be the answers for the uncertains in the reaction, for example, the formation of some neutral intermediates inferred from the lower acid content than predicted.
Figure 2-6 Equations of sulfonation process\textsuperscript{20}

Figure 2-7 Details in sulfonation process\textsuperscript{21}
Detailed studies on the properties of S-EPDM was made by Makowsk et al.\textsuperscript{19} In that paper, the influence of sulfonate content, metal cation, composition and structure of the base EPDM on the physical properties of the S-EPDM was studied. As reported by the authors, the modulus and elongation of S-EPDM increase with sulfonate content. The zinc neutralized S-EPDM had the lowest melt viscosity when compared with other cations neutralized S-EPDM such as Na and Mg.

2.4 Zinc stearate plasticized metal-sulfonate containing EPDM (Zn-S-EPDM)

Metal-sulfonate containing EPDMs thermoplastic elastomers with excellent mechanical properties gain high industrial interest. The association of metal sulfonate groups in the Zn-SEPDM is so strong that a low degree of sulfonation produces a significant enhancement of the mechanical properties. However this also produces an undesirable high melt viscosity which limits the processability of the material.

Zinc stearate was reported to be an ideal polar plasticizer for S-EPDM, which not only significantly reduces the melt viscosity at temperatures above its melting point, but also enhances the mechanical properties as a reinforcing filler at room temperature.\textsuperscript{22,23} The polar plasticizer can interact with the nanodomains, thereby reducing the density of physical crosslink junctions, which causes a reduction of viscosity. Stearic acid and other metal stearates are also able to increase the melt flow of the material, but they do not enhance mechanical properties\textsuperscript{22}. The
enhancement of the mechanical properties caused by zinc stearate is attributed to the formation of a crystalline phase of zinc stearate.\textsuperscript{24} The existence of specific associations between ZnSt and Zn-SEPDM and their influence on properties were verified using a differential scanning calorimetry and small-angle X-Ray scattering.\textsuperscript{25,26}

2.5 Birefringence

Birefringence is caused by the difference of indexes of refractions of a media setting between two orthogonal polarization planes. A media’s index of refraction is defined as the ratio of the speed of light in vacuum divided by the speed of light in the media. For isotropic materials, the refraction indexes remain constant for all directions. However, for deformed polymer films the refraction indexes change. When uniaxial stress was applied, the macromolecules of polymer film will extend and arrange, known as orientation, which leads to anisotropy and different refraction indexes. The material now shows double refraction or, in other word, is birefringent. Retardation will generate when a polarized light passes through the birefringent materials because of the phase difference of the light. Later, the different of refraction index was found as a function of principal stress. This gave rise to the stress-optical (Brewster’s) Law. When stress-optical Law was combined with retardation, the stress then can be calculate, as shown below.

\textbf{Stress-optical Law:}
\[(n_1 - n_2) = C_B(\sigma_1 - \sigma_2)\]

(2.1)

Where \((n_1 - n_2)\) is the difference of refraction index, \(C_B\) is the stress-optical (Brewster’s) constant, \((\sigma_1 - \sigma_2)\) is the difference of principal stress.

Calculation of Stress:

\[\sigma = \delta / d C_B\]

(2.2)

Where \(\sigma\) is the stress, \(d\) is the thickness of the sample film, \(C_B\) is the stress-optical constant, \(\delta\) is the retardation.

Based on discussed above, a new characterization method was established, known as mechano-optical analysis (or photoelasticity). The different of these two words was pointed out by Gurnee et al. \(^{27}\)

Cakmak and Sen designed an advanced real time spectral birefringence stretching machine,\(^{28,29}\) as shown in Figure 2-8, for the mechano-optical measurements. The birefringence was calculated from the retardation which was recorded by an optics test system. This real time spectral birefringence stretching machine can simultaneously measure the birefringence, true stress and true strain of the plane in the stretching direction, during stretching. This machine also equipped with enviromental chamber which allows temperature control. The experiments for mechano-optical studies of Zn-S-EPDM in this project is carried on this instrument.
2.6 Uniaxial true stress-true strain stretching

Engineering stress-strain stretching is the most conventional way to characterize the mechanical properties of the samples in material science. The equations for engineering stress-strain stretching is listed below.

\[
\sigma_e = \frac{P_t}{A_0}
\]

\[
\varepsilon_e = \frac{\Delta l}{l_0} = \frac{(l_t - l_0)}{l_0}
\]

(2.3)

Where \( l_0 \) is the initial length, \( l_t \) is the instantaneous length, \( P_t \) is the instantaneous load, \( A_0 \) is the initial cross-section area.
Although engineering stress-strain stretching is widely used in polymer field, in some case, it failed to reflect the real mechanical response of the samples, especially when tests went beyond the Hookean elastic region. If polymers experience “necking” phenomenon, the stress level in the “necking” area will be higher than other regions which cannot be well characterized by the traditional uniaxial stretching. Compared with engineering stress-strain tensile test, true stress-true strain tensile test was found as a more accurate way to describe the mechanical response of the polymers.

The real time spectral birefringence stretching machine built by our group allows simultaneously birefringence-true stress, birefringence-true strain, and true stress-true strain test on polymer films. With the assumption of incompressibility (the volume of the material stays constant), poisson’s ratio equal to 0.5, the equations of true stress and true strain are derived below.

\[ D_0 W_0 L_0 = D_t W_t L_t \]  
\[ (2.4) \]

\[ \frac{W_t}{W_0} = \frac{D_t}{D_0} \]  
\[ (2.5) \]

True strain \[ = \frac{L_t - L_0}{L_0} = \frac{\Delta L}{L_0} = \left( \frac{W_0}{W_t} \right)^2 - 1 \]

True stress \[ = \frac{F_t}{W_t D_t} = \frac{F_t}{\left( \frac{W_t}{W_0} \right) D_0} \]  
\[ (2.6) \]
Where $D_0$ is the initial thickness, $W_0$ is the initial width, $L_0$ is the initial length, $D_t$ is the instantaneous thickness, $W_t$ is the instantaneous width, $L_t$ is the instantaneous length, $F_t$ is the instantaneous load.
CHAPTER III

EXPERIMENTAL

3.1 Materials

In this section, the detail information of ethylene-propylene-diene monomer terpolymer (EPDM) used in our research was described in detail.

3.1.1 EPDM

The ethylene-propylene-diene monomer terpolymer (EPDM) with the third monomer 5-ethylidene-2-norbornene (ENB) was provided by Exxon Mobil and was used as received. The EPDM Vistalon™ 2502 is the only type that have used in this project. The description of the material was shown in table 1. The structure of ENB was shown in figure 3-1.

<table>
<thead>
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<th>Table 2-1 Product information of EPDM</th>
</tr>
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<tr>
<td><strong>Typical Value</strong></td>
</tr>
<tr>
<td>Mooney Viscosity 1+4, 125°C</td>
</tr>
<tr>
<td>Ethylene content</td>
</tr>
<tr>
<td>ENB content</td>
</tr>
</tbody>
</table>
The molecular weight of EPDM V2502 was measured by GPC and show in figure 3-2 and table 2. These date were kindly provided by Zhiyang Zhao.

Table 2-2 Molecular weight of EPDM

<table>
<thead>
<tr>
<th>Name</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM V2502</td>
<td>92800</td>
<td>170922</td>
<td>1.842</td>
</tr>
</tbody>
</table>
3.2 Synthesis and Sample preparation

Sulfonate group was introduce in EPDM by sulfonation on the unsaturated double of ENB part. The resultant polymeric acid was then neutralized by zinc acetate. Sample films were all made by compression molding.

3.2.1 Synthesis

EPDM was dissolved in hexane at a concentration of 40g/L. After 3 hours of stirring, a transparent and homogeneous solution was got and was then poured into the reactor. At first, acetic anhydride was added (at least 1.6 mol of acetic anhydride per mol of concentrated sulfuric acid). 20 minutes later, concentrated sulfuric acid was dripped in at room temperature to start the sulfonation. A set of mechanical stirrer was employed for efficient agitation (figure 3-3). The sulfonation process lasts for 30 minutes and was then terminated by the addition of methanol. For neutralization, zinc acetate (1.1 mol of zinc acetate per mol of concentrated sulfuric acid) was dissolved in methanol/water solution as neutralization reagent and was then dripped into the sulfonated cement. After 30 minutes of agitation, the zinc acetate sulfonated EPDM was washed in a blender with first cold water and then boiling water to eliminate acid and solvent. The resultant rubber particles were dried under vacuum at 50°C for 24 hours.
3.2.2 Sample Preparation

Sample films of Zn(St)$_2$ plasticized Zn-SEPDM and pure Zn-SEPDM were manufactured.

For Zn(St)$_2$ plasticized sample, solution mixing was carried out to uniformly disperse Zn(St)$_2$ into Zn-SEPDM. A cosolvent, a mixture of toluene and methanol 100/3.5 (w/w), was used to dissolve the Zn-SEPDM and Zn(St)$_2$. The solution was stirred overnight at 42°C. Zn(St)$_2$ was then added to produce 10 wt%, 20 wt% and 30 wt% (Zn(St)$_2$/Zn-SEPDM) mixtures (1 wt% = 1% znst in 100g sample). The well dispersed solution was first dried at room temperature in a fume hood and then by vacuum drying at 50°C.

Sample films of Zn(St)$_2$ plasticized Zn-SEPDM and pure Zn-SEPDM were
compression molded at about 170°C under vacuum. The sample was preheated for 5 min then pressed at 170°C for 15 min and finally cooled under system control as cooling rate 0.5°C/s.

3.3 Characterization

In this section, the details of experiment methods and devices were described. The purposes for the experiments were also discussed.

3.3.1 Fourier transform infrared spectroscopy (FTIR)

The chemical information of the resultant ionomers with different sulfonation levels was detected by Fourier transform infrared spectroscopy (FTIR). All the experiments were carried out on BRUKER ALPHA FT-IR Spectrometer. The transmission model was chosen for the experiments. The scan time was 256. The resolution was 16.

Sample films for the FTIR test was compression molded with thickness around 0.03mm. All sample films were dried under vacuum for 24 hours before the experiment.

3.3.2 Sulfur analysis

The sulfonation degree of the Zn-S-EPDM was measured by sulfur analysis. All experiments were conducted by Dr. Sotzing group in the University of Connecticut. The standard was ASTM D4239 Method B. All samples were dried under vacuum at
40°C for 24 hours before the test.

3.3.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC, TA instrument’s Thermo Scientific Q2000) was employed to study the thermal transitions of Zn-S-EPDM and crystallization and melting of Zn(St)$_2$ in Zn(St)$_2$ plasticized Zn-S-EPDM. All the samples were scanned in the temperature range from -85°C to 190°C which covers the glass transition temperature of the Zn-S-EPDM and the melting point of Zn(St)$_2$. The scanning rate for heating/cooling was 20°C/min. All the experiments were performed under a nitrogen atmosphere. The mass of samples approaches to 5mg.

3.3.4 Thermogravimetric Analysis (TGA)

The influence of sulfonation degree and zinc stearate content on the thermal stability of Zn-S-EPDM was investigated by thermogravimetric analysis (TGA) with TA Instruments’ Thermo Scientific Q50 analyzer. Also, by using TGA, the amount of zinc within the unplasticized Zn-S-EPDM (which was introduced by zinc acetate during neutralization process) and the amount of zinc stearate of plasticized Zn-S-EPDM were measured. The heating rates were chosen as 10°C/min for all samples. All experiments were operated under nitrogen atmosphere at a purge rate 40ml/min. Samples with weight around 5mg were heated from 25°C to 700°C.
3.3.5 Uniaxial tensile tests at Real-time spectral birefringence stretching machine

An advanced real time spectral birefringence stretching machine, named A2 (figure3-4), was used for the mechano-optical measurements. Two cross-heads move in opposite direction at the same rate to maintain the film position stationary in the optical path. The birefringence was calculated from the retardation which was recorded by an optics test system. The samples are placed in an environmental chamber to control the temperature. This real time spectral birefringence stretching machine can simultaneously measure the birefringence, true stress and true strain of the plane in the stretching direction, during stretching.

The temperature, stretching speed, sulfonation degree and concentration of ZnSt2 were chosen as variables for the tensile tests. The temperature was raised and the sample was maintained at that temperature for 3 min before the stretching was begun. The stretching speeds were 2mm/min, 20mm/min and 200mm/min. Three different sulfonation degree (14.1meq, 20.3meq, 28.1meq) samples were prepared. 0wt%, 10 wt%, 20 wt% and 30 wt% ZnSt2 containing Zn-SEPDM films were used. The test temperatures used were room temperature (~23 ºC) and 70ºC.

Dumbbell-shape specimens were cut from the compression molded films using a die with the dimensions shown in figure (3-5).
Figure 3-4 Real-time spectral birefringence stretching machine

Figure 3-5 Dumbbell-shape specimen
3.3.6 Small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering was employed to study the microstructure of the Zn-S-EPDM. The SAXS measurements were made on Rigaku S-MAX 3000 camera system using three pinhole collimation. The generator with energy 40kV emits CuKα radiation (λ=1.54). The sample to detector distance is 1.525m. The q (momentum transfer) range of the system is 0.0067 to 0.19 Å⁻¹. Ag behenate was used for q calibration. Glassy carbon was used for absolute intensity calibration. All experiments were done under vacuum with 5min scattering time for each sample. The background and thickness of the samples were normalized. Sample films with a thickness around 0.7mm were made by compression molding and were dried in vacuum for 24 hours before tests.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Color change

There is a color change observed in sulfonation process, shown in figure 4-1. At beginning, a transparent and homogeneous solution was got when EPDM was dissolved in hexane, however the color of the solution turned to light pink as the concentrated sulfuric acid was added. The light pink darkened with the sulfonation progress and finally turned to dark purple when the reaction time came to 15min. It was also found that the color of the solution not only darkens with the reaction time but also with the sulfonation level of the reaction system. As can be observed, 14.0meq sample appeared purple after 15min of reaction, however, for the sample over 30meq it showed dark blue (1meq= 1mmol H₂SO₄/100g sample).
The purple/blue faded when methanol was dripped in (to terminate the sulfonation) and the color gradually became light yellow/green at last (figure 4-2).

The color change during the sulfonation was thought to arise from the intermediates. As reported by Thaler\textsuperscript{21}, the reaction on the carbon-carbon double bond of ENB has been reported as a multiple-step reaction with intermediates, such as...
sultone, and one/many of which may lead to the unique color change. However, the relationship of the intermediates and the color change hasn’t been reported yet. The exact reason for the color change is still unknown. As the color change associates with the structure change of the carbon-carbon double bond within the ENB part during sulfonation, it can be chosen as an indication for successful sulfonation.

4.2 Fourier transform infrared spectroscopy (FTIR)

To confirm the existence of the sulfonate groups in Zn-S-EPDM, the Fourier transform infrared spectroscopy (FTIR) was used. The FTIR spectra were shown in figure 4-3. As can be seen, the zinc neutralized sulfonated EPDM samples shown four characteristic absorption bands which were absent in pure EPDM samples. These bands are assigned as follow: the 1200cm\(^{-1}\) band is due to the asymmetric vibration of the SO\(_2\) (V\(^a\)O=S=O). The 1050 cm\(^{-1}\) and 1028 cm\(^{-1}\) bands arise from the symmetric vibration of the SO\(_2\)(V\(^s\)O=S=O)\(^{30}\). The origin of the splitting is unknown. The 630cm\(^{-1}\) band is due to stretching mode of S-O\(^{31}\). The 608 cm\(^{-1}\) is attributed to the vibration of C-S bond.

One can also find that the intensity (integration of the peak areas) of the characteristic absorption bands of sulfonate groups increases with sulfonation degree (all the sample films are of same thickness as around 0.03mm). So the Fourier transform infrared spectroscopy (FTIR) is proposed as a qualitative method for analyzing sulfonation level of Zn-S-EPDM.
4.3 Sulfur analysis

The sulfonation degree was determined by sulfur analysis. Three sets of samples were synthesized. The sulfonation degree was calculated by the formula shown below. And the result was shown in table 3. The sulfonation degree was an important
variable for ionomer, because it was a measurement of density of physical crosslinks formed by ionic interaction.

\[ c = \frac{\alpha}{32} \times 1000 \]

c is the sulfonation degree, \( \alpha \) is the weight percent of sulfur.

(1meq=1mmol/100g sample)

Table 3-1 Results of sulfur analysis

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sulfur weight %</th>
<th>Sulfonation degree (meq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 meq</td>
<td>0.45</td>
<td>14.1</td>
</tr>
<tr>
<td>25 meq</td>
<td>0.65</td>
<td>20.3</td>
</tr>
<tr>
<td>35 meq</td>
<td>0.90</td>
<td>28.1</td>
</tr>
</tbody>
</table>

In spite of sulfur weight, another effective way to characterize sulfonation degree is the number of sulfonate groups per polymer chain. Base on the weight average molecular weight provided by GPC, we can calculate the number of sulfonate groups per polymer chain as follow.

The mole number of 100g EPDM is

\[ n_{EPDM} = \frac{m}{M_w} = \frac{100g}{170000} = 0.59\text{mmol} \]

Then the number of sulfonate groups per polymer chain (\( N \)) will be

\[ N = \text{Sulfonation degree}(\frac{\text{meq}}{100g})/n_{EPDM} \]
The result of sulfonate groups per polymer chain for all samples is listed in Table 4.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sulfur weight %</th>
<th>Concentration(meq)</th>
<th>Number of sulfonate group per polymer chain (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 meq</td>
<td>0.45</td>
<td>14.1</td>
<td>24</td>
</tr>
<tr>
<td>25 meq</td>
<td>0.65</td>
<td>20.3</td>
<td>35</td>
</tr>
<tr>
<td>35 meq</td>
<td>0.90</td>
<td>28.1</td>
<td>48</td>
</tr>
</tbody>
</table>

4.4 Thermogravimetric Analysis (TGA)

In this part, the thermal stability of both pure Zn-S-EPDM ionomer and zinc stearate filled Zn-S-EPDM were studied by Thermogravimetric Analysis (TGA).

4.4.1 Introduction

The influence of sulfonation degree and zinc stearate content on the thermal stability and degradation behavior of Zn-S-EPDM were investigated by thermogravimetric analysis (TGA). The 5% weight loss point was assigned as $(T_i)$. The peak decomposition temperature $(T_p)$ was designated as the maximum mass change rate point of the TGA curve and was characterized by the peak of the Derivative Thermogravimetry (DTG) curve.
4.4.2 TGA for Zn-S-EPDM

Thermograms of samples with varied sulfonation levels were shown in figure 4-4. As can be observed, the TGA curves shift towards lower temperature with increase of sulfonation degree, indicating that the introduction of sulfonation group has a negative effect on the thermal stability of the materials. This is because the ionic groups decompose below the temperature at which the EPDM decomposes. The weight loss curves for all samples shows only one stage indicates that the decomposition is a one-step process. For EPDM this one-step decomposition is the degradation of hydrocarbon. For Zn-S-EPDM there is no distinct stage for the decomposition of sulfonate groups which were supposed to have a lower thermal stability. This is because the amount of sulfonate groups within the Zn-S-EPDM is small (<2 wt%) and the decomposition temperature of sulfonate groups was close to and finally covered up by the decomposition temperature region of hydrocarbon part. The 5% weight loss point (T₁) and the peak decomposition temperature (Tₚ) of each sample were shown in table 3-3. As can be seen, the above two temperatures shift to lower region with increase of the sulfonation degree which, again, shows that sulfonation group introduced thermal instability to the materials. The zinc content of the Zn-S-EPDM samples can be quantified by analyzing the remaining mass of the TGA curve. The residue at the end of the thermal treatment is considered to be zinc oxide (although a little amount of zinc carbonate may also exists). The zinc content was calculated in table 3-4.
Figure 4-4 TGA curves for Zn-S-EPDM with varied sulfonation levels

Table 3-3 Onset/peak temperature of Zn-S-EPDM with varied sulfonation levels

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$T_i$ °C</th>
<th>$T_p$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>450</td>
<td>477</td>
</tr>
<tr>
<td>14.1 meq</td>
<td>435</td>
<td>470</td>
</tr>
<tr>
<td>20.3 meq</td>
<td>429</td>
<td>467</td>
</tr>
<tr>
<td>28.1 meq</td>
<td>419</td>
<td>466</td>
</tr>
<tr>
<td>Sample name</td>
<td>EPDM</td>
<td>14.1 meq</td>
</tr>
<tr>
<td>-------------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>Zinc weight %</td>
<td>0</td>
<td>0.34</td>
</tr>
<tr>
<td>Zinc concentration (meq)</td>
<td>0</td>
<td>5.2</td>
</tr>
</tbody>
</table>

4.4.3 TGA for Zinc stearate plasticized Zn-S-EPDM

Thermograms of Zn-S-EPDM with varied zinc stearate contents were shown in figure 4-5. As shown, the TGA curves shift to lower temperature region with the increase of zinc stearate content indicating that zinc stearate introduced thermal instability to the materials. This is because zinc stearate has a lower decomposition temperature than Zn-S-EPDM. For unplasticized Zn-S-EPDM, the weight loss curve shows only one stage. However for zinc stearate filled Zn-S-EPDM, especially the 30% zinc stearate loaded one, a clear stage at around 300 shows up which was corresponding to the degradation of zinc stearate. The zinc stearate amount was calculated from the weight remaining, as shown in table 3-5.
Figure 4-5 TGA curves for Zinc stearate filled Zn-S-EPDM

Table 3-5 Zinc stearate content

<table>
<thead>
<tr>
<th>Sample name</th>
<th>10% Zn(St)₂</th>
<th>20% Zn(St)₂</th>
<th>30% Zn(St)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Totally weight remain %</td>
<td>1.75</td>
<td>2.80</td>
<td>4.60</td>
</tr>
<tr>
<td>Zn(St)₂ Weight</td>
<td>7.89</td>
<td>16.73</td>
<td>29.42</td>
</tr>
</tbody>
</table>

4.5 Differential Scanning Calorimetry (DSC)

The thermal transition behaviors of Zn-S-EPDM and Zn(st)₂ filled Zn-S-EPDM were studied by DSC. The heating and cooling curves for the Zn-S-EPDM with different sulfonation degrees were shown in figure 4-6 and 4-7. Amorphous property was found for Zn-S-EPDM. With current ethylene content, no polyethylene crystal (whose melting point is 115–135 °C) exists in the Zn-S-EPDM for the absence of the corresponding melting/crystallization peaks in DSC curves. The possible disturbances
caused by polyethylene crystals in the morphology and mechano-optical tests can be eliminated.

The thermograms for Zn(st)$_2$ filled Zn-S-EPDM were shown in figure 4-8 and 4-9. The melting/crystallization behaviors of Zn(st)$_2$ was significantly affected by Zn-S-EPDM matrix$^{25}$. For pure Zn(st)$_2$, a sharp endothermic melting peak shows up at about 120°C. All Zn(st)$_2$ filled compositions showed broader endothermic melting peaks than pure Zn(st)$_2$ and the integral areas of these peaks increase with the addition of Zn(st)$_2$. Multiple melting/crystallization peaks were observed for higher Zn(st)$_2$ filled samples as marked by the dash lines indicating that: (1) Zn(st)$_2$ was compatible with Zn-SEPDM. (2) Zn(st)$_2$ crystals have a size distribution. The phenomena discussed above was thought due to the electrostatic interactions between carboxylate groups of Zn(st)$_2$ and the sulfonate.
Figure 4-6 DSC cooling curves for Zn-S-EPDM

Figure 4-7 DSC heating curves for Zn-S-EPDM
Figure 4-8 DSC cooling curves for zinc stearate filled Zn-S-EPDM

Figure 4-9 DSC heating curves for zinc stearate filled Zn-S-EPDM
4.6 Mechano-Optical analysis of Zn-S-EPDM

In this section, the real time true stress-true strain response and real time mechano-optical behavior of Zn-S-EPDM were studied by our Real time spectral birefringence stretching machine.

4.6.1 Mechanical property

The influence of sulfonation degree on the mechanical properties of Zn-S-EPDM was studied by uniaxial real time true stress-true strain tensile test. The experiments were carried out at room temperature with a stretching speed of 20mm/min. The true stress-true strain curves for Zn-S-EPDM with varied sulfonation levels were shown in figure 4-10.

Although the content of zinc-sulfonate groups was relatively low, it shows significant effects on the mechanical properties of the Zn-S-EPDM. When sulfonation level of the sample goes higher, the modulus will remarkably increase. This is because the rise of sulfonation level leads to a higher density of physical crosslinks which will reinforce the material. The modulus of pure EPDM was very low as no limitation of polymer chains’ relative movement by crosslinking exists. Increasing the sulfonation degree, decreases the elongation and tensile strength. This was caused by the disruption of the ionic domains when high level of loads were added, which led to the local defects of the sample films. Stress concentration on these defects gave rise to the crazes, and finally broke the films. The moduli, elongation, tensile strength were
given is table 3-6. In our study, the tensile strength for sulfonated samples decreased with sulfonation degrees which was opposite to Makowski and Lundberg’s report\textsuperscript{19} (they found that tensile strength increase with sulfonation degree). This is because their results were based on the engineering stress at the breaking point of sample films. However, for us, the true stress at the breaking point of sample film was considered as tensile strength. The true stress vs time and engineering stress vs time plots from one exactly same experiment were compared in Figure 4-11. Opposite trends were found and the latter one matched the trend reported by Makowski and Lundberg.

![True Stress vs True Strain](image)

Figure 4-10 True stress-true strain curves for Zn-S-EPDM stretching at room temperature with a stretching speed of 20mm/min
4.6.2 Mechano-optical behaviors

The birefringence-true stress and birefringence-true strain curves for Zn-S-EPDM with different sulfonation degrees were shown in figure 4-12 and 4-13. As shown, the birefringence had a linear relationship with both true stress and true strain. This indicates that there is no crystallization (which usually gives an up-turn in birefringence-true stress curve) happened during stretching. The birefringence-true stress curves, figure 4-13, for different samples didn’t show significant change as sulfonation level increased, and were close to each other. However, the birefringence-true strain curves’ become steeper in samples with higher sulfonation degrees. Increasing the sulfonation degree results in larger strain-optical constant. As shown, in order to get the same level of birefringence much lower strain is needed. From the birefringence-true stress and birefringence-true strain curves, we can infer...
that the ionic aggregates make orientation of chains easier during stretching. During
the deformation, polymer chains attached to the surface of ionic domains are forcibly
stretch out and orientate to a higher level. The chains uncombined with ionic domains
will also orientate, however to much lower levels than the combined chains whose
orientation induced by a pull action of the ionic domains. Multiple mechanical
parameters vs sulfonation degree plot and stress/strain optical constant vs sulfonation
degree plot were shown in figure 4-14 and 4-15.

Figure 4-12 Birefringence vs true strain curves for Zn-S-EPDM stretching at room
temperature with a stretching speed of 20mm/min
Figure 4-13 Birefringence vs true stress curves for Zn-S-EPDM stretching at room temperature with a stretching speed of 20mm/min

Table 3-6 Multiple Values for Zn-S-EPDM with varied sulfonation degrees

<table>
<thead>
<tr>
<th>Sulfonation Degree</th>
<th>Modulus (MPa)</th>
<th>Elongation (100%)</th>
<th>Tensile Strength (MPa)</th>
<th>Stress-optical constant</th>
<th>Strain-optical constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.57</td>
<td>2.61</td>
<td>0.55</td>
<td>0.0019</td>
<td>0.0013</td>
</tr>
<tr>
<td>14.1</td>
<td>2.05</td>
<td>3.52</td>
<td>10.34</td>
<td>0.0020</td>
<td>0.0039</td>
</tr>
<tr>
<td>20.3</td>
<td>2.50</td>
<td>2.03</td>
<td>6.11</td>
<td>0.0021</td>
<td>0.0050</td>
</tr>
<tr>
<td>28.1</td>
<td>4.35</td>
<td>1.25</td>
<td>5.41</td>
<td>0.0020</td>
<td>0.0069</td>
</tr>
</tbody>
</table>
4.7 Mechano-optical analysis of Zn(st)$_2$ filled Zn-S-EPDM

In this section, the real time true stress-true strain response and real time
mechano-optical behavior of zinc stearate plasticized Zn-S-EPDM were studied by our Real time spectral birefringence stretching machine.

4.7.1 Effect of Zn(st)$_2$ concentration

True stress-true strain curves at room temperature of samples with varying concentration of Zn(st)$_2$ and a stretching rate of 2 mm/min are shown (Figure 4-16). The true stress shows a more rapid increase with increasing concentration of ZnSt. The modulus increased with Zn(st)$_2$ content. This modulus increase is due to the supramolecular crosslinking caused by Zn(st)$_2$. The tensile strength also increased with Zn(st)$_2$ concentration, probably due to changes in the morphology of the film as the sample was deformed, which may provides a mechanism for energy dissipation. The significant difference of elongations between Zn(st)$_2$ filled Zn-SEPDM and neat Zn-SEPDM shows another mechanism of the improvement of the mechanical properties, that is the addition of Zn(st)$_2$ allows more perfect production of the films which reduces the possibility of breaking caused by stress concentration in the defects$^{22}$. 

A more complex phenomenon was seen at 70°C (Figure 4-17). Increasing the concentration of ZnSt first increased and then decreased the tensile strength and elongation to break. The modulus on the other hand increased monotonically with the ZnSt content. This behavior may be due to the complex crystallization behavior and
melting of the smallest crystals at 70ºC or plasticization of the ionomers from the melted crystals.

Figure 4-16 2mm/min, room temperature true stress-true strain plot for zinc stearate filled Zn-S-EPDM

Figure 4-17 True stress-true strain curve for 0%, 10%, 20%, 30% Zn(st)2 samples of stretch speed 2mm/min at 70ºC
The horizontal line in figure 4-18 shows that in order to achieve the same level of birefringence in each sample, more stress is required as the Zn(st)$_2$ concentration increases. This indicates that the addition of Zn(st)$_2$ makes the orientation of molecular chains harder. The reason is considered as the Zn(st)$_2$ weakens the interaction of ionic groups so the crosslink density effectively decreases. This associations maybe caused by the connection of molecular chains to the surface of the
Zn(st)$_2$ small crystals which works as physical crosslinks. And the interaction of Zn(st)$_2$ and metal sulfonate groups of Zn-SEPDM can also attribute to this reinforcement mechanism. However, further works needed to be done to confirm the origin and microstructure of the special associations between Zn(st)$_2$ and Zn-SEPDM by combining other characterization methods.

Figure 4-19 The birefringence-true strain curve for samples with different ZnSt concentration stretched at 2mm/min under room temperature
The strain-optical behavior of Zn(st)$_2$-containing Zn-SEPDM as a function of Zn(st)$_2$ content at room temperature is shown in figure 4-19. For a given level of birefringence, the true strain needed increases with addition of Zn(st)$_2$. That is to say, the strain-optical constant which is the slope of the birefringence-true strain curve increases with Zn(st)$_2$ content as shown in table 3-7. This may due to the change of the ionic domains inside Zn-SEPDM with addition of Zn(st)$_2$ which increases the motion of the chains and leads to more relaxation. A significant difference is shown in figure 4-20 for Zn-SEPDM with varying Zn(st)$_2$ content stretching at 70ºC. This indicates the increasing temperature increases the motion of polymer chains and the interaction of Zn(st)$_2$ with metal groups of Zn-SEPDM.

![Figure 4-20 The birefringence-true strain curve for samples with different Zn(st)2 concentration stretched at 2mm/min, 70ºC](image)
Multiple properties of the material as a function of Zn(st)$_2$ content has been drawn in figure 4-20. As can be seen, the modulus, elongation and tensile strength increase with addition of Zn(st)$_2$. However, the elongation and tensile strength reach a maximum at around 23% Zn(st)$_2$ content. On the other hand, the stress-optical constant and strain-optical constant decrease with Zn(st)$_2$ content. The values were shown in table 9.

<table>
<thead>
<tr>
<th>ZnSt content (wt%)</th>
<th>Modulus (Mpa)</th>
<th>Elongation (100%)</th>
<th>Tensile Strength(MPa)</th>
<th>Stress-optical constant</th>
<th>Strain-optical constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.60</td>
<td>0.92</td>
<td>2.43</td>
<td>0.0020</td>
<td>0.0054</td>
</tr>
<tr>
<td>10%</td>
<td>3.21</td>
<td>2.63</td>
<td>10.82</td>
<td>0.0016</td>
<td>0.0052</td>
</tr>
<tr>
<td>20%</td>
<td>6.24</td>
<td>4.22</td>
<td>29.01</td>
<td>0.0009</td>
<td>0.0048</td>
</tr>
<tr>
<td>30%</td>
<td>9.23</td>
<td>4.04</td>
<td>26.82</td>
<td>0.0007</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Figure 4-21 Multiple values for zinc stearate filled Zn-S-EPDM at room temperature
4.7.2 Nonlinearity of birefringence-true stress curve of ZnSt-filled Zn-SEPDM

Figure 4-22 Birefringence-true stress curve for 20% Zn(st)$_2$-containing Zn-SEPDM, stretched at 2mm/min at room temperature

Figure 4-22 shows that the birefringence-true stress relationship for the Zn(st)$_2$-filled sample is non-linear and can be divided into three regions. This indicates that the small Zn(st)$_2$ crystals and/or their specific association with the metal sulfonate groups of Zn-SEPDM or the amorphous chains influence the anisotropy of the material and are responsible for the non-linearity. Within the first region shown in Figure 4-22, the birefringence-true stress behavior is linear, which agrees with the stress-optical law. However, in region two, there is a positive deviation from linearity. This positive deviation may due to the orientation of network of Zn(st)$_2$ small crystals
connecting the metal groups of Zn-SEPDM and/or amorphous polymer chains. Coupling of the shear stresses between the Zn(st)$_2$ crystals and the ionomer chains may also contribute additional birefringence. Another possible mechanism is that the rotation of the bilayers of Zn(st)$_2$ crystals by the stretching changes the optical axes of the crystals and produces increased birefringence. In region 3, the chains may reach their maximum stretching level, and although the modulus increases due to stretching of bonds, no further orientation occurs. Increasing concentration of Zn(st)$_2$ t will make the transition of region 1 to region 2 more apparent as shown in figure 4-22. This, on the other hand, confirms the existent of the special associations between Zn(st)$_2$ and Zn-SEPDM.

4.7.3 Effect of Temperature

For Zn-SEPDM with same Zn(st)$_2$ concentration, the increasing temperature reduces the modulus, and tensile strength of the compound, as shown in figure 4-23. When temperature went to 80 degree the elongation increased, this is due to the weakening of ionic interaction which led to freer intermolecular slip. The mechano-optical behaviors of the ZnSt-filled Zn-SEPDM as influence by the temperature are shown in figure 4-24 and 4-25. According to figure 4-24, in order to get same level of birefringence much higher true strain is needed at higher temperatures which on the other hand leads to increase of true stress. The reason for these phenomenon may be that the increasing temperature weakens the dipole
interactions in the ionic clusters of Zn-SEPDM and increases the plasticizing effect of Zn(st)$_2$ by melting the crystals which weaken the interchain associations caused by the physical crosslinks. This explains the negative development of the mechanical properties of the material with increasing temperature. The molecular chains have more freedom to move as decrease of the interchain associations, and get more energy for motion as well. So the polymer chains are more likely to relax and disorientate which leads to the addition of true stress and true strain needed for orientation.

Figure 4-23 The true stress-true strain curve for samples with 20% Zn(st)$_2$ stretched at 2mm/min under different temperature
Figure 4-24 The birefringence-true strain curve for samples with 20% Zn(st)$_2$ stretched at 2mm/min under different temperature
Figure 4-25 The birefringence-true stress curve for samples with 20% Zn(st)$_2$ stretched at 2mm/min under different temperature

Stress-optical behavior for Zn-SEPDM with different concentration of Zn(st)$_2$ at 70°C is shown in figure 4-26. At higher temperatures more stress are needed to reach a given birefringence level with addition of ZnSt. The trend is the same with room temperature. However, at higher temperatures, the difference of the slopes of the birefringence-true stress for varying Zn(st)$_2$ amount samples is smaller when compared to the room tempetature. This indicates that the increasing temperature weakens the special association of the Zn(st)$_2$ and Zn-SEPDM.

Increasing temperature also makes the non-linear behavior of the birefringence-true stress curve less apparent. The transition between region 1 and region 2 is less obvious when compared to the room temperature’s. This on the other hand proves that it is the association of Zn(st)$_2$ and Zn-SEPDM causes the addition orientation at the transition point.
4.7.4 Effect of stretching speed

Figure 4-26 The birefringence-true stress curve for samples stretched at 2mm/min under 70°C

Figure 4-27 The true stress-true stress curve for samples with 20% Zn(St)$_2$ stretched at 2/20/200mm/min, under room temperature
Figure 4-28 The birefringence-true stress curve for samples with 20% Zn(st)2 stretched at 2/20/200mm/min under room temperature.

Figure 4-29 The birefringence-true strain curve for samples with 20% Zn(st)2 stretched at 2/20/200mm/min under room temperature.
As can be seen from figure 4-27 and figure 4-28, there is a stretch-hardening behavior shows up. That is, the material becomes hard to deform and needed more true stress to get equal birefringence level when the stretching speed increase. It is supposed that during high speed stretching there is no sufficient time for polymer chains to relax. The lack of method for energy dissipation at increasing stretching speed leads to higher modulus. The possibility for polymer chain to disorientate becomes smaller as the decreasing time for relaxation. So for given true strain the birefringence increases with addition of Zn(st)$_2$(figure 4-29).

4.8 Small-angle X-ray scattering (SAXS).

The existent of ionic domains in Zn-S-EPDM was confirmed by the Small-angle X-ray scattering (SAXS). Figure 4-30 was the 2D SAXS patterns for Zn-S-EPDM with varied sulfonation degrees. The SAXS pattern for pure EPDM was isotropic and showed no characteristic peak. One single ring appeared in 20meq and 30meq Zn-S-EPDM samples and was more distinct in latter one. This single ring was generally accepted as the evidence of ionic domains. The 1D SAXS intensity profiles for the samples were shown in figure 4-31. The ionic peak corresponding to a Bragg spacing of 63 Å and ranged from 40 Å to 120 Å. The maximum of the ionic peak increased with increasing sulfonation degree, however, changed little in the position. It can be inferred that, with sulfonation degree goes higher, the interference between
the ionic aggregates increases as the sizes of the domains raise, however the distance between the domains did not change a lot. To confirm the hypothesis, more work is needed in the future.
Figure 4-29 2D SAXS patterns for Zn-S-EPDM with varied sulfonation degrees

Figure 4-30 1D SAXS intensity profiles
Zn-S-EPDM with three different sulfonation levels were synthesized. The existent and exact amount of the sulfonate groups of the resultants were characterized by Fourier transform infrared spectroscopy (FTIR) and sulfur analysis respectively.

For unplasticized Zn-S-EPDM, the real-time true stress-true strain birefringence measurement showed that: (1) Increasing the sulfonation level increases the modulus of the Zn-S-EPDM, but lowers the elongation and tensile strength. (2) The ionic aggregates have a positive effect on the orientation of polymer chains. (3) The existence of the ionic domains were confirmed by SAXS as a single ring in 2D SAXS pattern corresponding to a Bragg spacing of around 40 Å.

For plasticized Zn-S-EPDM, the real-time true stress-true strain birefringence measurement showed that: (1) The Zn(st)$_2$ reinforces the material as a solid filler. The modulus, elongation, and tensile strengths increase with addition of Zn(st)$_2$, however, the elongation and tensile strength reach a maximum as the content grows to about 23%. (2) Increasing the amount of Zn(st)$_2$ makes the molecular chains of Zn-SEPDM harder to orientate. (3) There is a 3-region non-linear stress-optical
behavior of ZnSt-filledZn-SEPDM. There is a positive deviation from the first linear region which shows an additional orientation at the same value of true stress. A negative region at last shows that the molecular chains reach their maximum stretching level. (4) As the temperature rises, much higher true strain is needed to reach the given birefringence which, on the other hand, leads to the increase of true stress needed. (5) A stretching-hardening phenomenon is found when one raises the rate of stretching.
REFERENCES


8. Li, C.; Register, R. A.; Cooper, S.L., Direct observation of ionic aggregates in sulphonated polystyrene ionomers 1989, Polymer, 30, 1227.


