REINFORCEMENT OF ELASTOMERS BY REACTIVE IONIC

SURFACTANT FILLER

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Thesis

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ABSTRACT

Elastomers without reinforcement are too weak and soft to meet the requirements of practical applications. To achieve the necessary strength and stiffness, particulate fillers are used to reinforce thermoset rubber. For thermoplastic elastomers, microphase-separated hard domains play the role of stiffening and strengthening the elastomer. Our group recently reported reactive supramolecular fillers based on β alanine oligomers. This thesis focuses on the use of reactive fillers containing a mercaptan tail and an ionic head as supramolecular filler for cured rubbers. The reactive functional groups of the fillers can form covalent bond with elastomers' backbone. After the reaction, the elastomer becomes an ionomer, which is defined as polymers with bonded ionic groups that are used under conditions where the salt species are in condense state. Since the polar ionic groups are incompatible with the low nonpolar polymer, microscopic phase separation will occur. The alkyl chain is attached to the ionic species to improve the compatibility. Ionic nanodomains formed by the polar ionic moieties are anticipated. The ion interaction within ionic clusters can serve as physical crosslinks. The reversibility of the supramolecular interaction offers a mechanism for energy dissipation that should increase mechanical properties of rubber. The extent of reinforcement and the supramolecular structure of ioncontaining filler are studied.

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CHAPTER I

INTRODUCTION

1.1 Elastomers

Elastomers form a special class of materials having important properties, such as elasticity, flexibility, toughness and impermeability. Elastomers that can be crosslinked by vulcanizing agents are referred as rubbers. ¹Rubber has been emerged in Europe for more than 200 years. Ever since Charles Goodyear discover the vulcanization of rubber in 1839, it has been an important material that penetrated all aspects of modern life. The most important utility of rubber is in the automobile industry. In addition, rubber can be applied in engineering and medical application, such as seals, insulators, gaskets and medical implants.

From a survey in 2017², the consumption of rubber worldwide increases from 14.8 million tons in 1990 to 27.5 million tons in 2016. In 1990, nature rubber accounts for 35% in the total consumption while synthetic rubber occupies 65%. In comparison, the proportion is 46%: 54% in 2016. Although many synthetic rubbers emerge, natural rubber is still an indispensable material in human activities.

One reason is the special properties of natural rubber, such as crystallization upon stretching and high green strength. The unique behavior of strain-induced crystallization gives high tensile strength and tear resistance to natural rubber³. Compared with synthetic rubber, natural rubber contains natural proteins and phospholipids contributing to the high green strength that is vital for processing⁴. The other reason is the cost. Natural rubber is produced from the latex of Hevea brasiliensis and its price is determined by annual production, labor cost, transportation and so on.

The basic requirement of rubbery material is consisting of long, flexible polymer chains. These long chains can entangle with each other by weak intermolecular forces. They are unable to retract essentially to original shape after large deformation without vulcanization.⁵ To achieve permanent structures that can form a coherent solid and prevent the liquidlike flow of molecule chain, the elastomers are needed to be crosslinked.⁶ Due to the great length of chains, the quantity of such crosslink points is not sufficient enough to significantly impede the statistical fluctuations or movement of individual chains.⁷ By incorporating a small number of intermolecular crosslinks, three-dimensional network such as sulfur cured rubber network is formed as shown in FIGURE 1.1. Various curing agents are used to vulcanize raw elastomers. Initially, vulcanization has been introduced since 1906.⁹ Although sulfur vulcanization of rubber has been used in rubber industry for hundreds of years, the mechanism is still not figured out. There are two generally agreed mechanisms: free radical mechanism



FIGURE 1.1 Sketch of a crosslinked network¹⁰

and anionic mechanism. ¹¹ In addition, other curing agents such as organic peroxides,¹² resin and amines are also used.

1.2 Reinforcement of Elastomers

The properties of rubber products are influenced not only by the characteristics of elastomers, but also by the various additives and ingredients compounded with the elastomer. Elastomers can be reinforced to enhance properties, such as stiffness and toughness¹³, by the addition of reinforcement fillers. The low strength, low resilience, low tear strength and poor sticky without filler reinforcement are the drawbacks of elastomers, so it is usually reinforced to meet the needs of practical applications.¹⁴

Particulate fillers such as carbon black and silica are most conventional and common fillers.¹⁵ A great number of carbon black posttreatment study has been taken to increase the reinforcing effect. Such as surface oxidation by oxygen in elevated temperature, peroxide and ozone¹⁶ and functionalization by surface grafting of polymers.¹⁷ Their primary size is in nanometer range, but they exist in the form aggregates in a size of micrometer range as shown in FIGURE 1.2. The reinforcing effect depends mainly on the particle size, surface activity and structure. Due to the small size and large surface area, varies of nanofillers have been studied in recent years, such as layered silicates, talc, silica, nanobiofillers and carbon nanotubes.¹⁸



FIGURE 1.2 Schematic of carbon black aggregates¹⁹

A basic requirement to obtain optimum reinforcement and low hysteresis is sufficiently dispersed in the rubber matrix, which impart fine interaction and adhesion between filler and rubber. In addition, when the fillers are less than 100nm, it is efficient for the filler to reinforce rubbers. The reason is that the rubber matrix is confined between closely spaced particles and the large translational motion of chains to crack is restricted.²⁰ The smaller fillers have the larger surface area, resulting in an improved filler-matrix interaction.

The reinforcement mechanisms of filler are complicated and are still not well studied due to the complications of a heterogeneous system combining of multicomponent and the network structure of the crosslinked rubber. Furthermore, interactions between filler-filler and filler-rubber play an important role in the reinforcement and is a key feature that influence the mechanical properties of rubber compound.²¹ It is no doubt that the surface interaction between fillers and rubber involves a range of bond energies from relatively weak to comparable strong as covalent bond. In the physical sense, the difference in surface energy influence the adsorption degree. In the chemical sense, the affinity of rubber to filler can be improved by the organic functional groups on the surface of filler and the reactive functional group may provide chemical bonding between filler and rubber²². Therefore, the effectiveness of enhancement of the mechanical properties, such as the strength, commonly cannot be explained by one simple theory. In the present study, the reinforcement mechanism of the rubber still attracts a lot of interest with an emergence of promising fillers and various filler-rubber combinations.

6

1.3 Supramolecular

In 1987, Lehn defined the supramolecular chemistry as 'chemistry beyond the molecule' having the organized entities of higher complexity resulting from the association of two or more chemical species connected by intermolecular forces.²³ These intermolecular forces include hydrogen bonding, transition metal complexation, hydrophobic interaction, ionic attraction, or π - π stacking²⁴. Noncovalent interactions enormously vary in strength. Therefore, by tuning the interaction and the supramolecular network, the characteristics of supramolecular materials can be tailored. Supramolecular polymer networks combine the characteristics of chemical and physical networks are designed to specific needs. Starting from the original host-guest system, work in modern supramolecular chemistry expands to molecular machines, molecular recognition, self-assembly, self-organization and nanochemistry. ²⁵

1.3.1 Supramolecular fillers

Supramolecular fillers are relatively low molecular weight species that can assemble into hierarchical structures in the elastomer matrix by reversible supramolecular interaction. ²⁶ For example, in thermoplastic elastomers, urea groups usually serve as hard blocks because they can associate trough hydrogen bonding. In Bisurea-based TPEs, bisureas microphase-segregate into hard domains consisted of linearly aggregated bisureas. According to Eva Wisse's research, they add supramolecular fillers that can incorporate into that hard domains via bifurcated hydrogen bond (FIGURE 1.3). As a result, the Young's modulus was increased without the sacrifice in tensile strength or strain.²⁷



FIGURE 1.3 Proposed modular approach: the supramolecular filler (red) is incorporated into the PCLU4U hard domains (blue) via bifurcated hydrogen bonds. Reprinted with permission (from reference²⁷. Copyright (2018) American Chemical Society).

1.3.2 β-sheet crystals

As an example of supramolecular interaction, β -sheet is a common protein secondary structure. In the β -sheet, two or more peptide chains, or different sections of the same peptide chain form parallel or anti-parallel arrangement. The β -strands can form an extensive hydrogen bond network with adjacent strands and, in which the N-H groups in the backbone of one strand establish hydrogen bonds with the C=O groups in the backbone of the adjacent strands (FIGURE 1.4).

In the crystal of Nylon-3, the adjacent Nylon-3 chains form anti-parallel arrangement, in which the hydrogen bond between N-H groups and C=O groups are perpendicular to the chains. Parallel β -sheets stack to form a monoclinic unit cell (FIGURE 1.5)^{28, 29}. (d (010) = 0.478 nm, d (200) = 0.404 nm, and d (002) = 0.378 nm)

 β -sheet crystals in silk is an example that can manifest its ability to reinforce as a supramolecular filler. Sinan Keten has studied the β -sheet reinforcement in silk.³⁰ They found that the confinement in nanoscale of β -sheet crystals in silks is the key to achieve great stiffness, resilience and fracture toughness. Furthermore, the smaller size nanocrystals are stronger and the strength , modulus can be significantly increased if the dimensions of nanocrystal below 3 nm.

The reason is that when applied the constant lateral force on both large and small nanocrystals. The large one prefers to bend, which results in the formation of cracklike flaws under the tension on hydrogen bonds. In contrast, in the small one,



FIGURE 1.4 Parallel and anti-parallel chains in β -sheets.



FIGURE 1.5 Stacked β -sheet^{28, 29}

the hydrogen bonds break by stick-slip motion leading the homogeneous shear failure (FIGURE 1.6). Besides, the hydrogen bond is dramatically weaker in on-uniform tension than in uniform shear³¹, which leads to the significant difference of capacity to withstand deformation.

The other advantage of small β -sheet crystals is that the hydrogen bonds can be broken and reformed during the stick-slip motion until the complete fracture which can also protect the hydrogen bonds from water in the surround. Compared to most materials that rely on strong covalent bonds, the use of hydrogen bonds can selfassemble into crystals and the smaller crystals provide feature a self-healing ability attributed to hydrogen bond reform.



FIGURE 1.6 The constant lateral force applied on small and large β -sheet nanocrystal. **a**. small β -sheet nanocrystal(L=2.83nm) stick-slip motion. **b**. large β -sheet nanocrystal(L=6.56nm) bending. Reprinted with permission (from reference³⁰. Copyright (2018) Springer Nature).

1.3.3 Functionalized β-Alanine

Our group has studied the functionalized β -Alanine^{32, 33} which has a long alkyl chain that can increase the compatibility of filler and rubber (FIGURE 1.7a). It can form β -sheet crystalline domain and evenly dispersed in the rubber matrix. Tensile strength, elongation, modulus, and toughness were increased obviously. However, the improvement of mechanical properties is not enough for the practical need and there was no bound rubber formed, which showed the poor interaction between the rubber and filler. Therefore, Xin Tan added a thiol function group at the end of the long alkyl chain (FIGURE 1.7b), which can react with the double bond of unsaturated rubber and form covalent bond with the backbone of rubber.

The formed supramolecular networks provide a mechanism of energy dissipation by breaking and reforming noncovalent binding interactions that should significantly affect the mechanical properties of rubber. As can be seen from the TEM result, the supramolecular fillers form fibrous nanocrystal in the rubber matrix (FIGURE 1.8). The fibrous crystalline filler domains evenly distributed throughout the continuous SBR phase.

Thus, physically crosslink of rubber by the β -sheet crystals can be formed. As a result, these reactive fillers can remarkably improve the tensile properties of rubber as reinforcement fillers as shown in FIGURE 1.9. The superior mechanical properties are undoubtedly attributable to the improved filler dispersion and filler-rubber interaction as the result of chemical grafting SA1 to SBR via the thiol-ene reaction.³⁴⁻³⁶



FIGURE 1.7 Functionalized β -Alanine³²



FIGURE 1.8 TEM images of SBR/SA1 and SBR/PA1' composites. (a) SBR/15SA1-m; (b) SBR/30SA1-s; (c) SBR/30SA1-s; (d) SBR/30PA1'-s.³²



FIGURE 1.9 Stress-strain curve³²

1.4 Ionomer

Polymers form an indispensable class of materials having the largest production volume that exceed conventional materials such as metal and ceramics. ³⁷ The increase of the consumption and utilization of polymers is because of the constant study and innovation in the synthesis and well-defined molecular structure of polymers connecting to the material properties. An excellent example of this is the Surlyn ionomers produced by DuPont³⁸ which use non-covalent bond (ionic, hydrogen, and van der Waals) in copolymers of ethylene and methacrylic acid that combined with metal, the structure is shown in 17FIGURE 1.10. The supramolecular interaction intermolecularly remarkably affects the structure and function of the polymer system. The utilization of ionic bonding in synthetic polymers has been intensively investigated attracted widespread interest in recent years. ³⁹⁻⁴⁶

Ionomer is defined as a polymer with bonded ionic species that are used under conditions where the ion pairs are in a condensed state.⁴⁷ Such definition contains all traditional low ion content polymers. For examples, sulfonated polyisobutylene,⁴⁸⁻⁵⁰ butyl rubber based K-ionomer,⁵¹lightly sulfonated polystyrene⁴⁰ and sulfonated EPDM.^{41, 52} This definition also consists of relatively high ion content polymers that used in dry state where ion pairs are condensed. Polyelectrolyte solutions and water-swollen ionic membrane applications in which the ion pairs are solvated by solution are excluded from the definition of ionomers.



FIGURE 1.10 Chemical structure of Surlyn ionomers produced by DuPont, where x, y, and z denote mole fractions of ethylene, methacrylic acid and a metal–ion methacrylate, respectively. Note that (y þ z) ¼ (1–x). For, currently commercial products, M ¼ Li, Na, (Zn)1/2 and (Mg)1/2.⁴⁷



FIGURE 1.11 The most important noncovalent interactions along with their typical range of binding strength, in comparison with covalent bonds. Reprinted with permission (from reference⁵³. Copyright (2018) Springer Nature).

Ionomers are in inherently supramolecular considering their physical interaction such as ion-ion interactions, ion-diploe interactions and dipole-dipole interactions. Ion interactions are comparable with covalent bond in strength⁵⁴ as shown in FIGURE 1.11. As a result, polymers with ion groups can be tuned to exhibit different mechanical properties affected by the ion interactions form between various anions and cations.⁵³

1.4.1 Morphological structure

The similarity in morphology of different ionomers is based on various polymers overweight differences and whether the ionic motifs on the polymer backbones distribute evenly or randomly.³⁷ The invariance is because of the strong Coulombic attraction between ion pairs, which serves as the driving force for phase separation. It is generally agreed upon that ionic groups aggregate in ion-rich domains. Many techniques are used to study the size, shape and arrangement of the aggregates, such as infrared spectroscopy⁵⁵, small angle X-ray scattering,⁵⁶ extended X-ray absorption fine structure,⁵⁷ transmission electron microscopy⁵⁸ and so on.

The effect of the ion content of zinc-neutralized sulfonated polystyrene on the SAXS spectra was investigated.⁵⁹ Based on the original core-shell model⁶⁰ and depleted-zone core shell model^{61, 62}, Yarusso proposed a liquid-like hard sphere model that could qualitatively describe all features of an ionomer SAXS pattern and fit the SAXS data well. This interparticle model assumes that about half of the ionic pairs are

aggregated in liquid-like arranged domains with the remainder separate in the matrix. The radius of the closest approach doesn't depend on the ionic aggregate radius and is larger than the aggregate size. Physically, this corresponds to a layer of bulk polymer attached to the aggregate, offering steric restrictions on the approach of any two of aggregates. The electron density distribution of this model is shown in FIGURE 1.12. SAXS data and analyses show that the size of nanodomains are 2 nm in diameter and the shell of the polymer backbone divides two aggregates to more than 3.4 nm. The covalently bonded ion-pairs on the polymer chain make the aggregates behave multifunctionally and the properties and dynamics of materials are substantially affected by these physical crosslinks. Yarusso's model proposed that each ionic domain contains about 20 ion pairs. Thus, the functionality of the ''crosslink junction'' can be of the order of about 20.

Kirkmeyer et al.⁶³ used scanning transmission electron microscopy (STEM) to show a clear picture of a spherical nanostructure of ionomers that agree with SAXS data (FIGURE 1.13a).). But they also found some nanodomain that have an irregular shape, such as vesicles (FIGURE 1.13b). There are still many unknown problems with the microstructure of ionomers.



FIGURE 1.12 Schematic of Yarusso liquid-like hard sphere model⁵⁹



FIGURE 1.13 STEM micrographs of the nanodomains in a zinc salt of sulfonated polystyrene. (a) Spherical nanodomains observed in sample with 75% neutralization;
(a) Vesicle-shaped nanodomains observed in fully neutralized sample.⁶³

1.4.2 Mechanical properties

The physical crosslinks in ionomer are thermally reversible in nature. The supramolecular interaction of ion pairs and the supramolecular structure resulting from the ion interaction can be broken by stress and can reform when the stress is removed. The reversibility of the physical network structure of ionomers offers a mechanism for energy dissipation that can enhance the mechanical properties of materials.

Many investigations have been conducted to elucidate the relationship of structure and properties concerning on the melt viscosity⁴⁵ and the high temperature modulus^{42, 64}. Bagrodia et al⁴⁵ synthesized a triarm sulfonated polyisobutylene and studied the effect of molecular weight and excess neutralizing agent in the viscosity of ionomers. They measured the dynamic melt viscosity (FIGURE 1.14) and drew the conclusion that the zero-shear viscosity increases with an increase in the molecular weight and the amount of neutralizing agents.

Bellinger et al. ⁶⁵ studied the tensile fracture properties of sulfonated polystyrene. They found the fracture mechanism of the NaSPS changed with different ion content, which attributed to the different nanostructure of ionic domains. The tensile strength and toughness of various ion content ionomer are shown in FIGURE 1.15.

It is evident that the introduction of ionic groups in polymers can significantly change the mechanical properties compared with unmodified polymers. In addition, the size, structure of ionic aggregates is the key feature of these effects.



FIGURE 1.14 Dynamic melt viscosity as a function of frequency for unsulfonated precursor T-8.3-HC and ionomers materials at 180°C. The first symbol T indicates a triarm ionomer. The second symbol indicates the Mn. The third symbol, K, indicates the cation the ionomer contains. The fourth symbol, indicates the extent of excess neutralization past the equivalence point. Reprinted with permission (from reference⁴⁵.

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FIGURE 1.15 (a) Effect of ion content on the tensile strength of ionomers; (b) Effect of ion content on the toughness of ionomer: closed circles represent individual data points, and open circles represent average values.⁶⁵

CHAPTER II

REACTIVE IONIC SURFACTANT FILLER S2

2.1 Experiment

2.1.1 Materials

6-Mercapto-1-hexanol was purchased from TCI. Chlorosulfonic acid was purchased from Acros Organics. Anhydrous methanol, anhydrous diethyl ether and other solvents were purchased from Sigma-Aldrich. Sodium hydroxide is from BDH Analytical Chemicals. Curing agent DCP was provided by Akrochem. Synthetic polyisoprene latex was provided by Kraton Polymer as a gift.

2.1.2 Synthesis of sulfate S2

Into a 200 ml Schlenk flask equipped with a magnetic stirring bar were added 6mercapto-1-hexanol (6.71 g, 0.05 mol) and anhydrous diethyl ether (30ml) under a stream of nitrogen. Then, added chlorosulfonic acid (11.65 g, 0.1 mol) dropwise at 0° C, any heat generated being allowed to dissipate before the addition of the next drop. The mixture was stirred overnight at room temperature. The solution was concentrated to a syrup in vacuum. Methanolic NaOH (1 mol/L) was then added to neutralize the acid to pH 8-9. Precipitated salts were separated by filtration. The resulting solid was repeatedly triturated with hot methanol and combined methanol fractions with the filtrate. The solution was concentrated till cloudy by rotary evaporation at 60°C. Removed the small amount of salts by filtration of the hot methanolic mixture. Cooled the solution overnight at -50°C to give white powder S_2 .



Scheme 2.1: Synthetic route S2

2.1.3 Compounding of IR-S2-s composites by solution mixing and vulcanization

Synthetic polyisoprene was compounded with different filler loading. The formulations of rubber composites are shown in Table 2.1. The solution mixed compounds are designated as IR-S2 representing IR filled with X phr (part per hundred rubber) of filler. For example, IR-5S2 refers to IR filled with 5 phr of S2. Polyisoprene latex (8.14 g) containing polyisoprene rubber (5 g) was mixed with DCP (0.1 g/ml in hexane) and S2 (0.1 g/ml in deionized water). The mixed solution was stirred at room temperature overnight and most solvent evaporate. Then dried the compound in vacuum for two days. Milled the rubber by two-roll mill at 50°C. The finished compounds were compressed and cured for 160 °C to obtain rubber sheets of 1 mm thickness, the curing times are measured by moving-die rheometer.

Composites	IR	S2	DCP
IR-gum-s	100	0	1
IR-2.5S2-s	100	2.5	1
IR-5S2-s	100	5	1
IR-10S2-s	100	10	1
IR-15S2-s	100	15	1
IR-gum-m	100	0	1
IR-2.5S2-m	100	2.5	1
IR-10S2-m	100	10	1

TABLE 2.1 Formulations of IR-S2 composites

* The unit for the quantities in this table is phr (part per hundred rubber).

* The suffix "s" and "m" in IR-S2-s and IR-S2-m refers to solution mixed and melt compounded IR-S2 composites, respectively.

2.1.4 Compounding of IR-S2-m Composites by Mechanical Mixing and vulcanization

The formulations of rubber composites are shown in Table 2. 1, and the rubber compound mixed by an 80cc internal mixer Brabender using a filling factor of 0.8-0.85. Mechanical mixed IR-S2 composites are designated as IR-S2-m. The initial temperature was 160 °C, and the dumping out temperature was about 155°C. The rotor speed was 65 rpm. The mixing procedures were: 0-1 min IR, 1-3 min S2. Curing agent dicumyl peroxide was added on a two-roll mill. The finished compounds were compressed and cured for 160 °C to obtain rubber sheets of 1 mm thickness, the curing times are 90% of the maximum torque (t90) plus 10 minutes. The t90 is measured by moving-die rheometer.

2.1.5 Characterization Techniques

Nuclear magnetic resonance (NMR) spectroscopy was performed on NMRS 500M Hz.

Thermal gravimetric analysis (TGA) was done on a Q500 TA instrument. Each sample was prepared in Tzero aluminum pan for experiments about 10 mg in weight. Filler S2 was tested under N_2 to determine the onset decomposition temperature, a 10°C /min ramp rate was applied to raise the temperature from room temperature to 600°C.

Attenuated total reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra of the filler S2 was recorded with PerkinElmer Spectrum at 4 cm⁻¹ resolution

for 8 times.

2.1.6 Moving-Die Rheometer

Moving-Die Rheometer (MDR) was used to measure the curing curve of different rubber mixed compound IR-S2 (TABLE 2.1) at 160°C. Under a constant amplitude of oscillation at a given temperature, vulcanization is measured by the increase of torque which maintain the constant oscillation. During the procedure of vulcanization, the crosslink per unit volume rubber is also proportional to the torque.⁶

2.1.7 Tensile Test

Tensile specimens were cut with an ASTM 638 11-98 Type V dumbbell die. Dumbbell samples were held with a 40 mm gap distance and attached extensometer with the initial gap of 10 mm was applied to measure the strain. Three tensile specimens were tested in each case to avoid the experimental error using Instron A. The crosshead speed was 50 mm/min for IR-S2-s; 500mm/min for IR-S2-m.

2.2 Results and Discussion

2.2.1 Synthesis and Characterization of Ionic Filler S2

The reactive ionic surfactant filler S2 is synthesized according to Scheme 2.1. The 6-mercapto-1-hexanol can undergo sulfonation and oxidation reaction with chlorosulfonic acid^{66, 67}. After neutralization by sodium hydroxide, the filler with ion pairs is achieved. The proton Nuclear magnetic resonance spectrum of S2 in deuterated methanol (CD₃OD) is shown in FIGURE 2.1.



4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 f1 (ppm)

FIGURE 2.1 ¹H NMR spectra of S2 (500 MHz, 25°C, CD₃OD)

¹H-NMR (25°C, CD₃OD): δ=1.44 (m, 8H, CH2), 1.69(m, 8H, CH2), 2.70(t, 4H,

CH2), 4.00(t, 4H, CH2).

TGA was performed to determine the decomposition temperatures of S2. It was tested under nitrogen. The temperature, at which 95% of the weight remained (solvent is not counted), is considered the decomposition temperature. FIGURE 2.2 shows the TGA trace of S2 indicating the thermal decomposition temperature is 231°C. Thus, it is appropriate for compounding with rubber that can go through mixing and molding compression.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the functional group in S2 as shown in FIGURE 2.4. The assigned band is based on the study of Prosser et al.⁶⁸ The antisymmetric SO3 stretch is the largest band of the respective spectra, as it is a combination of several overlapping peaks, but is generally visible as a double band. The C-O-S stretch band is centered at 950 cm⁻¹.



FIGURE 2.2 TGA trace of S2 in N2



FIGURE 2.3 FTIR for S2 (room temperature)

2.2.2 Vulcanization condition

The appropriate vulcanization condition of IR-gum and compounded IR-S2 were derived from the curing curve carries out by moving-die rheometer. The results of solution mixing are presented in the following FIGURE 2.4 and TABLE 2.2. The results of mechanical mixing are shown in FIGURE 2.5 and TABLE 2.3.

From the results, compared with IR-gum-s, the torque of IR-S2-s compound are lower, and their equilibrium torque are similar. The lower of torque may be resulted from the consumption of DCP by S-S bond of the filler. The radical produced by DCP are supposed to react with S-S and double bond of elastomers. Fluctuations in the curves are attributed to the aggregation of ionic groups. The polar ion pairs are aggregated in ionic domains with the remainder dispersed in the hydrophobic matrix. But ionic dissociation will occur at elevated temperature resulting in the decrease of torque.

The difference of the torque at equilibrium between mechanical mixing sample (1.94) is larger than that between IR-gum-s and IR-2.5S2-s (0.68). Besides, the curves of mechanical mixing samples have no fluctuation that exists in all solution mixing samples with filler. The reason may be that during mechanical mixing at high temperature, the chain scission of polyisoprene will occur and radical will be produced. Then, the S-S bond can be opened in large-scale and react with the elastomers' backbone. Through the formation of covalent bonds between the polymer and ionic filler and the constantly shear in the internal mixer, the filler will be

distributed uniformly. Thus, in the IR-2.5S2-m there is no large size ionic aggregates that cause the fluctuation of torque.



FIGURE 2.4 Curing curve of solution mixing rubber.

			ts1	ts2				
phr	ML(dNm)	MH(dNm)	(min)	(min)	t10(min)	t50(min)	t90(min)	t100(min)
0	1.11	5.34	1.57	3.62	0.94	3.94	18.22	89.99
2.5	1.07	4.86	1.7	4.2	0.91	3.86	17.07	54.37
5	1.02	4.73	1.63	4.19	0.86	3.68	16.26	37.96
10	1	4.87	1.85	4.5	0.98	4.28	25.77	67.01
15	1.01	5.02	1.79	4.3	0.98	4.36	30.87	62.28

TABLE 2.2 Curing curve analysis of solution mixing rubber.



FIGURE 2.5 Curing curve of mechanical mixing rubber

			ts1	ts2				
phr	ML(dNm)	MH(dNm)	(min)	(min)	t10(min)	t50(min)	t90(min)	t100(min)
0	0.66	5.00	1.77	3.81	1.05	4.35	17.31	45.23
2.5	0.68	3.06	2.4	23.15	0.9	3.25	38.29	81.26

TABLE 2.3 Curing curve analysis of mechanical mixing rubber.

The compound IR-10S2-m cannot form a sheet in the two-roll mill but can be compressed to a film. The rubber is not sticky enough to form a sheet on the roll at 50°C and after milling the products are ground particles. Under high temperature, it is able to flow and be molded to get a film with shrinkage. That phenomenon may be resulted from the strong physical crosslinks formed by covalently bonded ionic species. When the filler loading is high, the rubber compound performs like thermoplastic elastomer⁴⁷.

2.2.3 Mechanical Properties

From the tensile test of solution mixed rubber composites as shown in FIGURE 2.6 and TABLE 2.4, it can be concluded that the tensile strength, elongation at break and toughness decrease with the addition of filler. This phenomenon can be explained by the aggregation of filler. Since the filler is amphiphile, the oleophilic alkyl chain is compatible with rubber matrix. However, the polar ionic groups are oleophobic, which prefer to interact with each other to form aggregates by relatively strong ion interaction. Therefore, the filler in rubber may not disperse well and may aggregate to form defects that importantly affect the mechanical properties of rubber.

The stress-strain curve and analysis of mechanical mixing samples are shown in FIGURE 2.7 below and TABLE 2.5. The fluctuations of the curve are caused by the machine's problems. As can be seen, the compound with filler has higher the elongation at break and toughness behaving like uncrosslinked rubber. Immersing the compound IR-2.5S2-m in toluene for five days, it dissolves mostly and remained part

is shapeless gel. Combined with curing curve, the IR-2.5S2-m is under cured. That can be caused by the reaction between disulfide and DCP that will consume DCP and decrease the crosslink density.

Based on the discussion above, the mixing procedure can significantly influence the effect of S2 filler on synthetic polyisoprene rubber. In order to achieve better dispersion, the mixing procedure that combines solution mixing and mechanical mixing is designed and will be tested in future work.



FIGURE 2.6 Tensile test of cured IR-gum-s, IR-S2-s.

phr	σb(Mpa)	εb(%)
0	8.64	532.22
2.5	1.13	98.47
5	1.34	93.53
10	1.36	98.77
15	1.28	90.77

TABLE 2.4 Tensile test results of solution mixing samples



FIGURE 2.7 Tensile test of cured IR-gum-m, IR-2.5S2-m.

TABLE 2.5 Tensile test results of mechanical mixing samples

phr	σb(Mpa)	εb(%)	Toughness(J/cm3)
0	7.72	618.45	14
2.5	3.80	1252.69	22

CHAPTER III

REACTIVE IONIC SURFACANT FILLER PNa

3.1 Experiment

3.1.1 Materials

6-Mercapto-1-hexanol was purchased from TCI. 1-octanol was purchased from Acros Organics. Phosphorus oxychloride, anhydrous methanol, anhydrous diethyl ether and other solvents were purchased from Sigma-Aldrich. Sodium hydroxide is from BDH Analytical Chemicals. Curing agent DCP was provided by Akrochem. Synthetic polyisoprene latex was provided by Kraton Polymer as a gift.

3.1.2 Synthesis of phosphate PNa

A Schlenk flask was loaded with anhydrous diethyl ether (70ml), phosphoryl chloride (0.03 mol), 1-Octanol (0.03 mol) and triethylamine (0.03 mol) and stirred 30 min under nitrogen. Precipitated triethylamine hydrochloride salt was filtered off. Added 6-mercapto-1-hexanol (0.03mol) and triethylamine (0.03 mol) and stirred overnight. Removed the salt by filtration and the filtrate was concentrated under vacuum. Dissolved the syrup in methanol and reacted with deionized water (0.06 mol) for 1 h. Solvent was removed in vacuo. The mixture was diluted with chloroform and

extracted with deionized water to get rid of residue HCl. Dried the solution, then diluted the residue by diethyl ether and neutralized with NaOH (1 mol/L in anhydrous ethanol) stoichiometrically. Mixed solvent (hexane with a little CHCl3) was used for recrystallization.



Scheme 3.1: Synthetic route PNa

3.1.3 Compounding of IR-PNa-s composites by solution mixing and vulcanization

Synthetic polyisoprene was compounded new phosphate filler. The formulations of rubber composites are shown in TABLE 3.1. The solution mixed compounds are designated as IR-PNa representing IR filled with X phr (part per hundred rubber) of filler. Polyisoprene latex (8.14 g) containing polyisoprene rubber (5 g) was mixed with DCP (0.1 g/ml in hexane) and PNa (0.1 g/ml in deionized water. Stirred at room temperature overnight to evaporate solvent. Then dried the compound in vacuum for two days. Milled the rubber by two-roll mill at 50°C. The finished compounds were compressed and cured for 160 °C to obtain rubber sheets of 1 mm thickness, the curing time (t90 plus 10 min) is measured by moving-die rheometer.

Composites	IR	PNa	DCP
IR-gum-s	100	0	1
IR-5PNa-s	100	5	1
IR-15PNa-s	100	15	1

TABLE 3.1 Formulations of IR-PNacomposites

- * The unit for the quantities in this table is phr (part per hundred rubber).
- * The suffix "s" in IR-PNa-s refers to solution mixed IR-PNa composites.

3.1.4 Characterization Techniques

Nuclear magnetic resonance (NMR) spectroscopy was performed on Varian Mercury 300M Hz.

Thermal gravimetric analysis (TGA) was done on a Q500 TA instrument. Ramp 10°C/min to 800°C.

Differential Scanning Calorimetry (DSC) was performed with filler PNa to obtain the melting temperature. The sample was prepared in aluminum hermetic pans with the weight about 5 mg. TA instrument model Q2000 was used in the experiment. For pure filler PNa, equilibrated at -30°C, then rise to 200°C, which is followed by the decrease to -30°C. This cycle repeated twice. All ramp rates were 10°C per minute.

3.1.5 Moving-Die Rheometer

Moving-Die Rheometer (MDR) was used to measure the curing curve of different rubber mixed compound IR-PNa (Table 3.1) at 160°C.

3.1.6 Swelling test

Crosslink densities of IR-gum and IR-PNa composites were measured by swelling tests. About 0.1 g cured film (Winitial) was weighed and immersed in 20 ml of toluene for one week at room temperature. Then, the swelled sample was wiped by paper towel and weighed (Wgel). Dried in vacuum oven at 70°C to achieve a constant weight (Wdry). The crosslink densities were calculated by Flory-Rehner Equation⁶⁹:

$$\rho\rho_{cc} = -\frac{1\ln(1 - vv_{rr}) + vv_{rr} + \mathcal{X}\mathcal{X}vv_{rr}^{2}}{\frac{1}{vv_{rr}^{3} - \frac{vv_{rr}}{2}}}$$

where

$$vv_{rr} = \frac{\frac{WWWWWWW}{\rho\rho WWWWW}}{\frac{WWWWWWW}{\rho\rho WWWWW}} \frac{WWWWWW}{\rho\rho\rho\rho\rho}$$

 vv_{rr} is the volume fraction of rubber in the swollen gel, $\rho\rho_{ddrrdd}$ is the density of dried rubber (0.91g/cm3), $\rho\rho_{ccssccccccccc}$ is the density of solvent (toluene: 0.862g/ml), $\rho\rho_{cc}$ is the crosslink density, vv_{ss} is the molar volume of the solvent (toluene: 105.29 cm3/mol), XX is the interaction parameter of the solvent and rubber (IR-toluene: 0.448)⁷⁰.

3.1.7 Stress-relaxation test

The compression-molded film was cut into a strip about 15mm, 5mm, 1mm (l, w, t). The stress relaxation test was performed by dynamic mechanical analyzer TA Q800 at room temperature. The preload force is 0.01N and the strain is 10%. The relaxation modulus and stress were recorded as a function of time.

3.1.8 Tensile Test

Tensile specimens were cut with an ASTM 638 11-98 Type V dumbbell die. The gap between crosshead is 40mm and extensometer with the initial gauge length of 10 mm was used to measure the strain. The specimens were tested by Instron A. The

crosshead speed was 50 mm/min for IR-PNa-s;

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of Ionic Filler PNa

The synthetic route of phosphate PNa is presented in Scheme 3.1. Since the phosphoryl chloride is not oxidative, the final product will maintain a more reactive thiol group. Thus, the ionic filler should react with the double bond of elastomers backbone via thiol-ene reaction. Besides, it contains longer alkyl chain than S2 which increase the compatibility with hydrophobic rubber matrix. The proton Nuclear magnetic resonance spectrum of PNa in deuterated methanol (CD₃OD) is shown in FIGURE 3.1.

TGA was conducted to measure the decomposition temperatures of PNa. It was tested under nitrogen. The temperature where 5% of the weight lost is considered as the decomposition temperature. FIGURE 3.2 shows the TGA trace of PNa indicating the decomposition temperature is 278°C. Therefore, it is stable during the mixing and molding.

DSC was used to determine the melting and crystallization temperature of the alkyl chain covalently connected with the phosphate group. As shown in FIGURE 3.3, the compound has two melting peaks that close to each other and one crystallization peak. It is assumed that the two long alkyl tails melt separately and when being cooled, they crystalized together.



FIGURE 3.1 ¹H NMR spectra of PNa (300 MHz, 25°C, CD₃OD)

¹H-NMR (25°C, CD₃OD): δ=0.90 (t, 3H, CH3), 1.31-1.62 (m, 20H, CH2), 2.49(t, 2H, CH2), 3.82(m, 4H, CH2).



FIGURE 3.3 DSC trace of PNa. The first heating-cooling cycle is gray, the second cycle is black. Heating and cooling rate are 10°C /min.

3.2.2 Vulcanization

The vulcanization condition of IR-gum and compounded IR-PNa were determined by the curing curve carries out by moving-die rheometer. The MDR results of solution mixed samples are presented in the following FIGURE 3.4 and TABLE 3.2.

From the results, the suitable curing condition is 160°C and 30min. With the increase of filler loading, the torque decrease. That may due to the thiol group can consume part of DCP, then reduce the number of chemical crosslinks.

Swelling test was performed to measure the crosslink densities of cured rubber composites. The results are listed in TABLE 3.3. The crosslink densities are almost the same for IR-gum-s and IR-5PNa-s, and somewhat lower for IR-15PNa-s. Since the calculation did not take filler-rubber interaction and the influence of solvent on physical crosslinks into account, the results are reference only and should not reflect the real situation.

Stress relaxation curves for IR-5PNa-s and IR-15PNa-s at 10% strain are shown in FIGURE 3.5 below. These materials reach a near plateau relaxation modulus after about 1 h behaving like viscoelastic materials. The plateau modulus level and plateau stress of IR-15PNa-s is larger than that of IR-5PNa-s. The explanation is that the added filler is rigid compared to the continuous phase that cause the difference of modulus.⁷¹



FIGURE 3.4 Curing curve of solution mixed rubber.

TABLE 3.2 Curing curve analysis of solution mixed rubber.

phr	ML(dNm)	MH(dNm)	ts1 (min)	ts2 (min)	t10(min)	t50(min)	t90(min)	t100(min)
0	1.11	5.34	1.57	3.62	0.94	3.94	18.22	89.99
5	0.98	4.76	1.63	4.04	0.83	3.67	17.04	90.06
15	0.72	4.18	2.05	5.21	0.99	4.06	18.58	85.08

phr	pc(mol/m3)	Mc(g/mol)
0	35.67	12754
5	35.51	12814
15	30.33	15002

TABLE 3.3 Crosslink densities of solution mixed rubber.



FIGURE 3.5 Stress relaxation behavior of IR-5PNa-s and IR-5PNa-s

3.2.3 Mechanical Properties



FIGURE 3.6 Stress-strain curves of cured IR-gum-s, IR-5PNa-s, IR-15PNa-s.

TABLE 3.4 Tensile test result	of solution	mixing samples	
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phr	σb(Mpa)	εb(%)	σ300%(Mpa)	σ400%(Mpa)	Toughness(J/cm3)
0	0.64	500.00	2.25	2.67	
0	8.64	532.22	2.35	3.67	14
5	13.36	653.77	1.76	2.32	20
15	14.48	738.94	1.43	1.56	22

The stress-strain curves and analysis of tensile test of solution mixed rubber composites as shown in FIGURE 3.6 and TABLE 3.4. The tensile strength, elongation at break and toughness increase with the growth of filler loading. It shows that the reactive ionic filler can reinforce polyisoprene rubber by simply solution mixing. The reason may be that the longer oleophilic chain helps the filler disperse uniformly in the rubber matrix. The reactive thiol group can react with rubber backbone in situ, which improve the rubber-filler interaction. Well-defined ion domains serve as physical crosslinks and form supramolecular networks that offers a mechanism of energy dissipation.

CHAPTER IV

CONCLUSION

Two kinds of reactive ionic surfactant filler have been synthesized and analyzed. They are designated as sulfate S2 and phosphate PNa separately. The important factor that affects the reinforcement by S2 is processing procedure. Tensile tests were carried out to study the reinforcing effect of sulfate S2 on synthetic polyisoprene rubber. By solution mixing, the fillers show tendency to aggregate in a rubber matrix resulted in defects that decrease the mechanical properties of rubber. However, the mechanical mixed rubber compounds resulted under cured compounds. The mechanical mixed compound with higher filler loading is able to flow and be processed at high temperature as a thermoplastic elastomer.

Compare to S2, the phosphate filler PNa is supposed to possess higher rubberfiller compatibility by its oleophilic tail. It has a reactive thiol group that can form covalent bond with the unsaturated rubber backbone that can enhance the rubber-filler interaction. Therefore, it can improve the properties of rubber by simply solution mixing. The strength, elongation at break and toughness are enhance by ionic filler PNa.

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