



Chapter I

Introduction

1.1 Natural Rubber (NR)

NR is planted in most southern areas in Thailand. The widely used NR comes from the Hevea Brasiliensis tree, a rubber tree native of Brazil. Natural-rubber consists of particles of rubber hydrocarbon and nonrubber material suspended in an aqueous serum phase. The composition of the Hevea latex differs between clones, tapping history and season. A typical composition of fresh latex is shown in Table 1.1. [1]:

Table 1.1. Typical Composition of Fresh Latex and Dry Rubber

	<i>Latex, %</i>	<i>Dry Rubber, %</i>
Rubber hydrocarbon	36	93.7
Protein	1.4	2.2
Carbohydrates	1.6	0.4
Neutral lipids	1.0	2.4
Glycolipids + phospholipids	0.6	1.0
Inorganic constituents	0.5	0.2
Others	0.4	0.1
Water	58.5	-

Hevea NR has a chemical structure of almost 100% cis-1,4-polyisoprene units having a chemical structure as illustrated in Figure 1.1.

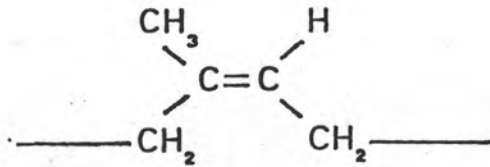
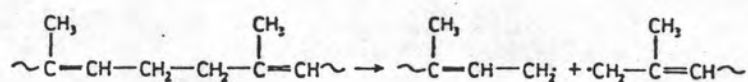


Figure 1.1 cis-1,4-polyisoprene

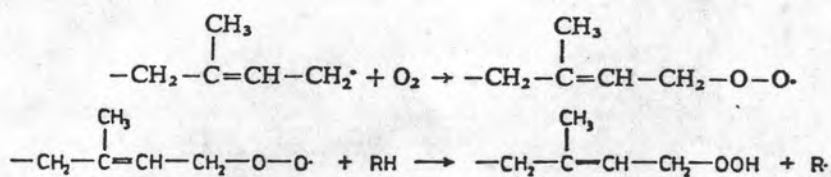
Its number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w), and molecular weight distribution (MWD) are significantly different between clones. A study [2] on \bar{M}_n and \bar{M}_w between 12 different clones, ranged between 0.5×10^6 to 2.7×10^6 for \bar{M}_n , and 3.4×10^6 to 10.2×10^6 for \bar{M}_w . The average MWD was found to be 6.7, whose value between individual clones ranged from 3.6 to 11.0.

In solution NR exhibits a solid and gel phase [1] in the dry rubber. During storage, the rubber hardens and stiffens spontaneously and the viscosity increases as a result of crosslinking reactions. These reactions usually increase at higher temperature and lower humidity. It is believed that aldehyde groups in the rubber are responsible for such reactions known to involve free radicals. These groups react with the amino groups of free amino acids and proteins to give crosslinks. Their reactivity can be deactivated with 0.15% of hydroxylamine salt. It was found that during storage the gel content (that is, the crosslinking density) increased as much as 50%, or even higher.

The gel is not a true network due to a high degree of entanglement and its content depends on the solvent used, usually it is lower in good solvents. Mastication is usually carried out in the presence of air to prevent crosslinking. During the process [3] the gel easily breaks down through oxidative degradation with heat and oxygen by using roller mills or plasticators (internal mixers). It is assumed that a homolytic bond scission occurred in the main chains leading to allyl type radicals as schematically represented below:



Oxygen usually reacts with macroradicals to form peroxy radicals which then abstract hydrogen atoms intra- or intermolecularly from rubber (RH), and leading to further degradation.



The decrease of \bar{M}_w as a function of the mastication time is shown in Figure 1.2. It indicates that the largest decrease in \bar{M}_w occurred during the first 20 minutes before reaching almost a plateau. This is very important to the tire industry in term of energy saving when using NR, for the rubber has to be masticated before being used due to its very high MW. As illustrated in Figure 1.3, the MWD also is narrowed by mastication.

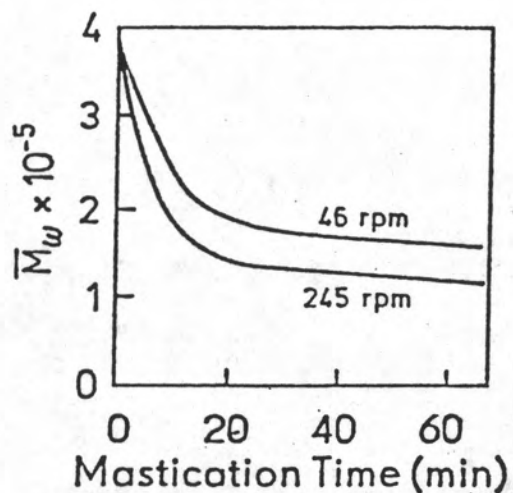


Figure 1.2. Mastication of NR in an internal mixer in the presence of air at 52 °C

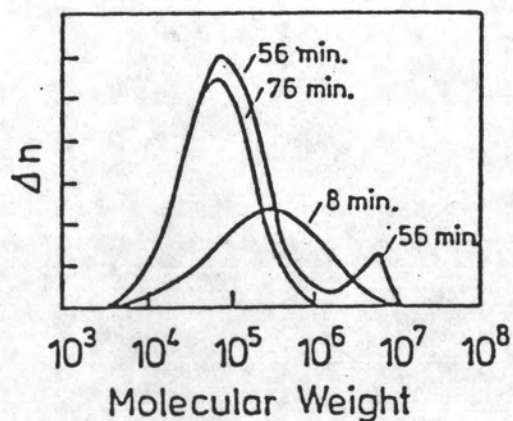
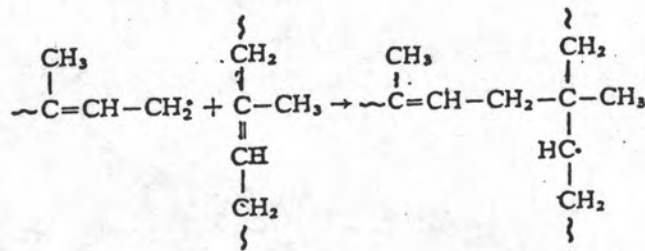


Figure 1.3. Gel permeation chromatography (GPC) analysis of masticated NR.

The GPC spectrogram illustrates that a rubber with a bimodal MWD, can be masticated into a material with a mono-modal MWD, and at the same time narrow the MWD.

In an inert atmosphere, on the other hand, mastication leads to intermolecular crosslinking as indicated by an increase of the \bar{M}_w and at a later stage by the formation of an insoluble and infusible 3-dimensional network. A possible crosslinking reaction is shown below:



1.2 Chemical Modification of NR

NR has mainly been used as a raw material for the tire industry. A list of natural rubber products is given in Table 1.2. [1]:

Table 1.2. Use of Natural Rubber in Products

Product	Percent ^a
Tire and tire products	70-72
Mechanical goods	9-10
Latex products	7-8
Footwear	4-5
Engineering products	3-4
Adhesives	1-2
Others	2-3

^aEstimated from different sources.

The small scope of applications and the increasing competition with synthetic rubber, has made researchers focus on new methods by modifying NR into materials with novel mechanical properties and applications. These methods are via chemical, mechanical and irradiation processes.

Among them chemical modification is the most attractive as it can be better controlled and be more specific regarding the choice of functional groups and/or monomers which can be used for modification. For example, graft copolymerization onto NR of vinyl monomers such as methyl acrylate [4] and methyl methacrylate have been carried out using either vanadium [5], potassium bromate/thiourea redox system [6] or cerium [7] as initiators. While ethyl acrylate and butyl acrylate have been grafted via a free radical mechanism onto the rubber using benzoyl peroxide [8].

Also, Heveaplus the generic name for a family of graft rubbers, were synthesized using acrylate monomers which were grafted onto NR at a concentration between 30-50% weight of acrylate content. These materials are self-reinforcing and can be added to natural or synthetic rubbers to impart high hardness and impact strength to nonblack materials. The most useful applications of modified NR are adhesives, either in the latex form of an organic solution, or as a dry rubber film. They have the ability to adhere many "like" and "unlike" surfaces together because the grafted rubber combines with both polar and nonpolar groups in the same material, which behave as chemical bridges.

1.3 Ionomers

In 1964, another type of material called "ionomer" reached the market. The term ionomer was introduced by the

Du Pont to describe a copolymers derived from ethylene and methacrylic acid, and in which the carboxyl groups were neutralized partially or completely with monovalent and divalent cations to form salts. The concentration of the salt groups varies and today, in general, the term ionomers refers to polymers with less than 10 mole % ion groups [9].

It was found that the neutralization of the acid groups creates ionic crosslinks exhibiting a pseudo-crosslinked elastomer behavior. The ionic group acts as a thermally reversible physical polymer network. There are two types of ionic crosslinks possible depending whether the cation is mono- or divalent. The cation acts as the counterion to carboxylated anion as represented in Figure 1.4.

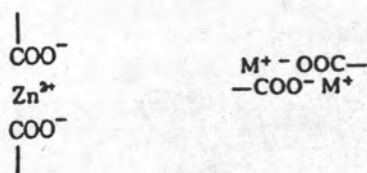


Figure 1.4. Chemical structures of two types of carboxylated elastomers neutralized by divalent and monovalent cation, respectively.

In reality, ionic groups coming from different polymer chains aggregate to form ionic domains as illustrated in Figure 1.5 [10].

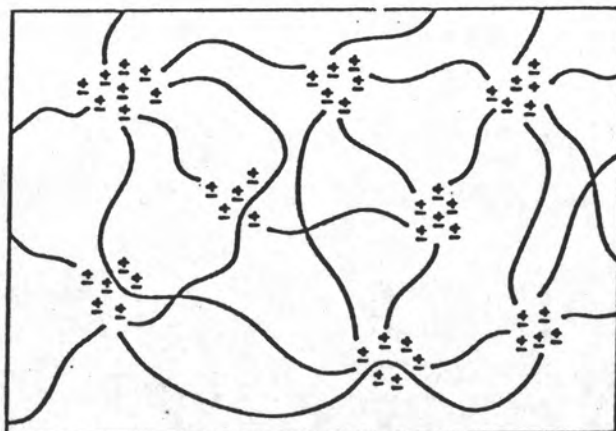


Figure 1.5. Domain structures in ionic elastomers.

An ionic domain, also called a multiplet, is defined as a spherical drop consisting of a group of ion pairs with the polymer chains outside the drop. Agarwal et al. [11] and Holliday [12] proposed that the maximum number of ion pairs in a multiplet is about 8, with the core of the multiplets being held together by electrostatic forces. Most ionomers have a maximum cluster distance of about 2-4.5 nm [13]. However, the driving force for the cluster formation is not very clear due to the nature of the polymer chain such as its stiffness and/or the presence of bulky side groups.

1.4 Synthesis and Properties of Ionomers

The most common route to synthesize such materials begins with the incorporation through copolymerization of a monomer containing two double bonds such as

5-ethylene-2-norbornene (ENB) in ethylene-propylene-diene-terpolymer (EPDM) [14] and then grafting a carboxylic or sulfonic groups onto the remaining double bond; or by simple copolymerization of a monomer already containing the acid group such as acrylic acid. These groups are then converted to their salt form by neutralization with a metal acetate such as zinc or calcium acetate.

The introduction of very small quantities of metal ions into such polymer systems does dramatically change the mechanical properties of the material when compared with nonionized systems [15]. The resulting polymer is a very tough, strong and truly thermoplastic material that can be successfully processed by conventional polymer processing techniques. The major property changes are the following [12]:

a. Glass Transition: The electrostatic forces between bonding ions in the polymer chains and the counterions reduce the segmental mobility and thus increases T_g . The higher the ionic bond content, the higher the T_g .

b. Melting Point and Melt Behavior: The ionic bonds affect the softening or melting behavior by requiring more energy to disrupt the polymer matrix, thus increasing the T_m as well.

c. Viscoelastic Properties: The viscoelastic properties of ionic polymers such as flow, stress-relaxation and creep, have also been affected by factors such as the lability of the ionic bond, the mobility of the main chain, the formation of ion multiplets, and the effect of ion aggregation on crystallization behavior when crystallizable main chains are present.

d. Hydrolytic Stability: The presence of strong ionic groups in an amorphous polymer will induce absorption of water through an osmotic effect. The degree of water absorption is affected by the type of cation and the number of salt groups in the chain. For example, Makowski et al. [14] neutralized sulfonated EPDM with different mono- and divalent cations and found the following results illustrated in Figure 1.6. Among the divalent ions, Zn^{2+} and Pb^{2+} cations gave the lowest water absorption while Ba^{2+} and Ca^{2+} indicate a higher absorption. On the other hand, monovalent cations such as Na^+ , Li^+ and Cs^+ showed water absorption ranging between those of the divalent cations.

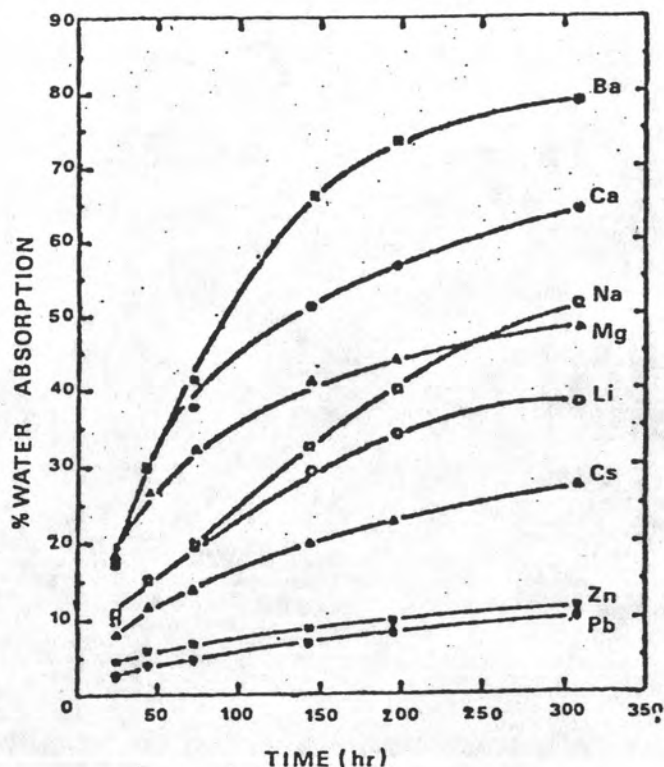


Figure 1.6. Percentage of water absorption of 31 meq. of a various metal ions per 100 g EPDM.

1.5 Effect of the Metal Ions on Ionomers

Macknight and Earnest [9], in their review paper on the properties of ionomers, suggested that their unique properties are due to the coulombic (electrostatic) interaction between the ionic moieties. As mentioned earlier, an important parameter that affects these interactions is the type of the metal cation used to neutralize the precursor acid. Eisenberg [16] proposed and demonstrated that the ionic potential q/a (charge to ion size ratio) is a critical parameter, and has

rationalized the behavior of ethyl acrylate-acrylic acid copolymers neutralized with various cations and other ionomer systems on the basis of this concept.

The energy, E , of coulombic attraction between two charged particles is proportional to the product of their charge, and inversely proportional to the distance between them. Specifically:

$$E = -(Z^+ Z^-) q^2 / 4\pi\epsilon_0 R$$

where Z^+ and Z^- is the charge of the cation and anion respectively, ϵ_0 is the dielectric constant of the medium, R is the distance between the two charged centers and q is the electrostatic charge.

Thus, the higher the q/a ratio of a cation, the more strongly it will be attracted by a given anion. In fact this concept works well for cations within the same group of the periodic table, as demonstrated by Eisenberg. However, Bagrodia and Wilkes [17] believe that the q/a ratio by itself is often insufficient to account for the observed behavior in various other ionomer systems neutralized with cations belonging to different groups in the periodic table. For example, Makowski et al. [14] have also studied the effect of the cation type on the rheological and physical properties of sulfonated EPDM materials. They observed that the behavior of Hg^{2+} and Ca^{2+} neutralized ionomers was drastically different, although

their ionic radii differ by only 2 pm (picometer) (the respective radii are Hg^+ 102 pm and Ca^{2+} 100 pm).

Clearly then there are other factors besides the ionic potential (q/a) that affect the association character of the final ionomers. Indeed, it has also been observed by Lundberg et al. that Zn^{2+} neutralized sulfonated EPDM have the lowest melt viscosity at higher temperature as compared to the same polymer neutralized with other cations such as Na(IA), Mg(IIA), Ca(IIA), Co(VIII), Li(IA), Ba(IIA), Pb(IVA), etc. However, Zn^{2+} neutralized EPDM's have comparable, if not better, tensile strength than those neutralized with many of the other cations listed above. Similar behavior has been observed in sulfonated polyisobutylene ionomers neutralized with either zinc acetate, potassium or calcium hydroxide [18, 19].

In line with the explanation offered by Lundberg et al. Bagrodia and Wilkes propose that besides the coulombic effect, an additional important parameter that deserves consideration is the electronic configuration of the cation which in turn governs its degree of ionic/covalent character. Specifically, the divalent zinc cation is more "covalent" than the corresponding divalent calcium, magnesium, or barium cation. Hence, at elevated temperatures the coulombic interactions in the case of Zn^{2+} neutralized ionomers are weaker than with Ca^{2+} , or the other divalent ions which are more ionic in character. This will also help explain the lower melt viscosity at

elevated temperatures in the case of the former.

Bonotto and bonner [20] have also investigated the melt rheology of mono- and divalent cation of ethylene based ionomers. They found that the melt flow index decreased as ionization increased, with less correlation on ion valency. They also found that, in the study of rubber such as polybutadiene when copolymerized with acrylic acid monomer and then converting the acid groups to their monovalent metal salts, a decrease in solubility with large permanent sets. A similar trend of the room temperature tensile strength, moduli and elongation was also apparent. When the testing temperature was increased the materials exhibited thermoplastic behavior, that is, a material which softens without chemical changes when heated and hardens again when cooled. Compared with divalent metal salts with smaller elongations and permanent sets, the polymer products were insoluble and in some cases, depending on the ion, were infusible, and had a higher tensile strength and moduli.

Some efforts were also made to study the effect of partial and excess neutralization of acid groups [17, 18, 21]. This, too, affected the melt rheological and mechanical behavior of the ionomers. Mohajer and coworkers [17, 18] investigated the neutralization of sulfonated EPDM with zinc acetate and tentatively explained the effect in terms of a combination of the following two phenomena: (a) the plasticization of the

ionic associations by zinc acetate at elevated temperatures, and (b) through the conversion of disulfonates $\text{SO}_3\text{-Zn-SO}_3$ to less strongly associating monosulfonates $\text{SO}_3\text{-Zn-OOC-CH}_3$ at high zinc acetate concentration.

Addition of excess neutralizing agents resulted in the absorption of the inorganic component in the polymer matrix. It is speculated that the retained excess salt increases the strength of the ionic association but has little influence on the number of ionic domains. The excess neutralization significantly influences bulk behavior, particularly at high elongations.

The difference of pendant acid groups also have affected the ionomers properties. Agarwal et al. showed that sulfonate ionomers differ significantly from the carboxylate ionomers in both physical and solution properties. The sulfonates exhibit more ionic association which results in a stronger physical network, and one which is more temperature resistant than the carboxylates [11].

1.6 Applications of Ionomers

The introduction of Surlyn by Du pont intrigued various academics and industrial research institutions because of its unique properties. These tough and transparent materials are well suited for a variety of applications, notably film packaging. They have high melt strength, puncture and abrasion resistance, and are

resistant to greases, oils and solvents. The combination of these properties offers potential applications where toughness and clarity are required. Examples of ethylene based ionomer applications are found in food packaging, either as a shrinkable film or in the form of a laminated film with nylon, foil, paper or any other barrier films, depending on the type of product to be packaged.

Also, Michaels et al. have prepared the poly (sodium-styrene sulfonate) (NaSS) - poly(vinyl benzyl trimethylammonium chloride) (VATAC) complex by simply mixing the appropriate solutions. The most promising field of application for these materials is in the area of medicine. It has been shown that they are very compatible with mammalian tissue and their particular ionic permeability and swellability encourage the hopes that they will make possible new artificial organs and implants [12].

1.7 Most Recent Works on Ionomers

Recently, a new type of ionomer was investigated by Mohajer and coworkers [18, 19]. It is a tri-arm-star polyisobutylene (PIB) carrying a sulfonic acid group at each end, as illustrated in Figure 1.7. Upon neutralization, this system led to a model network with ionic association only at the chain ends.

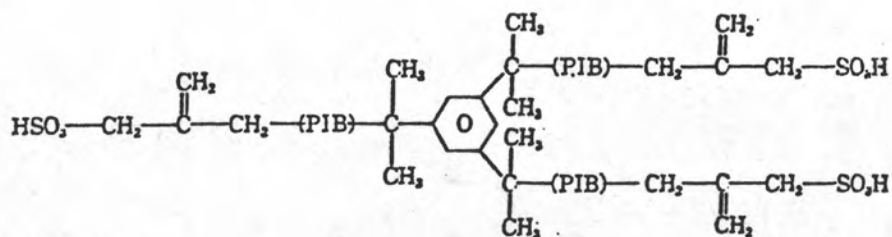


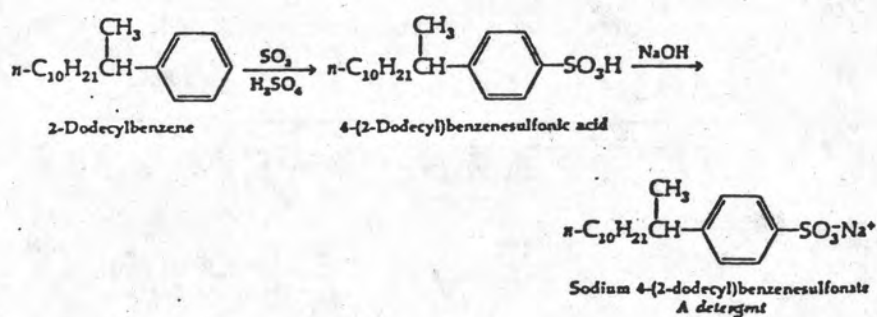
Figure 1.7. Tri-arm-star sulfonated polyisobutylene.

It is now widely recognized that the introduction of low levels of ionic groups onto a hydrocarbon chain results in substantial changes in physical properties. However, the particular question regarding the state of aggregation of ions and associated polymer molecules in organic polymer systems is complicated due to inapplicability of any directly available analytical tools. Today, despite the progress made in elucidating the physical state of ionic polymers, the results are still at variance and subject to different interpretations.

1.8 Sulfonation

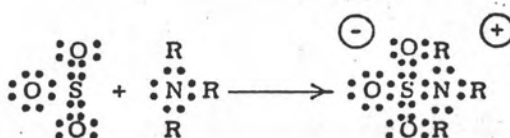
A key step in the development of ionomers is the introduction of acidic functional groups into the polymer backbone. Sulfonation, for example is the reaction which introduces the sulfonic group into unsaturated compounds containing olefinic double bond or an aromatic ring, using sulfonating reagents such as chlorosulfonic

acid and sulfur trioxide. This process probably was developed historically because of the ready availability of inexpensive sulfuric acid. Today, one of the largest uses for sulfonation is in the detergents industry [22]. The reaction scheme below illustrates a typical route to synthesize detergents:

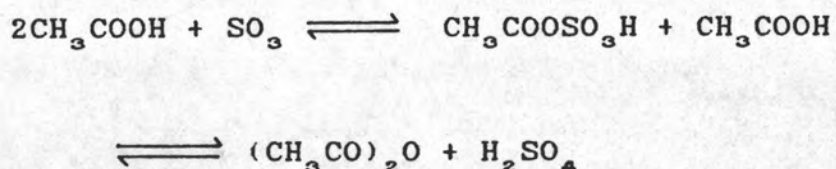


Sulfur trioxide (SO_3) is an excellent electrophile for such purpose, either in a free or as a complex form, by combination with other reagents such as pyridine, trimethyl- or triethylamines. The most common source of the electrophile is concentrated or fuming sulfuric acid, containing SO_3 .

The sulfur atom in SO_3 , being a strong electron acceptor or Lewis acid, combines with electron donors or Lewis bases, to form complexes. The associated bases may be tertiary amines. The stability of the complex varies directly with the base strength. When it is employed for sulfonation of an organic compound, the SO_3 is released and complexes with the base to form the salt of the new acid as shown below:



Alternatively, acyl sulfates is also widely used for sulfonation because it is easy to handle and is highly reactive by giving excellent yields. The reaction of sulfur trioxide with acetic acid below 0°C to form acetyl sulfate, is believed to form the following equilibrium [23].



On the other hand, similar results were obtained by reacting acetic anhydride with concentrated sulfuric acid. It is observed that the acetic anhydride function is simply to abstract water from sulfuric acid. All classes of unsaturated compounds sulfonate easily, forming various types of products as shown in Figure 1.8 [23]. The formation of these products depends upon factors such as reactant-reagent ratio, the sulfonating agent and the structure of the alkene.

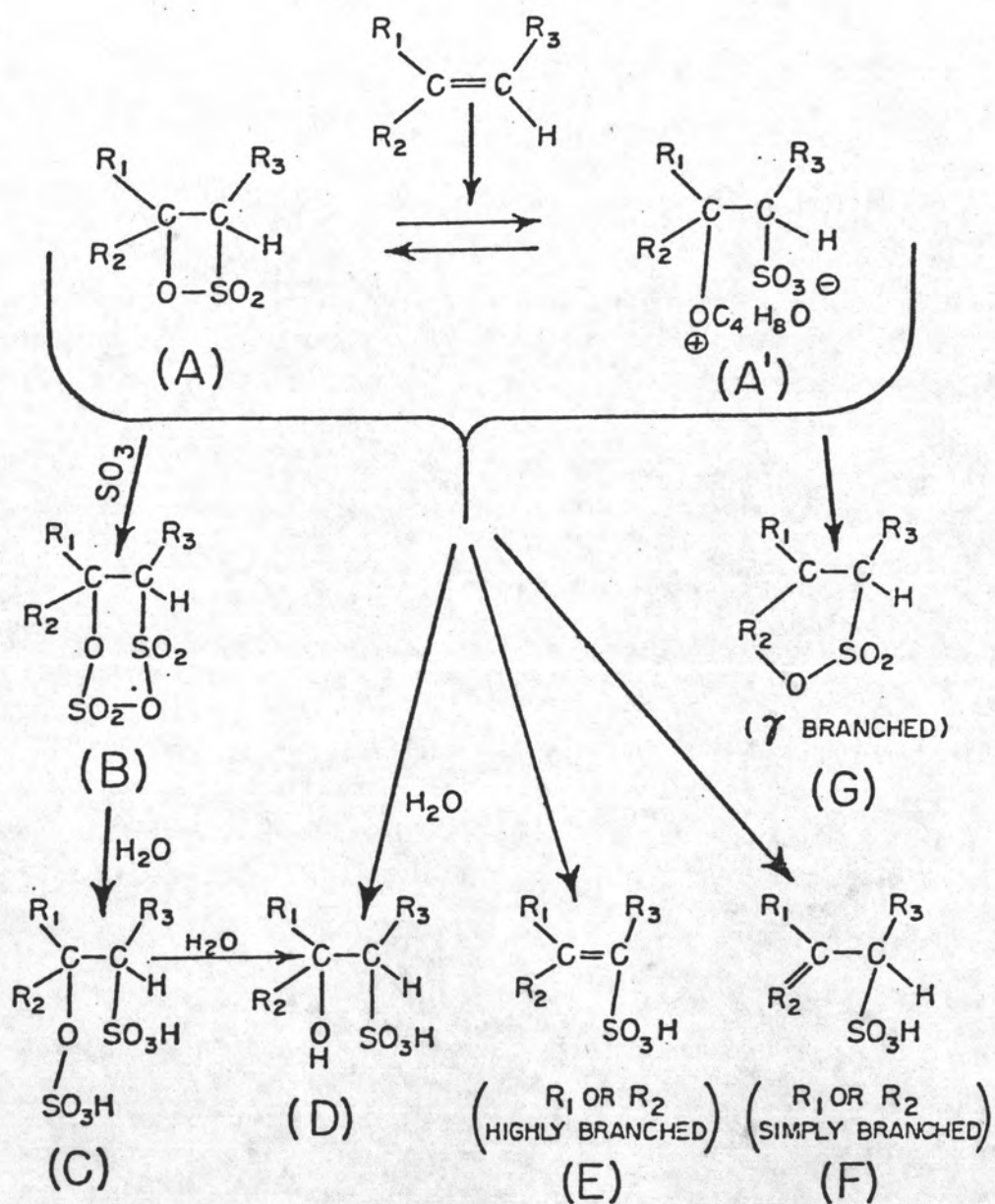


Figure 1.8. Various types of sulfonated products obtained from sulfonation of alkenes.

1.9 Purpose of Research

Due to the very interesting properties of commercial ionomers and since no attempt to form such material with NR has ever been made before, and it is of interest to investigate whether the synthesis of an ionomer-type NR is possible. Thailand being one of the largest producers of NR in the world, it is of economical interest to the country to develop new NR-derived products.

In view of the above background, this research will focus on the sulfonation of NR and the neutralization of the resulting polymer by zinc, magnesium and lead acetate. The resulting modified NR will be characterized by NMR and IR spectroscopy, and by dilute viscosity. The water absorption and plasticity properties of the neutralized sulfonated NR will also be determined.