

NATURAL RUBBER:

PART I: AN OVERVIEW

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ABSTRACT

Before the advent of synthetic rubbers and for many decades Natural Rubber (NR) remained a general purpose elastomer used in various applications. However after the commercial success of Styrene Butadiene Styrene thermoplastic elastomers in the late seventies, Natural Rubber producers could not afford not to follow this trend. Their concern was to face a virtual risk that the consumers would turn to synthetic rubbers in the event of Natural Rubber (NR) not being able to meet their needs or if NR is seen to create a kind of monopoly situation. It was believed that the only way to defend non-tire applications and insure continuous market outlets for NR, was to develop highly technical grades which could not easily be substituted by synthetic rubbers. Many studies have therefore been conducted in order to chemically modify Natural Rubber in order to produce new forms or grades. Examples of such grades are cyclized NR, which is used in adhesive and printing ink formulations, and chlorinated NR, which compensates for the poor oil resistance, inflammability and adhesion to metal substrates of the mother elastomer.

The first part of this paper discusses the structure and the properties of Natural rubber and outlines the different routes that were used in order to develop other grades through the chemical modification of the original elastomer.

The second part will be devoted to an extensive review of the main published work concerning the particular form of modified Natural Rubber which is Thermoplastic Natural Rubber (TPNR).

It is hoped that through this contribution, we make available to Algerian researchers from industry and academics, comprehensive material of interest to both scientists and technologists.

RESUME

Avant l'avènement des caoutchoucs synthétiques, Le Caoutchouc Naturel fut pendant plusieurs décennies un élastomère de commodité utilisé dans plusieurs applications. Néanmoins, après le succès commercial que les élastomères thermoplastiques à base de Styrène Butadiène Styrène ont connu vers la fin des années soixante dix, les producteurs du Caoutchouc Naturel ne pouvaient pas ne pas suivre l'évolution de cette concurrence. Leur souci était de faire face à un risque virtuel que les consommateurs se tourneraient vers ces caoutchoucs synthétiques en cas où le Caoutchouc Naturel ne satisferait pas leurs besoins. On pensait que le seul moyen pour assurer une commercialisation continue du Caoutchouc Naturel en dehors du secteur du pneumatique était alors de développer d'autres grades techniques qui ne pourraient pas être facilement substitués par les caoutchoucs synthétiques.

C'est dans ce contexte que les chercheurs ont entamé des études afin de modifier chimiquement le Caoutchouc Naturel pour pouvoir produire de nouveaux grades. Le Caoutchouc Naturel Cyclisé, qui est utilisé dans les adhésifs ou dans les formulations des encres d'impression, ou le Caoutchouc Naturel Chloré, qui possède une meilleure inflammabilité et adhésivité aux substrats métalliques que l'élastomère mère, sont deux exemples des nouvelles formes du Caoutchouc Naturel modifié.

Nous attelons donc, à travers cet article composé de deux parties, à présenter ce matériau unique en son genre. Dans la première partie, nous présentons la structure chimique et les propriétés du Caoutchouc Naturel, ainsi que les différentes voies qui ont été suivies pour la modification chimique de cet élastomère.

La deuxième partie sera consacrée à une recherche bibliographique sur les résultats des travaux de recherche publiés à travers le monde sur le grade particulier du Caoutchouc Naturel Thermoplastique.

Nous espérons, à travers cette contribution, mettre à la disposition des chercheurs Algériens un travail d'intérêt industriel et pédagogique.

KEY WORDS: Natural Rubber, chemical modification, Thermoplastic Natural Rubber.

1. INTRODUCTION

Over one hundred and fifty years ago, before the dawn of the plastics industry, Natural Rubber (NR) was the only polymer available commercially, and up to 1940 it was the only elastomer used in the rubber products sector [1]. Today it is competed with a great variety of synthetic rubbers, each of which having properties that allow them to be used in many applications. Hence there is a great need for more research and development efforts to upgrade the already excellent combination of physical properties; not only to strengthen its position but also to open new grounds of application [2].

Many studies have been carried out in order to chemically modify Natural Rubber in an attempt to produce new elastomers with enhanced chemical and physical properties, which will enable it to find applications in fields where specialty elastomers are normally employed. The epoxidation of Natural Rubber is one example of such studies; a useful modified natural rubber called ENR, Epoxidized Natural Rubber, was obtained and is commercially available [3]. Another route of modification of NR, which has gained great importance, as far as optimizing the material's performance and processing, is the development of Thermoplastic Natural Rubber (TPNR). Its outstanding feature, as for all Thermoplastic Elastomers (TPE), is its combined excellent processing characteristics of thermoplastic materials and the wide range of physical properties of the base elastomer at service temperature [4].

The aim of this paper is to make a presentation of Natural Rubber and to outline research concerning its two different forms, that is chemically modified NR's and Thermoplastic NR.

2. NATURAL RUBBER: Structure and properties

Natural Rubber (designation in ISO 1629: NR) is Cis 1,4 Polyisoprene (Figure 1) and has a number average degree of polymerization of about 5000 and a broad distribution of molecular weights varying between 200 000 and 500 000.

It can be obtained from more than 200 different species of plant. *Hevea Brasiliensis*, is however, the most commercially significant source of production of this elastomer.

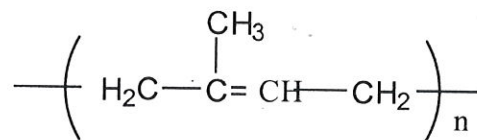


Figure 1: Chemical structure of Natural Rubber

Latex, an aqueous colloid of the rubber, is obtained from the tree by tapping into the inner bark and collecting the latex in cups. The latex contains 30-40 % dry rubber by weight, and 10-20 % of the collected latex is concentrated by creaming, or centrifuging, and used in the latex form. The remaining latex is coagulated, washed and dried by two processes. Crepe rubber results if a small amount of sodium bisulfite is added to bleach the rubber. The coagulum is rolled out into sheets about 1 mm thick and dried in air. If smoked sheets, the second grade of Natural Rubber, are to be made, the bleach is omitted and somewhat thicker sheets are rolled. These are dried in smokehouses at about 50°C in the smoke from burning wood or coconut shells.

The latex contains also a small level of highly important non-rubber constituents. Of these, the most important are the proteins, sugars, and fatty acids, which are antioxidants and activators of cure. Trace elements present include potassium, manganese, phosphorus, copper, and iron, which act as catalysts for oxidation.

Natural rubber can strain crystallize, which results in its compounds exhibiting high tensile strength and good tear strength.

Since the main chain of Natural Rubber contains unsaturation, it is susceptible to attack by oxygen, ozone, and ultraviolet light. Protection through compounding is therefore required.

Natural Rubber is not oil resistant and is swollen by aromatic, aliphatic, and halogenated hydrocarbons. It can be vulcanized by the use of sulfur, sulfur donor systems, peroxides, and by radiation. The sulfur vulcanization of Natural Rubber generally requires higher added amounts of sulfur, and lower levels of accelerators than the synthetic rubbers.

Natural Rubber requires a certain degree of mastication, that is reduction in molecular weight when subjected to severe mechanical working, to facilitate processing. Peptizers are often used to facilitate breakdown of the rubber during mixing [5].

The properties of Natural Rubber form the model for the ideal elastomeric properties, which include rapid extensibility to great elongations, high stiffness and strength when stretched, and rapid and complete retraction on release of the stress. In addition, it exhibits a low rolling resistance combined with a low degree of heat buildup, which makes it the ideal material for the tire industry [6].

3. CHEMICAL MODIFICATION OF NATURAL RUBBER

Owing to its outstanding properties, Natural Rubber is extensively used in tires, gaskets, seals, vibration mounts, and many other auto parts. However, NR is known to have poorer aging properties and weather resistance. Thus chemical modifications of NR were carried out not only to improve those drawbacks but also to extend its range of end uses.

The chemical modification, which can be carried out either in the latex form, in the solution form, or in the solid form, may be classified in three main categories; namely: modification by bond rearrangement without introducing new atoms, modification by attachment of new chemical groups through addition or substitution reactions at the olefinic double bonds, and grafting a second polymer onto the NR backbone [7,8].

3.1 Modification by bond rearrangement

Examples of this type of modification are carbon-carbon crosslinking, cyclization, cis/trans isomerization, and depolymerization. Cyclized NR, for example, was formed by treating NR with a proton donor such as sulfuric acid, sulphonic acid, or by heating Natural Rubber [9]. Cyclization can be carried out by milling the acid into the rubber on an ordinary mixing roller or by allowing acid to react with the rubber solution, or by adding sulfuric acid to NR latex. The reaction which can be carried out over the temperature range of 70°C - 100°C, yielded Cyclized NR with 40-50% unsaturation and having the structure shown below:

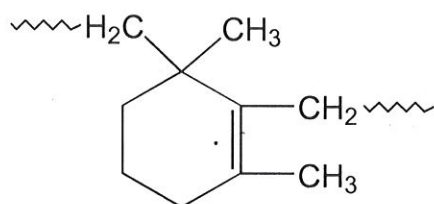


Figure 2: Chemical structure of Cyclized Natural Rubber

Cyclized NR is reported to be tough, hard and brittle but it still has some elastic behavior. It is used in adhesives and in printing ink. It is also mixed with Natural Rubber to give a higher modulus, and higher hardness blend [10].

Liquid Natural Rubber (LNR), which has a shorter polymeric chain is another form of the chemically modified NR that is the depolymerized NR. Methods used for depolymerization are chemical peptization, photolysis, and thermal, and mechanical mastication.

Thermal depolymerization yields LNR with broad molecular distribution. In the photolysis method a source of light such as solar radiation, ultraviolet light or visible light is used together with chain breaker compounds like nitrobenzene, hydrogen peroxide or photosensitizers. A great number of chemicals have been used for peptization. Examples include reducing agents like p-methyl benzene sulfuric acid, phenylhydrazine, sodium chlorite, sodium nitrite, and oxidizing agents like hydrogen peroxide or its derivatives. Liquid Natural Rubber can be used as a viscosity modifier, an adhesive, a tackifier, and as a plasticizer to improve the processability of rubbers used in rubber compounds [11].

3.2 Modification by attachment of new chemical groups

A typical example of such a modification is the chlorination which can be carried out in the solid rubber state or in the solution state or by letting the latex react with gaseous chlorine. As reported by Zhong et al. [12] Chlorinated Natural Rubber (CNR) was prepared by adding chlorine gas-saturated distilled water to stabilized NR latex with a suitable amount of potassium persulfate as a catalyst. Chlorine gas was passed continuously throughout the process, and after 45 hours chlorination up to 60% was achieved. Due to the presence of the polar Cl atom, CNR has good oil resistance, a better unflammability and a good adhesion to metal substrates. But as the level of chlorination is increased the resulting NR would become more difficult to process as the chain rigidity increases.

CNR is used as raw material for paint because of its resistance to acids and alkalis, and its wear

resistance, aging resistance, and corrosion resistance in seawater [13].

3.3 Modification by grafting

Many polymers have been grafted onto the NR chain. Grafting has been achieved using acrylonitrile, methyl methacrylate, methyl vinyl ketone, styrene, caprolactone and ethylene. However only methyl methacrylate and styrene were reported to be the most suitable monomers to yield high levels of grafting with NR.

When two grades of Methyl Methacrylate-Grafted Natural Rubber were used in a blend with Polymethyl methacrylate (PMMA) as impact modifier, the morphologies of the blend showed that the grafted NR acts as interfacial agent to improve the adhesion between the two phases. It was also found that the tensile strength, tear strength, and hardness of the blend increased with increasing level of grafting [14].

The graft polymerization of NR is not limited to the grafting of a single monomer only. Lately grafting of stearyl methacrylate and divinyl benzene onto NR has been carried out and the resulting products showed better light resistance and improved weatherability compared to those of Natural Rubber [15].

4. THERMOPLASTIC NATURAL RUBBER

The term thermoplastic elastomer (TPE) is currently used to describe a wide variety of materials that have elastomeric properties at ambient temperatures, but process like thermoplastics. The conversion process which allows a conventional rubber to behave like thermoplastics is not a simple one, and it is even more difficult with Natural Rubber, which already has predetermined chemical composition and structure.

However there are three possible routes which can be used to obtain Thermoplastic Natural Rubber (TPNR): either by the insertion of entirely new types of thermolabile crosslinks, or by the grafting of blocks of crystalline polymers onto NR chain, or by the physical blending of NR with a crystalline polymer [16].

The TPNR that will be referred to here is a mechanical blend obtained by melt mixing Natural Rubber with Polypropylene. It is therefore possible to obtain a variety of materials by this method ranging from soft TPNRs containing a high percentage of NR to semi rigid thermoplastics containing a high ratio of PP. Polypropylene was chosen mainly because of its high melting point which extends

the elastic and stiffness properties of the blend to a higher temperature level [17].

The blending of NR and PP can be carried out using the existing rubber mixing equipment such as an internal mixer. Francis Shaw [4] proposed a typical continuous line for the production of TPNR. It consists of an internal mixer, which discharges into an extruder fitted with a rod die, followed by a cooling bath, drying and pelletizing units. The internal mixer was fed with pieces of bale SMR (Standard Malaysian Rubber), pelletized Polypropylene, antioxidants and pigments and at a rotor speed of 125 rpm the machine gave a good melt blend in under 2 minutes. The material was dumped into the hopper and forced by a reciprocating ram into the extruder. By adjusting batch frequency and extruder throughput it was possible to make the process continuous.

Although any ratio of the two components is possible, efforts had been concentrated on two major TPNR grades, which are soft TPNR and hard TPNR. The former contains 65 % or more NR giving hardnesses in the range of 55 to 95 shore A and the latter contains less than 20 % of rubber.

For subsequent processing of TPNR, classical molding equipment may be used. This includes extrusion or injection molding. Compression molding would not be appropriate anymore. The optimal processing temperature in injection molding was found to be 180°C, for it would not cause excessive thermal degradation of the rubber, and molding distortion can be minimized through appropriate gate and runner designs [18]. Extensive details concerning the preparation and the properties of TPNR have already been covered in a previous publication [19].

5. CONCLUSION

Natural Rubber, which is an elastomer unique among solids owing to its particular structure, has high mechanical strength, outstanding resilience, excellent elasticity, and good low temperature resistance. In addition to these properties, its lower rolling resistance combined with high tack and low heat build up make it an ideal polymer for the tire industry. It is also used competitively with synthetic rubbers in many other engineering applications. However, NR has poorer aging properties, oil resistance, and wet grip resistance. Moreover, NR producers showed increased concern to widen its field of applications. Thus, there have been many

research projects that have sought to modify NR. Some of those studies that aimed to produce a modified form with greater oil resistance, low gas permeability, and improved damping properties, that is Epoxidized Natural Rubber, have achieved some commercial success. Others, such as those concerned with chemically modifying NR by grafting methyl methacrylate, found applications particularly as compatibilizers for some blends.

Another route for "modifying" NR to extend its range of end uses, which has gained great importance is the development of Thermoplastic Natural Rubber. TPNR's outstanding feature, as for all TPEs, is its ease of processing as well as a wide range of physical properties at service temperatures. This form of Natural Rubber, which does not alter the properties of the parent elastomer, offers great economical benefits since savings in time and energy consumption and perhaps also in the capital costs of machinery are made possible.

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