

NATURAL RUBBER: PART II: RECENT ADVANCEMENTS IN THE DEVELOPMENT OF NR-BASED TPES

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ABSTRACT

There are many reasons that made researchers investigate different ways to chemically modify Natural Rubber (NR). Before the advent of synthetic rubbers and for many decades Natural Rubber 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 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 second part of this paper is 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

Plusieurs raisons ont amené les chercheurs à modifier chimiquement le Caoutchouc Naturel (NR). Parmi lesquelles la concurrence de la part des producteurs des caoutchoucs synthétiques, et particulièrement ceux des élastomères thermoplastiques (TPE). 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.

La deuxième partie de cette publication est 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

Research on different types of Thermoplastic Elastomers is very extensive and many works have been published; among which those dealing with blends containing EPDM (Ethylene Propylene Diene Monomer) gained a great interest due to the versatility of the material, the simple preparation method and ease of tailoring the properties [1-11]. But concerning Natural Rubber-based Thermoplastic Elastomers, credit is to be given particularly to researchers of The Rubber Research Institute of Malaysia and those of The Malaysian Rubber Producers' Research Association [12] who published many works dealing with TPNR. The main fields of research on this subject can be summarized into three categories, which are:

1-The study of different crosslinking agents for the dynamic vulcanization of soft TPNR.

2-Development of different types of TPNR.

3-Investigations on the effects of the chemical modification of the NR phase in the blend.

However little work has been published on compounding TPNR.

Needless therefore to mention that the list of publications that will be briefly described in this paper is by no means exhaustive.

2. Development of Different Types of TPNR

As mentioned earlier Thermoplastic Natural Rubber can also be obtained by blending NR with different polymers other than Polypropylene. Example of such polymers is High Density Polyethylene. In this context, Coran and co-workers [13] studied the rheological and interfacial effects on the phase morphology of many rubber/plastic blends, including those of NR and HDPE, during molten state mixing, cold pressing, and compression molding. Their study was mainly concerned with soft rubbery compositions, which contained large concentration of the elastomeric phase. They revealed that the type of morphology of the blends varied with both the concentrations of the components and with the viscosity of the two phases.

Asaletha et al.[14] carried out research on another type of TPNR which was prepared from blends of Natural Rubber and Polystyrene. They studied the morphology and mechanical properties of these blends with special interest to the effect of blend ratio, processing conditions,

and vulcanizing systems. They found that the mechanical properties and morphology of the blends were much dependent on whether the samples were prepared by the melt mixing technique or by the solution casting method using chloroform, benzene, and carbon tetrachloride as the casting solvents. They also found that differences in mechanical properties and morphology were noted when varying the concentration of the crosslinking agents, which were sulfur, peroxide and mixed systems.

Latex waste is another form of recycled rubber that has been used to prepare a NR-based TPE. For example, Rajalekshmi and Rani [15] used latex waste products such as thread waste and glove waste, which contain hydrocarbon rubber of very high quality, and modified it into processable material and as a result of this modification thermoplastic elastomers were prepared by blending these modified waste materials with HDPE at different concentrations. They reported that the mechanical and rheological properties of the resulting blends were comparable to those of the Natural Rubber/High Density Polyethylene thermoplastic elastomer blends.

Shaban et al. [16] also used NR latex reclaim. They melt mixed it with PP to prepare TPNR. They examined the rheology of the blend with respect to reclaim concentration at different temperatures and found that the latex reclaim reduced the distortion of the extrudates.

Compounding ground rubber tire (GRT) with commercial polyolefins is a possible and effective way of recycling used tires and can provide new rubber/plastic TPE blend. Luo and Isayev [17] used devulcanized GRT as a blend with Polypropylene. Compounding and dynamic vulcanization were carried out using a twin-screw extruder and a Brabender internal mixer. They used sulfur, phenolic resin curing systems, and maleic anhydride grafted Polypropylene as a compatibilizer. Mechanical properties, rheology and morphology as well as thermal stability and melt behavior were evaluated. They reported that the resulting blends exhibited excellent processability along with impact strength higher than that of pure PP. They also found that the blends that were dynamically vulcanized with the phenolic resin cure system and those containing the maleic anhydride grafted PP

compatibilizer showed improved Young's modulus and tensile strength.

Suryadiansyah and Ismail [18] used recycled rubber (RR) as a fine rubber powder obtained from the sanding process of polishing rubber balls and "artificial eggs" to prepare a TPE blend of PP/RR. Their results indicated that at a similar rubber content, PP/RR blends had higher tensile strength and Young's modulus but lower elongation at break than PP/NR blends. Morphological examination of the fracture surface of the material indicated that a higher energy was needed to cause failure compared to PP/NR blends.

Another type of melt processable rubber, which softens reversibly and exhibits elastomeric properties, worth noting is the ternary blends of PP/EPDM/NR. Ashalatha et al. [19] investigated the properties of such a TPE and observed a double layered morphological structure. They particularly revealed that blends with low levels of elastomer content showed an interpenetrating co-continuous network type of morphology responsible for a remarkable improvement in impact strength.

Long term performance of NR-based thermoplastic elastomers is another aspect for which research has been devoted. For instance, Loennberg and Starck [20] who studied the weather resistance of many TPEs by measuring changes in physical and mechanical properties, found that while the tensile strength of the partially crosslinked blends decreased after prolonged exposure, the hardness and tensile modulus of some TPEs increased due to the desorption of oils. Furthermore, their results of the dynamic mechanical properties confirmed this behavior, for the differences in stiffness existing between different types of TPEs due to the exposure were consistent with the differences in hardness and tensile modulus.

3. Dynamic Vulcanization of TPNR

Rigid Thermoplastic Natural Rubber does not require a vulcanization step like classical rubbers. This factor eliminates the use of certain additives and consequently offers great economical benefits in terms of time and energy savings. Yet for soft grades where the Natural Rubber concentration is higher than 65%, partial crosslinking of the elastomer achieved during mixing is required. For this purpose many chemicals were used for the dynamic vulcanization of TPNR. For example, Elliot [21] reported that N,N' meta-

phenylene bismaleimide (HVA 2) gave well balanced properties in terms of thermal stability of the crosslinks, recovery behavior of the blend and at the same time had no oxidative side effects to Polypropylene. As a result the material has higher tensile and tear strengths, reduced stress relaxation and creep, and less swelling in oils and solvents.

In another publication [22], Elliot concluded that despite the presence of chemical crosslinks resulting from dynamic vulcanization by means of different agents ranging from sulfur, sulfur donors, and peroxides, the blends retain their thermoplasticity, and exhibited an important improvement in compression set compared to the reference SBS thermoplastic elastomer.

In an update on TPNR blends, Tinker [23] reported that the amount of peroxide, as a crosslinking agent, had a pronounced effect in the soft grade of TPNR containing 85% NR compared to a blend containing only 65% NR. He also concluded that dynamic vulcanization by 0.2% peroxide improved the compression set of the material.

It is possible to partially crosslink the rubber phase in a TPNR blend by physical means such as radiation. For instance, Ghazali and co-workers [24] investigated the suitability of foaming thermoplastic elastomer blends of NR and EVA using different chemical blowing agent. They reported that partial crosslinking was achieved by exposing the TPNR to different electron beam irradiation doses and that the foam density was dependent on the concentration of the blowing agent.

4. Chemical Modification of the NR Phase in the Blend

Research concerning TPE has recently been oriented towards using different modified forms of Natural Rubber. These include blends of Epoxidized Natural Rubber (ENR) with PVC, and PMMA grafted NR with NR. The distinct features of ENR which are its good air impermeability, excellent oil resistance, and improved compatibility with Nitrile rubber, Chloroprene rubber, and with PVC, made it attractive to produce useful TPE. In this context, Ishiaku and co-workers [25] studied the thermo-oxidative aging of thermoplastic elastomer blends of ENR with PVC. The preparation was carried out in the mixing chamber of a Brabender plasticorder, and unaged as well as aged blends were characterized by means of FTIR, tensile properties, tear strength, hardness

and dynamic mechanical analysis (DMA). They reported that the improvement in all the properties suggested that the ENR can be used to make stable TPEs which are much less sensitive to thermo-oxidative aging. Their DMA results gave a single Tg indicating compatibility of the two phases.

In another study, Ishiaku et al. [26] investigated the effects of an epoxidized plasticizer on the mechanical properties and thermo-oxidative aging behavior of PVC/ENR thermoplastic elastomers. They compared the properties of the epoxidized Soya oil (ESO) plasticized TPEs with those of the di-2-ethyl hexyl phthalate (DOP) plasticized counterparts. They found that the presence of epoxide groups in ESO had been shown to produce two conflicting effects. On one hand, the presence of excessive epoxide groups had resulted in poor aging behavior. On the other hand, it had resulted in a good interaction and compatibility with the blend. They also reported that the tensile strength of the ESO plasticized blends were comparable with the DOP plasticized ones, but the elongation at break of the ESO blends fell below that of the DOP blends. They concluded that despite the fact that the retention of both tensile properties for the ESO blends was poorer than for the DOP blends, and that hardening and embrittlement also occurred in the ESO blends, epoxidized Soya oil could be an ideal plasticizer for the ENR/PVC system as indicated by plasticizer performance and the greater efficiency of plasticization.

Mousa and co-workers [27-29] also investigated the thermo-oxidative aging of dynamically vulcanized PVC/ENR thermoplastic elastomers. The blends were prepared by melt mixing in a Brabender plasticorder in the presence of a plasticizer. Various concentrations of a semi-efficient sulfur curative system were added during the mixing stage. The effectiveness of dynamic vulcanization was studied using the Brabender plastograms, a Mooney disc rheometer, swelling index measurement, and Fourier Transform Infrared Spectroscopy and the data obtained were correlated with the mechanical properties of the materials. They found that all physical and mechanical properties increased continuously with increasing sulfur concentration. They indicated that a steady reduction in swelling index with increasing concentration of curatives was excellent evidence for a significant increase in

crosslink density. They also reported that the thermo-oxidative aging process resulted in a significant enhancement in the mechanical properties with the exception of elongation at break. This observation seemed to indicate that some microstructural changes, such as the formation of new crosslinks, had taken place in the aged TPEs.

In another publication, Mousa et al. [30] reported the results of the oil resistance studies of PVC/ENR thermoplastic elastomers. The blends which were dynamically vulcanized were exposed to two types of environments; namely air and oil under identical conditions. The effect of oil and thermo-oxidative aging on the tensile properties, tear strength, and hardness were determined at room temperature and at 100°C. They found that at ambient temperature the samples immersed in oil possessed similar properties to those which were exposed to air. Significant enhancement in mechanical properties were observed for both environments at 100°C. this trend had been attributed to the increase in crosslink density that was manifested by a steady reduction in the swelling index with increased sulfur concentration. They concluded that the excellent mechanical behavior of the Poly Vinyl Chloride/Epoxidized Natural Rubber TPE even after immersing the samples in oil at high temperatures provided a good indication of the oil resistance of the materials.

It is clear from the above papers that the solid form of ENR/PVC-based TPEs gained significant importance; however there has been little attention given to the cellular blends. In this context, it is worth noting two papers dealing with foamed NR-based TPEs. The first one which is reported by Metherell [31] presents the physical properties of expanded rubbers made from Natural Rubber, two grades of Epoxidized Natural Rubber and blends of the latter with PVC. In this study many formulations were prepared using fine particle size grade of talc in order to insure good nucleation of pores and uniform cell distribution, along with three different blowing agents which were benzene sulphonylhydrazide, para toluene sulphonylhydrazide, and azodicarbonamide. Materials with densities as small as 0.15 gr/cc were obtained, all with very fine closed cell structures. He reported also that the resulting TPEs possessed very low compression set and water absorption.

In the second study, Kropp et al. [32] conducted an experimental investigation on the foamability

of different TPEs using CO₂ as the blowing agent. For each material, different foaming temperatures as well as blowing and nucleating agent concentrations were examined. They reported that while the SEBS type of thermoplastic elastomer showed the best foamability, the PP/EPDM blend was most difficult to foam.

Concerning the second type of chemically modified NR-based TPE, Oommen and Thomas [33] used a ternary blend of Natural Rubber/Poly Methyl Methacrylate/Natural Rubber-grafted Poly Methyl Methacrylate. They investigated the mechanical properties and fracture behavior of the TPE as a function of composition, graft copolymer concentration, and mixing conditions. They found that the domain size of the dispersed phase decreased with graft copolymer concentration followed by a leveling off at higher concentration. They also reported that the mechanical properties attained a maximum value at the leveling point, which was an indication of interfacial saturation and the attainment of maximum interfacial adhesion between the homopolymers. The examination of the tensile and tear fractured surfaces by means of scanning electron microscopy revealed that the detachment of the dispersed domains from the matrix was an indication of no adhesion between the two phases in the case of uncompatibilized blends, while the presence of micro fibrils between the matrix and the dispersed phase indicated some type of interfacial adhesion between the phases in the case of compatibilized blends.

Structural variables of the rubber phase in the blend such as molecular weight and molecular weight distribution have also been investigated. Madkour and Mark [34], in their simulation of the effect of molecular weight and molecular weight distribution on the properties of thermoplastic elastomeric polypropylene, indicated that degrees of crystallinity and melting points should generally increase with increase in molecular weight and with decrease in polydispersity. They also concluded that the elastic modulus, based on the crystallites acting as temporary crosslinks in an elastomeric network, generally behaved similarly but were sensitive to those variables.

5. Applications

It has been estimated that 1.2 millions of tons of thermoplastic elastomers would be used in the year 2002 [1]. Their consumption is continuing

to increase by 10-12% per year [2]. Such a strong growth year after year is the result of the growth of existing applications, but even more, by the use of these materials in new applications. Their performance gets more and more accepted throughout the industry segments such as the automotive and construction sector in addition to many engineering applications. Due to their combined excellent processing characteristics and a wide spectrum of physical properties, they are now being used in fields that were the predominance of vulcanized rubbers or as partial substitute for them.

In view of the amount of rubber produced and consumed worldwide, it has been necessary to deal with the recycling of rubber rejects and waste. In this context and as was mentioned earlier, many studies [63-66] dealing with the development of rubber waste-based materials have concluded that these thermoplastic elastomers can contribute into providing adequate solutions to the recycling problems.

The impact of TPEs on rubber part economics and performance can best be seen by considering the following examples. The balance properties of hard TPNR grades are suitable for use in car components such as bumpers, body protection strips, and radiator grilles. The other potential usage is in items such as electric plugs, tool handles, railway pads, and floor tiles. The major potential usage of soft TPNR grades is in products such as footwear, sports goods, hose and tubing, and profiles for seals [35].

6. Conclusion

Thermoplastic Elastomers (TPE) are a unique class of materials which exhibit the outstanding physical and mechanical properties of elastomers and the excellent processing characteristics of thermoplastics.

Research concerning this type of materials is very extensive and a great number of works have been published. The investigations dealing with Natural Rubber-based TPEs, or Thermoplastic Natural Rubber (TPNR), focused on developing different types of TPNR, studying numerous crosslinking agents for dynamic vulcanization, and tailoring the chemical modification of the NR phase in the blends. Since the excellent properties of Natural Rubber are not lost through those various processes of modification, the advantages of using these

materials are enormous. Owing to their performance they are opening up new frontiers in polymer applications. Currently efforts are directed towards upgrading the performance of TPNR so that it would be used in the more lucrative field of automotive tire treads.

7. References

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