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An Analysis on Various Properties and Durability of Natural Rubber

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Abstract* – *The focus of this research was to investigate the effect of thermal degradation upon the mechanical properties of natural rubber compounds and apply those effects to the life prediction of off axis 2-ply cord rubber laminates. The work examined both the quasi-static and dynamic mechanical properties of two natural rubber vulcanizates, which had been subjected to isothermal anaerobic aging.

Thermal aging was performed on two different natural rubber vulcanizates. The thermal aging was conducted between the temperatures of 80 and 120°C for times ranging from 3 to 24 days. The effect of thermal degradation was measured from the changes in the chemical composition of the vulcanizates as functions of time at temperature. A master curve relationship between the changes in the chemical composition of the vulcanizates due to thermal degradation and their static and dynamic mechanical properties has been developed. This relationship allowed for the prediction of the vulcanizate mechanical properties after thermal aging. It was found that the mechanical properties correlated with the percentage of poly and monosulfidic crosslinks, where in general higher levels of polysulfidic crosslink gave rise to the highest mechanical properties.

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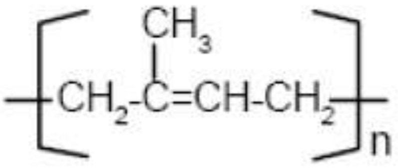
INTRODUCTION

Natural rubber is the prototype of all elastomers. It is extracted in the form of latex from the bark of the Hevea tree. The rubber is collected from the latex in a series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety of grades based on purity (color and presence of extraneous matter), viscosity, viscosity stability, oxidation resistance, and rate of cure. Modified natural rubbers are also available, with treatment usually performed at the latex stage. These include:

1. epoxidized natural rubber (ENR).
2. deproteinized natural rubber (DNR).
3. process oils have been incorporated.
4. Heveaplus MG rubber − natural rubber with grafted poly (methyl methacrylate) side chains.
5. Thermoplastic natural rubber (TNR) – blends of natural rubber and polypropylene.

The natural rubber polymer is nearly 100% cis-1,4 polyisoprene with Mwranging from 1 to 2.5 x 10^6. Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. Low temperature crystallization causes stiffening, but is easily reversed by warming. Crystallization gives natural rubber high tensile strength and resistance to cutting, tearing, and abrasion.



Natural rubber NR
Polyisoprene IR

Like other high polymers, natural rubber can be pictured as a tangle of randomly oriented sinuous polymer chains. The “length” of these chains is a function of their thermodynamic behavior and is determined as the statistically most probable distance between each end. This chain length reflects the preferred configuration of the individual polymer molecule. The application of force to a rubber sample effectively changes the chain length. When the force is removed, the chain tries to regain its preferred configuration. In simple terms, this can be compared to the compression or extension of a spring. This effect is the basis of rubber’s elasticity.

Elasticity is one of the fundamentally important properties of natural rubber. Rubber is unique in the extent to which it can be distorted, and the rapidity and degree to which it recovers to its original shape and dimensions. It is, however, not perfectly elastic. The rapid recovery is not complete. Part of the distortion is recovered more slowly and part is retained. The extent of this permanent distortion, called permanent set, depends upon the rate and duration of the applied force. The slower the force, and the longer it is maintained, the greater is the permanent set. Because of rubber's elasticity, however, the permanent set may not be complete even after long periods of applied force. This quality is of obvious value in gaskets and seals.

The rubber's polymer network allows elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched. The elastic nature of this network also accounts for the exceptional resilience of cured rubber products. This resilience means less kinetic energy is lost as heat during repeated stress deformation. Products made from natural rubber are less likely than most other elastomers to fail from excessive heat buildup or fatigue when exposed to severe dynamic conditions. This has secured the place of natural rubber as the preferred sidewall elastomer in radial tires.

As already noted, the rubber polymer network was originally an impediment to rubber processing. Mixing additives with a tough, elastic piece of raw rubber was a substantial challenge. The solution came with the discovery of its thermoplastic behavior. High shear and heat turn the rubber soft and plastic through a combination of extension, disentanglement, and oxidative cleavage of polymer chains. In this state it is considerably more receptive to the incorporation of additives so that the rubber's natural attributes can be modified and optimized as desired. The commercial utility of natural rubber has in fact grown from the ease with which its useful properties can be changed or improved by compounding techniques.

Another important and almost unique quality of uncured natural rubber compounds is building tack. When two fresh surfaces of milled rubber are pressed together they bond into a single piece. This facilitates the building of composite articles from separate components. In tire manufacture, for example, the separate pieces of uncured tire are held together solely by building tack. During cure they fuse into a single unit.

Natural rubber is used in the carcass of passenger car cross-ply tires for its building tack, ply adhesion, and good tear resistance. It is also used in the sidewalls of radial ply tires for its fatigue resistance and low heat buildup. In tires for commercial and industrial vehicles, natural rubber content increases with tire size. Almost 100% natural rubber is used in the large truck and earthmover tires which require low heat buildup and maximum cut resistance. Natural rubber is also used in industrial goods, such as hoses, conveyor belts, and rubberized fabrics; engineering products, for resilient load bearing and shock or vibration absorption components; and latex products such as gloves, and adhesives.

LITERATURE REVIEW

Natural rubber is a heavily researched material. Aspects of natural rubber that have been researched include the: fatigue of rubber, crack growth analysis and fracture, rubber filler interactions, rubber crystallization, aging of rubber, rubber reversion, molecular orientation of rubber and cord rubber composites. The review of the investigations performed by other researchers provides a foundation for this dissertation. This literature review will attempt to cover nearly all aspects of the research that has been conducted on natural rubber as well as other rubbery materials. An emphasis will be placed on the concepts of energy, temperature, crack growth and aging.

Fatigue of Rubber - Research into the fatigue of rubber has focused on the mechanics of fatigue failure as well as on the development of relations to predict failure. The work of Rivlin et al. was the most influential in changing how the fatigue failure of rubber was conceptualized. Rivlin et al. developed a criterion for the tearing of a rubber vulcanizate that was independent of the form of the test piece. This form was based upon the Griffith failure theory that describes the slow propagation of a crack as the conversion of elastic energy stored in the bulk to surface free energy. Griffith postulated that at constant overall deformation, the changes in the elastically stored energy due to an increase in crack length were balanced by the energy used in the creation of new surfaces. However, Rivlin et al. postulated that under the same conditions the changes in the elastically stored energy were balanced by changes in the internal energy. This energy was then the work expended irreversibly per centimeter increase in crack length and per centimeter thickness of the test-piece. This criterion of Rivlin et al. was deemed the tearing energy criteria and it was shown that this characteristic energy could be found experimentally for a particular vulcanizate and used to predict the force required to tear test pieces of that vulcanizate.

Crack Growth Analysis and Fracture - Application of the tearing energy criterion to the crack growth and fracture of NR has been performed. Lake et al. have further shown that the rate of crack growth is independent of sample shape and type of deformation when expressed in terms of the elastic energy. Their work was aimed at determining the mechanism of groove cracking in tire treads. Lake et al. applied a method which enabled the elastic energy to be estimated for a tire groove from measurements of the crack opening area upon an applied stress. The method also enabled Lake et al. to determine the strain within the sample. Lindley investigated three methods of determining the tearing energy: from changes in total energy, from crack surface displacements and by comparison with known values for the same crack growth rates. It was found that all three methods, when applied to plane stress specimens, were satisfactory in determining the energy for crack growth in model rubber components. Particularly, the crack-surface-displacement method, similar to Lake et al., was found to be the most satisfactory.

Rivlin et al. examined the effect of stress relaxation on the resistance of an elastomer to tearing. In their investigation, Rivlin et al. utilized a two-network model for an elastomers in which stress relaxation has already occurred.

Rubber Filler Interaction - The interaction between the rubber and the filler has been studied to determine the effects on failure of the compounds. Neogi et al. have researched the high temperature interaction between rubber and filler by using the strain amplification factor. When carbon black is added as reinforcement, the degrees of freedom of the rubber chains are decreased due to the interaction and adsorption of nondeformable carbon black onto the rubber. Upon an applied load the rubber must bear the total strain; however, the local strain within the rubber phase is greater than the global strain attained by the system.

Chung et al. investigated the effects of carbon black on the ultimate properties of an elastomer. They examined both the critical tearing energy as well as a critical J-integral. They found that for NR compounds, crystallization could be observed near the crack tip. Crystallization hindered the crack propagation through the thickness of the specimen. The level of carbon black loading moderately affected the To of the NR compounds, with the value ranging from 4.1 kN m^{-1} to 6.9 kN m^{-1}. The true modulus of the compound was found to increase with increasing levels of carbon black.

Aging of Rubber - The effects of aging on rubber have been studied to determine the time dependent effects on NR compounds. The bulk of the research into the aging of rubber has concentrated on the oxidative effects. Thermal effects on the properties of natural rubber will be discussed in the context of rubber reversion. Oxidative effects occur when oxygen attacks the unsaturated bond along the backbone of the polyisoprene, natural rubber, chain. Braden and Gent have defined the characteristics of static crack growth due to ozone. The research of Braden and Gent concluded that a critical tearing energy is necessary for cracks to grow, crack length increases linearly with time for $T > T_o$ and the rate of crack growth is similar and proportional to the ozone concentration.

REACTIVE COMPATIBILIZATION OF NATURAL RUBBER

Natural rubber (NR) is an important elastomer which exhibits excellent mechanical properties, and has been widely used in several areas of engineering and industry. However, due to its non-polar nature and reactive double bonds in the structure, the resistance of NR in oil and aging on exposure to oxygen, ozone and heat is poor.

In order to achieve properties that cannot be obtained by individual polymers, polymer blends are often used to combine the physical characteristics of both polymers. Thus, elastomer blends are frequently used in a wide range of engineering and industrial applications to obtain the best compromise in compound physical properties, processability and cost. However,except for a few polymer pairs that are known to be thermodynamically miscible, most polymer pairs are immiscible.

Immiscible polymer systems display lower mechanical properties than those of their components, due to their unstable morphology and poor adhesion between phases. The desired properties of immiscible polymer systems are not achieved without a third component, i.e., a compatibilizer, which reduces the interfacial tension and enhances the interfacial adhesion between component phases so that applied force can be effectively transmitted between component phases.

Over the years, traditional compatibilization strategies have been employed to alleviate the problem of poor interfacial adhesion between polymer phases, which involve the addition of a pre-made block or graft copolymers composed of the blocks or grafts, which are identical with or miscible with the component polymers. A more recent approach which has proved to be generally more effective and less expensive, and more frequently used for industrial applications is the reactive processing or the reactive blending, in which the block or graft copolymer can be generated in-situ at the interface between phases by the coupling reaction of functionalized components.

Basically, the performance of elastomer blends is largely governed by various factors which includes the nature of elastomers, blend compositions, phase morphology of elastomer blends, nature of compatibilizer and interfacial cross-linking in elastomer blends. For example, in a study by Kwaruethai et al., zinc salts of sulphonated natural rubber (Zn-SNR)(a rubbery ionomer) containing 17.5meq/100 of SNR was prepared and used as a new compatibilizer for the preparation of NR and chlorosulphonated polyethylene rubber (CSM) blends. Epoxidized natural rubber (ENR-20) was also used as compatibilizer for such blends. They found that the shear viscosity of the blends with ionomers was higher than that of the neat blends, suggesting strong interaction between rubber phases. They also reported a greater level of enhancement in 100% modulus, tensile and tear strength for the blends containing 17.57 Zn-SNR compared to those of ENR-20. Similarly, Sirinha et al. reported improved oil and thermal aging resistance when NR was blended with chlorinated polyethylene rubber.

Blends of NR with carboxylated styrene-butadiene rubber (XSBR) and ethylene-propylene-diene rubber (EPDM) were reported to have better aging and ozone resistance. Sirinha et al. have demonstrated that improved phase morphology in blends of NR and nitrile rubber (NBR) resulted in an increased oil resistant property of the blends. Blends of CSM and NR have been studied by Tanrattanakul and Petchkaew.. They reported that blends of NR and CSM were immiscible, except for NR-rich blends (70-80 wt% of NR), and that oil and ozone resistant properties of the blends increased with increase in CSM loading. They also found that further improvement in mechanical properties and compatibility of the blends could be obtained when a suitable compatibilizer, such as epoxidized natural rubber (ENR), was added to the blends.

Carboxylated nitrile rubber (XNBR) is an important elastomer which has found increasing use in many engineering and industrial applications due to its outstanding oil and solvent resistant properties. In the present study, the reactive compatibilization of NR/XNBR blends by maleic anhydride-grafted-polyisoprene (MAPI) and epoxy resin dual compatibilizers is reported. The presence of a multifunctional epoxy resin in the XNBR-NR-MAPI blend has the potential to produce XNBR-co-epoxy-co-MAPI copolymer at the interface, which is able to function as an effective compatibilizer.

To the author’s knowledge, there has been no attempt to use maleic anhydride-grafted-polyisoprene/epoxy resin as compatibilizer for NR/XNBR blends. However, Naskar et al. had reported a novel method for preparation of carboxylated nitrile rubber (XNBR)-natural rubber (NR) blends using Bis(diisopropyl)thiophosphoryl polysulphides as a compatibilizer. They found that oil resistance and mechanical properties of the NR/XNBR blends strongly depended on blend ratios and the degree of interfacial cross-linking between NR and XNBR components.

USE OF NANO ZINC OXIDE IN NATURAL RUBBER

Natural rubber (NR) is a high molecular weight polymer of isoprene (2-methyl-1,3-butadiene). It is the oldest known rubber and the most versatile one for fabrication of rubber products. The high and reversible deformability of natural rubber is of great industrial importance. However, its initial modulus and durability are low and an additional reinforcement is required for practical applications. Carbon black and precipitated silica have been extensively used for this purpose. In addition, CaCO3, ZnO, MgO, talc, mica etc. have also been used.

Zinc oxide is added to rubber compounds as an activator to activate sulfur vulcanization and thereby reduce the vulcanization time. Besides its effect on the curing process, ZnO has many beneficial effects on the physical properties of rubber. Furthermore, ZnO assists in the processing of uncured rubber. ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes. Nieuwenhuizen in his study proposed a mechanism in which the ZnO surface function both as a reactant and as a catalytic reaction template, activating and bringing together reactants. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed onto ZnO with the formation of intermediate complexes. Fatty acids are generally regarded as indispensable activators in conjunction with zinc oxide. The function of fatty acid activators such as stearic acid, is to solubilize the zinc oxide, a secondary effect is an increase in the amount of zinc sulphide produced. The zinc salts of fatty acids, which are a type of surfactant , also solubilize insoluble accelerators to form the actual catalyst.

In some rubbers such as natural rubber (NR) and ethylene-propylene diene rubber (EPDM), there is evidence that a considerable amount of ZnO is consumed and transformed into ZnS. The zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in rubber industry is, therefore, to reduce the zinc content in rubber products.

CONCLUSION

The focus of this research was to investigate the effect of thermal degradation on the mechanical properties of natural rubber compounds and apply those effects to the life prediction of 2-ply cord rubber laminates. The investigation focused on two different natural rubber compounds. Both compounds were 100 percent natural rubber with 65 pphr carbon black. The research into the mechanical properties was divided into two aspects quasi-static and dynamic. The quasi-static properties investigated were the ultimate stress, ultimate strain, shear strength and the modulus. The dynamic properties investigated were the R-ratio, fatigue life and crack growth rates.

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