EFFECT OF MECHANICAL PROPERTIES ON BLENDS OF ACRYLONITRILE-BUTADIENE RUBBER WITH STYRENE-BUTADIENE RUBBER

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ABSTRACT: *Acrylonitrile butadiene rubber (NBR) and styrene-butadiene rubber (SBR) are commonly used elastomers in the rubber industry. The blending of NBR being hard, oil-resistant, but expensive with SBR being stronger and cheaper can result in a relatively low-cost rubber compound with good mechanical properties along with some oil resistance. This project aims to study the effect of mechanical properties of the rubbery polymeric blend concerning variation in the NBR to SBR blend ratio. NBR/SBR blend samples with different NBR to SBR ratios were compounded on the industrial two-roll mill and cured on a hand-operated industrial compression set. Tensile and hardness tests were performed on each sample. The test results gave an insight into non-linear and somehow sinusoidal values of the tensile strength of the blends concerning the blend ratio. Results also highlighted the non-linear relation between hardness and % NBR in the blend composition. It was found that the immiscibility of the blend inconsistency in results can become more prominent. If the blending scheme is applied industrially, that can lead to significant property deviations from the desired set points. This blending technique cannot be used for producing engineering products due to the precisely excellent properties required in such products and is suitable for producing commodity products.*

Key Words: Acrylonitrile butadiene rubber; styrene-butadiene rubber; blends; tensile; hardness.

1. INTRODUCTION

Rubber or elastomer is a class of polymers defined as materials that can be repeatedly stretched to over twice their standard length and have the capability to return to their original length when released immediately. Elastomers can be either thermoplastics or thermosets, but if thermosets are so lightly cross-linked that substantial hardening does not occur. Crosslinking is sufficient that they cannot be melted after shaping [1]. Rubbers generally have long macromolecular chains with structural units arranged in a spatially oriented manner. This morphological characteristic enables the movement and rotation of the segments around the chemical bonds even at normal and room temperatures [2].

Natural rubber's essential ingredient is extracted from the sap of a specific plant and then further processed, whereas Synthetic rubbers are usually synthesized using different petrochemical compounds. For the area of application and general characteristics, the elastomers/rubbers can be divided into two categories: General purpose rubbers and specialty rubbers. General-purpose rubbers have properties that satisfy the requirements of a wide range of products. Such rubbers are relatively cheap and are produced in large volumes due to their high demand. Common examples include SBR, butadiene rubber, NR, and synthetic isoprene rubber. Specialty rubbers are along with basic elastic properties and have some special feature that distinguishes them from general rubbers. These features can be either aging resistance, chemical resistance, temperature resistance. These are generally in lower demand and have specific application areas; therefore, they are much costlier. Examples can be chloroprene, fluorine rubbers, epoxidized rubbers [3].

Unlike the thermoplastic elastomers that have recently begun to find their place in the rubber market, vulcanized rubbers (thermoset elastomers) have a long development history since the beginning of the 20th century. The quest for elastic materials with unique properties leads to the synthesis of new rubbers with special characteristics [4]. Along with new developments in the synthesis of new rubbers, rubber experts have done a lot in rubber additives such as fillers, softeners, antioxidants, colorants, and reinforcing materials. To achieve a combination of the unique properties of rubbers such as chemical resistance, mechanical strength, and cost. Through compounding of rubbers with additives, a combination of various properties can be achieved in the produced rubber parts such as sustainability over a wide range of temperature, low thermal conductivity, good compression and tear strength, low hardness along with high tensile strength, the good capability to elongated, resistance to chemicals such as oils and fuel, good electrically insulating capability and anti-static properties, compatibility with different materials (good metal adhesion) and vibration-damping capability. Numerous raw rubbers are available with distinct properties and capabilities according to their molecular structure and cross-linking capabilities. Several of them are listed here, along with some of their specialties [4, 5].

Natural rubber, or as its chemical structure is defined, poly-isoprene is rubber with a natural original from the sap of a plant named Hevea Braziliensis. It is the earliest rubber discovered in modern days. Products made from natural rubber have good mechanical strength and excellent elasticity. Its excellent dynamic mechanical properties make it a good choice for automobile tires, vibration mounts, and rubber springs. Its low cost and good abrasive strength enable it to be used in slurry pump liners, impellers, and tank linings. Synthetic polyisoprene is a counterpart of the natural rubber with properties similar to NR but with a petrochemical origin [6].

One of the first synthetic rubbers produced in the modern days is butadiene rubber. The rubber structure is similar to the poly-isoprene with four carbon atoms in the backbone of the repeating unit with a single double-bond. Its similarity results in similar cross-linking performance. There is also a difference in the structure of the two rubbers, which is the presence of two hydrogen atoms attached to the backbone carbon-carbon double bond instead of hydrogen and a methyl molecule (as in the case of poly-isoprene). The absence of a methyl group in the backbone of poly-butadiene results in poor tensile strength, tear-resistance, and tack than poly-isoprene. The advantages of poly-butadiene are low cost, improved low-temperature flexibility, compatibility with many other polymeric materials, and good metal adhesion. These advantages have led directly to some unique applications for unmodified poly-butadiene and the development of ways to modify poly-butadiene to improve its physical properties [7]. Butadiene-styrene rubbers (SBR) are among the most frequently used elastomers in the rubber industry. It is a copolymer of butadiene and styrene monomers. The arrangements of the styrene and butadiene monomer units form in the partial block. Its properties are affected by the structural arrangement of both the butadiene and styrene units. Figure 1 shows the chemical structure of the SBR.

The higher the styrene content is, the higher its T_g will be. Similarly, higher styrene content lowers the price but exhibits good wear and abrasion resistance and improves the blend properties [8]. The styrene in SBR contributes to the skid resistance in tires and through the damping effect. Generally, the bound styrene content in SBR is in the range of 23 – 40%. Mainly SBR is produced through radical copolymerization in the emulsion. It is also produced by anionic copolymerization in solution. Emulsion SBR has a high molecular weight, broad molecular weight distribution, and a high degree of branching. However, Emulsion SBR (E-SBR) has a lesser demand than solution SBR (S-SBR) because S-SBR exhibits better properties when used in high-performance tires. However, emulsion SBR grades account for more than 75% of the total world capacity of SBR production as of 2015 [8]. SBR's fatigue resistance, along with its properties at low temperatures, are lower concerning NR, while its heat aging properties and abrasion resistance are greater than those of natural rubber. SBR is more affected by thermal and oxidative degradation. Degradation usually occurs due to cross-linking during service life, which causes stiffness and embrittlement in the rubber product. SBR shows poor chemical resistance; therefore, it has lower solvent resistance and weathering properties than almost all the other rubbers. Like other unsaturated rubbers, SBR is also generally vulcanized through sulphur systems. It has a low strength which makes use of active fillers in its formulation necessary. The rate of degradation in SBR is lesser than NR, but still, there is a need to add anti-degradation agents. SBR is the highest produced synthetic rubber by volume. It is a premium material in drive couplings, haul-off pads, conveyor belts, and car tires. Its working temperature range is from -45°C to 107° C [8].

Nitrile butadiene rubber is a copolymer of butadiene and acrylonitrile monomers. NBR's unique properties include good chemical resistance against nonpolar solvents, diesel, gasoline, fats, and oil. The chemical structure of NBR is shown in Figure 2. The acrylonitrile content mainly dictates the significant characteristics of NBR. The increase in acrylonitrile content results in vulcanizers having improved resistance to swelling against polar solvents. The polymer becomes highly miscible with polar solvents and plasticizers. Elasticity and flexibility deteriorate, but workability improves simultaneously [9]. NBR has lower strength, shows lesser resistance to oxidation and ozone. It is only suitable for application at temperatures lower than 250°F. NBR finds its application in the oil and gas industry, automotive, bowling pinsetters, and sealing. Its working temperature range is from -40°C to 121°C [4].

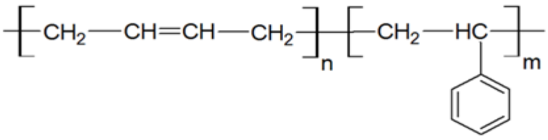


Figure 1. SBR chemical structure

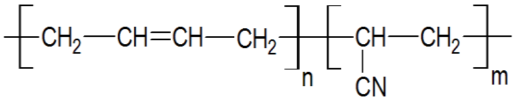


Figure 2. NBR chemical structure

These rubbers are synthesized by copolymerizing ethylene and propylene to get EPM (ethylene propylene monomer with a methylene backbone) and adding a non-conjugated double bond monomer to get EPDM (ethylene propylene diene monomers, also with a methylene backbone). In both EPM and EPDM, the backbone of the material is fully saturated; that is, there are no carbon-carbon double bonds. In this respect, EPM and EPDM differ from most of the other elastomers considered up to this point. EPM has excellent elongation, but the absence of cross-linking results in a prolonged and incomplete material recovery after the elongation. Therefore, cross-linking capability to this polymer was added by the addition of a non-conjugated diene monomer producing EPDM rubber.

Furthermore, other methods were developed to cross-link the EPM rubber to give it complete elastomeric properties. These rubbers have good thermal, UV, and anti-oxidative stability. Also, their nonpolar nature gives them excellent water resistance but low oil resistance. The main applications of these rubbers comprise automotive window seals, trunks and doors, roofing membranes, hose, tubing, and cable coatings [5].

Rubber Compounding

The raw form of rubber cannot be used in the pure form because of low mechanical properties and low working temperature range. Hence rubber gum is compounded with a set of materials and chemical agents that assist it in cross-linking and enhancing its properties to the desired level. These compounding materials are of different types and are responsible for various properties in the final rubber product. These can be divided into other classes. Synthetic elastomers have no inherent reinforcing properties, which result in low abrasion resistance, lower hardness, and lower strength; as a result, fillers are used, which are classified as reinforcing fillers and non- reinforcing fillers. The incorporation of filler thus improves the processability, performance properties, reduces cost, and imparts its color. There is a necessary condition for the filler reinforcement to occur, which is the interaction between the filler particles and the polymer. The interactions are termed as strong interactions when a covalent bond forms between the functional groups of the polymeric material and the filler surface. The interaction is termed as weak interaction in the case of attractive physical forces, and thus a need for a coupling agent arises [10].

Reinforcing fillers are a type of particulate material that, when added to rubber compounds, can improve the tensile properties, abrasive strength, and tear resistance of the resulting vulcanized products. Carbon black is one of the essential reinforcing fillers in the rubber industry. It is a type of colloidal form of hydrocarbon with good chemical stability and has a high surface area of about (6-15) m^2/gm, and is produced by thermal decomposition of hydrocarbon (soot) [11]. Carbon black improves the tensile strength, modulus of elasticity, the fatigue resistance of the final product formed.

The carbon black is composed of three colloidal particles morphological forms in rubber compounding, which includes (primary particle, aggregate, and agglomerate). The sizes of these morphological forms increase in the given order; particle < aggregate < agglomerate. Single carbon black particles usually have their particle size in 15nm - 300nm and are the fewest used in the rubber industry. The aggregates do not break during rubber compounding and have their particle size ranges 85nm – 500nm. The commonly used carbon black to rubber compounding as agglomerate consists of a group of aggregates and have their particle size ranges 1µm - 100µm. Requires a large amount of energy to be broken down during the rubber compounding process due to its high attractive forces among black carbon particles, as shown in Figure 3 [11].

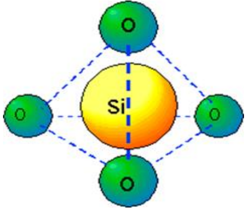


Figure 3. Silicon dioxide molecule

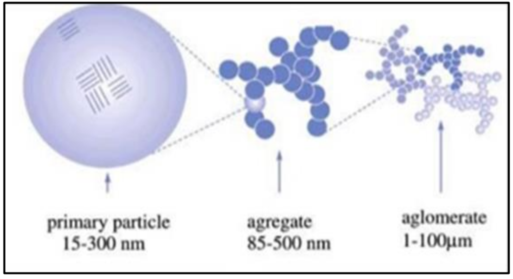


Figure 4. Carbon black particle size

Silica is referred to as silicon dioxide (SiO_2) formed by the four covalent bonding of four oxygen atoms and a central silicon atom, as shown in Figure 4. There exist two types of silica: precipitated silica and fumed silica. In the rubber industry, economic precipitated silica is used. Silica, used as the rubber reinforcing filler, has a specific surface area of 25–250m^2/g. The silica generally exists as aggregates and agglomerates. The silica usually exists as aggregates and agglomerates when it exits hydrogen on the silica surface, which causes severe problems in rubber compounding, such as poor dispersion of silica [11].

Unlike reinforcing fillers, this class of fillers is generally used for purposes other than reinforcing the final product. Typical examples are alumina fillers, talc, clay fillers, and titanium oxide. Alumina is commonly referred to as, consisting of aluminum oxide (Al_2O_3), which is a widely-used engineering – ceramic material. Al_2O_3 has strong inter-atomic bonding, which results in high compressive strength, good abrasion, and wear resistance, and also possesses fair corrosive and thermal resistivity when exposed to harsh environmental conditions. Alumina filler used in the industry have purity in the range of about 95 % to 99.99 % and has potential applications where abrasion resistance and dimensional stability is required at elevated temperature. Talc is a finely milled mineral consisting of Mg and Al silicate. As an inert filler, talc is mainly used in compounds requiring heat-resistant properties such as autoclave sealing. It also hinders the rubber surfaces from sticking to each other. The clay fillers are the class of fillers commonly used non-black fillers in the rubber industry. Clay minerals, when used, impart good reinforcement and improve processing. The main drawback concerned with the clay filler is that it possesses a large particle size which somewhat affects the final reinforcement effect. The primary clay material is Kaolin which is either categorized as hard or soft depending upon the particle size. Hard clay has a particle size in the range of 250 nm to 500 nm and, when introduced, provides high tensile strength & stiffness. Soft clay, which has a particle size range of 1000 nm to 2000 nm when used as clay filler in the rubber blends, provides low mechanical strength because of its relatively larger particle size. Titanium oxide TiO_2 has a somewhat reinforcing effect in the rubber product but mainly acts as a white coloring agent [10].

Plasticizers are usually mixed in the rubber compounds to enhance the processability of the material. Because of the incorporation of the reinforcing fillers, there is a massive increase in viscosity, and the material develops serious processability issues. Mineral oil is added to the rubber material after reinforcement as a plasticizer. Mineral oil has obtained firm the refining of the crude oil. Therefore various types of mineral oil are available based on the character and base of the crude oil used for their production [12]. The compatibility of the mineral oil with different rubbers is shown in Table 1. Therefore, for polar rubbers like NBR, there is a requirement for a compatible enough mineral oil; as a result, synthetic plasticizers are being designed to account for the fact mentioned above. These synthetic plasticizers are higher in cost but are employed for specified vulcanizers. Pthalic esters, which include (DOP) are especially suitable for NBR rubbers. Usually, the amounts reported are between 5 – 30 phr [10].

In the sulphur vulcanized rubber compounds, a mixture of rubber and free sulphur when heated, the formation of free radicals occurs because of the ring-opening phenomenon occurring in the eight-membered sulphur rings. These then react with the double bonds of the rubber material. Therefore, a diverse mixture of inter and intra-molecular sulfur-bridges is formed. Some of these sulfur-bridges change into real network cross-links, while the others become ineffective as they react with the same polymer chain at both ends. During vulcanization with sulphur, activators are used.

A typical example is zinc oxide. It is more effective if made soluble by adding small quantities of fatty acids like stearic acid. The activator's primary function is to cause a rapid onset of curing. Accelerators are the compounds added in the rubber blend due to the sluggish nature of the sulphur-crosslinking. During the curing of rubbers with sulphur, accelerators are sued along with activators to speed up the reactions. Other than that, accelerators are also used to improve and assist the vulcanization reaction. Some standard accelerators and their specifications are described in Table 2 and Figure 5.

Table (1): Compatibility of mineral oil with different rubbers

Properties	Polymers			
	NR	SBR	BR	NBR
Paraffinic	+	+	+	-
Relatively naphthenic	+	+	+	-
Naphthenic	+	+	+	0
Relatively aromatic	+	+	+	0
Aromatic	+	+	+	+
Strongly aromatic	+	+	+	+

Table (2): Common accelerators and their specifications

Accelerators	Chemical Group	Vulcanization Speed
BA, HMT	Aldehyde Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi ultra-fast
ZBDP	Thiophosphate	Ultra-fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast delayed action
ETU, DPTU, DBTU	Thiourea	Ultra-fast
TMTM, TMTD, DPTT, TBZTD	Thiuram	Ultra-fast

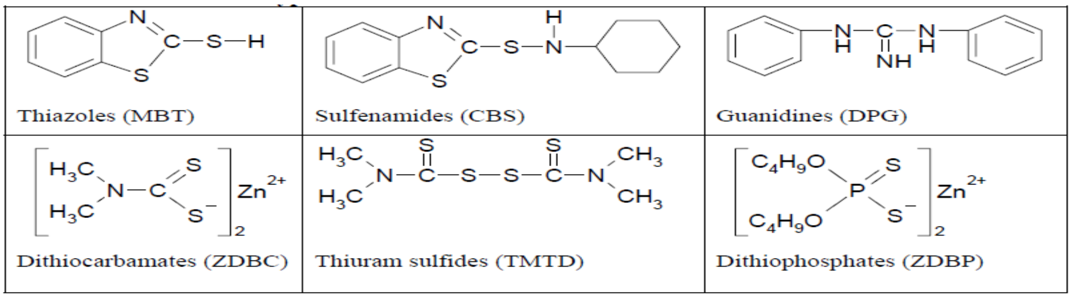

Thiazoles (MBT)
Sulfenamides (CBS)
Guanidines (DPG)
Dithiocarbamates (ZDBC)
Thiuram sulfides (TMTD)
Dithiophosphates (ZDBP)

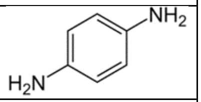
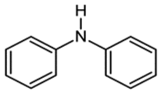
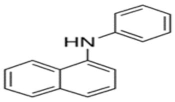
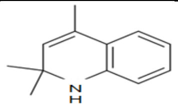
Figure 5. Chemical structures of some standard accelerators

Elastomers and rubber compounds containing carbon-carbon double bonds, which include (NR, BR, SBR, and NBR) are degraded by reacting with oxygen, ozone, and light, and heat. Thus these compounds shield the rubber against oxidization and ozone attack. These components are of immense importance and require due consideration of their incorporation for the rubber products to maintain their properties during service life. Ozone resistance is enhanced by the incorporation of antiozonants and through other physical methods that shield the rubber under static conditions. It is done by the addition of paraffinic waxes or mixing of ozone resistant polymers such as EPDM, polyethylene. The most efficient antiozonants are para phenylene diamines. Two different processes undergo degradation by oxygen and ozone and, therefore, create unique effects on the physical properties of rubber. Ozone degradation consists of discoloration and cracking phenomena. Oxygen degradation consists of the hardening or softening of the polymer [6]. Table 3 gives some examples of anti-degradants.

Rubber Blends

The type of application for the rubber part is designed will decide the set of properties that have to be achieved by the rubber compound, which will define the type of rubber, the types of fillers, and additives to be used, and their ratios. Since every rubber has some cons and inherent pros suitable for a specific application, the rubber experts continuously strive to find different techniques to achieve the properties required for a particular application. Other possibilities for achieving the desired properties other than by the synthesis of the new rubber resin system, additives, and manipulation in their ratios are copolymerization, alloying, and blending.

Table (3): Common anti-degradants

Chemical Name	Structure
Paraphenylene diamines	
Diphenylamines	
Naphylamines (PAN) (Phenyl-a-naphthylamine)	
Dihydroquinolines (TMQ) (2,2,4-Trimethyl-1,2-dihydroquinoline)	

Copolymerization combines two or more types of monomers such that the resulting polymer contains some of each. Although this process is not categorized as a blending process, it has a similar concept of combining different polymers as blending. Alloying combines two or more polymers after forming or of a polymer and a monomer into a single phase, homogenous polymer material. Some chemical attraction between the combined polymers is usually required to create an alloy. The term 'miscible blends' is sometimes interchangeably used with alloys. The blends or alloys produced by this method are miscible blends where the homogeneity is observed at the nanometer scale or molecular level as well—such type of blend exhibit one single glass transition temperature T_g. Alloys also form when two different metals combine [6, 10].

Blending or mixing combines polymers after they have formed so that the resultant polymer material is in two or more phases. Such blends exhibit a sharp and uneven morphology and poor adhesion between the blend phases. The physical blending of two or more polymers that are immiscible to attain optimum properties, this approach has acquired significant attention in recent years. Blending aims to develop products with improved properties not achievable when used individually. The blending method is quite useful because it utilizes the existing polymers and thus eliminates the need for the expensive development of new polymers by polymerization or copolymerization of monomers. Alloys and blends have become essential for many polymers. Estimates of polymer production indicate that blends and alloys represented over 20% of the total resin market. One of the advantages of alloying or blending is that new polymers can be developed without the vast investments of time and equipment required to make new polymers by polymerization or copolymerization of monomers.

Moreover, alloying or blending can be done by custom compounders and resin manufacturers, suggesting that the competition will tend to keep prices low. Another advantage is that the effort to develop a new alloy or blend can be justified based on much smaller potential sales than required to further polymerization. The diversity of alloys and blends, that is, the choices of polymers that can be combined and the many ratios of combination, provide far more property possibilities than are available from just pure resins. Alloys and blends can, therefore, be used to give tailored properties for specific applications [13].

The polymer materials can form miscible blends more easily if a chemical attraction between the molecules of the two species is known as compatibilization. It is observed that in some respect, the miscible blends usually have some properties that are superior to the properties of their pure resin systems. The reagents used for making the two rubber/polymer resins compatible with each other by these means are known as compatibility agents or compatibilizers. It is a general observation that if the two rubber/polymer compounds blended are immiscible, the properties resulting from the blended product will be, to some extent, averages of the properties of the individual rubbers/polymers that were combined to form the blend. The use of two compatible resin systems (miscible blend) or compatibility agents in immiscible blends is preferred to achieve better properties. However still, there is much work to be done in the field of compatibility agents, and the developments are still premature for specific blends. On the other hand, the feasibility factors for using immiscible blends for certain applications make this type of blend still popular [10].

The scope is to study the blend composition of the two incompatible/immiscible rubbers. The mechanical properties of the resulting blend of nitrile butadiene rubber (NBR) and styrene-butadiene rubber (SBR). The study has found many similar research articles in which the same phenomenon was studied with the effect of some compatibility agents. Still, the formulation of the rubbers was kept very simple, and their sample preparation was done in small batches at standard lab-scale equipment. In this study, a different approach and selected an industrially being used technique of the rubber compound and also prepared samples in larger batches using an industrial-scale two-roll mill. With this approach, it tried to reproduce and verify the results of lab-scale experiments of the previous research articles and their industrial applicability. In this study, any compatibility agent is not included and has worked only on the immiscible blend.

The utilization of mixes of elastic is broad, the reason for existing being to acquire balance properties, including cost, which one elastomer alone can't supply. Synthetic rubbers may be added to one another as parallel blends to improve one of the parts [14]. The search for new and fascinating polymeric materials with paired properties has, as of late, strengthened. A simple and financially savvy approach to creating another mix of properties is mixing. Most blends are immiscible and, along these lines, display poor physicomechanical properties. In this way, compatibilization is expected to acquire mixes with the ideal properties. The mechanical properties of contradictory polymers can be essentially improved by expanding a compatibilizer amid the treating stage [15]. Be that as it may, most polymer mixes are immiscible and, more often than not, display stage isolated morphology and poor interfacial grip between the stages [16]. These days, extensive research intrigue centers on new polymeric materials acquired by mixing at least two polymers. The significant element of such a procedure is that the intermediate properties are sometimes superior to those shown by the single parts. Most business polymer mixes have multiphase morphology, and much of the time, the palatable physical and mechanical properties of these materials.

Blends have been created to meet a few modern prerequisites, for example, the requirement for simpler preparing and widening of the properties run, either by changing the sort, relative sums, or morphology of every segment. These materials can be arranged to consolidate their high mechanical solidarity to better dimensional soundness and thermal resistance [12].

2. METHODOLOGY

Materials

The two rubbers selected for blending in this project were nitrile butadiene rubber (NBR) and styrene-butadiene rubber (SBR). These were compounded with curing reagents, accelerator, reinforcing material, and antioxidants according to a single formulation. The grade of nitrile butadiene rubber used in this project was NBR 6240, LG. NBR 6240 is a copolymer of butadiene and acrylonitrile manufactured by advanced emulsion polymerization technology of Goodyear and LG Chem. It has non-staining properties and medium to low Mooney viscosity with high acrylonitrile content specially designed to assist in processing operations such as calendaring and extrusion. NBR 6240 is recommended for packing, shoe products, chemically blown sponges, oil field products, industrial and automotive molded parts [3]. Some of its properties are listed in Table 4.

The styrene-butadiene rubber used was of the grade SBR 1502, Nipol. The 1502 grade of SBR has a 23.5% bound styrene content and is polymerized using a mixed acid emulsifier, non-staining stabilizer, and salt-acid coagulation. It exhibits good tensile strength, flexibility, abrasive strength, and elasticity. The non-staining and non-discoloring properties of the grade make it suitable for various applications. End-uses include white sidewall tires, footwear, light, and dark-colored mechanical goods, and miscellaneous items where excellent physical properties and minimum discoloration and staining are required [3]. Some of its descriptions are shown in Table 5.

The filler used in the formulation of the blend samples was of the reinforcing type, such as carbon black. Carbon black is one of the most common reinforcing fillers in the rubber industry, with good compatibility with most rubbers and low cost relative to other reinforcing materials. One of its main disadvantages is its black color which does not allow the final products to be of colors other than black. Carbon black comes in various grades classified according to its particle size. Standard grades are N-110, N-220, and so on, where N-110 is the finest grade with a particle size within nm. The grade used in the case was N-330 carbon black which was readily available in the local market within a relatively feasible price range.

It reduces the aging effect in the final product; different anti-degradants/antioxidants are added to the blend of the rubber compound. The antioxidant used in the formulation was 2, 2, 4-Trimethyl-1, 2-dihydroquinoline, polymerized (TMQ). The curing in the rubber industry is referred to as the vulcanization process or the cross-linking of elastomers. Elemental sulfur is the most broadly utilized vulcanization agent for rough rubbers that contain double bonds in their chains. Be that as it may, the response of elastic with sulfur is moderate even at high temperatures; in truth, for the most part, it requires a few hours. To build the vulcanization rate, it is essential to include accelerators and activators. The whole combination of accelerators, activators, and elemental sulphur is known as the cure system. Activators are commonly added in small amounts to increase the efficiency of accelerators. Stearic acid and zinc oxide are the most usually used activators.

Table (4): NBR 6240 properties

Properties	
Bound acrylonitrile content (%)	34 %
Ash (%)	Max. 0.5 %
Volatile matter (%)	0.3 %
Specific gravity	0.99
Mooney viscosity (ML 1+4, 100℃)	41

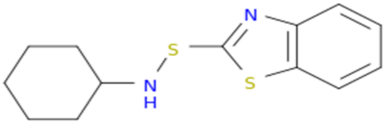


Figure 6. Chemical structure of N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)

Table (5): SBR 1502 properties

Properties	
Bound styrene content (%)	23.5 %
Ash (%)	Max. 1 %
Volatile matter (%)	Max. 0.5 %
Specific gravity	0.94
Mooney viscosity (ML 1+4, 100℃)	52

Some vulcanizing agents used for certain rubber kinds include, for instance, diamines, metal oxides, special resins, and bisphenol. Sulphur, also known as a yellow powder in the rubber market, is the main ingredient of the cure system. Almost all commodity rubber products produced locally use sulphur as the cross-linking agent. Also, there are several accelerators available in the market which have sulfur attached to their molecules, eliminating the need for elemental sulphur to be added separately in the method. However, by the aim of this study, a common type of ingredients are selected in this method, sulphur is one of them

The commonly used zinc oxide and stearic acid were used in this study. These react with each other during the vulcanization process to form zinc stearate, which speeds up the sulphur cross-linking process. Accelerators are chemical reagents included in the rubber formulation to enhance the vulcanization rate. To let the vulcanization process proceed at lower processing temperatures with greater efficiency. The accelerator is also used to reduce the sulphur requirements in vulcanization, resulting in improved resistance to the aging of the vulcanized product. The accelerator used in this method was N-Cyclohexyl-2-benzothiazole sulfenamide (CBS). It belongs to the sulfenamide class of accelerators, which have fast delayed action. Its chemical structure is shown in Figure 6.

Sample Preparation

A typical composition commonly used for NBR products was chosen. Five different samples were prepared with only varying the amount of each of the two rubbers without altering the rest of the composition. Table 6 shows the formulation for the rubber compound. Here the total raw rubber PHR was kept 100 with varying the NBR and SBR phr from 0 to 100, and the sample names were defined concerning % NBR present in the raw rubber part of the composition NBR 0%, NBR 25%, NBR 50%, NBR 75%, and NBR 100%. The different composition of blend samples is shown in Table 7.

Rubber compounding is accomplished with two roll mills or an internal mixer (Banbury Mixers). The internal mixer is a device used for mixing in large-scale rubber industries. Its strength can be assigned to a few variables, among which the great filler scattering accomplished and the extensive decrease of the blending time. There are two basic internal mixer designs, intermeshing rotor and tangential (non-intermeshing) rotor, and many variations on these two themes. The common characteristics in both designs are the set of two contra-rotating rotors; the ram. Which can be lifted to let the feeding, and lowered and pressurized to hold the rubber compound in the active mixing regions; the drop door, designed for the batch; and the channels in the chamber walls, the rotors, the drop door and (sometimes) the ram for circulation of cooling water.

Table (6): Formulation for rubber compound

Materials	PHR
NBR + SBR	100
N-330 Carbon Black	42
Stearic Acid	1
Zinc Oxide	5
Anti-Oxidant/Ozonant (TMQ)	1
Sulphur	1.5
CBS	1.5
Total PHR:	**152**

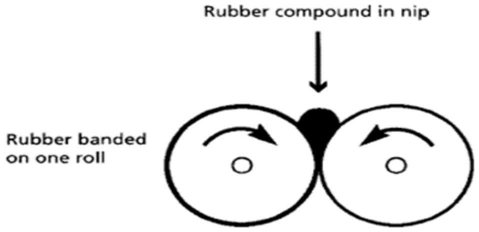


Figure 7. Schematic diagram of a two-roll mill

The two roll mill comprises two nearby solidified steel moves set on a level plane. The rolls turn at an alternate speed to create contact or crushing activity between them.

The blending procedure establishes chewing or separating the rough rubbers, as appeared in Figure 7. An even and smooth band is conformed to the front roll. When the rough elastic turns into delicate and plastic, different fixings are included. The two-roll mill is a mixing method in which the quality of mixing is entirely dependent on the skills and knowledge of the operator. In fact, during the processing, some of the chemical reagents that are primarily in powder form may not stick on the rubber on the roll and may drop into the mill tray. Since the method and formulation consist of these chemicals in very low weights concerning the whole sample, loss of even small amounts of these chemicals may change the formula completely, thereby resulting in a final product with a different set of properties. So, the operators must collect any dropped powder and add it back. Also, to form a uniform dispersion, the ingredient's cutting and folding are constantly done.

Locally in the small and medium scale industries, the two-roll mill is preferred as it can handle small-scale formulations easily. The use of Banbury mixers, on the other hand, being a high-capacity mixing machine, is not suitable as its minimum capacity is too large. The samples are compounded on a medium-scale industrial two-roll mill that will roll 10 inches. The diameter and a nip gap are set to about 10 mm at 25 rpm. The compounding of each sample was carried out for 15 minutes. After the mixing, the forming and the vulcanizing operation follows; sometimes, these could also coincide. With the forming step, the crude compounding will retain the shape imposed on it because it is predominantly plastic. The processing machine mainly used for forming are calendars and extruders. The calendar is equipped with two or more internally heated or cooled rolls. The latter rotate in opposite directions. The calendar is used essentially for producing rubbers sheets of different lengths and thicknesses.

The extruder is generally used to produce rubber tubes and weather-sealing strips. In this machine, a rubber compound is transferred along with a cylinder by a rotation screw. The green stock becomes hot and plastic as it moves to the exit end of the extruder, called a die, with the desired shape and dimensions. In this case, the two-roll mill was used to the calendar and formed the mixture into an 8 mm thick sheet.

Table (7): Different compositions for blend samples

Materials	**NBR**				
	0 wt. %	**25 wt. %**	**50 wt. %**	**75 wt. %**	**100 wt. %**
SBR	100	75	50	25	0
NBR	0	25	50	75	100
N-330 Carbon black	42	42	42	42	42
Stearic acid	1	1	1	1	1
Zinc oxide	5	5	5	5	5
Anti-Ox./Oz. (TMQ)	1	1	1	1	1
Sulphur	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5
Total PHR:	152	152	152	152	152

After the forming, the green stock is changed over into the three-dimensional elastic system. It is practiced by the vulcanization procedure, for the most part, directed under pressure at raised temperature, in which polymeric chains are chemically linked together. The physical properties of a vulcanized compound depend strongly on cross-link density. Modulus and hardness increase with increasing cross-link density, while the % elongation decreases. Fracture properties, such as tensile strength, pass through a maximum as cross-linking increases. The mixed/compounded, formed sheets were then molded into cured sheets of small size. It was done through small-scale hand-operated compression set with a heated plate below it. The curing was carried out at a temperature of 200°C with a 10 min curing time.

The characterization of rubber blends becomes more accessible due to the adequate testing methods known today. Physical testing of rubber vulcanizates like; hardness test, tensile stress/strain, tear test, accelerated aging, abrasion, rebound resilience, low temperature, and electrical properties.

Mechanical Testing

The mechanical testing of rubber vulcanizates is similar to the rest of polymers. The scale of mechanical properties such as tensile strength, hardness, and tear strength for rubbery polymers and elastomers is relatively smaller concerning standard polymers. Still, properties such as elongation have significantly high values. It necessitates the application of standards and procedures for rubber testing to be different from the standard polymers. This study emphasizes the mechanical properties of the composite rubber samples.

Tensile testing of the polymers and other materials is usually done through Universal Testing Machine (UTM). The universal testing machine has its name from the vast capabilities in testing such as tensile, compression, tear, and flexural strength. The main components of the UTM include load frame, load cell, cross-head, and output device. The parameters defined by the tensile test performed by UTM are tensile strength, modulus, % elongation at break. Tensile strength is the force per unit area of the original cross-section of the sample required to stretch a rubber test piece to its breaking point [5]. Modulus is the tensile stress-strain necessary to stretch a rubber test piece to a predetermined elongation. Elongation at break is an elongation of the specimen at 100% strain at the point of rupture of the specimen. It is expressed in the form of % elongation concerning initial length.

The standard test performing procedures are usually different for different materials, as discussed earlier. In our case, the material to be tested was a type of vulcanized rubber; therefore, according to the ASTM, the standard operating procedure to be applied was selected to be ASTM-D412 which is typical for vulcanized rubbers. According to ASTM-D412, the test specimen should be in the dumbbell shape with a specified gauge length, grip geometry, and thickness. For this purpose, the cured samples we had produced were cut into the desired dumbbell shapes, using an ASTM-D412C standard cutting die and pneumatic press. Three specimens for each sample (composition) were prepared with dimensions of the specimen defined in Figure 8.

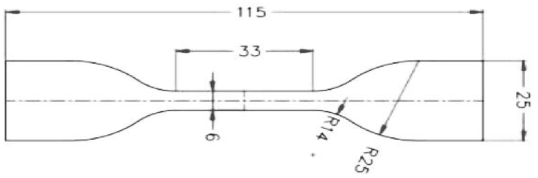


Figure 8. Tensile test specimen geometry (ASTM-D412C)

The testing of the tensile properties of the dumbbell-shaped specimens was done on a Zwick Tensile Testing Machine (Model Z005). The gauge length was defined as 25mm, and the cross-head speed, which determines the strain rate of the specimen, was kept at 500mm/min. There was no conditioning environment done during the testing procedure, and all the tests were performed at an ambient temperature of around 27°C. Three specimens of each sample were tested, and mean values were computed.

The hardness of a material is the measure of the resistance it shows against penetration. The hardness test involves measuring the extent of penetration of a special indenter (usually specified by the standard being followed) under defined conditions of applied load and time. The force applied can be either through dead weight or by a spring. The value obtained from the result is usually utilized to measure the hardness of a particular rubber or as a means of quality control.

The durometer hardness tester is the most common hardness testing equipment and is often used to define the relative hardness of soft materials. The durometer scale differs for different materials depending upon their relative hardness and the geometry and type of indenter used in the test. Standard scales for rubber and elastomers are shore A and shore D, where generally Shore A is used for softer rubbers, and Shore D is used for the harder ones. The shore hardness scale of the Durometer is calibrated between values of 0 and 100, where 0 represents very soft material and 100 represents very hard material. If the hardness test result at any shore scale is given to be 100 or 0, this means that an improper shore scale has been selected, resulting in extreme values, and a harder or a softer scale should be selected for obtained value.

According to the literature reviewed and ASTM standards, the shore A hardness scale was selected. The ASTM D2240 testing procedure for the shore hardness was followed. Two specimens from each composition were prepared and tested with a specimen thickness of 5mm. The process followed included placement of the specimen on the hard flat surface of the Durometer, releasing of the stopper of the indenter allowing a 1000g load to be applied on the specimen, and observation of the reading within one second of firm contact with the specimen.

3. RESULT & DISCUSSION

Tensile strength

Figure 9 shows the tensile strength results of the individual samples plotted to their corresponding compositions taking NBR % as the basis of the composition. The data points are joined by a continuous curve to identify a hypothetical trend between the tensile strength and %NBR incorporation in the blend. The resulting trend represents no direct relation between the percent NBR incorporated in the rubber and the tensile strength, an inherent characteristic of immiscible blends. The tensile results at 0% NBR and 100% NBR can be treated as the basis as these samples represent pure SBR (at 0% NBR) and NBR (at 100% NBR) compounds with no blending. The tensile strength of the pure SBR compound is greater than that of pure NBR. This result can be different for different grades of SBR and NBR used. The strength does not follow a linear relationship; it decreases to 25% NBR to its minimum value and reaches its maximum at 50% NBR composition. It again follows a decreasing trend passing through 75% NBR and 100% NBR composition data points.

The dips occurring in the trend at 25% and 75% NBR composition can be due to the possibility that the NBR to SBR ratio of 25:75 and inverse that is 75:25 raise the probability of non-uniform mixing the two rubbers. On the other hand, the tensile strength at the NBR to SBR ratio of 50:50 is greater than the two different blend compositions. It can be because of the similar composition of the two rubbers, which can enhance the chances of uniform mixing of the blend. This somehow sinusoidal trend is identical to that observed in the literature review with just slight differences in the magnitude of the strength, which can be due to the difference in the grades of the rubbers used and formulation variations [2]. Though, the tensile strength of SBR with NBR blend vulcanizes compatibility with elemental sulphur and N-cyclohexyl-2-benzothiazole sulfenamide (CBS) revealed a positive deviation from the additive rule. The change in the tensile strength was due to improved interfacial adhesion of SBR/NBR blends by decreasing the interfacial energy among phases due to the incorporation of CBS [2, 3, 15].

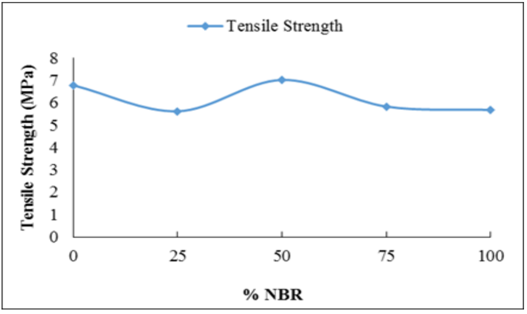


Figure 9. Effect of tensile strength with the increasing % of NBR in the SBR blend

Modulus

Figure 10 represents the modulus of samples at 100% strain against the composition of the blends. It was found that the increasing composition of NBR in SBR shows a slight change in the modulus of the mixtures. The resulting data points were joined with a continuous line to examine the developed hypothetical trend. The modulus of the 100% SBR compound was smaller than the modulus for the 100% NBR compound. The NBR to SBR blending ratio was increased from 0:100 to 25:75 and 50:50; there is an increase in the respective modules. At the 50:50 ratio, the modulus is at its peak value. At higher ratios, the modulus decreases slightly. It was probable that the styrene group in SBR, and acryl nitrile group in NBR, can act as a donor-acceptor and henceforth allow compatibility of polar NBR and nonpolar SBR. The results show that NBR is incompatible with SBR [7, 9, 12, 14].

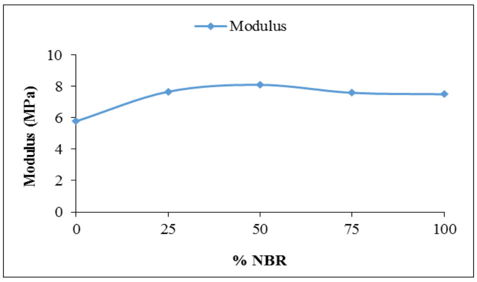


Figure 10. Effect of modulus with the increasing % of NBR in the SBR blend

Percentage Elongation at Break

The % elongation at break was also plotted similarly as tensile strength and modulus. Figure 11 portraits that with the increasing composition of NBR in the SBR blend, its elongation at break decreases due to the less flexible nature of NBR. It might be due to the dipole-dipole interaction of the sulfenamide groups in N-Cyclohexyl-2-benzothiazole sulfenamide and NBR nitrile groups. It has enhanced the interfacial adhesion between gross-phase-separated polymer pairs. Although, the carbon black in SBR/NBR compatibilized with elemental sulphur and N-cyclohexyl-2-benzothiazole sulfenamide (CBS) vulcanizate reveals the least change in 100% modulus, confirmed the highest thermal stability as shown in the elongation at break and tensile strength results obtained [5, 6, 12, 16].

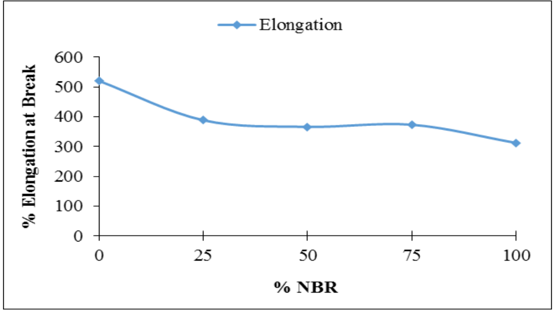


Figure 11. Effect of elongation at break with the increasing % of NBR in the SBR blend

Hardness Test Results

Figure 12 displays the results were obtained from the shore a hardness test performed on the individual samples. The results indicated that 100% has a lower hardness than the 100% NBR compound. The NBR to SBR blend ratio of 25:75 represents the lowest hardness level which can be again due to the probability of lower mixing efficiency in the compound and a greater ratio of the softer rubber that is SBR. At 50:50 and 75:25, the hardness level is increased somehow. It can be ascribed to the increase of the additional thermally stable acrylonitrile content due to the dominating effect of the NBR portion. The incorporation of carbon black increased the viscosity of the rubber. The carbon filler produces heat in the compounds under shear conditions; the mixture tends to be more viscous. As a result, vulcanization reactions can occur more rapidly to increase viscosity. This finding is due to the good interaction between rubber and filler. While the rubber blended well with carbon black, rubber chains have an assured probability of interacting with carbon black, affecting the chains to be entangled in the voids of carbon black aggregates [2, 3, 15]. The results in a summarized form on each sample are given in Table 8.

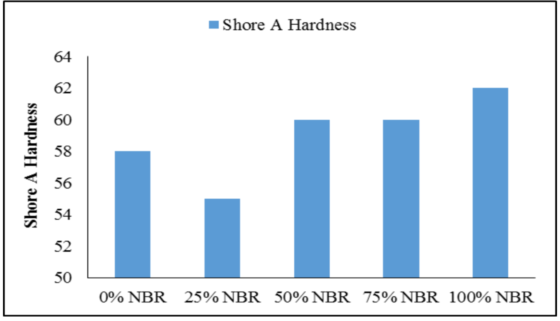


Figure 12. Effect of the shore hardness with the increasing % of NBR in the SBR blend

The results obtained through the mechanical tests performed on different samples with different blend ratios are much larger than the literature available [2, 3, 10, 12]. There are although some dissimilarities, such as the magnitude of the results and some trends. The distinctions in the results and results of previous researches can be because of the inefficiencies present in the industrial equipment used in sample mastication and hand-operated compression set. The temperature of the heating plate and applied pressure for closing the mold were manually controlled. Apart from these dissimilarities, the non-linear relations between blend ratio and mechanical properties are a result of the immiscible nature of the blend. From the results, it can be concluded that if a mix of these rubbers is to be used, and NBR to SBR blend ratio of 50:50 has optimum properties. In the small-scale cottage industries working locally, low batch consistencies are inevitable due to the limited resources available and lack of robust equipment. Therefore, these industries can utilize such blends and compounds to produce commodity products and products requiring lower standards of mechanical properties.

Table (8): Mechanical properties results of all samples

Polymers	**% Blend Composition (PHR)**				
NBR	0	25	50	75	100
SBR	100	75	50	25	0
Mechanical Properties					
Tensile strength (MPa)	6.78	5.62	7.02	5.83	5.68
100% Modulus (MPa)	5.78	7.66	8.10	7.59	7.50
Elongation at break (%)	520	388	366	373	312
Shore A hardness	58	55	60	60	62

4. CONCLUSION

The mechanical properties of tensile strength, hardness, and tear strength were successfully evaluated for SBR/NBR polymer blends. Incorporating filler, antioxidants, and activators into SBR/NBR blends improves the mechanical properties. The non-linear relations between mechanical properties and blend ratio show the immiscible nature of the blend. Moreover, for all mechanical properties tested, it could be concluded that if a blend of these rubbery polymers (NBR to SBR) is used, the blend ratio of 50:50 provides the optimum properties. The results obtained through the mechanical tests performed on different samples with different blend ratios are too much extent. If engineering products are produced using a blend of these rubbers, there will be a need to use a robust compatibilizer and appropriate mixing equipment for mastication. NBR/SBR blends can be used advantageously over applications where a low-cost rubber material with good oil resistance is required.

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