

INFLUENCE OF INTERRUPTED VULCANIZATION ON RUBBER TO METAL BONDING STRENGTH

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Master Thesis
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MASTER'S THESIS ASSIGNMENT

(PROJECT, ARTWORK, ARTISTIC PERFORMANCE)

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Thesis Guidelines:

The theoretical part of the Diploma Thesis will deal with description of vulcanization curve, processes occurring during the vulcanization, interrupted vulcanization curve and effect of this process on the rubber to metal bonding quality. The rubber mixtures suitable for the use in stabilizers systems differing in hardness will be suggested as well. The effect of interrupted vulcanization of suggested rubber mixtures in various degrees on the final strength of the rubber to metal bonding will be investigated in the practical part of the Diploma Thesis. Furthermore, the effect of interrupted vulcanization on the rubber component of the bonding as such will be investigated.

1. Make a literature review on the given topic
2. Prepare rubber mixtures differing in their composition
3. Perform vulcanizations of suggested rubber mixtures interrupted at different degrees
4. Measure the stiffness of prepared rubber to metal bonding
3. Evaluate and interpret obtained results

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1. **WHITE, J., DE, S.K., NASKAR, K.:** Rubber Technologist's Handbook, Volume 2. Smithers Rapra Technology, 2009. Online version available at:
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3. Online databases accessible from TBU in Zlín.

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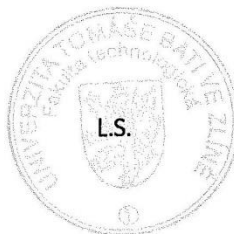
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ABSTRACT

The Master Thesis deals with the description of vulcanization curve, processes occurring during the vulcanization, interrupted vulcanization curve and the effect of this process on the rubber to metal bonding quality. The rubber mixtures suitable for the use in stabilizer systems differing in hardness will be suggested as well. The effect of interrupted vulcanization of suggested rubber mixtures in various degrees on the final strength of the rubber to metal bonding are investigated in the practical part of the Master Thesis. Furthermore, the effect of interrupted vulcanization on the rubber component of the bonding is investigated as well.

Keywords: rubber, interrupted vulcanization, rubber mixture, rubber to metal bonding.

ABSTRAKT

Diplomová práce se zabývá popisem vulkanizační křivky a procesech, které nastávají při vulkanizaci, přerušovanou vulkanizací a vlivem této metody na kvalitu spoje pryž–kov. Dále jsou popsány kaučukové směsi o různých tvrdostech jako vhodné systémy pro použití ve stabilizátorech. V praktické části je zkoumán vliv stupně přerušování vulkanizace navržených kaučukových směsí na finální pevnost spoje pryž–kov.

Klíčová slova: pryž, přerušovaná vulkanizace, kaučuková směs, pojení pryž–kov.

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INTRODUCTION

Rubber and metals products in corporation with each other are widely been used in automotive industry as well in household applications. The connection or adhesion between rubber and metal is quite a concerned topic nowadays in industries. Rubber has always been a crucial part of automobile industry as it is used in tires. Rubber is used with metal particularly to reduce the vibrations, thus causing reduction in shock. The connection between rubber and metal is of high importance.

It is expected that vulcanization plays an important role in this connection of rubber to metal bonding. In this Master Thesis, the main focus is on rubber to metal bonding with different degree of vulcanization or in other words interrupted vulcanization which plays a major role in bonding. Different samples are being examined in connection with each other to evaluate which has better connection of metal to rubber bonding. In some tests a bonding agent is used whereas in some tests it is not used and results are discussed.

The purpose of these tests is to see whether or not different degree of vulcanization has some effect on rubber bonding with metal. Firstly rubber with different degree of vulcanization is bonded with metal plate without bonding agent and the effect has been studied. Secondly rubber with different degree of vulcanization is bonded with metal plate with the help of a bonding agent and effects are studied.

I. THEORY

1 RUBBER HISTORY

Rubber is a kind of polyisoprene i.e. polymers made up of 5 carbon isoprene units. These carbon units can be linked either in cis or trans conformations resulting in polymers that leads to very different properties. For instance, rubber with cis-linked units tends to forms an amorphous structure which is highly elastic. Gutta Percha on the other hand, which is a polyisoprene compound made of all trans-linked isoprene units, forms linear structure which tends to form crystalline structure which have plastic properties, but are not elastic. This case is generally or basically for natural rubber but as we know there are also different kinds of rubber as per the application changes. These are called synthetic rubbers or man-made rubbers as they have been developed with recent scientific development in this field. [1]

The first use of rubber was in the form of an eraser. In 1839 Goodyear discovered vulcanization, quite by accident leads to better properties in rubber. In 1815 an interesting incident happened, a humble sawyer - Hancock - became one of the leading manufacturers of rubber products in the UK. He invented a rubber mattress in association with Macintosh, he produced the popular water-proof coat named as the "Macintosh". Manufacturing of elastic balls was also discovered by Hancock. In 1842, Hancock learned vulcanized rubber produced by Goodyear, learning the secret of vulcanization that brought him lots of wealth. It happened in year 1845 when tire was invented by R.W. Thomson along with the inner tube and textured tread. [1–3]

In 1850, solid and hollow balls for golf and tennis were being made from rubber as well as toys. Finally, Bouchardt discovered the polymerization of isoprene between 1879 and 1882, resulting in products with properties matching rubber. The first bicycle tire was invented back in 1830, and in 1895 Michelin dared to go further with rubber tires in automotive industry. [1]

Since then, rubber has taken an outstanding position on the global market. As rubber is an important raw material which plays a leading role in modern world, chemists soon became curious to know more about its composition in order to synthesize it and make progress in this field. The Germans and the Russians grabbed fresh ground in their efforts to manufacture rubber. But the resulting products did not have same quality as that of natural rubber. It was the time of World War I that Germany - pressured by unfavorable circumstances had needed to develop the industrialized product of the synthetic rubber. This was the bar set by Germans for the development of the synthetic rubber industry all over the world, producing elastomers. [1]

2 TYPES OF RUBBER

2.1 Natural rubber

Natural rubber as a non-synthetic type of rubber is being used for commercial purpose since 20th century. Natural rubber can be tapped from *Parthenium argentatum*, *Taraxacum kok-saghyz*, *Hevea brasiliensis* as latex. It is biodegradable. Tensile strength, abrasion resistance and elongation are excellent over a wide hardness range. Polyisoprene is the chemical identity of natural rubber. It has also good tear strength, fatigue resistance and excellent compression set. Weathering resistance is good as well. Natural rubber compounds are not suitable for exposing them to oils and fuels based on petroleum. It has poor resistance to high temperatures and is prone ozone attack unless mixed with anti-ozonants. Typical applications include anti-vibration mounts, hoses, belts, drive couplings and haul-off pads. [4–9]

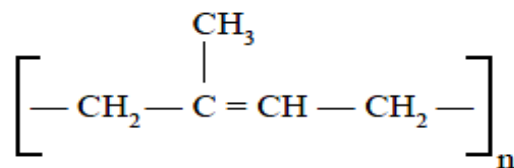


Figure 1: Chemical structure of natural rubber. [10]

2.2 Butyl Rubber

Butyl rubber is also known as Isobutylene-isoprene (IIR) and is a synthetic rubber developed in the 1940s. It has an excellent low gas permeability making it ideal for inner tubes and high pressure/vacuum sealing applications. It has very low resilience that makes it suitable for shock and vibration damping purposes. Its chemical unsaturation property gives it excellent resistance towards heat, ozone, and weathering, dilute acids and alkalis. It is not suitable for use in mineral or petroleum based fluids.[11] Typical applications are bottle closures, gaskets, inner tubes, seals, diaphragms and O-rings. [12]

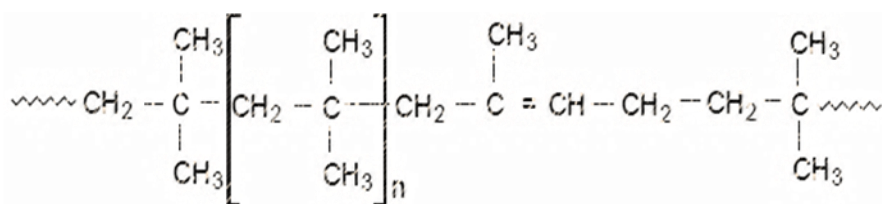


Figure 2: Chemical structure of butyl rubber. [13]

2.3 Ethylene propylene diene monomer

Ethylene Propylene Diene Monomer (EPDM) is a copolymer of propylene and ethylene and a smaller amount of diene monomer which forms chemically unsaturated ethylene groups pendant from the main saturated chain. These provide cross-linking reactions which do not affect the integrity of the polymer backbone. This provides EPDM excellent resistance to chemicals, ozone and heat. Physical properties are excellent as well as the resistance to polar fluids. Low temperature resistance is also very good and EPDM can be formulated to give excellent electrical resistance. EPDM is not suitable for exposure to di-ester lubricants and petroleum based fluids. [11] Typical applications include gaskets, accumulator bladders, seals, cable connectors, hoses, insulators, diaphragms. [14]

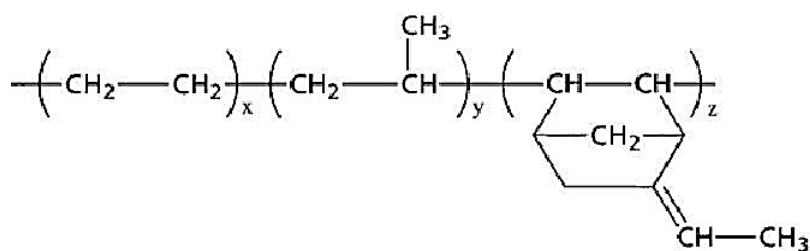


Figure 3: Chemical structure of ethylene propylene diene monomer rubber. [15]

2.4 Nitrile rubber

Acrylonitrile Butadiene Rubber, also known as Nitrile rubber (NBR), was developed in 1941 as the oil resistant rubber. NBR grades with high acrylonitrile content have better oil resistance whereas low acrylonitrile content gives better low temperature flexibility and resilience respectively. NBR has moderate physical properties but quite good resistance to abrasion.

Permeability to gas is low for NBR. Resistance to ozone and electrical properties are not in exceptionally good. Use with polar solvents as well as for flame is not appropriate. Certain grades can be formulated with polyvinylchloride to improve ageing, petrol, flame and ozone resistance. Carboxylate grade of NBR has good physical properties and higher temperature resistance. Potable water compounds are available as well as mixes suitable for use in the food and pharmaceutical industries. [11] Typical applications include seals, hoses, gaskets, diaphragms, liners. [16]

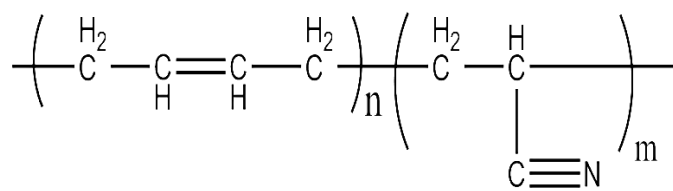


Figure 4: Chemical structure of nitrile rubber. [17]

2.5 Chloroprene Rubber

Chloroprene Rubber (CR), better known as Neoprene is a synthetic rubber that is considered as rubber resistant to oil. On the other hand CR is not good for resistance against oils derived from petroleum. It has excellent balance of physical as well as chemical properties to be used for general purpose. In comparison to NR, resistance against chemicals, heat, oil ozone is quite good but loses to physical properties of NR. It absorbs water and electrical properties are quite poor. It has low permeability; resistance to flame is exceptionally good, Chloroprene has self-extinguishing property. Neoprene has excellent rubber-metal bonds and resilience is also good. It may crystallize and become hard if stored. [11] Typical applications include belting, gaiters, coated fabrics, seals. [18]

3 COMPOUNDING OF RUBBER

A rubber compound is basically obtained by mixing a number of rubbers starting from a common polymer and mixture of all other additives. The choice of the rubber and the additives is directly linked to the application need and desired properties. The end product is non-vulcanized entity or compound. The quantity of additives used varies from 20 to 130 % as a percentage on the weight. [28]

3.1 Compounding Ingredients

For a system under consideration, the compounding ingredients can be respectively classified in the following groups. However, the classification is somewhat complex since some ingredients may act in more than one way possible. A brief classification of these chemicals is given with detailed discussion respectively. [28]

3.1.1 Raw rubber

Raw rubber can be classified either as natural or synthetic. Smoked sheets and pale crepe are the standard grades of NR. Pale Crepe is practically colourless and is used in products where delicate colour, extreme whiteness and transparency are requested. Smoked sheet is the rubber preferably used in products which are subjected to wear and tear such as automotive tyre treads and carcasses, inner tubes, footwear, soles, cable covers, roll covers, tank lining and wire insulation. The lower grades of NR are estate brown crepe or amber crepe. These are used alone or in combination with smoked sheets either to reduce costs or to increase the plasticity of friction and skim-coated products or compounds used in the extruding machine or calendering machine. There are many kinds of synthetic rubbers available including general purpose such as styrene butadiene rubber and poly-butadiene rubber as well as special purpose rubbers such as CR, NBR, EPDM and BR and many specialty synthetic rubbers respectively. [29]

3.1.2 Vulcanizing agents

Three vulcanizing agents have a large role in rubber industry: peroxides, sulphur or insoluble sulphur, and peroxides. The mostly used agent is rhombic sulphur. The advantage with this is that it does not require any special handling and storage need. Sulphur is soluble in NR at levels up to 2.0 phr. If concentration is higher than mentioned one, insoluble sulphur must be used to prevent migration of sulphur to the compound surface, i.e., sulphur bloom. Sulphur is a cheaper and the most practical chemical available for effective vulcanization. In the 19th century the

practical amount of sulphur for vulcanization was 6 to 10 parts per hundred parts of rubber (phr). Due to the advancement of accelerators it was reduced to about 0.5 to 4 phr. Later sulphur less vulcanizing system was also developed. General rubber-sulphur ratios for various products are given below in Table 1. [30]

Table 1: Rubber-sulphur ratio for various products. [30]

Type of use	Rubber-sulphur ratio [phr]
Rubber lining	2.5 to 2.75
Rubber roll covering	3 to 15
Tyre carcass	2.5 to 3.5
Tyre tread	2.75 to 3.25
Moulded tubes	0.75 to 2.5
Footwear	2.00 to 2.50
Soles and heels	3 to 4
Mechanical goods	2.5 to 3.5
Ebonite or hard rubber	20 to 40

3.1.3 Accelerators of vulcanization

Accelerators are second in importance only to sulphur in the vulcanization process. Their function is the acceleration of normally slow rubber-sulphur reaction, increase the rate of vulcanization, and also increase productivity. Accelerators are classified into two main classes, i.e., organic and inorganic. The inorganic accelerators such as lime, litharge and other lead compounds and magnesia were being used extensively before the introduction of organic accelerators. Inorganic ones are still used mainly to produce hard rubber or ebonite products. Litharge is used in rubberized fabrics, insulated wires and cables and shoe compounds as well as chemical resistant rubber products for accelerating vulcanization. Organic accelerators are considered as the backbone of rubber industry for their extensive use and remarkable role. Their use is practically universal. The main commercial types of organic accelerators are:

- Benzothiazole derivatives
- Thiuram disulphides

- Salts of thio acids
- Guanidine derivatives
- Aldehydeamines

The first three groups of accelerators are called ultra- or semi ultra-accelerators because they lead to higher rates of vulcanization. The last two groups are called slow-accelerators. Apart from controlling the time and rate of vulcanization during curing process, it also controls the number and type of sulphur crosslinks which are formed. [31, 32]

3.1.4 Accelerators activators

Accelerators are mainly unable to exercise their maximum effect unless the rubber compound contains certain ingredients called as activators of accelerators. There are two kinds of these activators such as metallic oxides and organic acids. Both are frequently used activators for accurate acceleration with most accelerators. Zinc Oxide (ZnO) is the most common metal oxide and is added to nearly every compound in the range of at least 1 to 5 phr. Lead oxide (litharge) action is also similar as ZnO but is less commonly used since it activates some accelerators to such extent that it tends to induce pre-vulcanization or scorching. Secondly, litharge imparts dark colour. Hence, litharge as such can be used only in black coloured products. Various grades of ZnO with different particle size and varying degrees of purity are also available. Finer particles size ZnO are more effective than coarse size particles during active vulcanization. [33]

3.1.5 Vulcanization retarders

The rate of vulcanization of many of the industrial rubber compounds is very rapid. This is because of demands, production and need of higher productivity, competition and cost consideration and using high temperatures of curing. One of the well-known retarder is Salicylic acid for NR compounds. Excessive use of retarders may lead to porosity in compounds. The quicker a compound vulcanizes the more prone it gets to premature vulcanization or scorching. Scorching is defined as the onset of vulcanization at an undesirable stage of processing, making further processing difficult or rather impossible. The use of slow accelerators, which is employed by the desire to vulcanize certain types of products at low temperatures because of scorching problems, aggravates the tendency to pre-vulcanize the compounds since the process temperature is high at about 90 °C throughout the processing parameters and operations in mill, calender and

extruder. Nowadays better methods of mixing and processing, improved machine or equipments designs and use of better cooling devices have reduced this catastrophe in many modern factories. However, it has become important to use some ingredients which have a retarding effect on the rate of vulcanization at processing temperatures as a source of eliminating or reducing scorching. Certain organic acids such as salicylic, phthalic, benzoic and even stearic acid in excess and phenols have negative or better to say retarding action. It is to be considered that salicylic acid accelerates vulcanization of neoprene compound. Though, the use of retarders is rare. A effective method of preventing scorching while storage and during processing is proper combination of accelerating system, reduction of rubber to sulphur ratio, use of adequate plasticizers, considerable cooling of the stock after mixing and subsequent processing and using the compounded stock within a proper time limit and adequate storage temperature below room temperature at around 20 °C. [28,33]

3.1.6 Antioxidants or ageing agents

This class of rubber ingredients has popped out into use because of the desire or urgency to reduce the deteriorating effects of the rubber products during storage and service life. This class consists of a number of organic materials without praise-able accelerating activity that retard deterioration and increase the service life of the rubber products. Anti-oxidants must have the following properties, in order to fulfil their role:

- Thermal stability and non-volatility at processing temperatures
- It must be miscible in the polymer
- It should not leach out of the polymer on contact with solvents
- It should not corrode the processing equipment with acidic decomposition products
- It must be odourless, tasteless and not coloured (including its degradation products)

They act mainly as negative catalysts retarding oxidation reaction. The quantity of antioxidants usually added to a rubber compound varies from 0.5 phr to 2 phr. Some of the antioxidants are being used for protection against flex-cracking, increasing heat resistance and for reducing ozone cracks. Chemical agents which protect rubber products against ozone attack are called antiozonant. The antioxidants have no remarkable or significant role in the vulcanization process. They are incorporated to increase the life-span of vulcanized rubbers. The use of antioxidants in several cases in corrosion and wear applications is subjected or optional. But it has become a

trend to add these ingredients in most compounds, because they have advantages to retard the oxidation of rubber, thus reducing cost. [28,33]

3.1.7 Plasticizers and softeners

Rubber mastication requires time and high power and thereupon generates heat. It has essentially become necessary to accelerate mastication with addition of certain ingredients which will soften and plasticize it so that it will decrease heat generation, power consumption and generates absorption of the various compounding ingredients. The softening is initiated by the swelling of the rubber by the softeners. Mineral and vegetable oils, waxes, tars, resins etc., falls under this class of ingredients. These organic ingredients are of different degree and softening action on the rubber. Their effectiveness from one ingredient to another and the proportions in which they are added to rubber vary over a wide range considerably and effectively. Some of them are used to aid plasticization and reduce the temperature of processing, others to impart tackiness or stickiness to the unvulcanized rubber. Some act as lubricants reducing internal friction during filler addition and following processing operations rather than actual plasticization of rubber. Stearic acid is added for activation that helps in plasticization and lubrication of rubber stock. Inadequate plasticization leads to non-homogeneous mixing and scorching and thus leads to non-uniform thickness and dimensions of sheets and profiles in the calendering process as well as extruding machine with tremendous shrinkage. On the other hand, excess plasticization makes the compounds too soft and sticky that leads to problems in handling. The fact that plasticization of rubber in the mixing mill is the result of oxidation implies that oxygen is indispensable for the same. Chemical agents which accelerate oxidation along with effecting plasticity to a desired Mooney viscosity level are called peptizing agents. [34–36]

3.1.8 Anti-softeners or stiffeners

These are compounds which when added in very small quantity to the compound stock produce a slight stiffening effect or decrease in plasticity. Benzidine and para-aminophenol are examples of organic chemicals that consist of these properties. Litharge is an inorganic stiffener. These agents are used in compounds to reduce sagging or plastic flow during lining activity, wire insulation and hose compounds after calendering or extrusion and during vulcanization. Benzidine gives maximum effect in concentrations of about 0.1 phr. [28]

3.1.9 Reinforcing fillers

There are two types of fillers, reinforcing and non-reinforcing fillers. Those fillers which have a pronounced effect on the physical properties of rubbers, such as tensile strength, abrasion resistance, tear resistance, and fatigue resistance, are called reinforcing fillers. Fillers that do not have an influence on the above mentioned properties are called inert fillers (e.g., ebonite dust, graphite powder). They perform a number of important functions such as increasing chemical resistance, heat resistance, and ease of processing, providing rigidity or hardness to products, and most important of all reducing the cost of the compound. Carbon black is commonly used as reinforcing filler. This is also the reason why most rubbers are black. Calcium carbonate is an example of non-reinforcing filler. Some typical rubber fillers are namely clays, calcium carbonate, silica, etc. Carbon black is used to improve the strength of the rubber. The performance of carbon black incorporated into rubber largely depends on its oil number. Tires contain over 30 weight percentage of carbon black which is quite significant amount. Some of the inert fillers include whiting, barites, lithopone, talc, etc., apart from ebonite dust and graphite powder. [28,29,32]

3.1.10 Pigments and colours

Ingredients that belong to this class give colouring effect to rubber products. ZnO and titanium dioxide produce light coloured articles and are used as a base for addition of other colouring ingredients. Organic dyes impart bright and glossy colours, and they can be used in smaller proportions than mineral pigments. Most of the dyestuffs used in textile industry can be used for manufacturing coloured rubber products. [28,37]

3.1.11 Factice

Factices are products generated by heating vegetable oils with sulphur (brown factice) or by reacting them with sulphur chloride in a suitable solvent (white factice). They are called rubber substitutes because of their use. They have a low softening action and are used in quite small quantity to as processing aid in extrusion and calendering operations. Factices are used in the production of erasers and soft rollers. Brown factice in small quantity has a slight activating effect on vulcanization, on the other hand, white factice has a retarding effect. Elastic bituminous substance derived from petroleum asphalt is called as mineral rubber which has a softening effect and as such is known a softener. Due to low specific gravity and cost asphalt is regarded as a cost

reducing substitute. Its main disadvantage is that it can be used only in black coloured compounds. Hard asphalt has high dielectric strength and low dielectric constant and hence it is used in wire insulations extensively. [28,38]

3.1.12 Blowing agents for sponging

The manufacturing of sponge rubber products such as gaskets for heat exchangers is based on the introduction in the compound of chemicals which cause gas formation during vulcanization and thereby produce the desired porosity. Sodium bicarbonate and ammonium bicarbonate are examples of popular blowing agents. [28,39]

3.1.13 Abrasives

These are special mineral ingredients used to impart abrasive power to rubber products, used for abrading, grinding or polishing such as rubber erasers and hard or soft rubber grinding wheels such as carborundum. [28]

3.1.14 Processing aids

The term process aid is a general description for any material that will improve one or more aspects of the processing behaviour of rubber. These materials generally improve the flow behaviour, providing smooth surface finish to calendared or extruded products. Typical process aids include the following materials: [40]

- Wax
- Fatty acids
- Soaps emulsified
- Esters
- Polyethylene waxes

4 VULCANIZATION OF RUBBER

Vulcanization is the key or approach of inserting chemical cross-links between the long chains of rubber molecules to form a network. The vulcanization process is necessary for producing most useful rubber articles, like tires and mechanical goods. Un-vulcanized rubber is generally weak, does not retract primarily to its original shape after a large deformation, and it could be very sticky. In short, un-vulcanized rubber can have the same inert nature as chewing gum. [41,42]

The first commercial method for vulcanization has been contributed by Charles Goodyear. His process (heating NR with sulphur) was first practised in Springfield, Massachusetts, in 1841. Thomas Hancock repeated essentially the same process about a year later in England. Since the early era, there has been tremendous continuous progress toward the improvement in process and in the resulting vulcanized rubber products. Along with NR, over the years, many synthetic rubbers have been incorporated. Also, in addition to sulphur, other ingredients have been introduced as components of curing (vulcanization) systems. [42]

The accelerated-sulphur vulcanization of synthetic rubbers along with the vulcanization of other rubbers, which are vulcanized by closely related technology, comprises more than 90 % of all vulcanization. These rubbers include EPDM, IIR, halo butyl rubbers, and NBR. Nevertheless, some consideration is also given to vulcanization by the action of other vulcanization agents such as organic peroxides, phenolic curatives, and quinoid curatives. [42]

4.1 Definition of rubber vulcanization

Vulcanization, in general, is a process implied to rubbery or elastic materials. These materials come back or retract to their approximately original shape after a mechanically imposed deformation. Vulcanization can be defined as a process that increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization tends to increase elasticity while it causes reduction in plasticity. It is generally accompanied by the formation of a cross linked molecular network or structure. According to the theory of rubber elasticity, “the retractile force to resist a deformation is proportional to the number of network-supporting polymer chains per unit volume of elastomer”. A supporting polymer chain is considered as a linear polymer molecular segment between network junctures. An increase in the number of junctures or crosslinks provides an increase in

the number of supporting chains or network. In an un-vulcanized linear high polymer (above its melting point) only molecular chain entanglements constitute junctures. Vulcanization, thus, is a process of chemically producing network junctures by the introduction of crosslinks between polymer chains. A crosslink may be a group of sulphur atoms in a short chain, a single sulphur atom, a carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. [42]

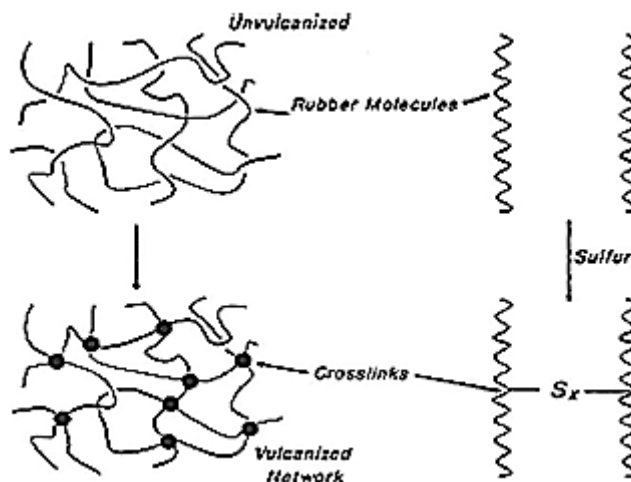


Figure 8: Network formation during vulcanization. [42]

4.2 Effects of vulcanization on vulcanizate properties

Vulcanization causes recommendable significant changes at the molecular level. The long rubber molecules (molecular weight usually between 100,000 and 500,000 Daltons) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4000 and 10,000 Daltons. Because of network formation or crosslinking, essentially the rubber becomes insoluble in any solvent, and it cannot be processed by any means that requires it to flow, like processing in a mixer or extruder; on a mill or calendar; or during shaping, forming or molding. Thus, it is highly mentioned that vulcanization occurs only after the rubber article is in its final stage of geometric form. Effects of vulcanization on end-use properties are illustrated in Figure 9. [42]

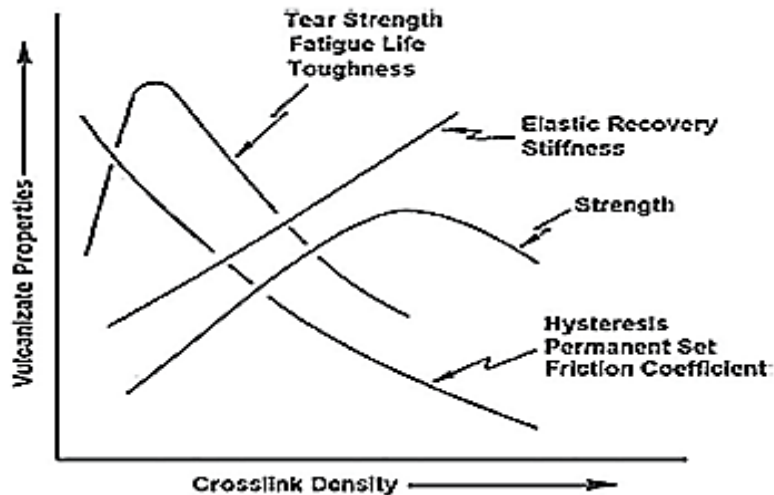


Figure 9: Vulcanizate properties as a function of the extent of vulcanization. [42]

Crosslink formation greatly reduces hysteresis. Hysteresis is defined as the ratio of the rate dependent or viscous component to the elastic component of deformation resistance. It is also defined as a measure of deformation energy, which is not stored (or borne by the elastic network), but is converted to heat. Vulcanization then causes a change or trade-off of elasticity for viscous or plastic behaviour. Tear strength, fatigue life, and toughness are related to the breaking energy. Extent of the properties increases with small amounts of crosslinking but they are reduced by further crosslinking. Properties related to the energy to break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density. [42]

It should be noted that the properties are not related only of crosslink density. The type of crosslink, the type of polymer, and type and amount of filler, as such also affects them considerably. [42]

Reversion is a term or phenomenon generally applied or observed to the loss of network structures by non-oxidative thermal aging. It is usually linked with isoprene rubbers vulcanized by sulphur. It can be the result of quite long vulcanization time (over curing) or hot aging of thick sections. It is most extreme at temperatures above 155 °C. It occurs in the case of

vulcanizates containing a large number of polysulfide crosslinks. Though its mechanism is quite complex. [42]

4.3 Characterization of the vulcanization process

The time elapsed before crosslinking starts, the rate of crosslink formation once it starts, and the extent of crosslinking at the end of the process, are important characteristics related to the vulcanization process. There must be sufficient or significant delay or scorch resistance (resistance to premature vulcanization or prolonged time for initiation for vulcanization) to permit mixing, shaping, forming, and flowing (e.g., in the mold) of the rubber before vulcanization. [42, 43]

After this necessary delay, or induction period, the formation of crosslinks should be rapid and the extent of crosslinking must be controlled. Scorch resistance is usually measured by the time required, at a given temperature, for the onset of crosslink formation, as indicated by an abrupt increase in viscosity. The Mooney viscometer can be used for this purpose (Figures 10 & 11). [42]

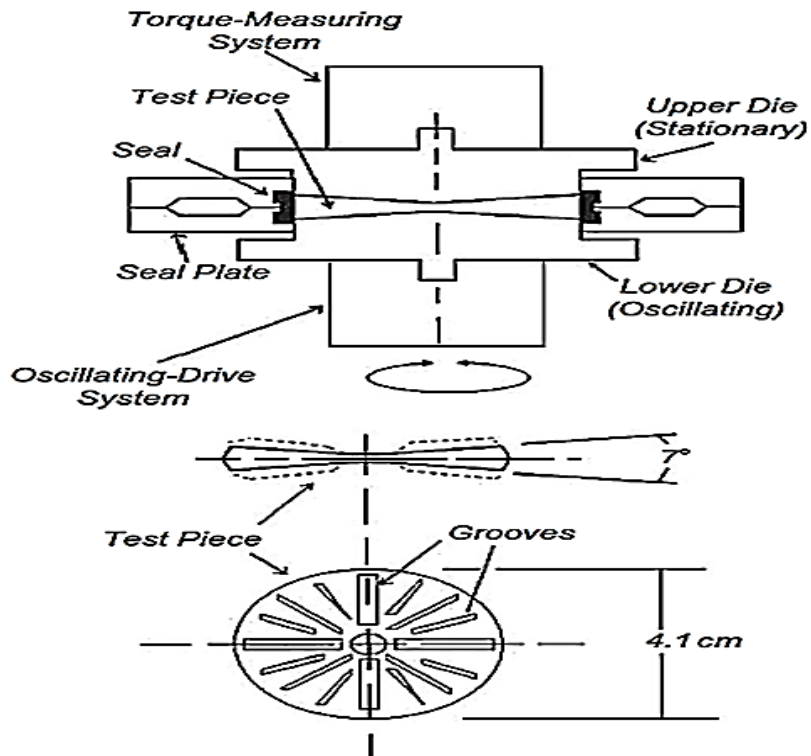


Figure 10: Moving disc rheometer. [42]

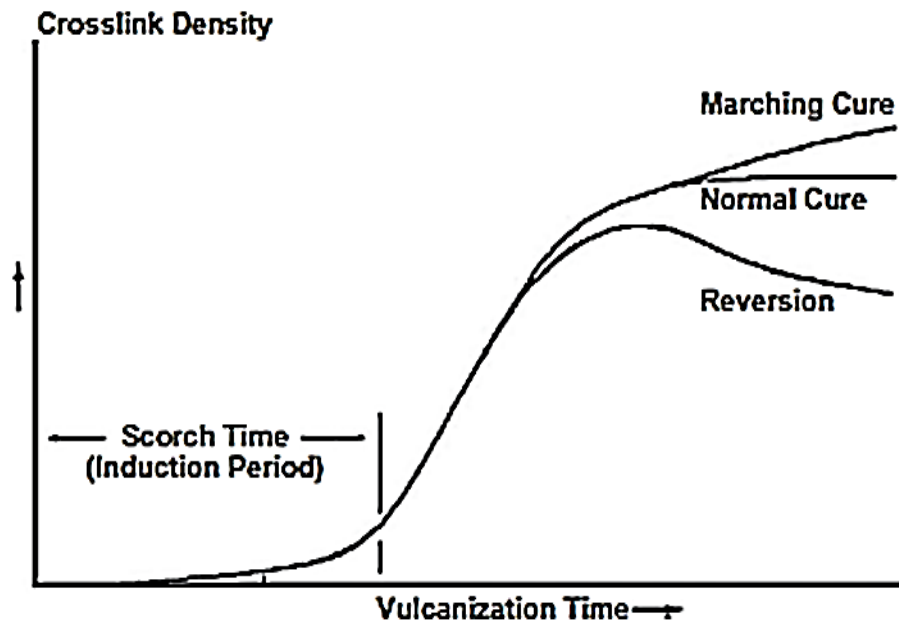


Figure 11: Rheometer cure curve. [42]

During this test, the fully mixed but un-vulcanized rubber is put or contained in a heated cavity. Imbedded in the rubber is a rotating disc. Viscosity is continuously measured (by the torque required to keep the rotor rotating at a constant rate) as a function of time. The temperature is selected to be characteristic of rather severe processing (extrusion, calendaring, etc.). Both the rate of vulcanization after the scorch period and the final extent of vulcanization are measured by using devices called cure meters using above rheometer in Figure 10. [42]

5 METHODS OF CROSS- LINKING

Vulcanization of rubber is a chemical process, and is slightly complicated one at that, and any attempt to anticipate the volatile by-products can avoid the chemistry involved. For a step-by-step, it is simple to start with peroxide vulcanization. The basic features of sulphur vulcanization will be developed from this basis. [44]

5.1 Peroxide crosslinking

Peroxides are used in the vulcanization of various kinds of rubber, especially the ethylene-propylene and silicone rubber. The reaction depends on the activation of the rubber molecule when a hydrogen atom is abstracted from it by peroxide action. The advantage of peroxide crosslinking is formation of C-C cross-linked bond. In below case the hydrogen is abstracted by free radicals generated from the peroxide breakdown. The following steps show the sequence from dialkyl peroxide (X-O-O-X), represented in equation 1. [44,45]

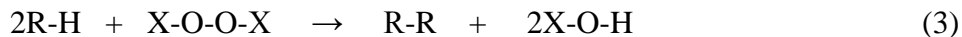
Peroxide breakdown:



Hydrogen abstraction (rubber polymer represented as R-H) in equation 2. [44]



On this basis the first volatile product produced is an alcohol, and further breakdown products follow. Rubber crosslinking can take place by radical coupling, in which case the complete reaction can be represented in equation 3. [44]



The above equation represents the simplest chemical model of vulcanization: the volatile by-products depend on the peroxide used and on peroxide decomposition in the reaction. The characteristic smell of peroxide vulcanizations arises from the ketones present in the volatile mix. [44]

5.2 Sulphur crosslinking

The above equation for peroxide crosslinking provides the simplest model of sulphur vulcanization represented in equation 4. [44]



In this case the sulphur is shown in polyatomic form (rhombic sulphur is S_8) and the crosslink that forms is represented as polysulphidic. Accelerators are now an important part of any sulphur vulcanization system: accelerators increase the rate of vulcanization and change the sulphur content of the cross-linked entity. The most important curative is sulphur which produces (polymer)-S_x-(polymer) crosslinks. [44, 46]

In general, the most widely used technique in curing various industrial applications is the accelerated sulphur curing method, since it provides better physical properties, provides a considerable fast crosslinking rate and it has the capability to provide the delayed actions needed for processing, shaping, and forming before the formation of the rubber vulcanized network.

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5.2.1 Vulcanization by sulphur without accelerator

Initially, vulcanization was achieved by using elemental sulphur at a concentration of 8 phr. It required 5 hours at 140 °C earlier. The incorporation of ZnO reduced the time to 3 hours nowadays. The use of accelerators, in quantity as low as 0.5 phr, has therefore reduced the time to as short as 1–3 min. [42]

5.2.2 Accelerated sulphur vulcanization

Accelerated-sulphur vulcanization is the most widely used method. For many applications, it is the only rapid crosslinking technique that can, in a practical manner, give the delayed action required for processing, shaping, and forming before the formation of the intractable vulcanized

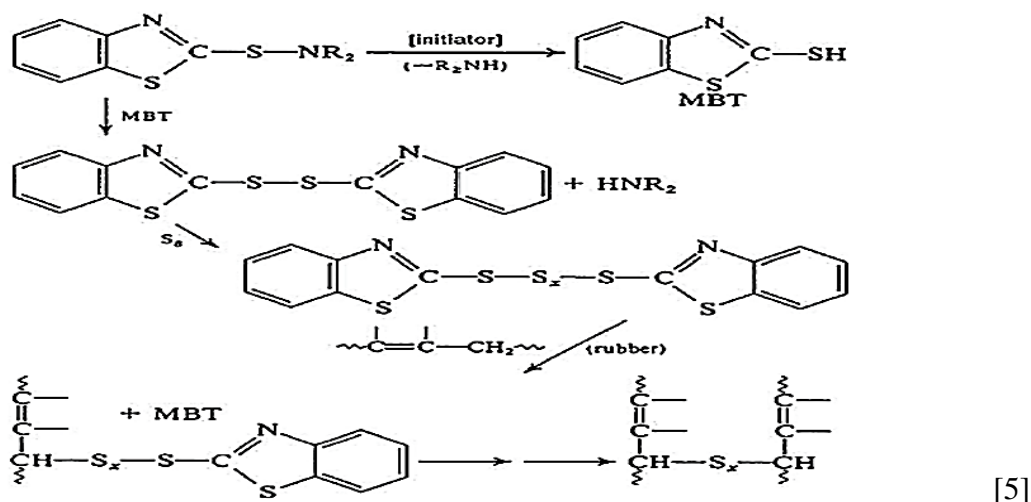
network. It is used to vulcanize NR, IR, SBR, NBR, IIR, CIIR, Bromo Butyl Rubber (BIIR), and EPDM. More often, mixtures of accelerators are used. Typically, a benzothiazole type is used with smaller concentration of a dithiocarbamate (thiuram) or an amine type. The result of using a mixture of two different types of accelerators can be that each activates the other and more desired results can be obtained. Mixing accelerators of the same type gives average or intermediate results. [42]

Compound	Abbreviation	Structure
<i>Benzothiazoles</i>		
2-Mercaptobenzothiazole	MBT	
2,2'-Dithiobisbenzothiazole	MBTS	
<i>Benzothiazolesulfenamides</i>		
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-butylbenzothiazole-2-sulfenamide	TBBS	
2-Morpholinothiobenzothiazole	MBS	
N-Dicyclohexylbenzothiazole-2-sulfenamide	DCBS	
<i>Dithiocarbamates</i>		
Tetramethylthiuram monosulfide	TMTM	
Tetramethylthiuram disulfide	TMTD	
Zinc diethylthiocarbamate	ZDEC	
<i>Amines</i>		
Diphenylguanidine	DPG	
Di-o-tolylguanidine	DOTG	

Figure 12: List of accelerators for sulphur vulcanization. [42]

The general reaction path of accelerated-sulphur vulcanization is thought to be accelerator reacts with sulphur to give monomeric poly-sulphides of the structure $Ac-S_x-Ac$ where Ac is an

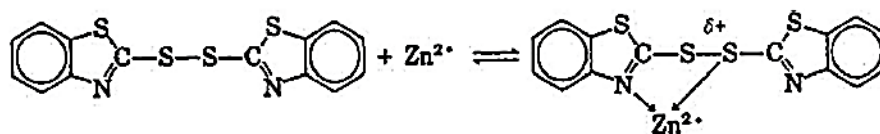
organic radical derived from the accelerator (e.g., benzothiazoyl). The monomeric poly-sulphides react with rubber in the compound to form polymeric poly-sulphides (e.g., rubber-S_x-Ac). During this reaction, formation of 2-mercaptobenzothiazole (MBT) takes place, if the accelerator is a benzothiazole derivative and if the elastomer is NR. When MBT works as an accelerator in NR, it first disappears then reappears with the formation of rubber-S_x-Ac. Finally, the rubber poly-sulphides react directly or through an intermediate, to give crosslinks, rubber-S_x-rubber. A reaction scheme is shown in equation 5. [42]



There are practically visible differences between accelerated vulcanization and un-accelerated vulcanization. Higher crosslinking efficiencies and higher crosslinking rates can be noted with accelerated vulcanization. But there are more unique differences. Results from the reactions with curing ingredients shows that sulphur becomes attached to the rubber hydrocarbon almost exclusively at allylic positions. This is not the case with un-accelerated sulphur vulcanization. [42]

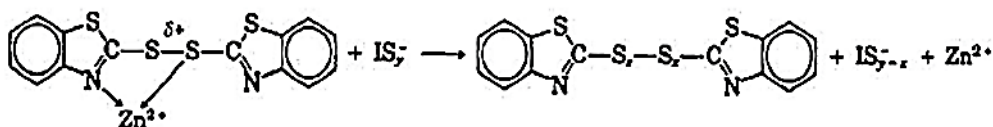
5.3 The role of zinc benzothiazole accelerated vulcanization

An increase in the concentration of fatty acid and that results in increase of concentration of available Zn^{2+} leading an increased overall rate in the early reactions (during the delay period), which leads to the formation of rubber-S_x-Ac. However, it leads to a decrease in the rate of crosslink formation but an increase in the extent of crosslinking otherwise. The increase in the rates of the early reactions is explained by the following interaction [42]:



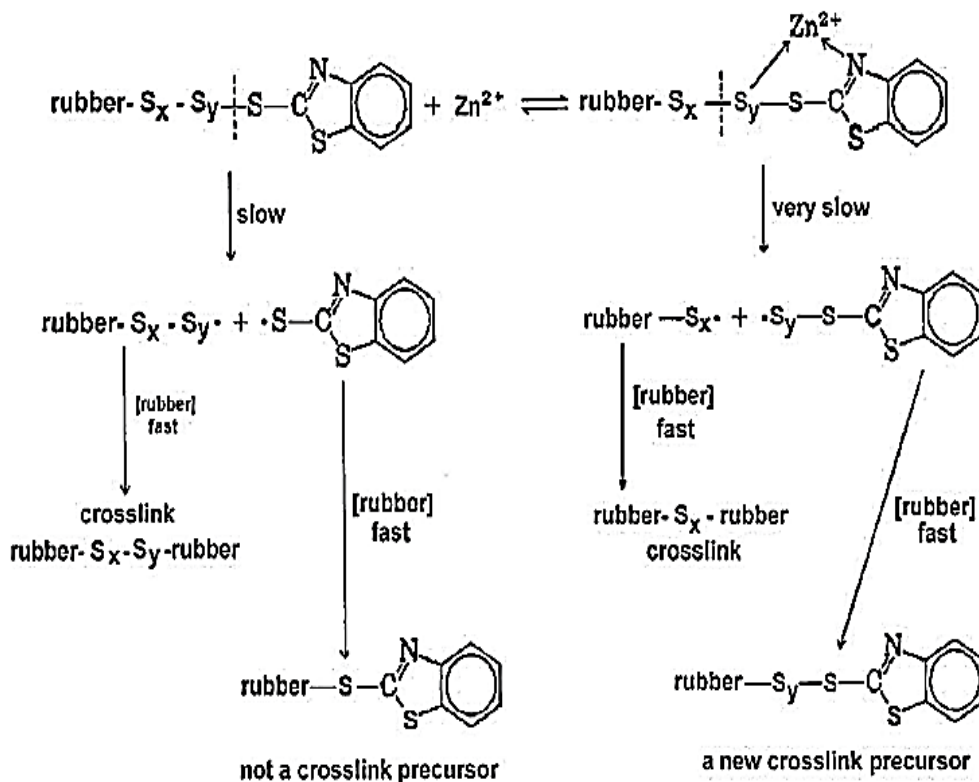
[6]

The chelated form of the accelerator is more reactive than the free accelerator during the early reactions:[42]:



[7]

Here, I-S_y is an ionized form of linear sulphur. It could be rapidly formed in a reaction between sulphur and any number of initiating species. Ignatz Hoover proposed that the presence of Zn²⁺ can increase the rate of sulphurization through the formation of complexes. The decreased in specific rate of crosslink formation, and the increased extent of crosslinking due to the presence of Zn²⁺ in benzothiazole accelerated vulcanization [42]:

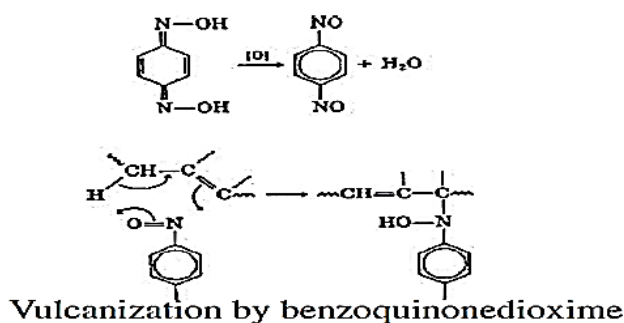
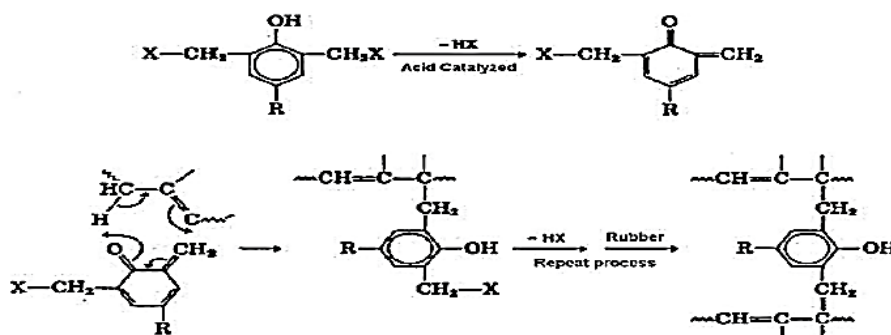


[8]

Zinc chelation can change the position of the S-S bond most prone to break. Suggested, a stronger bond must break, the rate will slow down. Though the crosslinking rate is slow, the extent of crosslink formation is increased since less sulphur is used in each crosslink. Thus the resulting, crosslinks are of lower sulphide rank. The presence of zinc compounds can also initiate the reduction of the sulphur rank of crosslinks preferably in high-temperature aging of the vulcanizate, for example, during reversion. In some cases zinc compounds actually promote the decomposition of crosslinks. [42]

5.4 Vulcanization by phenolic curatives, benzoquinone derivatives

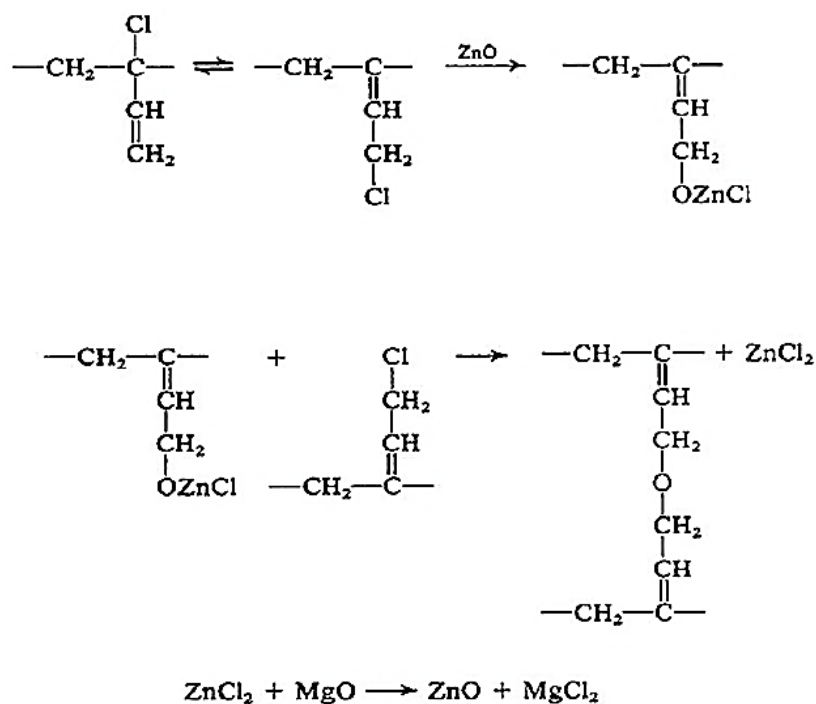
Diene rubbers like NR, SBR, and BR are vulcanized by the action of phenolic compounds substituted by $-\text{CH}_2\text{-X}$ groups where X is an $-\text{OH}$ group or a halogen atom substituent, respectively. A high-diene rubber is vulcanized by the action of a dinitrosobenzene, which forms in situ by the oxidation of a quinonedioxime, incorporated into the rubber in company of oxidizing agent, lead peroxide. The attack on rubber molecules by the vulcanization system can be described in a similar way to that which was stated for the sulphurization of the rubber molecules by the action of accelerated sulphur vulcanization systems. Reaction depiction is following [42]:



M-phenylenebismaleimide is another vulcanizing agent for high-diene rubbers. A free radical catalytic source such as dicumylperoxide or benzothiazyl disulphide is usually used to initiate the reaction. [42]

5.5 Vulcanization by metal oxides

Chlorobutadiene or CR are mostly vulcanized by the use of metal oxides. The crosslinking agent is commonly ZnO, which is used along with magnesium oxide. CR is vulcanized in the presence of ZnO alone; though, magnesium oxide is necessary to give scorch resistance. A mechanism, which has been written for the vulcanization of CR by the action of ZnO and magnesium oxide, is following [42]:

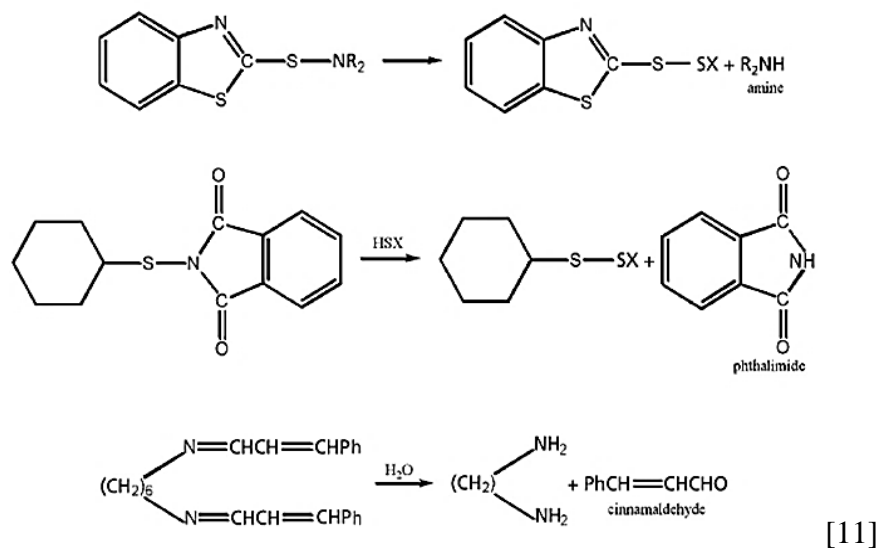


[10]

5.6 Amines and delayed action cures

In this involved reaction a chemical change must predate the actual vulcanization, and there are formations of volatile by-products which are not necessarily involved in any subsequent step in the reaction. These can therefore pop out as major emissions from the cure. The examples in equation 11 show the release of an amine from a sulphenamide, phthalimide from N-

(cyclohexylthio) phthalimide (PVI), cinnamaldehyde from N,N' -dicinnamylidene-1,6-hexanediamine.[44]



Considering the range of sulphenamides in particular use, a variety of amines may be released. These include both primary ($-NH_2$) as well as secondary ($>NH$) types. Amines, which can also be formed from the action of thiurams and dithiocarbamates are therefore important by-products of accelerated sulphur cures. Some prominent examples are listed in Figure 13. [44]

Table 2: Primary (10) and secondary (20) amines from accelerators and curing agents. [44]

Ingredient		Amine evolved	Boiling point (°C)
Tetramethyl thiuram disulfide	TMTD	Dimethylamine (2°)	7.4
<i>N-tert</i> -Butyl-2-benzothiazole sulfenamide	TBBS	<i>tert</i> -Butylamine (1°)	44
Tetraethyl thiuram disulfide	TETD	Diethylamine (2°)	56
<i>N,N</i> -Diisopropyl-2-benzothiazole-sulfenamide	DIBS	Di-isopropylamine (2°)	84
4,4'-Dithiodimorpholine	DTDM	Morpholine (2°)	128
<i>N</i> -Oxydiethylene-2-benzothiazyl sulfenamide	NOBS	Morpholine (2°)	128
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide	CBS	Cyclohexylamine (1°)	135
Tetrabutyl thiuram disulfide	TBTD	Dibutylamine (2°)	159
Diphenyl guanidine	DPG	Aniline (1°)	184

6 RUBBER TO METAL BONDING

Rubber to metal bonding is a vast field underlying a number of interlinked processes. The products from these processes are employed as metal bonded oil seals, engine mounts for the reduction of noise and vibration in automotive and engineering applications, rubber lined mild steel tanks, and instruments that are safe from corrosion, so can be used for long run. [50]

Rubber industry is over 150 years old; it is during the last few decades that design engineers came with an idea to apply the strength of metals with the elasticity of rubber in combination with each other for a number of applications. Earlier mechanical means were used to bond rubber with metal. Hard rubber technique was employed to achieve the first rubber-metal bond. The first commercially successful bonding process was achieved by the brass plating technique during the 1920s. The hard rubber bonding system is applicable in some applications, such as rubber rollers and tank linings. [50]

In chemical bonding technique, three important elements that form the core of the process are; the rubber compound, the bonding agents and the substrate. Polymer base selection and linked compound depends mainly on the product utility. Provided that the rubber can flow into the mold without developing significant levels of cross-linking (less than 2 %), a bond can be formed from any rubber compound. There are no limitations on compounding ingredients, but still it is safe enough to avoid substances that will bloom rapidly on the surface of the un-cured compound stock. It is generally evident that that bonding of rubber with metal happens through both physical and as well as chemical method. Since metals are polar, polar rubbers will have great affinity to form bond rather than non-polar rubbers. The higher the polarity, the more willingly the rubber bonds with metals when using a single coat adhesive system. The lower the polarity, the greater is the requirement for using a two-coat system – a primer to provide good bonding with metal, and a secondary or top adhesive coat to provide good bonding with rubber. Many bonding agents are available and the most important are listed below [50]:

- polyisocyanates
- chlorinated rubber
- phenol formaldehyde resins

For few decades, bonding agents were a primer coat based on phenolic-style resin, and a top-coat formed from solutions of polymers and other ingredients. Bond formation is in the connection with the initiation of a very high modulus in the rubber layer quickly adjacent to the surface of the bonding metal. [50]

The selection of bonding agents extensively based on the kind of rubber to be bonded, the modulus of the rubber and the design of the component. The selection process is critical to the resilience of the bond. After the introduction and much development concerning water-based types of bonding agents, these are now effective replacements for the solvent-based agents. Bond stand to be up to 10 % weaker, but components show good resistance to normal conditions found in automotive applications. Application methods for water-based bonding agents are similar to those for the solvent systems, but inserts have to be preheated to 60–80 °C before applying the primer, and then again re-heated before applying the top-coat. Drying times are surprisingly short and no obstacles arise if high volume demand for production is required. [50]

The choice of substrate depends primarily with the component designer, who must think about the necessary strength and durability requirements for the desired use. The conventional substrate is steel, in all its forms and grades, but recommended is the use of aluminium alloys and polyamides to reduce weight. Almost any material could be bonded to rubber, just to make sure that it can withstand the heat and pressures of the molding process, for desired practical purposes. Polyacetal inserts can be bonded, but require careful etching and use of rubber molding temperatures below 150 °C. Polytetrafluoroethylene (PTFE) provides a useful low friction material for use in anti-roll bar bushes as well as fluid seals. It can be bonded successfully to rubber by chemically etching the surface of the plastic prior to application of bonding agents. Its use in such applications has, however, been largely superseded by woven PTFE fibre material, which offer a better mechanical bond. [50]

6.1 The bonding process

6.1.1 Substrate cleaning

The first key step in the process for metal inserts is to clean them properly. Necessarily all remains of oil, any grease and lubricant should be cleaned from the metal surface for strong bonding. [50]

Wet blasting followed by phosphate conversion treatment is of greater acceptance as a cost-effective process and is gaining popularity, and it also provides the added benefit of improved corrosion resistance. Whatever process route is adopted, the focus should be on control, to ensure that the consistency in the results should be met. De-greaser plants need to be examined carefully to minimize any build-up of contaminants, or change in pH. In practice, use of neutral stabilized trichloroethylene is apt for vapour degreasing. The grade of grit applied in shot-blast operations is salient, and will affect the environmental resistance of the finished product. The profiling of particle sizes is a primary tool to examine machine effectiveness, and fortifies that dust levels remain low during blasting. Routine sampling will show if fresh grit is being fed to the machine and so detect a failure in the mechanism of dust extraction. Surface profile differences due to the changes in the size range of the grit will not lead to failure in the bond, but the presence of dirt and debris in the grit will lead to the same failure. Dust inclines to the newly cleaned metal surfaces and is very onerous to remove, even with a second degreasing operation. [50]

6.1.2 Application of bonding agents

Methods for applying bonding agents are subject to frequent review. The process requires the application of a primer coat and then a top-coat. In high volume method of production, other mechanistic faults may allow the production of components without the necessary primer just beneath the top-coat. Such parts in the beginning will show a good bond, but will be likely to failing service. The best method to date is to ensure that the primer is sprayed over a slightly wider area than the top-coat to show that it is there. However, this does not work for inserts that need to be bonded over 100 % of their surface. If service conditions are exceptionally severe, as is the case for bonds which are subject to dynamic strain, or in contact with oils, solvents, boiling water or corrosive chemicals, then a two-coat adhesive system is preferred. When using a two-coat system, it is essential that there should be good compatibility between coats. Lack of compatibility is likely if primer and top or cover coat are obtained from separate source. [50]

6.2 Metal treatment

The bonding mechanisms of the multiphase systems involved in making a rubber to metal component are complex and the chemistry of the reactions involved not totally disclosed or understood. In the region of the metal contact the interactions are deemed to be a combination of mechanical and chemisorption processes. [51]

Rubbers and resins act as barriers to the migration of external corrosion catalysts of the metal surface. The resins and rubbers probably form an interpenetrating network of polymer chains within the adhesive system, thus giving strength and structure to the primer and rubber bonding coats. Bond quality depends to a large extent on the ability of all interfaces to freely exchange chemical entities. Any contamination of surfaces will ruin the surface chemistry at that point and will reduce the bond strength. Some techniques are used to overcome this problem and are discussed below. [51]

The quality of bond achieved during the manufacture of the component must be of sufficient integrity, not only to be stronger than the rubber itself, but also to outlast the active life of the rubber constituent of the components. To this end, the design of the component and metal part must be carefully considered to ensure that no undue stress concentrations are created in the area of the bond between the rubber and the metal. Components consisting of molded rubber bonded to metal, carried out during high temperature vulcanization, can have inherent stresses simply due to shrinkage of the rubber when cooling from the vulcanization temperature and the coefficient of thermal expansion relationship of the rubber-metal combination. The 'shrinkage' of the rubber in the system will be different for each type of rubber being used and is dependent also upon the compound hardness, or degree of filler presented. Allowances for the rubber shrinkage must be made in determining the shape of the mould cavity and hence the component's final shape. [51]

The environment in which the component will work is also affecting the stresses to which the rubber-metal bond will be subjected. Few oil and solvent environments will penetrate a bond at the interface and thus may weaken or destroy the integrity of the bond until the stress becomes relieved by failure. One major problem can also be the corrosion of the metal component of the bonded unit by salt environments and thus due concern and allowance must be made for the service conditions in which the rubber to metal component will be resistant. Corrosion of the bonded metal under the bonding system can also occur if the metal pre-preparation is carried out with acidic degreasing fluids. Care must be taken to degreasing fluids since their remaining proportion should be neutral in pH throughout their use in the application. Recovery of used solvents and redistillation can significantly change the pH of a solvent. This can be a particular

problem with chlorinated solvents, where after re-distillation the distillate can be acidic in nature. [51]

Post-vulcanization bonding is a type of bonding which includes adhesive bonding and vulcanizing bonding agents under the effect of heat and pressure, in the cases regarding the plastics component needs to be adhered to the preformed vulcanized rubber. This may be the only adequate method of manufacture for some products and there is a collection of adhesives available for plastics. The main adhesives for bonding plastics to rubbers include cyanoacrylates, two-part urethanes, two-part epoxies, hot melt reactive urethane pre-polymers, heat reactive contact cements and silane treatments. [51]

In order to get good long-lasting bonds between rubber and metals it is essential that both materials presented to the interface are clean and free from detritus. The presence of oils and the possibility that compounding ingredients can exude or bloom from the rubber surface, before or after moulding, or during the service life of the component must also be taken into consideration and remedied. In the following section we will discuss very briefly some essential metal pre-treatments ways. [51]

6.2.1 Mechanical

Metals, especially the more common iron and steel, come from the foundry and metal plate stamping shop and are coated with oil, grease and most often with a generous layer of oxide and rolling mill scale which are formed on the exposed surfaces. Oxide films can be further developed during the storage prior to use by the bonding shop. All these materials must be removed from the surface and from the voids in the metal to ensure that the oils and greases which otherwise may be trapped unseen cannot exude under the increased temperature of vulcanization, when they become more mobile or volatile. Surface oxides must be removed since they are frequently only loosely structured in their attachment at the metal substrate and will rupture and detach themselves under duress. This will subsequently cause the metal-adhesive bond failure. Once the original oxide layer has been removed, the freshly exposed metal will immediately start to build a new oxide film which must be minimized by rapid degreasing and application of primer/adhesive coating. [51]

Possible mechanical pre-treatment used are:

- Initial degreasing
- Alkaline removal of oils and greases
- Solvent dip methods for large scale removal of greases
- Removal of surface oxides

6.2.2 Chemical

The alternative metal pre-treatment processes to grit blasting use a variety of different chemical routes. The usual chemical pre-treatment systems consist of acid etching of the surface which is then followed by several water dips and subsequent phosphate or in some cases or circumstances cadmium plating and passivating (render inert). Many of these treatments are done by the metal processor and are not the rubber bonder's processes. [51]

Below mentioned are chemical pre-treatments used [51]:

- Treatment for stainless steels
- Phosphate coating
- Zinc coating or galvanizing
- Aluminium – anodizing
- Metal preparation for waterborne bonding systems

II. ANALYSIS

7 AIM OF WORK

The aim of this master thesis is

- To prepare the different rubber samples with different degree of vulcanization and evaluating their bonding strength on a metal surface without a bonding agent.
- To prepare the different rubber samples with different degree of vulcanization and evaluating their bonding strength on a metal surface with a bonding agent.
- To evaluate the best degree of vulcanization for rubber to metal bonding with and without a bonding agent.

8 COMPOSITION OF RUBBER SAMPLES

Rubber samples were supplied from the company and all the information about them which can be published are listed in Table 3.

Table 3: List of samples with their composition

SAMPLE	SBR (%)	NR (%)	CARBON BLACK
1739 A (R1)		confidential	
1791-1 (R2)	27	41	23
102B-1 (R3)	17	39	28
CK1-1	EPDM vulcanized via sulphur		

9 EXPERIMENTAL SET UP

9.1 Determination of vulcanization curve

For the determination of vulcanization curve for all samples under investigation commercially available rubber processing analyzer (RPA 2000) invented by Monsanto in 1992 was used (Fig 14). The RPA has die design same as moving disk rheometer. However, unlike other rotor-less cure meters, the RPA performs tests or moves with the lower die with direct drive motor. Through a computer the operator can programme tests in which the oscillation frequency, strain amplitude and test temperature that are valid during a test can be set. Special foil heaters that are part of RPA enable fast temperature increase while a forced air system reduces temperature quickly. These features impart the RPA to function as a true dynamic mechanical rheological tester (DMRT) that can test stocks before during and after cure, raw polymer or master batches. Thus it can be used as [52]:

- a raw polymer tester
- a processibility tester
- an advanced cure meter
- DMRT that measures cure dynamic property at temperature below the cure temperature



Figure 13: Rubber process analyzer. [53].

The RPA can apply enough strain and frequency during oscillation to break up carbon black aggregates network of various rubber compounds. [52] RPA measures the dynamic viscosity of developing a sinusoidal deformation of the uncured rubber inserted in a sealed and pressurized chamber.

9.2 Reduction of samples thickness for molding

Two roll mills were used to reduce the thickness of rubber mixtures supplied by the company for sufficient vulcanization into plates of suitable thickness. This device has two large metal cylinders mounted closely in parallel with each other, which rotate toward one another, creating a narrow gap between the two rolls (Fig 19). The surfaces of the metal cylinders are heated by steam hot water or oil circulating through the rolls. The temperature for all samples was set to 50 °C. Pre-blended material is dropped into the nip gap of the cylinders. The pre-blend melts and forms a drape on metal cylinders. The gap between the cylinders is reduced until desired thickness of the material is achieved. As the material processes on the two roll mill, it is folded over again and again repeatedly to homogenize the material as they are getting mixed up in the process. The material can be taken out of the cylinders once it is mixed properly. [52]

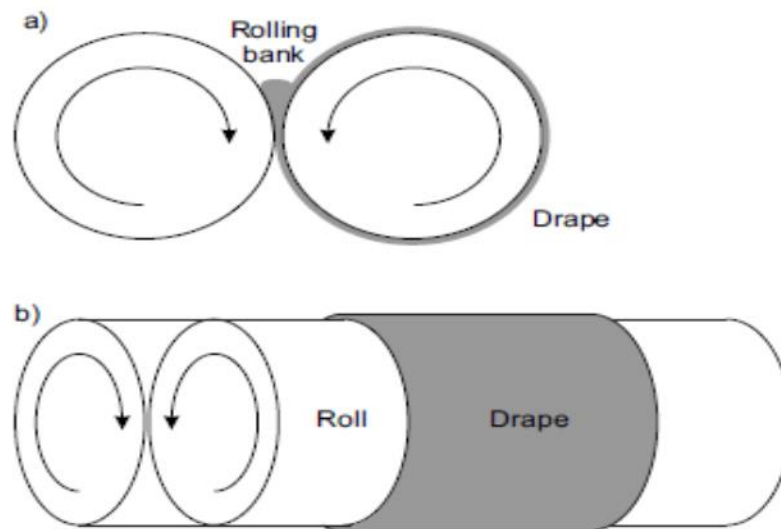


Figure 14: Schematic diagram of two roll mill: a) cross-section view b) drape formation on rolls.

[52]

9.3 Compression molding

A calculated amount of rubber samples is taken, and introduced into a heated mould, which is then closed under pressure, forcing the material into all areas of the cavity while it is melting. Raw material was supplied in either powder or liquid resin form [54]. For compression molding, temperature used is 160 °C. Thickness of the sample is 2mm and amount of rubber used is 55 grams. The rubber samples are compressed for the time mentioned in Table 5 below.



Figure 15: Compression molding press.

Table 4: List of rubber mixtures with respect to their degree of vulcanization and time.

Sample	Degree of Vulcanization (%)	Time (sec)
1739 A	30	61
	40	81
	50	101
	60	121
	70	142
	80	175
	90	192
	120	256
1791-1	30	58
	40	77
	50	96
	60	116
	70	135
	80	168
	90	186
	120	248
102B-1	30	62
	40	83
	50	104
	60	125
	70	146
	80	176
	90	190
	120	253
CK1-1	30	122
	40	162
	50	203
	60	243
	70	284
	80	398
	90	582
	120	776

After the preparation of rubber samples they were put to rest for 16 hours to perform further use according to the standard relating to the rubber to metal bonding.

9.4 Peel test- ASTM D 429 TYPE B

This test is primarily used for determining the bonding strength of rubber to metal bonding agents. The results are obtained by measuring the force necessary to separate a rubber from a metal surface. The data obtained indicate the strength of adhesion along a line across the width of the rubber strip being separated from a metal plate at a 90°. The test provides valuable data for development and control of rubber compounds and test methods of bonding, and it also serves as a screening test for the evaluation of various bonding agents or techniques, or both. [55]



Figure 16: Showing standard peel test machine.

9.4.1 Testing Machine

A power driven test machine equipped to produce a uniform rate of grip separation shall be used for measuring the strength of adhesion. The head of the machine shall travel at the uniform rate of 0.83 ± 0.08 mm/s. [55]



Figure 17: Peel test.

9.4.2 Fixture

Any suitable fixture for holding the test specimen to the upper head of the machine may be used provided the direction of pull to cause separation shall be, at all times during the test, as nearly perpendicular as possible, that is, making a 90° with the top holding fixture. [57] Any suitable grip may be used, provided it does not slip or rupture the rubber strip. [55]

9.4.3 Standard Test Specimen

The standard test specimen shall consist of a strip of rubber $6.3 + 0.1$ mm in thickness, $25 + 0.05$ mm in width, and 125 mm in length adhered to the face of a metal strip $1.6 + 0.1$ mm in thickness, $25 + 0.05$ mm in width, and $60 + 1$ mm in length. [55]

10 PREPARATIONS OF RUBBER SAMPLES

10.1 Cutting of rubber samples

Rubber samples are cut according to ASTM D 429 -TYPE B [56] and marked for the further testing (Fig. 18). Rubber samples are cut by hand with the help of a scissors.

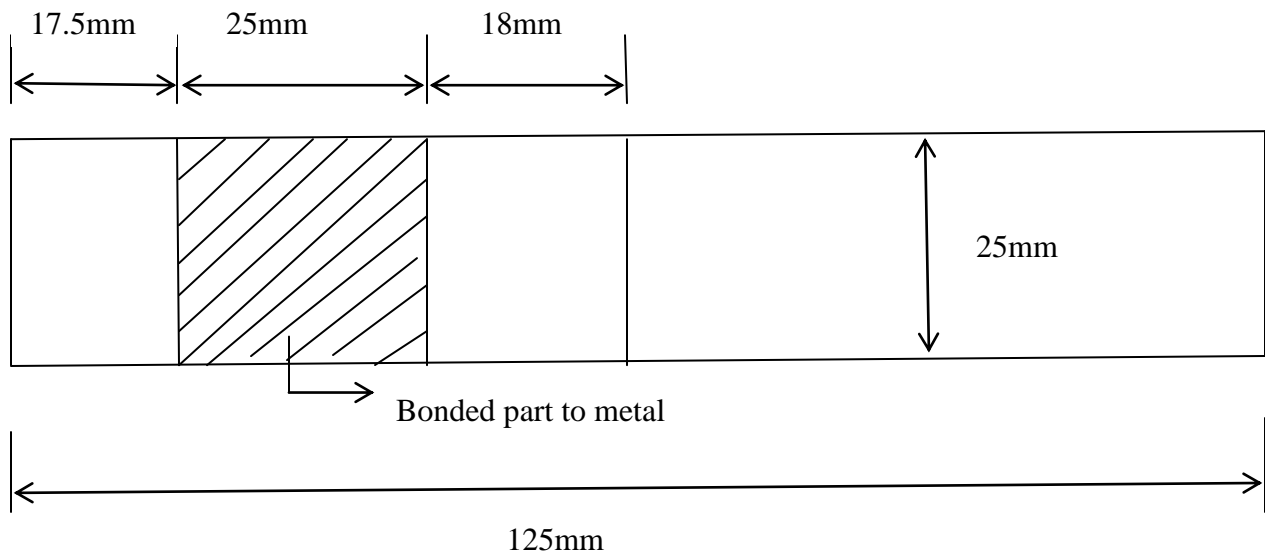


Figure 18: General view of rubber sample for rubber to metal bonding.

10.2 Chemosil

Chemosil NL 256 is often applied for painting the surface of the rubber which is bonded with the metal. Chemosil 256 NL is lead free, versatile, heat activated bonding-agent, which will bond a numerous types of rubber compounds to metal and plastic substrates. [57]



Figure 19: Rubber sample's surface painted with Chemosil.

Single coating is applied in many applications. Chemosil NL 256 bonds elastomer compounds such as NR, CR, EPDM, BR, IR, SBR, NBR, ECO, and IIR rubber to metals. The bonding is established during the vulcanization process of the rubber using cure temperatures typically between 130 and 180 °C. The bond exhibits good resistance against heat, oil and aggressive media. [57] After painting of the rubber samples using a brush they were put to rest for 16 hours to perform further use.

10.3 Metal plate preparation for bonding with rubber

Metals plates were coated with epoxide to protect them from corrosion.



Figure 20: Metal plate before mechanical treatment

Metal plates are marked in same dimension as rubber sample for their easy bonding by compression molding.

After marking the dimensions on the surface of metal plates, they were rubbed with sand paper cube to make the surface uneven so that when the compression molding was done by putting rubber sample on top of the metal plate it sticks. The sand paper was used to rub the metal surface several times in order to remove the basic epoxide coating from the desired area for a good bond between rubber and metal surface.

After rubbing the surface of the metal plate, the rubber samples were placed in accordance with the marking on each other before putting them in compression mould. The temperature of the compression molding was 160 °C and the heating time was 3 min inside compression machine. After 3 min these were cooled for 2 min.



Figure 21: Rubber sample bonded to metal plate after compression molding.

11 RESULTS AND DISCUSSIONS

11.1 Rubber to metal bonding without bonding agent

All three rubber samples were prepared to bond with metal plates at different interrupted vulcanization degree. The result has been summarised in the Table 5.

Table 5: Rubber to metal bond with different degree of vulcanization

Rubber Samples			
Degree of vulcanization	R1	R2	R3
30 %	Too soft and no bonding	Too soft and no bonding	Too soft and no bonding
40 %	Too soft and no bonding	Too soft and no bonding	Too soft and no bonding
50 %	Too soft and no bonding	Too soft and no bonding	Too soft and no bonding
60 %	Soft and No bonding	Soft and No bonding	Soft and No bonding
70 %	No bonding	No bonding	No bonding
80 %	No bonding	No bonding	No bonding
90 %	No bonding	No bonding	No bonding
120 %	No bonding	No bonding	No bonding

All the rubber samples were compressed and bonded with metal plates. Starting from 30 %, 40 %, 50 %, 60 % degree of vulcanization, the samples were too soft and once they were compressed in compression molding machine, they covered the entire metal plate and even out of the plate area and there was no sign of bonding.

In the rest of the vulcanization degrees, there was no bonding with metal plates even with the change of time in compression molding. This process was repeated for 15 days with different time (the post-vulcanization time till 100% degree was also tried for each separate rubber sample) again and again, but it was noticed that there was no bonding of rubber to metal plates.

11.2 Rubber to metal bonding with bonding agent

All the rubber samples were compressed and bonded to metal plates. Starting from 30 %, 40 %, 50 %, 60 % degree of vulcanization, the samples were again too soft and once they were compressed in compression molding machine, they covered the entire metal plate and even out of the plate area which was not good for the next step, i.e. for peel test, as the samples were not in desired condition explained in Table 6.

Table 6: Rubber to metal bond with different degree of vulcanization for bonding with bonding agent.

Rubber Samples			
Degree of vulcanization	R1	R2	R3
30 %	Too soft	Too soft	Too soft
40 %	Too soft	Too soft	Too soft
50 %	Too soft	Too soft	Too soft
60 %	Soft	Soft	Soft

However, starting from 70 %, 80 %, 90 % and 120 % degrees of vulcanization, all the samples were bonded properly with the metal plates and, thus, the results of bonding quality are discussed below.

The bonding strength for the sample pre-vulcanized to 70 % (Fig. 22) is maximum, far greater than rest followed by 80 %, 90 % and 120 % for sample R1. It can be clearly stated that for R1 70 % the bonding quality is much better than for other vulcanization degrees. The ups and downs in the graph indicate that there was always new bonding to break.

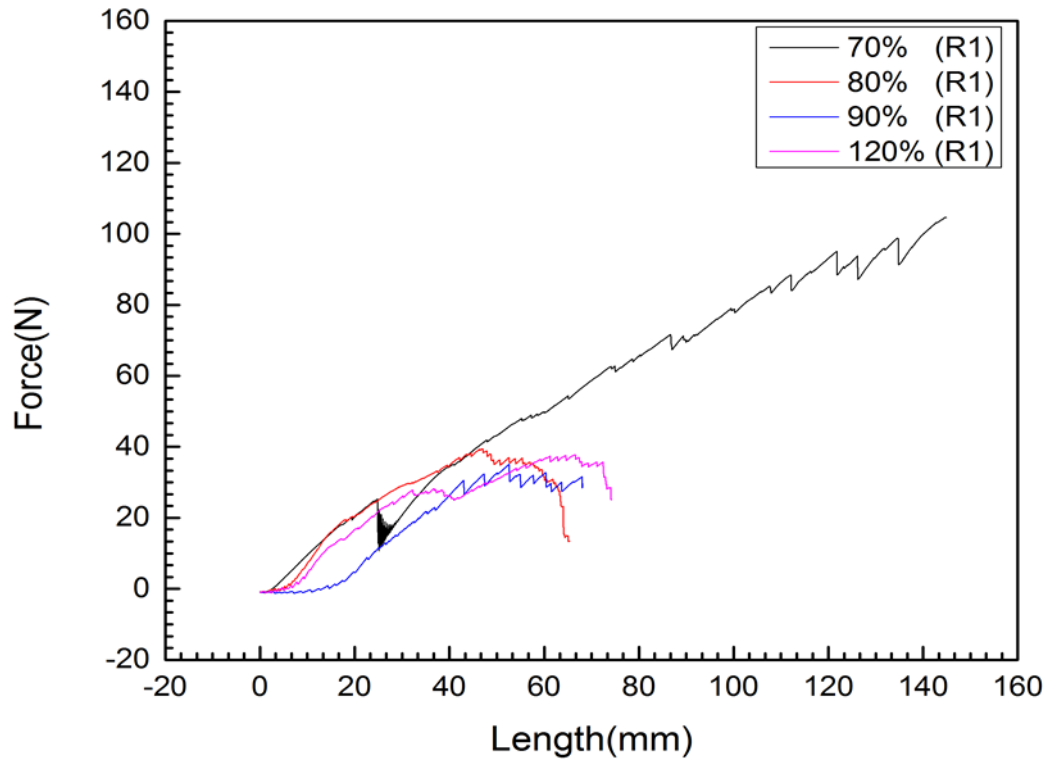


Figure 22: Comparison of rubber to metal bonding strength for Sample R1 with each degree of vulcanization.

The bonding strength for the sample pre-vulcanized to 70 % is maximum, far higher than rest followed by 80 %, 90 % and 120 % for sample R2 (Fig. 23). Evidently, the bonding quality for 70 % interrupted sample is far better than rest of the vulcanization degree.

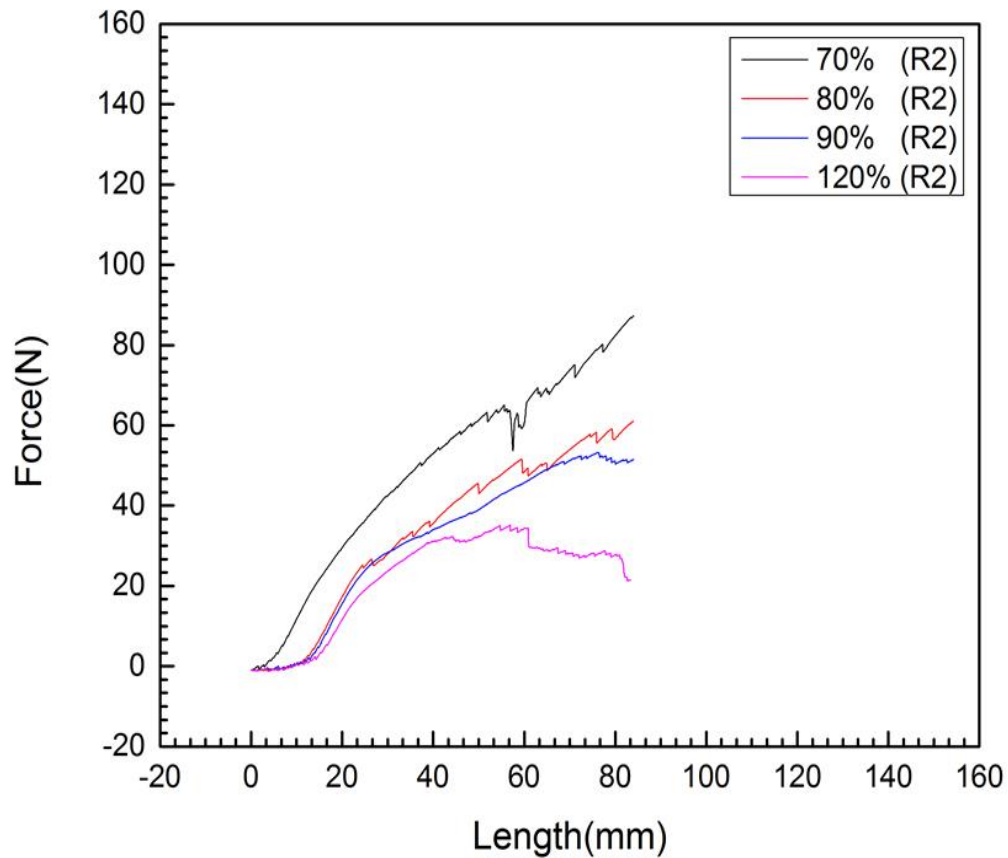


Figure 23: Comparison of rubber to metal bonding strength for Sample R2 with each degree of vulcanization.

The bonding strength for the sample pre-vulcanized to 80 % is surging head of 70 % for R3 rubber sample (Fig. 24), which was the highest till now for the R1 and R2 rubber samples. In here 90 % and 120 % are also quite good but when the force reached a higher level, bonding ruptured suddenly. The force is around 80 N when these two degrees of vulcanization suddenly ruptured

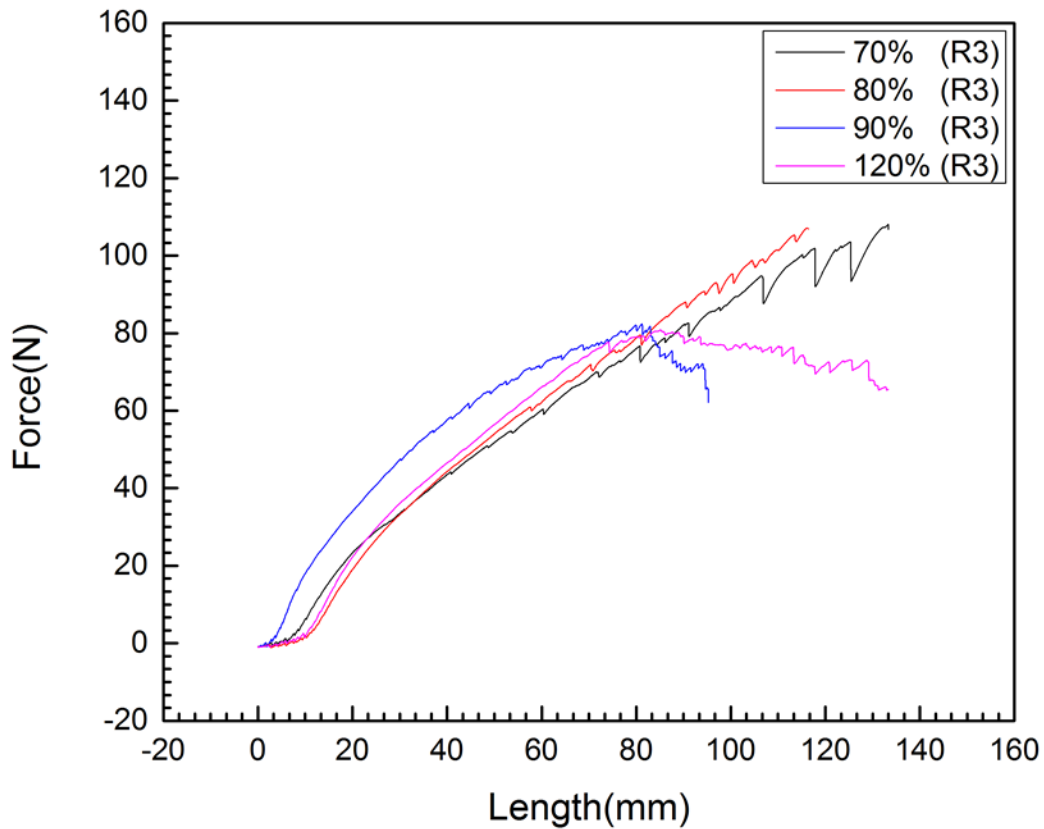


Figure 24: Comparison of rubber to metal bonding strength for Sample R3 with each degree of vulcanization.

It can be concluded that for R3 rubber sample, 70 % degree of interrupted vulcanization is best followed by R2 and R1 (Fig. 25). It can be seen that R2 rubber sample initially has the best bonding strength followed by R3 and R1 rubber samples, but as the force is increasing R2 rubber sample got ruptured and could not stand the increasing force. On the other hand in the case of R1 and R3 rubber samples lost to increased force at a certain area, in this case R3 rubber sample has greater strength than R1 one

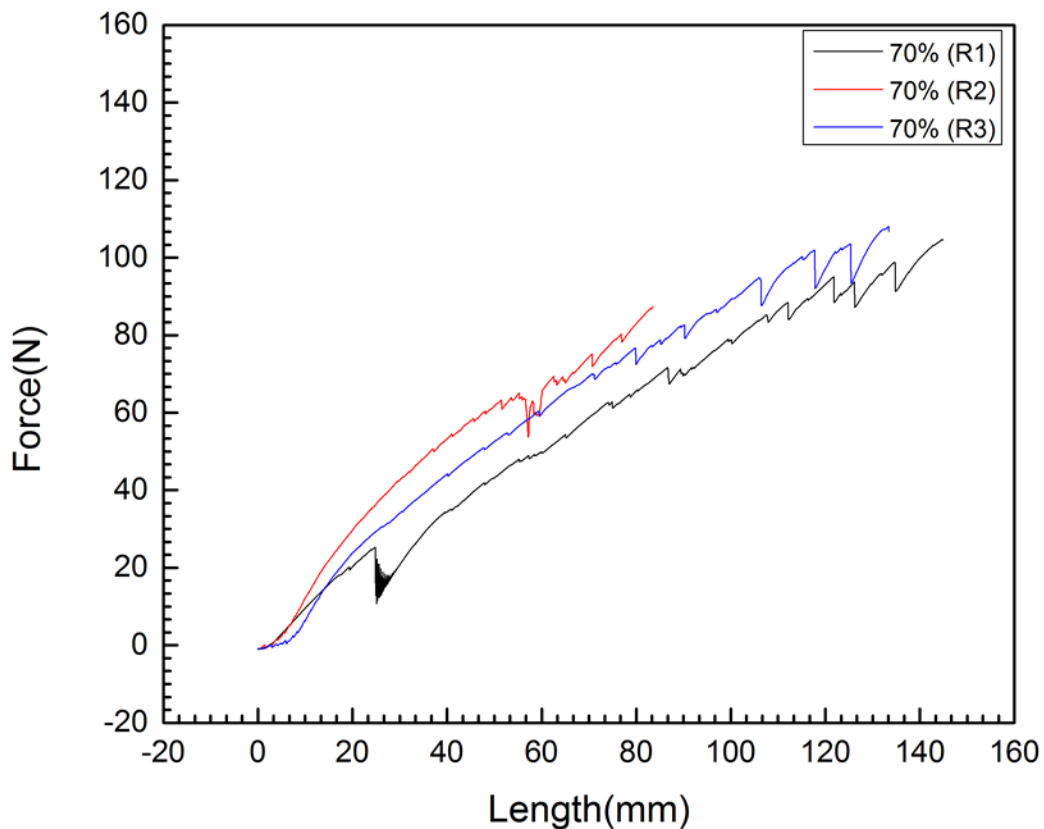


Figure 25: Comparison of rubber to metal bonding strength for 70 % degree of vulcanization for each sample.

It can be further concluded that for R3 rubber sample, 80 % (Fig. 26) degree of interrupted vulcanization is the best followed by R2 and R1 rubber samples. In general we can see that strength is not that good for all three samples but out of three R3 rubber sample has the best strength at this vulcanization degree. R1 rubber sample got ruptured around 30 N, R2 one at 50 N and out of all samples R3 one got ruptured at 75 N, which is eventually the best one for this degree of vulcanization.

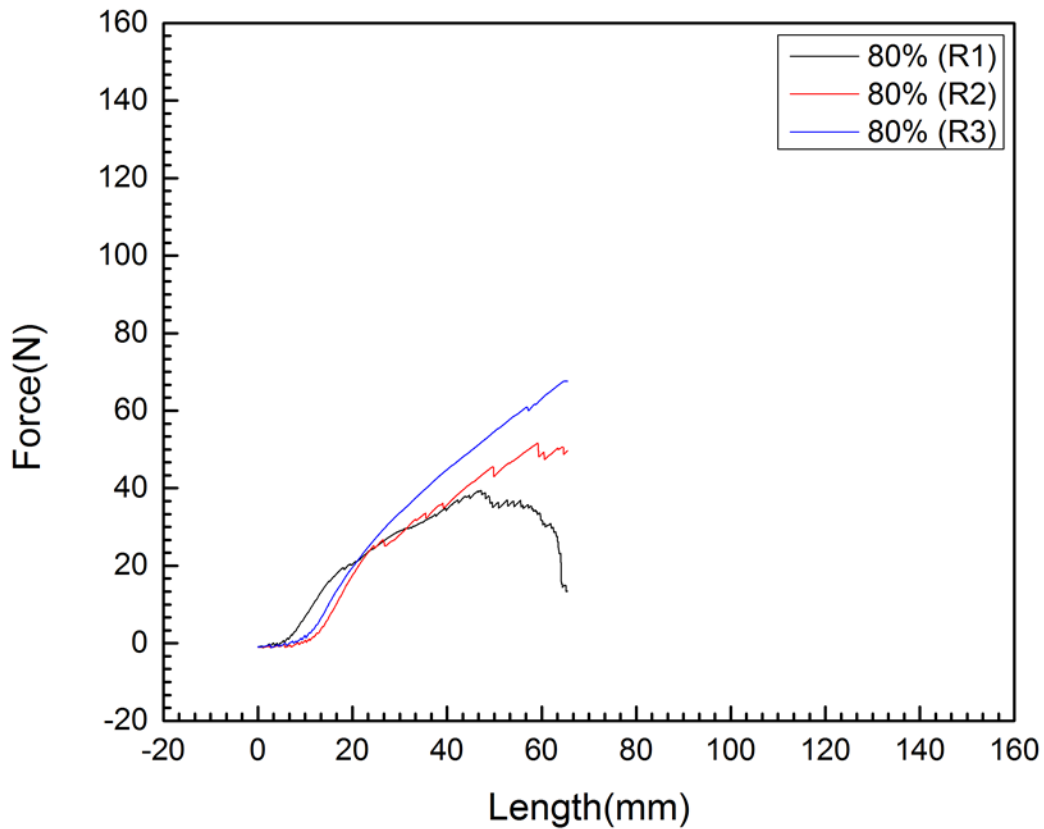


Figure 26: Comparison of rubber to metal bonding strength for 80 % degree of vulcanization for each sample.

In the case of 90 % interrupted vulcanization, the bonding quality is the best for R3 rubber sample followed by R2 and R1 rubber samples, respectively (Fig. 27). In other words, R3 rubber sample has clearly the best strength for among all three. Rubber sample marked R1 is really weak at this degree of vulcanization.

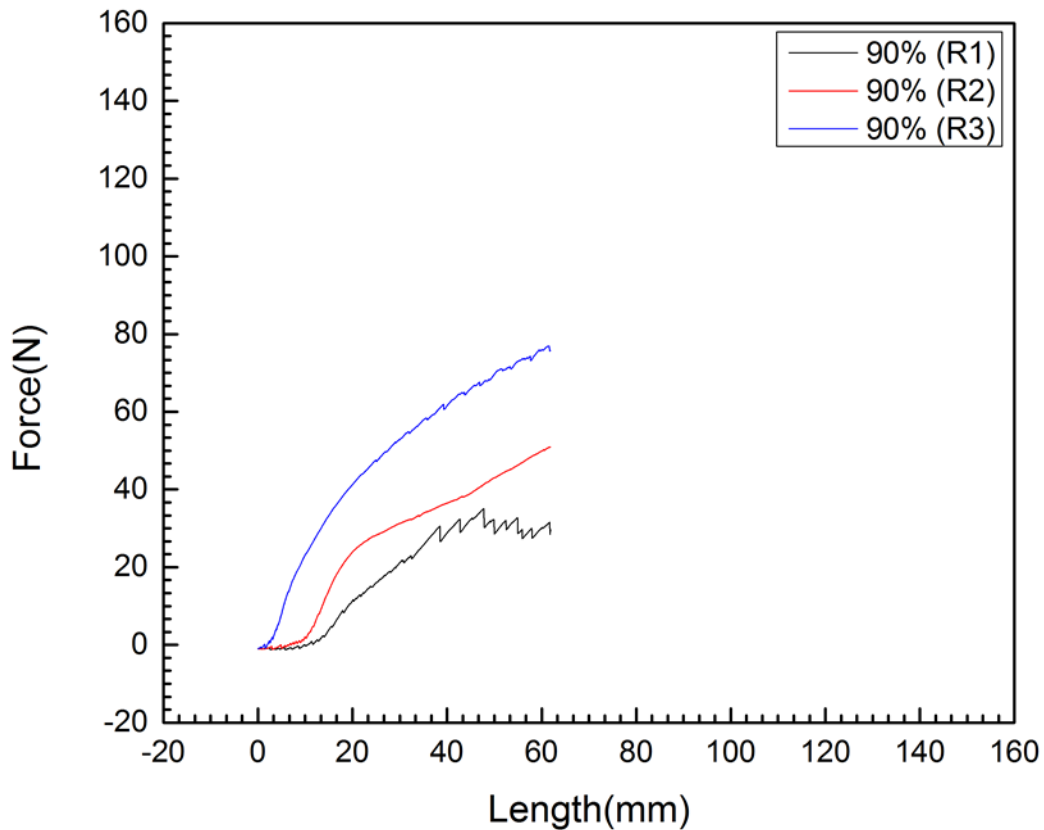


Figure 27: Comparison of rubber to metal bonding strength for 90 % degree of vulcanization for each sample.

The trend observed in previous cases of interrupted vulcanization degrees is confirmed also for 120 % pre-vulcanized rubber samples, where R3 rubber sample is the best followed by R2 and R1 rubber samples, respectively (Fig. 28).

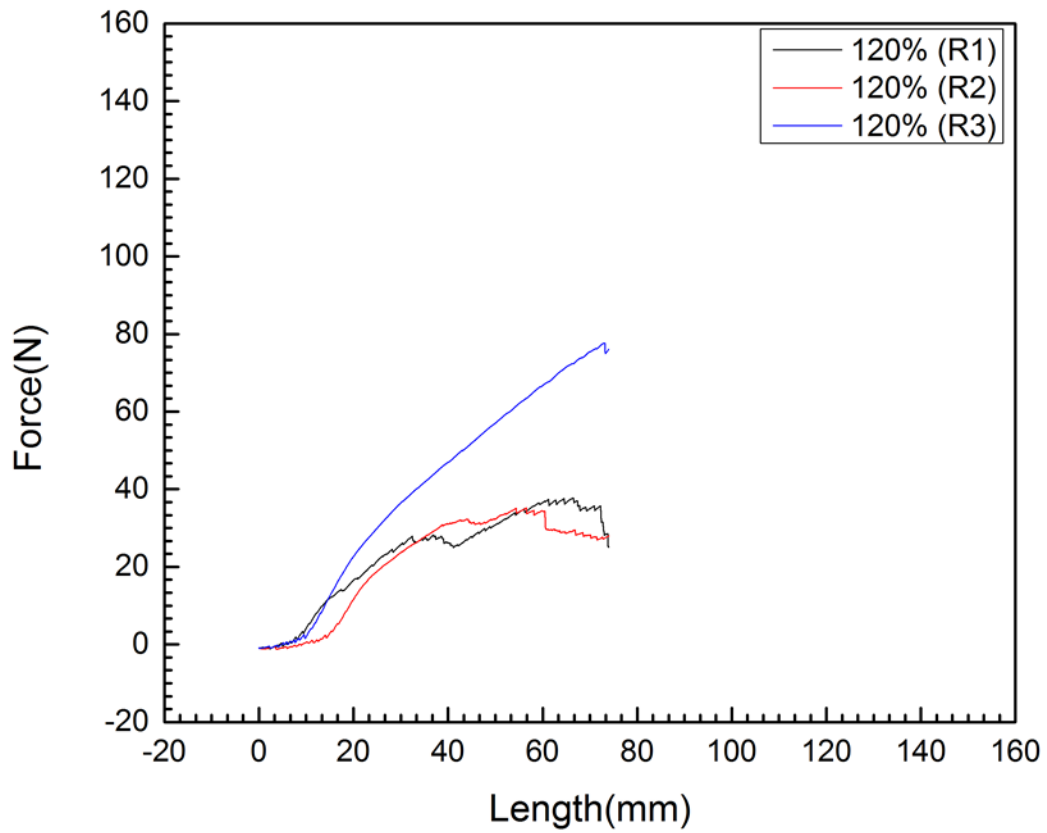


Figure 28: Comparison of rubber to metal bonding strength for 120 % degree of vulcanization for each sample.

CONCLUSION

Three rubber mixtures supplied by the company and marked as R1, R2 and R3 were used for analysing rubber to metal bonding i.e. peel test. Sample CK1 was not suitable for this kind of bonding since its composition based on EPDM rubber did not allow its proper vulcanization in demanded times followed by unacceptable bonding to metal plates. Necessary vulcanization time for each of rubber sample under investigation was calculated through the rubber process analyser. Each sample was subsequently pre-vulcanized at 30–90 % with the step of 10 % and 120 % by compression moulding. The surface of metal plate was then treated properly before bonding of pre-vulcanized rubber samples. Prior to any testing the final rubber to metal bonded all samples were kept for 16 hours according to the ASTM standard employed before further testing.

Despite of several attempts there was no observable bonding between rubber and metal plates for any type of rubber sample and at any percentage of interrupted vulcanization without bonding agent. It was revealed that the bonds were so weak that it was broken very easily. In addition to that at lower vulcanization degree like 30 %, 40 %, 50 % and 60 % the samples were too soft (the internal crosslinks were not too dense) and got deformed when compressed with metal plate in compression molding. The bonding was so weak that it was not significant to further perform any test.

Due to the fact that without the use of bonding agent very poor or even no bonding took place between rubber and metal plates, it was then decided to use a thin layer of bonding agent (Chemosil 256 NL) on the rubber sample. The rubber samples were again vulcanized at all mentioned degrees and significant results were observed which can be concluded in three parts as follow:

- Interrupted vulcanization at 30 %, 40 %, 50 % and 60 % was not favourable as the rubber samples deformed resulting in lower bond strength.
- It was revealed that interrupted vulcanization degree of 70 % was best out of all, as higher bond strength and good dimensional stability of rubber samples were observed. It could be concluded here that 70% has more sulphur than the other degree of vulcanization. So sulphur is the prime reason that resulted in best bonding strength.

- As mentioned in the previous point that 70 % was the most suitable one, bonding strength of different rubber samples namely R1, R2 and R3 were compared. It was observed that R3 rubber sample showed better bond strength, followed by R2 and R1 being the least favourable in all tested degree of vulcanization. This could be linked to the low composition of SBR and high composition of NR.

Based on previous it can be concluded that R3 rubber sample vulcanized at 70 % shows the highest rubber to metal bonding quality, hence it is the most suitable option to be used for stabilizer bars.

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12 LIST OF ABBREVIATIONS

NR	Natural rubber
BR	Butyl rubber
IIR	Isobutylene Isoprene rubber
ECO	Epichlorohydrin rubber.
NBR	Nitrile rubber
EPDM	Ethylene propylene diene monomer rubber
CR	Chloroprene rubber.
SBR	Styrene butadiene rubber.
MBTS	Dithiobis (benzothiazole)
Phr	Parts per hundred ratio
PTFE	Polytetrafluoroethylene
ZnO	Zinc Oxide
N	Newton
mm	millimeter
RPA	Rubber process analyser

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