International Journal of Interdisciplinary Innovative Research &Development (IJIIRD)
ISSN: 2456-236X
Vol. 06 Issue 01 | 2021

Devulcanization of rubber industry waste and incorporation of devulcanized rubber into virgin rubber compound.

Prof. S. P. Choudhari
Lecturer Plastic and Polymer Engg Dept. Government polytechnic college, Nashik

ABSTRACT

In this era of rapid development and economic growth, waste management is of high concern for humans. According to statistics, a great amount of rubber waste materials are produced annually. The major amount of these waste rubber materials comes from scrap product. Only a few percent of the waste rubber materials are recycled and made into new products. Recycling of waste rubber has a certain problems: the crosslink structure of thermoset rubbers.

Due to the presence of three-dimensional crosslink structures in rubber products, they cannot be reprocessed by application of heat, like we do for thermoplastic materials. In order to recycle and reuse the vulcanized rubber we have to find a way to cleave the crosslink bonds. This technique which can be break down the crosslink bonds in the rubber is called devulcanization. Different devulcanization processes are utilizing heat, chemicals ultrasound, and mechanical stresses in order to break down the crosslink structure of vulcanized rubber and convert the insoluble thermoset rubber into soft and sticky materials which can be processed and vulcanized again.

Comparing various devulcanization processes, the thermo-mechanical devulcanization process which applies mechanical force with effect of devulcanizing agent ie DV-5 helps to break down the crosslink network of rubber is very effective and. One of the common ways to maintain the required shear stresses and mechanical forces to cleave and break down the crosslink structure of vulcanized rubber is utilizing the two roll mill process.

Keywords :- Divulgating agent (D.V-5) , Mixing time, characterization of compound.

1. INTRODUCTION

Waste: -It is defined as, the material which releases toxic substances into the environment and which is hazardous to environment and human being. In recent years the accumulation of waste materials has been a big problem for mankind and waste disposal management is of high importance. The problem is more serious especially for polymeric materials which due to their chemical structure cannot decompose easily in nature. Recycling of waste rubber is even harder and takes a very long time due to the three dimensional cross linked structure and presence of different additives and stabilizers that make the recycling process very difficult. Finding a solution for recycling waste rubber has two important aspects: first to stop the wasting the valuable rubber materials and second to prevent environmental pollution.

Rubber waste

Introduction to rubber recycling:- The concept of sustainability has been garnering much needed public attention and interest in recent years. The increase of waste has serious environmental implications, and waste management must be carefully considered. There is now focus on a sustainable practices in almost any industry-including rubber industry. The rubber industry has been faced with its own unique challenges when it comes to recycling. Synthetic rubber is difficult to manage due to three main factors:

- Large volume of waste
- Durability of the material
- Hazards involving handling and storage

Until recently, the technology and infrastructure to deal with this waste did not exist, despite the hazards. Fortunately, decades of concerted effort have culminated in effective rubber recycling programs. Old tires can find new life as playground surfaces, floor mats, or even impact-resistant parking stops. The success of rubber recycling sheds light on a promising future in non biodegradable waste management. Rubber has been recycled for about a century, but the market has greatly expanded in the past two decades due to an increased demand for scrap tires in a wide range of settings, including in hospitals, agricultural, sports, playground, infrastructure, and even household items. Rubber recycling is not a recent issue and its history goes back to more than 100 years ago when rubber was a very precious material and resources were very scarce. The cost of an ounce of rubber in 1910 was the same as the cost of an ounce of silver. But after production of synthetic rubber the capacity of rubber production increased, and the price of rubber decreased.

Types of rubber waste

- Industrial waste.
- Domestic waste
- Agricultural waste
- Automotive waste.

Sources of rubber waste:

- Used product that contain vulcanized rubber.
- Waste produced during manufacturing processes
- Discarded rubber.

Synthetic rubber: In order to meet the increasingly constraining demand of industry from the automotive point of view, need of synthetic rubber This development of new rubber came with the develop of petrochemical industry.

Nitrile Butadiene Rubber

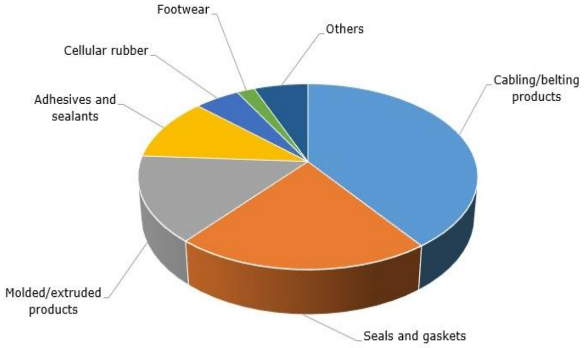
NBR- Acrylonitrile Butadiene copolymers commonly known as Nitrile rubbers.

India has consuming this rubber for over four decades; however, the consumption remained small and restricted to mainly the products requiring oil resistance properties. The picture changed rapidly since 1970 as the combined properties of abrasion resistance even at high temperatures was used for making products like rice dehusking rolls. Today over maximum wattage of NBR is used in this single application the growth of automotive industries.Nitrile rubbers are high molecular weight copolymers of 1,3-butadiene and acrylonitrile,copolymer can be largely linear to highly branch depending upon condition of polymerization, The percentage of acrylonitrile content can be varied from 18% to 50%, and will influence the performance characteristics of the polymer, The great variation in acrylonitrile content possible with nitrile rubber, allows for compounds to be customized to highlight specific required properties.

Application of Nitrile butadiene Rubber

NBR is one of the most widely consumed rubbers worldwide. It's applications in different fields are discussed below.

Automotive industry, Oil & gas industry, In Fuel Tubes / Hoses, In Military Application Consumption of nitrile rubber:



2. DEVULCANIZATION OF RUBBER - VULCANIZED RUBBER AND RECYCLING:

A rubber is a polymeric material which has an elastic behavior. This behavior is the result of the long chain characteristics of the rubber macromolecules. “Rubber materials are elastic, flexible, tough and relatively impermeable to both water and air. Unvulcanized nitrile rubber does not have enough strength and dimensional stability to make it applicable for rubber products and it's very sticky. It becomes soft and sticky in hot temperatures and stiff in hard and cold temperature. Virgin nitrile rubber (before vulcanization) is considered a liquid, but the viscosity is very high sot it may appear like solid. After the vulcanization process of nitrile rubber, a network between the polymer chains forms and the nitrile rubber cannot flow anymore. The crosslink bonds the polymer chains together and they prevent chains to slip on top of each other.

Curing is a general definition which we can used for all kinds of thermoset polymers, but vulcanization is generally applied for elastomers or rubbers. The vulcanization process produces a chemical network between the rubber chains by bonding the chains together and increases the elasticity and dimensional stability of the polymer. Following figure is a schematic of the vulcanization process, in which sulfur bonds the rubber molecules to form a vulcanized network. These chemical bonds are formed by a group of sulfur atoms or a single sulfur atom, carbon-carbon bonds an organic radical, an anionic cluster or a polyvalent metal ion.

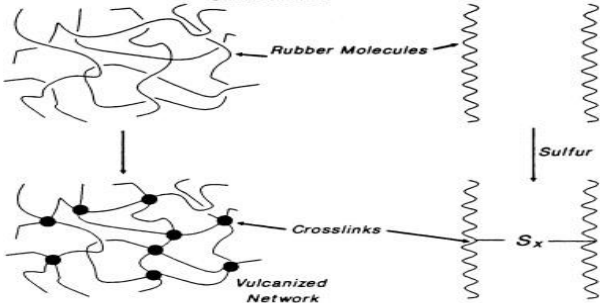


Fig no. (1) Cross linking of rubber molecules

Devulcanization:

Rubber industry worldwide is using on an average 50% of raw materials. This material produces more extreme environmental hazards. The waste rubber problem is of great magnitude and has far reaching environmental and economic implications. There are some ways for recycling of rubber, such as reclaiming technology, surface treatment, grinding and pulverization technology, devulcanization technology. Methods of devulcanizing rubber (or elastomers) have been researched almost since the time of the discovery of the rubber vulcanization process. By devulcanization process the cross-links in the structure of rubber are broken and devulcanized rubber can be revulcanized into a raw material for rubber industry, which is highly valued form of waste rubber.

Need of devulcanization of rubber:

Rubber has less strength and it will be soft over a wide range of temperature, we can't produce enough rubber to meet all our needs. So, to overcome these properties the rubber needs devulcanization.

To decrease the environmental pollution produced by rubber waste we need devulcanization of rubber.

3. METHODS OF RUBBER DEVULCANIZATION

The term devulcanization refers to a process in which the crosslink bonds in the vulcanized rubber cleave totally or partially. By cleaving these crosslink bonds, the vulcanized rubber can be revulcanized and utilized again like a virgin rubber material. To have better properties, it is preferable to avoid main chain scissions during the devulcanization process.

3.1 Thermo-mechanical devulcanization process:

In the thermo-mechanical devulcanization process, shear and elongation stresses are used to break down the crosslink bonds. Extruders and open mills are common equipment's which are suitable for this purpose. The process usually involves heating to increase the cleavage performance of crosslink chemical bonds. However, shear and elongation stresses alongside high temperature can easily breakdown the main chains of polymer which results in a significant decrease in molecular mass and poor physical properties. To cleave the crosslink bonds selectively, the characteristics of equipment and the processing parameters are very important.

3.2 Ultrasound devulcanization:

Another important method for rubber devulcanization is ultrasound devulcanization process. To break the carbon-sulfur and sulfur-sulfur chemical bonds, the ultrasound devulcanization process uses a high energy level ultrasound source. "An ultrasonic field creates high frequency extension-contraction stresses in various media". In a continuous ultrasound devulcanization process, an extruder is utilized for passing the crumb rubber through a narrow gap between the stationary die and the vibrating horn. There are three different types of ultrasonic devulcanization reactors, coaxial, barrel and grooved barrel ultrasonic reactors.

The coaxial reactor consists of an extruder and a coaxial ultrasonic die attachment. There is a power supply, an acoustic converter, booster, and a cone-tipped horn in the ultrasonic system. When the nitrile rubber crumb flows in the gap of the die the horn vibrates longitudinally and the material is exposed to the ultrasonic waves which propagate vertically to the flow direction.

3.3Microwave process:

In the microwave devulcanization method a certain amount of microwave energy with specified frequency is needed to cleave the crosslink bonds of vulcanized rubber. The presence of polar groups in the waste rubber is essential to absorb the microwave energy and generate the enough heat required for the devulcanization process most of the time, this process involves extrusion and mixing.

3.4 Thermo-chemical process:

The devulcanization of rubber waste poses a challenging economic environmental and social problem. We proposed a new devulcanization process to use the rubber waste, it is a mechano- chemical process (MCP), where the waste is devulcanized by combination of mechanical shearing, heat (45-50ºC) and the use of de-vulcanization agent (DV-5).In this process crosslink breakage is carried out by a combination of heat and chemical reagents.the process was carried out by blending the devulcanizing agent with crumb rubber in a two roll mill or an internal mixer. The vulcanized rubber compound was ground with the help of open two roll mixing mill at 45-50ºC ,simultaneous addition of the devulcanizing agent ie DV-5 and the process oil milled in an open mixing mill at the same temperature for 30/60/90 min. The main function of this mill is to reduce lump size. The advantage of the above milling technique is that it gives a fine elastic rubber powder.shear force can cleavge sulphur crosslinks and product would be an unvulcanized or devulcanized. Devulcanized sulphur cure nitrile rubber by using different doses (phr) of devulcanizing agent for different time period of milling.the chemical devulcanizing agent are dv-5. The sole , gel fraction and were determined .sole fraction increses with increasing milling time..

4. EXPERIMENTAL WORK

Materials :- Rubber scrap of Nitrile product and DV-5

Rubber scrap:

Formulation of Nitrile Rubber Compound.	
Ingredients	**Phr**
Nitrile 3345	100
Zno	5
stearic Acid	1.5
TDQ	1.5
Wood Rosin	3
Rubaid 1640	3
FEF	58
Austin Black	8
DOP	10
TMT	1
CBS	1
Sulphur	1

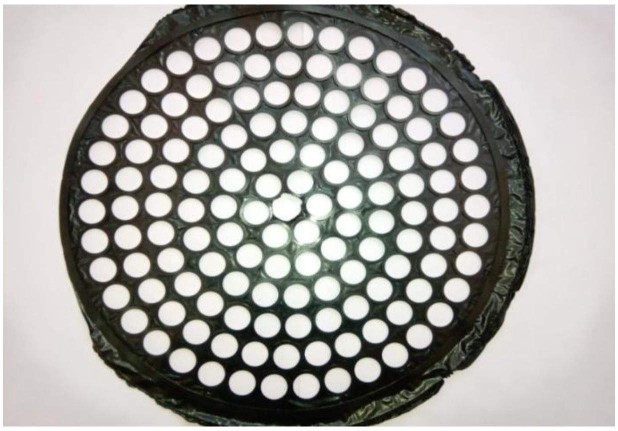


Fig. Nitrile Rubber Scrap

Rubber scrap from above given formulation.

DV 5 (De-vulcanizing agent) chemical.

De-vulcanizing agent is used to reclaim waste rubber by mechanical shearing until fine powder is produced. The devulcanizing agent contains two types of components: 1) amino acids, 2) ashless inorganic salts as Anti-stick additives for subsequent size reduction of rubber particles and preventing them from sticking. In a form of powder the reclaim rubber shows much better technical properties than in a form of sheet, bale or other bulk solids.

Physical properties of Dv -5	
Density	1.5
Appearance	White powder
Melting point	Decompose above 220oc
solubility	Partial soluble in solvent /water.

Equipment ;- Two Roll Mill

A schematics of the two roll mill shows three main zone of the machine

- The nip region between the rolls, where the rubber is subjected to high power densities
- The rolling bank above the nip ,which act as a reservoir to feed the nip and also provides encapsulating flows for additives incorporation
- The band, returning the rubber from the nip to the rolling bank and both cooling it and allow it to relax it in the transition.

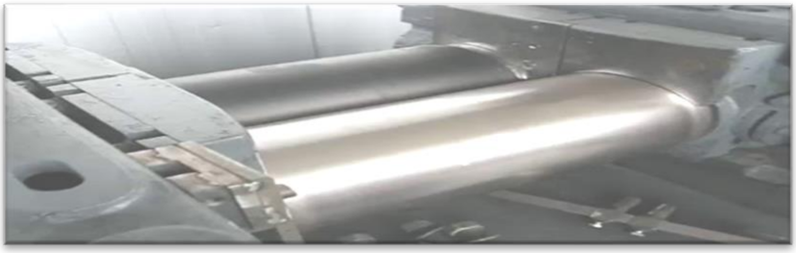


Fig. Two roll mill

<u>Procedure of devuclanization by mechanochemical method</u>

The mechano-chemical devulcanization process is carried out by mixing the the rubber scrap on two roll mill with de vulcanizing chemical agent (DV-5). The chemical is mixed with this mixing process for plasticizing the rubber compound / for softening the rubber compound to convert into useful rubber.

- Take the rubber waste in the form of scrap.
- Convert the rubber scrap into rubber crumb on two roll mill
- Add devuclanizing agent with plasticizer to plasticized the rubber waste.
- Mixed the substances upto complete dispersion
- Prepared the sheet as per required thickness.

Experimental variables. –

- Mixing Time ie 30/60/90 min.
- Phr of Devulcanizng agent ie 2phr, 3 phr and 4 phr.

Temperature :- Select appropripate temperature for devulcanization process can help for cleavegae of sulphur bonds in vulcanized rubber.excess heating may results in degradation of rubber and low physical properties of rubber. In order to achieve best physical properties in devulcanized performance best temperature must be selected.

Testing Method :-

Hardness Test:-

The test is carried out according ASTM D2240 Std, Shore A scale is the preferred for measuring hardness of rubbers. It measures the resistance of rubber toward indentation and provides a hardness value.

Tensile Test:-

Tensile test were examine on dumble shape specimen, the measurement were carries out at 25^{o}c on universal tensile testing machine with grip separation 40 mm at cross head speed of 500 mm/min as per ASTM D-412 & as per ASTM D-624 .respectively.

Crosslink density and degree of devulcanization measurements:

To characterize the performance of the devulcanization process we calculate the network crosslink density of several samples. The procedures for crosslink density and degree of devulcanization measurements are described in ASTM D 6814-02 standard.

The Flory-Rehner equation is used for the calculation of crosslink density as follows:

$$v = \frac{-\left[\ln\left(1-V_r\right)+V_r+xV_r^{2}\right]}{V_s\left(V_r^{\frac{1}{3}}-V_r/2\right)}$$

Where V_r, x_1, v_1, and v_e are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of solvent and the crosslink density (effective number of chains in a real network per unit volume) of the rubber sample.

The rubber volume fraction is calculated using the following relation:

$$Vr = \frac{(weight\ of\ dry\ rubber\ /density\ of\ rubber)}{\frac{weight\ of\ dry\ rubber}{density\ of\ dry\ rubber} + \frac{weight\ of\ solvent\ absorbed\ by\ sample}{density\ of\ solvent}}$$

Density of the rubber sample are measure using an electronic densitometer, it basically measures the weight of the rubber in the atmosphere and while it is immersed in water. Using the buoyancy role, the density of the rubber can be calculated.

Following the crosslink density determination, the percent devulcanization can be determined by using the following equation:

$$\%\ \text{Devulcanization} = 1 - \frac{\textbf{crosslinking density of devulcanized rubber}}{\textbf{crosslinking density of product}}$$

Acetone extraction:

Acetone extraction was conducted using a Soxhlet apparatus to separate the low molecular weight content such as free sulfur, acetone soluble plasticizers, processing oils or waxes, organic accelerators, and fatty acids. Also, bituminous substances, vulcanized oils, high molecular mass hydrocarbons, and soaps can be removed by acetone extraction.

In this method the Soxhlet extraction apparatus is used, which consists of an electric heater, 500ml round boiling flasks, extraction tubes, and a condenser. The electric heater has three positions for three 500 ml round flasks. The heating rate can be adjusted using an electrical controller located on the right side of the heater. The acetone boils and evaporates and when it gets to the condenser it cools down, condensed by the cool water which is circulating in the condenser. This procedure must be continued for 16 ± 1 hour according to ASTM D 297 to completely remove all acetone extractable contents from the rubber sample.

After extraction, the sample is removed from the extractor and dried overnight in a ventilated oven at 72°C.The difference between the weight of the sample before extraction and after drying gives us the weight value of acetone soluble contents which was present in the sample. By dividing this value over the total weight of the rubber before extraction and multiplying by 100 we can find out the percentage of acetone soluble part of the rubber sample.

Fig. Soxhlet apparatus

Sol and gel contents measurements:

After acetone extraction, the sol and gel part of the rubber is separated by swelling the rubber sample in acetone. The gel part is the fully cross-linked part or some of the polymer chains which are still attached to the network from one side (in case of devulcanized rubber) and cannot be dissolved by acetone. The fraction of rubber sample which consists of free polymer chains that can be dissolved in acetone is called the sol fraction.

By immersing the rubber samples in benzene for 72 hours we can separate the sol and gel fraction of rubber. We can also use the Soxhlet extraction with acetone to separate the sol and gel fraction After 72 hours we remove the sample from benzene and put it in an air ventilated oven at 72°C over night to dry it to constant weight. The sol and gel fractions can be calculated using this equation:

$$\text{Sole fraction (\%)} = \frac{\text{weight before swelling} - \text{weight of dried sample}}{\text{weight before swelling}} \times 100$$

$$\text{Gel Fraction (\%)} = 100 - \text{Sole fraction (\%)}$$

Ageing Test for blend Compound

Determination Properties of blend after Hot air Aging

Ref: - ASTM D-573

This test method describes a procedure to determine the influence of elevated temperature in presence of air and ASTM Oil no 1 & 3 on the physical properties of vulcanized rubber as per ASTMD -573

5. RESULT AND DISCUSSION

Effect of mixing time and D.V Phr on hardness value

	Mixing Time		
Dv phr	30 min	60min	90min
	Observed hardness (Shore A)		
2 Phr	67	67	67
3 Phr	69	68	68
4 Phr	70	68	68

As the phr of Devulvanizing agent are increases hardness values is increases but there is not much more effect of devuclanizing agent on harness value.

% of Retaining of Tensile strength :

Mixing Time	30 min	60 min	90 min
Phr of DV	% Retention in Tensile Strength		
2 Phr Dv	72%	83%	82%
3 Phr Dv	84%	84%	85%
4 Phr Dv	60%	60%	58%

As the % of Devulcanizing agent is increases retention in tensile in increases, minimum phr of Devulcanizing agent ie 2 phr will also give satisfactory results. High dose of Dv agent will retard the curing property and also observed that drop in tensile strength.

% Swelling of Dv Compound: - (Medium – Benzene)

Mixing Time	**30Min**	**60min**	**90min**
Dv phr	Observations		
2 Phr	115.36%	117.42%	119.97%
3 Phr	117.22 %	118.37%	121.12%
4 Phr	120.73 %	125.45%	128.79%

Crosslinking Density:

Original sample cross linking density in benzene Medium	12.98*10-4

Cross linked density of Dv Compound in Benzene medium:

Mixing Time	**30min**	**60min**	**90min**
Dv phr.	Observations.		
2 Phr -dv	6.31*10-4	6.08*10-4	5.75*10-4
3 Phr -dv	6.20*10-4	5.90*10-4	5..71*10-4
4 Phr -dv	5.47*10-4	4.63*10-4	4.46*10-4

Above result shows % of Devulcanizing agent is increases swelling % is increases and crosslinking density is less due to breakdown of sulphur cure bond by devulcanizing agent.but high doses of dv agent will show dissolution of rubber in solvent .

% of devulcanization in benzene:

Mixing Time	**30 min**	**60 min**	**90 min**
Phr of DV	% Devulcanization		
2 Phr Dv	50%	52%	55%
3 Phr Dv	65%	67%	68%
4 Phr Dv	70%	71%	74%

The result shows as the phr of Devulcanizing compound is increases , % devulcanization is also increases. High phr of devulcanizng agent will give high % of devulcanization.

Ageing Test :- Testing of 70/30 blend after post curing at 150 oc /3o min.

(Blend of 30% Devulcanized compound with original compound)

Test Parameters	Specification	Observations	Remark
Hardness shore A	70+-5	69	Ok
Tensile strength	120kg/cm2	140.44	Ok
%Elongation	250%	358	Ok
Heat Ageing at 100oc for 72 hrs			
Change in Hardness	8	5	Ok
%Change in Tensile	"+/-15	0.73	Ok
%Change in Elongation	"+/-20	-11.39	Ok
ASTM Oil no-3 at 100oc for 72 hrs			
Change in Hardness	"+5/-10	4	Ok
%Change in Tensile	-20	-6.58	Ok
%Change in Elongation	-30	-8.1	Ok
% swelling	+10	+2.22	Ok
ASTM Oil no-1 at 100oc for 72 hrs			
Change in Hardness	"+10/-5	7	Ok
%Change in Tensile	-20	6.4	Ok
%Change in Elongation	-40	-15.91	Ok
% swelling	+5-10	-7.3	Ok
compression set at 100oc /22 hrs			
% compression set	25	13.71	Ok

Remark :- All test results are within specification , blending of 30% devulcanized compound with vergin compound will show the test results of ageing test are within specification value. devulcanized rubber has 80% retention of properties of traditional materials.

5. CONCLUSION

The devulcanization process convert the waste into compound of premium product , result in significant cost saving also this process is not release any toxic chemicals not creat pollution but protect the environment by converting the waste into useful product.the thermomechanical method is very simple and economical process and Devulcanizing agent DV -5 is the chemical agent help to cleave the sulphur cure bond . the doses of Dv -5 agent can be vary depend upon type of vulcanization system and type of elastomeric material. the blending of 30% devulcanized rubber with virgin rubber gives testing results within specified limit so it will be accepted to produced the useful product , it save the 30% cost of virgin material.

6. REFRENCES

[1] Said Seghar lucia asaro- Thermomechanical devulcanization and recycling of rubber industry waste - Published in Elsevier 2016.
[2] Adrain macsiniuc, annie rochette –effect of SBR rubber partical size distribution on its thermochemical regeneration. Journal of progress in rubber , plastic recycling technology , volume 29 no-3,2013
[3] Devon William Edward,bart danon –Quantifying and comparing the selectivity for crosslink scission in mechanical and mechanochemical devulcanization process –Journal of Applied polymer science 2016
[4] Jianbo sui ,Dong xiang –devuclanization waste tires rubber vulcanizate through mechanochemical pan milling at ambient temp – journal of advanced material research volume 239-242(2011)
[5] G.k.jana and C.k .das –devuclanization of automobile scrap tyres by mechanical process – journernal of material science 2005
[6] Gautam .K.Jana and Ram mahaling –Mechano chemical recycling of sulphur cured natural rubber – journal of material science 2007
[7] mohammad meysami -A study of scrap rubber devulcanization and incorporation of devulcanized rubber into vergin rubber compound by – thesis of chemical Engg dept.
[8] Handbook of rubber technology by Steven blow.
[9] General rubber compounding by ram charan
[10] Rubber technology handbook by J.R.White
[11] Rubber testing std –ASTMD 2000.
[12] Rubber recipes by Brydson.
[13] www.businessimpactenvironment.wordpress
[14] www.recycledrubberfacts.org
[15] www.marketsandmarkets.com.