



Studies on Aramid Short Fibers Reinforced Acrylonitrile Butadiene Rubber Composites

H. Sheik Mohammed^{1*}, K. Elangovan², V. Subrahmanian²

¹Department of Rubber and Plastics Technology, Anna University/Madras Institute of Technology, Chennai, Tamil Nadu, India. ²Department of Rubber and Plastics Technology, Anna University/Madras Institute of Technology, Chennai, Tamil Nadu, India.

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ABSTRACT

The gasket applications employ ethylene-propylene diene-rubber, natural rubber, acrylonitrile butadiene rubber (NBR), chloroprene rubber elastomers with reinforcing effects of asbestos, certain synthetic fibers like nylon. The ban of asbestos due to its hazardous nature and the advancement in fibers has led to the development of short fiber (nonasbestos) reinforced elastomers for gasket applications. This study aims at the improvement of some properties of NBR reinforced by short aramid fiber. The usage of bonding systems such as resorcinol/hexamethylenetetramine/silica (HRH) enhances the fiber/NBR adhesion and maintains optimum composite strength properties. Mechanical properties of composites, namely, tensile strength, hardness, and modulus at 100% elongation, compression set can be enhanced by adding aramid fibers. In addition to this, thermal stability of the composites, properties after aging and after fluid interactions are the main objectives of this study.

Key words: Acrylonitrile butadiene rubber, Aramid short fibers, HRH bonding system.

1. INTRODUCTION

Composite materials play a key role in the aerospace industry, automobile industry, and in other engineering applications because they exhibit outstanding strength to - weight and modulus-to-weight ratios. Short-fiber-reinforced rubber composites have attracted much attention because of better processability, improved physical and mechanical properties, and economic advantage [1-5]. Short fiber-reinforced rubber composites have been successfully used in the production of V-belts, hoses, tire treads, seals, and complex-shaped mechanical goods [6-10]. Synthetic fibers such as glass, rayon, nylon, aramid, and asbestos have been used by a number of scientists in natural and various synthetic rubbers and resins. Fiber-matrix adhesion in short fiber-rubber composites has been a field of extensive research. Properties of short fiber elastomer composites critically depend on the interfacial bonding between the fiber and the matrix. In the case of short fiber reinforced rubber composites, the load is not directly applied to the fiber; rather, it is applied to the matrix. To obtain a high-performance composite, the load must be effectively transferred to the fiber, which is possible only when the fiber-matrix interface is strong. The adhesion between the fiber and the matrix should be

such that the failure occurs in the matrix rather than at the interface. Compared to the adhesive dipping process, the use of a tricomponent dry bonding system consisting of hexamethylenetetramine, resorcinol, and fine particle hydrated silica (HRH system) is easier as the constituents can be added to the rubber matrix like any other compounding ingredient, and additional processes, such as dipping and drying, can be avoided. Wazzan *et al.*, Ismail *et al.*, Geethamma *et al.*, and Sreeja *et al.* have described the various aspects of short fiber adhesion to rubber in the presence of the dry bonding system. In all these studies, they have used conventional precipitated silica with particle size in microns. The role of silica is to improve wetting of the fiber surface. As small particles have a higher surface area, nanosilica can be more effective in improving the wet ability of the fibers. In this work, we report the effect of nanosilica on the properties of short nylon fiber reinforced acrylonitrile butadiene rubber (NBR) composites. The silica is used as a component in the dry bonding system and also as additional filler.

1.1. NBR

NBR (nitrile rubber) is a copolymer of acrylonitrile and butadiene, and it is a polar specialty rubber. NBR

*Corresponding Author:
E-mail: sheik980@gmail.com

has good resistance to a wide variety of oils and solvents and hence is widely used for products such as oil seals, pipe protectors, and blowout preventers, etc. Major properties of NBR depend on the acrylonitrile content (ACN) which usually vary from 20% to 50% by weight. Commercially available nitrile rubbers differ from one another in three respects: Acrylonitrile content, polymerization temperature, and Mooney viscosity. NBR has high viscosity that can be reduced by mastication.

1.2. Aramid Fiber

The name "aramide" is a generic term for a manufactured fiber, in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings as defined by US federal trade commission. Aramid fibers have some characteristics properties:

- Excellent tensile properties
- High glass transition temperature
- Very small shrinkage at elevated temperatures
- Low creep
- Corrosion resistant
- Nonconductive
- Resistant to most chemicals, except strong acids and bases
- Sensitive to compression, the fiber yields at, 0.5% compression
- Sensitive to radiation from ultraviolet and radioactive sources
- High tensile fatigue
- High cut resistance.

Aramid short fibers come in two principally different shapes: Pulp and staple fibers.

1.3. HRH Bonding System

The dry bonding system commonly used in rubbers is the HRH system consisting of hydrated silica, resorcinol, and hexamethylene tetramine to create adhesion between fiber and rubber matrix. Compared to adhesive dipping, the use of a tricomponent dry bonding system is easy. This is because the constituents of the dry bonding system can be added to the rubber matrix like any other compounding ingredients and extra processes such as dipping and drying can be avoided.

2. EXPERIMENTAL

2.1. Materials used

NBR used in this study was N553 grade with 33% acrylonitrile content supplied by M/S LANXESS Ltd., India. Aramid fiber was obtained from Twaron Ltd., Aramid BV, Netherlands, and was chopped to approximately 6 mm length. Zinc oxide, stearic acid, MBTS, TMTD, Carbon Black (HAF Grade) sulfur, hexamethylenetetramine (hexa), and the resorcinol used were of commercial grade.

2.2. Preparation of the Composites

The formulation of mixes is given in Table 1. NBR - 100 phr, zinc oxide - 5 phr, stearic acid - 2 phr, MBTS - 1.5 phr, TMTD - 0.2 phr, carbon black - 30 phr and sulfur - 2.5 phr were common to all mixes. The mixing was done per ASTM D-3184 (1989) standard on a two-roll laboratory size mixing mill. Aramid fibers were added in small increments to obtain uniform dispersion. After complete mixing, the stock was finally sheeted out through a tight nip to orient the fibers in one direction. The thin sheet obtained was cut in the required dimension and stacked one above the other to the desired volume. The sheets were vulcanized in the hydraulic press at 150°C and 1500 kgf pressure to their optimum cure times, as determined using an oscillating disc rheometer.

3. MEASUREMENT OF PHYSICAL PROPERTIES

The tensile properties were measured using a Shimadzu universal testing machine model AG-1, 10 kN according to ASTM D 412 standard at a crosshead speed of 500 mm/min. The test specimens were punched out with fibers oriented along milling direction and the mechanical properties were determined. The tear strength was determined according to ASTM D 624 (Die C). The hardness (Shore A) was determined as per ASTM D2240-86 using a Durometer. Rebound resilience was determined by the vertical rebound method according to ASTM D 2832-88. Compression set at constant strain was measured according to ASTM D 395-86 method B.

4. RESULTS AND DISCUSSION

4.1. Cure Characteristics

Variations of minimum torque with fiber loading at various silica contents are shown in Figure 1. The

Table 1: Formulation of the mixes.

Mix no.	Ingredients (Phr)				
	Aramid fiber	Silica	Resorcinol	Hexa	Black
1	0	0	0	0	30
2	2	10	5	2	0
3	2	0	0	0	30
4	2	10	5	2	30
5	5	10	5	2	30
6	10	10	5	2	30
7	12	10	5	2	30
8	15	10	5	2	30
9	20	10	5	2	30

1: NBR compound, 2: NBR gum with 2 phr fiber, 3: NBR with 2 phr fiber and without HRH, 4: 2 phr fiber content, 5: 5 phr fiber content, 6: 10 phr fiber content, 7: 12 phr fiber content with, 8: 15 phr fiber content, 9: 20 phr fiber content. From mix no 4-9, bonding agent was added according to formulation. Phr: Parts per hundred rubber

minimum torque increases with fiber loading for all the mixes, indicating that the processability of the composite is adversely affected by the introduction of fiber and silica. Mix no. 3 shows fall in torque value because of bonding agent absence. The higher viscosity of the nanosilica composites may be due to the better interaction between silica and the rubber matrix. The lower particle size silica has a higher surface area and, hence, can have improved interactions. Figure 2 gives the variations of scorch time with silica content and fiber loading. Scorch time decreases with fiber loading and silica content for all the mixes. This indicates that aramid fiber has an accelerating effect on cure reaction. Similar results in the case of short nylon fiber reinforced NBR composite using an epoxy-based bonding agent have been reported earlier. Cure time increases with fiber content for all the mixes (Figure 3). This is due to the interaction of silica with the accelerators, and this interaction is found to be more for nanosilica. Figure 4 shows the rate of cure reaction with fiber loading. Cure rate increases with fiber loading. An increase in the cure rate with fiber content is due to the accelerating effect of aramid fiber on the cure reaction.

4.2. Mechanical Properties

Aramid short fibers were incorporated in NBR rubber mixes with different concentrations up to 20 phr as

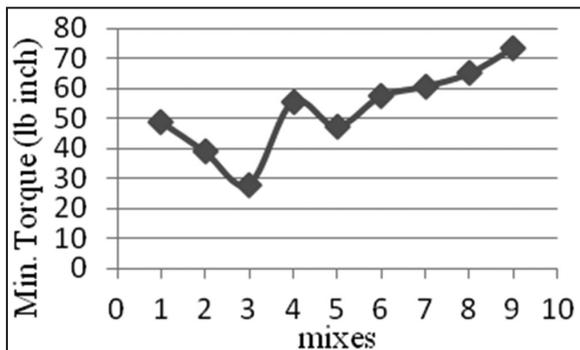


Figure 1: Different mixes versus min. torque.

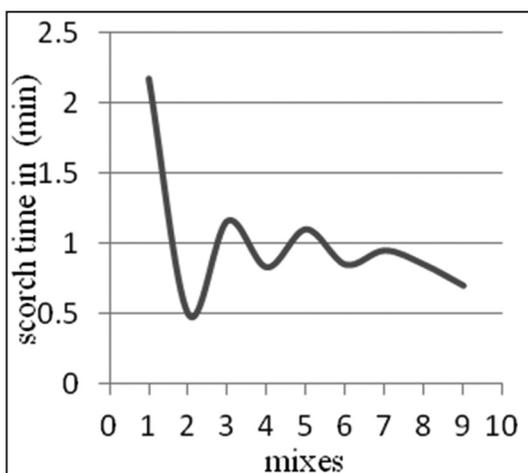


Figure 2: Different mixes versus scorch time.

shown in Table 1 The physic-mechanical properties were determined and presented in Figures 5-7. It is clear that there is a sharp decrease in tensile strength for gum compound and without bonding agent compound followed by an increase in the tensile strength with the increase in fiber content.

Figure 6 shows the dependence of the elongation at break versus the fiber concentration. It is clear from the figure that addition of fiber leads to a sharp decrease in the elongation at break in both directions up to 10 phr, then, the elongation remains decrease with further increase in fiber concentration. On the other hand, it indicates that the fibers were well oriented in the rubber matrix in the mill direction. Based on this discussion of results, it can be concluded that the adhesion of aramid short fibers to rubber mixes leads to rubber vulcanizates with high stress at low strain. Figure 7 shows the tear strength of the each mixes. It shows that tear strength increases with level of fiber concentration.

Figure 8 shows a surface properties (hardness) of different rubber mixes. The concentration of the fiber increases with the hardness of the compound.

4.3. Compression Properties

Figure 9 Shows the compression forces required for 5% deflection of the cylindrical specimen. It shows

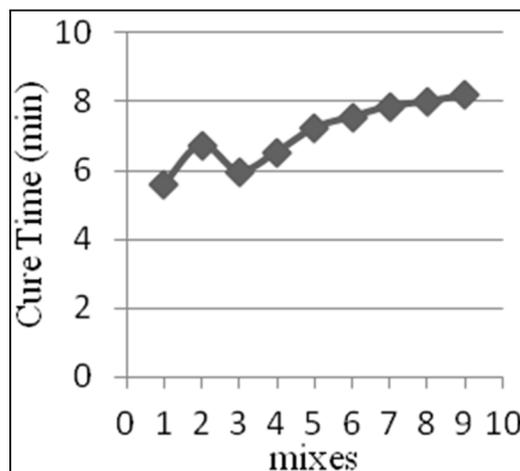


Figure 3: Different mixes versus cure time.

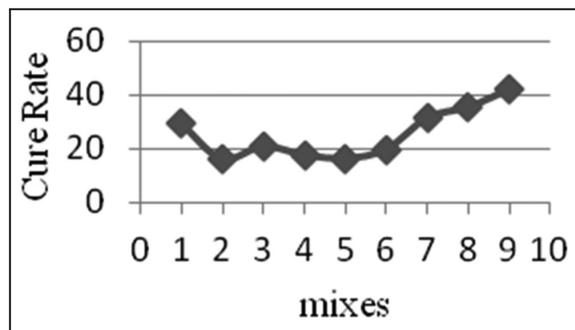


Figure 4: Different mixes versus cure rate.

higher load for 10 phr loading of aramid fiber with bonding agent in the compound.

Figure 10 shows a resilience behavior for various loading of aramid short fibers.

4.4. Rebound Resilience

Resilience, an indication of the material elasticity, decreases with fiber content for all mixes. The

dissipation of energy at the fiber-matrix interface results in lower resilience values of composites.

4.5. Compression Set

Compression set is the important properties for gasket applications. Figure 11 shows the compression set of different mixes. It indicates that the set percentage decrease with increase of fiber content.

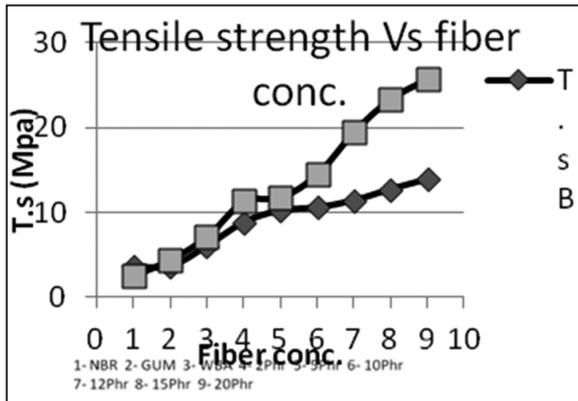


Figure 5: Different mixes versus tensile strength Mpa.

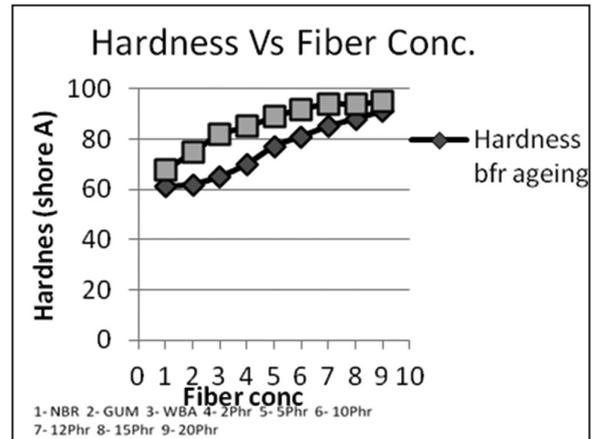


Figure 8: Different mixes versus hardness.

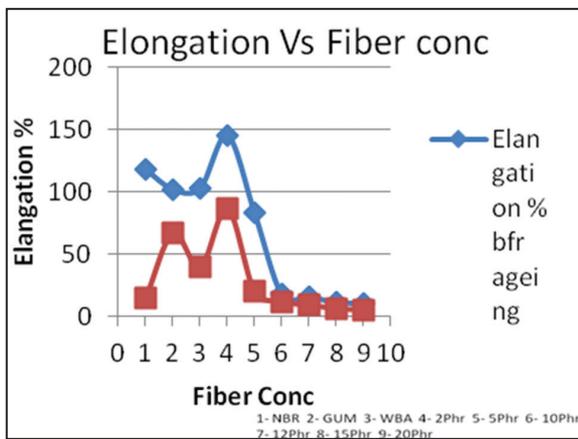


Figure 6: Different mixes versus elongation %.

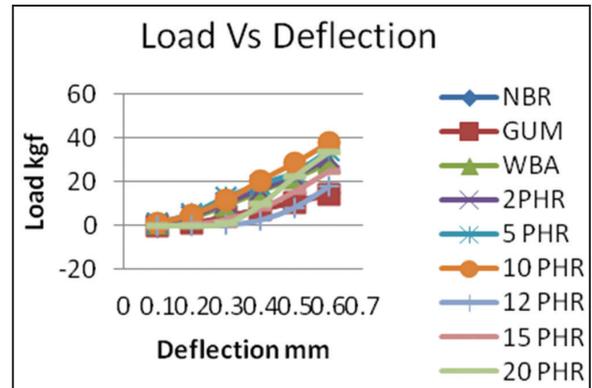


Figure 9: Different mixes versus load required for 5% deflection.

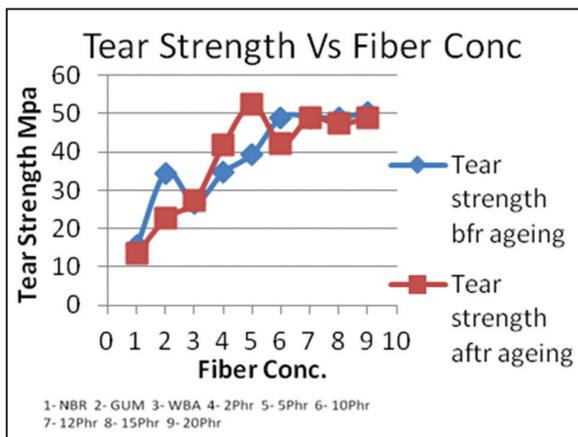


Figure 7: Different mixes versus tear strength.

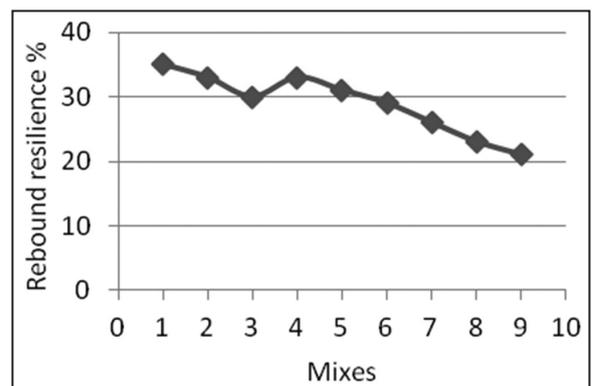


Figure 10: Different mixes versus rebound resilience %.

4.6. Swell Study

Figure 12 shows that the effect of fluid interaction of different composites. The cured samples were subjected to a fluid to check the resistance towards fluids as per the ASTM standard D471, with the reference fuel - B (Isooctane 70% + toluene 30%) set aside for 70 hours maintained at an ambient temperature

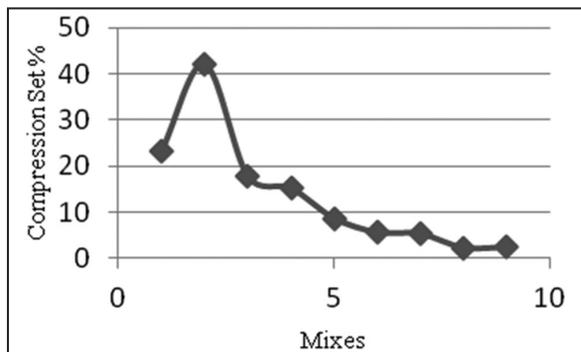


Figure 11: Different mixes versus compression set %.

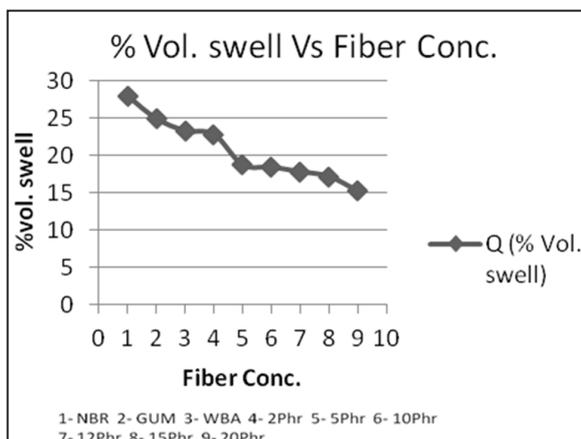


Figure 12: Different mixes versus volume swell %.

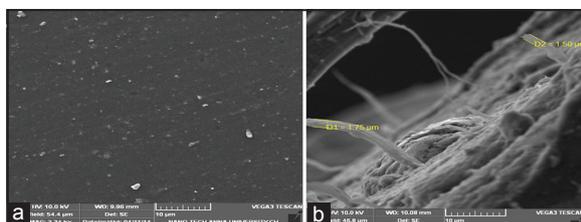


Figure 13: (a and b) Scanning electron microscope analysis with bonding agent.

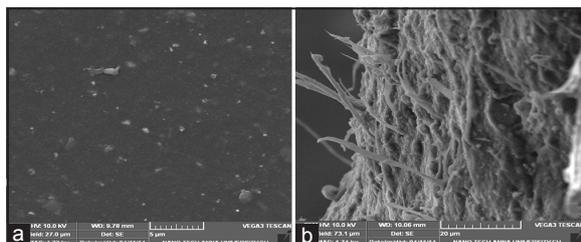


Figure 14: (a and b) Scanning electron microscope analysis without bonding agent.

of 23°C. Volume swell is observed and calculated for each sample whose values are as follows:

4.7. Micro Structure Analysis (Scanning Electron Microscope [SEM])

Figures 13 and 14 show that the SEM analysis of the samples which gave the best and optimum results were characterized using SEM to study the fiber orientation, fiber interaction into the rubber matrix. The SEM images showed a good interaction between the fiber and the rubber. The interaction of the fibers and the orientation are linear for the samples with a bonding agent, whereas for the samples without bonding agent shows the irregular orientation of the fibers. As results, the samples with bonding agents are only viable to make the products like gaskets so that the properties are good and as desired.

5. CONCLUSION

The following conclusions can be drawn from the experimental data presented in the paper:

1. The presence of aramid short fibers increases the efficiency of the reinforcement of NBR rubber vulcanizates.
2. The best volume fraction of reinforcing fiber that leads to high stress at low strain was found to be 10 phr.
3. The presence of reinforcing aramid fibers and the adhesion system greatly improves mechanical properties of the rubber vulcanizates. This may be attributed to the further formation of cross-linked resin, which balances the degradation that occurs during aging.

6. REFERENCES

1. S. R. Ryu, D. J. Lee, (2001) Effects of fiber aspect ratio, fiber content, and bonding agent on tensile and tear properties of short-fiber reinforced rubber, *KSME International Journal*, **15(1)**: 35-43.
2. A. Seema, S. K. N. Kutty, (2007) Characterization of short nylon-6 fiber/acrylonitrile butadiene rubber composite by thermogravimetry, *International Journal of Polymer Analysis and Characterization*, **10(3-4)**: 169-178.
3. A. A. Wazzan, (2010) Physico-mechanical properties of epdm/nylon-6 short fiber composites, *International Journal of Polymeric Materials and Polymeric Biomaterials*, **53(1)**: 59-67.
4. J. Li, Y. C. Xia, (2010) Interfacial characteristics of an epoxy composite reinforced with phosphoric acid-functionalized kevlar fibers, *Mechanics of Composite Materials*, **46(2)**: 211-221.
5. G. S. Shibulal, K. Naskar, (2011) RFL coated aramid short fiber reinforced thermoplastic elastomer: Mechanical, rheological and morphological characteristics, *Journal of polymer Research*, **18**: 2295-2306.
6. G. Gao, Z. Zhang, X. Li, Q. Meng, Y. Zheng,

- (2010) An excellent ablative composite based on PBO reinforced EPDM, *Polymer Bulletin*, **64**: 607-622.
7. R. S. Rajeev, S. K. De, A. K. Bhowmick, (2011) Atomic force microscopy studies of short melamine fiber reinforced EPDM rubber, *Journal of Materials Science*, **36**: 2621-2632.
8. A. M. Khalil, K. F. El-Nemr, A. I. Khalaf, (2012) Effect of short polyethylene terephthalate fibers on properties of ethylene-propylene Diene rubber composites, Springer Science Business Media, *Journal of polymer Research*, **19**: 9883.
9. P. N. B. Reis, J. A. M. Ferreira, J. D. M. Costa, M. J. Santos, (2012) Fatigue performance of Kevlar/epoxy composites with filled matrix by cork powder, *Journals of Fibers and Polymers*, **13(10)**: 1292-1299.
10. K. S. Mazumdar, (2002) *Composites Manufacturing, Materials, Product, and Process Engineering*, Washington, DC: CRC Press, p1-20.

***Bibliographical Sketch**



The author of paper Mr. Sheik Mohammed is presently working as a Teaching Fellow in the Department of Rubber and Plastics Technology, Madras Institute of Technology, Chennai, India. He acquired degree both at graduate (B.E – Mechanical Engineering) and post graduate level (M.Tech. - Rubber Technology). He is pursuing his doctoral work in the field of rubber science at Anna University, MIT Campus, Chennai. He has 3 years of teaching experience in the field of rubber science and polymer composites technology. He has published one paper as following, I. V SUBRAHMANYAN, SHEIK MOHAMMED, PRABHUKUMAR, “Energy efficient functionalization of low Tg polymers and their properties”, Indian Journal of Advances in Chemical Science, Vol. 4, Issue 4, (2016).