Effect of MMT Nanoclay on The Thermo-Mechanical Properties of Acrylonitrile-Butadiene/Polychloroprene Rubber Blends

Mohd Gulam Waris Khan[1], Rizwan Hussain[2]
[1]Dept of Mechanical Engineering
[2]Dept of Polymer and Coating Technology
[1]University Polytechnic, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India-202002
[2]Community College, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India-202002

Abstract- *In the present research work the effect of montmorillonite (MMT) nanoclay (loading 1, 3, 5 phr) was examined on the mechanical properties, thermal stability and morphology of Acrylonitrile-butadiene rubber/Polychloroprene rubber (NBR/CR) of 50:50 ratio rubbers blends. Nanocomposite has been prepared by two roll mill, then specimen compression moulded. The results reveal that 5phrcontent of MMT nanoclay ina rubber matrix gives the highest mechanical properties, thermal stability carried out through TGA. The modification in various properties can be attributed to better interfacial adhesion between reinforcement and rubber matrixes examined by Scanning Electron Microscopy.*

Keywords- NBR CR; montmorillonite (MMT) nanoclay; thermo mechanical properties.

I. INTRODUCTION

Polymer nano-clay composites found to have greater interest for researchers and scientists as they exhibit many industrial applications. Materials with a mixture of nano-sized organic / inorganic materials and polymers expected to give properties of the individual components with the reinforcing components are nano-clay, nano-silica, nano graphite, carbon nanotubes (CNT) etc. Polymer nanocomposites are materials, where the reinforcements uniformly distributed in nanometre scale within the polymer matrix. Elastomers were reinforced with fillers to improve their performance by incorporating conventional fillers. The resulting polymer nano composites thus comprise nano fillers embedded in a polymerized medium that can be subsequently cross-linked, to obtain vulcanized rubber nanocomposites. Nano-composites made out of nano fillers had shown to afford remarkable property enhancements compared to conventional micro composites that were made using conventional filler. [1-5]

Polymer nano-composites with layered silicates [6-10] and carbon nanotubes [11–13] have attracted major interest for the improvement of structural a property and the development of new materials having different functional properties. NBR-Nano graphite polymer nano composites were found to increase its thermal stability [14]. Dispersion of nanosilica in NBR polymer was studied by Rajkumar et.al. [15] In general, the degree of dispersion of the clay platelets into the polymer matrix determines the superstructure of the nanocomposites.

Many authors have been working on this way, Botros et. al. Reported, CR/NBR blend ratios investigated, the 50:50 blend possesses the best mechanical properties with high thermal stability [16].Prem Ranjan et. al shown work the Effect of DOP as Dispersion Medium on MMT- nano Clay in NBR Polymer Matrix and Dispersion Studies Of Nanosilica In NBR Based Polymer Nanocomposite, nano-clay in NBR matrix show improved mechanical properties and better dispersion with increasing loading of clay nanofiller [1-2] Tengteng Wang et. al has been determined compatibility of NBR/CR blends by modulated DSC, DMA analysis and done the Research on Mechanical Properties, Compatibility, Flame Retardancy, Hot-Air Ageing Resistance of HNBR/CR Blends[17]. M. A. Kader et. al have been prepared and determined the properties of nitrile rubber/Montmorillonite nanocomposites via latex blending. [18]

In this research work we have try to implement the above authors work in the form of enhancing properties, reducing cost and deciding the application area for prepared material. Various properties of rubber materials can be re-engineered by incorporating different types of fillers in the matrix to obtain suitable technological applications in future like automobile, defence, missile, aerospace and space technology. The production of NBR/CR/MMT Nanocomposites remarkably takes notice of due to their well-balanced mechanical and thermal properties and relatively low cost. Acrylonitrile Butadiene Rubber (NBR) which has excellent properties such as resistance to petroleum oils and aromatic hydrocarbons, as well as being highly resistant to mineral oils, vegetable oils, and many acids. NBR is generally attacked by ozone, ketones, esters, aldehydes, chlorinated and nitro hydrocarbons. Polychloroprene Rubber (CR) has a better resistance to swelling in mineral, animal and vegetable oils and fats when compare to hydrocarbon rubbers except NBR. The chlorine atoms also impart to CR a better flame retardancy, weather and ozone resistance than that normally encountered with diene rubbers. The blend of NBR/CR are miscible because both have to exhibits in polar form and also the viscosity of CR can improve the processibility of NBR, therefore, it's helpful to investigate the properties of blends of NBR/CR. The incorporation of MMT's in NBR/CR matrix may also contribute to enhance the mechanical, thermal, and various other properties with high performance range.

II. EXPERIMENTAL

2.1.Materials

Acrylonitrile -butadiene/Nitrile rubber (NBR) was obtained from M/s. Japan Synthetic Rubber grade JSR 220 having acrylonitrile content of 38%.Polychloroprene rubber was obtained from DuPont USA grade W-M1.Montmorillonite (MMT Nanoclay) was obtained from Aldrich Chemistry.Zinc Oxide, Stearic Acid, 2, 6 Ditert-butyl-4-methyl phenol, 2-Mercaptobenzothiazole (MBT),Dicumyl Peroxide, Thiourea, this was procured from E. Merck Germany and Di-octyl-Phthalate obtained from S. R. Chemical Kanpur, India.

2.2. Methods of preparations

NBR and CR rubber blend they were masticated separately and then mixed together in definite ratio [19] along with other ingredients (Table 1.). Mixing was carried out in a conventional laboratory open two mill (150 x 330 mm) at 140-150Ċ. NBR was masticated for 3 min and blended with CR. After homogenization of the rubber blend for about (7 min), the other ingredients are added. The processing time after each component addition was about 2 min. The compound rubber was allowed to stand overnight before vulcanization. The compounded blends have been moulded to obtain sheet (3.5 mm) thickness using an electrically heated hydraulic press at 150 ° C for 20 min at a pressure of 2400 Psi. These cured sheets have to condition before testing (24 h maturation at 250C). The sheets were developed by compression moulding from prepared nano-composites by blending of rubber and MMT. The specimens were cut from prepared sheets of different compositions according to respective ASTM standard. These samples were utilized for evaluating the thermal, mechanical and morphological performance of the nano-composite.

Table 1: Formulation of the nanocomposite based on NBR/CR rubber blends

Sample code	NBR/CR (Wt. %)	Formulation, phr (parts per hundred)							
		ZnO	Stearic Acid	Antioxidant	Thiourea	MBT	DCP	DOP	MMT
A	50/50	5	2	1.75	2	1.5	2	10	0
B	50/50	5	2	1.75	2	1.5	2	10	1
C	50/50	5	2	1.75	2	1.5	2	10	3
D	50/50	5	2	1.75	2	1.5	2	10	5

III. METHODS OF CHARACTERIZATION

The various characterization techniques used for the purpose of different types of study can be divided into following categories:-

3.1 Mechanical Properties: (a)Tensile Strength(b) Tensile Modulus (c) Elongation at break(d) Hardness
3.2 Morphological Characterization: Scanning Electron Microscopy (SEM).
3.3 Thermal Characterization: Thermo gravimetric analyzer (TGA).

3.1. Mechanical Properties

The mechanical tests were performed on a universal testing machine (INSTRON, USA) with the maximum load capacity 100KN. Tensile tests were conducted according to ASTMD-412. For each composition, five measurements were taken and average values of strength, modulus and elongation were reported. Hardness was measured by Shore- A Durometer according to ASTM D 2240.

3.2. Thermo gravimetric analysis (TGA)

In the present study, the degradation, pattern and thermal stability of the various rubber nanocomposites were determined by Pyres TGA-I (Perkin Elmer, USA) thermal analyzer. The weight loss of the samples was analysed as a function of temperature through TGA. The quantity of the sample for each test was near about 4mg and they were heated from 50^0C to 650^0C at the controlled heating rate of 10^0C/min. under an inert atmosphere.

3.3. Scanning Electron Microscopy (SEM)

This technique was employed to study the morphology of the nano-composites of NBR/CR/MMT. Prior to SEM analysis the fractured samples obtained after tensile analysis was gold coated with the help of gold sputtering unit to avoid the charging effect and enhance the emission of secondary electrons. SEM studies were carried out with Zeiss EVO-50 VP Low-vacuum scanning electron microscopes.

IV. RESULTS AND DISCUSSION

4.1 Mechanical Properties

The results shows from Table 2, it is interesting to see that there is a significant improvement in the tensile properties of NBR/CR MMTs nanocomposite. Incorporation of MMTs in NBR/CR matrix leads to an increase in tensile strength by a greater extent. This might be attributed to the higher aspect ratio of MMT nano-composites. It has also been observed that both tensile modulus and elongation at break increases. This may be because of direct bonding of coated MMTs and polymer chains, thus providing better wetting or adhesion at the interface of two phases. Hardness of NBR/CR/MMT has been increased at 1 and 3 phr but at 5 phr there is no change in hardness.

Table 2: Mechanical properties of the NBR/CR rubber blends reinforced with MMT.

Sample code	Tensile strength (MPa)	Tensile Modulus (MPa)	Elongation at break	Hardness (Shore- A)
A	1.18	0.58	450	56
B	1.36	0.66	467	61
C	1.55	0.79	583	63
D	1.77	0.91	673	63

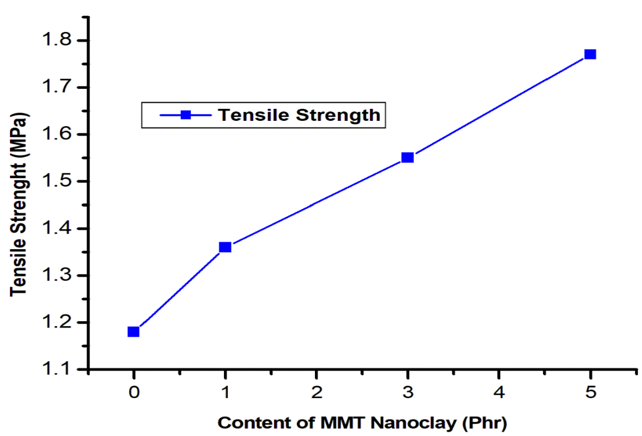

Figure 1: Tensile Strength of NBR/CR rubber blends with different loadings of MMT

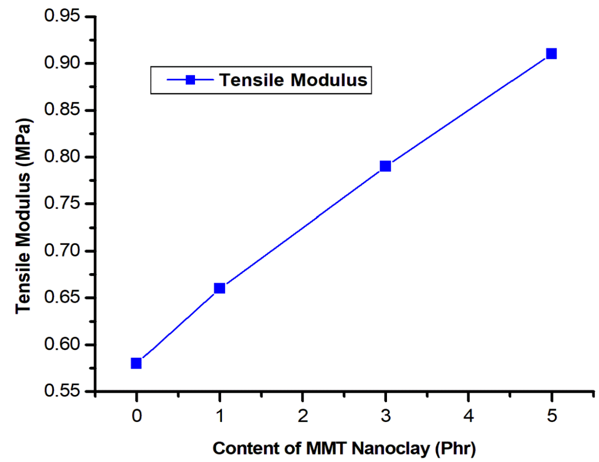

Figure 2: Tensile Modulus of NBR/CR rubber blends with different loadings of MMT

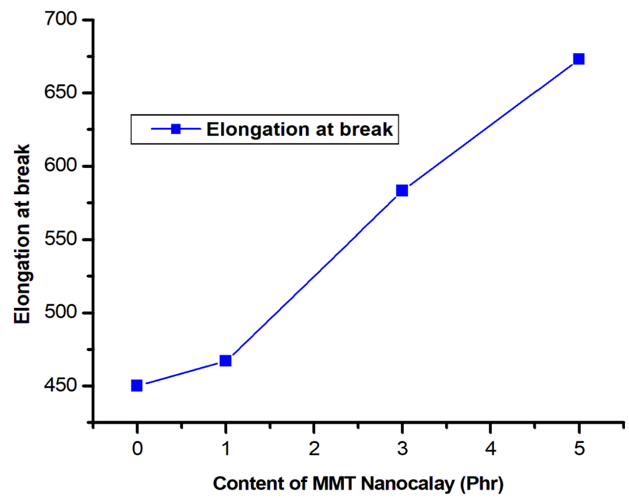

Figure 3: Elongation at break of NBR/CR rubber blends with different loadings of MMT

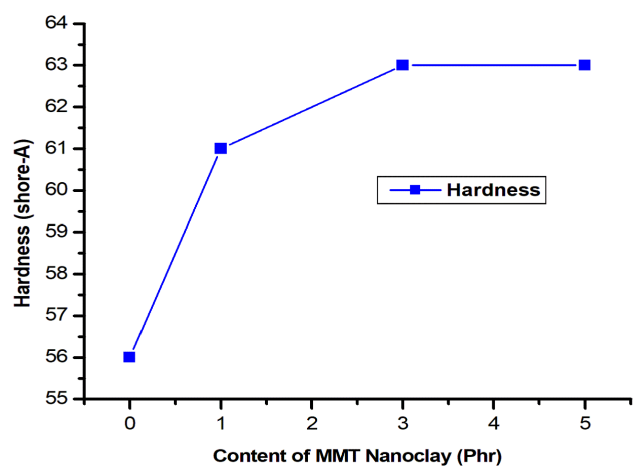

Figure 4: Hardness of NBR/CR rubber blends with different loadings of MMT

4.2 Thermal Characterization by Thermo gravimetric analysis (TGA):

It is obvious from TGA results that the thermal stability of NBR/ CR blend is enhanced with the incorporation of MMT as compared to virgin NBR/CR blend. It is also evident that highest thermal stability has been achieved at 3 and 5 phr loading of the nanofiller. This remarkable effect of nanocomposite is likely to be due to reduction of chain mobility of NBR/CR matrix by providing a large number of restriction sites which has resulted in reducing the thermal vibration of active bonds. Thus we can say that the developed nanocomposites are in need of much more thermal energy for the decomposition of NBR/CR matrices which enhances the thermal stability.

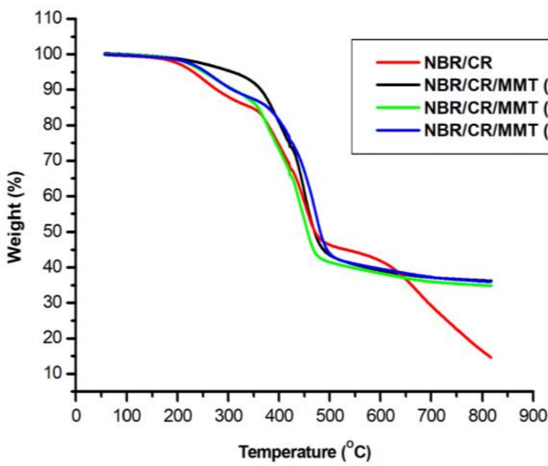

Figure 5:TGA curve of NBR/CR blends at different loadings of MMT

4.3 Morphological Characterization

Scanning Electron Microscopy (SEM) Figure 6, 7(a), 7(b) and 7(c) clearly indicates the inhomogeneous distribution of dispersants with aggregations in the absence of MMT. Figure 7(a) depicts the surface morphology after introducing 1 phr MMT in the matrix of compatibilised NBR/CR, no or very less aggregation are observed with homogeneously distributed filler. Figure 7(b) is an SEM micrograph for sample having loading 3 phr, where uniform distribution of filler is seen. It is clearly evident in the higher magnification image that in all the vulcanizates the dispersants and stabilizers are well dispersed. The absence of vacuoles in the vulcanizates indicates a high level of interaction between the filler and the rubber which may result in the improved strength of vulcanizates. Figure 7 (c) is an SEM micrograph for sample having loading 5 phr, where the fractured surfaces which is very rough, but demonstrate homogenous pattern.

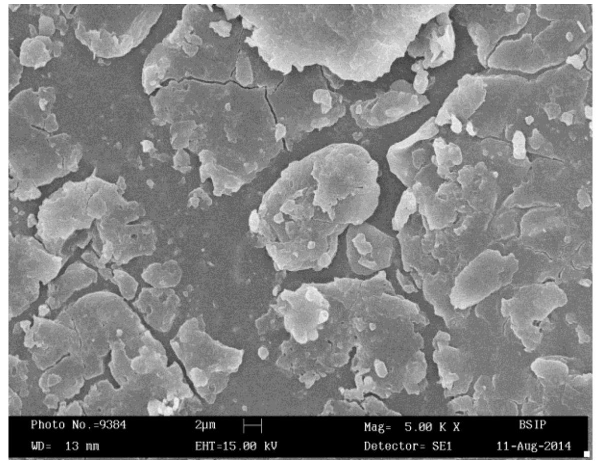

Figure 6: SEM micrograph of NBR/CR

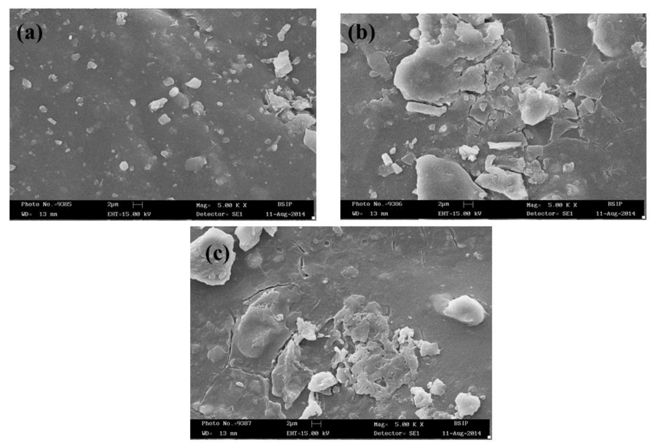

Figure 7: (a) SEM micrograph of 1 Phr MMT/NBR/CR**(b)** 3 Phr MMT/NBR/CR (b) 5 Phr MMT/NBR/CR

V. CONCLUSIONS

Mechanical properties such as tensile strength increases as the loading of MMT are increased and reach to the maximum (at 5 phr of MMT).This showed a remarkable enhancement when compared to virgin NBR/CR blends.TGA studies reveal that thermal stability increases appreciably with the incorporation of higher content of coated MMT into the matrix of NBR/CR blends. SEM studies demonstrate a better dispersion of MMT into the matrix of NBR/CR due to better interfacial adhesion between MMT and the rubber matrix.

REFERENCES

[1] K. Rajkumar,et al. Effect of DOP as Dispersion Medium on MMT- nano Clay in NBR Polymer Matrix, Indian Journal of Applied Research, 2014;vol:4; issue 02- ISSN-2249-555X.

[2] K. Rajkumar, P. Ranjan, P. Thavamani, P.Jeyanthi and P. Pazhanisamy, Dispersion Studies Of Nanosilica In Nbr

Based Polymer Nanocomposite, Rasayan J Chem. 2013; Vol. 6; No.2; 122-133

[3] B. M. Novak, (1993) Hybrid Nanocomposite Materials—Between Inorganic Glasses and Organic Polymers. Advanced Materials, 5, p422-433.

[4] J.E. Mark, Ceramic reinforced polymer and Polymers modified ceramics, Polym Eng Sci.; Willey, 1996, 36, p2905.

[5] D. Vollathand D.V. Szabo, Synthesis and properties of nanocomposites, Adv. Eng. Mater; WILEY-VCH, 2004,6, p117.

[6] P.B. Messersmith,E.P. Giannelis, Polymer-layered silicate nanocomposites: in situ intercalative polymerization of «-caprolactone in layered silicates. 1993, Chem. Mater. 5, 1064–1066.

[7] E. P. Giannelis, Adv. Mater; John Wiley & Sons, Ltd. 1996, 8, p29.doi:10.1002/adma.19960080501

[8] C. Zilg, R. Thomann, J. Finter, R. Mulhaupt, Macromol Mater Eng.: 2000, 41, p280.

[9] S.S. Ray, and M. Okamoto, Polymer/Layered Silicate Nanocomposites: A Review from Preparation to Processing. Progress in Polymer Science, 2003, 28, 1539-1641.

[10] A. Usuki, N. Hasegawa, M. Kato, Adv. Polym Sci.; 2005, 179, p135.

[11] Y. P. Wu, Y.Q. Wang , H.F. Zhang, Y.Z. Wang, D.S. Yu, L.Q. Zhang& Yang, J. - Compos. Sci. Technol; 65, p.1195 (2005). http://dx.doi. org/10.1016/j.compscitech.2004.11.016

[12] P. M. Ajayan, O.Z. Zhou,Topics. Appl. Phys.; 2001, 80, p391.

[13] L. Dai, A.W.H. Mau,Conjugated Polymers for Light-Emitting Applications, Adv. Mater,: WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001,13, p899.

[14] J.N. Coleman, U. Khan, Y.K. Gunoko,Mechanical Reinforcement of Polymers Using Carbon Nanotubes, Adv. Mater, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, 18, p689.

[15] K. Rajkumar, N. Kumari, P. Ranjit, S.K. Chakraborty, P. Thavamani, P. Pazhanisamy, P. Jeyanthi,High temperature resistance properties of NBR based polymer nanocomposites, Int. J. Chem Tech Res. 2011; 3:1343-1348.

[16] S.H. Botros, A.E. Younan and M.E. Mohamed, Ageing and Oil Resistance of Fiber-Reinforced CR/NBR Blends, *Mol. Clysr and Liq. Clysr*, 2000; 354: 409-420.

[17] T. Wang, G. Zhong, L. Zhou, Research on Mechanical Properties, Compatibility, Flame Retardancy, Hot-Air Ageing Resistance of HNBR/CR Blends, *Adv. Mat. Re*, 2013; 750-752: 816-819.

[18] M.A. Kader, K. Kim, Y.S. Lee andC. Nah Preparation and properties of nitrile rubber/Montmorillonite nanocomposites via latex blending, Received: 10 March 2005; Accepted: 2 December 2005; Published online: 19 September 2006 Springer Science+Business Media, LLC 2006.

[19] B. H. Samir, A.F. Younan and M.M. ESSA, Aging and oil resistance of fibres reinforced CR/NBR blends. Mol. cryst. and Liq. Cryst. 2000, Vol 354 pp 4029-420