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INFLUENCE OF DUAL FILLER REINFORCEMENT ON THE CURING AND TRIBO-MECHANICAL BEHAVIOUR OF NATURAL RUBBER NANOCOMPOSITE FOR TIRE TREAD APPLICATION

A huge amount of carbon black (40-60 phr) was commonly used as a reinforcing material in manufacturing of tires to improve the technical properties of pure rubber. Carbon black causes severe health hazard like skin cancer, respiratory problem due to its fly loss property. This study focusses on reducing the usage of carbon black by replacing it with minimal quantity of nanoclay to compensate the technical properties of rubber. Natural Rubber nanocomposites are fabricated using solution and mechanical mixing method in presence and absence of compatibilizer. Cure characteristics, wear test and mechanical properties were examined. NR nanocomposite with dual filler in presence of compatibilizer showed enhancement in torque values, mechanical and wear resistant property. Wear resistance, tensile strength and modulus of dual filler nanocomposite was increased by 66.7%, 91% and 85% when compared to pure NR. Hence NR nanocomposite with dual filler in presence of compatibilizer was found as a proving and possible nanocomposite for tire application.

Keywords: Natural Rubber, Nanoclay, Carbon black, Composites, Tire

1. Introduction

Natural rubber (NR) and synthetic rubber are most commonly utilized in tire manufacturing industry. Natural rubber possess various prominent properties such as resistance to oil, good gas barrier properties, low rolling resistance, high elasticity, tensile strength, etc. [1]. Synthetic rubbers are used as substitute for natural rubber to improve the properties [2]. In tire manufacturing industries rubber blends are commonly used to improve the performance of tires. Reinforcement of carbon black and blending of rubbers are the techniques used in tire manufacturing process [1,3]. Even though other number of numerous reinforcing fillers are commonly available such as silica, nanoclay, etc. Carbon black is more popular due to its unmatched performance [3,4]. Carbon black has mostly inter-related structure and their properties depends on particle size and surface area. The primary objective of the reinforcement is to enhance the strength, abrasion resistance, hardness, improvement in processing techniques and reducing cost of the material [2-5]. Polluting nature, fly loss and bulk usage of carbon black are major limitation seen while using as reinforcing filler and it leads to severe health issues to the workers [6,7]. Hence, many

research works are focused to find the replacement of carbon black by using inorganic reinforcing agent such as silica, carbon nanotubes, nanoclay [6]. Major hurdle in finding the alternate filler is due to the reinforcement technique because inorganic fillers are incompatible with organic rubber compounds [5,8,9]. So, this research work aims in reducing the amount of carbon black used in tire manufacturing process.

Minimum loading of nanofiller in to rubber matrix shows greater improvement in mechanical, optical, gas barrier, thermal and electrical properties [10]. Montmorillonite (MMT) nanoclay is inorganic, hydrophilic in nature and mostly seen as a preferred reinforcing agent in polymer matrix. MMT was organically modified with a quaternary ammonium salt in-order to increase the compatibility between rubber and nanoclay [8,11]. Since this work aims in reducing the amount of carbon black in tire manufacturing, reduction in technical properties of tire was compensated by adding small amount Cloisite 30B. Cloisite 30B is a type of MMT nanoclay belongs to polar group due to the presence of hydroxyethyl groups in add-on to carbon and hydrogen atom [12]. Natural rubber belongs to non-polar group since it contains only carbon and hydrogen atoms. Preparation of nanocomposite by adding nanoclay and natural rubber becomes a challenging

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task owing to poor compatibility between clay layers and polymer matrix [13,14]. Properties of the nanocomposite is enhanced by homogenous distribution of nanoclay in rubber matrix [4]. Homogeneous distribution is achieved using preparation method and compatibility match between nanoclay and rubber matrix [6,13]. Nanoclay can easily be dispersed in to polar rubber when compared to non-polar rubber [15]. To increase the compatibility between nanoclay and natural rubber, epoxidized natural rubber (ENR) was utilized as a compatibilizer [16-18]. Polarity and glass transition temperature of ENR is increased by epoxidation of 1,4-polyisoprene [15]. Polar groups in ENR can form strong bonding with nanoclay. Similarly, presence of non-polar groups in ENR can interact with natural rubber to form strong adhesion bonding. Minimal content Cloisite 30B was added in to ENR via solution mixing and bulk quantity of carbon black were added in to NR along with ENR-Cloisite 30B film through two roll mill. Curing behaviour of rubber, mechanical properties, wear study and HR-TEM images have been examined for the prepared specimens and compared with properties pure NR.

2. Materials

Natural rubber (RMA-1X) was received from Rubber Board, Kottayam, Kerala. Epoxidized natural rubber containing 47% epoxidation unit was purchased from Agricultural Product Processing Research Institute, Zhangjiang, PR China. Cloisite 30B an organically modified montmorillonite clay by ammonium salt was purchased from Southern clay products, USA. N234 grade carbon black procured from Hi-Tech. Other compounding materials like Sulphur, zinc oxide, stearic acid, N-cyclohexyl-2-benzothiazyl sulphonamide and tetramethylthiuram disulphide were procured from Bayer.

3. Preparation method

Natural rubber nanocomposite were developed by two step process, (i) solution mixing and (ii) mechanical mixing. Using solution mixing method ENR-nanoclay composites are prepared. Toluene was used as a solvent to dissolve ENR and Cloisite 30B.

Both ENR and Cloisite 30B were dissolved separately with 1:3 weight ratio between ENR, Cloisite 30B and solvent. Magnetic stirrer was used for dissolving rubber and Cloisite 30B in solvent which is operated at 500 rpm. Again both ENR-toluene and nanoclay-toluene solution are mixed by using magnetic stirrer for 1 hour and ultrasonicated for 15 minutes. Then the ultrasonicated solution is poured in to pet disc and kept at room temperature for the evaporation of solvent which results in the formation transparent thin film. ENR-clay film, natural rubber and carbon black were feed in to two roll mill. Gap between the two rollers were maintained with a ratio of 1:1.4 and it is operated at room temperature. Based on the results obtained from rheometer studies, NR compounds were vulcanized at 150°C. Specimens were prepared according to the formulation depicted in Table 1. Fig. 1. Shows the mechanism of adding nanoclay in to NR matrix and the preparation method used for the preparation of specimens.

4. Characterization methods

4.1. Rheometer study

Monsanto Rheometer R-100 instrument is used to find out cure rate index, scorch and cure time along with minimum and maximum torque values for the natural rubber compounds. Rheological studies were carried out at 150°C with 3° arc for 30 min.

4.2. Wear Test

Wear analysis were carried out for the NR composite using abrasion tester according to the standard ASTM: D5963-04 (2010).

4.3. Rock-rubber wear test

Wear analysis was carried out on experimental setup which is available in IIT Kharagpur. Experimental set up is specially designed and fabricated to carry out wear analysis of rubber with

Formulation of Rubber Compounds

TABLE 1

Sample no	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16	R17	R18
Ingredients	Content /phr*																	
NR	100	100	100	100	97	94	93	91	100	100	100	100	100	97	94	91	90	88
Carbon Black	—	—	—	—	—	—	—	—	40	20	20	20	20	20	20	20	20	20
Cloisite 30B	—	1	2	2.5	1	2	2.5	3	—	1	2	2.5	3	1	2	3	3.5	4
Compatibilizer ENR	—	—	—	—	3	6	7.5	9	—	—	—	—	—	3	6	9	11	12
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
CBS+	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Zinc oxide	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Sulphur	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

*phr – Parts per hundred rubber by weight

+CBS – N-cyclohexyl-2-benzothiazyl sulphonamide

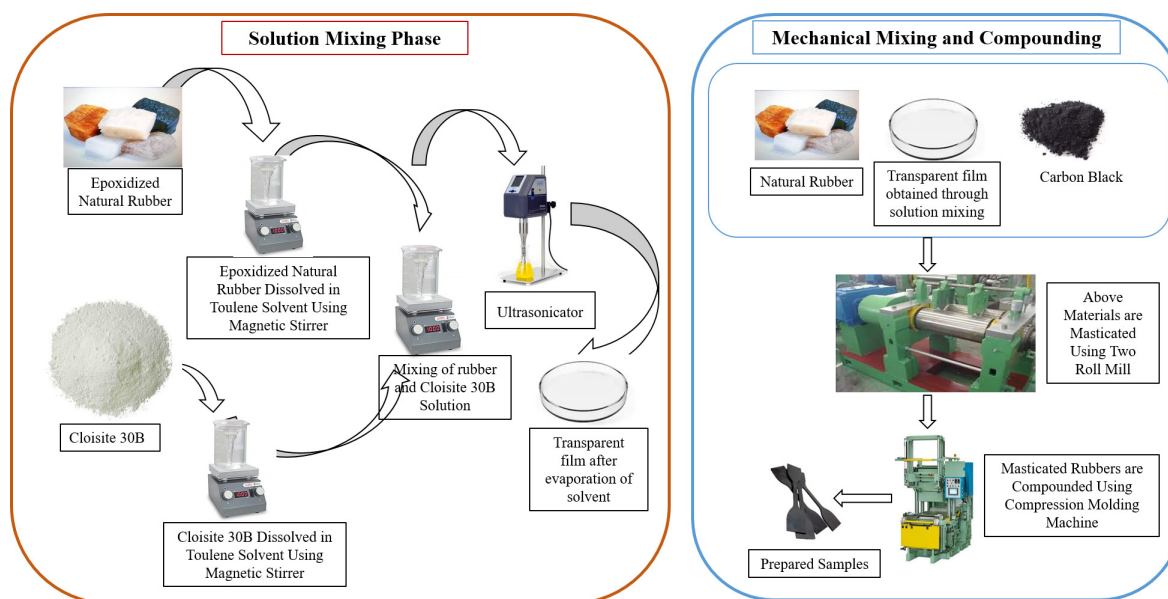


Fig. 1. Preparation method of NR compounds

different rocks shown in Fig. 2. The Cerchar abrasivity test is a laboratory method to quantify the rock abrasivity. It allows to determine an index called Cerchar Abrasivity Index (CAI) for the rock's abrasivity which can be used for evaluate the wear behaviour. Wear studies were made by considering three rock such as sand stone, granite and coal. Specific gravity of coal, sand stone and granite are 1.5, 2.08 and 2.74 respectively. The CAI value of tested sandstone sample is 2.50 and granite sample is 4.10. Coefficient of friction of coal, granite and sandstone is 0.40, 0.33 and 0.28 respectively. Thus, coefficient of friction and the CAI value of rock majorly influences the wear behaviour of rubber samples which significantly affects the weight loss values. Rubber sample is mounted on the specimen holder by using set-screw and the rock samples are fixed in the rock holder. Projection of the rock sample is adjusted in such a way that cantilever beam is in horizontal condition. Shaft is connected to a single phase 0.2 kW electric motor and the speed adjustments can be made by step cone pulley. Speed of the shaft is maintained at 246 rpm.

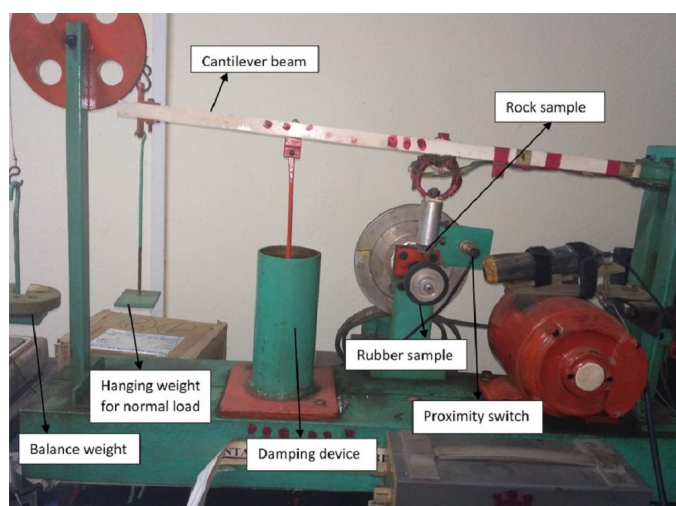


Fig. 2. Experimental setup for rock-rubber wear test

A damping device is connected to the cantilever beam to avoid vibrations. Instrument cluster is connected to the experimental setup to ensure the duration of contact between rubber and rock. Number of revolutions is also monitored by using a proximity switch. A weight of 450 g is hanged on the one of cantilever beam to develop a normal load of 4.41 N at the rubber and rock interface region. Weight of the specimens were measured before and after carrying out the test at room temperature.

4.4. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of the NR rubber samples were determined using DMA 2980 instrument model. Storage modulus of the NR composite were examined at 0.1% strain rate between the temperatures ranging from 30° to 80°C with a frequency of 1Hz.

4.5. Mechanical properties

Specimens for mechanical testing were prepared as per ASTM standard D412-06 with the gauge length of 25 mm. UTM is used to carry out the tensile test and the machine is operated with a speed of 500 mm / min at room temperature.

4.6. High Resolution Transmission Electron Microscopy (HR-TEM)

JEOL 2100 high resolution transmission microscope were used to study the dispersion morphology of nanoclay for the prepared NR nanocomposite. Ultramicrotome fitted with diamond knife were used for preparing the samples. Samples were placed in grid of the microscope and held at -80°C.

5. Results and discussion

5.1. Rheometer study

Table 2. shows the outcomes of rheometer studies of natural rubber (NR) composites. Curing study reveals that compatibilized rubber nanocomposite (R5, R6, R7, R8, R14, R15, R16, R17, R18) shows enhancement in values when compared to other rubber compounds. Cure time and scorch time of compatibilizer rubber nanocomposite decreases when compared to uncompatibilized nanocomposite and pure rubber. Due to the homogeneous distribution of Cloisite 30B in to NR matrix and cross linking between the molecules enhances the minimum and maximum torque [11,19-22]. Hence, usage of ENR as compatibilizer enhances the compatibility between the nanoclay. Maximum and minimum torque value in the Table 2 shows the viscosity and storage modulus of NR compounds [18,20,23]. Torque difference can be compared with degree of crosslinking [18,20,24]. Cure time and scorch time of dual filler nanocomposite (R10, R11, R12, R13, R14, R15, R16, R17, R18) has reduced drastically when compared to single filler nanocomposite (R2, R3, R4, R5, R6, R7, R8, R9). Cure and scorch time was reduced due to the presence of ammonium groups in Cloisite 30B [11,19-21]. Curing rate increases as weight percentage of nanoclay increases. Curing rate increases further for dual filler nanocomposite and it is due to the hybrid effect of carbon black and Cloisite 30B in NR matrix. Since carbon black possess large surface area, it promotes curing process in hybrid composites [21,25]. Formation of zinc element in cross linking process resulted in enhancement of cure rate [11,20,21,26,27]. Faster curing time and cure rate was achieved due to the presence of Cloisite 30B in NR matrix.

5.2. Wear Test

Fig. 3. indicates the wear analysis of NR compounds using din abrasion tester. Wear resistance of NR composite increases as weight percentage of carbon black and Cloisite 30B increases in NR matrix. Wear loss of dual filler NR nanocomposite (R10, R11, R12, R13, R14, R15, R16, R17, R18) is high when compared to single filler NR nanocomposite (R2, R3, R4, R5, R6, R7, R8, R9). It is also found that compatibilized rubber compounds shows better low wear loss when compared to uncompatibilized rubber compounds. It is due to the strong adhesion between Cloisite 30B and NR matrix. Increase in interfacial bonding between NR matrix and Cloisite 30B was achieved due to polar-polar interaction between ENR and nanoclay for the compatibilized NR nanocomposite. Wear loss of R18 rubber compound was reduced by 77.95% when compared to pure NR [22,28,29].

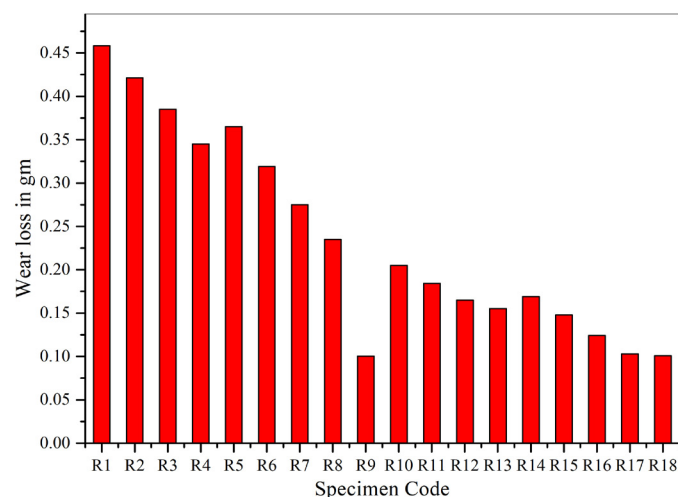


Fig. 3. Din-Abrasion test of NR compounds

TABLE 2

Curing Characteristics

Samples	Min Torque (dN.m)	Max Torque (dN.m)	Torque Diff (dN.m)	Scorch time (min)	Cure time (min)	Cure rate index (min ⁻¹)
R1	5.33	49.33	44	2.3	12.3	10.00
R2	8.44	51.83	43.39	1.45	11.15	10.31
R3	8.67	52.11	43.44	1.15	10.45	10.75
R4	9.17	48.16	38.99	1	10.15	10.93
R5	8.4	52.55	44.15	1.3	11	10.31
R6	8.9	53.77	44.87	1.15	10.3	10.93
R7	9.33	54.65	45.32	1	10	11.11
R8	9.61	55.01	45.4	0.45	9.15	11.49
R9	5.78	56.94	51.16	2.3	10.3	12.50
R10	6.6	55.85	49.25	2	10	12.50
R11	6.93	56.45	49.52	1.3	9.3	12.50
R12	7.55	57.34	49.79	1.15	9	12.74
R13	8.01	58.01	50	1	8.3	13.70
R14	5.11	54.83	49.72	1.45	9.15	12.99
R15	6.78	57.32	50.54	1.3	8.3	14.29
R16	7.07	58.01	50.94	1.15	8	14.60
R17	7.45	58.83	51.38	1	7.45	15.50
R18	7.89	59.32	51.43	0.45	7	15.27

5.3. Rock-rubber wear test

Fig. 4. depicts the wear analysis of NR nanocomposite, tested with different rocks such as coal, granite and sand stone. Among the three rocks, NR nanocomposite shows less wear resistant in sand stone rock and it is due to the less coefficient of friction as 0.28 and low CAI value as 2.50. Wear analysis were also carried with granite and coal rocks and it is observed that wear loss is increased by 4.3% and 27.5% for R18 when compared to nanocomposite tested with sand stone rock. Wear loss were increased for granite and coal due to its high coefficient of friction and high CAI value when compared to sandstone [3,15,30]. Similar trend is also observed when comparing with din abrasion wear test.

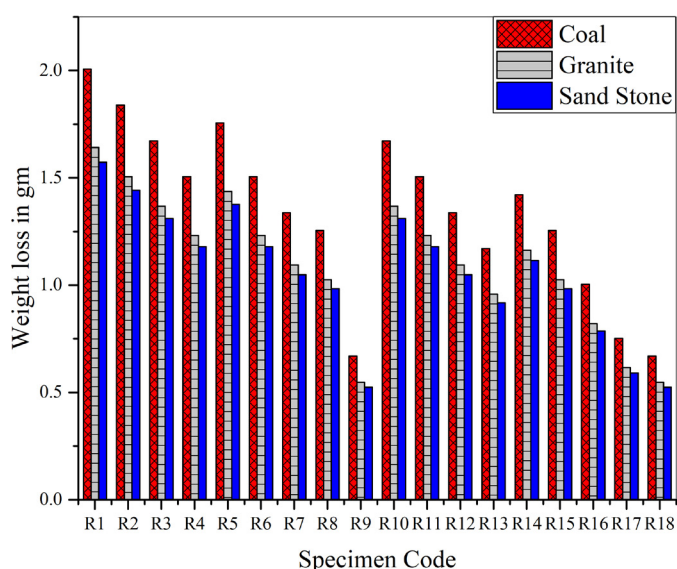


Fig. 4. Rock-rubber wear test NR compounds

5.4. Dynamic Mechanical Analysis (DMA)

Fig. 5. depicts the results of storage modulus with respect to temperature. DMA studies were carried out for the NR rubber samples R4, R6, R9, R16 and R17. Storage modulus were observed to increase when carbon black and Cloisite 30B were introduced in to NR compounds in presence and absence of compatibilizer. Due to the even dispersion of Cloisite 30B and carbon black in NR matrix with compatibilizer (R6, R16 and R17) shows increase in storage modulus. Storage modulus curve of R9 and R17 rubber samples are found to be similar [19].

5.5. Mechanical properties

Fig. 6. and Fig. 7. shows the tensile strength, modulus and percentage of elongation of NR nanocomposite. Compatibilized nanocomposite (R5, R6, R7, R8, R14, R15, R16, R17, R18) shows superior tensile strength and modulus when compared to uncompatibilized nanocomposite (R2, R3, R4, R10, R11, R12,

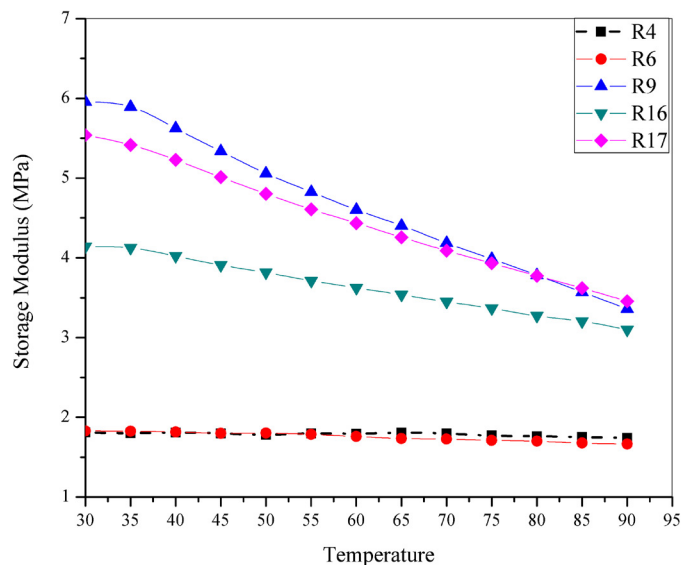


Fig. 5. Storage Modulus NR compounds

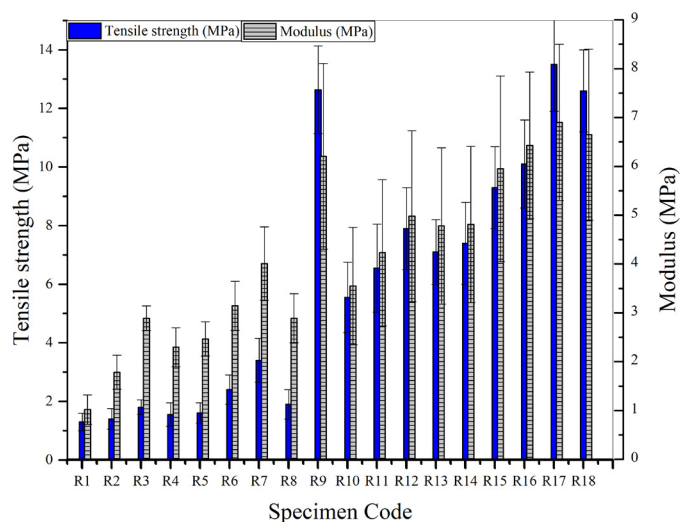


Fig. 6. Tensile Strength and Modulus NR compounds

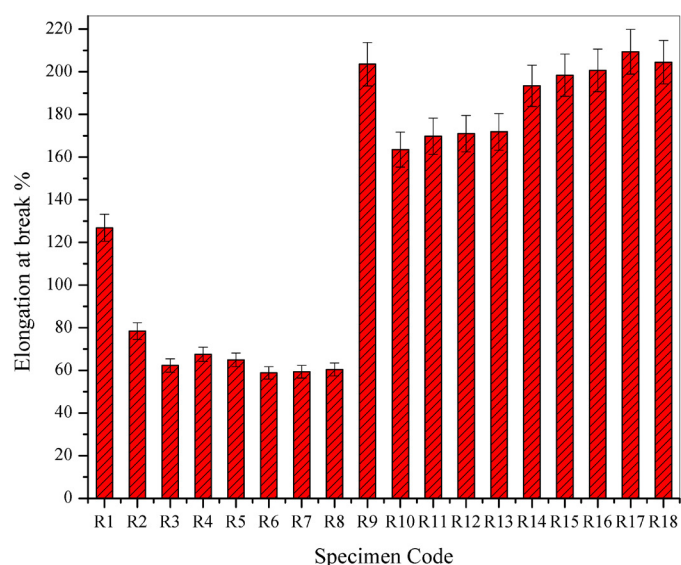


Fig. 7. Elongation at Break NR compounds

R13) and pure rubber [18]. Uncompatibilized nanocomposite shows poor results due to poor compatibility between Cloisite 30B and NR. Tensile strength and modulus of dual filler nanocomposite (R17) was enhanced by 91% and 85% when compared to pure NR (R1). Similarly, tensile strength and modulus of compatibilized single filler and dual filler nanocomposite is increased by 18.4%, 20.4%, 47.4% and 30.7% respectively. Presence of carbon black in the dual filler nanocomposite and homogeneous distribution of Cloisite 30B in the NR matrix results in increased mechanical properties [20,22,29]. Strong interfacial bonding between carbon black and NR was achieved due to the larger surface area of carbon black [21]. Addition of carbon black along with Cloisite 30B in NR matrix breaks the aggregated nanoclay platelets resulted in homogeneous distribution of nanoclay. Hence dual filler nanocomposite (R17) shows maximum intake of 3.5 phr Cloisite 30B in NR matrix. Tensile strength and modulus of dual filler nanocomposite (R18) was decreased by 6.67% and 3.6% when compared to R17 due to weight content of Cloisite 30B increases to 4 phr. Reduction in mechanical properties was observed due aggregated nanoclay platelets resulted in weaker spots. Same trend is also observed for percentage of elongation also.

5.6. High Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM images of dual filler reinforced compatibilized nanocomposite R17 and R18 are shown in Fig. 8 and Fig. 9. Rounded areas shown in the Fig. 8. points out the exfoliated structure of nanoclay platelets. Homogeneous dispersion of Cloisite 30B was achieved due to the addition of carbon black resulted in exfoliated structure [31,32]. Exfoliated nanoclay platelets and carbon black got agglomerated during increase in loading of nanoclay from 3.5 phr to 4 phr which is observed from Fig. 9. Technical properties of NR nanocomposite (R18) decreases due to the agglomeration of nanoclay.

6. Conclusion

Compensation of tribo-mechanical properties of NR nanocomposite is achieved by adding small weight percentage of nanoclay for minimizing 20 phr of carbon black in tire manufacturing process. NR nanocomposites were developed by two step mixing method (i) solution and (ii) mechanical mixing method. Compatibility between polar based Cloisite 30B and non-polar NR was achieved using ENR as a compatibilizer. Curing study reveals faster cure rate and increment in torque values for the both single and dual filler nanocomposite. Increase in torque and decrease in cure rate is achieved due to the uniform distribution of filler in nanocomposite. Single and dual filler compatibilized nanocomposite shows increment in mechanical and wear resistance when compared to uncompatibilized and pure rubber N1. Interfacial bonding between filler

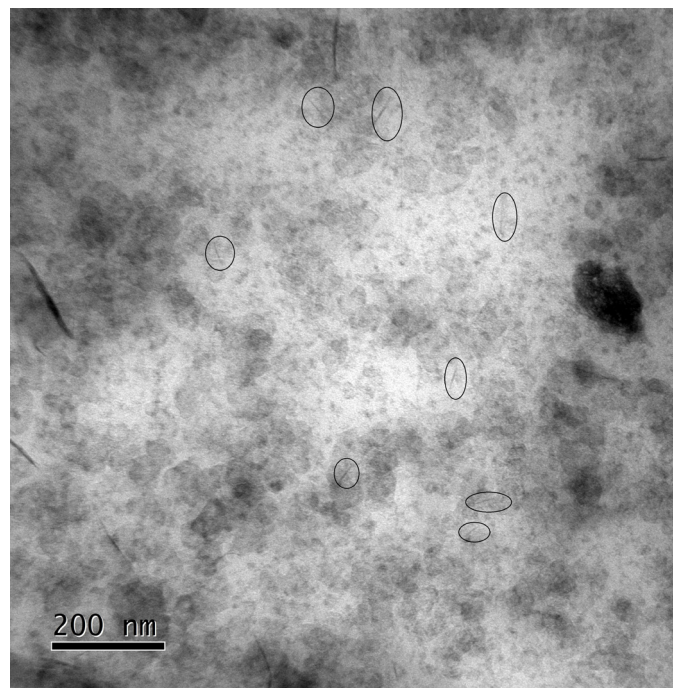


Fig. 8. HR-TEM images of R17 nanocomposite NR compounds

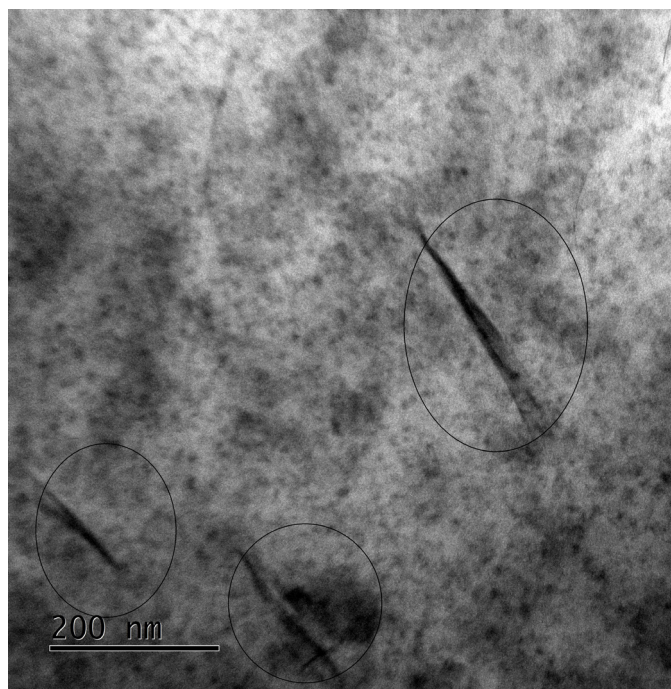


Fig. 9. HR-TEM images of R18 nanocomposite NR compounds

and NR matrix was achieved for compatibilized nanocomposite. Technical properties of dual filler based compatibilized NR nanocomposite containing carbon black (20 phr) and nanoclay (3.5 phr) was comparable to nanocomposite (R9) contains 40 phr carbon black. Hence, minimum content of Cloisite 30B addition in NR matrix with compatibilizer via two step mixing method rendered desired technical properties resulted in considerably minimizing the weight content of carbon black in tire manufacturing process.

REFERENCES

- [1] K. Pal, R. Rajasekar, D.J. Kang, Z.X. Zhang, S.K. Pal, C.K. Das, J.K. Kim, *Mater. Des.* **31** (2), 677-686 (2010). DOI: <https://doi.org/10.1016/j.matdes.2009.08.014>
- [2] K. Pal, R. Rajasekar, T. Das, D. Kang, S. Pal, J. Kim, C. Das, *Plast., Rubber Compos.* **38** (7), 302-308 (2009). DOI: <https://doi.org/10.1179/174328909X435393>
- [3] K. Pal, R. Rajasekar, D.J. Kang, Z.X. Zhang, J.K. Kim, C. Das, *Mater. Des.* **30** (10), 4035-4042 (2009). DOI: <https://doi.org/10.1016/j.matdes.2009.05.021>
- [4] K. Roy, S.C. Debnath, P. Potiyaraj, *J. Elastomers Plast.*, (2019).
- [5] S.J. He, Y.Q. Wang, J. Lin, L.Q. Zhang, *Adv. Mater. Res.* 28-31 (2012).
- [6] S. Ahmadi Shooli, M. Tavakoli, *J. Macromol. Sci., Part B*, **55** (10), 969-983 (2016). DOI: <https://doi.org/10.1080/00222348.2016.1230464>
- [7] R. Sengupta, S. Chakraborty, S. Bandyopadhyay, S. Dasgupta, R. Mukhopadhyay, K. Auddy, A. Deuri, *Polym. Eng. Sci.* **47** (11), 1956-1974 (2007). DOI: <https://doi.org/10.1002/pen.20921>
- [8] A. Malas, C.K. Das, *J. Mater. Sci.* **47** (4), 2016-2024 (2012). DOI: <https://doi.org/10.1007/s10853-011-6000-z>
- [9] Q.-X. Jia, Y.-P. Wu, P. Xiang, Y. Xin, Y.-Q. Wang, L.-Q. Zhang, *Polym. Polym. Compos.* **13** (7), 709-719 (2005).
- [10] H. Nabil, H. Ismail, *Int. J. Polym. Anal. Charact.* **19** (2), 159-174 (2014). DOI: <https://doi.org/10.1080/1023666X.2014.873597>
- [11] R. Rajasekar, G. Heinrich, A. Das, C.K. Das, *J. Nanotechnol.* **2009**, 1-5 (2009). DOI: <https://doi.org/10.1155/2009/405153>
- [12] Y.-W. Mai, Z.-Z. Yu, *Polym. Nanocompos.*, Woodhead publishing, (2006).
- [13] R. Rajasekar, G. Nayak, C. Das, *Plast., Rubber Compos.* **40** (3), 146-150 (2011). DOI: <https://doi.org/10.1179/1743289810Y.0000000010>
- [14] Y. Liang, Y. Wang, Y. Wu, Y. Lu, H. Zhang, L. Zhang, *Polym. Test.* **24** (1), 12-17 (2005). DOI: <https://doi.org/10.1016/j.polymertesting.2004.08.004>
- [15] K. Pal, R. Rajasekar, S.K. Pal, J.K. Kim, C.K. Das, *J. Nanosci. Nanotechnol.* **10** (5), 3022-3033 (2010). DOI: <https://doi.org/10.1166/jnn.2010.2170>
- [16] R. Iyer, S. Suin, N.K. Shrivastava, S. Maiti, B. Khatua, *Polym.-Plast. Technol. Eng.* **52** (5), 514-524 (2013). DOI: <https://doi.org/10.1080/03602559.2012.762024>
- [17] P. Saramolee, K. Sahakaro, N. Lopattananon, W.K. Dierkes, J.W. Noordermeer, *J. Elastomers Plast.* **48** (2), 145-163 (2016). DOI: <https://doi.org/10.1177/0095244314568469>
- [18] N. Hayemasae, I. Surya, H. Ismail, *Int. J. Polym. Anal. Charact.* **21** (5), 396-407 (2016). DOI: <https://doi.org/10.1080/1023666X.2016.1160970>
- [19] R. Rajasekar, C. Das, *Plast., Rubber Compos.* **40** (8), 407-412 (2011). DOI: <https://doi.org/10.1179/1743289810Y.0000000039>
- [20] A. Malas, C.K. Das, *Mater. Des.* **49**, 857-865 (2013). DOI: <https://doi.org/10.1016/j.matdes.2013.02.040>
- [21] R. Rajasekar, G. Nayak, A. Malas, C. Das, *Mater. Des.* **35** (1), 878-885 (2012). DOI: <https://doi.org/10.1016/j.matdes.2011.10.018>
- [22] R. Mahaling, S. Kumar, T. Rath, C. Das, *J. Elastomers Plast.* **39** (3), 253-268 (2007). DOI: <https://doi.org/10.1177/0095244307076495>
- [23] P. Teh, Z.M. Ishak, A. Hashim, J. Karger-Kocsis, U. Ishiaku, *Eur. Polym. J.* **40** (11), 2513-2521 (2004). DOI: <https://doi.org/10.1016/j.eurpolymj.2004.06.025>
- [24] H. Ismail, H. Chia, *Eur. Polym. J.* **34** (12), 1857-1863 (1998). DOI: [https://doi.org/10.1016/S0014-3057\(98\)00029-9](https://doi.org/10.1016/S0014-3057(98)00029-9)
- [25] T. Mohan, J. Kuriakose, K. Kanny, *J. Ind. Eng. Chem.* **17** (2), 264-270 (2011). DOI: <https://doi.org/10.1016/j.jiec.2011.02.019>
- [26] M.S. Kim, G.H. Kim, S.R. Chowdhury, *Polym. Eng. Sci.* **47** (3), 308-313 (2007). DOI: <https://doi.org/10.1002/pen.20709>
- [27] A. Khalil, S.N. Shaikh, Z.R. Nudrat, S. Khaula, *Adv. Mater. Phys. Chem.* **2012**, (2012).
- [28] G.C.N. R. Rajasekar, C.K. Das, *Materials Science & Technologies*, 575-590, (2011).
- [29] B.P. Kapgate, C. Das, D. Basu, A. Das, G. Heinrich, *J. Elastomers Plast.* **47** (3), 248-261 (2015). DOI: <https://doi.org/10.1177/0095244313507807>
- [30] K. Pal, T. Das, R. Rajasekar, S.K. Pal, C.K. Das, *J. Appl. Polym. Sci.* **111** (1), 348-357 (2009). DOI: <https://doi.org/10.1002/app.29128>
- [31] M. Balachandran, S. Bhagawan, *J. Polym. Res.* **19** (2), 9809 (2012). DOI: <https://doi.org/10.1007/s10965-011-9809-x>
- [32] Y. Liu, L. Li, Q. Wang, *Plast., Rubber Compos.* **39** (8), 370-376 (2010). DOI: <https://doi.org/10.1179/174328910X12691245469871>