

Effect of concentration of Halloysite nanotubes on the Mechanical, Thermal and electrical properties of NBR/PP Elastomer nanocomposites

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Abstract

Preparation of nanocomposites from immiscible polymer blends system has been investigated in this work. Natural clay named halloysite nanotubes are incorporated in the immiscible blend system using melt mixing process to prepare halloysite based nanocomposites comprising of PP/NBR blend system. FTIR studies have been carried out to establish the structure properties relationship. Nanocomposites are characterized by SEM for morphological studies. The thermal stability of nanocomposites has been evaluated by TGA and it found that maximum thermal stability occurs at 3 wt% of HNTs in polymer matrix. Mechanical Properties results have demonstrated maximum tensile strength and hardness at 3wt% loading of HNTs. The above investigation reveals that HNT act as a reinforcing with nucleating agent in the present investigated blend system. Electrical properties results depict that there is appreciable enhancement in arc resistance and dielectric strength as the content of HNT is increased in the blend system.

Keywords: Nanocomposites, tensile strength, dielectric, PP, SEM.

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INTRODUCTION

In the present scenario, polymers/coated silicates nano-composites have attracted a great deal of attention because they demonstrate significant development in materials when compared to intrinsic polymers or conventional composites. These developments can include high modulus¹⁻⁶, improved strength also heat resistance⁷, reduced gas permeability⁸⁻¹² flammability¹³⁻¹⁷ biodegradability of biodegradable polymer¹⁸. Nowadays, tubular halloysite clays have attracted immense interest of researcher's because of its multipurpose structures. This nanomaterial can be used as nanofiller in polymer reinforcement of thermoplastic matrices with HNT have been investigated in big way by various research groups. HNT may be used in polymer nanocomposites to develop high-tech nanocomposites with significant improvements in various properties i.e.

mechanical, thermal, morphological, etc. truly speaking, halloysite is consisted of aluminium and silicon 1:1 ratio with chemical formula of $Al_2Si_2O_5(OH)_4nH_2O$ where $n= 2$ and 0 , conforming the hydrated also dehydrated HNTs^{19, 20}. HNTs have high aspect ratio, area and length varies from (500-1000nm) and (15-100nm) correspondingly.

Polypropylene is most commonly used polymer globally because it's simple processability and cheap. It has good mechanical and physical properties however its inferior characteristics (impact strength, minimum UV resistance, and breakable at low temperature) confine its utilized in engineering applications. Various investigators have paid their consideration on the effect of PP/HNTs composites²¹⁻²⁴. NBR rubber is commonly unaffected to fuel, oil and chemicals. Its propriety to withstand range of temperature

from (-40°C to 108°C) types a perfect material for automotive applications Nitrile (NBR, Buna-N) rubber is commonly unaffected to aliphatic hydrocarbon.

The purpose of current research work to development blend of PP and NBR by melt mixing process. It is well established fact that generally the combines of polymers are immiscible in nature. To make them compatible, HNT has been incorporated in blend system at varied loadings. Nowadays, nanofiller are thought to be compatibilizer for any blend system. We focused on the mechanical, thermal also electrical properties after adding of HNTs.

MATERIALS AND METHODS

Materials

NBR rubber was obtained from M/s. Japan Synthetic rubber grade JSR 220 having acrylonitrile content of 38%. Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene. PP-ICP (C015EG) grade having MI 1.50 g/10 min. Halloysite nanotubes (HNT's) were obtained from Sigma-Aldrich. Zinc oxide, stearic acid and sulphur, employed in this study were obtained from E. Merk, Germany.

Samples preparation

The compounding of rubber and plastics were done by using open two roll mill (Neoplast, TRM 155) of length (300 mm), (170 mm) diameter at a rpm of slow roll (18 revolutions^{min}⁻¹) and friction proportion of (1.4), composite was compassed 8-9 times by rollers having a tight nip space of < 1mm. The composite ingredients were added as per technique given the following sequence: filler, activator, accelerator and curing agents maintaining roller temperatures between (100-120°C) with the cooling water heat removal function. Meanwhile the amount of HNT's

was varied accordingly. Simultaneously the formulations of rubber additives used are tabulated in Table 1. The nanocomposite thus obtained was then molded in the form of a sheet (12cm x 12cm x 3 cm) at 160°C at 1138 psi or 80 kg/cm² in a compression moulding press (made Deepak Poly Plast Pvt Ltd, Delhi, India). All specimens were then cut into form of testing sheets.

TESTING AND CHARACTERIZATION

Mechanical properties

Dumbbell designed samples for tensile testing are designed from molded sheet by using punching press or ASTM Die-C. Tensile strength has been noticed according to (ASTM D412-98) utilizing a (INSTRON, U.S.A.) Universal Testing Equipment the extension rpm of (500 mm/min) at 25±2°C through an initial gauge length of 25 mm. Hardness of the rubber samples have been determined by Durometer Hardness test of Shore-A type having indentation in the form of truncated cone. The reading is to be taken after 15 seconds of indentation when the firm contact is established between the specimens test data reported here average of the result for test run-on at least four samples.

Thermal gravimetric analysis (TGA)

Thermalgravimetric Analyzer (TGA) (Model Perkin Elmer TRA7-6000,US) was utilized to evaluated the moisture content, fixed carbon and volatile matter present in composite, 5 gm of the composite sample was transferred in the ceramic crucible of the analyzer. It calculates the quantity and degree of bulk variation as effects of temperature to resolve the thermal stability and decay kinetics of a material, temperature range at 50°C temperature to 700°C at heating rate of 10°C/min in nitrogen environment.

Table 1: Compounding formulations of NBR/PP-HNTs nanocomposites.

Sample Code	NBR (wt.%)	PP (wt.%)	(ZnO) (wt.%)	Stearic Acid (wt.%)	Sulphur(wt.%)	HNT's(wt.%)
NPH-0	50	50	2	1	2.5	0
NPH-1	50	50	2	1	2.5	1
NPH-2	50	50	2	1	2.5	2
NPH-3	50	50	2	1	2.5	3
NPH-4	50	50	2	1	2.5	4

Scanning Electron Microscopy (SEM)

The surfaces morphology of NBR/PP blends filled with the different loadings of HNTs have been analyzed utilizing (model no. JEOL, JSM-6490 LV SEM). SEM technique used to justify the HNT presence in the composite the dispersion of HNT in the matrix of NBR/PP blend. Prior to SEM analysis the fractured samples obtained after tensile analysis have been gold coated with the help of gold sputtering unit to avoid the charging effect and enhance the emission of secondary electrons.

Fourier Transform Infrared spectroscopy (FTIR)

FTIR studies were carried out with the help of Agilent Carry 600 in a humidity free atmosphere at room temperature from 4000-450 cm^{-1} to investigate the possible interaction between polypropylene and nitrile rubber.

Electrical Properties

The dielectric strength of an insulating material is defined as the maximum voltage required to produce a dielectric breakdown evaluated as per ASTM D 149. Arc resistance is the ability of a plastic material to resist the action of a high-voltage electrical arc, and is usually stated in terms of time required to form material electrically conductive evaluated as per ASTM D 495.

RESULTS AND DISCUSSION

Mechanical properties

Mechanical properties results of NBR/PP reinforced with HNT nanocomposites are presented in Table 2. It is observed from the mechanical properties results that there is enhancement in tensile strength and elongation at break with increasing amount of HNT upto 3 wt% loading of HNT and the values have been found to decrease as the level of HNTs is increased beyond 4 wt%. The decrease in tensile properties at higher loading is attributed to filler-filler interaction and poor filler dispersion in the polymer matrices. The enhancement in tensile properties may be due to the improvement in interfacial interaction of HNTs and rubber molecules and also the higher aspect ratio and surface area of HNT. This interaction delays the de-attachment between HNTs and rubber molecules and

promotes the rise of stress during tensile process.

The hardness of developed nanocomposites has been found to be increased directly proportion with increasing amount of HNT. The hardness values of nanocomposites are higher as compared to that of NBR rubber and PP blends. This can be due to the strong interaction between HNTs and polymer matrices.

Table 2: Mechanical properties results of NBR/PP-HNTs nanocomposites.

Sample Codes	Tensile Strength (MPa)	Elongation at break (%)	Hardness (Shore A)
NPH-0	6.24	1210	65
NPH-1	6.56	1356	68
NPH-2	6.64	1595	69
NPH-3	7.12	1660	72
NPH-4	6.90	1615	72

Thermo gravimetric analysis (TGA)

The results of TGA analysis of the NBR/PP blend reinforced with HNT^s nanocomposites have been shown in Figure 1. It is obvious from thermo gram that in the temperature range 100-200°C. Nanocomposites containing organic moiety degrades slightly faster causing slight weight loss in nanocomposites. The improvement in thermal stability with increasing HNTs loadings shows the ability of nanofiller in retarding the heat diffusion into the rubber matrix. When the HNTs content has been increased beyond 3wt%, a minute decrease in the weight of residue has been observed. The improvement in thermal stability may be attributed to the delay in diffusion of volatile materials from the nanocomposites structure at 3wt% loading of HNTs in rubber matrix. Thus, a conclusion can be drawn by saying that nano composites having 3 wt% loading of HNTs possesses excellent thermal stability.

Scanning Electron Microscopy (SEM)

SEM micrographs of pure blend also nanocomposites shown in Figure 2 (a-e). In the micrographs of pure blend reveal the immiscibility and a coarse morphology. It is evident from Figure 2 (a) that the surface of the pure blend is rough in nature having some

voids and cavities. From SEM micrographs Figure 2(b-e), it is evident that there is no phase separation which confirms the homogeneity between both the component of polymers i.e. polypropylene and NBR rubber. It is also observable from SEM micrographs that the high level of compatibilization imparted by the incorporation of HNTs has played imperative character in the improvisation of mechanical and thermal properties of NBR/PP/HNTs nano composites. Thus, it can be concluded that HNTs acts as a compatibilizer for the developed nanocomposites which provides excellent interfacial adhesion and polymer-polymer-HNTs interactions.

Fourier Transform Infrared spectroscopy (FTIR)

The FTIR spectra, a comparative study of HNTs, NBR and NBR/PP/HNTs blends are depicted in Figure 3. The peaks at 3632 and 3252 cm^{-1} show the presence of $-\text{OH}$ groups. 2924 and 2851 cm^{-1} peaks are assigned to $-\text{CH}$ stretching due to the presence of propyl group. The bending peak of $-\text{OH}$ group is present at 1614 cm^{-1} . The broad band represents $-\text{SiO}_2$ at 1014 cm^{-1} . The presence of nitrile group can be confirmed by the characteristic peak at 2236 cm^{-1} and out of plane bending vibration

from $=\text{C}-\text{H}$ bond at 968 cm^{-1} . In NBR/PP/HNTs nanocomposites, peaks at 3789 cm^{-1} can be assigned to $-\text{OH}$ due to presence of HNT. It is also observable that the $-\text{CH}$ peaks shift from 2924 cm^{-1} to 2919 cm^{-1} and from 2851 cm^{-1} to 2850 cm^{-1} . The decreased intensity in characteristic peak at 2236 cm^{-1} (nitrile group) confirms the blending of NBR/PP and HNT.

Electrical Properties

Electrical properties results of NBR/PP reinforced with HNT nanocomposites are presented in Table 3. It is observed from the Table 3 dielectric strength and arc resistant that there is remarkable enhancement in dielectric strength and arc resistant with increasing amount of HNT upto 3 wt% loading of HNTs and the values have been found to decrease as the level of HNTs is increased beyond 4 wt%. The decrease in dielectric strength and arc resistant at higher loading is attributed to filler-filler interaction and poor filler dispersion in the polymer matrices. The dielectric strength and arc resistant values of nanocomposites are higher as compared to that of NBR rubber and PP blends. This can be due to the strong interaction between HNTs and polymer matrices.

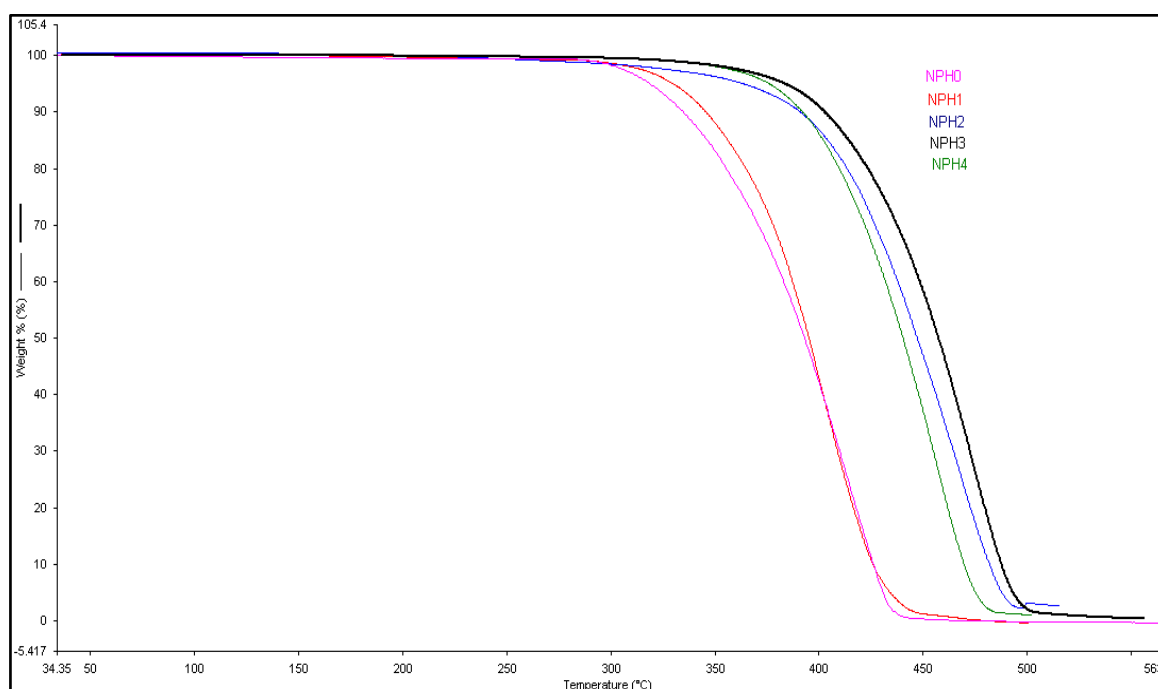


Fig.1: TGA Thermogram of NBR/PP blends with varied loadings of halloysite nanotubes.

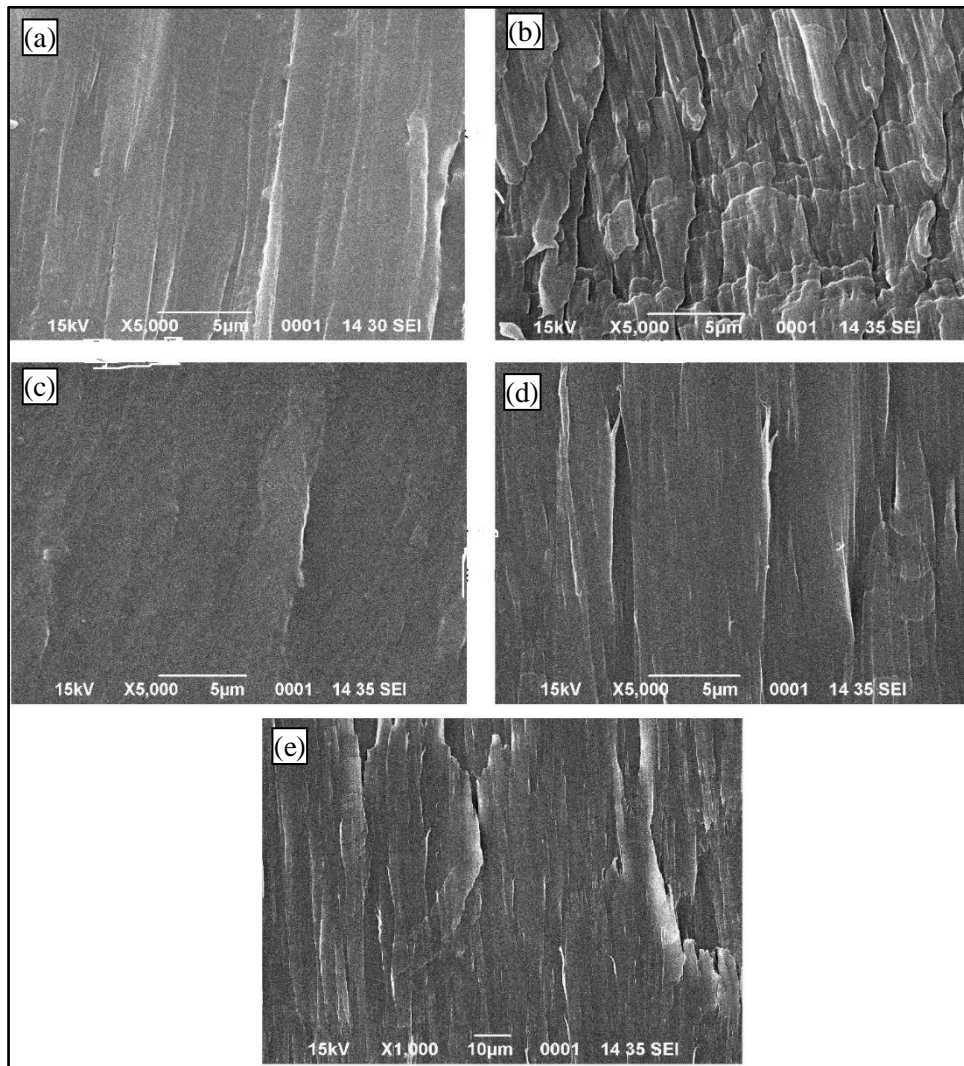


Fig. 2: (a-e) SEM micrographs of NBR/PP blend with different loadings of halloysite nanotubes.

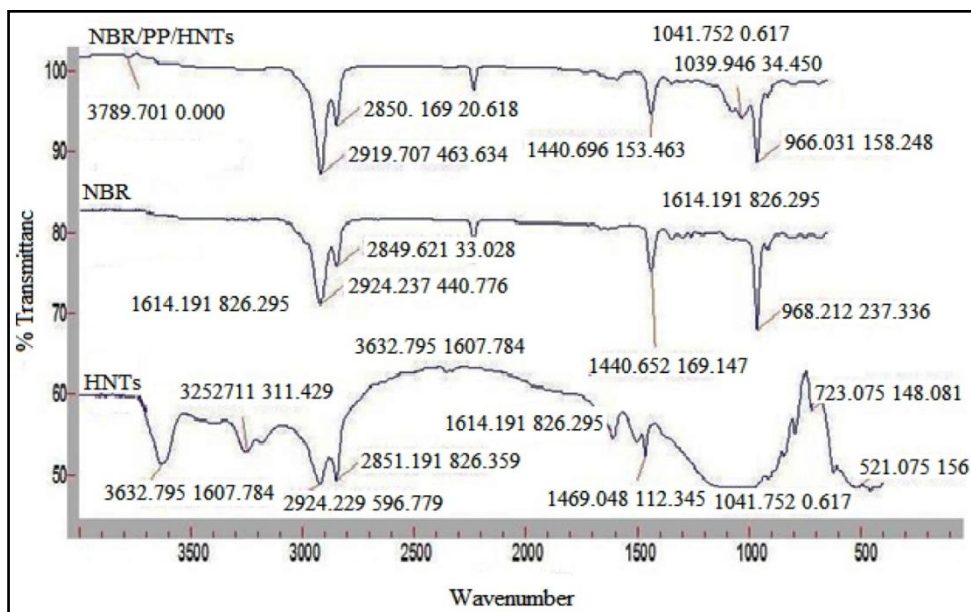


Fig. 3: FTIR spectra of NBR/PP, NBR and HNTs nanotubes.

Table 3: Dielectric strength and arc resistant of NBR/PP-HNTs nanocomposites.

Sample Codes	Dielectric Strength (mv/m)	Arc Resistant
NPH-0	3250	170
NPH-1	3520	172
NPH-2	6510	175
NPH-3	6845	178
NPH-4	6625	176

CONCLUSION

The nanocomposites based on NBR/PP filled with various loadings of HNTs nano clay have been prepared by melt mixing process using two roll mills. It has been found that HNTs nano clay in the polymer matrix shows the prominent effect on the performance of polymer nanocomposites due to better dispersion of nano clay. Better dispersion of HNTs results in the enhancement of thermal, mechanical and morphological properties of nanocomposites at 3wt% of HNTs when compared with pure blend of PP/NBR. FTIR analysis confirms the blending of NBR/PP and HNT.

REFERENCES

1. A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, and O. Kamigaito: 'Synthesis and properties of nylon-6/clay hybrids', Polymer based molecular composites. MRS symposium proceedings, Pittsburgh, 1990, 45.
2. E. P. Giannelis, *Advanced materials* (1996) 29.
3. E. P. Giannelis, R. Krishnamoorti, and E. Manias: 'Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes', in 'Polymers in confined environments', 107; 1999, Springer.
4. P. C. LeBaron, Z. Wang, and T. J. Pinnavaia, *Applied Clay Science* (1999) 11.
5. R. A. Vaia, G. Price, P. N. Ruth, H. T. Nguyen, and J. Lichtenhan, *Applied Clay Science* (1999) 67.
6. M. Biswas and S. S. Ray: 'Recent progress in synthesis and evaluation of polymer-montmorillonite nanocomposites', in 'New polymerization techniques and synthetic methodologies', 167; 2001, Springer.
7. E. P. Giannelis, *Applied organometallic chemistry* (1998) 675.
8. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *Journal of Materials Research* (1993) 1185.
9. K. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito, *Journal of Polymer Science Part A: Polymer Chemistry* (1993) 2493.
10. P. B. Messersmith and E. P. Giannelis, *Journal of Polymer Science Part A: Polymer Chemistry* (1995) 1047.
11. R. K. Bharadwaj, *Macromolecules* (2001) 9189.
12. R. Xu, E. Manias, A. J. Snyder, and J. Runt, *Macromolecules* (2001) 337.
13. F. Dabrowski, M. Bras, S. Bourbigot, J. Gilman, and T. Kashiwagi, *Proceedings of the Eurofillers* (1999) 6.
14. J. Gilman, T. Kashiwagi, M. Nyden, J. Brown, C. Jackson, S. Lomakin, E. Giannelis, and E. Manias, *Chemistry and technology of polymer additives* (1999) 249.
15. J. W. Gilman, *Applied Clay Science* (1999) 31.
16. S. Bourbigot, M. L. Bras, F. Dabrowski, J. W. Gilman, and T. Kashiwagi, *Fire and Materials* (2000) 201.
17. J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, *Chemistry of materials* (2000) 1866.
18. S. Sinha Ray, K. Yamada, M. Okamoto, and K. Ueda, *Nano Letters* (2002) 1093.
19. M. Du, B. Guo, and D. Jia, *Polymer International* (2010) 574.
20. L. Guimaraes, A. N. Enyashin, G. Seifert, and H. A. Duarte, *The Journal of Physical Chemistry C* (2010) 11358.
21. Z. Lin, M. Peng, and Q. Zheng, *Journal of Applied Polymer Science* (2004) 877.
22. M. Du, B. Guo, and D. Jia, *European Polymer Journal* (2006) 1362.
23. N.-y. Ning, Q.-j. Yin, F. Luo, Q. Zhang, R. Du, and Q. Fu, *Polymer* (2007) 7374.
24. K. Prashantha, M.-F. Lacrampe, and P. Krawczak, *Express Polymer Letters* (2011).

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