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GRT Golden Research Thoughts

PREPARATION AND CHARACTERISATION OF COMPOSITES OF NATURAL RUBBER -PEO BLOCK COPOLYMER AND MULTIWALLED CARBON NANOTUBES

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ABSTRACT

A series of composites were prepared using polyethylene oxide (PEO- Molecular weight 4000), hydroxy terminated liquid natural rubber (HTNR) and multiwalled carbon nanotubes (MWNT) by solution polymerization. Different composites were prepared by varying amounts of MWNT (1g, 2gand 3g). Mechanical properties of these composites were determined and compared with that of GUM (without filler) sample. The morphology of these block copolymers was confirmed by Scanning Electron Microscopy (SEM).

KEYWORDS :*NR, PEO, HTNR, Block copolymers, multiwalled carbon nanotubes, SEM.*

1.INTRODUCTION

Natural Rubber nanocomposites have fascinated a huge scientific interest because they allow the design of high-performance materials that exhibit noteworthy enhanced properties with regard to the pure polymer. The outstanding properties of the carbon nanotubes make them promising filler material to improve mechanical, thermal and electrical properties of polymers. The input point is to convey the potential properties of CNTs to the polymer composites. Due to the strong attractive long-ranged Vander Walls interaction, nanotubes tend to aggregate and form bundles or ropes, usually with highly entangled network structure. The extent of improvement generally depends on several parameters including the size of the particles, their aspect ratio, state of dispersion and their surface chemical characteristics that determine the interaction between the filler and the polymer chains and thus the interface of the polymer-filler system [1, 2]. In fact, one of the biggest challenges is to obtain a homogeneous dispersion of CNTs in a polymer matrix because Van der Waals interactions between individual tubes lead to significant aggregation and agglomeration that reduce the expected property improvements [3–5]. A homogeneous distribution and a good dispersion are essential for mechanical reinforcement of polymers [6, 7]. The influence of multiwall carbon nanotubes (MWNTs) contents on electrical and mechanical properties of MWNTs-reinforced natural rubber (NR) composites is studied. The volume resistivity of the composites decreases with increasing the MWNTs content and the electrical percolation threshold is reached at less than 1 phr of MWNTs (phr = parts of filler by weight per hundred parts of rubber). This is caused by the formation of conductive chains in the composites. Electrical measurements under uniaxial deformation of a composite carried out at a filler loading above the percolation threshold indicate a gradual disconnection of the conducting network with the bulk deformation [16, 17]]. The drop in the storage modulus G′ with the shear strain amplitude (Payne effect) is also attributed to a breakdown of the filler network [8]. Considerable improvement in the stiffness is obtained upon incorporation of MWNTs in the polymer matrix but the main factor for reinforcement of NR by MWNTs appears to be their high aspect ratio rather than strong interfacial interaction with rubber. The tensile strength and the elongation at break of the composites are reduced with regard to the unfilled sample. This is probably due to the presence of some agglomerates that increase with the nanotube content. This hypothesis is confirmed by a cyclic loading of the composites where it is seen that the deformation at break occurs at a much higher level of strain in the second stretch than in the first one. The overall significant property improvements are the result of a better nanotube dispersion attributed to the combined use of tip sonication and cyclohexane as dispersion aids during composite processing. [9] .In fact, it is one of the major attributes of carbon nanotubes to provide electrical conduction at a very low filler loading, this property being required in commercial applications to dissipate electrostatic charge. Since their discovery in 1991 [3,5], carbon nanotubes (CNTs) have attracted enormous attention for their fundamental behavior and for their use in a wide variety of applications in nanoelectronic devices [10-12], probe tips for scanning probe microscopes [[13-18] or in the automotive and aerospace industries for the dissipation of electrostatic charges [19]. Owing to their structural characteristics and their electrical and mechanical properties, one of the most important opportunities in the future is the emergence of a new generation of composite materials since relatively low carbon nanotube loading.

This paper reports the preparation of composites of Natural Rubber /PEO block copolymer and Multi Walled Carbon Nanotubes. The state of nanotube dispersion is evaluated from Scanning Electron Microscopy. Mechanical properties are determined and optimized.

2.EXPERIMENTAL

2.1.Chemicals and Materials

Natural crumb rubber (ISNR – 3L) supplied by Rubber Research Institute of India, Kottayam, Kerala was used for making all the natural rubber (NR) derivatives in the present study. Hydrogen peroxide (30% w/v, E-Merck, India) was used without purification. Toluene (E-Merck, India) was used as solvent without further purification. Toluene diisocyante (TDI) (80/20 mixture of 2, 4 and 2, 6 isomers, Aldrich) was used as received. PEO 4000 (SISCO Research Laboratory, India), was used as received. However the PEOs were dried in vacuum oven below their melting point before using them in the synthesis of NR – PEO block copolymers. Dibutyl tin dilaurate (DBTDL, Merck, India) was used as catalyst without further purification. Chloroform (Qualigens, India, synthetic grade) was used as such. Methanol supplied by Qualigens, India was used as such. Multiwalled Carbon NanoTubes was supplied by Intelligent material Pvt. Ltd, Chandigarh. Sodium docyl sulphate (SDS) was supplied by Merck, India.

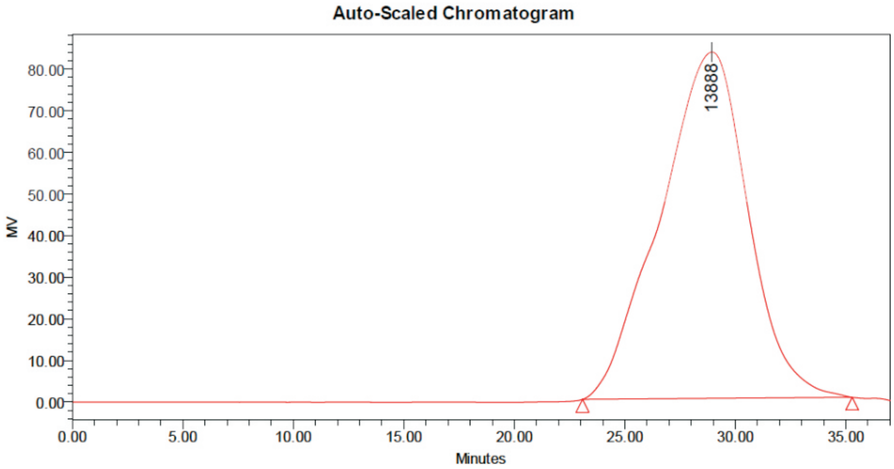
2.2. Method of preparation

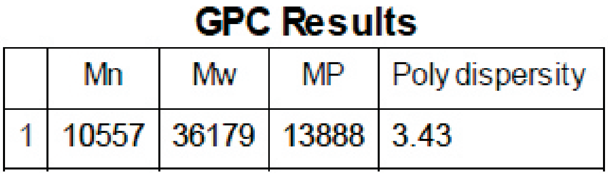
2.2.1. Preparation of Hydroxyl Terminated Natural Rubber (HTNR) or Liquid Natural Rubber (LNR)

The terminal hydroxylation of NR was achieved by solar radiation assisted reaction. The hydroxylation was effected by reaction with Hydrogen Peroxide. 400 gms of natural crumb rubber was masticated for 30 minutes at 40 degree Celsius and dissolved in Toluene. The solution was charged into a flat bottomed flask; Hydrogen Peroxide was added and thoroughly mixed with the rubber solution. The mixture was homogenized to a certain extent by the addition of methanol. The whole assembly with the material for irradiation was placed in sun light and continuously stirred. After an exposure of 72 hours, the upper clear layer comprising LNR in Toluene was distilled to remove the Toluene and recover the LNR or HTNR. The sample for block copolymerization was purified by repeated precipitation with methanol from Toluene solution and dried in a vacuum oven.

2.2.2. Determination of molecular weight by Gel permeation chromatography

Gel Permeation Chromatography was done to determine the average molecular mass of the prepared HTNR.





GPC Results

	Mn	Mw	MP	Poly dispersity
1	10557	36179	13888	3.43

2.2.3. Synthesis of NR/PEO block copolymer

Overall composition of the reactants is given in Table 1.

HTNR was dissolved in chloroform (23% w/v) and dibutyl tin dilaurate catalyst (0.3 % by wt of HTNR) was added. The solution brought to reflux with stirring [20]. The stoichiometric amount of TDI was added in drops. It was followed by drop by drop addition of the required amount of PEO as a solution in chloroform (23% w/v) for a period of 1.5 hrs followed by 2 hrs of the reflux. The excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone releasing agent. The sheet was removed from the tray after 12 hrs and kept in a vacuum oven at 600C to remove the traces of solvent present. It was then cured at 700C for 24 hrs, followed by one week ageing at room temperature in a moisture free atmosphere.

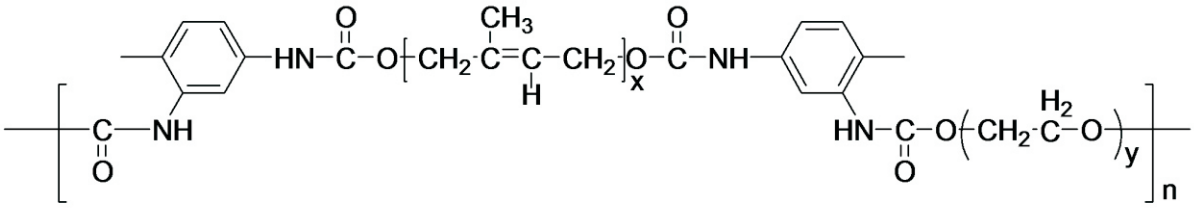
2.2.4. Synthesis of NR/PEO block copolymer-CNT composites

In the third part of the procedure the NR/PEO block copolymer – CNT composites was synthesized. The HTNR was dissolved in Chloroform (23% w/v). 10 drops of Dibutyl tin dilaurate (catalyst) was added and the solution was stirred. The stoichiometric amount of TDI was added in drops. The required amount of PEO 4000, dissolved in Chloroform was added drop by drop for 1.5 hours and followed by 2 hours of refluxion. The sonicated Multiwalled Carbon Nanotube (MWCNT) and Sodium docyl sulphate (SDS) in the ratio 1:1.5 was then added. The viscous content was cast in trays coated with silicone. After 24 hours, the sheet was removed from the tray and kept in a vacuum oven at 60 degree Celsius to remove the traces of solvent. The sheet was then cured at 70 degree Celsius for 24 hrs, and aged for one week at room temperature in a moisture free atmosphere. Sheets with various filler loadings of MWCNT'S (1%, 2%, 3 %) were prepared.

Table-1
Compositions of the block copolymers and MWCNT

Sample Code	Weight % of PEO	Weight % of NR	Weight % of MWNT
GUM	55.99	44.01	0
C1	55.99	44.01	1
C2	55.99	44.01	2
C3	55.99	44.01	3

Following the above procedure, a series of composites of polyether-diene block copolymers and MWCNT were prepared. The polyether is the PEO part and the polydiene is liquid natural rubber (LNR) which provides the nonpolar part. The block copolymers were prepared by solution polymerization method and their structure is shown below:



2.2.5. MECHANCAL TESTS

2.2.5.1. Tensile strength, modulus and elongation of the samples at break were measured at room temperature, on an Instron 4411 Universal Testing Machine with a cross head speed of 500mm/min following the ASTM D 412 standard. Five dumbbell samples were punched out from the molded sheets with a die, in the milled direction, in a single impact stroke. A Testing Machine Inc. thickness gauge with precision of ±0.05 mm was used to measure the dimensions of the dumbbell samples. For each sample, the thickness was measured at three locations, one at the center and one each at the ends of the reduced section. The median reading was used for calculating the cross sectional area. The distance between the cutting edges of the die in the center was taken as the width. The maximum strength, modulus and elongation were determined by taking the average values for five samples per compound. The testing of tear strength was conducted according to ASTM method D624 using an Alpha Technologies Tensometer 2000. Three samples from the solution processed vulcanized sheets were cut using a die. The thickness of the samples was measured using a Testing Machine Inc. thickness gauge with a precision of ±0.05mm. The tear testing was done at room temperature at the rate of 500 mm/min.

2.2.5. 2.Abrasion tests

The abrasion resistance was measured using a procedure in IS 3400 (Part-3) (dry abrasion) using a Zwick DIN Abrader. The rotating drum covered by an abrasive paper was given a test load of 10 Newton. It was ensured that the abrasive belt was in uniform contact with test specimens during the traveling distance of 40m. The measurement of abrasion resistance, was done by the weighing the sample before and after subjecting it to a known abrasive stress for a known time period.

2.2.5.3. Tear tests

The testing of tear strength was conducted according to ASTM method D624 using an Alpha Technologies Tensometer 2000. Three samples from the solution processed vulcanized sheets were cut using a die. The thickness of the samples was measured using a Testing Machine Inc. thickness gauge with a precision of ±0.05mm. The tear testing was done at room temperature and at the rate of 500 mm/min.

2.2. 6. Morphology of the samples

2.2.6.1. Scanning electron microscopy (SEM)

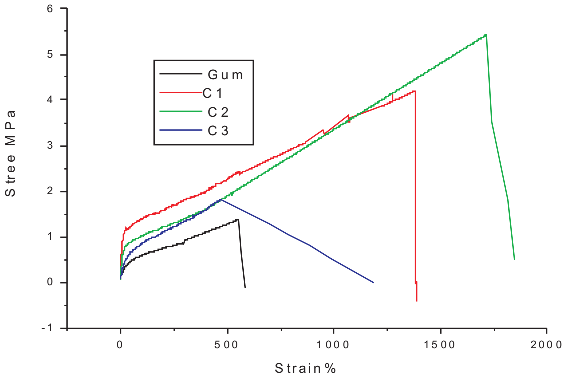
SEM studies were carried out by SEM JEOL JSM 6390 to find the extent of dispersion and agglomeration of nano fillers within the NR/PEO matrix. Prior to observation, the fracture surfaces were coated with a thin layer of platinum by means of a Polaron Sputtering apparatus.

3. RESULTS AND DISCUSSION

3.1. Mechanical Tests

3.1.1. Tensile test of the Gum and composites

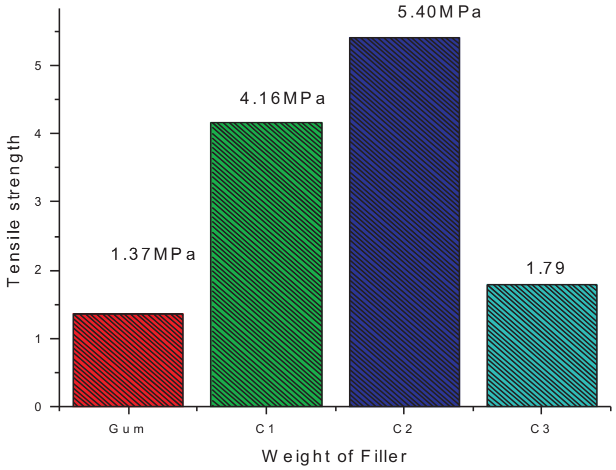
It is observed that the tensile strength is highest in C2 composite with the 2g filler loading. There is an increase of 203% in tensile strength in C1 with respect to GUM. However there is an increase of 294% in maximum tensile strength in C2 with respect to GUM. For the C3 composite, though there is an increase in its tensile strength with respect to GUM, it shows a tremendous decrease in its tensile strength. It is observed that C2 composite displays the maximum elongation at break. This increase in tensile strength in C2 composite suggests that there is thorough mixing and uniform distribution of CNT in the block copolymer matrix. SDS functions as a surfactant to prevent agglomeration. Agglomeration is the biggest challenge in the preparation of Nano composite using fillers. But as the filler content increases there is the possibility for agglomeration and the decrease in tensile strength. This is the reason for the decrease in tensile strength in C3. A complete picture of the morphology can be achieved through TEM examination. The tensile strengths of this are shown in Table 3.



A plot of Stress Vs Strain in Gum and dfferent MWNT Composites

Table 2.
Tensile strengths and Modulii at different percentages and Elongation at break

Sample code	Maximum Tensile Strength	Modulus at 100% elongation	Modulus at 200% elongation	Modulus at 300% elongation	Elongation at break
Gum	1.37	0.547	0.67	0.867	552
C1	4.16	1.346	1.60	1.76	1390
C2	5.40	0.995	1.155	1.40	1714
C3	1.79	0.83	1.15	1.346	467



A comparison of tensile strength in Gum and different composites

Table -3
Comparison of tensile strength of composite with respect to GUM

Sample code	% increase in Tensile strength with respect to GUM
C1	203.6
C2	294.2
C3	30.7

3.1.2. Tear test

Table-4
Tear strength

SAMPLE CODE	TEAR STRENGTH in Kg f/cm^2
GUM	65
C 1	85
C2	92
C3	79

The tear strength also showed the same gradation as tensile strenghth.C2 has the higher tear strength.

3.1.3 Abrasion Resistance

In the series of composites based on MWNT, thickness loss was the least in sample C2. Two factors contribute to this resistance to abrasion. MWNT on the surface of the sample appears to protect it from abrasion. Disaggregation using SDS gave a uniform dispersion of MWCNT in the block copolymer matrix which supported thorough mixing and thereby facilitated abrasion resistance. Thickness loss and weight loss was higher in GUM. There is a notable decrease in thickness loss and weight loss in C1 and C2 and an increase in C3. The reason for this may be due to the agglomeration of MWCNT as the weight of it increases. Agglomeration continues to be the biggest challenge in the preparation of nanocomposites.

Table -5
Abrasion Resistance

SAMPLE CODE	Weight loss %	Thickness loss %
GUM	6	3.9
C 1	2.3	1.2
C2	1.1	0.6
C3	1.9	0.9

3.1.4. Hardness

Table -6
Hardness

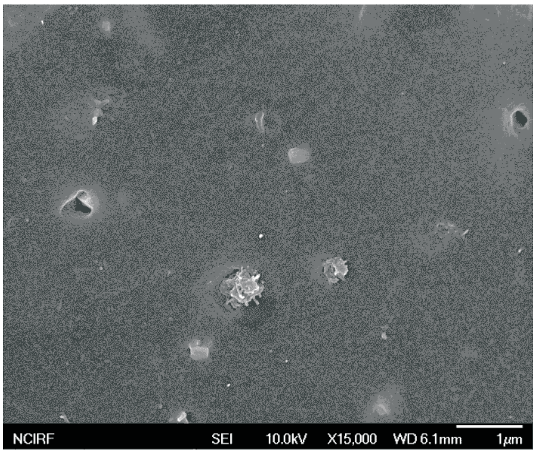
SAMPLE CODE	Hardness Shore	% increase in hardness w.r.t to gum
GUM	48	
C 1	68	9.6
C2	79	14.88
C3	87	18.72

Hardness of the composite increased almost linearly with the increase in filler loading .The percentage increase in hardness with respect to gum is as shown in Table -7.

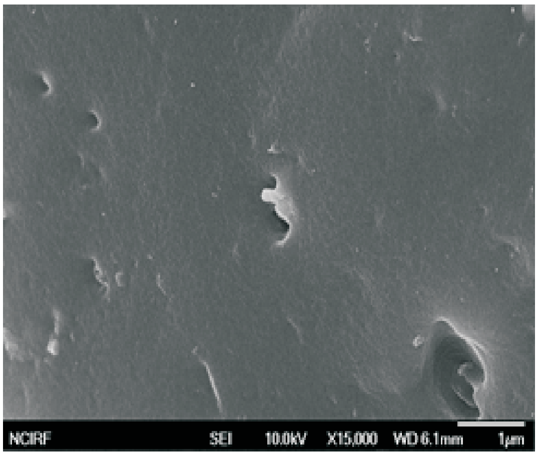
4.MORPHOLOGICAL STUDIES

Scanning Electron microscopy (SEM)

SEM images of the tensile fractured composite samples elucidate the even dispersion of the incorporated nanotubes into the host polymer matrix.



SEM image of C1



SEM of C3 showing agglomeration

CONCLUSION

Liquid Natural Rubber was prepared composites of NR/PEO block copolymer and MWCNT also successfully fabricated. These composites were prepared with 1-3 wt % Multi Walled Carbon Nanotubes (MWCNTs) fillers. While there is an increase of 203% in tensile strength in C1 with respect to GUM there is an increase of 294% in maximum tensile strength in C2 with respect to GUM. But it is observed that though there is an increase in tensile strength with respect to GUM, elongation at break is the maximum in C2 suggests that there is thorough mixing and uniform distribution of CNT in the block copolymer matrix.SDS functions as a surfactant to prevent agglomeration. But as the filler content increases there is the possibility for agglomeration and the decrease in the tensile strength in C3. There is a notable decrease in thickness loss and weight loss in C1 and C2 and an increase in C3. The reason for this may be due to the agglomeration of MWCNT as its weight increases. Hardness of the composite increased almost linearly with the increase in filler loading. The results indicates that, by increasing the amount of CNTs added to the rubber, the ductility decreased and the material become harder. The clear trend observed here is that as nanotube load increases, the fiber breaking strain decreases.

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REFERENCES

1. E. Lahi, R. Leahy, N. J. Coleman, and W. J. Blau. Carbon, 44:1624-1652, 2006
2. D. S. Bethune, C. H. Kiang, M. S. Devries, G. Gorman, R. Savoy, and J. Vazquez. Nature, 363:605-607, 1993.
3. S. Iijima and T. Ichihashi. Nature, 363:603-605, 1993.
4. L. Ci, Z. Zhou, D. Tang, X. Yan, Y. Liang, D. Liu, H. Yuan, W. Zhou, G. Wang, and S. Xie. Chem. Vap. Dep., 9:119-121, 2003.
5. S. Iijima. Nature, 354:56-58, 1991.
6. Peigney, A., Laurent, C., Flahaut, E., Bacsa, R.R., Rousset, A. (2001) Carbon, 39 (4), pp. 507-514.
7. Jonathan N. Colemana,, Umar Khana, Werner J. Blau , Yurii K. Gun'kob; Carbon ,Volume 44, Issue 9, August 2006, Pages 1624–1652
8. Liliane Bokobza , Polymer 48 (2007) 4907-4920
9. EXPRESS Polymer Letters Vol.6, No.3 (2012) 213–223
10. Bachtold A, Hadley P, Nakanishi T, Dekker C. Science 2001;294:1317.
11. Derycke V, Martel R, Appenzeller J, Avouris Ph. Nano Letters 2001;1: 453.
12. Rotkin SV, Zharov I. International Journal of Nanoscience 2002;1:347
13. Akita S, Nishijima H, Nakayama Y, Tokumasu F, Takeyasu K. Journal of Physics D: Applied Physics 1999;32:1044.
14. Cheung CL, Hafner JH, Odom TW, Kim K, Lieber CM. Applied Physics Letters 2000;76:3136.
15. Wilson NR, Cobden DH, Macpherson JV. Journal of Physical Chemistry B 2002;106:13102.
16. Yenilmez E, Wang Q, Robert RJ, Wang D, Dai H. Applied Physics Letters 2002;80:2225.
17. Ye Q, Cassell AM, Liu H, Chao K-J, Han J, Meyyappan M. Nano Physical Chemistry B 2002;106:1310.
18. Breuer O, Sundararaj U. Polymer Composites 2004; 25:630. 4918
19. Wise KE, Park C, Siochi EJ, Harrison JS. Chemical Physics Letters 2004; 391:207.
20. R. Chandrasekharan Nair; Block copolymers from liquid natural rubber and polyethers. Ph D Thesis, School of Chemical Sciences, October 1998

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