

# Role of Surface Modified Nano Calcium Carbonate as Filler and Linseed Oil as an Extender in the Vulcanization of Acrylonitrile Butadiene Rubber (NBR) Nanocomposites

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**Abstract**—The present study mainly focuses on the effect of surface modified nano calcium carbonate ( $\text{CaCO}_3$ ) as filler and linseed oil as extender on the cure, mechanical and thermal properties of acrylonitrile butadiene rubber (NBR) nanocomposites. The surface modification of nano  $\text{CaCO}_3$  is confirmed using Fourier transform infrared (FTIR) spectra. Only surface modified nano  $\text{CaCO}_3$  is able to give little enhancement in the cure and mechanical properties of NBR nanocomposites in comparison to unmodified nano  $\text{CaCO}_3$ . But the incorporation of surface modified nano  $\text{CaCO}_3$  along with linseed oil as an extender provides greater amount of enhancement in cure, mechanical and properties of NBR nanocomposites in comparison to unmodified nano  $\text{CaCO}_3$  at same phr (Parts per hundred parts of rubber) level. The incredible improvement in the properties of NBR nanocomposites is the part of great interest for rubber researcher regarding the application of surface modified nano  $\text{CaCO}_3$  as filler along with linseed oil as extender for NBR nanocomposites.

**Keywords**-Surface modification, linseed oil, cure characteristics, mechanical properties.

## I. INTRODUCTION

In practical application, rubbers are mostly applied with reinforcing fillers not only enhanced mechanical properties of rubber but also reducing the cost of the final product in industry, which is commercially interesting. Among the different types of filler, Carbon black (CB) is most widely used and the oldest filler in rubber materials. Since, the source of CB is petroleum, the preparation and processing of CB is hazardous. Carbon black not only causes pollution but also imparts black coloration in the rubber materials. Thus, the use of nano  $\text{CaCO}_3$  as filler is an interesting way to substitute carbon black in rubber compounding [1-5]. Nano  $\text{CaCO}_3$  is also important from environment point of view due to its low level of toxicity and less polluting nature [6].

Among the various types of rubber, the excellent oil and fuel resistance properties of NBR are utilized in many industry such as belts, hoses, O rings etc. Homogeneous dispersion of nano  $\text{CaCO}_3$  within the rubber matrix is mandatory to achieve proper enhancement in NBR nanocomposites. Now, due to its hydrophilic nature a problem arises in the uniform dispersion of nano  $\text{CaCO}_3$  within the rubber matrix [5]. Thus, surface modification of nano  $\text{CaCO}_3$  by hydrophobic species is necessary for the wide use of nano  $\text{CaCO}_3$  as filler in rubber industry. In this respect, application of stearic acid as surface modifier for nano  $\text{CaCO}_3$  is an interesting way [4].

To accomplish far better dispersion of nano  $\text{CaCO}_3$  within the rubber matrix linseed oil has been used as extender for styrene-butadiene rubber (SBR), natural rubber (NR) [1, 7]. Linseed oil is an important extender for rubber industry due to higher linoleic concentration [1]. With our best knowledge till now no vast study has been reported regarding the application of surface modified nano  $\text{CaCO}_3$  as filler in combination with linseed oil as extender on the properties of NBR. The present work aims to examine the effect of surface modified nano  $\text{CaCO}_3$  and linseed oil on the cure, mechanical and thermal properties of NBR nanocomposites.

## II. EXPERIMENTAL SETUP

### A. Materials and physical measurements

Acrylonitrile butadiene rubber (NBR KNB 35L) is supplied by Shilton Rubber Industries, Liluah. Zinc oxide (Merck), stearic acid (Loba Chemie, India), sulfur (Loba Chemie, India), tetra benzyl thiuram disulfide (TBzTD) (Apollo tyre, Ltd. India), calcium chloride (Merck), poly(ethylene glycol) (PEG; molecular weight 6000), potassium bicarbonate (Merck) and toluene (Merck) are used as received. Nano  $\text{CaCO}_3$  is synthesized using the procedure given by Mishra et al. [1].

X-ray diffraction (XRD) pattern of nano  $\text{CaCO}_3$  is recorded on a Xpertpro-Panalytical X-ray diffractometer. FTIR spectra ( $\text{cm}^{-1}$ ) of surface modified nano  $\text{CaCO}_3$  are recorded on a Perkin-Elmer L 120-000A spectrometer ( $\text{cm}^{-1}$ ) on KBr disks. The cure characteristics of the different stocks are obtained using the Monsanto Rheometer R-100 at 3 degree arc for 160 °C. The stocks are cured under pressure at 160 °C for optimum cure time ( $t_{90}$ ), keeping vulcanizates for 24 hrs at ambient temperature before measuring the modulus at 100% ( $M_{100}$ ) elongation, tensile strength (T.S.) and elongation at break (E.B. in %) according to ASTM D 412-51 T using dumbbell shaped test pieces in an Amsler (Sweden) tensile tester. Hardness (shore A) of the vulcanizates is measured by a Hiroshima Hardness Tester as per ASTM D 1415-56T. Thermogravimetric analysis (TGA) is carried out in order to study the thermal behavior of NBR vulcanizates. TGA scans are performed using a TA instrument (Q 5000) under nitrogen flow from 20 °C to 800 °C with a heating rate of 10 °C/min.

### B. Synthesis of $\text{CaCO}_3$ nanoparticles

Nano  $\text{CaCO}_3$  is synthesized by a procedure given by Mishra et al. [1]. At first, 110 g of calcium chloride is dissolved in 100 ml of distilled water. Then, 248 g of PEG is dissolved in 100 ml of water under mildly heated condition. A complex is then prepared by the mixing of calcium chloride and PEG in a molar ratio 1: 32. A solution of  $\text{K}_2\text{CO}_3$  is prepared by dissolving 106 ml of  $\text{K}_2\text{CO}_3$  in 100 ml of distilled water. Then, the solution of  $\text{K}_2\text{CO}_3$  is added to the previously prepared complex and the mixture is digested for 12 hrs. The resulting precipitate is filtered, washed with water and dried in a vacuum oven to obtain nano  $\text{CaCO}_3$  nanoparticles [1].

### C. Preparation of NBR composites

NBR is masticated in a two-roll mixing mill, and then Zinc oxide (ZnO) and stearic acid are added and again masticated. After that accelerator and sulfur are incorporated to the rubber matrix and the mixing is done near about for 10 minutes. At last different types of filler with and without linseed oil are added and the mixing done for sufficient time. Mixing composition of different ingredients is presented in Table 1.

## III. RESULTS AND DISCUSSION

### A. Nanoparticle characterization using X-Ray Diffraction (XRD) analysis

The XRD pattern of synthesized nano  $\text{CaCO}_3$  is recorded in Figure 1. The detected XRD pattern is found to be similar with the earlier report [1]. The nano size of  $\text{CaCO}_3$  particle is confirmed from XRD pattern using well known Scherrer equation [1, 7]. The Scherrer equation is given as:

$$d (\text{\AA}) = K \lambda / (B \cos \theta)$$

Here, d is the particle size, K is a constant nearly about to unity,  $\lambda$  is 1.542, B is the integral half-width, and  $\theta$  is the diffraction angle. The particle size for the synthesized nano  $\text{CaCO}_3$  is found to be  $40 \pm 5$  nm.

### B. Evaluation of surface modification using FTIR analysis

The FTIR spectrum of stearic acid modified  $\text{CaCO}_3$  nanoparticles is shown in Figure 2. The peak nearly  $1680 \text{ cm}^{-1}$  is due to the appearance of carboxylic salt and thus, this peak clearly indicates stearic acid is present on the surface of  $\text{CaCO}_3$  nanoparticles via an ionic bond [5]. The peaks nearly at  $2916 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$  characterize C-H stretching frequency [5]. The peaks nearly at  $875 \text{ cm}^{-1}$  and  $711 \text{ cm}^{-1}$  characterize the presence of long alkyl chain on the surface of nano  $\text{CaCO}_3$  [5].

C. Cure characteristics of NBR vulcanizates

Cure parameters of NBR vulcanizates in presence of unmodified nano  $\text{CaCO}_3$ , surface modified nano  $\text{CaCO}_3$  with and without linseed oil are calculated at 160 °C and the results are presented in Table 2. The highest value of maximum rheometric torque (R ) is obtained in mix no 6 containing 4 phr surface modified nano  $\text{CaCO}_3$  as filler along with linseed oil. The result indicates maximum level of interaction of rubber chain with nano filler occurs in mix no 6 due to the plasticizing effect of linseed oil [7].

The cure enhancement of NBR vulcanizates in presence of linseed oil becomes clear from the value of cure rate index (CRI). At the same level of filler loading, the value of CRI remains unchanged for NBR vulcanizates containing unmodified and surface modified nano  $\text{CaCO}_3$ . But the presence of linseed oil along with surface modified nano  $\text{CaCO}_3$  successfully increases the value of CRI of NBR vulcanizate. This is mainly due to the homogeneous dispersion of nano  $\text{CaCO}_3$  within the rubber matrix in presence of linseed oil.

Thus, for NBR nanocomposites surface modified nano  $\text{CaCO}_3$  with linseed oil causes much greater cure enhancement in comparison to surface modified nano  $\text{CaCO}_3$  without linseed oil.

Table 1: The formulation of studied vulcanizates in parts per hundred parts of rubber (phr)

Ingredients	Mix No					
	1	2	3	4	5	6
NBR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TBzTD	4.896	4.896	4.896	4.896	4.896	4.896
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5
Unmodified nano $\text{CaCO}_3$	0	2	4	6		-
Surface modified nano $\text{CaCO}_3$	-	-	-	-	4	4
Linseed oil	-	-	-	-	-	2

Table 2: Cure characteristics of NBR vulcanizates at 160 °C in presence of unmodified and surface modified nano  $\text{CaCO}_3$

Mix No	Maximum rheometric torque, R (dNm)	Optimum cure time, $t_{90}$ (min)	Scorch time, $t_2$ (min)	Cure rate index, $\text{CRI} = 100 / (t_{90} - t_2)$ ( $\text{min}^{-1}$ )
1	29	10	3	14.28
2	30	10	3.25	14.81
3	32.5	9.5	3.5	16.66
4	29.5	9.5	3.25	16
5	33	9.5	3.5	16.66
6	35	9	3.25	17.39

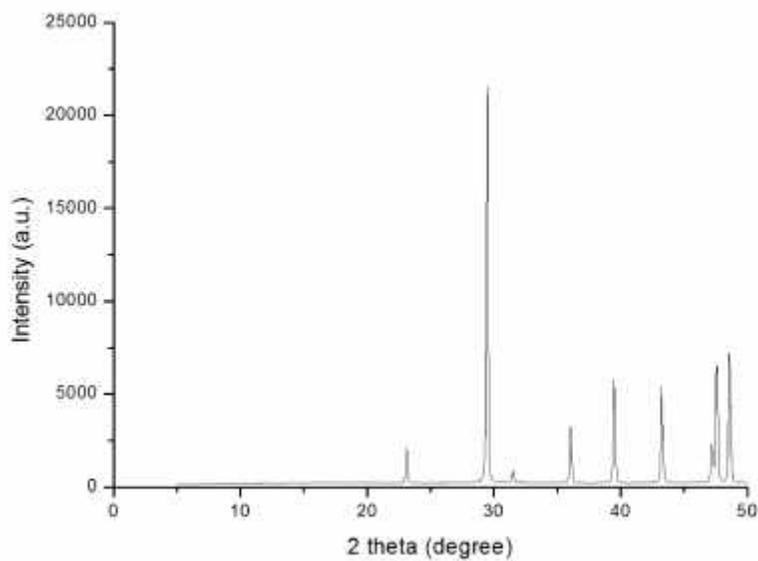


Fig 1. XRD pattern of nano CaCO<sub>3</sub>

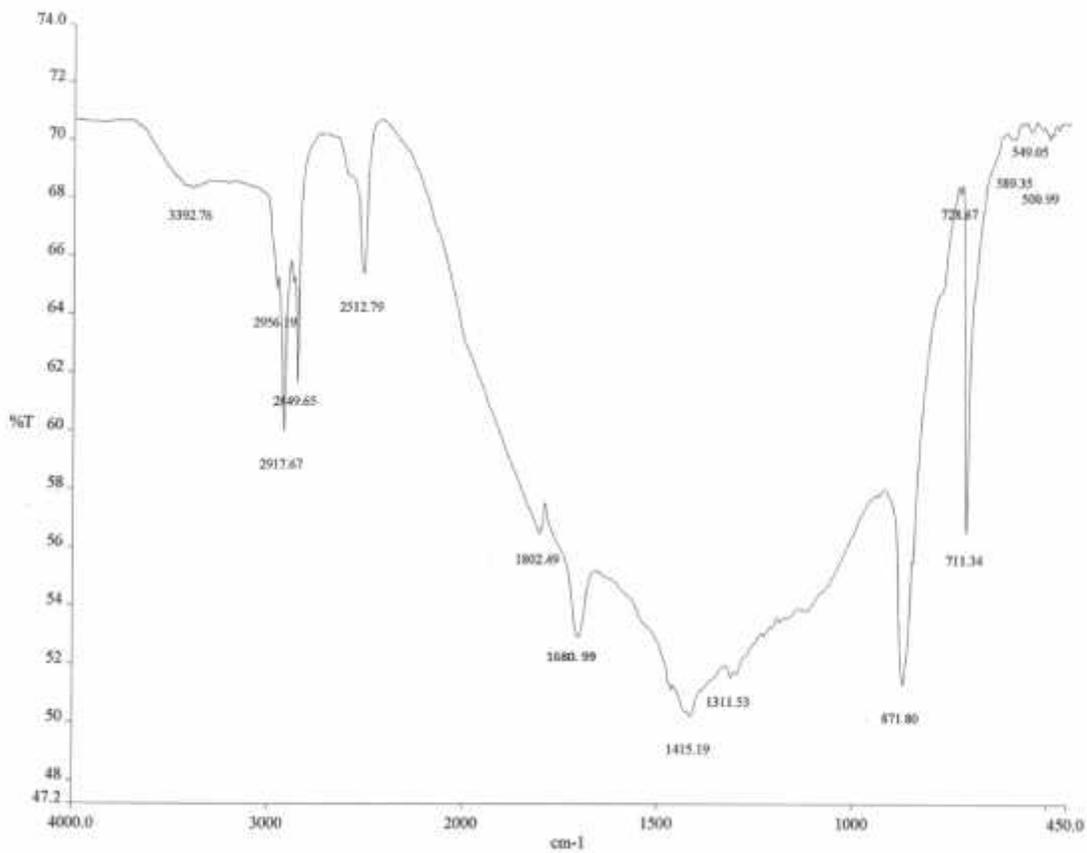


Fig 2. FTIR spectrum of stearic acid modified nano CaCO<sub>3</sub>

#### D. Mechanical properties of NBR vulcanizates

The mechanical properties of various NBR vulcanizates (mix no 1-6) are also studied and shown in Table 3. For NBR vulcanizates, with increasing the amount of unmodified nano  $\text{CaCO}_3$ , the modulus value at 100% elongation ( $M_{100}$ ) increases upto 4 phr filler loading. Above 4 phr filler loading,  $M_{100}$  value decreases due to agglomeration of filler particles [1, 7]. On the other hand, surface modified nano  $\text{CaCO}_3$  shows an enhancement in the  $M_{100}$  value of NBR nanocomposite in comparison to unmodified nano  $\text{CaCO}_3$ . Further large enhancement in the  $M_{100}$  value is observed when surface modified nano  $\text{CaCO}_3$  is used as filler in combination with linseed oil as extender. This is described by the better dispersion of nano filler within the rubber matrix in presence of linseed oil, which results greater interfacial interaction between nano fillers and rubber chain [7].

Like  $M_{100}$  value, the value of tensile strength also increases upto 4 phr filler loading. The variation of tensile strength of NBR vulcanizates containing different types of filler are shown in Figure 3. The presence of linseed oil plays a vital role on the improvement of tensile strength of NBR vulcanizates and 4 phr surface modified nano  $\text{CaCO}_3$  along with linseed oil shows an increment by 18.30% in the value of tensile strength in comparison to 4 phr unmodified nano  $\text{CaCO}_3$ . The variation of elongation at break is analogous with tensile strength.

#### E. Swelling studies

The swelling indexes of mix no 3 (containing 4 phr unmodified nano  $\text{CaCO}_3$ ), mix no 5 (containing 4 phr modified nano  $\text{CaCO}_3$ ) and mix no 6 (containing 4 phr modified nano  $\text{CaCO}_3$  with linseed oil) are represented in Table 4. The value of swelling index is lower for mix no 6 in comparison to other two mixes. Thus, from the values of swelling index it is clear that uniform dispersion of surface modified nano  $\text{CaCO}_3$  occurs within the rubber matrix in presence of linseed oil and it results in greater amount of crosslinking of rubber for mix no 6 [1].

Table 3: Mechanical properties of NBR vulcanizates cured at 160 °C

Mix No	$M_{100}$ (MPa)	T.S. (MPa)	E.B. (%)	Hardness (shore A)
1	0.956	1.861	440	56
2	1.018	2.252	450	57
3	1.058	2.617	550	58
4	1.047	2.442	500	58
5	1.074	2.890	550	58
6	1.122	3.097	600	58

Table 4: Variation in swelling index and thermal properties of NBR vulcanizates

Mix No	Swelling index (Q)	$T_i$ (°C)	$T_{max}$ (°C)
3	2.42	397	442
5	2.27	398	442
6	2.14	405	444

#### F. Thermal properties of NBR vulcanizates

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) curves of NBR vulcanizates (mix no 3, 5, 6) are shown in figures 4a and 4b. TGA study indicates rapid degradation region shifted towards little higher temperature for mix no 6 (containing linseed oil as extender) than other two mixes. However, only surface modified nano  $\text{CaCO}_3$  without linseed oil is not able to enhance the thermal stability of NBR vulcanizate in comparison to unmodified nano  $\text{CaCO}_3$ .

The little thermal enhancement of mix no 6 over other two mixes (mix no 3 and 5) is confirmed from DTA analysis. The onset decomposition temperature ( $T_i$ ) and the temperature at which the rate of decomposition is maximum ( $T_{\text{max}}$ ) are calculated from DTA curve and represented in Table 4. Although  $T_{\text{max}}$  values are almost same for three mixes (mix no 3, 5, 6), but the  $T_i$  value of mix no 6 shifted towards higher temperature in comparison to mix no 3 and 5. This data clearly reveals the greater thermal stability of NBR nanocomposite containing modified nano  $\text{CaCO}_3$  as filler along with linseed oil as extender in comparison to NBR nanocomposite containing only modified nano  $\text{CaCO}_3$  or unmodified nano  $\text{CaCO}_3$  as filler.

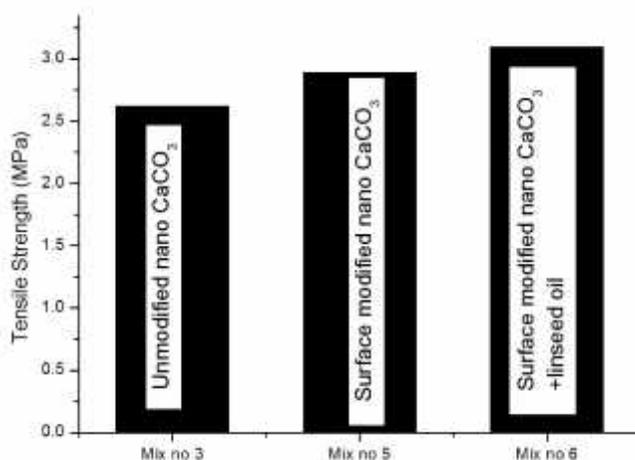


Fig 3. Variation of tensile strength of NBR nanocomposites

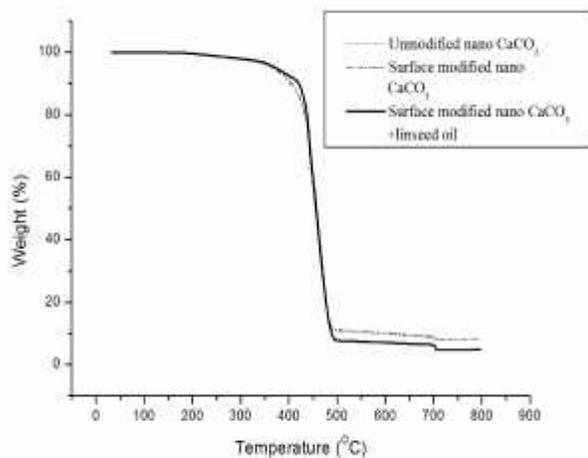


Fig 4a. TGA analysis of NBR vulcanizates

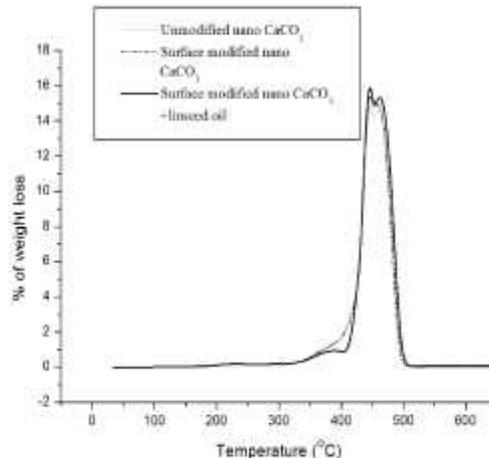


Fig 4b. DTA curve of NBR vulcanizates

#### IV. CONCLUSION

The present study describes the importance of linseed oil as extender for better filler dispersion in NBR nanocomposites. Only surface modified nano  $\text{CaCO}_3$  provides a little enhancement in the cure and mechanical properties of NBR nanocomposites in comparison to unmodified nano  $\text{CaCO}_3$ . Furthermore, the presence of linseed oil along with surface modified nano  $\text{CaCO}_3$  results an extraordinary improvement in the cure and mechanical properties of NBR nanocomposites. Only surface modified nano  $\text{CaCO}_3$  is not able to enhance thermal stability of NBR nanocomposites, although the use of linseed oil along with surface modified filler produces little thermal stability in NBR nanocomposites. Thus, the application of nano  $\text{CaCO}_3$  in combination with linseed oil will be an important approach for the industrial use of NBR nanocomposites.

#### V. ACKNOWLEDGEMENTS

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