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Technological Properties of Nano Ni-Co Mixed Oxide Filled NR Composites

Chemistry

KEYWORDS : Natural Rubber; mixed oxide nanoparticles, technological properties

SHAJI.P.THOMAS Post graduate Department of Chemistry, B.A.M College, and Affiliated to M.G. University Kerala, India.

SALINEY THOMAS School of Chemical Sciences, Mahatma Gandhi University, Kottayam, India

ABSTRACT

Here an attempt has been made to synthesize nano Ni-Co mixed oxide by sol-gel process with an objective to check its dual function as an activator and filler for accelerated sulfur vulcanization of natural rubber (NR). Characterization techniques like FTIR, XRD, SEM and TEM have been used to throw light on the nature and dispersion of the nanoparticles in the rubber matrix. Technological properties like tensile strength, tear resistance, and compression set were found out and compared with that of NR composite containing nanoclay. The nano Ni-Co mixed oxide exhibited considerable effect in enhancing the technological properties of the NR vulcanizates.

Introduction

Nieuwenhuizen proposed that surface of ZnO acts dually as a reactant and catalytic reaction template by activating and bringing together the reactants. The particles of accelerators, fatty acid and sulfur diffuse through the polymer matrix and finally get adsorbed on to the surface of ZnO forming intermediate catalyst complexes. Inspite of its capacity to enhance efficiency of vulcanization and vulcanizate properties, ZnO has some major disadvantages icluding poor affinity towards elastomer matrix and mould fouling1.Therefore, presenting alternatives for reducing the dosage of ZnO in sulfur vulcanization of elastomers will be technologically advantageous.The extent of improvement of technological properties of elastomer composites depends on the nature of filler particles, particularly its size, aspect ratio and ability to establish stronger interactions with the matrix. In the preparation of elastomer nanocomposites for achieving maximum desirable effects including mechanical reinforcement and inclusion of anisotropic electrical conductivities, finer and homogeneous dispersion of filler particles in the elastomer matrix is essential2. The filler-matrix interactions play a key role in producing fine and uniform filler dispersion and also in increasing the adhesion of filler particles on the polymer matrix, by which it can further increase the effective filler volume.This will help the transfer of stress from the elastomer matrix to the filler on mechanical deformation3 .The recent studies have shown that many novel nano particles including layered silicates, expanded graphite, polyhedral oligomeric silsesquioxane and carbon naotubes are effective in improving the technological properties of elastomers on lower dosages4.

In this paper we report the synthesis of nano Co-Ni mixed oxide by sol-gel precipitation and evaluation of the effect of the as prepared nanoparticles on the mechanical properties natural rubber (NR), with a view to partially substitute ZnO without scarifying the technological properties of the finished goods. Characterization techniques like FTIR, XRD, SEM and TEM have been used to throw light on the nature and dispersion of the nanoparticles in the rubber matrix.

2. Experimental

2.1. Synthesis of nano Ni-Co mixed oxide

Cobalt nitrate, nickel sulphate (GR), NaOH pellets, dichloromethane (DCM) as supplied by Cimsons scientific syndicate, Kottayam, India were used.

Method

0.1mol of cobalt nitrate was dissolved in a 2:1 hot binary mixture of water and DCM in a 250 ml beaker and in another 250 ml beaker by similar method 0.1 molar solution of nickel sulphate was also prepared and sonicated for 15 minutes. To this mixture, 0.2 molar solution of NaOH dissolved in 2:1 hot binary mixture of water and DCM was added in thin stream and sonicated for another 30 minutes. The gel was transferred to a filter and washed many times with water to remove the un reacted materials and the pale green solid was heated in an air oven at 100^0C for 3 hrs and powdered in a ball mill.

2.2. NR formulations

Different NR mixes were prepared using NR of grade ISNR-5, as per the Table 1. The mixes NM1 to NCR contain 100 g of NR, 1.32 g of CBS,2g commercial ZnO,2 g commercial stearic acid and 1.5 g of rubber grade sulfur. In addition to this NM1 to NM4 contain 1 to 4 g of nano Ni-Co mixed oxide .The mix NCR contains 5 g nanoclay in place of nano Ni-Co mixed oxide. The various mixes were prepared on a laboratory size two- roll mixing mill (15.3 x 30.5 cm, Indian Expeller) as per ASTM designation D3182-89, first by masticating NR for 10 min and then mixing other ingredients in the order as shown in Table 1. Mixing was continued for a further 3 min and the batch was homogenized by passing it in single direction to ensure orientation of chains and to preserve mill direction before molding.

Ingredients *phr	Mixes				
	NM_1	NM_2	NM_3	NM_4	NC_R
NR	100	100	100	100	100
ZnO	2	2	2	2	2
Stearic acid	2	2	2	2	2
Nano Ni-Co mixed oxide	1	2	3	4	0
Nanoclay	0	0	0	0	5
CBS	1.32	1.32	1.32	1.32	1.32
S	1.5	1.5	1.5	1.5	1.5

Table.1.NR formulations

***parts per hundred parts of rubber**

2.3. Evaluation of the cure properties

The optimum cure time (t90) of the mixes (time to reach the 90 % of the maximum torque) was determined on a Goettfert elastograph; model Vario (German) at 150^0C at CFSE,Changanasserry,Kerala. The cure properties were obtained directly and the values are given in the Table 2. Elastographic scorch time (Ts2) is the time required for two units to raise above the minimum torque (about 10% of vulcanization).The compounds were then vulcanized up to the optimum cure time in an electrically heated laboratory

type hydraulic press (Indian Expeller) at 150^{0}C at a pressure of 120 Kg.cm^{-2}.

2.4. FTIR analysis of nanoparticles
FTIR spectrum was taken on Perkin Elmer spectrophotometer in the range 4000 – 500 cm-1 at CUSAT, STIC, Kerala.

2.5. X-ray diffraction studies
X-ray diffraction patterns of the vulcanized rubber samples were taken on Bruker AXS D8 advance model XRD instrument , with source Cu, wavelength 1.5406 A0 and Si (Li) PSD detector at CUSAT, STIC, Kerala.

2.6. Scanning electron microscopy
Scanning electron microscopic images of the vulcanized rubber samples were taken using Jeol SEM (10 KV) at CUSAT, STIC, Kerala.

2.7.Transmissiom electron microscopy(TEM)
TEM of nano mixed oxide was taken using high resolution transmission electron microscope of model Jeol/JEM 2100 at CUSAT, STIC, Kerala.

2.8 . Tensile Properties and Tear Resistance
The tensile properties of the vulcanized samples were determined on a Universal Testing Machine, Instron Corporation, series IX model 1034, using a crosshead speed of 500 mm/min. as per ASTM D412-87, using dumbbell specimen at CFSE, Changanasserry, Kerala.

2.9. Hardness
Hardness (Shore A) was measured as per ASTM D2240-86 using a Zwick 3114 hardness tester on unstressed molded cylindrical samples (30mm diameter x 6mm thick).For each vulcanized sample three measurements were taken and the result was reported as the average.

2.10. Compression Set
Compression set was determined as per ASTM D395-89 (method B) using the apparatus Prolific Engineers India Ltd. The molded samples (1.25cm thick and 2.8 cm diameter) in duplicate compressed to constant deflection (25%) were kept for 22 h at 270C. The samples were taken out and final thickness was measured after keeping for 30 min. The compression set % was calculated as in equation (1)

$$\text{Compression set \%} = \frac{(t_0 - t_1) \times 100}{t_0 - t_s} \qquad (1)$$

Where t0 and t1 are the initial and final thickness of the specimen and ts is the thickness of the space bar used.

For each molded sample, average of the duplicate measurements was reported as the final results.

2.11. Swelling value
Swelling values of the vulcanizates were determined using circular samples of approximately 1cm diameter and 0.2cm thickness punched out from the central portions of the vulcanizates using the equation;

$$Q = \left(\frac{W_S - W_d}{100 W_1}\right) W_R \qquad (2)$$

where Ws is the weight of the solvent-swollen samples,Wd is the weight of the deswollen samples, W1 is the weight of the pre-swollen samples, and WR is the weight of the recipe (total weight of all of the components in the mix, including rubber).

The circular samples were allowed to swell in toluene for 24 hours. The swollen samples were taken out and weighed again after removing the solvent from the surface of the samples using blotting paper. The samples were allowed to de-swell in vacuum and the weight of the de-swollen samples was again noted.

RESULTS AND DISCUSSIONS
3.1. Characterization
3.1.1. FTIR studies
The FTIR peaks of the nano mixed oxide are given in fig.1.The broad absorption peak at 3477 cm^{-1} is due to entrapped or coordinated water molecules5.The band around 657 cm^{-1} is due to bending vibrations of cobalt oxide and that around 560 cm^{-1} is due to bending vibrations of nickel oxide.These IR peaks are characteristics of cubic spinels.

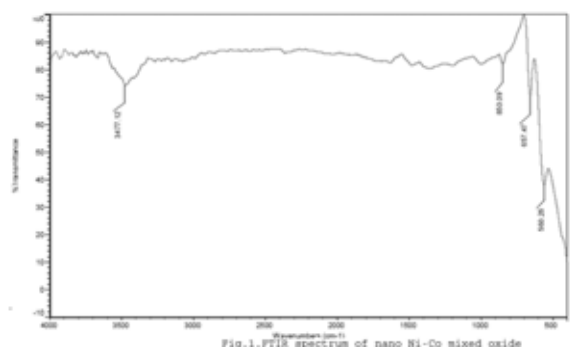


Fig.1.FTIR spectrum of nano Ni-Co mixed oxide

3.1.2. XRD curves
The XRD peaks are shown in the fig.2.The less intense peaks at 37.0240 is due to (311) planes and that at 32.50 is due to (220) planes of face centred cubic cryatals of Ni-Co mixed oxide6.

The lowering of intensity and shifting towards lower 2 theta values are attributed to the intercalation of the ruibber layers into the nanorods of the mixed oxide as found in the SEM [fig 4] and TEM [fig.5]. Other peaks are due to other ingredient particles like ZnO, CBS etc. The XRD peaks indicate spinel structure for the nano mixed oxide.

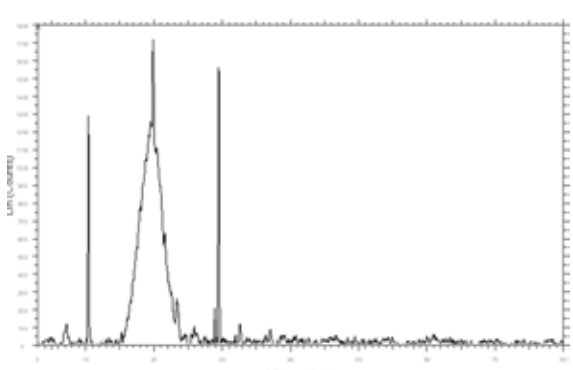


Fig.2.XRD curves of nano Ni-Co mixed oxide filled NR vulcanizate

3.1.3. Microscopic analysis
The SEM image of nano Ni-Co mixed oxide filled NR composite is shown in fig.4.The image shows nanorods of

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mixed oxide of average diameter 50 nm and 1μm length. Other agglomerated particles of microscopic ZnO, CBS etc are also seen in the picture. The nanorods are ascertained by the TEM image (fig.5) which shows that the rods are below 50 nm in diameter. But there are chances of agglomeration of the rods as seen in the fig.5.The high aspect ratio of the rods make them suitable candidates as reinforcing filler for elastomer nanocomposites.

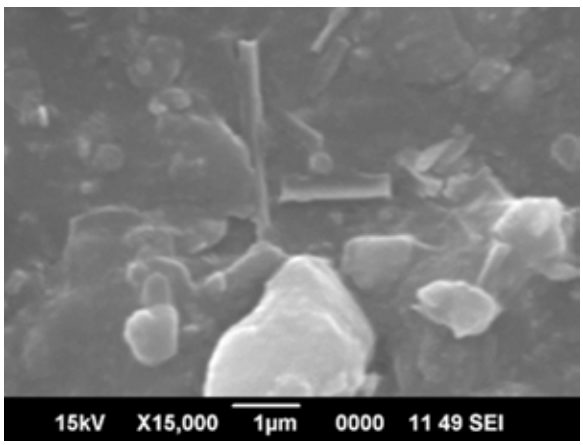


Fig.4.SEM image of nano Ni-Co mixed oxide filled NR composite

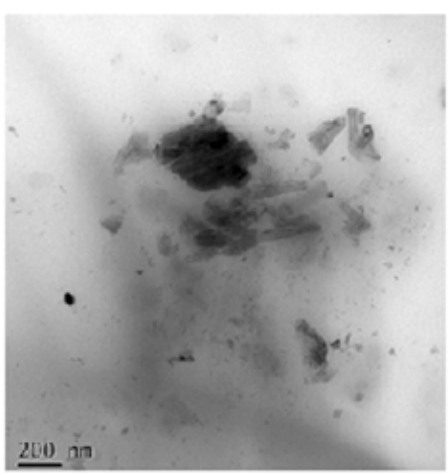


Fig.5.TEM image of nano Ni-Co mixed oxide

3.2. Cure and Mechanical properties of vulcanizates

The nano Ni-Co mixed oxide filled NR vulcanizates exhibited lower cure time compared to the clay filled as in table 2. This may be attributed to the superior ability to form complexes with accelerator moities. Like zinc, nickel and cobalt ions have definite ability to form active sulphurating species during sulfur vulcanization7.Also, the nanoclay could have adsorbed the curatives on its surface, making its access to the rubber chains restricted.

The nano Ni-Co mixed oxide filled NR vulcanizates showed superior tensile strenght values as given in table 2, compared to the 5 phr nanoclay filled vulcanizate NCR except the sample NM1 which contains only 1 phr of nano Ni-Co mixed oxide, which seems insufficient for the reinforcement of rubber matrix. There is an increase in the tensile strength on the increase in the dosage of the mixed oxide from 1 phr in NM1 to 4 phr in NM4. The observed enhancement in the tensile strength value can be ascribed to improved rubber–filler interactions for the mixed oxide particles. The increased hydrodynamic effect arising from the inclusion of rigid particles in the rubber matrix caused an increase in the modulus values. The expected high aspect ratio, anisometry of the mixed oxide particles and efficient dispersion might have caused improvement in filler-rubber interactions leading to the enhancement of modulus and elongation at break percent values8 .The mixes NM2 to NM4 exhibited higher tear resistance values (as shown in table 3) than the NCR containing 5 phr of nanoclay. This is also attributed to significant improvement in filler-matrix-interfacial bonding, and better dispersion of the filler particle in the matrix leading to an increase in the efficiency of stress transfer from matrix to filler phase.There is almost 20 % increase in the tear resistance value on the increase in the dosage of the mixed oxide from 1 phr in NM1 to 2 phr in NM2 up to 3 phr in NM3 with a reduction in the value at 4 phr in NM4. Above 3 phr, there may be agglomeration of the mixed oxide nanoparticles.The shore A hardness values are also in agreement with the tensile properties. As the dosage of the mixed oxide increases from 1 phr in NM1 to 4 phr in NM4, there is almost 27% increase in the hardness value (table 3).This can also be ascribed to the strong filler- matrix interfacial bonding than in the nanoclay filled sample NCR which exhibited a lower hardness value. The mixed oxide filled vulcanizates showed good compression set values than the clay filled sample.There is a reduction in the set values as the dosage of the mixed oxide has been increased from 1 to 4 phr. This is due to the increase in elasticity of the vulcanized samples containing mixed oxide nanoparticles.

The swelling values of the vulcanizates (table 3) are in tune with the mechanical properties observed. The decrease in the swelling value from 4.368 for NM1 to 2.918 for NM4 is an obvious indication of the increase in crosslink density of the samples on the increase in filler content and it also supports the reinforcing action of the mixed oxide nanoparticles.

Table.2. Cure and Tensile properties of NR mixes filled with Nano Ni-Co mixed oxide

Mixes	Tear resistance N/mm	Hardness (Shore A)	Compression set %	Swelling value
NM_1	25.10	33	7.02	4.368
NM_2	30.29	37	6.07	4.256
NM_3	34.10	38	4.91	4.178
NM_4	29.10	42	3.59	2.918
NC_R	26.98	39	10.52	4.504

Table.3. Other mechanical properties of NR mixes filled with Nano Ni-Co mixed oxide

Mixes	T_{90} min	Tensile strength, MPa	100% modulus, MPa	200% modulus, MPa	300% modulus, MPa	Elongation at break %
NM_1	6.07	13.43	0.63	1.31	2.58	332
NM_2	6.70	17.77	0.88	1.68	3.05	431
NM_3	7.12	18.03	0.91	2.29	4.84	454
NM_4	7.81	18.33	0.94	2.37	4.92	464
NC_R	13.61	15.05	0.98	2.55	4.99	256

4. Conclusions

Co-Ni mixed oxide nanoparticles can be conveniently prepared by sol-gel process. The XRD and FTIR peaks indicate cubic spinel structure for the nano Ni-Co mixed oxide. The microscopic studies reveal that the nanoparticles are below 50 nm in diameter and they are almost rod like structures. The nanoparticles are found effective in enhancing the mechanical properties of NR like tensile strength, tear resistance, hardness etc compared to nanoclay on a lower

dosage. Thus,the nano Ni-Co mixed oxide can partially substitute ZnO in the sulfur vulcanization of elastomers. These are all attributed to the superior ability of the mixed oxide nanoparticles to get dispersed in the polymer matrix in a better and uniform manner, by virtue of its nature and geometry. The higher aspect ratio of the mixed oxide naoparticles increases the probability of particle-particle contacts .

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