Cure Characteristics and Rheological Properties of Organically Modified Lanthanum Oxide-Natural Rubber Composites

Sreevalsa S\textsuperscript{a}, Sruthi Sreekumar\textsuperscript{b}, Sreedha Sambhudevan\textsuperscript{a} Balakrishnan Shankar\textsuperscript{b}

\textsuperscript{a} Department of Chemistry, Amrita University, Amritapuri, India.
\textsuperscript{b} Department of Mechanical Engineering, Amrita University, Amritapuri, India.

Email: sreedha@am.amrita.edu

Abstract: The present work emphasizes on the cure features and rheological behaviour of organically modified gadolinium oxide-Natural rubber vulcanizates. The main aim of incorporating gadolinium oxide is to impart X-ray shielding property to rubber composites. Earlier lead based materials were used for this purpose, but due to high toxicity of lead, lanthanum based materials can be an excellent alternative. Gadolinium oxide was organically modified with methacrylic acid and is used as filler in rubber vulcanizates at different loadings from 0-40 parts per hundred rubbers. Modification was done to increase the adhesion between an inorganic gadolinium oxide and natural rubber matrix. Characterization of modified gadolinium oxide using X-ray diffraction shows that the particle size got reduced to nano regime which highly influences the vulcanizates properties. The increase in torque minimum and torque maximum with filler loading is in covenant with mechanical property studies. The swelling index and swelling co-efficient decreases while cross link density enhances with filler percentage which reveals that a better interaction in molecular level is occurring between the modified filler and natural rubber than the unmodified one.

1. Introduction

Incorporation of nano-sized fillers into rubber composites is a well-practised technology to improve the performance of materials without much expensive procedures [1-4]. The rubber composites containing lanthanides are found to be a new system for over all and efficient X-ray shielding materials. Composite materials are used for many reasons such as low cost, light weight, durability, shielding protection etc. Besides, organic materials with higher numbers of hydrogen atoms in a given volume such as poly isoprene act as an outstanding support for X-Ray shielding. Due to the very fine size of particles, rare earths possess weak interaction with rubber matrix and hence the dispersion of these inorganic particle in organic rubber matrix is a very crucial step [5-6], particularly for a upper loading which eventually leads to the lessening of the chance of interferences among the dispersed phase and an X-ray beam. The main aim of rare earth modification organically is to attain an assured amount of enhancement in distribution and hence compatibility.

The aim of the present work is to prepare X-ray shielding natural rubber composites where gadolinium oxide in its modified form is used as the radiation absorbing material. Usually high-dense particles are strongly tangible than low-dense alternatives for lessening the intensity of gamma and X radiation which possess higher energy levels. Due to its high atomic number, lead is the most
accepted material for reducing the impact of gamma rays and x-rays. Atomic number means
thenumber of protons present in an atom with a corresponding number of electrons. Lead with higher
number of elecronswill hinder the gamma and x-ray particles that may pass through a lead shield and
the level of shielding can be enhanced with thicker shielding barriers. The present work discusses the
use of gadolinium in its oxide form as a promising radiation shielding material instead of lead.

2. Materials and methods

Gd$_2$O$_3$, methacrylic acid (MAA) and Dicumyl peroxide (DCP) were purchased from Sigma
Aldrich. Natural rubber (ISNR 5) was, obtained from the Rubber Research Institute of India.
Gadolinium oxide prior to mixing with rubber was modified using methacrylic acid. Gd$_2$O$_3$, MAA and
water in the molar ratio 1:12:12 is taken in a 50 ml RB and the reaction was carried out by refluxing at
75°C for 90 minutes. The solution after filtration was thickened by distilling water for 3 h. A white
precipitate was obtained after the addition of excess methanol to the liquor and leaving it overnight.
The resultant compound was characterized using FTIR. The modified Gd$_2$O$_3$ was incorporated into
the rubber matrix according the following recipe for sulphur vulcanization.

| Ingredient | Composition(pphr) |
|------------|-------------------|
| NR         | 100               |
| Filler     | 0 to 40           |
| ZnO        | 5                 |
| Stearic acid| 1                |
| TDQ        | 1                 |
| CBS        | 1                 |
| Sulphur    | 2.5               |

Table 1 : Recipe for sulphur based cure system

The system was also cured with DCP (Dicumyl peroxide) to compare the effect of curing system
in vulcanize properties.

The XRD pattern of the samples were collected at room temperature on a Bruker AXS D8
advance diffractometer, equipped with X-ray source Cu of wavelength 1.5406 Å with step size of
0.020 2θ and step time 32.8 sec. The surface morphology was studied using FEI Quanta 200 scanning
electron microscope. The cure charactersitics was studied using an oscillating Disc Rheometer (ODR)
model 4308, Zwick, Germany. The parameters measured includes Torque minimum (M_l) and torque
maximum (M_h).

3. Results and discussion

3.1 FTIR Spectroscopy:

The modified gadolinium oxide was characterized using FTIR as shown in figure 2. The
stretching frequency of ester carbonyl group is observed at 1696 cm$^{-1}$ and vinyl stretching frequency
at 1635cm$^{-1}$. The Gd-O stretching band is retained at around 947 cm$^{-1}$. The stretching frequency of
ester group as seen in the FTIR spectrum confirms the fact that modification has been carried out
successfully.
Figure 1: FTIR spectrum of modified Gd$_2$O$_3$

### 3.2 X-ray diffraction

Figure 2 depicts the XRD profile of gadolinium oxide before and after organic modification. A broad peak at around 29° is identified as the 222 reflection of cubic Gd$_2$O$_3$. The broadening of peaks and decrease in peak intensity may be attributed to the lowering of particle size to nano regime [7]. The peak positions and 2θ values are well agreeing with the early reported one for Gd$_2$O$_3$ nano particles [8]. In general, the atomic scattering factor is high for atoms with high atomic number (Gd : Z=64), but the low peak intensities observed for the Gd$_2$O$_3$ sample in Figure 2 is probably also a consequence of gadolinium fluoresce [9]. X-ray analysis reveals the crystalline nature of Gd(MAA)$_3$.. The well - defined diffraction peaks establish the crystalline nature of the sample after modification. The basic structure of Gd$_2$O$_3$ is retained with an increase in the crystalline nature after modification.

![XRD spectrum of (a) before modification and (b) after modification](image)

Figure 2 : XRD spectrum of (a) before modification and (b) after modification

### 3.3 Cure characteristics

The cure characteristics of natural rubber vulcanizates are shown in figure. It was found that the torque minimum increases apparently with rise in filler loading for all vulcanizates. As the torque minimum is a direct measure of stock viscosity, the presence of nano sized fillers imparts additional resistance to flow owing to the restricted molecular mobility of the nano composites [10]. Or in other words presence of modified filler increases the viscosity of the samples. According to Einstein, Guth and Gold equation [11]
\[ \eta_f = \eta_u (1 + 2.5 c + 14.1 c^2) \]

Where \( \eta_f \) and \( \eta_u \) are the viscosities of modified and unmodified natural rubber composites and \( c \) is the volume fraction of the filler. The torque maximum increases with increase in filler loading which clearly shows that incorporation of modified filler particles apparently enhance the stiffness of nano composites. Torque difference which is an indirect measure of cross link density of nano composites also rises with filler loading reveals that there is an increased collaboration among the rubber matrix and filler.

![Figure 3: Cure Characteristic of modified Gd2O3 based natural rubber composites](image)

### 3.4 Swelling measurements

The swelling experiments of the samples were carried out according to ASTM D471. Anisotropic swelling studies directly relates to the amount of distribution of fillers in the rubber matrix. Swelling index is estimated using the equation

Swelling index\% = \( \frac{(W_2 - W_1)}{W_1} \times 100 \)

where \( W_1 \) and \( W_2 \) are the initial and final swollen weights of the sample.

The swelling nature of the composites can also be studied using the swelling coefficient values and is given by the equation

Swelling coefficient \( \alpha = \frac{A_s}{m} \times \frac{1}{d} \)

where \( A_s \) is the weight of the solvent absorbed at equilibrium swelling, \( m \) is the mass of the sample before swelling and \( d \) is the density of the solvent used.

The cross link density of vulcanizates \( \nu \) can be calculated from the Flory-Rehner equation [12-13].

\[ \nu = \frac{-\ln[(1 - \nu_r) + \nu_r + \chi \nu_r^2]}{\nu_s \times \left( \frac{1}{\nu_r} - \frac{\nu_r}{2} \right)} \]

where \( \nu_r \) is the volume fraction of the polymer in the swollen gel, \( \chi \) is the polymer – solvent interaction parameter, \( \nu_s \) is the molar volume of the solvent.

| Filler loading (phr) | Swelling Index (%) | Swelling Coefficient | Cross link density |
|----------------------|--------------------|----------------------|--------------------|

![Table](image)
The values clearly show that rise in filler percentage enhances the cross linking between the particles and rubber matrix. Larger cross Link density values is a direct evidence of enhanced restriction on the network and thus leads to a lowering of swelling because of the existence of fillers.

4. Conclusions

The present study deals with the cure characteristics and swelling measurements of modified Gd$_2$O$_3$-Natural rubber nano composites. It is concluded that the presence of fillers increases all the properties and there is a dramatic increase with filler loading also.

Table 2 : Swelling characteristics of vulcanizates.

|   | $\times10^{-3}$cm$^3$/g | $\times10^2$g/cm$^3$ |
|---|------------------------|---------------------|
| 0 | 329.10                 | 3.79                |
| 10| 310.92                 | 3.59                |
| 20| 283.46                 | 3.25                |
| 30| 274.62                 | 3.17                |
| 40| 240                    | 2.77                |

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