

Preparation of zinc-oxide-free natural rubber nanocomposites using nanostructured magnesium oxide as cure activator

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ABSTRACT: The effect of sol-gel synthesized magnesium oxide (MgO) nanoparticles as cure activator is studied for the first time in the vulcanization of natural rubber (NR) and compared with conventional zinc oxide (ZnO) in terms of cure, mechanical, and thermal properties. The NR vulcanizate with 1 phr (Parts per hundred parts of rubber) nano MgO shows an excellent improvement in the curing characteristics and the value of cure rate index is about 400% greater for NR vulcanizate containing 1 phr nano MgO in comparison to the NR vulcanizate with 5 phr conventional ZnO. Both mechanical and thermal properties of NR vulcanizate are found to be satisfactory in the presence of 1 phr nano MgO as cure activator in comparison to conventional NR vulcanizate. This study shows that only 1 phr nano MgO can successfully replace 5 phr conventional ZnO with better resulting properties in the sulfur vulcanization of NR. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42705.

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INTRODUCTION

In order to improve some of the vulcanizate properties or to facilitate the manufacturing operations and to reduce the product cost, various ingredients are incorporated into the rubber matrix during mixing. In sulfur vulcanization of natural rubber (NR), the basic ingredients are ZnO, stearic acid, accelerators, and sulfur. The ZnO is used as an activator in rubber vulcanization and increases the efficiency of the vulcanizing or crosslinking system. It is assumed that stearic acid accelerates the activity of ZnO which further accelerates the action of accelerator and sulfur in the vulcanization process.

For industrial use, ZnO is produced at levels of 10^5 tons per year and about 50–60% ZnO is used in rubber industry.¹ In the vulcanization of rubber, the conventional amount of ZnO is 5 phr. Now the replacement of ZnO by other nontoxic metal oxide in rubber industry is very important from environmental point of view as at the end of the products life excess ZnO is released into the lithosphere during degradation of rubber.¹ Zinc oxide is also released in the environment through leaching in land-fill sites. More importantly, soluble zinc compounds have toxic effect on aquatic environment.² Environmental protection agency has classified ZnO as hazardous chemical for the environment and has suggested that its application in rubber compounds should be reduced.³ To solve this environmental problem, very recently several studies^{4–14} have been made by different researchers for the reduction of ZnO level in rubber

vulcanization by introducing nano ZnO as cure activator. Sahoo and Bhowmick⁴ reported that nano ZnO is much more effective curing agent for carboxylated nitrile rubber (XNBR) in comparison to conventional ZnO. Bhowmick and colleagues⁶ also studied the effect of nano ZnO on the cure and mechanical properties of natural rubber (NR) and nitrile rubber (NBR). It was confirmed that the tensile strength (T.S.) of NR vulcanizate was improved by 80% in the presence of nano ZnO as cure activator in comparison to rubber grade ZnO.⁶ Zhang and colleagues⁸ described nano ZnO as novel thermal conductive reinforcing filler for ethylene propylene diene monomer (EPDM) composites. Panampilly and Thomas¹⁰ investigated the suitability of nano ZnO as cure activator in the sulfur vulcanization of NR. In another work, Taghvaei-Ganjali *et al.*¹¹ used surface-modified nano ZnO to enhance the physico-mechanical properties of rubber compounds. But the research work covering complete substitution of ZnO with other less toxic metal oxide in the vulcanization of rubber is very scanty.

Among the various techniques sol-gel method is important one for the preparation of nanoparticles mainly due to its easy mechanism, small cost, and low fabricating temperature.¹⁵ Several works^{9,16–19} have been done to synthesize nanoparticles using sol-gel technique. In the present century, it is very reasonable to consider sol-gel technology as the crucial technology for the development of rubber industry. Nowadays, the commercialization of sol-gel technology becomes the part of great

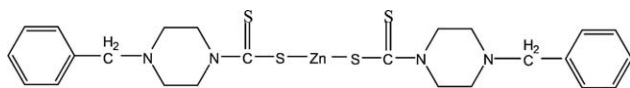


Figure 1. Structure of ZBPDC.

attention for the modern rubber researchers as it brings the proper advancement of rubber chemistry from industrial point of view.^{9,20}

In the present work, nano sized MgO is prepared via sol-gel auto-combustion technique and this nano MgO is used as cure activator in the sulfur vulcanization of NR. In our earlier work,⁹ we have reported that sol-gel-derived nano ZnO can successfully reduce the ZnO level in the sulfur vulcanization of NR. Now, it was already reported that MgO particles are very much less toxic than ZnO particles.²¹ Thus, the aim of the present study is to investigate the effect of nano MgO as cure activator in the vulcanization of NR and also to substitute ZnO by nano MgO in rubber compounding. It is noticeable that exceptionally high value of cure rate index and satisfactory value of mechanical properties of NR vulcanizate with 1 phr sol-gel-derived nano MgO are extremely important from both industrial and environmental point of view. In this way, nanotechnology will provide developed and innovative route for the preparation of more environment and economic friendly rubber nanocomposites with complete reduction of harmful environmental pollution produced by rubber compounds, especially conventional ZnO.

EXPERIMENTAL

Materials and Physical Measurements

NR (RMA-1X), zinc oxide (specific surface area 5–6 m²/g, Merck), stearic acid (Loba Chemie, India), sulfur (Loba Chemie, India), 2-Mercapto benzothiazyl disulfide (MBTS) (Apollo tyre, India), and toluene (Merck) are used as received. Nano MgO is synthesized using the procedure given by Fang *et al.*²² Zinc (N-benzyl piperazino) dithiocarbamate (ZBPDC) is prepared in the laboratory.²³ The structure of ZBPDC is represented in Figure 1.

Field-emission scanning electron microscopy (FESEM) images are obtained on instrument JSM 6700F. X-ray diffraction (XRD) pattern of nano MgO is recorded on Xpertpro-Panalytical X-ray diffractometer. The cure characteristics of the different stocks are obtained using the Monsanto Rheometer R-100 at 3 degree arc for 140°C. The stocks are cured under pressure at 140°C for optimum cure time (t_{90}), keeping vulcanizates for 24 h at ambient temperature before measuring the modulus at 100% (M_{100}) elongation, modulus at 300% (M_{300}) elongation, 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 Hirosima Hardness Tester as per ASTM D 1415-56T. Thermogravimetric analysis (TGA) is carried out in order to study the thermal behavior of NR 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.

Synthesis of MgO Nanoparticles

Nano MgO is prepared by sol-gel auto-combustion method via the procedure given by Fang *et al.*²² In a typical experiment, citric acid is added to a 0.4 mol/L solution of Mg(NO₃)₂·6H₂O (magnesium nitrate) to make the molar ratio of citric acid to nitrates as 4 : 1. A small amount of ammonia is added to the solution to adjust the pH value to about 4, then the solution is evaporated at 80°C in a thermostatic water bath followed by drying at 120°C in a vacuum oven, until it becomes into dry gel. The dried gel is precalcined at 350°C for 1.5 h and then calcined at 600°C for 3 h. The resulting powder is then cooled to reach room temperature in a deccator.

Preparation of NR Vulcanizates

NR is masticated in a two-roll mixing mill, and then conventional ZnO and stearic acid are added and again masticated. After that accelerators and sulfur are incorporated to the rubber matrix and the mixing is done near about for 10 min. Total concentration of the accelerator is fixed at 9 mM per 100 g of rubber. The whole compounding of NR is done at room temperature. The speed of one of the roll is maintained at 10 rpm and that of the other at 12 rpm, to get friction ratio of 1 : 1.2. In the present study, ZBPDC–MBTS binary accelerators system at 3 : 6 milli molar ratio is used as an effective accelerator system for the vulcanization of NR.²³ The same procedure is repeated to prepare NR nanocomposites containing different amount of nano MgO instead of ZnO. Mixing composition of different ingredients is presented in Table I. For the different mixes, NR indicates natural rubber, number indicates amount in phr, N indicates nano particle, C indicates conventional particle, as for example, mix of NR/0.5 NMgO represents NR vulcanizate containing 0.5 phr nano MgO.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

The XRD pattern of synthesized nano MgO is recorded in Figure 2. The detected XRD pattern is found to be similar with the earlier report.^{22,24} The diffraction peaks of (111), (200), and (220) are well observed at $2\theta = 37.1^\circ$, 43.1° , and 62.5° .²⁴ The average crystallite size is measured from XRD pattern using well known Scherrer equation.^{9,20} The Scherrer equation is given as:

$$C_s = K\lambda / (B\cos\theta)$$

Here, C_s is the average crystallite size, K is a constant nearly about to unity, λ is the wavelength of X-ray (0.154 nm for the CuK α), B is the integral half-width, and θ is the Bragg angle.

The average crystallite size is found to be 9.18 nm for the synthesized nano MgO. The specific surface area of nano MgO can be calculated according to the formula:^{25,26}

$$S = 6/\rho L$$

where S is specific surface area, ρ is the density, and L is the mean size of the particles. The specific surface area of nano MgO is found to be 182.56 m²/g.

Field-Emission Scanning Electron Microscopy (FESEM)

The FESEM image of MgO nanoparticles is shown in Figure 3. The particle size of MgO nanoparticle varies from 20 to 80 nm.

Table I. The Formulation of Studied Vulcanizates in Parts per Hundred Parts of Rubber (phr)

Formulation	Compound designation			
	NR/0.5 NMgO	NR/1 NMgO	NR/2 NMgO	NR/5 CZnO
NR	100	100	100	100
Conventional ZnO	-	-	-	5
Nano MgO	0.5	1	2	-
Stearic acid	2	2	2	2
ZBPDC	1.7	1.7	1.7	1.7
MBTS	1.992	1.992	1.992	1.992
Sulfur	0.5	0.5	0.5	0.5

Cure Characteristics of NR Vulcanizates

Cure parameters of NR vulcanizates in the presence of nano MgO and conventional ZnO are measured at 140°C and the results are presented in Table II. The cure curves of various NR vulcanizates are shown in Figure 4. The curing characteristics are expressed in terms of scorch time (t_2), optimum cure time (t_{90}), and cure rate index (CRI). The t_{90} value of NR vulcanizates containing low amount (0.5–2 phr) of nano MgO are very small compared to NR vulcanizate containing 5 phr conventional ZnO. Thus, the significant decrease of t_{90} value indicates that nano MgO performs as an effective crosslinking agent and better cure activator for the vulcanization of NR compared to conventional ZnO. The crosslinking efficiency of nano MgO is further confirmed from the value of cure rate index (CRI) of different NR vulcanizates. The value of CRI is about 400% greater for NR vulcanizate containing 1 phr nano MgO (NR/1 NMgO) in comparison to NR vulcanizate having 5 phr conventional ZnO (NR/5 CZnO).

Now the crucial step of vulcanization process in the presence of ZnO as cure activator is the formation of zinc accelerator complex.^{27,28} This resulting complex then reacts with sulfur or sulfur donor to produce active sulfurating agent.²⁹ In the next step, large numbers of crosslink precursors are produced by the reaction between active sulfurating agent and allylic sites of rub-

ber chain.²⁹ The crosslink precursors then react with additional polymer chain to produce greater number of crosslinks. Borrós and colleagues³⁰ proposed that the mechanism of the formation of the active sulfurating agents with MgO as cure activator differs markedly from the pathway that follows when ZnO is used as cure activator. In the presence of MgO, the active sulfurating species are formed via sulfur insertion in the active accelerator species and sulfur is consumed much quickly as compared to the systems with ZnO due to the higher affinity of MgO for sulfur.^{30,31} As a result, the active sulfurating agents are formed more quickly when nano MgO is used as cure activator.^{30,31} Furthermore, the breakdown of the accelerator occurs much faster when nano MgO substitutes ZnO as the activator and this is mainly due to the interaction of nano MgO with sulfur.^{30,32,33} The faster breakdown of accelerator significantly contributes to the quick formation of the active sulfurating agents. Additionally, the specific surface area of nano MgO is many times (~36 times) greater in comparison to conventional ZnO. As a result, due to large increase of interfacial area for reaction, the formation of active sulfurating agent occurs very quickly when nano MgO is used as cure activator. More significantly, due to very quick formation of active sulfurating complex the value of CRI is extraordinarily higher when nano MgO is used as cure activator in the sulfur vulcanization of NR.

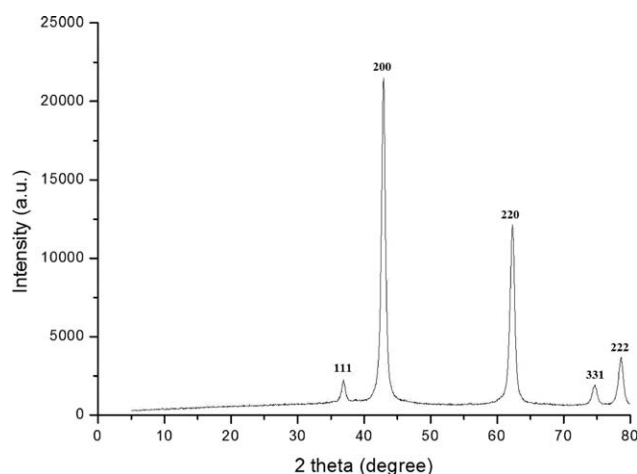
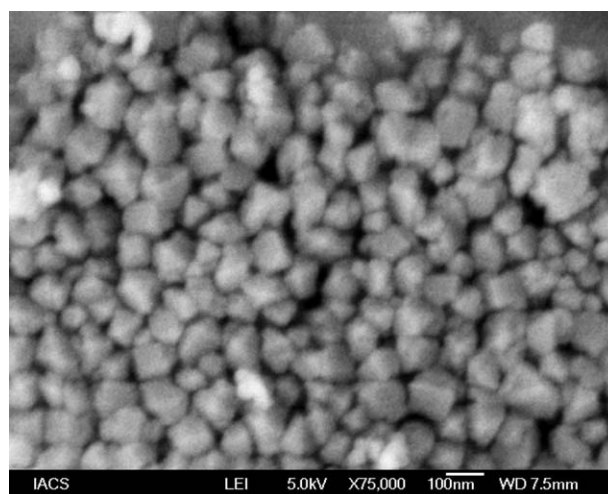
**Figure 2.** XRD pattern of nano MgO.**Figure 3.** SEM image of nano MgO.

Table II. Cure Characteristics of NR Vulcanizates at 140°C in the Presence of Nano MgO and Conventional ZnO

Compound designation	Optimum cure time, t_{90} (min)	Scorch time, t_2 (min)	Cure rate index, $CRI = 100/(t_{90} - t_2)$ (min^{-1})
NR/0.5 NMgO	5.75 ± 0.25	3 ± 0.25	36.36
NR/1 NMgO	5.25 ± 0.25	2.75 ± 0.25	40
NR/2 NMgO	5.75 ± 0.25	2.75 ± 0.25	33.33
NR/5 CZnO	21 ± 0.25	8.5 ± 0.25	8

Moreover, considering very small cure time and high cure rate index value it is concluded that only 1 phr nano MgO can successfully replace 5 phr conventional ZnO in sulfur vulcanization of NR.

Mechanical Properties of NR Vulcanizates

The mechanical properties of various NR vulcanizates are also studied and shown in Table III. The value of modulus at 100% elongation for NR/1 NMgO is slightly greater in comparison to NR/5 CZnO. Thus, modulus value is almost comparable when only 1 phr sol-gel produced nano MgO is used as cure activator instead of 5 phr conventional ZnO in the sulfur vulcanization of NR. This is due to the fact that nano MgO has high surface area in comparison to conventional ZnO and as a consequence it has an ability to interact far better with polymer chain than conventional ZnO.

Again, there is an obvious improvement in the value of T.S. when 1 phr nano MgO instead of 5 phr conventional ZnO is used as cure activator in the vulcanization of NR. The T.S. value shows an increment by 8.21% for NR nanocomposite containing 1 phr nano MgO in comparison to NR vulcanizate containing 5 phr conventional ZnO. The increase in the T.S. is due to uniform dispersion of nano MgO within the rubber matrix. As a result, the interaction with rubber matrix is greater in the presence of nano MgO instead of conventional ZnO. An increase in the T.S. is observed up to addition of 1 phr nano MgO. The decrease in the T.S. is observed when 2 phr nano MgO is used as cure activator. This may be due to agglomeration of MgO nanoparticle above the amount of 1 phr.⁹ The agglomeration of MgO nanoparticle is also detected in the scanning electron microscopy (SEM) images of nanocomposites later. However, it is clear from the results that only 1 phr nano MgO is sufficient to enhance T.S. to a greater extent as com-

pared to 5 phr conventional ZnO. The variation of E.B. is analogous with that of T.S. The E.B. shows an increment by 13.33% for NR nanocomposite containing 1 phr nano MgO in comparison to NR vulcanizate containing 5 phr conventional ZnO.

Moreover, from the above discussion it is reasonably concluded that only 1 phr nano MgO can able to successfully replace 5 phr conventional ZnO with the acceptable values of mechanical properties in the sulfur vulcanization of NR. Like cure characteristics, this point also helps to clarify the importance of nano MgO in the preparation of ZnO-free NR nanocomposites.

Morphology of Nanocomposites

The phase morphology of NR vulcanizates containing nano MgO is studied to evaluate the extent of dispersion of the nano MgO within the rubber matrix and also to explain the sudden decrease in the CRI value and mechanical properties of NR/2 NMgO as compared to NR/1 NMgO. The SEM images of NR nanocomposites are shown in Figure 5(a, b). The black phase indicates rubber matrix and white dot represents agglomerated MgO nanoparticle. From Figure 5a, it is notified that uniform dispersion of nano MgO occurs throughout the rubber matrix in the case of NR/1 NMgO (containing 1 phr nano MgO). But in the SEM image of NR/2 NMgO (Figure 5b), agglomeration of MgO nanoparticle is detected as white dot. Due to the agglomeration of MgO nanoparticle, there is also a reduction in the rate of formation of active sulfurating complex. As a result, the cure rate index value of NR/2 NMgO is lower than NR/1 NMgO. Also, due to agglomeration, the extent of dispersion of nano MgO within the rubber matrix decreases. This fact causes the reduction in the mechanical properties of NR/2 NMgO compared to NR/1 NMgO.

Variation of Elastic Gibbs Free Energy (ΔG) and Conformational Entropy (ΔS) of NR Vulcanizates

Thermodynamic effects are also analyzed to determine the rubber-filler interaction in the nanocomposite.¹⁰ The variation of thermodynamic parameters ΔG and ΔS is represented in Table IV. The elastic Gibbs free energy (ΔG) is calculated from the Flory–Huggins equation,³⁴

$$\Delta G = RT [\ln (1 - V_r) + V_r + \chi V_r^2]$$

where R is the universal gas constant, T is the absolute temperature, V_r is the volume fraction of swollen rubber, and χ is the rubber solvent interaction parameter.

The volume fraction of a rubber network in the swollen phase V_r is calculated from equilibrium swelling data using Flory–Rehner equation,³⁵

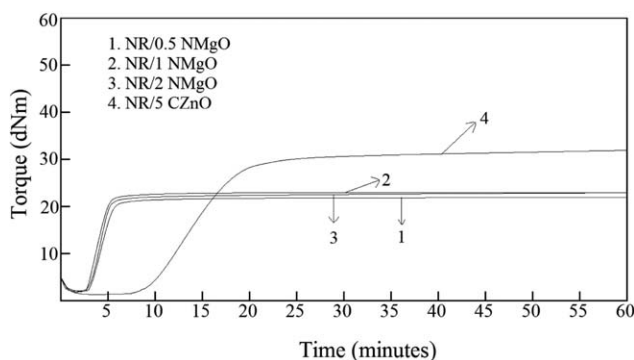
**Figure 4.** Cure curves of NR vulcanizates.

Table III. Mechanical Properties of NR Vulcanizates Cured at 140°C

Compound designation	M ₁₀₀ (MPa)	M ₃₀₀ (MPa)	T.S. (MPa)	E.B. (%)	Hardness (shore A)
NR/0.5 NMgO	0.809 ± 0.01	1.457 ± 0.01	18.613 ± 0.10	850 ± 10	51 ± 0.5
NR/1 NMgO	0.905 ± 0.01	1.766 ± 0.01	20.634 ± 0.10	850 ± 10	51 ± 0.5
NR/2 NMgO	0.865 ± 0.01	1.557 ± 0.01	17.295 ± 0.10	820 ± 10	51 ± 0.5
NR/5 CZnO	0.882 ± 0.01	1.639 ± 0.01	19.069 ± 0.10	750 ± 10	51.5 ± 0.5

$$V_r = (W_2/d_2) / [(W_1/d_1) + (W_2/d_2)]$$

where W_1 is the weight fraction of the solvent, d_1 is the density of the solvent, W_2 is the weight fraction of the polymer in the swollen specimen, and d_2 is the density of the polymer. For the NR–toluene system, $\chi = 0.3795$,³⁶ the molar volume of toluene V_s is 106.2 cm³/mol,³⁶ and the density of toluene is 0.87 g/cm³.

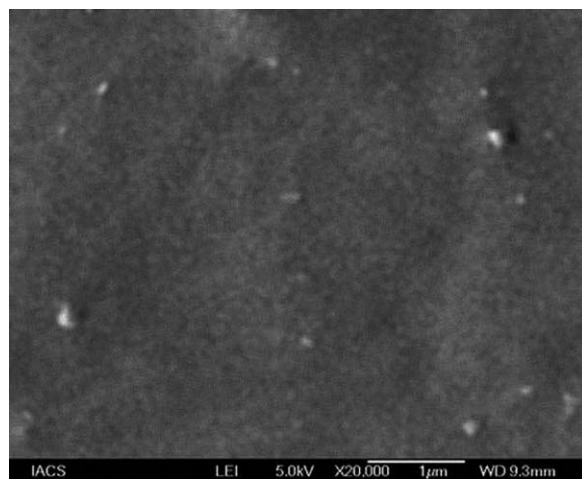
Now, according to statistical theory of rubber elasticity, ΔS is related to ΔG by the following equation, $\Delta G = T\Delta S$, here it is assumed that there is no change of internal energy of rubber

network during stretching.¹⁰ The data represented in Table IV indicates the conformational entropy (ΔS) of NR/1 NMgO is higher than NR vulcanizates containing 5 phr conventional ZnO. Both the high surface area and uniform dispersion of nano MgO within the rubber matrix are responsible for the higher value of ΔS in NR nanocomposite.¹⁰ The value of ΔG indicates that NR/1 NMgO has greater elastic behaviour in comparison to NR/5 CZnO as ΔG is closely linked to the elastic behaviour of the material.¹⁰ The better elastic behavior of NR/1 NMgO is explained by considering better compatibility between rubber matrix and nano MgO.¹⁰

Thermal Properties of NR Vulcanizates

Thermal study clearly reveals the substantial improvement in the thermal stability of NR/1 NMgO over NR/5 CZnO. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) curves of NR vulcanizates are shown in Figure 6(a,b). The TGA study indicates rapid degradation region shifted toward higher temperature for NR/1 NMgO in comparison to NR/5 CZnO. This is an indication of better thermal stability of NR nanocomposite than NR/5 CZnO.

The considerable enhancement in the thermal stability of NR nanocomposite over NR/5 CZnO is also observed from the DTA study. The onset decomposition temperature (T_i) and the temperature at which the rate of decomposition is maximum (T_{max}) are calculated from DTA curve and defined in Table IV. Both T_i and T_{max} values of nano MgO cured NR vulcanizate are shifted toward higher temperature as compared to NR/5 CZnO. Thus, it is clearly established from DTA study that nano MgO imposes greater thermal stability in NR vulcanizate than conventional ZnO. Both the reasons, the decrease in the thermal motion of polymer chain within the network structure and the greater heat absorption by the large surface area of MgO nanoparticles, are responsible for the improvement in the thermal stability of NR nanocomposite over NR/5 CZnO.³⁷ Due to the greater heat absorption by the large surface area of MgO nanoparticles, there is a physical barrier between the polymer and superficial zone. As a result, MgO nanoparticle prevents



(a)



(b)

Figure 5. (a) SEM image of NR/1 NMgO and (b) SEM image of NR/2 NMgO.**Table IV.** Variation in Thermodynamic Parameters and Thermal Properties of NR Vulcanizates

Compound designation	ΔG (J/mol)	$\Delta S \times 10^{-2}$ (J/mol)	ΔS	
			T_i (°C)	T_{max} (°C)
NR/1 NMgO	-13.12	4.33	286	390
NR/5 CZnO	-10.42	3.43	274	376

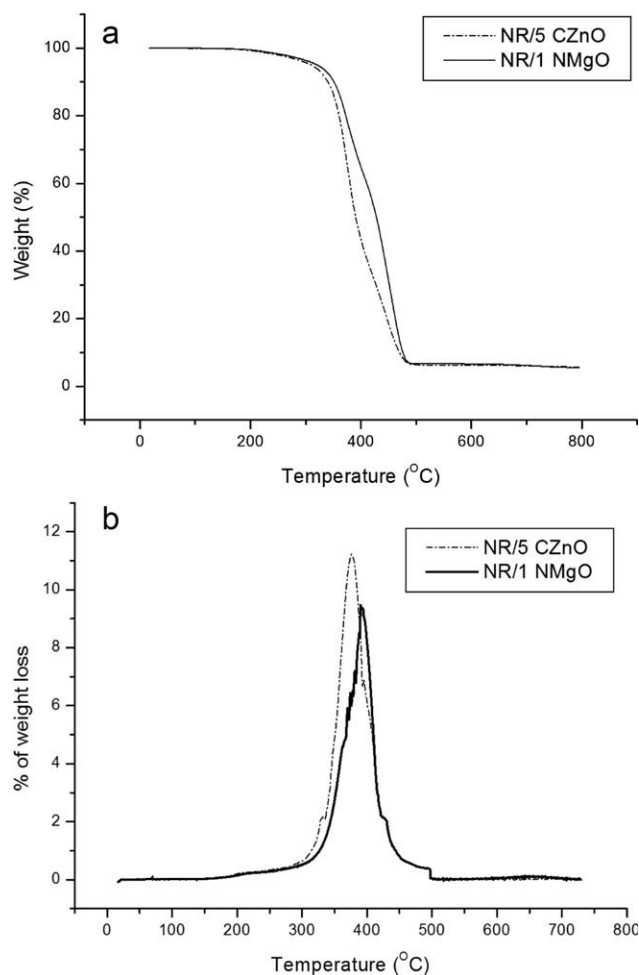


Figure 6. (a) TGA curve of NR vulcanizates and (b) DTA curve of NR vulcanizates.

departing the volatile product generated during decomposition and thermal degradation delays.^{37,38}

CONCLUSIONS

In this present paper, the effects of nano MgO as cure activator in the sulfur vulcanization of NR are investigated. From the above results, it is found that addition of 1 phr nano MgO in NR causes significant decrease in the optimum cure time and very large increase in the cure rate index in comparison to 5 phr conventional ZnO. Both the reasons, the high affinity of nano MgO for sulfur and large surface area of nano MgO, are responsible for outstanding enhancement of CRI value in NR/1 NMgO. Again, for NR vulcanizate mechanical properties are also satisfactory in the presence of 1 phr nano MgO as cure activator and the value of T.S. shows an increment by 8.21% for NR/1 NMgO in comparison to NR/5 CZnO. This is mainly due to the high surface area and uniform distribution of nano MgO within the rubber matrix. The value of ΔG indicates that NR/1 NMgO has greater elastic behaviour in comparison to NR/5 CZnO as ΔG is closely related to the elastic behaviour of the material. The better elasticity of NR/1 NMgO is explained by considering better compatibility between rubber matrix and nano MgO. TGA study reveals the

better thermal stability of NR nanocomposite as compared to NR vulcanizate containing conventional ZnO. The increase in thermal stability is attributed to the decrease in the thermal motion of polymer chain within the network structure and the greater heat absorption by the large surface area of MgO nanoparticle.

From this study, it is concluded that only 1 phr nano MgO can wholly replace 5 phr conventional ZnO in the sulfur vulcanization of NR. Thus, the present work provides an innovative route for the preparation of more environment friendly ZnO-free rubber nanocomposites. We expect that this paper makes a vital contribution on the development of rubber chemistry with the help of sol-gel science and technology. More significantly, the complete replacement of ZnO by nano MgO with five times reduction of cure activator level in rubber industry is important from both environmental and economic point of view. However, the role of ZBPDC-MBTS binary accelerators system on the property enhancement of nano MgO cured NR vulcanizates is still not clear. Detailed mechanistic studies for the preparation of totally zinc-free rubber nanocomposites will be done in our forthcoming publication.

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