

Carboxylated Nitrile Elastomer/Filler Nanocomposite: Effect of Silica Nanofiller in Thermal, Dynamic Mechanical Behavior, and Interfacial Adhesion

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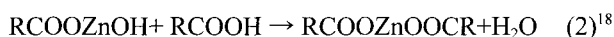
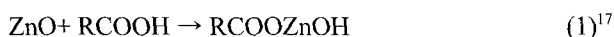
Abstract: Surface modified nanofillers are often used as curative-cum reinforcing agents for functional polymers. The polymer nanofiller interaction depends on the curative systems used. In the present study the carboxylic group of the carboxylated nitrile elastomer participated in the reaction with Zn-ion coated nanosilica filler producing a type of ionomeric elastomer. The interaction at the molecular level thus produced a high modulus vulcanizate. In this case, the S and MBT system, as curative, had an edge over the MDA and DPG curative system. Interfacial adhesion was enhanced in the presence of Zn-ion-coated nanosilica filler associated with dynamic mechanical behavior. The inferior properties obtained in the case of the MDA and DPG curative system were due to the decreased reactivity of the silica surface, thus reducing interfacial adhesion.

Keywords: vulcanizate, carboxylated nitrile elastomer (XNBR), nanofiller, silica, Zinc-ion.

Introduction

The filler dispersion is a critical problem to solve to make good compounds out of silica filled mixes. A good dispersibility can improve tensile strength, elongation at break, abrasion resistance and fatigue resistance. The adsorption of curatives by silica results in delay of the scorch time and reduction of the state of cure. Zn-ion on the surface of the nanosilica used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface.

The nanostructural materials often, exhibit combinations of specific and conventional materials.^{1,2} Carboxylated elastomers are commonly cured with ZnO, which neutralizes acid groups thereby producing ionomeric elastomers, whose properties have been studied extensively.³⁻¹⁶ Complete neutralization consists of two steps:



In this paper we have examined the effect of Zn-ion coated nanosilica filler on the cure behavior, thermal stability and dynamic modulus and surface morphology in presence of sulfur and amine curative systems.

It is normally, difficult to have in the same material both properties of high strength to sustain high loads and toughness to absorb a large amount of energy during fracture, which occurred by breaking of primary or secondary bonds, depending upon the structure of materials,¹⁹ Inorganic fine particles have a general use to act as fillers or reinforcing agents. When it is used as filler, it serves to reduce the cost of the composite. However, reinforced polymers, with minerals, showed an increase in modulus, hardness, tensile strength, abrasion, tear resistance and resistance to fatigue and cracking.²⁰

The nanoscale materials have inspired the scientist and technologists, in the field of composites, by the fact that they often gave rise to drastically improved properties than their macro counterpart. Polymer nano-filler composites have been widely investigated in recent years due to their unique properties such as stiffness, strength, and barrier action.^{21,22} In recent years nanocomposites have become a major part of new synthetic materials all over the world.^{23,24} Inorganic-organic nanocomposites are generally organic polymer composites with inorganic nanoparticles. In the polymer based nanocomposites field the surface atoms of nanoparticles are used to modify synthetic polymers. This kind of nanocomposites have attracted more and more attention.²⁵⁻²⁷ Nano-sized silicas, as individual particulate fillers have application to improve heat deflection temperatures and to increase the

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tensile strength and the modulus of composite materials. These nanosized silicas are very useful in the reinforcement of thermoplastics and thermosetting polymers if they are dispersed well into polymer matrices.^{28,29} Primarily the formation of aggregates due to the incompatibility of the silica particle with many matrix polymers has caused considerable concern.^{30,31} Due to the large surface area of nanoparticles the benefits that can be achieved such as reinforcement at low nanofiller loading. Some of these improvements can be achieved with conventional fillers but at 20-50% loading compared to 3-5% loading with nanofiller. Sahoo *et al.* have used Zn-ion coated nanosilica filler as the vulcanizing aid for sulfur curing of styrene butadiene rubber and also Sahoo *et al.* explored the possibilities of using Zn-ion coated nanosilica filler as curing agent for halogen containing polymers like chlorosulphonated polyethylene and polychloroprene rubbers.^{32,33}

Experimental

Formulations of the mixes used in the present work were shown in Table I. Composites were prepared by using a laboratory two roll mixing mill. XNBR was masticated on the mill for 2 min followed by addition of the ingredients. The nip gap, mill roll speed ratio and number of passes were kept constant in all the mixes. The samples were milled for sufficient time to disperse the fillers as well as other ingredients. Three different kind of silica fillers are being used, which were developed in our laboratory i.e. Zn-ion coated nanosilica filler, nanosilica and normal silica.³² ATR (Attenuated Total Reflection) spectroscopy experiments were done using NEXUS 870 FTIR (Thermo Nicolet) at room temperature on pure elastomer and elastomer filler samples with a 4 cm resolution and 32 scan signal. Average spectra were taken from 4600 to 400 cm^{-1} in the transmission mode using a DTG-TEC detector. Vulcanization of the mixes was done at 150 °C by the help of compression molding up to the optimum extent (t_{90}) under a pressure of 20 MPa. The physical properties were measured on this vulcanized sheet. The cure characteristics of the mixes were investigated by using a Monsanto Rheometer R-100. Stress strain measurements were carried out using a universal testing machine at a cross

head speed of 50 cm/min. Modulus, tensile strength and elongation at break were determined according to ASTM test method (D412-68) and hardness was measured at room temperature by using a shore-A hardness tester according to ASTM test method (D-2240). Percent of volume swell was studied by immersing the sample in the *N,N*-dimethyl formamide up to equilibrium. Differential thermal analysis (DTA) / thermo gravimetric analysis (TGA) studies were carried out using a Shimatzu-DT-40 instrument in presence of nitrogen at a heating rate of 20 °C/min within the temperature range of 50-500 °C. Fracture mechanism was studied by scanning electron microscope (SEM) (JSM-5800 of JEOL Co.), after auto sputter coating of the fracture surface with gold at 0° tilt angle. Dynamic mechanical properties of the samples were studied on compression-molded films using a TA instruments (DMA 2980) in the tensile mode. The samples were tested in a temperature range from 40 to 200 °C, temperature sweep was carried out in the auto strain mode. AFM (atomic force microscopy) images are obtained using a nanoscope scanning probe microscope of digital instruments (Santa Barbara, CA).

Results and Discussion

The cure characteristics and thus processibility of the compounds have been studied from the rheographs and the parameters were shown in Table II. The maximum torque in the rheographs is a measure of crosslink density and the

Table II. Curing Characteristics

Sample Code	T_{min} (dN · m)	$T_{(max-min)}$ (dN · m)	$t_{5(min)}$ (scorch time)
A1	11	6	14
A2	3	32	6
A3	3	31	6
B1	13	8	18
B2	4	36	7
B3	4	36	18

T: torque, *t*: time.

Table I. Formulations

Ingredients Sample Code	XNBR	Nano-Silica	10%Zn++ coated nano-Silica	Normal Silica	ZnO	Sulphur	MBT	DPG	MDA
A1	100		5			1	1		
A2	100	5			0.62	1	1		
A3	100			5	0.62	1	1		
B1	100		5					1	1
B2	100	5			0.62			1	1
B3	100			5	0.62			1	1

stiffness of the XNBR matrix. In general, for all mixes, the torque initially decreased and then increased and finally leveled off. The initial decrease in torque to a minimum value was due to the softening of the rubber matrix while the increase in torque was due to the crosslink of the rubber. The leveling off was an indication of the completion of curing. It was found that generally the presence of fillers increased the maximum torque. It was reported that the increase in torque is directly proportional to crosslink density.³⁴

The minimum torque was observed for Zn-ion coated nanosilica, in both the curative systems such as, S/ MBT and MDA/DPG. When ZnO was added from outside, high state of cure was observed for MDA/DPG curative system with nanosilica and normal silica respectively, due to very fast onset of vulcanization.

The self-crosslinks of XNBR, without added curative, probably due to the bimolecular condensation of acid groups, which forms anhydride crosslinks. Apparently some carboxyl groups have reacted with the ZnO (added from outside), thereby reducing self crosslinking. The first neutralization step [eq. (1)] did not produce elastically effective networks chains but it decreased the concentration of acid groups available to participate in anhydride formation. The dependency of the cure rate on ZnO particle size indicated diffusion controlled reaction. With the smaller size ZnO, the neutralization was rapid as in the case of Zn-ion coated nanosilica filler.

In the case of MDA/DPG system, the state of cure was higher as well as increased scorch time, but this cure system showed less physical properties such as tensile strength and tear strength. This may be due to lack of rubber filler interaction. The state of cure was maximum as observed in case of ZnO added from outside in both the curative systems but as we have seen earlier that the effect of rubber filler interaction was more in the case of Zinc-ion coated nanosilica in comparison to ZnO added from outside. Zinc-ion coated nanosilica contained composite showed better tensile strength as well as tear strength in comparison to ZnO added from outside with nanosilica and normal silica for S/MBT system. If we closely examine the tear and tensile strength, the S/MBT system showed better properties with Zinc-ion coated

nanosilica. The volume swell values in organic solvent also showed less percentage of swelling. Hence, it is evident from the Table III, that the Zn-ion coated nanosilica was more reactive than the ZnO added from outside. From the above findings we can say that sulfur curative system was better than MDA/DPG in presence of Zn-ion coated nanosilica filler.

In Figure 1(a), assignment of stretching vibration band of carbonyl group (-C=O) bond was observed at 1726 cm^{-1} and -OH stretching at 3328 cm^{-1} . In Figure 1(b), XNBR itself having hydrogen bonding formation, in the case of nanosilica filled XNBR, the -OH stretching bond is shifted towards lower wavenumber side (3295 cm^{-1}) due to secondary bond formation (H-Bonding) between XNBR and SiOH (Silanol) groups of nanosilica. ATR analysis of the compounds containing elastomers and only nanosilica filler with and without Zn-ion coated suggested that there is some interaction between filler and elastomers. In the case of Zn-ion coated nano silica filled XNBR, Zn-ion act as a catalyst to form secondary molecular interaction between nanosilica filler and XNBR.

The DTA (differential thermal analysis) and TGA (thermogravimetric analysis) plots of the elastomer samples were shown in Figure 2. The data from the graphs were shown in the Table IV. In case of Zinc-ion coated nanosilica, Figure 2(a), and nanosilica, ZnO added from outside, Figure 2(b), and Figure 3(c), with normal silica ZnO added from outside. The on-set temperature of first degradation and completed temperature of degradation has been increased in the case of S/MBT curative system. But the percentage of weight loss, in the case of Zn-ion coated nanosilica was less. Hence it may assumed that there was a strong interaction between the Zinc-ion coated nanosilica and elastomer for Sulfur and MBT system but in case of MDA/DPG curative system, when we are adding ZnO to the normal silica from outside and also in the case of nanosilica, showed higher on set temperature of degradation as well as completed degradation temperature, but this is not true in the case of Zn-ion coated nanosilica filler system, although it showed higher physical properties.

If we closely examine the DTA figures, the broad exothermic peak in thermogram was due to oxidative degradation

Table III. Physical Properties of Vulcanizates

Sample Code	100% Modulus (MPa)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (N/cm ²)	Hardness (ShoreA)	Volume Swell (%)
A1	1.7	3.5	7	1050	36	40	128
A2	0.9	1.4	6	1184	38	60	140
A3	0.8	1.4	5.7	1204	29.1	52	182
B1	0.7	1.1	5.3	3043	23.5	52	210
B2	0.2	0.3	5.4	1144	33.8	56	457
B3	1.3	2.1	5.6	644	27.7	46	571

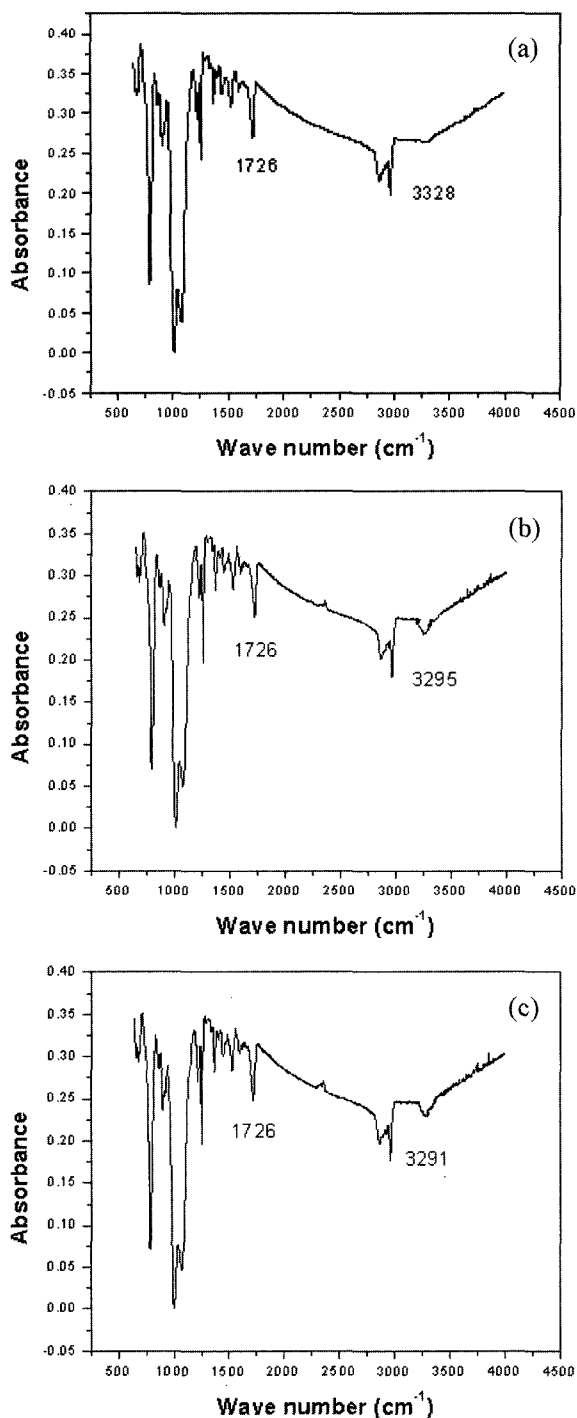


Figure 1. ATR spectra of (a) pure XNBR, (b) XNBR and nanosilica, (c) XNBR and Zn-ion coated nanosilica.

of the XNBR. TG plots showed that the maximum weight loss occurred in this region. As the oxidative degradation process is a complex one, the degradation of low level cross-linked phase, volatile matter formation, degradation of unused curatives etc, are also occurring and hence we got some more peaks.

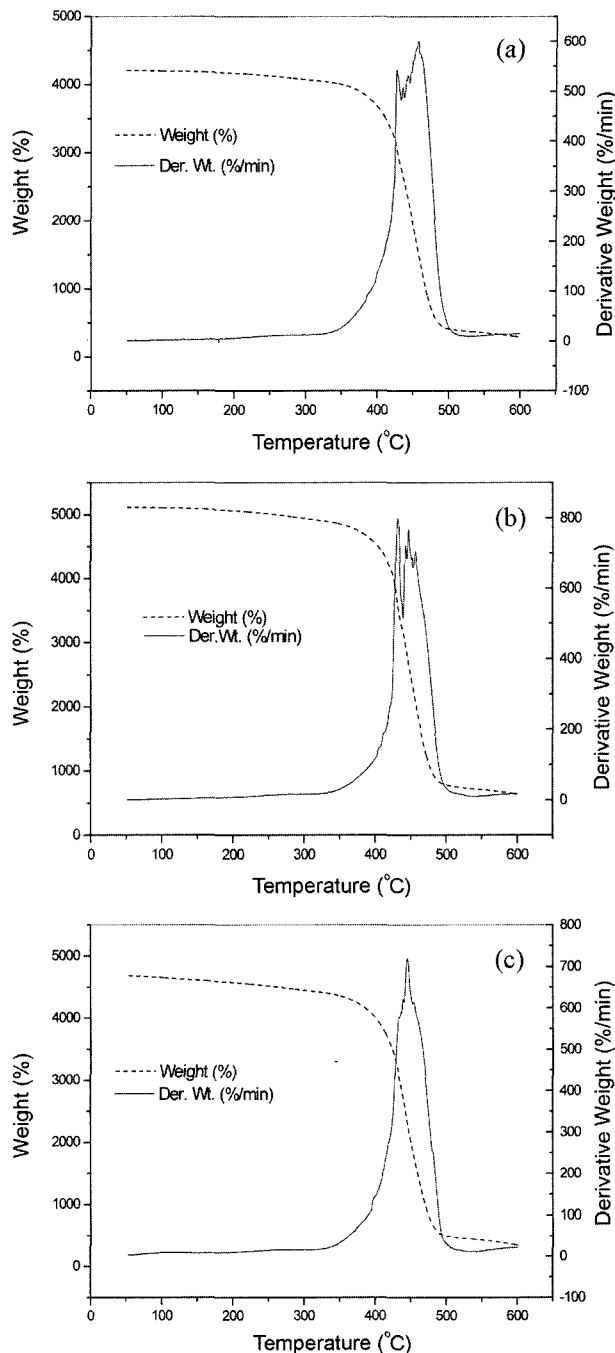
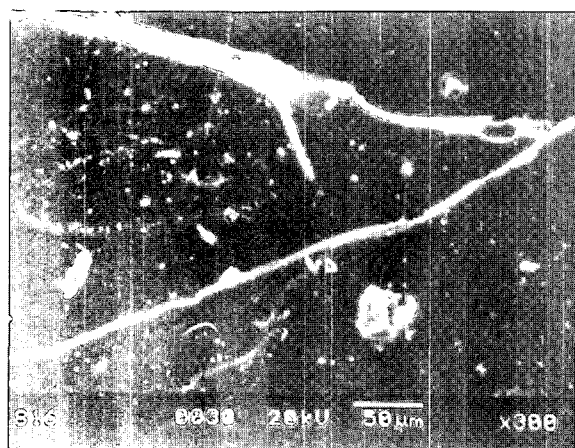


Figure 2. DTA/TGA graphs of carboxylated nitrile butadiene rubber (XNBR) with different curatives and filler. (a) Zn-ion coated nanosilica filler +S+MBT, (b) nanosilica+ZnO+S+MBT, and (c) normal Silica+ZnO+S+MBT.

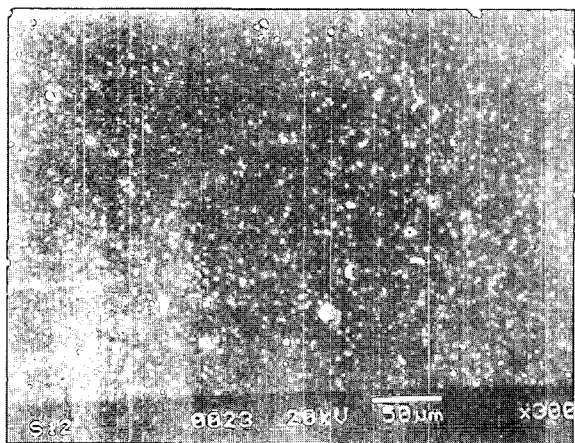
SEM study revealed, in presence of the curatives MDA and DPG, the nanosilica with ZnO added from outside showed the channel type cracks in different layers and it is unidirectional. However, comparatively smooth rubbery failure was observed in the case of Zinc-ion coated nanosilica filler. The flow of the matrix was not observed. When

Table IV. DTA/TGA Parameters

Sample Code	On-set Temperature of Degradation (°C)	Completed Temperature of Degradation (°C)	Loss of Wt (%)
A1	320	515	80
A2	300	500	84
A3	280	500	89
B1	250	370	77
B2	280	500	80
B3	270	495	87



(a)



(b)

Figure 3. SEM Photographs Carboxylated nitrile butadiene rubber (XNBR) with different curatives and filler. (a) Zn-ion coated nanosilica filler +S+MBT and (b) nanosilica+ZnO+S+MBT.

the normal silica filler replaced the nanosilica filler, smooth rubbery failure was observed which was associated with a deep crack mark with low elongation at break. Zinc-ion coated nanosilica filler showed a very high elongation at break may be due to the flow of the matrix and ionic interaction between Zn-ion coated nanosilica with XNBR.

When the curative system has been changed, the fracture mechanism was changed drastically. In the presence of sulphur and MBT as curatives, the channel cracks are observed which tend to merge at a particular point associated with high tensile and modulus values, Figure 3(a). However the presence of nanosilica filler with ZnO added from outside, Figure 3(b) a smooth rubbery failure has been observed with uniformly distributed ZnO, through out the matrix.

It is well known that dynamic modulus of a crosslink rubber does not generally decrease with increasing temperature.³⁵ As observed from the graph, dynamic modulus decreased with increasing temperature, suggesting insufficient cross-linking or a lack of adequate interfacial adhesion in the case of both curative systems.

The analysis of storage modulus, loss modulus, and $\tan \delta$ curve are useful in ascertaining the performance of the sample under stress and temperature. Zn-ion coated filler-elastomer nanocomposites exhibited higher storage moduli after 50°C range of the study, [40-200°C], Figure 4(a), for S/MBT curative system but for the MDA/DPG curative system it showed higher storage moduli over the entire temperature range, Figure 4(b). Zn-ion coated nanosilica showed higher interfacial adhesion as compared to nanosilica filler and normal silica filler when ZnO added from outside.

The decrease in storage modulus was observed in all the cases due to insufficient crosslinking. However, above this temperature (50°C) the decrease in storage modulus very low compared to other filler system and Zinc-ion coated filler system was more effective which is due to the more reinforcing nature of Zinc-ion in presence of S and MBT curative system, Figure 4(a). The decreasing trend of dynamic modulus showed predominant interfacial adhesion rather than chemical crosslink. The same trend was observed in the loss modulus, Figure 4(c).

The increase in the modulus was attributed to the presence of filler particles in the XNBR matrix. However, when nanofiller was used along with the crosslinking agent, the same increase was obtained at low filler content. The significant enhancement observed in the storage modulus of XNBR-filler nanocomposites, can be related to the nano-scale dispersion of filler in XNBR matrix.

In the case of Zinc-ion coated filler, Figure 4(b), with MDA/DPG curative system showed poor modulus values compared to other filler systems. The maximum value was observed in nanosilica and Zinc oxide added from outside. The loss modulus of the nonosilica filler system, and normal silica showed higher value than the Zinc-ion coated system in the case of S/MBT system. The maximum $\tan \delta$ value was observed in the case of nanosilica at 50°C, suggesting more damping characteristics in the system as compared to other filler system of S and MBT. However, in the case of MDA and DPG curative system the maximum $\tan \delta$ was observed in the Zinc-ion coated system and this value increased with increasing temperature due to the insufficient

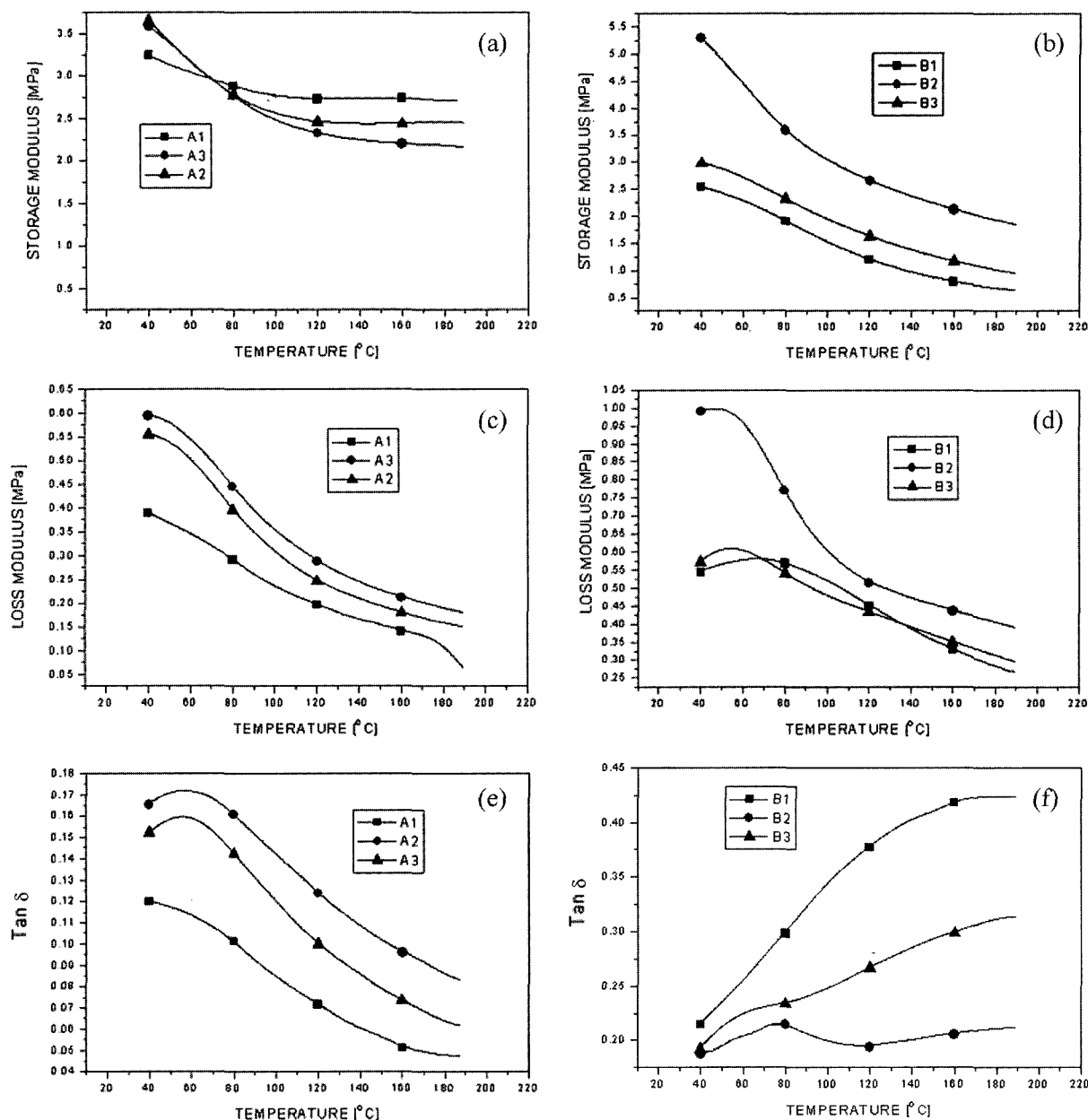


Figure 4. DMA graphs of Carboxylated nitrile butadiene rubber (XNBR) with different curatives and filler. (a) Zn-ion coated nanosilica filler+S+MBT, (b) nanosilica+ZnO+S+MBT, (c) normal silica+ZnO+S+MBT, (d) Zn-ion coated nanosilica filler+MDA+DPG, (e) nanosilica+ZnO+MDA+DPG, and (f) normal Silica +ZnO+MDA+DPG.

adhesion between filler and rubber consequently at that interface much energy must be dissipated as heat. When ZnO was added from outside the damping characteristics have goes high as compared to Zn-ion coated nanosilica filler.

The surface morphology of XNBR/nanosilica and XNBR/Zn-ion coated nanosilica was analyzed by AFM and the corresponding two-dimensional and three-dimensional pictures are shown in Figures 5 and 6, respectively. The surface roughness of XNBR/Zn-ion coated nanosilica (30.364 nm)

was reduced as compared to XNBR/nanosilica (48.446 nm). The surface of XNBR/Zn-ion coated nanosilica becomes smooth, this may be due to the surface silanol groups reacted with Zn-ion and reducing the polarity and reactivity of the silanol groups.

Conclusions

Zn-ion coated nano silica filler acts as a better reinforcing cum curative than with out Zn-ion coated nanosilica filler

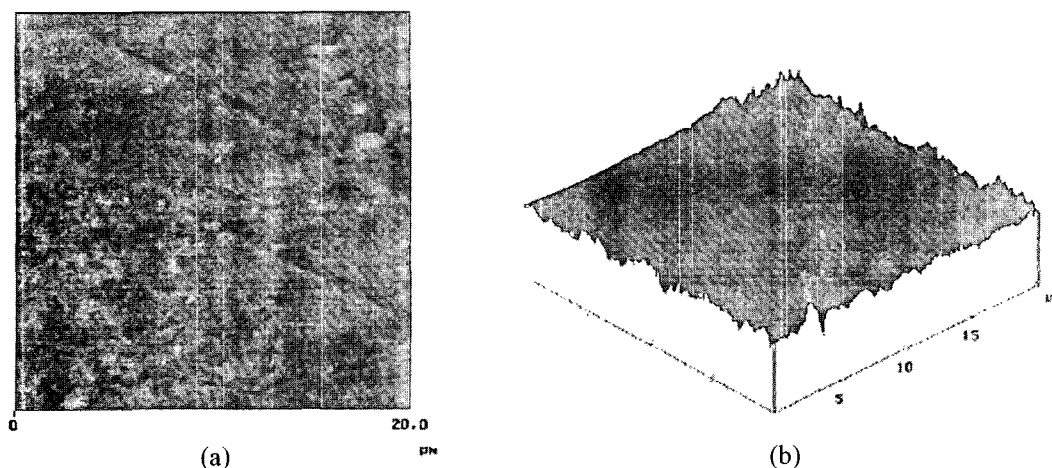


Figure 5. (a) AFM photographs (2D) of carboxylated nitrile rubber (XNBR)/ Zn-ion coated nanosilica and (b) AFM photographs (3D) of carboxylated nitrile rubber (XNBR)/ Zn-ion coated nanosilica.

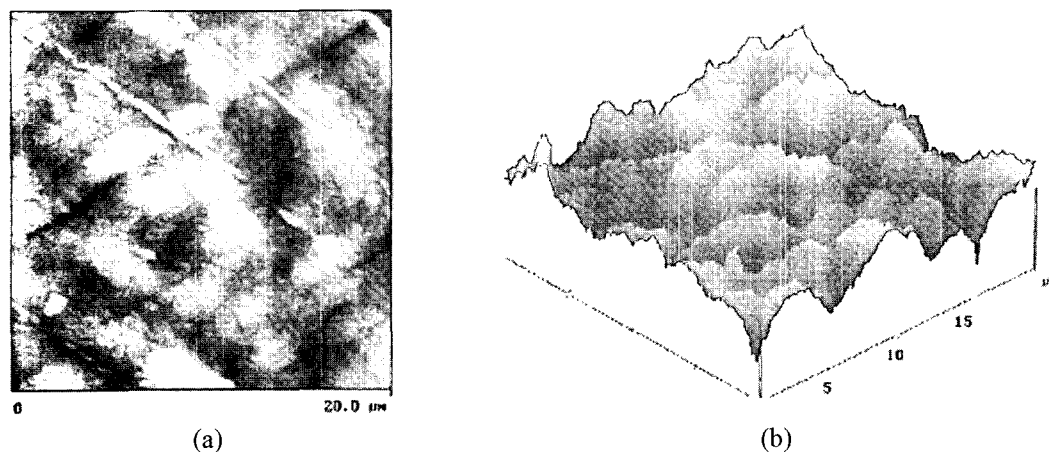


Figure 6. (a) AFM photographs (2D) of Carboxylated nitrile rubber (XNBR)/ nanosilica and (b) AFM photographs (3D) of carboxylated nitrile rubber (XNBR)/ nanosilica.

for carboxylated nitrile elastomer. This Zn-ion coated nanosilica improved the thermal stability of the vulcanizates. S/MBT curative system was seemed to be good, as filler-elastomer interaction through Zn-ion on the surface enhanced the technical properties. Sulphur system offers better thermal stability because of improved elastomer filler surface interaction in presence of Zn-ion coated nanosilica filler. Dynamic modulus was more in the case of Zn-ion coated nanosilica filler, which may be due to the effect of phase interaction at the filler elastomer interface. Interfacial adhesion was more in the case of Zn-ion coated nanosilica filler.

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