

Nanofiller as Crosslinker for Halogen-Containing Elastomers

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Abstract: A Zn ion-coated nanosilica filler has been developed and tested, in chlorosulfonated polyethylene (CSPE) and polychloroprene (CR), as a vulcanizing activator, cum was reinforcing filler. In this study, ZnO was replaced by the Zn ion-coated nanosilica filler with an aim of studying the dual role of this nanofiller in CSPE and CR. In the case of CSPE vulcanizates, the presence of MgO deteriorated the state and rate of cure when the Zn ion-coated nanosilica filler was used, but in the case of CR it improved the state of cure and enhanced the modulus and tensile strength. The Zn ion-coated filler proved to be a better reinforcing-cum-curing agent than was externally added ZnO and NA-22 also proved to be a better curative in the presence of the Zn ion-coated nanosilica filler for both CSPE and CR.

Keywords: vulcanization, chlorosulfonated polyethylene, polychloroprene, nanofiller, silica, zinc ion.

Introduction

Nanostructured composites consisting of layered inorganic solids and organic polymers have been widely investigated in recent years due to their interesting mechanical, thermal, optical, magnetic and barrier properties.¹ For polymer/clay nanocomposites, tremendously large interface surfaces are responsible for the benefits such as reinforcement with a 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. Thus relatively small amounts of plate like clay particles, provided they are well dispersed into individual platelets, can result large improvements in composite properties.²

The intercalation and exfoliation chemistry of epoxy-clay^{3,4} nanocomposites have been successfully transferred to a thermoset polyurethane system.⁵ Amine terminated butadiene-acrylonitrile (ATBN) intercalated clay has been used to form acrylonitrile-butadiene rubber (NBR)-nanocomposites.⁶ Poly(styrene-butadiene) copolymer nanocomposites have been prepared using similar approach from modified clay.⁷ Previous literatures suggested the use of layered clay for making the composites, but very little information is available regarding the use of other nanofillers in the composite preparation specially their use as vulcanizing/curing aids.

Recently Das *et al.*⁸ have used Zn-ion coated nano silica filler as the vulcanizing aid for sulfur curing of styrene butadiene rubber (SBR) and suggested the dual action of such nano filler both as vulcanizing aid and rubber reinforcing agent.

In this study we explore the possibilities of using Zn-ion coated nano silica filler as curing agent for halogen containing polymers like chlorosulphonated polyethylene and polychloroprene. Rubber-nanofiller composites, thus prepared, were assessed for their technical properties.

Experimental

Chlorosulphonated polyethylene (CSPE), from Du Pont (USA) and polychloroprene rubber (CR), from Bayer (Germany), were mixed with nanofiller along with NA-22 from Du Pont (USA), and MgO from Loba Chemie (India), in a two roll open mixing mill at a fixed nip gap at around 35 °C. The nanofiller was Zn-ion coated silica having average particle size 20 nm, which has been developed following the chemical process. The mixed compound was sheeted out from the two roll mixing mill and vulcanized by compression molding at 150 °C up to the optimum extent (t_{90}) under a pressure of 20 MPa. All technical properties were measured on this vulcanized sheet. Cure characteristics of the compounds were measured with a help of Monsanto Rheometer R-100 at 150 °C. Percent volume swell was studied by immersing the sample in the toluene up to equilibrium. Tensile

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properties of the compounds were carried out with the help of a universal tensile tester 1.3D Kmi India at test speed of 50 cm/min. Differential thermal analysis (DTA)/thermogravimetric analysis (TGA) studies were carried out using a Shimadzu-DT-40 instrument in presence of air at a heating rate of 20°C/min within the temperature range of 20-1,020°C. Differential scanning calorimetry (DSC) was carried out using Perkin-Elmer DSC7 instrument in presence of nitrogen to study the heat of reaction between the polar groups of the halogen containing polymers and Zn-ion in the nano silica filler. Fracture mechanism was studied by scanning electron microscope (JSM-5800 of JEOL Co.), after auto sputter coating of the fractured surface with gold at 0° felt angle.

Results and Discussion

The compounding formulations are shown in Table I. The curing parameters and the other physical properties are shown in Table II. It is evident from the Table II that the Zn-ion coated nano silica is more reactive than the ZnO added from outside. In the case of chlorosulphonated polyethylene vulcanizates, the presence of MgO deteriorated the state and rate of cure when Zn-ion coated silica nanofiller is used. The swelling co-efficient values in organic solvent confirmed the above findings. 200% modulus follows the same trend

as the state of cure. Tensile strength is higher when Zn-ion coated silica nanofiller is used. NA-22 proved to be better curative in presence of Zn-ion coated nanosilica filler.

In polychloroprene elastomer the Zn-ion coated silica filler showed more reinforcing characteristics than the ZnO added from outside. In this case, contrary to chlorosulphonated polyethylene, the presence of MgO improved the state of cure and enhanced the modulus and tensile strength. NA-22 in polychloroprene elastomer is not as effective as in chlorosulphonated polyethylene elastomer. Here again the Zn-ion coated silica filler proved to be better reinforcing cum curing agent than the ZnO added from outside.

IR analysis of the compounds containing only elastomers and nano silica filler with and without Zn-ion coated suggested that there is some interaction between filler and elastomers. The IR spectrum of CSPE-without Zn-ion coated nano silica filler, showed symmetric and asymmetric stretching frequency of SO₂ group at 1159 and 1361 cm⁻¹, which were shifted to 1164 and 1366 cm⁻¹ in the case of CSPE-Zn-ion coated nano silica filler. The C-Cl stretching frequency of CSPE-without Zn-ion coated nano silica filler appeared at 613 cm⁻¹, which was absent in CSPE-Zn-ion coated nano silica filler owing to the change in environment of the SO₂ and Cl groups. In the case of CR-without Zn-ion coated nano silica filler the IR spectrum showed C-Cl stretching frequency at 667 cm⁻¹ was shifted to 662 cm⁻¹ in the case of

Table I. Compounding Formulations

Ingredients	Mixture Number									
	A	B	C	D	E	F	G	H	I	J
Hypalon-40	100	100	100	100	100	-	-	-	-	-
Neoprene-W	-	-	-	-	-	100	100	100	100	100
SiO ₂ (Zn ⁺⁺)	10	10	10	-	-	10	10	10	-	-
SiO ₂ (N)	-	-	-	9	9	-	-	-	9	9
ZnO	-	-	-	1.2	1.2	-	-	-	1.2	1.2
MgO	-	-	0.40	-	-	-	-	0.40	-	-
NA-22	-	0.40	-	-	0.40	-	0.40	-	-	0.40

Table II. Physical Properties and Processing Parameters of the Compounding

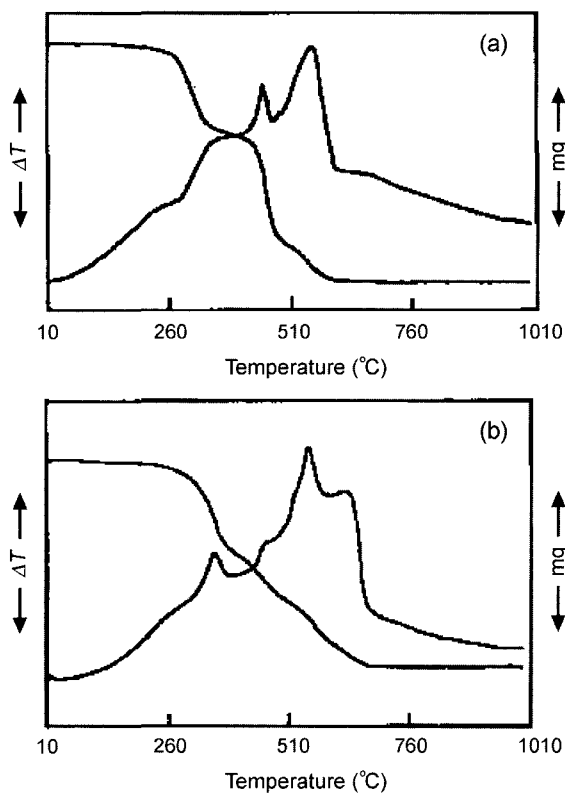
Physical Properties	Mixture Number									
	A	B	C	D	E	F	G	H	I	J
Tensile Strength (kgf/cm ²)	35.0	130.0	48.0	20.0	112.0	22.0	57.0	40.0	16.0	18.5
Modulus (200%) (kgf/cm ²)	16.0	20.0	11.0	8.4	18.2	7.4	15.0	12.0	6.2	8.8
Tear Strength (kgf/cm)	3.0	10.1	2.6	2.2	6.2	2.0	10.8	1.8	1.4	7.9
Elongation at Break (%)	2000	1400	2200	900	750	2200	1500	2000	1200	850
Hardness (Shore-A)	26	41	30	34	54	18	34	20	24	45
T _{max} -T _{min} (dn.m)	13	34	8	6	24	7	29	9.5	3	8.5
Swelling Coefficient	9.1	3.0	10.0	10.6	4.2	6.7	2.5	6.5	6.0	2.9

Table III. DTA/TGA Parameters

Mix. No.	1 st deg. Temp. (°C)	2 nd deg. Temp. (°C)	T_{50} (°C)	% wt. Loss (1 st step)	% wt. Loss (2 nd step)
B	214.7	412.0	447.5	40.0	45.0
C	124.2	410.0	445.0	39.0	42.2
E	158.0	418.0	427.0	42.0	33.0
G	224.2	413.3	436.6	45.0	34.0
H	120.0	403.3	445.0	46.0	25.4
J	212.0	416.0	418.0	31.0	48.0

CR-Zn-ion coated nano silica filler, which is due to the filler and the elastomer interaction.

The thermal stability of the vulcanizate have been studied by DTA/TGA and the results are shown in Table III and Figure 1. As shown from the Table III, the thermal stability of the vulcanizates is enhanced when NA-22 is used as curatives for both the elastomers. The 1st degradation temperatures were shifted towards higher temperature side when NA-22 was used as curatives. However the percent weight loss after the 2nd stage degradation showed the higher loss for NA-22 cure system in the case of both the elastomers. This may be due to some sulfur crosslinks introduced from NA-22. However, it needs more experimentation to conclude the above interpretation.

**Figure 1.** DTA/TGA plots of samples B (a) and G (b).

DSC analysis of the compounds containing only elastomers and nano silica filler with and without Zn-ion coating suggested the interaction between the polar groups (Cl) of CSPE and CR to different extents. In both the cases a wide exotherm was observed having the heat of reaction values as 6.19 and 10.12 J/g for CR-Zn-ion coated nano filler and CSPE Zn-ion coated nano filler suggesting the interactions at the filler surfaces. However without Zn-ion coated nano filler are characterized by an endotherm at comparatively lower temperatures for both the rubbers, which may be due to the elimination of chlorine groups. This is more prominent in the case of CR (at comparatively lower temperature) than that in the case of CSPE may be due to very low content of Cl in CSPE. The DSC results are shown in Table IV and Figure 2. It is quite evident from the Table IV that the onset temperatures of degradations were higher in the case of Zn-ion coated nano silica filler for both the elastomers. The heat of degradation values suggested the lower extent of degradation in the case of Zn-ion containing nano silica filler for polychloroprene rubber. However, for chlorosulfonated polyethylene the degradation mechanism is entirely changed depending on the presence of Zn-ion in the system. When Zn-ion coated nano silica filler is used, the system is characterized by exothermic degradation, when ZnO is added separately in the presence of nano silica filler, the endothermic degradation was observed this suggested the predominant thermal degradation for the later system at comparatively lower temperatures.

In order to understand the failure mechanism the SEM of the tensile fractured surfaces have been shown in Figure 3. Comparing the tensile fractured surfaces of chlorosulphonated polyethylene with two curative systems, the more reinforcing character of Zn-ion coated silica in presence of

Table IV. DSC Parameters

Mix. No	Onset Deg. Temp. (C)	Heat of Deg. (J/g)
B	254.76	-422.56
E	176.00	+151.97
G	334.20	-175.49
J	319.95	-205.23

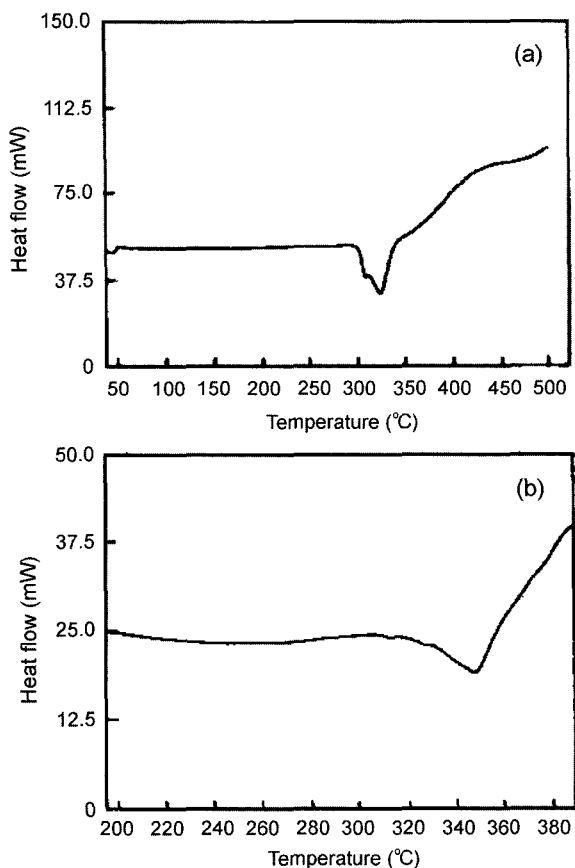


Figure 2. DSC plots of samples B (a) and G (b).

NA-22 has been demonstrated in Figure 3(a, b). More number of crack paths suggests the reinforcing character of the silica.

In the case of polychloroprene elastomer (Figure 3(c, d)) the similar observation holds good. In the presence of Zn-ion coated nano silica filler, the more reinforcing effect gave rise to high modulus and high tensile and tear strength values, however, the matrix flow in the case of both the polymers. Here the ductile failure accompanied by rubber matrix flow is observed in the case of MgO containing vulcanizate. The matrix flow was associated with higher elongation at break and lower technical properties. The fracture mode is changed completely when Na-22 is used as the curative systems. Here again Figure 3(c) the more number of fracture lines are evident although to a lesser extent than that observed in chlorosulphonated polyethylene. When the ZnO is added from outside in the presence of nano filler, both the polymers showed different factograms, lower number of crack paths and matrix flow is observed in the case of chlorosulfonated polyethylene rubber Figure 3(e) resulting lower technical properties with higher swelling value suggesting lower state of cure Table II. However, the Figure 3(f) suggested the smooth rubbery failure with minimum crack path which was associated with lower elongation at break and lower technical properties as compared to the Zn-ion coated nano silica filler compounds.

Conclusions

Zn-ion coated nano silica filler acts as a better reinforcing cum curative than without Zn-ion coated nano silica filler for halogen containing elastomers. This Zn-ion coated nano silica filler improve the thermal stability of the vulcanizates, when NA-22 is used as curative for both the elastomers. Filler-elastomer interaction through Zn-ion on the surface

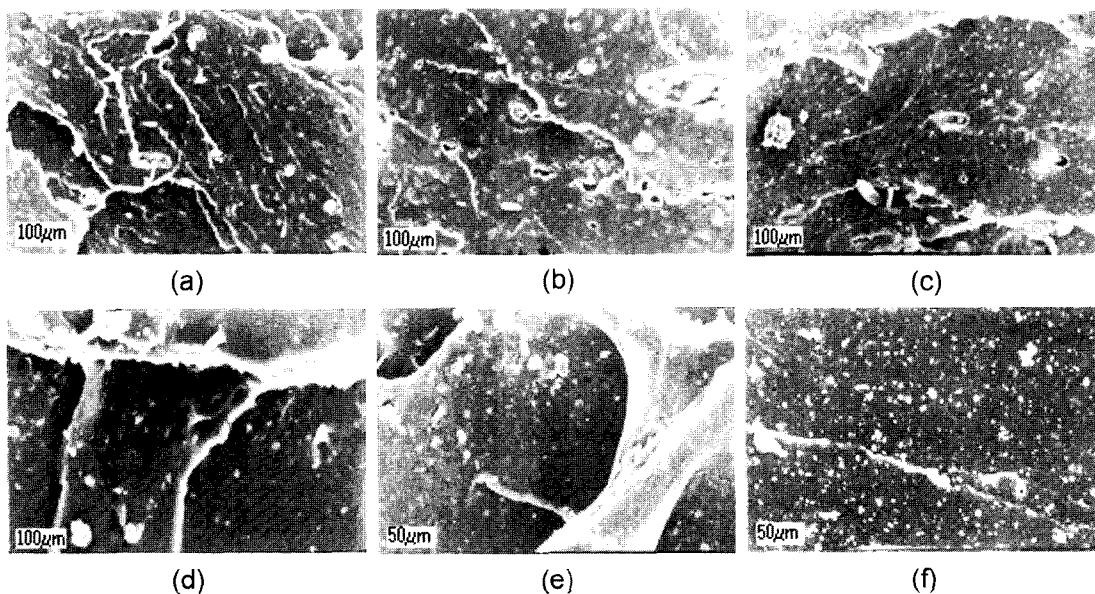


Figure 3. SEM photographs of tensile fractured surface of E (a), J (b), B (c), C (d), G (e), and H (f).

enhanced the technical properties. The curing mechanisms seem to have changed entirely in the presence of Zn-ion coated nano silica filler. Elimination of Cl is probably restricted in the presence of this Zn-ion coated nano filler thus keeping the polar properties of the elastomers intact.

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