HAF/SILICA/NANOCLAY “TERNARY” MASTERBATCH AND HAF/SILICA BINARY MASTERBATCH FROM FRESH NATURAL RUBBER LATEX

SASIDHARAN KRISHNAN,[1,*] ROSAMMA ALEX,[1] THOMAS KURIAN[2]

[1]RUBBER RESEARCH INSTITUTE OF INDIA, KOTTAYAM-686009, KERALA, INDIA
[2]DEPARTMENT OF POLYMER SCIENCE & RUBBER TECHNOLOGY, COCHIN UNIVERSITY OF SCIENCE & TECHNOLOGY, KOCHI-686022, KERALA, INDIA

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ABSTRACT

A process for production of carbon black/silica/nanoclay ternary filler masterbatch from fresh natural rubber (NR) latex was standardized. The fillers, nanoclay, carbon black, and silica were incorporated in fresh NR latex by a modified coagulation process. The latex, mixed with filler dispersions, coagulated immediately on addition of acids. The coagulum containing fillers was dried at 70 °C in an air oven to get the latex filler masterbatch, which was further processed in the conventional way. The masterbatch compounds containing only silica/carbon black showed a higher level of vulcanization as compared with the corresponding dry mixes. The mechanical properties, such as tensile strength, modulus, tear strength, abrasion resistance, and hardness, increased with the proportion of nanoclay in the mixes up to 5 phr, and with a greater amount, the change was only marginal. Lower tan delta values were observed for all of the masterbatches containing nanoclay in the ranges of 3 to 10 phr compared with the control dry mix containing 25/25 carbon black/silica. The improvement in mechanical properties and dynamic properties shown by the masterbatches over the conventional mill-mixed compounds was attributed to factors related to filler dispersion, as evidenced from the data from dispersion analyzer images, X-ray diffractograms, and a higher level of vulcanization. [doi:10.5254/rct.13.87908]

INTRODUCTION

The key factors for reinforcement by fillers such as silica and carbon black are smaller particle size, better polymer–filler interaction, and good dispersion.[1,2] Carbon black has remained the most promising filler in the tire sector. Silica gained importance in the tire sector because of the lower hysteresis possible in the presence of a silane-coupling agent.[3–5] Mixing of carbon black, silica, and nanoclay is a very energy-consuming process and is accompanied by pollution of the surrounding air due to flying of particles into the atmosphere. In the case of silica and nanoclay, it is extremely difficult to disperse these highly aggregate fillers in natural rubber (NR) using a mixing mill. Further lower particle-sized fillers, especially silica, have tendency for filler networking.[6,7] For carbon black, preparation of a latex–carbon black masterbatch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid the problems of mixing filler and to provide vulcanizates with enhanced properties.[8] Masterbatch has been prepared from fresh latex, centrifuged preserved latex, modified latex, and deproteinized latex and prevulcanized latex.[9–11] In most of the processes, coagulation is achieved by high-velocity mixing of filler slurry and latex.[8,12] To be economically viable, fresh NR latex obtained from the field has to be mixed with carbon black slurry, and it is essential to ensure that both latex and the carbon black slurry coagulate simultaneously to avoid loss of filler during coagulation. One of the approaches for the production of a carbon black masterbatch is mixing NR latex with carbon black slurry and then coagulating the mixture chemically. With this process, the coagulation and mixing time were higher.[13] However, the mismatch in the rate of coagulation of fresh field latex and the carbon black slurry led to the poor dispersion of carbon black in the rubber as well as a significant loss of filler during the coagulation, making the process economically unviable. It has been reported that the coagulation time of latex is reduced because of the presence of suitable surfactants.[14,15] When carbon black/silica/nanoclay

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[*]Corresponding author. Email: sasidharan@technologist.com

TABLE I
COMPOSITION OF FRESH NATURAL RUBBER LATEX

Ingredients	Percentage
Rubber	41.5
Protein	2.2
Resin	1.3
Sugar	1.2
Ash	0.8
Water	55.0

filler–incorporated latex is coagulated quickly by the addition of acids, it is expected that the fillers are uniformly distributed in the rubber matrix as compared with conventional coagulation methods. There has been no systematic study on the production of filler batches from fresh NR latex through a quick coagulation process. In this article, an attempt is made to prepare a latex carbon black/silica/nanoclay triple filler masterbatch from fresh NR latex by a modified coagulation process. Incorporation of nanoclay into polymer matrix provides different structures such as conventional, partially intercalated and exfoliated, fully intercalated and dispersed, fully exfoliated and dispersed, and so forth.

EXPERIMENTAL SECTION

MATERIALS

Fresh NR latex used in the study was obtained from the Rubber Research Institute of India, Kottayam (Table I). High abrasion furnace black (N330) was obtained from M/s Phillips Carbon Black Limited (Kochi, India; Table II). Precipitated silica used ULTRASIL VN3 grade obtained from M/s Degussa AG (Essen, Germany; Table III). Cloisite 93A obtained from M/s Southern Clay Products (Austin, TX; Table IV) was used for the study. Other ingredients used were rubber-grade chemicals.

TABLE II
PROPERTIES OF HAF (N330)

Parameter	ASTM	HAF
Iodine number, g/kg	D1510	81.6
DBPA, mL/100 g	D2414	100.5
No. 325 sieve residue, %	D1514	0.048
No. 100 sieve residue, %	D1514	0.003
No. 35 sieve residue, %	D1514	0.0004
Heat loss, %	D1509	0.4
Fines, %	D1508	0.8
Pour density, kg/m^3	D1513	380
Compressed DBP, mL/100 g	D3439	89

TABLE III
SPECIFICATIONS of ULTRASIL VN_3

Parameter	Value
Specific surface area (N_2), m^2/g	175
pH	6.2
Heating loss, %	5.5
Tapped density, g/L	220
SiO_2 content, %	98

PREPARATION OF CARBON BLACK/SILICA/NANOCLAY MASTERBATCHES BY THE QUICK COAGULATION METHOD

Twenty-five percent dispersions of carbon black and silica were prepared separately by the ball milling process for 24 h. Ten percent dispersion of nanoclay was prepared using a mechanical stirrer at 400 rpm for 15 min. The dispersion was added slowly to the fresh NR latex and coagulated by adding suitable coagulants in the required proportion to produce the mixed filler masterbatch (Scheme 1). Filler–latex dispersion is coagulated chemically almost immediately after addition of suitable coagulant. The coagulation behavior was similar to that of conventional NR latex concentrates. The coagulation time varied from about 3 to 5 s after addition of the required quantity of coagulants, as reported earlier.[15] It is proposed that the change in coagulation behavior of fresh latex is due to a change in the latex colloid stabilization system. Along with proteins, the surfactants of the latex–filler dispersion system also provide colloidal stability.

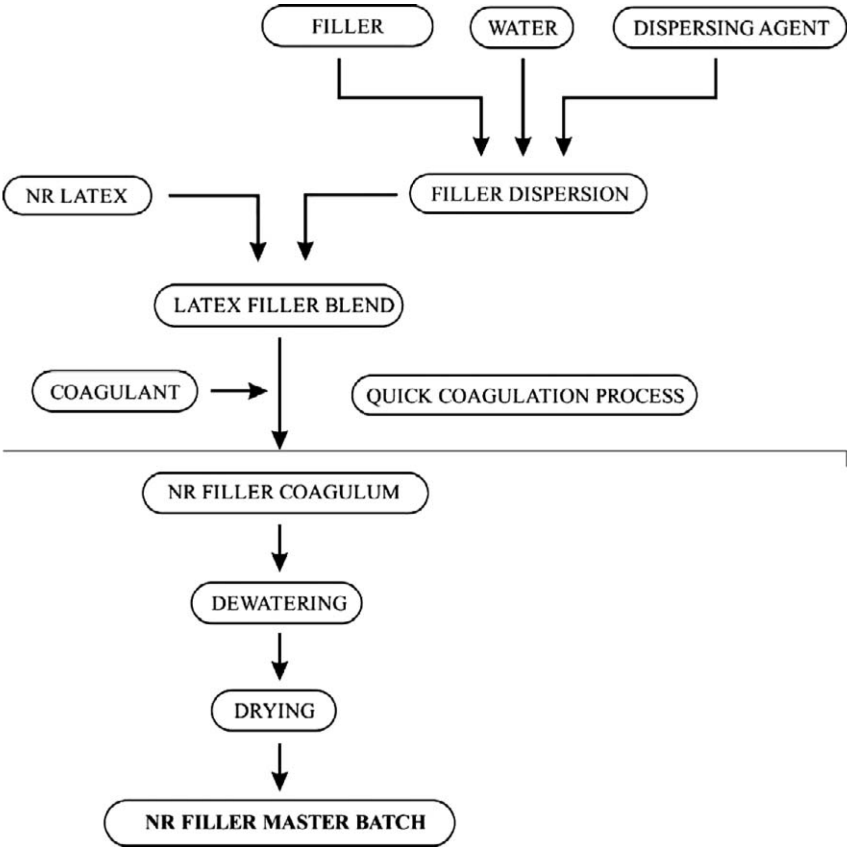
Because the modified coagulation ensured the simultaneous coagulation of latex and filler slurry, there was a practically negligible or no loss of filler during coagulation. The coagulum was washed well to remove the acid and dried in an air oven maintained at 70 °C. The fillers were incorporated in latex so as to have levels of 50 to 60 parts per hundred of dry rubber (phr). The dried masterbatch and control were mixed as per formulations given Tables Va and Vb by using a two-roll mixing mill, and vulcanizates were prepared by using a hydraulic press at 150 °C for the optimum cure time.

The particle size of filler dispersions and latex was determined using a particle size analyzer model Nanosizer (Malvern, Worcestershire, UK), based on the dynamic light-scattering technique. The cure behavior was determined at 150 °C using a moving die rheometer model MDR2000 from ALPHA Technologies (Akron, OH). The mechanical

TABLE IV
SPECIFICATIONS OF CLOISITE 93A (NATURAL MONTMORILLONITE MODIFIED WITH A TERNARY AMMONIUM SALT)

Treatment/properties	Organic modifier[a]	Modifier concentration	% Moisture	% Weight loss on ignition
Cloisite 93A	M2HT	95 mEq/100 g clay	<2	39.5
Dry particle sizes (μm, by volume), 10% less than 2 μm, 50% less than 6 μm, 90% less than 13 μm				
Density	Loose bulk, g/mL = 0.17	Packed bulk, g/mL = 0.29	Density, g/mL = 1.88	

[a] M2HT, methyl, dihydrogenatedtallow ammonium.



SCHEME 1. — Flow chart showing production of latex-filler masterbatch.

properties and the aging tests were determined using relevant ASTM standards. The dynamic properties were determined using a dynamic mechanical analyzer (model 01 dB DMA 50N, Metravib, Lyon, France). The test was conducted at a frequency of 10 Hz and dynamic strain of 0.12%. Filler dispersion was studied on vulcanized films using the dispersion analyzer from Tech Pro (Roseville, MN). Thermogravimetric analysis (TGA) of the samples was recorded using a thermogravimetric analyzer (TGA 4000, PerkinElmer, Inc., Waltham, MA). Approximately 5 mg of samples was heated at a rate of 20 °C/min from +50 to +550 °C. The Mooney viscosities were measured using a Mooney Viscometer (Mooney MV 2000, ALPHA Technologies), which is designed for measuring the shearing viscosity of polymers and compounds by a disc in a cylindrical cavity set at 100 °C as per ASTM D1646 (2007). The results of samples were expressed ML (1 + 4) at 100 °C. The X-ray diffraction analysis (XRD) was used to determine the interspatial distance between the clay platelets. The XRD patterns were obtained by a D500 diffractometer (Siemens, München, Germany) using Ni-filtered Cu K_α radiation ($\lambda = 0.1542$ nm).Volume fraction of rubber in toluene was swollen as per standard procedure using the following equation[16]:

$$V_r = \frac{(D - FT)\rho r^{-1}}{(D - FT)\rho r^{-1} + Ao\rho s^{-1}} \tag{1}$$

Table Va
FORMULATION OF THE MIXES FOR THE MASTERBATCH[a]

Ingredient	Quantity
Masterbatch[b]	100
Zinc oxide	5
Stearic acid	1.5
HS	1
HAF/silica/nanoclay	25/25, 30/30, 25/25/3, 25/25/5, 25/25/10
DEG	1
MBTS	1.0
DPG	0.2
Sulphur	2.5

[a] HS, 2.2.4-trimethyl-1,2-dihydroquinoline; DEG, diethylene glycol; MBTS, mercapto benzothiazole disulphide; DPG, diphenyl guanidine.
[b] Excluding.

where *T* is the weight of the test specimen, *D* is its deswollen weight, *F* is the weight fraction of insoluble component, *Ao* is the weight of the absorbed solvent corrected for the swelling increment, and ρ_r and ρ_s are the densities of rubber and solvent, respectively.

RESULTS AND DISCUSSION

COAGULATION CHARACTERISTICS

The particle size distribution of dispersions of nanoclay, carbon black, and silica are shown in Figure 1a–c. The particle size of carbon black varies from 150 nm to 290 nm and that of silica varies

TABLE Vb
FORMULATION OF THE MIXES FOR THE DRY MIX[a]

Ingredient	Quantity
Natural rubber (sheet 1X)	100
ZnO	5
Stearic acid	1.5
HS	1
HAF/silica/ nanoclay	25/25/0.25/25/3, 30/30/0
DEG	1
MBTS	1.0
DPG	0.2
Sulphur	2.5

[a] HS, 2.2.4-trimethyl-1,2-dihydroquinoline; DEG, diethylene glycol; MBTS, mercapto benzothiazole disulphide; DPG, diphenyl guanidine.

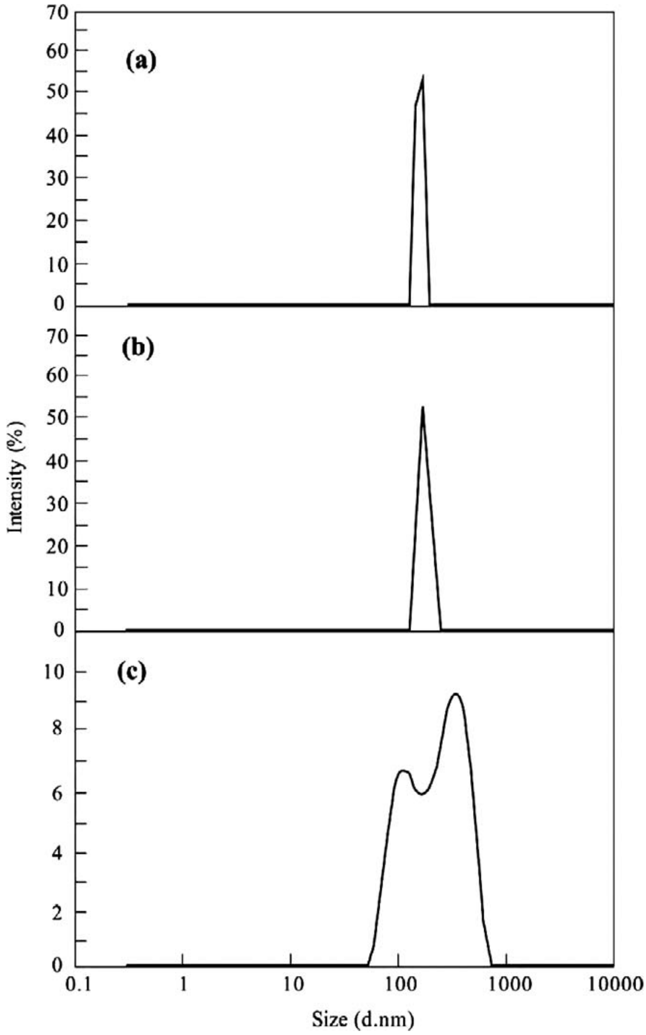


FIG. 1. — Particle size distribution of dispersions of (a) carbon black, (b) silica, and (c) nanoclay.

from 150 to 220 nm. Nanoclay dispersion has wide variation in particle size. The size varies from 70 to 700 nm. It is expected that when these dispersions are added to latex, they will mix uniformly with latex as the particle size of dispersions is comparatively low. Filler dispersion–fresh latex mixture coagulated immediately upon addition of acid, leaving an almost clear serum, as shown in Figure 2. There are earlier reports that proteins adsorbed on latex adversely affect the polymer–filler interaction and need to be removed while producing masterbatches.[17] In the presence of added surfactants, there is a displacement of proteins from the rubber–particle surface, which makes the latex more sensitive to coagulation and helps in better dispersion of fillers. On addition of acids to surfactant containing latex, the latex becomes more sensitive to coagulation by acids. As a consequence, the latex coagulates immediately.[14,18] Due to quick coagulation, it is expected that the uniformly mixed fillers remain unaggregated during coagulation and further processing.

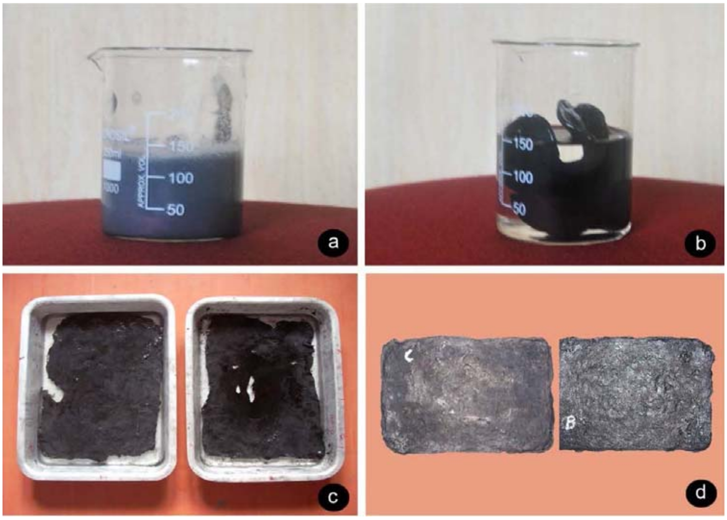


FIG. 2. — Preparation of masterbatch using quick coagulation and dried samples (a) latex-fillers dispersion, (b) masterbatch coagulum, (c) more quantity of masterbatch coagulum after coagulation, (d) dried masterbatches.

VULCANIZATION CHARACTERISTICS

The vulcanization characteristics are shown in Table VI. The cure time and scorch time were comparable for masterbatch and control mixes. The incorporation of clay did not adversely affect cure characteristics such as cure time and scorch time. The masterbatch mixes containing 25/25 and 30/30 carbon black/silica fillers (M1 and M5) recorded higher rheometric torque compared with the corresponding dry mixes (C1 and C5). The masterbatch mixes containing nanoclay (M2, M3, and M4) recorded higher rheometric torque compared with dry mixes that contain only carbon black/silica. During the preparation of masterbatches, the filler–latex mixture co-coagulates along with a portion of the surfactant that got converted into the corresponding fatty acid. This helps in better vulcanization characteristics of rubber, as fatty acids are activators of vulcanization.[19]

TABLE VI
VULCANIZATION CHARACTERISTICS AT 150 °C

	Latex masterbatch					Dry mill mix		
Carbon black/ silica/nanoclay	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
Torque max, dNm	22.67	23.04	25.33	25.54	24.10	21.03	22.40	21.40
Torque min, dNm	2.43	2.41	2.84	2.08	2.20	2.39	2.34	2.18
Optimum cure time t_{90}, min	9.39	9.0	9.01	9.19	5.40	9.06	8.85	6.27
Scorch time, ts_2, min	1.41	2.13	2.04	2.02	1.09	2.06	1.98	1.19
Volume fraction, Vr	0.2905	0.2915	0.2990	0.3140	0.3308	0.2845	0.2884	0.3120

TABLE VII
MOONEY VISCOSITY OF THE MASTERBATCHES AND RUBBER

	Latex Masterbatch				
Parameter	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)
Mooney viscosity, ML(1+4) at 100 °C	110	112	115	120	116

MOONEY VISCOSITY

The Mooney viscosity of the masterbatch after drying was measured using the Mooney viscometer, and the data are provided in Table VII. The masterbatches recorded a higher Mooney viscosity than pure, raw NR. An earlier report shows that the masterbatch has a high viscosity relative to pure rubber.[3] However, the Mooney viscosity of the masterbatch is not as high as expected. It is assumed that because of the presence of fatty acid soap in the masterbatch, there is good filler dispersion and comparatively low Mooney viscosity by lubrication at the molecular level. Fatty acid soaps have been shown to improve the process ability of NR compounds.[20]

FILLER DISPERSION CHARACTERISTICS

DisperGrader. — The filler dispersion images are presented in Figure 3 and rated in Table VIII. Comparatively better dispersion and lower aggregation are shown by masterbatch vulcanizate as compared with mill-mixed vulcanizate.

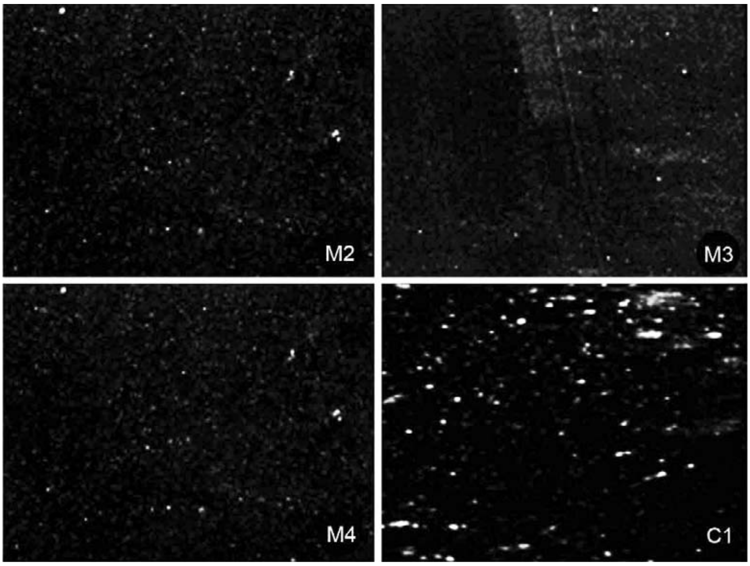


FIG. 3. — Dispersion image rating for masterbatch and dry mix.

TABLE VIII
RESULTS OF DISPERSION RATING

Sample name	Dispersion (X)	Agglomerate dispersion (Y)
25/25/3 Masterbatch (M2)	9.2	9.5
25/25/5 Masterbatch (M3)	9.8	9.9
25/25/10 Masterbatch (M4)	8.7	9.4
25/25/0 Dry mix (C1)	7.0	7.8

X-ray diffraction. — The XRD patterns of carbon black/silica/nanoclay masterbatches are shown in Figure 4 XRD patterns of Cloisite 93A containing a sharp peak at $2\theta = 3.697°$, corresponding to a basal spacing of 23.88Å. This peak is shifted to a lower 2θ angle 2.809°, suggesting that a basal spacing corresponds to the clay basal spacing of 31.43Å. The above result implies that the Cloisite 93A is an intercalated structure in the masterbatch. The characteristic XRD peak of the clay cannot be seen in samples M2 and M3. It might be possible that the clays are exfoliated in the nanocomposite membranes. Latex stage incorporation of nanoclay had been found to be beneficial in enhancing the mechanical properties of NR.[21] Exfoliated nanocomposites exhibit better properties owing to the maximum polymer–filler interaction. In the exfoliated structure, the entire surfaces of the layers are available for the interactions with the polymer.

MECHANICAL PROPERTIES

The HAF/Silica/nanoclay "ternary" masterbatch showed significantly improved properties such as modulus, tear strength, abrasion resistance, and heat buildup (Table IX). Thus, at comparable filler loading, addition of nanoclay (3–10 phr) showed lower abrasion loss, lower heat buildup, higher hardness, higher tear strength, higher modulus, lower elongation at break, and higher tensile strength when compared with the conventional mill-mixed compound containing

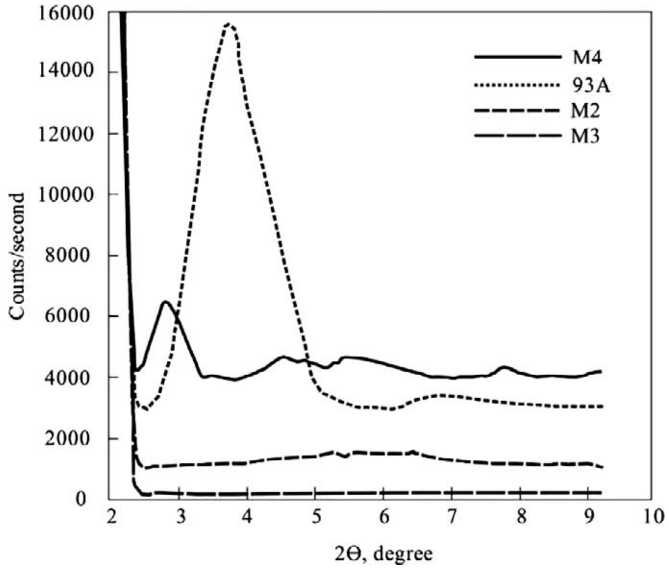


FIG. 4. — X-ray diffraction patterns of masterbatches and nanoclay (Cloisite 93A).

TABLE IX
COMPARISON OF MECHANICAL PROPERTIES OF THE MASTERBATCH AND DRY MILL MIX

	Latex Masterbatch				Dry Mill Mix			
Parameter	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
300% Modulus, MPa	10.80	11.69	14.85	12.10	14.80	7.20	10.25	12.70
Tensile strength, MPa	25.30	25.74	25.85	25.40	25.60	24.50	24.80	24.70
Elongation at break, %	570	553	471	527	460	620	580	484
Tear strength, kN/m	103	105	106	104	105	88	89	95
Hardness, Shore A	66	68	74	70	68	58	60	64
Heat buildup, ΔT, °C	16	13	16	16	17	21	20	22
Abrasion loss, mm^3	107	97	87	92	113	143	126	132

carbon black and silica. The 5 phr nanoclay incorporated vulcanizate showed elongation at break 471% and modulus at 300% 14.85 MPa. The 10 and 3 phr nanoclay incorporated vulcanizate showed elongation at break 527% and 553% and modulus at 300%, 12.1 and 11.69. The specific surface area is one of the reasons why the reinforcement imparted by these materials in rubber vulcanizates, even at very low filler loading (<10 phr), is very high.[22] In rubber vulcanizates, the properties are dictated by the bulk properties of both matrix and filler. The interaction between the filler particles and the polymer decides the stiffening of the vulcanizates. In the case of the rubber vulcanizates filled with nanofillers, the polymer–filler interaction is concentrated at the interface. Terms such as *bound polymer* and *interface* have been used to describe the polymer at or near the interface. The interfacial structure is known to be different from the bulk structure, and in polymers filled with nanofillers possessing extremely high specific surface area, most of the polymer is present near the interface, despite the small weight fraction of filler. If the interaction at the interface is a strong one, or if the structure of the interfacial polymer is very different from the bulk, markedly different properties in the material as a whole can be observed. The changes have a fundamentally different origin than those found in the rubber vulcanizates filled with conventional fillers.[3,23] The mechanical properties obtained after aging the samples at100 °C/3 days are given in Table X. The masterbatch mixes showed a higher tensile strength and modulus compared with conventional mixes. The enhancement in mechanical properties and aging behaviors is attributed to the better filler dispersion along with higher level of cross-linking.

TABLE X
COMPARISON OF MECHANICAL PROPERTIES OF THE MASTERBATCH AND DRY MILL MIX AFTER AGING (100 °C FOR 3 DAYS)

	Latex Masterbatch				Dry Mill Mix			
Parameter	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
300% Modulus, MPa	11.58	12.46	16.0	14.07	15.8	10.55	12.50	14.5
Tensile strength, MPa	22.0	24.28	23.8	23.9	23.5	21.78	22.80	23.0
Elongation at break, %	525	541	415	472	445	590	480	412

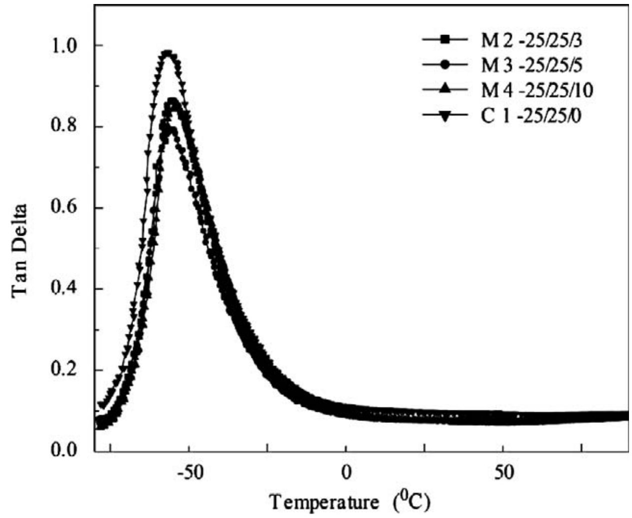


FIG. 5. — Damping characteristics of masterbatch and control mix containing carbon black/silica/nanoclay (M2, M3, M4, and C1).

DYNAMIC MECHANICAL ANALYSIS

Damping characteristics from –90 °C to +100 °C for the trifiller masterbatch and control mixes containing 50 phr fillers are given in Figure 5. The plots of storage modulus versus temperature and loss modulus for the masterbatches and control mix are shown in Figure 6 and Figure 7. For the masterbatch mix, there is a lowering of tan delta peak height compared with the control mix,

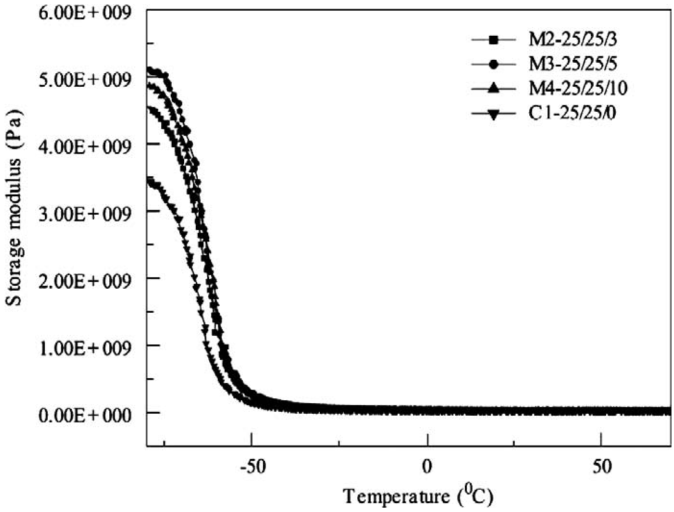


FIG. 6. — Storage modulus of masterbatch and control mix containing carbon black/silica/nanoclay (M2, M3, M4, and C1).

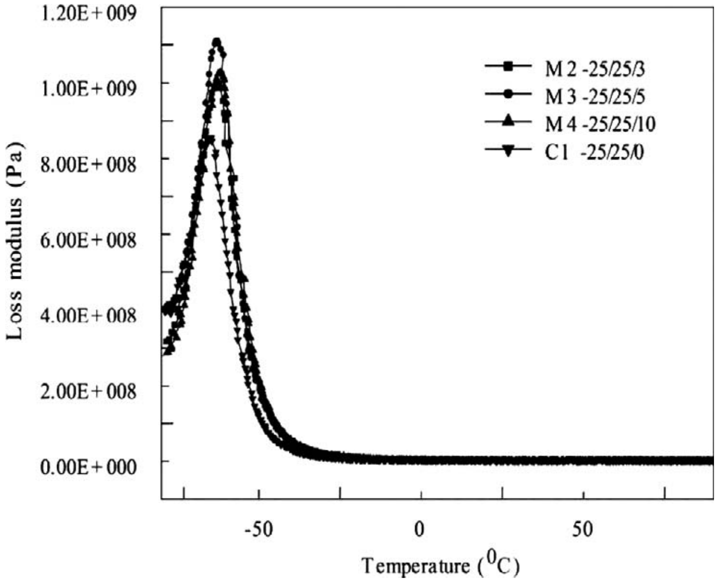


FIG. 7. — Loss modulus of masterbatch and control mix containing carbon black/silica/nanoclay (M2, M3, M4, and C1).

showing that there is better polymer–filler interaction for the masterbatch than the control mix. Within the three doses of nanoclay, the mix containing trifiller in the proportion of 25/25/5 silica/carbon black/nanofiller showed the lowest peak height. However, at higher loading, the tan delta peak height increases, but it is lower than the dual-filler dry mix system. The storage modulus and loss modulus are also higher for the masterbatch mixes compared with the control. This is in line with the observations on the tensile properties. The ideal filler for tire tread compounds are those that possess high polymer–filler and low filler–filler interactions. The former ensures higher

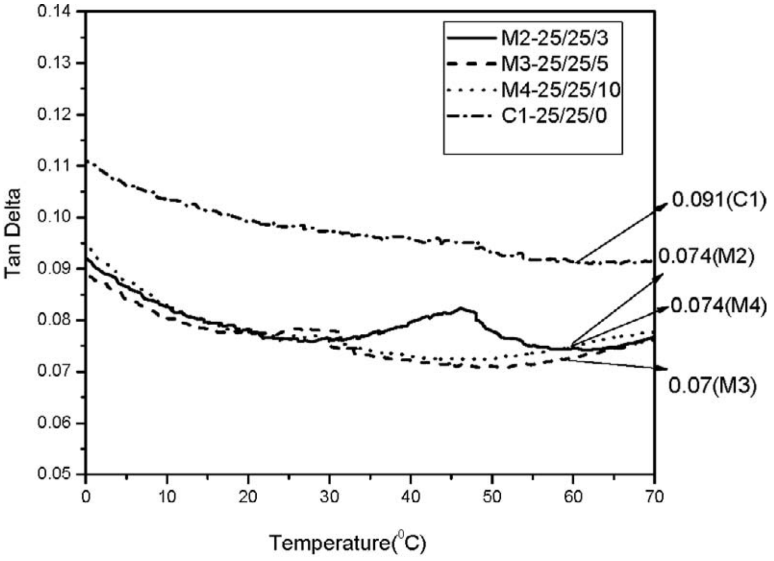


FIG. 8. —Tan delta at 60 °C of masterbatch and control mix containing carbon black/silica/nanoclay (M2, M3, M4, and C1).

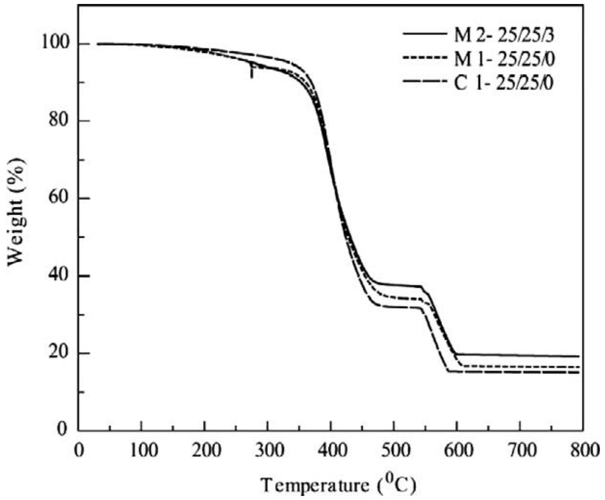


FIG. 9. — Thermogravimetric analysis: thermogram of masterbatches and dry mix (M1, M2, and C1).

abrasion resistance, and the latter is necessary for lower rolling resistance or lower tan delta.[24–26] The tan delta values for the masterbatch and control 60 °C are shown in Figure 8. It is observed that a lower tan delta at 60 °C is obtained for the masterbatch compared with the control, showing a lower rolling resistance for the masterbatch.

THERMOGRAVIMETRIC ANALYSIS

The thermograms of the masterbatch and the conventionally prepared mix, recorded on a thermogravimetric analyzer, are given in Figure 9 and the data in Table XI. Although the peak decomposition temperature for the nanoclay compound (M2) is a bit less than that of the masterbatch (M1), the percentage retention is greater here. That is, the rate of decomposition is slower in the nanoclay vulcanizate. This is further supported by the fact that the final dissociation temperature (also time) for the nanoclay vulcanizate is more than that of masterbatch M1 and control C1.

CONCLUSION

A novel method of preparing NR-based masterbatch containing a carbon black/silica/nanoclay trifiller system from fresh NR latex is described. The vulcanizate properties of the nanoclay

TABLE XI
DATA FROM THERMOGRAVIMETRIC ANALYZER FOR CARBON BLACK/SILICA/NANOCLAY MASTERBATCH AND DRY MILL MIX

Sample	Final decomposition temperature, °C	Time for full decomposition, min	Peak decomposition temperature, °C	% Retention
Masterbatch 25/25/3 (M2)	436	65.7	396.14	70.50
Masterbatch 25/25 (M1)	432	64	401.34	68.13
Dry mix 25/25 (C1)	432	63.8	401.34	68.07

containing masterbatches prepared by latex stage mixing showed excellent improvement in abrasion resistance, lowering of heat buildup, and lower tan delta at 60 °C as compared with a conventional mill mixing. These compounds can be used to manufacture tire treads with better fuel efficiency and improved wear resistance.

ACKNOWLEDGEMENTS

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