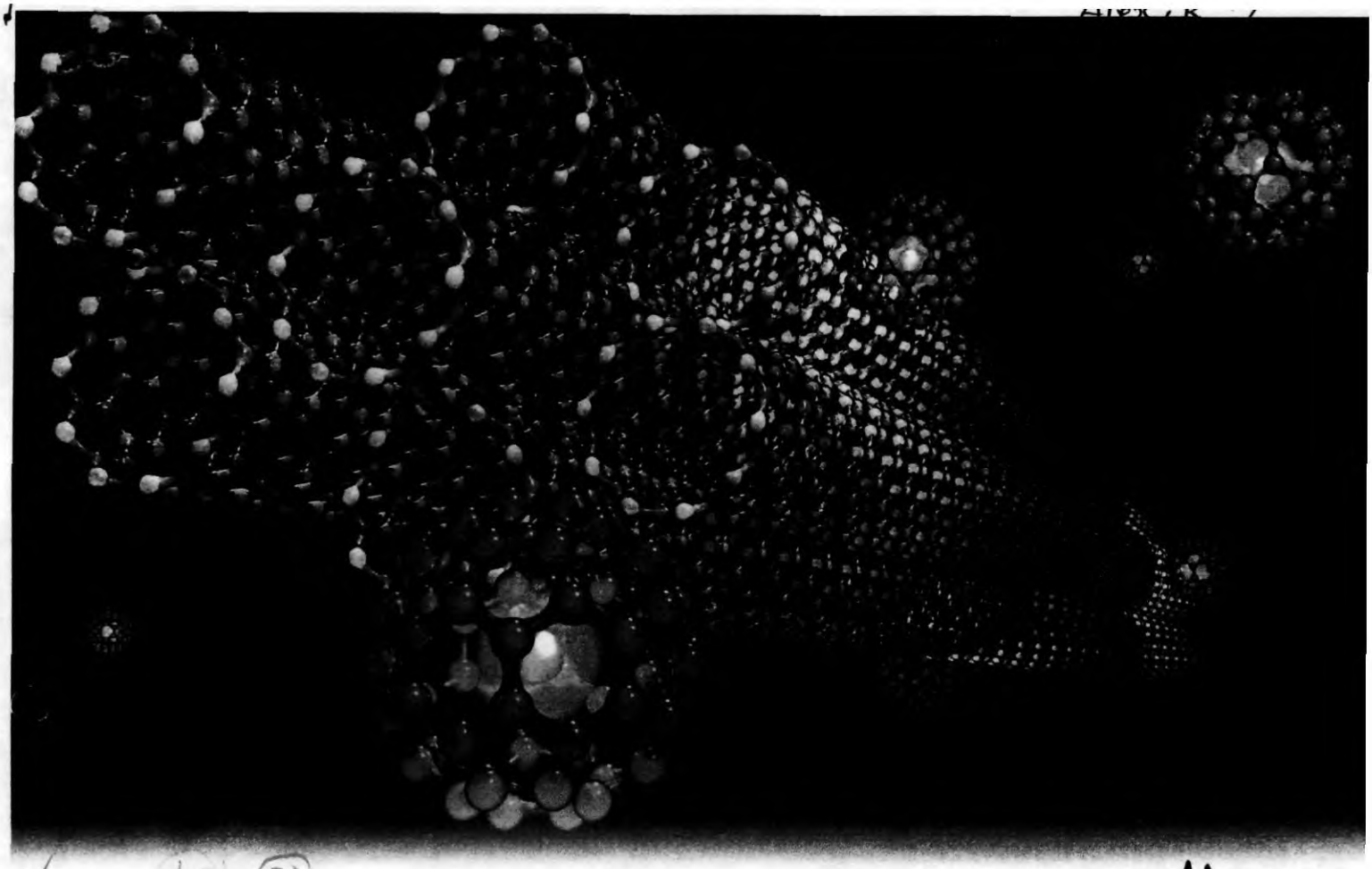

Carbon Black/Silica Master Batch From Fresh Natural Rubber Latex

Rosamma Alex[a], K.K Sasidharan[a] and Thomas Kurian[b] Arup Kumar Chandra[c]

A new process for production of carbon black/silica master batches with enhanced mechanical properties has been developed. The unit operations in the process are the preparation of filler dispersion, in presence of suitable surfactant, addition of the dispersion to the fresh natural rubber latex under stirring, coagulation of the mixture by the addition of acid, dewatering of the coagulum, and drying to obtain filler incorporated NR. Mixed filler containing master batch prepared by the new process showed good cure characteristics as compared to the dry rubber incorporated mix. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness were superior for the vulcanizates prepared by the new method. The heat build – up values were considerably low for the latex filler master batches. Comparatively better ageing resistance was also recorded by these vulcanizates. The improvement in mechanical properties shown by the silica/carbon black master batches over the conventional mill mixed compounds was attributed to better filler dispersion evidenced from the result of filler dispersion data.

INTRODUCTION

The level of dispersion of fillers like carbon black and silica in a rubber matrix is an important issue in a large variety of rubber products [1]. Further, there are issues such as air pollution and higher energy consumption when incorporated in dry rubber. During the conventional mixing process silica is highly aggregated due to filler-filler interaction resulting in a dispersion which is not favorable for reinforcement [2]. In the case of carbon black, production of latex-carbon black master batch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid some of these problems. [3,4]. One of the approaches for production of carbon black master batch was by mixing NR latex with carbon black slurry and then coagulating the mixture chemically. With this process the coagulation and mixing time were higher [5].

It has been reported that the coagulation time of latex is reduced due to presence of suitable surfactants [6]. When carbon black and silica filler incorporated latex is coagulated quickly by addition of acids it is expected that the fillers are uniformly distributed in rubber matrix as compared to conventional coagulation methods. There has been no systematic study on the production of filler batches from fresh natural rubber latex through a quick coagulation process. In this paper an attempt is made to prepare latex carbon black/silica dual filler master batch from fresh NR latex by a modified coagulation process.

Experimental

Fresh natural rubber latex used in the study was obtained from the Rubber Research Institute of India, Kottayam. High abrasion furnace black (N330) was obtained from M/s. Phillips Carbon Black Limited, Kochi, India. Precipitated silica used was ULTRSIL VN3. Other ingredients used were rubber grade chemicals. The surfactant used was based on alkali salts of fatty acids.

Preparation of carbon black master batches by quick coagulation method.

Dispersions of carbon black and silica were prepared separately by the conventional ball milling process in presence of a suitable surfactant. The dispersion was added slowly in to fresh natural rubber latex under stirring and coagulated by addition of acid to produce the filler master batch. In this new method the filler latex mixture is coagulated chemically almost immediately after addition of acids.

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 40-50 parts per hundred parts of dry rubber (phr). The dried rubber was mixed as per formulation given Tables 1a and 1b, and vulcanized by conventional methods. A control mix with loadings of 40 phr and 50 phr fillers added by conventional mill mixing process was also prepared. The cure behavior was determined using moving die rheometer Monsanto (MDR2000) at 150°C. The particle size of filler dispersion and latex was determined based on dynamic light scattering technique, using a Malvern Nanosizer, U.K. Filler dispersion was studied on vulcanized films using Dispersion Analyser from Tech Pro USA. The Mechanical properties the ageing tests were determined from relevant ASTM standards.

Results & Discussion

Coagulation Characteristics

The particle size distribution of carbon black dispersion, silica dispersion and latex-filler mixture is shown in Figures 1a 1b and 1c. Both silica and carbon black dispersions contains filler particles that have comparatively lower size (average 100 nm). The particle size of fresh NR latex-carbon black slurry mixture varies from about 90-6000nm. This shows that after addition fillers to latex the size of filler particles increased to a small extend due to a certain degree of aggregation. However it is expected that there is uniform mixing of filler in the latex stage.

Filler dispersion-fresh latex mixture coagulated immediately on addition of acid leaving a clear serum. On addition of surfactants to latex they cause displacement of protein and get strongly absorbed on rubber particles. In this way the protein stabilized latex gets transformed into a surfactant stabilized system. On addition of acids to surfactant containing latex the absorbed anions react with acid to form un-dissociated surfactant, and deprive the latex particles of stabilizers. As a consequence, latex coagulates immediately [6] Due to quick coagulation it is expected that the uniformly mixed carbon black remains unaggregated during coagulation and further processing.

Vulcanization Characteristics

The cure characteristics are shown in Tables 2a and 2b. In the master batch mixes containing 40 phr of silica/carbon black dual fillers a comparatively higher torque is recorded when the carbon black content is higher. In the same filler loading the master batch recorded a higher rheometric torque and lower cure time as compared to dry rubber mixed one showing higher levels of vulcanization at 40 phr and 50 phr concentrations of fillers. For pure silica system a lower minimum torque and lower scorch time is recorded for the master batch as compared to mill mixed one. When surfactant (fatty acid soap) is added to latex it disperses uniformly in latex due to absorption on rubber particles. During coagulation the surfactant gets converted into the corresponding fatty acid. This helps in better vulcanization characterizes of rubber as fatty acids are activators of vulcanization [7].

Mechanical Properties

The vulcanizates prepared from master batches by the new method showed higher tensile strength higher modulus, hardness, tear strength along with lower heat build-up and abrasion loss. (Tables 3a and 3b). The improvement in mechanical properties is attributed to better filler dispersion and higher level of vulcanization. The filler dispersion characteristics are presented in Figure 2a and 2b. Comparatively better dispersion and lower aggregation is shown by master batch mix as compared to mill mixed one.

The mechanical properties obtained after ageing the samples at 100°C/3days are given in Table 4. The master batch mixes showed a higher tensile strength and modulus compared to conventional mixes. The enchancement in mechanical properties and ageing behaviors is attributed due to better filler dispersion along with higher level of cross linking [8].

Conclusion

A uniformly mixed filler dispersion and latex in presence of suitable surfactant coagulates quickly an addition of acids. The filler master batch prepared by this new method shows enhanced cure characteristics, filler dispersion and superior mechanical properties as compared to conventionally prepared mixes. This is a simpler and cheaper method of master batch preparation as compared to the earlier methods.

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Table 1a Formulation of the mixes for the master batch

Ingredient	Quantity
NR filer master batch *	100
ZnO	5
Stearic Acid	1.5
HS **	1
MBTS ***	1.0
DPG ****	0.2
Sulphur	2.5

* excluding filler
** 2.2.4-tri methyl – 1,2-dihydroquinoline
*** Mercapto benzothiazole disulphide
**** Diphenyl guanidine

Table 1b Formulation of the mixes for the control mixes	
Ingredient	**Quantity**
NR	100
ZnO	5
Stearic Acid	1.5
HS	1
HAF Black/silica	10/30,0/40,25/25,30/30
DEG [a]	1
MBTS ***	1.0
DPG ****	0.2
Sulphur	2.5

[a] Diethylene glycol

Table 2a Cure characteristics at 150°C of mixes with 40 phr fillers

Parameters	Master batch (Silica/carbon black)				Mill mixed (Control) Silica/carbon black	
	10/30	20/20	30/10	40/0	10/30	40/0
Torque Max, dNm	19.44	20.01	17.06	23.51	14.96	18.98
Torque Min, dNm	1.68	1.63	0.81	1.47	1.08	3.89
Optimum cure time t_{90}, minutes	6.19	7.31	6.51	7.0	6.47	8.54
Scorch time, ts_2, minutes	1.0	1.29	1.38	1.39	1.01	2.08

Table 2b Cure characteristics at 150°C of mixes with 50 phr fillers		
Parameters	Masterbatch	Mill mixed
Silica/carbon black	25/25	25/25
Torque Max, dNm	22.67	21.03
Torque Min, dNm	2.43	2.39
Optimum cure time, t_{90} minutes	9.39	9.06
Scorch time, ts_2, minutes	1.41	2.06

Table 3a Mechanical properties of the mixes with 40 phr fillers

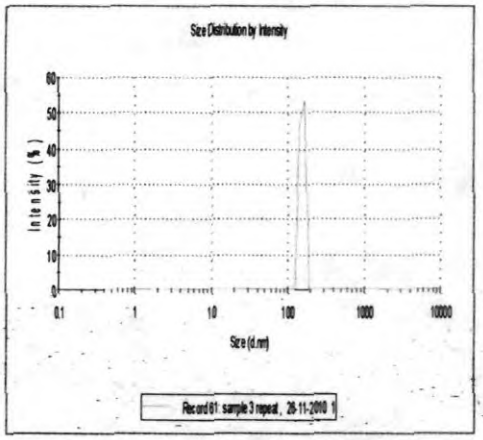
Parameters	Master batch				Mill mixed (Control)	
Silica/ carbon black	10/30	20/20	30/10	40/0	10/30	40/0
Modulus 300%, MPa	17.5	14.03	7.0	4.22	10.8	3.0
Tensile strength, MPa	27.6	28.2	30.6	27.6	26.6	21.5
Elongation at break, %	400	560	550	7.0	550	8.54
Tear Strength, kN/m	86.9	70.7	75	70	80.8	53
Hardness, Shore A	68	64	58	58	58	54
Heat Build-up,ΔT,°C	14	13	10	12	17	18
Abrasion loss, mm^3/h	98	118	140	153	110	270

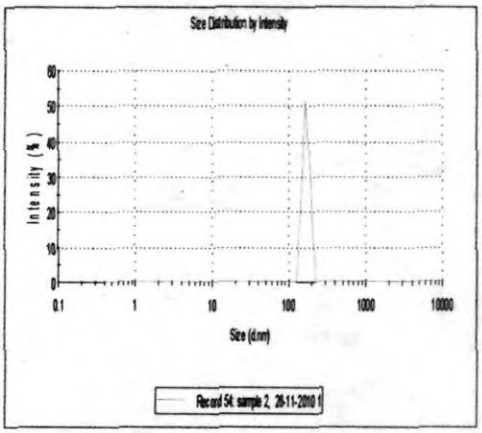
Table 3b Mechanical properties of the mixes with 50 phr fillers

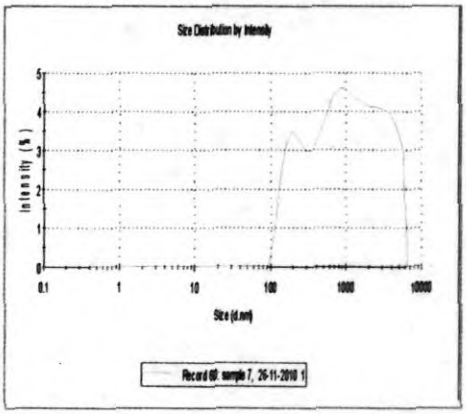
Parameters	Master batch	Mill mixed
Silica/carbon black	25/25	25/25
Modulus 300%, MPa	10.8	7.2
Tensile strength, MPa	27.3	24.5
Elongation at break, %	570	620
Tear Strength, kN/m	103	88
Hardness, Shore A	66	58
Heat Build-up,ΔT,°C	16	21
Din abrasion loss, mm^3/h	107	143

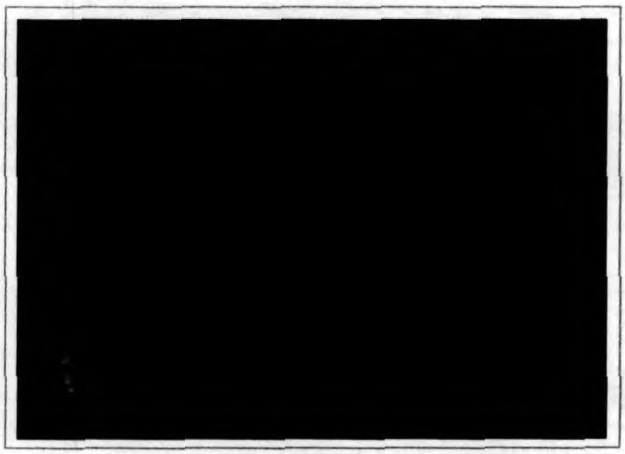
Table 4 Mechanical properties of the vulcanizates after ageing at 100°C for 3 days								
Parameters	Master batch					Mill mixed (Control)		
Silica/carbon black	10/30	20/20	30/10	40/0	25/25	10/30	25/25	40/0
Modulus 300%, MPa	16.6	10.9	6.25	5.6	8.58	10.5	6.85	3.0
Elongation at break, %	336	480	520	600	525	510	590	650
Tensile strength, MPa	21.3	22.3	26.7	23	24.5	22.6	21.6	15

Fig 1. Particle size of (a) carbon black in the carbon black dispersion (b) silica in the silica dispersion, (c) rubber particles and dispersions of carbon black and silica (20/20) in latex-filler mixture.

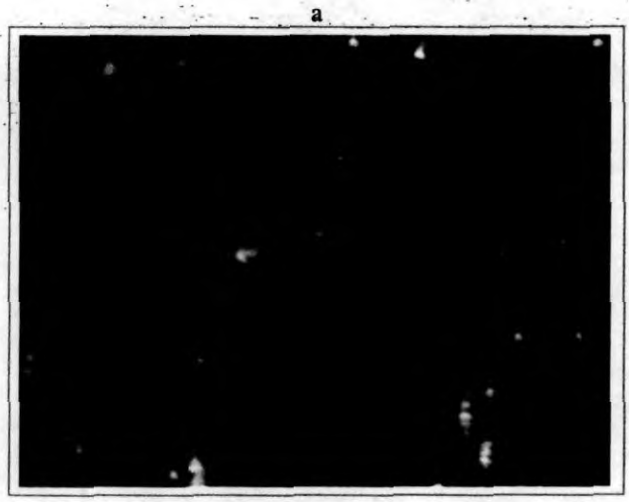








a



b

Figure 2. Dispersion rating 25/25 silica/carbon black mixes.

a. Master batch X = 8.8 Y = 9.3

b. Mill mixed X = 7 Y = 9.2

(Y = 10 denotes no agglomerate) X denotes filler dispersion and Y denotes agglomerate dispersion. Particles above 23 microns is considered as an aggregate0

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