939

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A METHOD FOR PRODUCING CARBON BLACK SILICA MASTER BATCH

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ABSTRACT

A method for production of carbon black/silica master batches through a modified coagulation technique of filler latex mixture that gives vulcanized with enhanced mechanical properties has been developed. The carbon black used was of Super Abrasion Furnace (SAF) and Intermediate Super Abrasion Furnace (ISAF) grades. Though they are expected to give enhanced mechanical properties like modulus tensile strength and abrasion resistance generally these properties are not fully realized as it is difficult to disperse these grades of carbon black due to the very small particle size being in the nano range. Further it is very difficult to disperse silica because compared to carbon black, with similar surface area and structure, silica shows a very low polymer- filler interaction and there is a strong tendency to agglomerate (without suitable filler modification or use of coupling agent) due to filler –filler interactions.

The method consists of 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. The filler-latex mixture coagulated immediately on addition of acids. Mixed filler containing master batch prepared by this method showed better 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 lower 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/SAF carbon black master batch or silica/ISAF carbon black master batches over the conventional mill mixed compounds (in the absence of any coupling agent) was attributed to better filler dispersion as evidenced from the result of filler dispersion data and enhanced level of vulcanization.

The filler master batch prepared by this method showed enhanced cure characteristic, 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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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) These fillers cause a considerable change in the dynamic mechanical properties, both modulus and hysteresis in rubber vulcanizates. Further, the fine dust of carbon black pollutes the air and the surroundings. Incorporation of carbon black is a high energy consuming process and requires the use of plasticizers especially when the loading of filler is high. During the conventional mixing process silica is highly aggregated due to filler –filler interaction resulting in a dispersion which is not favourable 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 times were higher (5). However, the mismatch in rate of coagulation of fresh field latex and the filler slurry led to the poor dispersion of carbon black in rubber as well as there was significant loss of filler during the coagulation, making the process economically unviable. A solution to this mismatch rate of coagulation is through a modified and quick coagulation process(6)

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. Super Abrasion furnace black (N134) Intermediate Super Abrasion Furnace black (N220) and High Abrasion Furnace black (N330) were obtained from M/s Phillips Carbon Black Limited Kochi, India. Precipitated silica used was ULTRSIL VN3. Other ingredients used were rubber grade chemicals.

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 required quantity of dispersions were 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 ^{0} C. The fillers were incorporated in latex so as to have levels of 50 parts per hundred parts of dry rubber . The dried rubber was mixed as per formulation given Tables 1a and 1b, and vulcanized by conventional methods. A control mix with loadings of 50 phr fillers added by conventional mill mixing process was also prepared.

The cure behavior was determined using moving Monsanto Oscillating disk rheometer (R100) at 150°C. The particle size of filler dispersions 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 were determined from relevant ASTM standards.

RESULTS & DISCUSSION

Coagulation Characteristics

The particle size distribution of carbon black dispersion (ISAF black), silica dispersion and latex- filler mixture is shown in Figures 1 a b and c. Silica dispersion contains filler particles that have comparatively small size (average 200 nm).However ISAF carbon black

dispersion has higher particle size (90 to 6000 nm). The particle size of fresh NR latex filler mixture also varies from about 90-6000 nm. Thus, after addition fillers to latex the size of filler particles remain almost the same. 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 adsorbed 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 adsorbed anions react with acid to form un-dissociated surfactant, and deprive the latex particles of stabilizers. As a consequence, latex coagulates immediately (7, 8) Due to quick coagulation it is expected that the uniformly mixed fillers remain unaggregated during coagulation and further processing.

Vulcanization Characteristics

The cure characteristics are shown in Table 2. The master batch mixes containing 50 phr of silica/carbon black dual fillers (ISAF and SAF grades) recorded a higher torque as compared to the corresponding dry mill mixed compounds. Between the two dry mixes a lower torque is recorded for SAF black containing mix compared to ISAF black filled mix and this could possibly be due to poor dispersion of lower particle sized filler. It is well known that as particle size decreases it is more difficult to disperse them in rubber. When surfactant is added to latex it disperses uniformly in latex due to adsorption on rubber particles and during vulcanisation this help in attainment of higher level of vulcanisation (9).

Mechanical Properties

The vulcanizates prepared from master batches by the new method showed higher tensile strength, higher modulus, hardness, and tear strength along with lower heat build-up and abrasion loss compared to conventional mill mixed compounds (Tables 3). For the master batches the hardness follows the order SAF> ISAF>HAF. Also SAF black filled mix showed higher tear strength than ISAF black filled compound. However within the three filler systems, HAF black /silica system showed superior properties for the master batch and the expected effect of higher reinforcement for lower particle sized carbon black filler is not observed in the carbon black/silica combinations. For conventionally mixed compounds also the expected effect of higher reinforcement for lower particle sized carbon black filler is not observed. It should be noted that for both master batch and dry mixed compounds additives like process oil and coupling agents were not used.

The improvement in mechanical properties for the master batch containing HAF black/silica filler system is attributed to better filler dispersion. The filler dispersion characteristics of HAF black /silica filler system are presented in Figures 2 a and 2b. Comparatively better dispersion and lower aggregation is shown by master batch mix as compared to mill mixed one.

CONCLUSION

A uniformly mixed filer dispersion and latex in presence of suitable surfactant coagulates quickly on addition of suitable coagulants. 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 maste rbatch

Ingredient	Quantity
NR filer master batch *	100
ZnO	5
Stearic Acid	1.5
HS **	1
DEG [a]	0.8
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 1bFormulation of the mixes for the control mixes

Ingredient	Quantity
NR	100
ZnO	5
Stearic Acid	1.5
HS	1
CarbonBlack/ silica	25/25
DEG [a]	1
MBTS***	1.0
DPG ****	0.2
Sulphur	2.5

[a] Diethylene glycol

Table 2. Cure characteristics – Silica/SAF and Silica/ISAF mixes

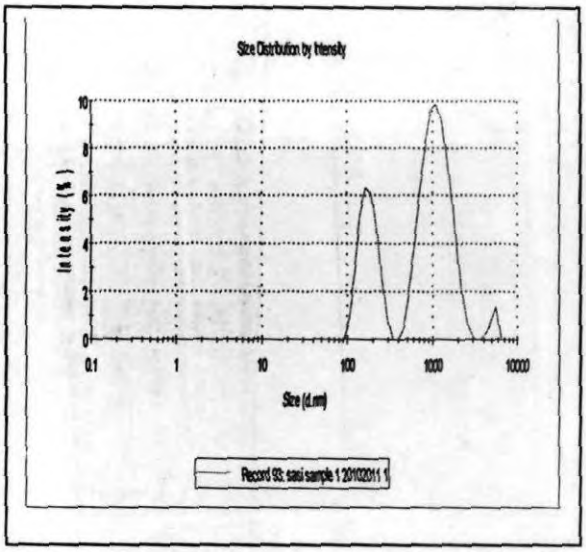
Parameter	SAF black /Silica		ISAF black /Silica	
	Sample Master	Control	Master batch	Control
Mini. torque, dN.m	16.9	25.3	14.1	20.0
Max. torque, dN.m	105.1	73.9	86.4	83.5
Δ, Rheometric torque, dN.m	88.2	48.7	72.3	63.5
Optimum cure time (t_{90}) at 150°C, min	15.1	15.9	14.4	10
Scorch time (ts_2) at 150°C, min	2.1	3.5	2.7	2.0

Table 3a. Mechanical properties – Silica/SAF, Silica/ISAF and Silica/HAF mixes (filler master batch)

Parameters	Master batch		
	SAF/Silica	ISAF/Silica	HAF/Silica
300 % Modulus, MPa	9.9	9.08	10.88
Tensile strength, MPa	22.9	22.65	27.3
Elongation at break, %	606	650	570
Tear strength, N/mm	105	100	103
Hardness, Shore A	70	68	66
Abrasion loss, mm3	135	139	118
Heat build-up, ΔT°C	20	16	16
Compression set, %	59	47	45

Table 3b. Mechanical properties – Silica/SAF, Silica/ISAF and Silica/HAF mixes (mill mixed)

	Mill mixed		
Parameters	SAF/Silica	ISAF/Silica	HAF/silica
300 % Modulus, MPa	3.5	4.4	7.2
Tensile strength, MPa	19.2	25.8	24.5
Elongation at break, %	775	748	620
Tear strength, N/mm	82	102	88
Hardness, Shore A	52	60	58
Abrasion loss, mm3	211	159	143
Heat build-up, ΔT°C	23	21	19
Compression set, %	68	51	48



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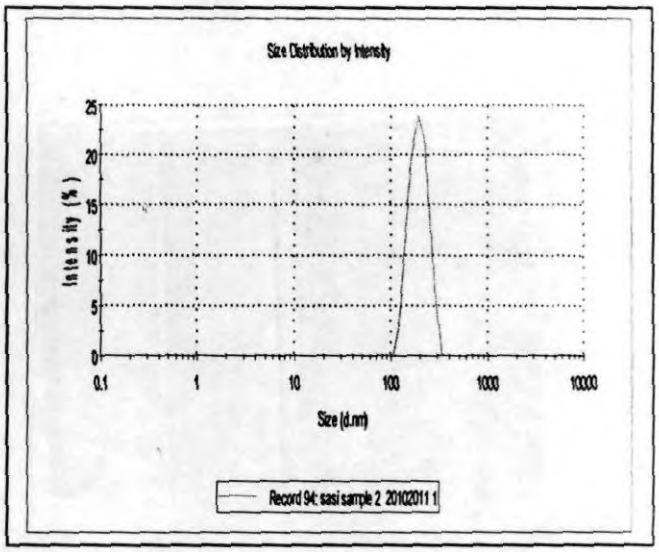

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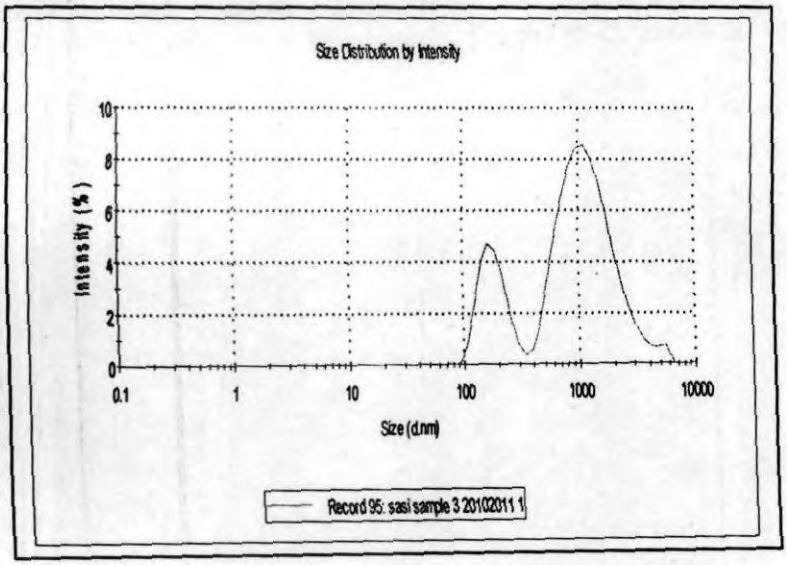
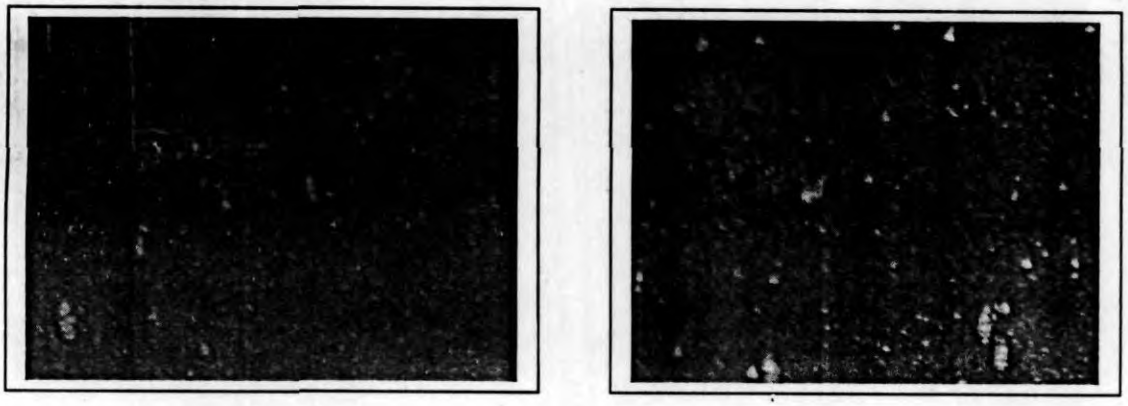


c

Fig 1. Particle size of (a) ISAF carbon black in the carbon black dispersion (b) silica in the silica dispersion, c rubber particles and dispersions of carbon black and silica(25/25) in latex-filler mixture



a b

Figure 2. Dispersion rating for 25/25 silica/HAF 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 aggregate