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CARBON BLACK MASTERBATCH USING DIFFERENT FORMS OF NATURAL RUBBER LATEX

K.K. Sasidharan, Rosamma Alex and Thomas Kurian*

Rubber Research Institute of India, Kottayam - 686 009, Kerala, India
*Cochin University of Science & Technology, Kochi - 686022, Kerala, India

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Different forms of natural rubber latex like fresh latex, preserved and concentrated latex were used for producing carbon black masterbatch with fluffy carbon black. Factors like particle size, zeta potential, colloidal stability, rubber content, non-rubber ingredients, sensitivity to acids and raw rubber properties are different for these forms of latex. These parameters can affect the processing and quality aspects of the carbon black masterbatch. Though fresh natural rubber (NR) latex does not coagulate immediately on addition of acids, it can be sensitized for coagulation with acids by addition of suitable surfactants. It was observed that surfactant treated fresh latex, preserved latex and latex concentrate containing filler dispersion coagulated to a consolidated mass quickly on addition of acids. It was observed that the coagulation was more uniform for fresh field latex compared to the other forms. This could be attributed to the type of anions adsorbed on the surface of rubber particles in the latex. A higher rheometric torque and cure time was observed for the masterbatches compared to the conventional dry mix. Within the masterbatches higher rheometric torque was recorded for fresh latex and preserved field latex (PFL) containing skim latex and this could be due to the presence of comparatively higher amount of surfactants in latex. It is found that a higher modulus, tensile strength, hardness, tear strength along with lower compression set, heat build-up and abrasion resistance were recorded for the masterbatches made from fresh latex, PFL and latex concentrate compared to the control dry mixed vulcanizate. Better ageing resistance was also observed for the masterbatches. The over-all mechanical properties shown by masterbatch prepared from fresh field latex was superior to others. The improvement in mechanical and ageing characteristics are attributed to the higher crosslinking and better dispersion of filler as observed from the filler dispersion data.

Key words: Carbon black, Fresh natural rubber latex, Latex concentrate, Latex masterbatch

INTRODUCTION

Latex is a colloidal dispersion of rubber particles in an aqueous medium obtained from latex vessels of *Hevea brasiliensis* with particle sizes varying from 80-3000 nm. Along with rubber particles, latex contains non-rubber ingredients like proteins, phospholipids, carbohydrates, metal ions and inorganic cations (Gomez and Hamzah, 1989; Yip and Gomez; 1980). The composition of non-rubber ingredients changes after latex leaves the tree and the obvious consequence of this is the coagulation of latex within a few hours. This is called spontaneous coagulation. (Van Gils, 1947). Another change that takes place in

Correspondence: K.K. Sasidharan (sasidharan@technologist.com)

latex at a later stage is called putrefaction which is followed by development of bad odour. To prevent spontaneous coagulation, latex is preserved with suitable preservatives. During concentration of latex by centrifuging process the comparatively bigger particles along with lower proportion of non-rubber ingredients separate into the latex concentrate and smaller particles along with greater proportion of non-rubber ingredients separate as skim fraction (Blackley, 1997) Factors like particle size, zeta potential, colloidal stability, rubber content, non-rubber ingredients, sensitivity to coagulation by acids and raw rubber properties are different for these forms of latex. (Jitlada *et al*., 2011).

Normally rubber is recovered from latex by a slow coagulation process after the addition of coagulants. Earlier reports showed that process of spontaneous coagulation, which occurs in the absence of added coagulants, can be accelerated by addition of suitable surfactants (Blackley, 1997). The mechanism of this is believed to be due to displacement of protective layer of proteins by added surfactant anions followed by their interaction with divalent metal ions which are either initially present or formed in latex. Hence sensitization of latex with suitable surfactants could reduce the time of coagulation of latex by the conventionally used coagulants.

There are several reports on production of carbon black masterbatch using natural rubber latex. (Janssen and Weinstock 1961; Laliamma *et al*., 1997; Wang 2005; Shekhar, 2008). M/s. Cabot Corporation, USA uses high speed mixing equipment for production of masterbatches (Wang *et al.*, 2002).

Generally a high Mooney viscosity is recorded for carbon black masterbatches which can be reduced by the addition of chemical additives during the mixing process. The main drawback of earlier reported methods is the long mixing and coagulation time. (Zainul *et al*., 1984). However there are no systematic reports on the production of masterbatch from different forms of NR latices that vary in non-rubber ingredients, colloidal stability, molecular structure and particle size.

In this work an attempt was made to study the effect of different forms of NR latex like fresh field latex, PFL, centrifuged latex and skim latex for the production of carbon black masterbatch by latex stage incorporation of fluffy black.

MATERIALS AND METHODS

The fresh latex (40 per cent drc), preserved field latex (38 per cent drc), concentrated latex (60 per cent drc) and skim natural rubber latex(5 per cent drc), used in the study were obtained from the Rubber Research Institute of India, Kottayam. Fluffy carbon black (high abrasion furnace or N330) was obtained from M/s. Phillips Carbon Black Limited, Kochi, India. Dispersion of fluffy carbon black was prepared using a mechanical stirrer rotating at a frequency of 400 rpm in presence of a suitable

Table 1**. Details of masterbatch**

Samples	Composition
A	Fresh natural rubber latex + 30 phr fluffy HAF black
B	Preserved field latex +30 phr fluffy HAF black
C	Centrifuged latex + 30 phr fluffy HAF black
D	75 parts preserved field latex + 25 parts skim latex +30phr fluffy HAF black
E	Conventional dry mix (dry rubber + 30 phr fluffy HAF black)

Table 2. **Formulation for masterbatch and dry mix**

Ingredient	A	B	C	D	E
Natural rubber masterbatch	130	130	130	130	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
TmQ*	1	1	1	1	1
HAF(fluffy black)	-	-	-	-	30
Naphthenic oil	1.5	1.5	1.5	1.5	1.5
CBS**	0.75	0.75	0.75	0.75	0.75
Sulphur	2.5	2.5	2.5	2.5	2.5

*2.2.4-tri methyl -1,2- dihydroquinoline

** N-cyclohexyl-2-benzothiazole sulfenamide.

surfactant. The filler dispersion was added slowly in to the natural rubber latex (Table 1) at 50 rpm with suitable surfactants. The mixes were stirred for 15 min and then coagulated (Van Gils, 1947, [1]Alex *et al*., 2011). The loss of filler through water during coagulation was negligible. The coagulum was washed well to remove the acid and dried in an air oven at 70^0 C. The dried masterbatch and control mixes were prepared as per the formulation given in Tables 2 using a two-roll mixing mill and vulcanizates were prepared by curing at 150 ^{0}C to the respective optimum cure time.

The particle size of the filler dispersion and latex was determined using a particle size analyzer (Malvern Nano S particle analyser, U.K) based on dynamic light scattering technique. Zeta potential was measured using Zeta potential analyser (Malvern, Nano Z, U.K). The buffer solution in the pH range of 4-9 was freshly prepared for dispersing the natural rubber latex as reported earlier (Jitlada *et al.*, 2011).

The cure behaviour was determined at 150 ºC using a moving die Rheometer (MDR2000 ALPHA Technologies, USA).The mechanical properties and the ageing tests were determined as per the corresponding ASTM standards. The Mooney viscosity was measured using a Mooney Viscometer (Mooney MV 2000, ALPHA Technologies, USA), as per ASTM D 1646 (1981).

Volume fraction of rubber in toluene swollen gel (Vr) was determined as per standard procedure using the following equation (Ellis and Welding, 1964)

$$Vr = \frac{(D\text{-}FT)P_r^{-1}}{(D\text{-}FT)\,P_r^{-1} + A_o P_s^{-1}}$$

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

Filler dispersion in the valcanisates was studied using a Dispergrader (Tech Pro, USA) as per ISO 11345 method B. This technique is based on interferometric microscopy (IFM) and utilizes the interference fringes between in-phase light beams reflected from the rubber sample and a smooth reference surface to measure the three-dimensional surface topography. The

peaks and valleys present on the fresh-cut surface are representative of the carbon black agglomerates and are used to characterize the dispersion. A set of ten image standards has been established for each of the different reference scales in the Dispergrader. To each of these reference images a numerical rating 1-10 (the x-value) has been assigned.

RESULTS AND DISCUSSIONS

a. Raw latex and rubber characteristics

The size of rubber particle varies from about 80 to 2000 nm for fresh latex, (FL) 85-2000 nm for preserved field latex (PFL), 100-3000 nm for latex concentrate (CL) and about 80-400 nm for skim latex (Figure1) (Gomez and Hamzah, 1989). As the skim fraction has smaller particles it is expected that non rubber ingredients present are also higher. Zeta potential data for different forms of natural rubber latex are presented in Fig. 2 and Table 3. It was observed that the fresh latex showed a higher zeta potential value than preserved and centrifuged latex. The zeta potential values decreased with decreases in pH. The negative value of zeta potential in all cases is attributed to the negatively charged ions adsorbed on rubber particles. It is known that zeta potential values decrease with the decrease of pH because at lower pH the latex reaches the isoelectric point when rubber particles have almost no charge. The higher zeta potential shows that there is greater proportion of long-chain fatty acids and proteins adsorbed on the rubber particle. (Jitlada *et al*., 2011).

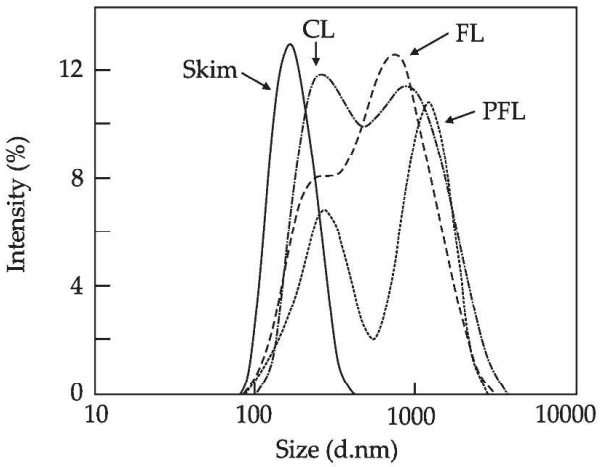

Fig. 1. Particle size distribution of NR latex [fresh (FL), preserved (PFL), skim and centrifuged latex (CL)]

b. Coagulation characteristics

It was observed that surfactant treated fresh latex, preserved latex and latex concentrate containing filler slurry coagulated to a consolidated mass quickly on addition of acids. However, it is observed that the coagulation was more uniform for fresh field latex compared to the other forms. From the values of zeta potential, it was observed that fresh field latex had a higher zeta potential than other forms of latex. The nitrogen content which is a measure of proteins was also higher for fresh latex compared to latex concentrate (Table 4). This shows that the types of adsorbed anions on the rubber particles in different forms of latex are different. In presence of suitable surfactants there is displacement of less active surfactants by the more active ones, leading to an increased tendency for colloidal destabilization by coagulants (Van Gils, 1947; Alex *et al*., 2011). The difference in coagulation behavior latex-fluffy black mixture is attributed to this. Due to the quick coagulation the well dispersed carbon black

Table 3. **Zeta potential value of natural rubber latex at pH 9**

Samples	Zeta potential (mV)
Fresh latex	- 62
Preserved field Latex	- 58
Centrifuged latex	- 55

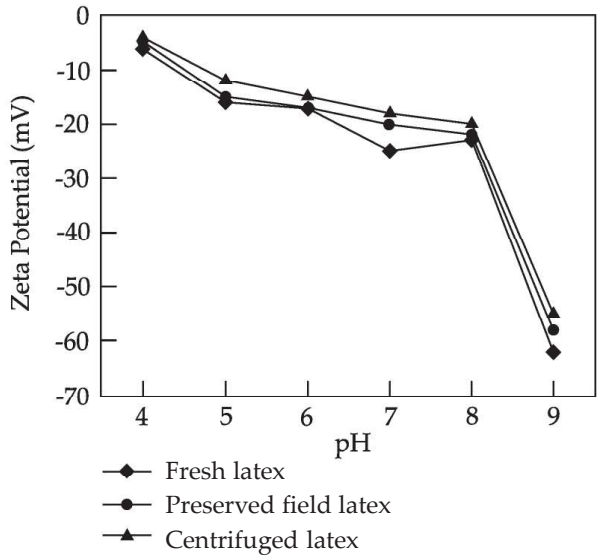

Fig. 2. Zeta potential values at different pH values.

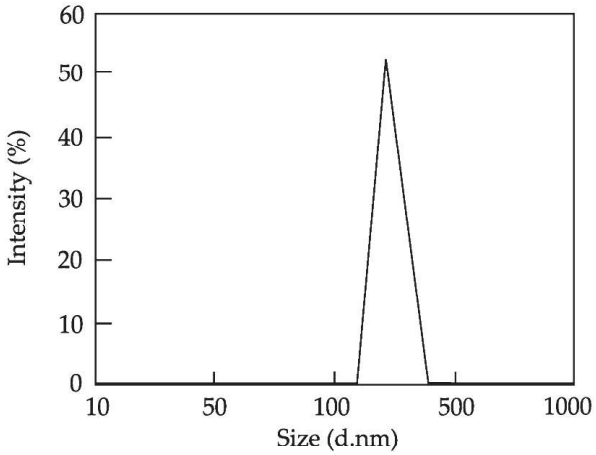

Fig. 3. Particle size of fluffy carbon black dispersion.

added to latex was expected to remain unaggregated in the latex coagulum (Fig. 3).

Mooney viscosity of masterbatch compounds are given in Table 4 which follows the order centrifuged latex > PFL > PFL containing skim > fresh field latex. In latex concentrate and PFL during preservation there can be chain entanglements and long chain branching leading to an increase in viscosity. In skim latex the rubber molecules are found to be linear without long chain branching whereas the non rubber ingredients are comparatively higher. Both these factors affect the Mooney viscosity. (Kawahara *et al.*, 2000) Further Mooney viscosity values are within the range due to the presence of in-situ formed plasticizers.

Table 4. **Mooney viscosity of mixes**

Samples	ML(1+4) 100 ^{0}C
A	90
B	101
C	102
D	99
Natural rubber (without filler)	78

c. Cure characteristics

The masterbatch based mixes showed a higher level of vulcanization as obtained from a higher rheometric torque compared to the control (Table 5). Within the masterbatch mixes higher rheometric torque was recorded for fresh latex and PFL containing skim latex compared to latex concentrate and PFL. The higher rheometric

Table 5. **Cure characteristics of masterbatche and dry mix**

Parameters	A	B	C	D	E
Torque Min, dNm	0.42	0.37	0.64	0.75	0.39
Torque Max, dNm	17.6	16.0	15.5	18.0	10.2
Optimum cure time, t90 at 150 ^{0}C, min	9.17	9.49	9.28	9.48	5.52
Volume fraction, Vr	0.266	0.258	0.263	0.261	0.234

Table 6. **Raw rubber properties**

Parameters	Fresh latex	Latex concentrate	Skim latex
Acetone extract, %	4.1	3.1	5.5
Nitrogen, %	0.45	0.39	2.1

torque of skim latex containing PFL is attributed to higher level of proteins present. This is because during concentration of latex, smaller rubber particles with higher amount of surfactants get separated as skim latex. The proteins present in skim latex help in attaining a higher level of vulcanization. The acetone extract is also higher for skim latex as shown in Table 6.

The control compound showed a comparatively lower cure time and rheometric torque due to the presence of lower content of surfactants.

d. Mechanical properties

It is found that a higher modulus, tensile strength, hardness, tear strength and lower compression set, heat buildup and abrasion resistance were recorded for the masterbatche made from fresh latex, PFL and latex concentrate compared to the control (Table 7). Among the masterbatches fresh field latex based vulcanizate showed higher tensile strength, higher elongation and a lower heat build-up and abrasion loss than other mixes. The vulcanizate based on blend of PFL and skim latex showed comparatively lower tensile strength, tear strength, and abrasion resistance along with higher compression set and modulus values. The higher modulus of vulcanizates containing skim rubber is due to presence of higher amount of proteins.

Table 8. C**arbon black dispersion rating**

Sl. No.	Sample name	Carbon black dispersion(X)	Agglomerate Count(Y)
1	Master batch A	7.0	8.3
2	Master batch B	6.8	8.0
3	Master batch C	6.5	7.6
4	Master batch D	6.0	7.0
5	Dry mix E	4.5	6.0

The filler dispersion data of mixes containing 30 phr filler is given in Fig. 4 and

Table 7. **Mechanical properties of masterbatch and dry mix**

Parameters	A	B	C	D	E
100 % Modulus, Mpa	2.4	2.2	2.2	4.1	1.9
300% Modulus, MPa	9.5	9.0	11.4	13.1	8.1
Elongation at break,%	545	515	536	408	631
Tensile strength, MPa	25.5	24.2	25.0	19.0	23.1
Hardness, Shore A	54	53	54	53	50
Compression set, %	36	37	35	38	39
Heat build-up, "T, ºC	22	24	23	28	25
Abrasion loss, mm^3	102	105	104	130	120
Resilience, %	75	75	76	70	75
Tear strength, kN m^{-1}	63	58	59	52	56

Table 9. **Mechanical properties of masterbatch and dry mix after ageing 3 days at 100 ^{0}C**

Parameters	A	B	C	D	E
300% Modulus, MPa	10.8	10.3	11.0	14.4	10.5
Elongation at break,%	510	480	500	380	520
Tensile strength, MPa	23.5	21.7	22.4	18.1	20.5

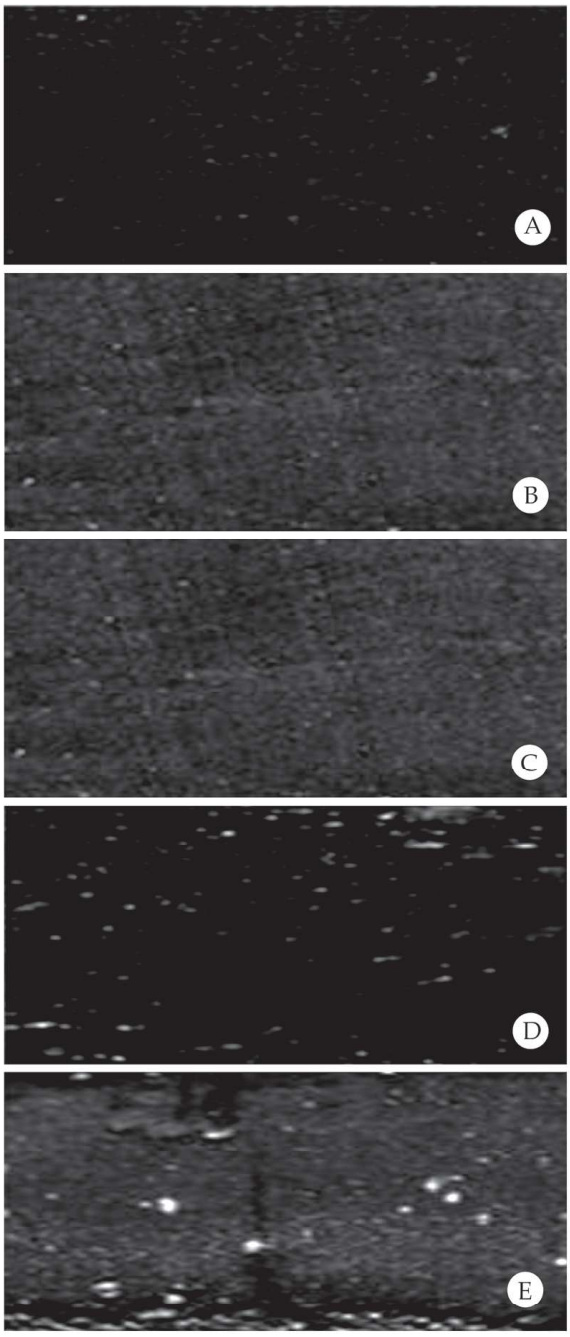

Fig. 4. Images of vulcanizates (A, B, C, D and E) as per rating in Table 8.

Table 8. It is observed that the filler dispersion is better in masterbatches than the control mix. Dispersion was uniform for field latex compared to other forms. It is expected that there is better dispersion of fillers when they are mixed in the latex stage and coagulated quickly by a modified coagulation process compared to mixing of carbon black using conventional mill mixing technique. The mechanical properties obtained after ageing the samples at 100 ^{0}C per 3 days are given in Table 9. Higher retention and lower variation of tensile strength during ageing is observed for vulcanizates based on carbon black masterbatch.

The improvement in mechanical properties and ageing characteristics is attributed to higher level of crosslinking (Table 6) and better dispersion of filler. (Wang *et al*., 2001; 2002)

CONCLUSIONS

Different forms of natural rubber latics were used to prepare carbon black masterbatch. Fresh latex based masterbatch, has very good mechanical properties compared to masterbatches prepared from preserved field latex, latex concentrate and skim latex. This is attributed to a more uniform coagulation of fluffy carbon black-latex mixture, The masterbatch mixes showed higher level of vulcanization and better dispersion of filler in the vulcanizates.

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