

Studies on Latex Stage Carbon Black Masterbatching of NR and its Blend with SBR

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ABSTRACT

Carbon Black is incorporated in natural rubber latex in the presence of polyethylene glycol. The dispersion of carbon black in the vulcanizates is analyzed using polaroid M_{p4} and camera. The mechanical properties of the carbon black masterbatched NR/SBR blend is compared with that of conventional NR/SBR blend before and after ageing. The resilience, flex resistance and hardness are found to be superior for N-LCM/SBR compounds. The compression set and abrasion resistance are comparable for both types of blends. The processability and die swell of these blends at different shear rates are also compared.

Key Words: natural rubber latex, latex stage masterbatching, NR/SBR blends, dispersion, mechanical properties

INTRODUCTION

The major advantages of adding filler to rubber compounds are the reduction in cost of the products and the reinforcement. Many studies have been published explaining the reinforcing properties of carbon black in rubber [1, 2]. But incorporation of carbon black in dry rubber presents problems like difficulty in maintenance of cleanliness in the factory and huge power consumption [3]. So attempts are made to mix carbon black with natural rubber (NR) in the latex stage. But the use of fillers in latex products is limited, since they affect the mechanical properties adversely [4].

The reduction in vulcanizate properties may be due to the lack of proper distribution of filler in the latex [5]. However, it is possible to incorporate modifiers to improve the rubber-filler interaction and hence to develop filled latex products [6].

N. Radhakrishnan Nair et al. have studied the role of certain surface modifying agents like diethylene glycol, triethanolamine and bis (triethoxysilylpropyl) tetrasulphide in improving the mechanical properties of the rubber compound [7].

From the earlier works, it is clear that latex masterbatch process can deliver a premix which can be given a shorter mixing cycle and still result in an extremely well dispersed compound.

Blending of two or more elastomers is an attractive method for attaining properties not available in a single elastomer [8-11]. It appears that in elastomer blends the sequence of blending and carbon black addition are of utmost importance for the distribution of the carbon black in the blend, which in turn, largely determines the physical properties of vulcanizates [12-14]. It is, therefore, important in reinforcing elastomer blends with carbon black to determine those mixing procedures which yield optimum physical properties of the vulcanizates.

In the present study, we have prepared NR-latex carbon black masterbatches. The latex stage mixing of carbon black is carried out more efficiently by mixing NR latex with 1 phr polyethylene glycol. The carbon black distribution in the masterbatch is examined. The extent of rubber-carbon black interaction is studied by measuring the bound rubber content. These masterbatches are blended with styrene butadiene rubber (SBR). The mechanical properties of the NR carbon black masterbatch/SBR blends are compared with carbon black filled dry NR/SBR blends. The processability of these blends are compared with that of NR/SBR blends.

EXPERIMENTAL

Materials

Natural rubber used was ISNR-5 grade (Mooney viscosity ML (1+4) at 100 °C, 85.3) obtained from Rubber Research Institute of India, Kottayam. NR latex used was field latex containing 30% dry rubber content, and the SBR was 1502 grade (Mooney viscosity ML (1+4) at 100 °C, 49.2). Carbon black-HAF N-330 and the compounding ingredients zinc oxide, stearic acid, sulphur and aromatic oil were of commercial grade.

Tetramethylthiuram disulphide and *N*-cyclohexylbenzothiazole-2 sulphenamides were supplied by Bayer India Ltd. Polyethylene glycol with molecular weight of 300 was Analar grade supplied by E. Merck India Ltd.

A 20% dispersion of carbon black was pre-

pared by ball milling for 20 h without any dispersing agent. In order to study the effect of ball milling on particle size, the iodine adsorption number of carbon black was determined before and after ball milling as per ASTM D 1510. To understand the structure of carbon black in the dispersion, the dibutyl phthalate (DBP) absorption test was conducted as per ASTM D 2 414-65.

Preparation of NR-Latex Carbon Black Masterbatches

Field latex was mixed with 1 phr polyethylene glycol (a surface active agent) [6] and 10, 20, 30, 40 and 50 phr each of carbon black dispersion, using a high speed mechanical stirrer (4000 rpm) for 2 min. The masterbatches were prepared by coagulating the latex carbon black mixture with 2% acetic acid. Hereafter this mixture is referred to as N-LCM (NR-latex carbon black masterbatch). These masterbatches were compounded in a two roll mill according to formulation given in Table 1. Similarly, NR-carbon black mixes were also prepared, using a two roll mixing mill according to ASTM D 3182 (1982).

Bound Rubber Content Determination

The bound rubber content of both mixes were determined according to the following method:

The solvent used for the bound rubber determination was toluene. Approximately 0.2 g of the compound was cut into small pieces and placed into a stainless steel wire mesh cage of known weight. The cage was then immersed in 25 mL of solvent for seven days at room temperature and the solvent was renewed after three days. After extraction, the rubber and the cage were dried for one day in air at room temperature and then for 24 h in an oven at 105 °C. The bound rubber of the polymer (R_B) was then calculated as described by S. Wolff et al. [15] according to the following equation:

$$R_B = [W_{fg} - W[m_f/(m_f + m_p)] \times 100] / W[m_p/(m_f + m_p)]$$

where W_{fg} is the weight of the carbon black and gel, m_f the weight of the filler in the compound, m_p

Table 1. Formulations of NR-carbon black and N-LCM mixes.

Mixing compound	NR-carbon black mixes					N-LCM mixes (NR-latex carbon black masterbatch)				
	100	100	100	100	100	110	120	130	140	150
NR										
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
NA 4020	11	1	1	1	1	1	1	1	1	1
HAF	10	20	30	40	50	—	—	—	—	—
Aromatic oil	—	—	—	5	6	—	—	—	—	—
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
S	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

the weight of the polymer in the compound and W is the weight of the specimen.

Optical studies of both N-LCM vulcanizates and dry NR vulcanizates, both containing 50 phr carbon black, were carried out by using Polaroid M_p4 land camera at a magnification of 30.

Preparation of N-LCM/SBR Blends

The N-LCM/SBR compounds were prepared using a two roll mill, varying the N-LCM/SBR ratio as 80/20, 60/40, 40/60 and 20/80. N-LCM was first masticated in the mill for 2 min and then SBR was added, and they were compounded according to

ASTM D 3182 (1982). The formulations are given in Table 2.

Preparation of Filled NR-SBR Blends

NR was first masticated in a two roll mill for 1 min and then SBR was added. These NR/SBR blends were compounded according to ASTM D 3182 (1982) as per the formulation given in Table 2. The optimum cure time T_{90} (time to reach 90% of the maximum torque) of these compounds were determined on a Göttfert model 67.85 at 150 °C.

Both blends of N-LCM/SBR and NR/SBR were each moulded in a laboratory hydraulic press

Table 2. Formulations of NR-SBR and N-LCM/SBR blends.

Mixing compound	NR/SBR Blends				N-LCM mixes (NR-latex carbon black masterbatch)			
	80	60	40	20	120	90	60	30
NR								
SBR	20	40	60	80	20	40	60	80
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
HAF	50	50	50	50	10	20	30	40
Aromatic oil	6	6	6	6	1.2	2.4	3.6	4.8
A.O.	1	1	1	1	1	1	1	1
CBS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMTD	0.24	0.28	0.32	0.36	0.24	0.28	0.32	0.36
S	2.4	2.3	2.2	2.1	2.4	2.3	2.2	2.1

Table 3. Iodine number and DBP absorption of carbon black.

Carbon black	Iodine number	DBP absorption (m/100 g)
Original	87	102
In dispersion	87	102

at 150 °C upto their respective optimum cure times. The tensile properties of the vulcanizates were evaluated as per ASTM D-412 (1980). The samples were aged at 100 °C for 24 and 48 h, and ageing resistance was studied.

Samples for hardness test, compression set, abrasion resistance, rebound resilience, heat build-up and flex cracking were moulded and tested as per relevant ASTM standards.

Rheological study of these blends without curatives were carried out using a capillary viscotester (Götfert viscotester 1500). The temperature inside the barrel and capillary was kept at 150 °C. The crosshead speed was varied in the range of 0.02 to 3 mm/min. Small pieces of the samples were put into the barrel of the rheometer and forced down to the capillary by the piston. After a warm-up period of 4 min, the sample was extruded through the capillary at different speeds. Forces corresponding to specific plunger speeds were measured. The apparent shear stress and shear rate were also calculated. The extrudates were collected, and the extrudate swelling was calculated.

RESULTS AND DISCUSSION

Ball milling helps in obtaining a high degree of dispersion of the carbon black added to the latex. The iodine adsorption number of carbon black is found to be the same before and after ball milling. This shows that there is no change in particle size during ball milling. The DBP absorption study shows that the structure of carbon black is not changed during ball milling (Table 3).

Addition of polyethylene glycol to latex improves its stability so that carbon black disper-

Table 4. Bound rubber of N-LCM and NR-carbon black mixes.

Sample	Carbon black loading	Bound rubber (%)
NR-carbon black mixes	10	17.0
	20	22.5
	30	39.0
	40	41.0
	50	50.0
N-LCM mixes	10	37.5
	20	53.0
	30	57.0
	40	60.0
	50	66.0

sion can be mixed with NR latex with proper mechanical stirring [16]. In the absence of polyethylene glycol, uniform distribution of carbon black dispersion in the latex will be difficult as the latex coagulates during mechanical agitation.

The bound rubber content value is found to be higher for N-LCM than NR-carbon black mixes (Table 4). This proves that there is more rubber-filler interaction in the case of NR-latex carbon black masterbatches.

Figure 1 shows the photographs of the NR-latex masterbatch and NR-black with 50 phr carbon black. The carbon black distribution is

Table 5. Cure characteristics of N-LCM/SBR blends and NR/SBR blends.

Sample	Blend ratio	Scorch time (min)	Cure time (min)
N-LCM/SBR blends	80/20	1.64	3.90
	60/40	1.76	3.88
	40/60	2.12	3.76
	20/80	2.04	3.04
NR/SBR blends	80/20	1.76	3.72
	60/40	1.76	3.76
	40/60	2.36	3.72
	20/80	1.98	3.20

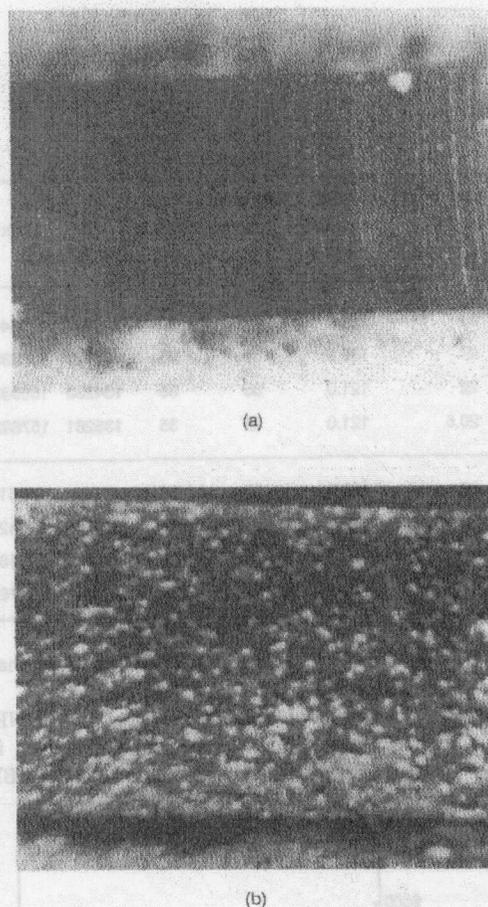


Figure 1. Photographs of N-LCM vulcanizate with 50 phr carbon black at a magnification of 30 (a); and NR-carbon black vulcanizate with 50 phr carbon black at a magnification of 30 (b).

found to be more uniform for latex masterbatches. Table 5 shows the cure characteristics of N-LCM/SBR blends and NR/SBR blends. N-LCM/SBR blends are found to cure at a similar rate compared to NR/SBR blends.

Figure 2 shows the tensile strength of both N-LCM/SBR and NR/SBR blends before and after

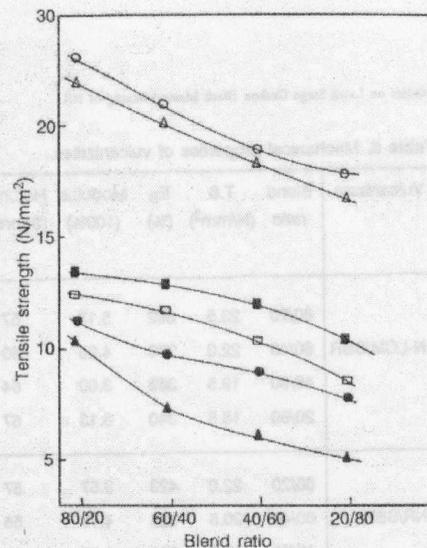


Figure 2. Variation of tensile strength with blend ratio. (○) N-LCM/SBR, (Δ) aged at 100 °C for 24 h, (■) aged for 48 h, (●) NR/SBR, (▲) aged at 100 °C for 24 h, (▲) aged for 48 h.

Figure 2. Variation of tensile strength with blend ratio.

ageing. The tensile strength of N-LCM/SBR blends are better than that of NR/SBR blends, before and after ageing. This may be due to the uniform distribution of carbon black in latex masterbatches. N-LCM/SBR blends are having higher modulus and lower elongation at break compared to the conventional NR/SBR blends (Table 6). This may be due to the higher polymer filler interaction in the case of latex/SBR blends. The resilience, flex resistance and hardness are superior for N-LCM/SBR compounds (shown in Table 6). The compression set and abrasion resistance are comparable for both types of blends. The heat build-up is lesser in the case of N-LCM/SBR blends. All these confirm uniform filler distribution and higher polymer filler interaction in the latex blends.

Figures 3 and 4 show the variation of shear viscosity with shear rate of N-LCM/SBR blends and NR/SBR blends, respectively, at 150 °C. As the shear rate increases, shear viscosity decreases. This confirms the pseudoplastic behaviour of these

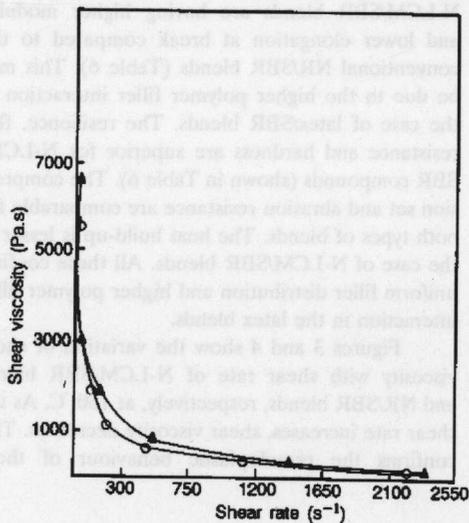
Table 6. Mechanical properties of vulcanizates.

Vulcanizate	Blend ratio	T.S (N/mm ²)	E _B (%)	Modulus (100%)	Hardness (Shore A)	Compression set (%)	Abrasion resistance index	Resilience (%)	Heat build-up (°C)	Flexing min	Flexing max
N-LCM/SBR	80/20	23.5	392	5.13	57	27	121.0	72	30	146927	182543
	60/40	22.0	370	4.20	60	24	120.6	69	35	137927	165930
	40/60	19.5	368	3.60	64	22	121.0	65	35	134233	150533
	20/80	18.5	340	3.13	67	20.5	121.0	62	35	135281	157892
NR/SBR	80/20	22.0	423	3.57	57	32	120.0	52	36	40624	66851
	60/40	20.5	385	4.11	58	28	119.0	55	34	16792	32342
	40/60	19.0	381	3.20	62	26	119.0	55	35	11154	22913
	20/80	17.5	379	3.04	64	24	121.0	55	35	25432	50676

compounds. Figure 5 shows the variation of shear viscosity with blend ratio. As SBR content increases, shear viscosity increases in both cases, although the increase in viscosity is less for N-LCM/SBR, compared to NR/SBR. Therefore, the process-

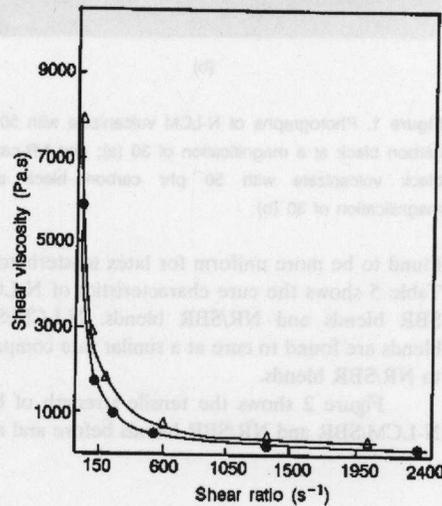
ability of N-LCM/SBR will be easier than NR/SBR blends.

Die swell of N-LCM/SBR blends and NR/SBR blends at different shear rates are given in Table 7. In all cases, the die swell of N-LCM/SBR blends are lower than that of NR/SBR blends.



(○) 80/20 N-LCM/SBR, (△) 20/80 N-LCM/SBR.

Figure 3. Variation of shear viscosity with shear rate of N-LCM/SBR, at 150 °C.



(●) 80/20 NR/SBR, (▲) 20/80 NR/SBR.

Figure 4. Variation of shear viscosity with shear rate of NR/SBR, at 150 °C.

Table 7. Die swell of the extrudates at different shear rates.

Sample	Blend ratio	Die swell at shear rates (s^{-1})				
		29	110	230	520	1200
N-LCM/SBR blends	80/20	2.56	2.45	2.49	2.48	2.47
	60/40	2.47	2.40	2.44	2.47	2.51
	40/60	2.47	2.40	2.46	2.53	2.57
	20/80	2.30	2.27	2.25	2.37	2.72
NR/SBR blends	80/20	2.70	2.52	2.56	2.62	2.58
	60/40	2.50	2.43	2.54	2.48	2.64
	40/60	2.64	2.50	2.57	2.69	2.63
	20/80	2.57	2.49	2.40	2.56	2.78

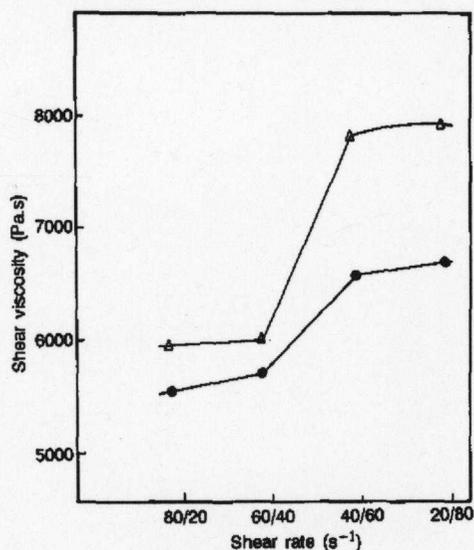
CONCLUSION

Latex stage blending can improve the dispersion of carbon black in natural rubber. The NR-latex carbon black masterbatch of SBR blend vulcanizate shows superior mechanical properties before and after ageing in comparison to an NR/SBR

blend vulcanizate. The processability of the N-LCM/SBR blend is found to be better than that of NR/SBR blend.

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(●) 80/20 N-LCM/SBR, (Δ) 20/80 NR/SBR.

Figure 5. Variation of shear viscosity with blend ratio at shear rate of $29 s^{-1}$.