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Natural Rubber-Carbon Black Masterbatches from Field Latex. II. Effect of Carbon Black Grinding

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The preparation of natural rubber-carbon black masterbatches directly from natural rubber field latex involves the acid coagulation of a mixture of ammonia-stabilised field latex, carbon black slurry, and antioxidant and oil at an elevated temperature. The carbon black is ground during preparation of the carbon black slurries. The mechanical grinding process causes loss of structure of the pelletised carbon black. This occurs primarily during the first hour of grinding. The effect of this break-down in structure of the carbon black on the vulcanisate properties of the natural rubber-carbon black masterbatches is discussed.

During the masterbatching process of natural rubber-carbon black (NR-CB) masterbatch *via* the latex route, the carbon black is ground prior to addition as a slurry to the natural rubber latex. The mechanical grinding process does not transform pelletised black into its original fluffy state but will break up the aggregates in which the size of the dispersed aggregate is of the same order of magnitude as the ultimate particle size of the carbon black[1]. Similarly, it has been well established that transient structures decrease markedly on intensive milling of the carbon black[2]. As the degree of structural change depends on the average number of particles fused together per aggregate the resultant Mooney viscosity of the raw masterbatch depends very much on the size of the aggregates[3].

The production of NR-CB masterbatch has been described previously[4] but the masterbatch has the disadvantage of high viscosity which is not acceptable to consumers. The high viscosity could be reduced by the addition of chemical additives, particularly peptisers, during the masterbatching process[5]. Another parameter which could affect the viscosity of the masterbatch would be the extent of mechanical grinding that the carbon black is subjected to during the preparation of aqueous carbon black slurries. The effect of carbon black grinding would also affect the physical properties of the masterbatch.

The purpose of this study is to determine quantitatively the degree of structural breakdown which occurs when carbon black is mechanically ground and the effect of carbon black grinding has on the properties of the NR-CB masterbatch.

EXPERIMENTAL

Materials

Bulk field latex was obtained from the Rubber Research Institute of Malaysia Experiment Station in Sungai Buloh. Carbon blacks (Machem ISAF N220 and Machem HAF N330) were obtained from Malaysian Carbon Sendirian Berhad, Renacit VII from Bayer (Malaysia) Sendirian Berhad, and other

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chemicals from various local chemical suppliers.

Preparation of Carbon Black Slurries

Dispersant-free carbon black slurries were prepared by wet grinding the pelletised carbon black with a triclover grinding pump for determined periods[4]. At the end of the determined periods, samples of the carbon black slurries were taken out, recovered by sedimentation and dried at 100°C. The hardened carbon black samples were then crushed into powders and sent for analysis. Samples were analysed by Malaysian Carbon Sendirian Berhad, Port Dickson.

Preparation of Natural Rubber-Carbon Black Masterbatch

The NR-CB masterbatch was prepared by a continuous process in the same manner as was described previously[4]. The carbon black slurry (5% total solids) and the latex/oil mixture were separately metered and mixed in a coagulator[4] with simultaneous injection of steam and formic acid. The strength of acid was kept at about 2% (weight/weight) and the pH of coagulation was at 4.0 ± 0.5. The coagulum was then crumbled using a creeper with thorough washing and dried at 100°C ± 5°C for 5 h.

Masterbatch Formulation

The masterbatch having the following composition was prepared:

	Parts by weight
Natural rubber	100
Carbon black	50
Aromatic oil (Dutrex 737 MB)	5
Antioxidant [Flectol H (Monsanto)]	1

The carbon black content determined analytically[6] was found to be in the region of 50 ± 1 p.h.r.

Preparation of Rubber Vulcanisate

Compounds of the following formulation were prepared:

	Parts by weight
NR-CB masterbatch	156.2
Zinc oxide	5
Stearic acid	2
Santoflex 13	1
Santocure MOR	0.6
Insoluble sulphur 60	2.5

The mixes were prepared on a two-roll mill at a batch weight of 2 kg each. The masterbatch was first masticated on the two-roll mill followed by the addition of zinc oxide, stearic acid, Santoflex 13 and finally Santocure MOR and sulphur. The compounds were cured at the optimum cure times.

RESULTS AND DISCUSSION

Carbon Black Properties

Tables 1 and *2* summarise the analytical data of the recovered Machem ISAF N220 and Machem HAF N330 after aqueous grinding.

The dibutylphthalate (DBP) absorption test is generally accepted as a measure of the structure of carbon black. The size and the packing density of these aggregates are factors which govern the absorption of DBP[3]. The structure of carbon blacks, as measured by the ASTM D2414 method, is generally known to be decreased by mechanical forces such as those taking place during mixing[2]. Compression of sample prior to testing, although not practical for quality control purposes, has been used to indicate retained structure (ASTM D3493 test method). Accordingly, the drop in DBPA shown by the ground samples, compared to typical Machem HAF and ISAF, is not surprising[1, 7].

It appears that the loss of structure occurs primarily in the first hour of grinding. There are no significant differences in DBPA values of

TABLE 1. PROPERTIES OF GROUND MACHEM ISAF N220 BLACK

Item	I_2No. (mg/g) ASTM No. D1510	I_2SA (mg/g) -	DBPA (ml/100g) ASTM No. D2414	Moisture (%) ASTM No. D1509	pH ASTM No. D1512	Discolouration (% toluene) ASTM No. D1618	Ash (%) ASTM No. D1506
Typical Machem ISAF N220	122	93	115	0.2	6	99	0.15
Grinding time							
1 h	104(103)	91	110(109)	4.0(2.1)	–	–	–
2 h	105(103)	92(74)	106(106)	3.0	–	–	–
3 h	105(108)	92	108(110)	3.2	3	-	–(0.5)
4 h	105(109)	92(78)	109(112)	3.3	–	–(53)	–
5 h	105(107)	92	107	3.2(2.5)	–	99	–

Figures within brackets show results with the incorporation of Renacit VII at 0.30% (wt/wt) on carbon black.

TABLE 2. PROPERTIES OF GROUND MACHEM HAF N330 BLACK

Item	I_2No. (mg/g) ASTM No. D1510	I_2SA (mg/g) -	DBPA (ml/100g) ASTM No. D2414	Moisture (%) ASTM No. D1509	pH ASTM No. D1512	Discolouration (% toluene) ASTM No. D1618
Typical Machem HAF N330	82	60	102	0.2	6	99
Grinding time						
1 h	72	–	93	1.9	–	–
2 h	71	–	92	–	–	–
3 h	71	59	92	–	–	–
4 h	71	–	93	–	3	–
5 h	71	–	93	3.2	–	97

the carbon black containing Renacit VII compared to normal carbon black.

The particle size of carbon black as measured by ASTM D1510 method is assumed to be essentially non-porous and clean. Porosity increases the iodine number (I_2No.) relative to a given particle size and surface impurities decrease the I_2No. Oxidation of carbon black surface is known to decrease the I_2No. and reduce pH value[8].

The substantially decreased I_2No. values obtained with both the Machem HAF and Machem ISAF *(Tables 1* and *2)*, indicate the formation of surface impurities. Furthermore, the reduction of pH suggests that this is due to oxidation.

Unlike the I_2No., the iodine surface area number (I_2SA) requires the carbon black surfaces to be cleaned of volatiles at 927°C prior to testing. Hence, the value obtained is independent of oxidation. With Machem ISAF containing Renacit VII particularly, it is apparent that the depression of the I_2No. might be due to the incorporation of Renacit VII.

The I_2SA values of the Renacit VII-free carbon black are much closer to normal. The increase in ash content and the decrease in toluene extractable material as observed in the Renacit VII-free Machem ISAF is consistent with this observation. Machem ISAF is more prone to adsorption of impurities than Machem HAF because of the much greater surface area available for a given mass of carbon black[8]. The drop in I_2No. of both blacks recovered after aqueous grinding might also be due to oxidation during the drying stage.

Subsequent work involves the production and evaluation of latex carbon black masterbatches using only one carbon black grade, namely, HAF N220.

Raw Masterbatch Properties

As expected the carbon black masterbatch, after drying, appears to be free from loose blacks and can be obtained in the form of stiff mass or sheet whose viscosity is too high to be measured on the Mooney Viscometer even with the small rotor. However, in order to evaluate the effect of black grinding time on masterbatch viscosity each of the product obtained was subjected to six passes on a mill after which Mooney viscosity measurements were made. Results *(Table 3)* show that varying grinding times between 1 h and 5 h did not affect the viscosity of the masterbatch. This observation is consistent with the DBPA values and I_2No. of the recovered carbon black subjected to various grinding times, as discussed earlier.

TABLE 3. EFFECT OF GRINDING OF CARBON BLACK ON VISCOSITY OF NR-CB MASTERBATCH

Grinding time (h)	Mooney viscosity (ML 1+4 at 100°C)
1	–
2	120
3	119
4	119
5	120

The high viscosity of the carbon black masterbatch produced in this manner necessitates extra care during further processing. Before the masterbatch could be further processed it has to be carefully warmed and plasticised after which subsequent incorporation and mixing of the rest of the compounding ingredient can be produced in the normal manner, *i.e.* free from pollution due to loose blacks.

Physical properties of uncured final compound such as tack, *etc.* are similar to the control.

Processing and Vulcanisate Properties

As shown in *Table 4,* cure behaviour, namely the optimum cure times and cure rates, of the latex carbon black masterbatches with carbon black that has been subjected to various grinding times appear to be similar to that of the control. However, with respect to Mooney scorch latex carbon black masterbatches are to a small degree better than the control.

While grinding time may not have any significant effect on raw masterbatch viscosity it substantially influences the final compound viscosity *(Table 4)* — the longer the grinding time the lower would the final compound viscosity be. This could be very important as normal mixing with dry rubber would require an additional premastication stage in order to have a final compound with low viscosity. Moreover the lower compound viscosity attributed to long grinding times does not have any effect on other physical properties, such as tensile strength, elongation at break, hardness, *etc.*, which are found to be comparable to those of the control.

CONCLUSION

Mechanical grinding of ISAF and HAF carbon blacks during the preparation of aqueous black slurry causes loss of structure only in the first hour of grinding. Varying the grinding times

TABLE 4. TECHNOLOGICAL PROPERTIES OF NR-CB MASTERBATCH[a]
(USING MACHEM HAF N330)

Property	Grinding time				
	2 h	3 h	4 h	5 h	Control[b]
Cure behaviour at 150°C					
Rheometer t_{90} (min)	14.1	14.2	14.5	14.5	13.3
Rheometer torque (Nm)	2.83	2.82	2.80	2.94	2.78
Rheometer cure rate (min)	10.6	10.5	10.8	10.7	9.6
Cure time (min)	14	14	15	15	14
Mooney scorch, t_5 at 120°C (min)	17.0	25.3	16.2	16.4	14.9
Compound viscosity (ML 1 + 4 at 100°C)	73.5	67.0	66.0	46.5	82.0
Elongation at break (%)	550	545	540	535	540
M100 (MPa)	2.3	2.6	2.6	2.5	3.0
M300 (MPa)	12.7	12.5	12.8	13.2	13.8
Rebound resilience (%)	50.3	50.0	59.1	54.0	60.1
Hardness (IRHD)	54.4	53.1	60.7	56.6	55.5
Crescent tear (N/mm)	142	123	165	122	144
Akron abrasion (m^3/1000 rev)	65	67	67	67	66
Air ageing, 7 days at 70°C (% retention)					
Tensile strength	105	101	101	92	100
Elongation at break	93	92	96	94	94
M300	122	120	117	114	118

[a] NR, 100; HAF N330, 50; Dutrex R, 5; Flectol H, 1

[b] CBMB from dry mixing with SMR L

from 1 h to 5 h does not affect the raw masterbatch viscosity which still remains very high and necessitates extra caution during further processing. However they influence the final compound viscosity by reducing it substantially. The reduced final compound viscosity does not in any way affect other physical properties and could improve stream processes such as extrusion, calendering, *etc.*

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