A PROCESS FOR PREPARATION OF CARBON BLACK / SILICA / NANOCLAY MASTERBATCH FROM FRESH NATURAL RUBBER LATEX

Sasidharan Krishnan,[1*] Rosamma Alex,[1]

and Thomas Kurian [2]

[1] Rubber Research Institute of India, Kottayam, India

[2] Dept. of Polymer Science & Rubber Technology, Cochin University of Science & Technology, Kochi, India

Carbon black masterbatch had received lot of attention in earlier days due to :

1. To minimize air pollution
2. To get better mechanical properties

The main problems of carbon masterbatch were

1. There was loss of filler during processing
2. Better mechanical properties were not realized
3. The process was generally energy intensive

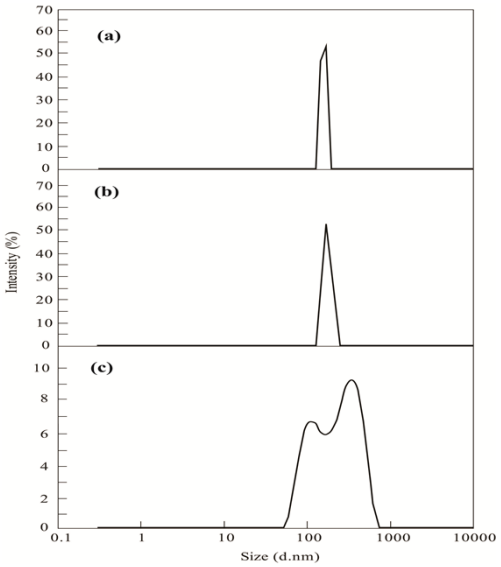
Materials

Chemicals	Supplier
Fresh NR latex	RRII farm
Carbon blacks, HAF	Philips Carbon Black, Kochi
Precipitated Silica (Ultrasil VN3	Degussa A.G., Germany
Nanoclay (Cloisite 93A)	Southern Clay Products USA

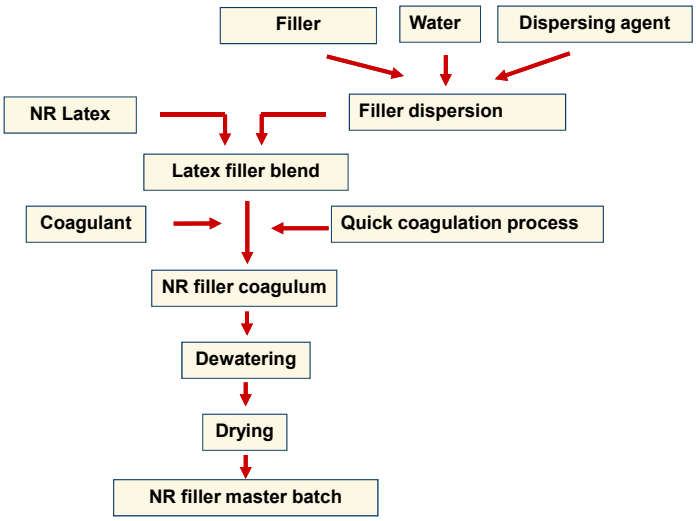
Preparation Latex
Carbon black/ Silica /Nanoclay Master batches

- 25% HAF black dispersion
- 25% silica dispersions
- 10% Nanoclay dispersion
- Fresh NR latex was mixed with carbon black , silica and nanoclay dispersion under stirring for 2- 3 min
- Coagulation using acid; washed and dried at 70^0C

The particle size distribution of (a) carbon black, (b) silica, (c) nanoclay dispersions



Flow chart showing preparation of latex filler black



Patent Filed

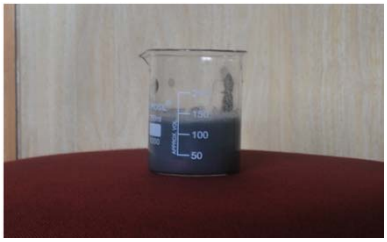
Mechanism of Coagulation

- On addition of surfactants to the 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 the surfactant containing latex, the adsorbed anions react with acid to form an undissociated surfactant and deprive the latex particles of stabilizers. As a consequence, latex coagulates immediately.

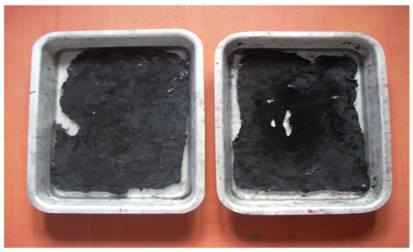
Preparation of latex filler master batch

Fresh NR latex and filler dispersions before acid coagulation



Master batch coagulum & clear serum after coagulation

Master batch coagulum after coagulation



Master batch after drying

Characterization of the Composites

- ✓ Particle size was determined using a Malvern Nanosizer,
- ✓ The Optimum cure time (t90) was determined by Monsanto Rheometer (MDR 2000).
- ✓ Filler Dispersion was studied using Dispersion Analyser from Tech. Pro, USA
- ✓ The dynamic mechanical properties were determined using DMA model 01 dB DMA 50N of Metravib, France.
- ✓ The mechanical properties were done as per relevant ASTM standards.
- ✓ XRD was determined using a D500, diffractometer (Siemens, München, Germany)
- ✓ TGA was determined using a PerkinElmer TGA 4000, (PerkinElmer, Inc, Waltham, USA).
- ✓ The Mooney viscosities were measured using Mooney viscometer (Mooney MV 2000, ALPHA Technologies, Akron, USA)

Formulation for master batch compound

Ingredients	Quantity
Natural Rubber *	100
Zinc Oxide	5
Stearicacid	1.5
HS**	1
HAF/Silica/Nanoclay	25/25/0 [M1], 25/25/3 [M2] 25/25/5 [M3], 25/25/10 [M4], 30/30/0 [M5]
DEG***	1
MBTS****	1.0
DPG*****	0.2
Sulphur	2.5

*excluding
**2.2.4-tri methyl -1,2- dihydroquinoline
*** Diethylene glycol
**** Mercapto benzothiazole disulphide
***** Diphenyl guanidine

Formulation for the dry mill mix compound

Ingredients	Quantity
Natural rubber	100
ZnO	5
Stearic acid	1.5
HS	1
HAF/Silica/Nanoclay	25/25[C1], 30/30[C5]
DEG	1
MBTS	1.0
DPG	0.2
Sulphur	2.5

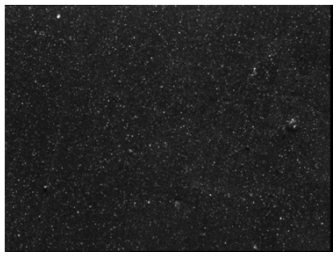
Cure characteristics, of mixes

Carbon black/silica/ nanoclay	Latex Master Batch					Dry Mill Mix	
	25/25/0 (M1)	25+25+3 (M2)	25+25+5 (M3)	25+25+10 (M4)	30+30+0 (M5)	25/25/0 (C1)	30+30+0 (C5)
Torque Max, dNm	22.67	23.04	25.33	22.67	24.1	21.03	21.4
Torque Min, dNm	2.43	2.41	2.84	2.08	2.2	2.39	2.18
Optimum cure time t_{90} , minutes	9.39	9.0	9.01	9.19	5.40	9.06	6.27
Scorch time,ts_2, minutes	1.41	2.13	2.04	2.02	1.09	2.06	1.19
Volume fraction, Vr	0.29	0.29	0.30	0.31	0.33	0.28	0.31

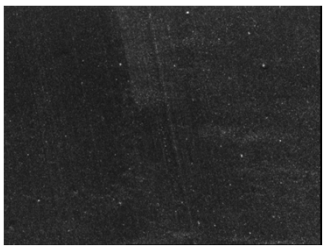
Mooney viscosity, ML(1+4)100 ˚C

Parameter	Latex Masterbatch				
	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)
Mooney viscosity, ML(1+4) 100^0 C	110	112	115	120	116
Mooney viscosity, ML(1+4) 100^0 C of NR =78					

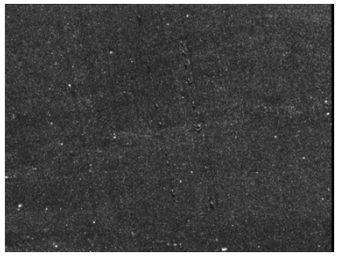
Disper grader image of Master batch and control



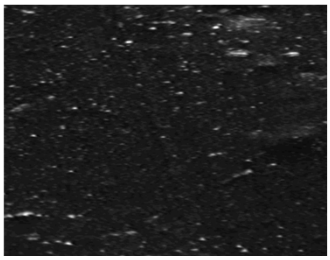
M2



M3



M4



C1

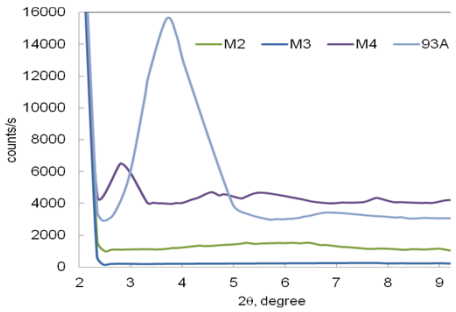
Results of Dispersion

S/N	Sample name	Classification of filler distribution (X)	Agglomerate Count (Y)
M2	25/25/3 master batch	9.2	9.5
M3	25/25/5 master batch	9.8	9.9
M4	25/25/10 master batch	8.7	9.4
C1	25/25/ Dry mix	7.0	8.2

X- value 1 represents poor dispersion while a rating of 10 represents excellent dispersion. Y- value 1 represent maximum number of large agglomerates while a rating of 10 represent the total absence of agglomerates

Comparatively better dispersion and lower aggregation is shown by master batch mix as compared to mill mixed one.

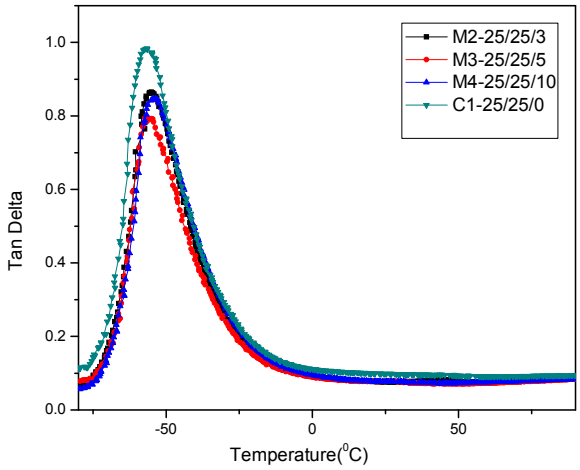
XRD spectra of Cloisite 93A & Cloisite 93A mixed Master batch



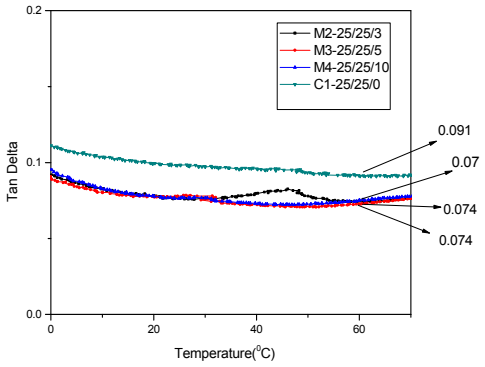
C/S/NC – 25/25/3 - M2
25/25/5 - M3
25/25/10 - M4

Sample	Peak at 2θ	Basal spacing	Observation
Cloisite 93A	3.697°	23.87799 A^0	
M4	2.809°	31.42916 A^0	Rubber intercalation in to the clay gallery & partial exfoliation
M3	Nil	-	Full exfoliation!
M2	Nil	-	Full exfoliation!

Dynamic mechanical analysis

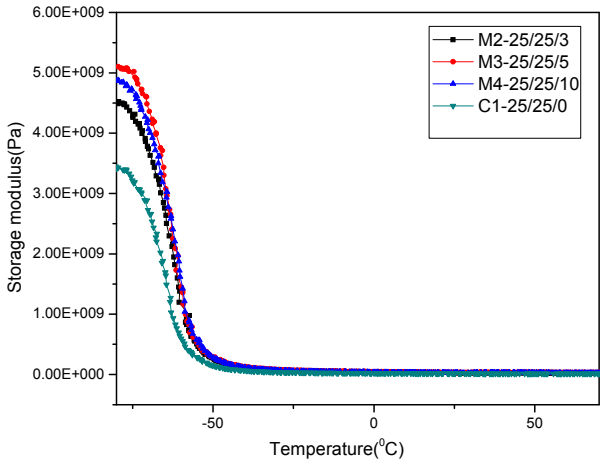


tan δ values at 60 ˚C

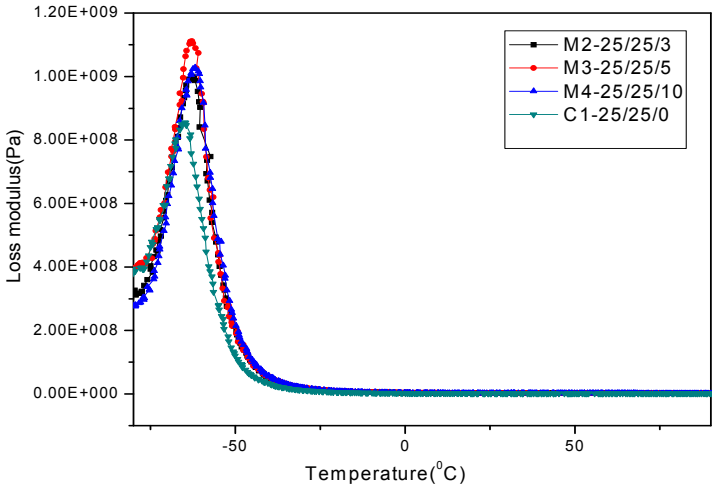


Sample	tan δ at 60^{0}C	% reduction
C1	0.091	-
M2	0.074	18.7
M3	0.070	23.1
M4	0.074	18.7

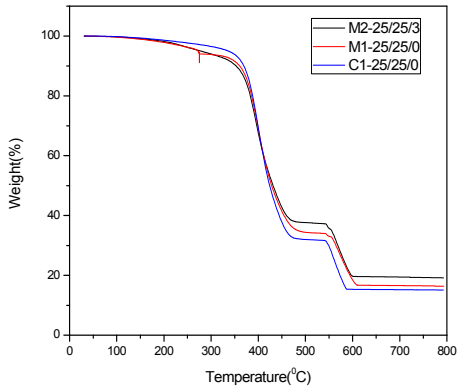
Plots of storage modulus (E') versus temperature



Plots of Loss modulus (E'') versus temperature



TGA plots of masterbatch & Dry mix



Sl.No.	Sample ID	Dissociation temperature	% age Retained at decomposition temperature
1	M2	398	70
2	M1	402	68
3	C1	401	68

Mechanical properties

Parameters	Latex master batch					Dry mill mix	
Silica/carbon black/nanoclay	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	30/30/0 (C5)
Modulus 300%, MPa	10.8	11.69	14.85	12.1	14.8	7.2	12.7
Tensile strength, MPa	25.3	25.74	25.85	25.4	25.6	24.5	24.7
Elongation at break, %	570	553	471	527	460	620	484
Tear Strength, kN/m	103	105.4	106	104.8	105	88	95
Hardness, Shore A	66	68	74	70	68	58	64
Heat Build-up, ΔT, ^{0}C	16	13	14	16	17	21	22
Abrasion loss, mm^3	107	97.3	87.5	91.8	113	143	132

Comparison of vulcanisate properties after ageing
(100^{0}Cfor 3days)

Parameters	Master Batch					Mill Mix	
Silica/carbon black/nanoclay	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	30/30/0 (C5)
Modulus 300%, MPa	11.58	12.46	16.0	14.07	15.8	10.55	14.5
Tensile strength, MPa	22.0	24.28	23.8	23.9	23.5	21.78	23.0
Elongation at break, %	525	541	415	472	445	590	412

OBSERVATIONS

The vulcanizates prepared from master batches by the new method showed

- ✓ higher tensile strength, higher modulus, hardness, and tear strength
- ✓ lower heat build-up, lower tan delta and abrasion loss
- ✓ between master batch M3(25/25/5) & conventional mill mixed C1(25/25/0) are given below.
  - ✓ Abrasion loss = -38.8% ,
  - ✓ Tan delta = - 20.42%,
  - ✓ Heat build up = -33.3%
  - ✓ Hardness = + 28%, Tear strength = +20.45%
  - ✓ Tensile strength = +4%, M300 = +100%

It should be noted that for both master batch and dry mixed compounds additives like process oil and coupling agents were not used

CONCLUSION

1. NR latex filler master batch can be prepared by an easy process consisting chemical assisted coagulation of NR latex filler mixture

2. By this process the fillers can be easily dispersed in rubber latex

CONCLUSION……

3. NR latex filler master batch prepared by chemical assisted coagulation has

- ► Higher level of vulcanisation
- ► Higher hardness and modulus
- ► Higher abrasion resistance and tear resistance
- ► Lower heat build-up
- ► Lower tan delta

Thank you

Composition of fresh Natural rubber latex

Sl. No.	Ingredients	Percentage (%)
1	Rubber	41.5
2	Protein	2.2
3	Resin	1.3
4	Sugar	1.2
5	Ash	0.8
6	Water	55.0

Properties of high abrasion furnace carbon black (HAF or N330)

Sl. No.	Parameter	ASTM	HAF
1	Iodine number, gm/kg	D1510	81.6
2	DBPA, cc/100gm	D2414	100.5
3	No.325 sieve residue,%	D1514	0.048
4	No.100 sieve residue,%	D1514	0.003
5	No.35 sieve residue,%	D1514	0.0004
6	Heat loss,%	D1509	0.4
7	Fines, %	D1508	0.8
8	Pour density, kg/m3	D1513	380
9	Compressed DBP, cc/100 gm	D3439	89

Specifications of Ultrasil VN3

Sl. No.	Parameter	Value
1	Specific surface area (N_2), m2/g	175
2	p H	6.2
3	Heating loss,%	5.5
4	Tapped density, g/l	220
5	SiO_2 content, %	98

Specifications of Cloisite 93A
(Natural montmorillonite modified with a ternary ammonium salt.)

Treatment/Properties	Organic Modifier (1)	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® 93A	M2HT	95 meq/100g clay	< 2%	39.5%
Dry Particle Sizes: (microns, by volume),10% less than: 2µm, 50% less than: 6µm , 90% less than: 13µm				
Density	Loose Bulk, lbs/ft3= 10.56	Packed Bulk, lbs/ft3 =18.03	Density, g/cc =1.88	

(1) M2HT: methyl, dihydrogenatedtallow ammonium