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BLENDS OF POLYBUTADIENE WITH NATURAL RUBBER LATEX MASTERBATCH

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The fillers such as carbon black and silica were incorporated in to the fresh natural rubber (NR) latex by a modified coagulation process. The coagulum containing fillers was dried in the conventional way to get latex filler masterbatches. NR/BR blend compounds were prepared by mixing the master batch with the required quantity of BR and other compounding ingredients. The compounds were vulcanized and characterized for mechanical and dynamic properties.

It was observed that blends prepared from master batches had better mechanical properties like tensile strength, modulus, tear strength, abrasion resistance, hardness and lower heat build-up compared to blends prepared using dry rubber mixing technique. As the proportion of BR in the blend increased the abrasion loss reduced while the hardness and heat build-up increased for all the blends, due to the unique micro structure of *cis*-1, 4-polybutadiene rubber. There was reduced filler-filler interaction on blending NR with BR for the blends based on masterbatches. Filler dispersion data indicated that filler dispersion was not adversely affected on blending. From the plots of tan δ versus temperature it was observed that for the pure materbatch there was a lowering of tan δ peak height indicating better polymer-filler interaction, compared to the mill mixed compound. The tan δ value at 60 ^{o}C and hence the rolling resistance was lower for the 80/20 NR/BR blend prepared using the masterbatch.

Keywords: Carbon black, Latex masterbatch, Natural rubber latex, Polybutadiene rubber, Silica

INTRODUCTION

Blends based on natural rubber and polybutadiene rubber are extensively used in tyre sector due to the enhanced mechanical properties like low heat build-up, excellent abrasion resistance and low rolling resistance. Silica in combination with silane coupling agent offers reduced rolling resistance and enhanced wet traction for tyres.

However in comparison with carbon black, silica imparts lower wear resistance and dry traction performance. Further silica is non conductive in nature and when used as single filler in tyres there can be accumulation of static electric charge. Due to these reasons silica along with carbon black, have attained great significance for tyre sector (Wang and Michael, 2009; Rothon 2002; Wang *et al.,* 2001; Donnet *et al.,* 1993). Due to filler-filler interactions existing in reinforcing fillers it is difficult to disperse them uniformly either in a single polymer or in blends. The dispersion of these fillers is the crucial parameter that controls the

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dynamic and mechanical properties of rubber vulcanizates (Gerspacher and Farrel, 2001; Wang, 1998).

It is well known that wear resistance is improved by enhancement in polymer-filler interactions either by physical adsorption of polymer chains on filler surface or through chemical linkages between polymer and filler. Both polymer- filler and filler- filler interactions contribute towards hysterisis of rubber vulcanizates. (Wang *et al.,* 2001). The loss factor or tan δ which is the ratio of loss modulus by storage modulus is related to hysterisis. Higher filler networking result in higher viscous modulus. Higher the filler-filler interactions, higher will be the loss factor and so higher will be the rolling resistance.

Many attempts have been made in the past to add filler as dispersion to latex and then to coagulate the latex filler slurry to get filler incorporated coagulum (Wang, 2005; Wang *et al.,* 2002; Leblance, 2002; Prasertsri and Nittaya, 2012). However the expected benefit was not realized in many of the methods standardized earlier (Zainul *et al*., 1984). Different forms of rubber like pre-vulcanised latex, modified latex and centrifuged natural rubber latex were used for masterbatch preparation. A method to prepare pre-vulcanized latex coated carbon black powder has been described earlier (Shekhar, 2008). In many of the methods coagulation was effected by high speed mixing of filler slurry and latex. Cabot Elastomer Composite is a NR carbon black masterbatch with good mechanical properties prepared using a technique of unique continuous liquid phase with mixing/coagulation process (Marby *et al.*, 2000; Kazuhiro *et al*., 2005). Takashi *et al*. (2009) have patented a process in which the filler slurry is irradiated with high amplitude ultrasonic waves having amplitude of 80 μ or more, and then mixed with concentrated natural rubber latex under same condition. It was expected that the proteins adsorbed on rubber particles would interfere with polymer filler interactions and the amide bonds of latex were cleaved before preparing the masterbatch (Hiroshi and Kazuhiro, 2011).

Masterbatches attain more significance when used in blends with polybutadiene rubber as the latter improves the wear resistance of tire compounds. Filler distribution in blends is influenced by filler addition, mixing method, surface polarity of filler and other factors like un-saturation, viscosity and polarity of blend components. The incorporation of carbon black in a 50/50 elastomer preblend indicated that black affinity decreased in the order, BR>SBR>CR>NBR>NR>EPDM>IIR (Corish and Powell, 1974; Callan *et al*., 1971).

It is expected that if carbon black is first incorporated in NR matrix and then blended with BR the filler distribution would be more uniform and would deliver vulcanizates with improved mechanical and dynamic properties. There are very few reports on use of filler masterbatch for preparation of rubber blends. In the present study, an attempt is made to prepare NR/BR blends using NR filler masterbatch.

MATERIALS AND METHODS

Natural rubber latex used in the study was obtained from Rubber Research Institute of India, Kottayam. *Cis*-1,4-polybutadiene rubber (CISSAMER) was obtained from M/s Indian Petrochemicals Corporation Ltd, Vadodara, Gujarat, India.

High abrasion furnace black (N330) was obtained from M/s Phillips Carbon Black Limited, Kochi, India. Precipitated silica used was ULTRSIL VN3 grade. Other ingredients used were rubber grade chemicals.

a. Preparation of carbon black/silica masterbatch by a modified coagulation process

Dispersions of carbon black and silica were prepared separately by the conventional ball milling process in presence of a suitable surfactant. The dispersion was added slowly into fresh natural rubber latex under stirring and coagulated by the addition of an acid to produce the filler masterbatch. In this method the filler -latex slurry is coagulated chemically almost immediately after addition of acids. The fillers were incorporated in latex so as to have levels of 50 parts per hundred parts of dry rubber (phr).The coagulum was washed well and dried in an air oven at 70 °C. The dried rubber was mixed with polybutadiene rubber as per formulation given in Table 1. Control mixes with conventional mill mixing process were also prepared.

b. Preparation of NR/BR blends

NR filler masterbatch and BR were separately masticated and mixed with the required quantity of carbon black and silica on a mixing mill so as to have 25 phr each of carbon black and silica in 80/20 and 60/40 NR/BR blends. Rubber compounds were prepared in the conventional way.

c. Characterization of pure and blend mixes

The cure behavior was determined at 150 °C using a moving die rheometer model MDR2000 of ALPHA Technologies USA. The Mechanical properties were determined using relevant ASTM standards. The dynamic properties were determined using a Dynamic Mechanical Analyzer model 01 dB DMA 50N of Metravib, France. The test was conducted at a frequency of 10 Hz and at a dynamic strain of 0.12% from -80 to 90 °C. The Payne effect was studied by evaluating the storage modulus at dynamic strain varying from 0.0001 to 0.1. Filler dispersion was studied on vulcanized films using Dispersion Analyser from Tech Pro USA. Thermo gravimetric analysis (TGA) was recorded with a thermo gravimetric analyzer, Perkin Elmer model TGA 4000 USA. Approximately 10 mg of samples were heated at a rate of 20 °C/ min from 30 to 550 °C.Volume fraction of rubber in toluene swollen gel was determined as per standard procedure using the following equation (Ellis and Welding, 1964).

$$Vr = \frac{(D - FT)\rho r^{-1}}{(D - FT)\rho r^{-1} + Ao\rho s^{-1}}$$

where, T is the weight of the test specimen, D its deswollen weight, F the weight fraction of insoluble component and Ao 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.

RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics are shown in Table 2. The masterbatch mixes containing 50 phr of silica/carbon black fillers for both pure and blends recorded a higher rheometric torque, lower cure time and lower scorch time as compared to the

Table 1. **Formulation of the mixes**

Ingredient	Masterbatch			Dry mix (Control mixes)		
	NR/BR 100/0	NR/BR 80/20	NR/BR 60/40	NR/BR 100/0	NR/BR 80/20	NR/BR 60/40
Natural Rubber masterbatch	150	120	90	-	-	-
Natural Rubber	-	-	-	100	100	100
Polybutadiene Rubber	0	20	40	-	20	40
Zinc Oxide	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	2	2	2
HAF black	0	5	10	25	25	25
Ultracil VN3	0	5	10	25	25	25
Antioxidant HS	1	1	1	1	1	1
MBTS	1.4	1.5	1.6	1.4	1.5	1.6
DPG	0.25	0.25	0.25	0.25	0.25	0.25
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 2. **Cure characteristics blends at 150 °C & volume fraction of rubber**

Parameter	Masterbatch , NR/BR			Dry mix (Control mix), NR/BR		
Blend ratio	100/0	80/20	60/40	100/0	80/20	60/40
Torque Min, dNm	1.27	1.61	2.55	1.39	1.98	2.20
Torque Max,dNm	20.52	22.80	23.07	18.88	13.17	13.90
△ Torque	19.25	21.19	20.52	16.49	11.85	12.00
Optimum cure time, t90, min	12.50	9.75	9.45	12.90	12.75	12.80
ts_2 (scorch time)	2.20	2.20	2.60	3.90	4.00	4.10
Vr	0.32	0.39	0.38	0.30	0.29	0.30

corresponding mill mixed compounds. The maximum torque does not show much variation for the pure and blend mixes in the case of masterbatch based mixes. The masterbatches are prepared using a modified coagulation process and the additives added are expected to give better filler dispersion and higher level of vulcanization (Sasidharan *et al*., 2011; Blackley, 1997; Van Gils, 1947). Due to this, a higher volume fraction is also recorded by the blends based on masterbatch.

Mechanical properties

The pure and blend vulcanizates prepared from the masterbatches showed a higher tensile strength, modulus, hardness and tear strength along with lower heat build-up and abrasion loss compared to conventionally prepared mixes. In all blends as the proportion of BR increased there was a decrease in modulus, tear strength and tensile strength along with an increase in heat build-up. The abrasion resistance improved as the BR content increased

Table 3. **Mechanical properties of the masterbatch mixes with BR blends**

Parameters	Masterbatch			Dry mix		
Blend ratio	100/0	80/20	60/40	100/0	80/20	60/40
Modulus 300%, MPa	10.8	8.0	7.8	7.2	5.3	5.2
Tensile strength , MPa	27.3	28	24.7	24.5	20.0	18.8
Elongation at break,%	540	625	680	620	700	660
Tear strength, kN/m	100	94	77	88	68	60
Hardness, Shore A	66	69	68	58	60	65
Heat Build-up, $\triangle T$, ^{o}C	15	16	18	17	18	20
Abrasion loss, mm^3	107	93	88	143	99	95

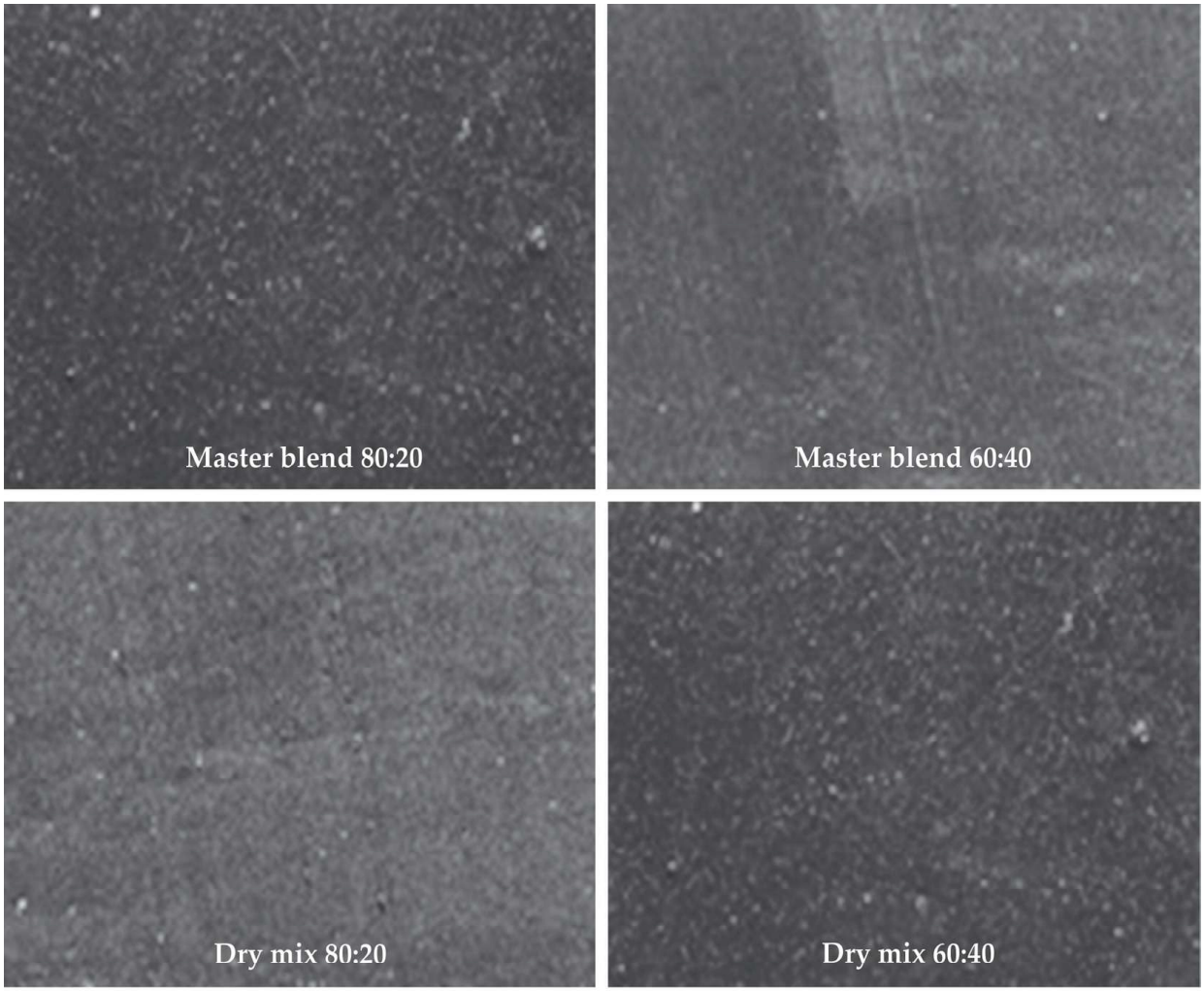

Fig.1. Filler dispersion photographs obtained from Dispersion Analyser
80:20 NR/BR blend based on masterbatch (Master blend 80:20)
60: 40 NR/BR blend based on masterbatch (Master blend 60:40)
80:20 NR/BR blend based on dry mix (Dry mix 80:20)
60: 40 NR/BR blend based on dry mix (Dry mix 60:40)

(Table 3.) These are attributed to the unique micro structure of *cis*-1, 4-polybutadiene rubber like molecular weight and branching. It is well known that addition of small quantity of *cis*-1, 4- polybutadiene rubber improves the abrasion resistance of the compound due to the inherent high elasticity on account of the very low glass transition temperature which is lower than that of NR.

Table 4. **Results of carbon black dispersion**

Sample name	Carbon black dispersion (X)	Agglomerate Count (Y)
Masterbatch 80:20	8.9	9.3
Masterbatch 60:40	9.0	9.5
Masterbatch 100:0	8.8	9.3
Dry mix 80:20	7.2	8.4
Dry mix 60:40	7.5	8.5
Dry mix 100:0	7.0	7.8

The filler dispersion characteristics are presented in Figure 1 and Table 4. Comparatively better dispersion and lower aggregation is shown by masterbatch mix as compared to mill mixed one. Filler dispersion characteristics do not show much variation on blending with BR in both 80/20 and 60/40 proportions for the mixes based on masterbatches. It is inferred that the filler distribution is not adversely affected on blending though carbon black has a tendency to migrate to BR phase and silica to NR phase in blends of NR/BR as reported earlier (Hess *et al.*, 1971; Jeon *et al.*, 2003). During masterbatch preparation both the fillers are incorporated in the NR phase. So the migration to butadiene phase on mixing with BR is expected to be low as the fillers are incorporated in the latex stage. The improvement in mechanical properties is attributed to better filler dispersion and higher level of vulcanization for the mixes prepared using the masterbatches.

Dynamic mechanical properties.

a) Payne effect – Filler-filler interactions

The filler-filler interactions can be evaluated from the strain dependence of elastic modulus. Generally for filled vulcanizates the elastic modulus decreases with strain amplitude and this phenomenon is known as Payne effect (Payne and Whittaker, 1971). The plots of storage modulus versus strain amplitude for the blends prepared from latex masterbatches

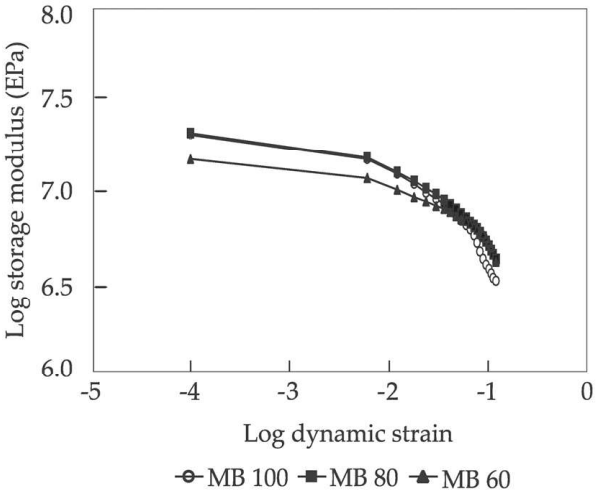

Fig. 2. Strain dependence of storage modulus of Pure masterbatch (MB 100, NR/BR 80/20 blend(MB80) and NR/BR 60/40 (MB 60)

is shown in Figure 2. It is observed that Payne effect is not increasing on blending. Though there is a decrease in the modulus, the Payne effect also decreases as the proportion of BR in the blend increase. This shows that the filler-filler interaction is reduced on blending with BR. It is to be observed that comparatively good tensile properties are obtained for all the blends when compared to pure rubber.

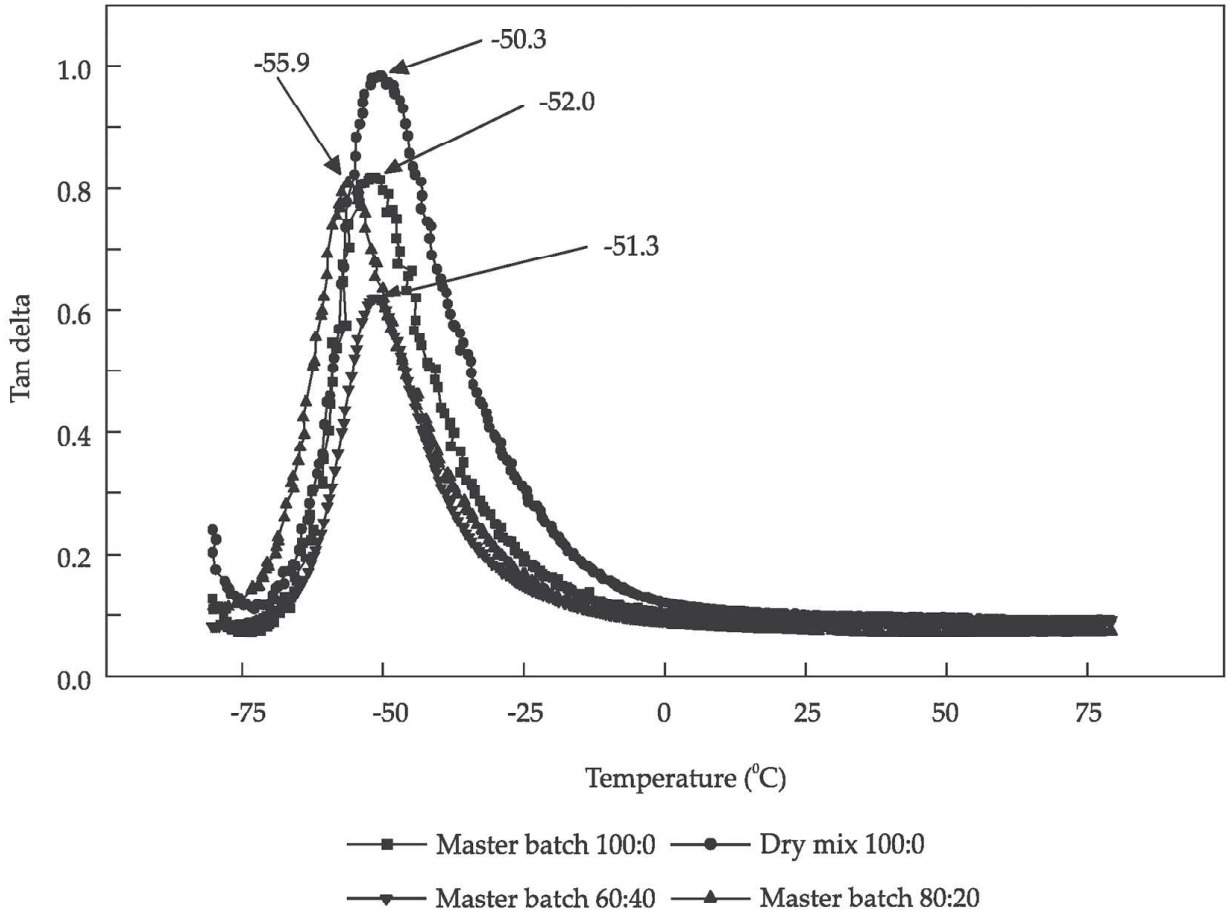

Fig.3. Plots of tan delta versus temperature for pure master batch, (Masterbatch 100:0) conventional dry mix (Dry mix 100:0), and NR/BR blends based on masterbatch, 80:20 and 60:40 (Masterbatch 80:20 and Masterbatch 60:40)

b) Tan δ in cyclic deformations – Polymer - filler interaction

Damping characteristics from -80 to 100 °C for the pure masterbatch, control mix and the blends are given in Figures 3 and 4. For the masterbatch mix there is a lowering of tan δ peak height compared to the control mix showing that there is better polymer filler interaction. For the 80/20 blends it is observed that the temperature showing the maximum tan δ is lower for masterbatch than control and a similar observation is shown for the storage modulus since the loss factor or tan δ is the ratio of loss modulus by storage modulus. The transition in storage modulus also occurs at a lower temperature for blend based on masterbatch compared to control mix. It is observed that a lower tan δ at 60 °C is also obtained for the blend based on masterbatch compared to the control. These observations reveal that there is higher chain flexibility for the masterbatch based mixes, and this is possibly due to factors like preserving a higher molecular weight, better filler dispersion and more uniform mixing of the two rubbers. Higher chain flexibility is known to correlate with higher abrasion resistance and lower heat build-up

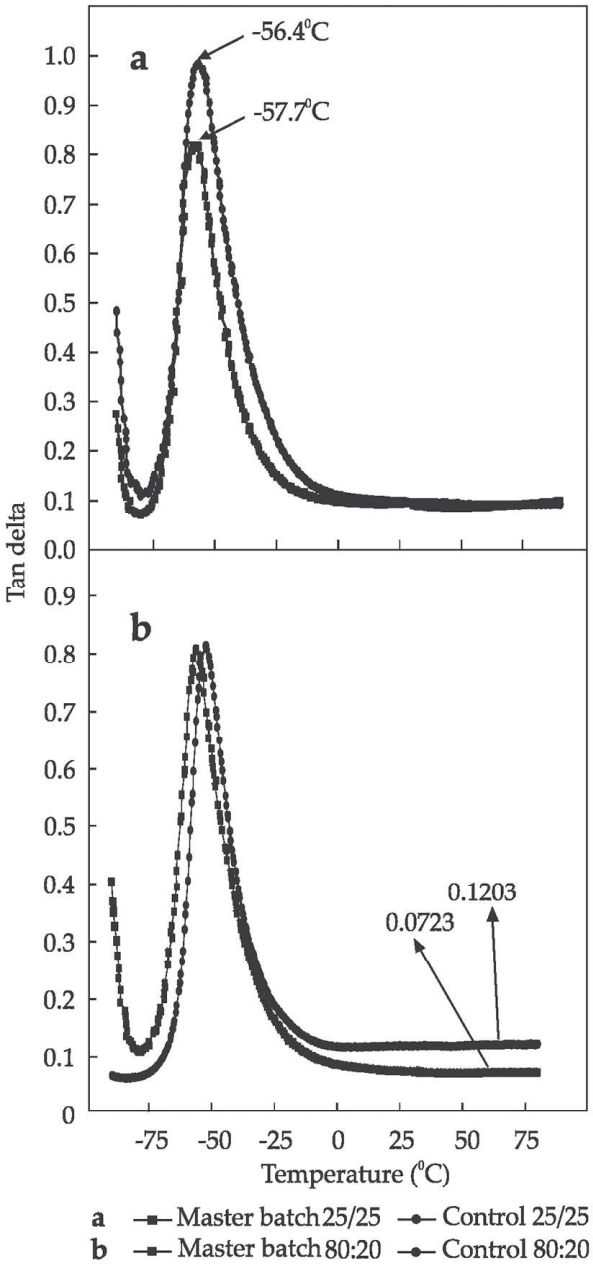

Fig.4. Plots of tan delta versus temperature for (a). Pure masterbatch and control mix, (b). NR/ BR 80/20 blends based on master batch and conventional dry rubber (control)

characteristics. Ideal filler for tyre tread compounds are those which possess high polymer-filler and low filler-filler interactions. The former ensures higher abrasion resistance and the latter is

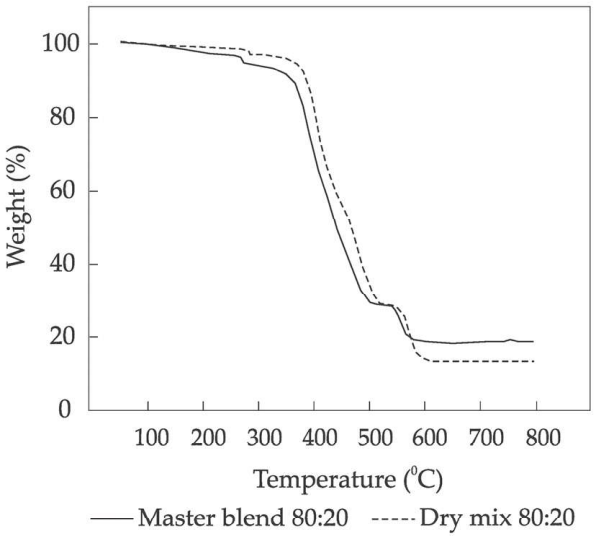

Fig.5. Thermograms of 80:20 NR/BR blends based on masterbatch and dry mix

necessary for lower rolling resistance or lower tan δ (Wang *et al.*, 2001). It is well known that the tan δ at 60 °C is a measure of the degree of rolling resistance (Wang *et al.*, 2002). It is clearly inferred that there is a lower rolling resistance for the masterbatch based mixes compared to the conventional mixes.

Thermo gravimetric analysis

The thermograms of the masterbatch and the conventionally prepared mix, recorded on a thermogravimetric analyzer are given in Figure 5 and Table 5. It is

Table 5. **Thermo gravimetric analysis data of blends**

Sample	Dissociation temperature (°C)	% retained at decomposition temperature
Master 80:20	401466	75.043.4
Dry mix 80:20	396.8	79.0
	478.7	41.0

inferred that thermal stability of carbon black/silica BR blend masterbatch and the conventional mix were the same.

CONCLUSIONS

Latex-filler masterbatch can be prepared by latex stage incorporation of filler and using a modified coagulation process. Such a masterbatch offers precise advantages in blends with *cis*-1, 4 polybutadiene rubber. They show very good polymer-filler interactions, lower filler–filler interactions and high level of vulcanization. Due to this NR/BR blends show superior mechanical and dynamic properties compared to blends prepared by the conventional mixing.

REFERENCES

Blackley, D.C. (1997). Polymer Latices, Science and Technology, Vol.2 *Types of lattices,* Second Edition, Chapter 9 , Chapman & Hall, UK.

Callan, J.E., Hess, W.M. and Scott, C.E. (1971). Elastomer Blends, Compatibility and Relative Response to Fillers. *Rubber Chemistry and Technology*, **44**: 814-837.

Corish, P.J. and Powell, B.D.W. (1974). Elastomer Blends. *Rubber Chemistry and Technology*, **47:** 481-509.

Donnet, J.B., Bansal, R.C. and Wang, M.J. (1993). Composite Materials, In: *Carbon black Science and Technology* 2nd edition, Marcel Dekker, New York.

Ellis, B. and Welding, G.N. (1964). Estimation, from Swelling, of the Structural Contribution of Chemical Reactions to the Vulcanization of Natural Rubber, art II. Estimation of Equilibrium Degree of Swelling. *Rubber Chemistry and Technology*, **37**: 571 -581.

Gerspacher, M. and Farrel, C.P.O. (2001). Tire Compound Materials Interactions. *Kautchuk Gummi Kunststoffe,* **54**(4):153-158.

Hess, W.M., Scott, C.E. and Callan, J.E. (1967). Carbon black distribution in elastomer blends. *Rubber Chemistry and Technology*, **40**:371.

Jeon, I. H., Kim, H. and Kim, S. G. (2003). Characterization of Rubber Micro-Morphology by Atomic Microscopy (AFM). *Rubber Chemistry and Technology,* **76**(1): 1-11.

Leblance, J. L. (2002). Rubber-filler interactions and rheogical properties in filled compounds. *Progress in Polymer Science*, **27**(4): 627-687

Marby, M.A., Rumpf, F.H., Podobnik, J.Z., Westveer, S.A., Morgan, A.C., Chung, B. and Andrew, M.J. (2000). *U. S. Patent, 6048923 2000.*

Miyasaka, T., Uri, T., Narita, H. and Hyashi, H. (2009). Method for producing Rubber-filler composite, Toyo Tire & Rubber Company Ltd. *Patent No 20090036596.*

Payne, A.R. and Whittaker, R.E. (1971). Low Strain Dynamic Properties of Filled Rubbers. *Rubber Chemistry and Technology,* **44**: 440-478.

Prasertsri, S. and Rattaasom, N .(2012). Fumed and precipitated silica reinforced natural rubber composites prepared from latex system: Mechanical and dynamic properties. *Polymer Testing*, **31**(5): 593 -605.

Rothon, R.N. (2002). Particulate fillers for Polymers, *Rapra Review Report No.141,* ***12****, No.9.*

Sasidharan, K.K., Alex, R., George, B. and Jacob, J. (2011). A Novel process for the preparation of carbon black/silica/nanoclay masterbatch from fresh natural rubber latex. *Indian Patent application No.2564/ CHE / 2011, (G602B).*

Shekhar, B.C. (2008). Carbon Black Masterbatches and Method for making the same. *US Patent 20080262123.*

Van gils, G.E. (1947). Spontaneous coagulation of Hevea Latex. *Transaction of Institution of Rubber Industries*, **23**: 74-76.

Wang, M. J. and Morris, M. (2009). Advances in Fillers for Rubber Industry In: Rubber Technologist's Handbook (Eds. J. White, S. K. De and K. Naskar), Smithers RAPRA Technology, **2**: 59-95 & 189-218.

Wang, M.J. (1998**).** Effect of Polymer- Filler and Filler - Filler Interactions on Dynamic Properties of Filled Vulcanizates. *Rubber Chemistry and Technology*, **71**(3): 520-599.

Wang, M.J. (2005). New Developments in Carbon Black Dispersion. *Kautchuk Gummi Kunststoffe,* **12**: 626-631.

Wang, M.J., Wang, T., Wong, Y.L., Shell, J. and Mahmud, K. (2002). NR/carbon black masterbatch produced with continuous liquid phase mixing. *Kautchuk Gummi Kunststoffe,* **55**(7-8): 388-396.

Wang, M.J., Kutzovsky, Y., Zhang, P., Murphy, L.J., Laube, S. and Mahmud K. (2002). New Generation Carbon-Silica Dual Phase Filler Part I. Characterization and application to Passenger Tir**e.** *Rubber Chemistry and Technology***,** **75**: 247-263.

Wang, M.J., Zang, P. and Mahumd, K. (2001). Carbon-Silica Dual Phase Filler, A new Generation Reinforcing Agent for Rubber: Part IX. Application to Truck Tire Tread Compound. *Rubber Chemistry and Technology*, **74**: 124-137.

Wang, M.J., Kutzovski, Y., Zhang, P., Mehos, G., Murphy, L.J. and Mahmud, K. (2001). Presented at "Functionalised Tyre Fillers 2001", Fort Louderdale, Florida, January 29-31, 2001.

Yamada, H. and Yanagisawa, K. (2011). US patent 7960466B2.

Yangisawa, K., Someno, K. and Mukai, U. (2005). *US Patent 6841606,841,606 B2.*

Maidunny, Z.A.B., Bin Mohd. Nor, M.R., Dulngali, S.B., Othman, S.B. and W.I. Bin Wah Yaacob. (1984). Carbon black masterbatch using field latex. *Journal of Rubber research institute of Malaysia*, **32**(2): 103 -112.