Improvement of Polymer Blend Properties by Changing Sequence of Mixing

R. Maji,[1] S. Bhattacharyya,[1] S. Dasgupta,[1] S. Bandyopadhyay,[1] R. Mukhopadhyay,[1] A. S. Deuri[2]

[1]Material Compound Group (MCG), HASETRI, Rajsamand, Rajasthan, India
[2]R & D Centre, J. K. Tyre, Rajsamand, Rajasthan, India

ABSTRACT: The basic objective of this article is to improve the polymer blend properties by changing mixing sequence. Blending of two elastomers does not lead to a molecularly homogeneous blend (true solution), but to a heterogeneous system in which both polymer phases are present. In this article, the detailed study of heterogeneous distribution of carbon black as well as blend inhomogenity and the physicomechanical including dynamic mechanical properties of the blend has been carried out. The choice of the blend was natural rubber/polybutadiene rubber as 85:15. Heterogeneous carbon black distribution study was also performed in differential scanning calorimeter. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2735–2742, 2007

Key words: compounding; blending; differential scanning calorimeter; modulus; rubber

INTRODUCTION

Elastomer blends continue to play an important role in the manufacturing of rubber products. Four major reasons for utilizing blends were listed and included enhanced product performance, better processing, reduced product cost, and improved manufacturing of tires. Several reviews on the extensive literature of elastomer blends have been published by McDonel et al.,[1] Roland,[2] Hess et al.,[3] and Corish.[4] The use of elastomer blends in tire application has also been reviewed by McDonel et al.[1]

Mechanical mixing is still mostly used to prepare elastomer blends. The resulting mixing of the two elastomers is usually an endothermic process with small entropic contribution,[5] which results in a micro-heterogeneous blend. Complete miscibility of the elastomers is not required and to some level of micro-heterogeneity is actually desirable to preserve the properties of the individual elastomers used in the blend.[6]

Natural rubber (NR) is the adequate choice when good tensile and tear strengths are demanded, since these characteristics can be developed owing to the capability of this rubber to crystallize under stress.[7–11] Polybutadiene rubber (BR) is characterized by its superior abrasion resistance, so that blends of NR and BR that combine the excellent processing and physical properties of the former with the superior abrasion resistance of the latter are largely used in the tire industry for the production of treads and also in conveyor belt cover compound.[12–15] However, the rubber performance is determined not only by the right choice of the formulation components but also by such design factors as constituent patterns and fabrication process parameters. The final properties will be strongly influenced by the additive distribution in each elastomeric phase and by the interfacial compatibility between the components.[16]

It is generally recognized that blending of two elastomers does not lead to a molecularly homogeneous blend (true solution), but to a heterogeneous system in which both polymer phases are present.[17] The zone-size of the phases in such blends is mainly dependent upon the relative compatibility of the elastomers and on the processing conditions.

The heterogeneity present in polymer blends is further magnified on addition of compounding ingredients if the affinity of the polymers for these ingredients is unequal. This may lead to a heterogeneous carbon black distribution, as is the case for NR/BR blend. More recent work has shown that the difference in carbon black distribution in blend components can be further increased, in some cases, by varying the sequence of elastomer and black addition.[18]

In this article, the detailed study of heterogeneous distribution of carbon black as well as blend inhomogenity and the physicomechanical including dynamic mechanical properties of the blend has been carried out. The choice of the blend was NR/BR as 85 : 15. Heterogeneous carbon black distribution study was also performed in a differential scanning calorimeter (DSC7) equipment.

TABLE I
Material and Suppliers

Material	Supplier
Natural rubber, Sheet Rubber, RMA no. 4	J K Supplying Agency, Cochin, Kerala, India
Poly butadiene rubber (BR), BR 01	Indian Petrochemical Corporation, Vadodara, India
Penta chloro pthio phenol (PCTP) based Peptiser, PEPTIZOL-7	Acmechem, Ankeleshwar, India
High abrasion furnace black, High Structure (HAF-HS, N339)	Cabot India, Mumbai, India
Aromatic oil, RPO 701	Sah Petroleum, Daman, India
Red seal zinc oxide	Zinc–O–India, Alwar, Rajasthan, India
Stearic acid	Godrej Industries, Mumbai, India
Antiozonant 1, 3 dimethyl butyl para phenylene diamine, 6PPD, PILFLEX 13	NOCIL, Thane, India
Antioxidant 1, 2 di hydro 2, 2, 4 trimethyl quinoline, TMQ, PILNOX TDQ	NOCIL, Thane, India
Microcrystalline wax (MC Wax)	Gujarat Paraffins, Gujarat, India
Rubber makers sulfur (soluble sulfur)	Jain Chemicals, Kanpur, India
Accelerator, N-oxydiethylene benzo thiazyl sulfenamide, (NOBS), PILCURE MOR	NOCIL, Thane, India
Scorch Inhibitor, N-Cyclo hexyl pthio pthalimide, CTP, PVI 100, ACCITARD RE	ICI, Rishra, India

EXPERIMENTAL

Material used

The details of all the materials used in this study are given in Table I.

TABLE II
Rubber Compound Formulation

Ingredients	Parts per hundred parts of rubber (phr)
RMA-4	85
BR	15
PCTP	0.15
Black (N339)	50
Aromatic oil	7
ZnO	4.5
Stearic acid	3
6PPD	2.4
TMQ	0.75
MC wax	1.25
Sulfur	2.25
NOBS	0.55
PVI	0.2

TABLE III
Mixing Sequence for Control Compound

Parameter for master batch	Time (min)	Parameter for Remilled batch	Time (min)
RMA-4 and PCTP	0.0	Master compound loading	0.0
BR	0.5		
N-339 and ZnO	1.0		
Oil, St. acid, 6PPD, MC Wax and TMQ	4.5	Batch Dumping	2.5
Batch Dumping	6.0		

Temperature control unit (TCU): 90°C (master) and 70°C (remilled); Rotor rpm: 60 (master compound) and 30 (remilled compound); Ram pressure: 4.9×10^4 kgf/m².

Compound mixing and characterization

Mixing of rubber compound was carried out using a two-wing rotor laboratory Banbury mixer of 1.5 L capacity (Stewart Bolling, USA) following master, remilled, and final batch mixing mode. The compound formulation taken into use is shown in Table II.

The control as well as experimental batches were mixed as per the mixing sequences described in Tables III–VI. The mixing sequence for preparing the final batch for all the compounds were kept same and are described in Table VII. The various mixing sequences were chosen for heterogeneous distribution of different material used in the mix, particularly, the carbon black in the NR as well as in the soft BR phase. It was also decided that the mixing sequences would be applied in the actual shop floor conditions in a rubber product manufacturing industry.

The dump temperature of the master/first master batches was found to be within 140–150°C and that of the remilled/second master batches were 105–115°C. The dumped batches were sheeted out in a laboratory two-roll mill from Santosh Industries,

TABLE IV
Mixing Sequence for Experimental Compound (Sample 1)

Parameter for first master batch	Time (min)	Parameter for second master batch	Time (min)
RMA-4 and PCTP	0.0	First Master and BR	0.0
40 phr black	1.0	Rest black, rest oil, ZnO, and St. acid	1.0
5 Phr oil + chemical	2.0	Batch dumping	2.5
Batch dumping	5.5		

Temperature control unit (TCU): 90°C (first master) and 70°C (second master); Rotor rpm: 60 (first master) and 30 (second master); Ram pressure: 4.9×10^4 kgf/m².

TABLE V
Mixing Sequence for the Master Batch Experimental Compound (Sample 2)

Parameter for first master batch	Time (min)	Parameter for second master batch	Time (min)
RMA-4 and PCTP	0.0	First master, BR, and other chemicals	0.0
All black and oil	1.0	Batch dumping	2.5
Batch dumping	6.0		

Temperature control unit (TCU): 90°C (first master) and 70°C (second master); Rotor rpm: 60 (first master) and 30 (second master); Ram pressure: 4.9×10^4 kgf/m^2.

New Delhi, India. The master/remilled batches were further mixed after a maturation period of 8 h.

The dump temperature of the final batches was maintained within 95–105°C. The final batches were also sheeted out in the laboratory two-roll mill. The final compounds were matured for 8 h before further testing.

Rheological properties

Rheometric properties were determined at 141°C over a period of 60 min using a 0.5° arc in a MDR 2000E instrument, in accordance with ASTM D 5289. The Mooney viscosity, ML (1 + 4) at 100°C was determined in a MV 2000E, as per ASTM D 1646. Both items of equipment were from Alpha Technologies, USA.

Study of filler dispersion and polymer–filler interaction in Rubber Process Analyzer

Dispersion of filler was determined using Rubber Process Analyzer, RPA 2000 from Alpha Technologies, USA, in accordance with ASTM D6204. Strain sweep of unvulcanized compound at 1.667 Hz and at 50°C was carried out from 1% to 25% strain to

TABLE VI
Mixing Sequence for the Master Batch Experimental Compound (Sample 3)

Parameter for first master batch	Time (min)	Parameter for second master batch	Time (min)
RMA-4 and PCTP	0.0	First Master and BR	0.0
All black	1.0		
Oil and all other chemicals	3.5	Batch dumping	2.0
Batch dumping	6.0		

Temperature control unit (TCU): 90°C (first master) and 70°C (second master); Rotor rpm: 60 (first Master) and 30 (second master); Ram pressure: 4.9×10^4 kgf/m^2.

TABLE VII
Mixing Sequence for Final Compound

Parameter for final compound	Time (min)
Master/remilled compound and curative package (sulfur, accelerator, and scorch inhibitor)	0.0
Batch dumping	2.5

Temperature control unit (TCU): 60°C; Rotor rpm: 30; Ram pressure: 4.9×10^4 kgf/m^2.

understand the filler–filler networking—''Payne effect.''[19]

Another experiment in the RPA was also done according to Coran and Donnet[20] to understand the carbon black dispersion quality in the compound. The configuration of the experiment is shown in Table VIII.

Polymer–filler interaction

More recently, an interaction parameter, defined[21] by σ/η, has been proposed for the measurement of the interactions between carbon black and rubber. The σ term is the slope of the stress–strain curve in linear regions and at typical extension ratios varying from 1 to 3. The moduli in these deformations relate the carbon black–polymer interaction. The nondimensional term, η, is the ratio of the dynamic modulus E' at 1% and 25% strain, and it is related with the carbon black–carbon black interactions.

Physical properties

The green rubber compounds were cured in accordance with ASTM D 3182 in an electrically heated hydraulic curing press from Hind hydraulics, New Delhi, India, using compression molding technique. The molding conditions followed to prepare different samples are given in Table IX.

TABLE VIII
Test Configuration in RPA 2000

Parameter	Strain (%)	Frequency (cpm)	Temperature (°C)
Conditioning of the rubber compound	1	100	50
10 s static delay	0	0	50
High strain	50	100	50
10 s static delay	0	0	50
Low strain, repeated until stable[a]	1	100	50
60 s delay[b]	0	0	50

[a] Repeat last two steps until G' reaches plateau.
[b] After 10 s G' was measured.

TABLE IX
Molding Conditions for Test Sample Preparation

Sample	Temperature (°C)	Time (min)	Pressure (kg/cm^2)
Tensile slab including for tear specimen having approximately 2.0 mm thickness	141	45	150
Abrasion loss	141	60	150
Heat build up	141	60	150
Demattia fatigue test sample	141	60	150

The tensile and tear properties were measured using a Zwick UTM 1445 (Zwick, Germany), in accordance with ASTM D 412 and ASTM D 624. The hardness was measured with a Durometer from Prolific Engineers (New Delhi, India), in accordance with ASTM D2240. Demattia cut initiation and cut propagation was tested as per ASTM D 430 and ASTM D813 using a Demattia Flexon tester (UK). The heat build up property of the samples was determined using Goodrich Flexometer (BF Goodrich, USA), in accordance with ASTM D623. The abrasion loss was determined using Din Abrader (Zwick, Germany) using $10N$ loads in accordance with ASTM D5963. The rebound resilience at room temperature was determined in a Rebound Resilience Tester (Zwick, Germany), as per SS ISO 4662. The dynamic mechanical properties were also determined for the cured specimen (cured at 141°C for 45 min) at 0.5° arc, 100 cpm frequency using RPA 2000. The measurement was done at 5% strain and 1.667 Hz frequency in torsional shear mode. The dynamic properties were measured at 30, 70, and 100°C. The temperature scanning from −100°C to +100°C was done through a dynamic mechanic analyzer VA 4000 (Metravib R.D.S, France), in accordance with ASTM D5992.

Heterogeneous filler distribution in *NR/BR* blend

The heterogeneous filler distribution in the blend was studied using DSC 7 from Perkin–Elmer USA, in accordance with ASTM E 1356. The test configuration followed in the study was as follows:

1. The sample was hold in the sample pan for 5 min at −140°C.
2. Heating of the sample was started from −140°C to 50°C at 20°C/min heating rate.
3. The sample was cooled from 50°C to −140°C at 20°C/min cooling rate.
4. Once again the sample was hold in the sample pan for 5 min at −140°C and heated from −140°C to 50°C at 20°C/min heating rate.

RESULTS AND DISCUSSION

The rheological properties are shown in Table X.

The minimum torque of Sample 3 was found to be the lowest as compared with others and accordingly the Mooney viscosity also was the lowest. The maximum torque for all the compounds was comparable. Sample 2 was found to be the fastest cure compound, while Sample 1 and Sample 3 showed comparable cure characteristics. The scorch safety of Sample 1 and Sample 3 was found better than control. This may be due to the presence of more curatives predominantly in the softer BR phase as compared with the NR phase.

RPA study

The test result of strain sweep in RPA is shown in Figure 1 and Table XI.

From the figure it is clear that the difference in G' at 1% and 25% strain level was found to be lower for all the experimental compounds as compared with the control. Sample 3 had the lowest value, followed by Sample 1, Sample 2, and Control. This clearly indicates that the filler–filler interactions and consequently the Payne effect were less in the experimental compounds as compared with the control. Among the experimental samples, Sample 3 was found to be the best as the value of the $\Delta G'$ was lowest and consequently the lowest filler–filler interaction in that compound. In Sample 3, carbon black was added in the much earlier stage of the mixing, and because of the availability of more black incorporation time the filler could be dispersed much better. This might be the reason for lower filler–filler interaction as well as more heterogeneous distribution of the carbon black filler.

The test result of the RPA study carried out following Coran and Donnet[20] is given in Table XII.

TABLE X
Rheological Properties of the Compounds

Test parameter	Control	Sample 1	Sample 2	Sample 3
Min TQ (dN-m)	2.38	2.43	2.46	2.25
Max TQ (dN-m)	14.83	15.19	15.11	14.93
Scorch safety time, t_{s2} (min)	13.22	17.31	12.52	17.03
Optimum cure time, t_{c90} (min)	29.12	33.55	27.82	33.05
ML (1 + 4) at 100°C	58.0	59.0	62.0	53.0

The rheometric properties reported above is the averages from three test specimens. Measurement error for: ML (1 + 4) at 100°C: ±1.2; minimum torque: ±0.02 dN-m; maximum torque: ±0.15 dN-m; scorch safety time, t_{s2}: ±0.01 min; optimum cure time, t_{c90}: ±0.02 min.
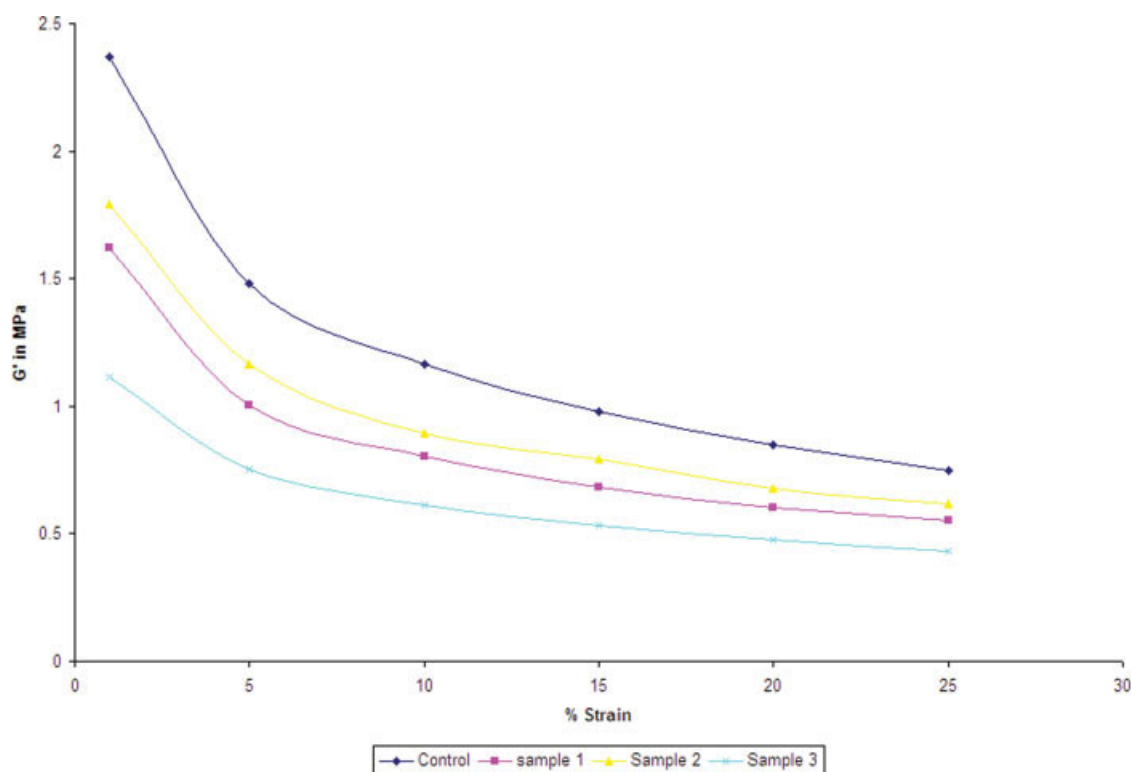
Figure 1 Strain sweep of compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE XI
RPA Study for Filler–Filler Interaction

Parameter	G' in MPa			
% Strain	Control	Sample 1	Sample 2	Sample 3
1	2.37	1.62	1.79	1.12
5	1.48	1.00	1.16	0.75
10	1.17	0.80	0.89	0.61
15	0.98	0.69	0.79	0.53
20	0.85	0.60	0.68	0.48
25	0.75	0.55	0.62	0.43
G' (1–25%)	1.62	1.07	1.18	0.68

Measurement error for G': ±0.01 Mpa.

TABLE XII
RPA Study to Understand Filler Dispersion

Parameter	Control	Sample 1	Sample 2	Sample 3
G' (MPa) at 1% strain	1.65	1.53	1.56	1.36
G' (MPa) at 50% strain	0.41	0.36	0.44	0.32
G' (MPa) at 1% strain	1.29	1.16	1.27	1.02
G' (MPa) at plateau level	1.32	1.24	1.34	1.10
Fraction recovery of G' ($G'_{\text{at plateau}}/G'_{\text{initial}}$)	0.80	0.81	0.86	0.81

Measurement error for G': ±0.01 MPa.

Higher is the fraction recovery of G', better is the quality of filler dispersion. So, the dispersion quality of the control compound was found to be poor as compared with experimental compounds. This is also supported by the facts as mentioned before.

The test result related to polymer–filler interaction parameter is shown in Table XIII.

Once again the experimental compounds, Sample 1 and Sample 2, had shown higher polymer–filler interaction as compared with the control and Sample 3 had the closer polymer–filler interaction to that of the control compound.

Physical properties

The original stress–strain properties including tear strength, hardness, abrasion loss, and heat build up are shown in Table XIV. The result of the Demattia cut growth study has been shown in Figure 2.

TABLE XIII
Polymer–Filler Interaction Parameter

Parameter	Control	Sample 1	Sample 2	Sample 3
η	2.56	2.33	2.54	2.43
σ	0.044	0.048	0.047	0.046
σ/η	0.017	0.020	0.019	0.018

Measurement error for $\eta = \pm 0.01$ and $\sigma = \pm 0.001$.

TABLE XIV
Physical Properties

Test parameter	Control	Sample 1	Sample 2	Sample 3
Modulus at 100% elongation (MPa)	2.3	2.3	2.5	2.1
Modulus at 300% elongation (MPa)	11.1	11.8	11.9	11.0
Tensile strength (MPa)	26.8	26.5	26.6	25.9
Elongation at break (%)	590	566	574	582
Hardness (shore A)	63	63	63	62
Tear strength (N/mm)	100	91	102	90
Abrasion loss at 10N load (mm^3)	78	78	78	78
HBU at 100°C/30 min (°C)	17	15	15	15

The stress–strain properties, including hardness, reported above are the averages from five test specimens. Abrasion loss, heat build up, and rebound resilience are averages from three test specimens.

Measurement error for: tensile strength: ±0.3 Mpa; modulus at 100% elongation: ±0.1 MPa; modulus at 300% elongation: ±0.2 MPa; elongation at break: ±13%; hardness: ±1 shore A; abrasion loss: ±5 mm^3; HBU: ±1°C.

Comparable stress–strain properties were observed for all the compounds. No difference in abrasion loss was also observed. Marginal improvement in heat build up property was observed in case of the experimental samples as compared with the control. The marginal improvement in heat build up may be due to the higher polymer–filler as well as lower filler–filler interaction as exhibited by the experimental compounds.

The cut growth property of the Sample 2 was found to be the best. This may be due to the higher tear strength as well as higher polymer–filler interaction as exhibited by Sample 2. This is also supported by the DSC data, where Sample 2 has shown lower shift of glass transition temperature (T_g) in BR phase and higher shift of T_g in NR phase. The energy for crystalline melting for BR was also comparatively less affected in Sample 2. This indicates that more black was distributed in NR phase than in the BR phase in Sample 2, and consequently BR will also form a sheathing layer over the NR phase. This will help in improvement of cut growth property by distributing the stress concentration on the crack tip toward the softer BR phase.

Sample 1 and Sample 3 showed inferior cut growth property as compared with the control compound.

Dynamic mechanical property

The dynamic mechanical property of the samples is shown in Table XV.

The Tan δ values obtained at three different temperatures for all the experimental compounds were
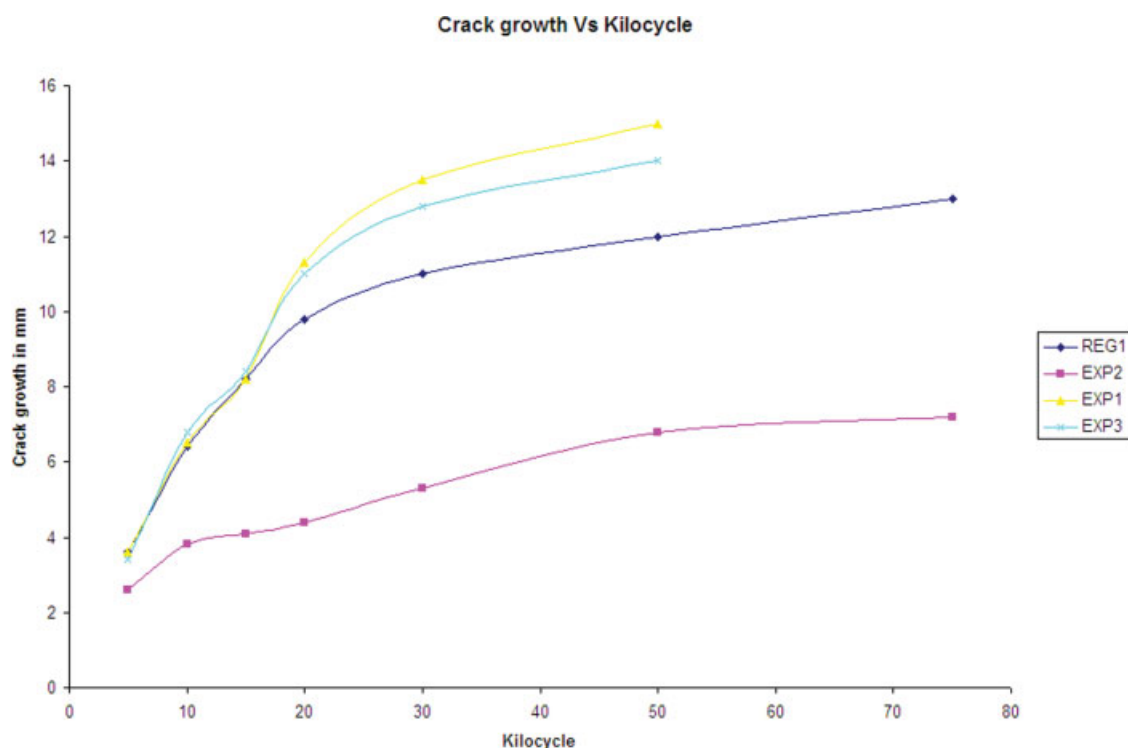

Figure 2 Demattia cut propagation of compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE XV
Dynamic Mechanical Property Measured in RPA 2000

Test parameter	Control	Sample 1	Sample 2	Sample 3
Measured at 30°C				
G* (MPa)	1.57	1.58	1.53	1.59
G′ (MPa)	1.54	1.55	1.50	1.57
G″ (MPa)	0.31	0.27	0.27	0.28
Tan δ	0.20	0.17	0.18	0.18
Measured at 70°C				
G* (MPa)	1.41	1.40	1.39	1.39
G′ (MPa)	1.39	1.38	1.37	1.37
G″ (MPa)	0.23	0.20	0.20	0.20
Tan δ	0.17	0.14	0.14	0.15
Measured at 100°C				
G* (MPa)	1.24	1.25	1.23	1.23
G′ (MPa)	1.24	1.24	1.22	1.23
G″ (MPa)	0.15	0.13	0.13	0.13
Tan δ	0.12	0.10	0.11	0.11

TABLE XVI
DMA Data

Parameter	Control	Sample 1	Sample 2	Sample 3
T_g (°C)	−51	−44	−40	−50

found to be lower as compared with control. This may be due to the higher polymer–filler interaction as well as lower filler–filler interaction in the experimental compounds. The elastic modulus at room temperature of Sample 2 was found to be lower as compared with control, whereas for the other two experimental samples it was found higher. This may be the reason for better-cut growth property as exhibited by Sample 2. In all the experimental compounds the carbon black was added in earlier stage of the mixing cycle for which the filler incorporation time was found to be more. In case of the experimental compounds as the black was incorporated along with NR in the first master stage and BR was added in the second master stage so a heterogeneous distribution of the filler is also assumed.

The T_g measured through VA 4000 is shown in Table XVI. The plot of tan δ versus temperature is shown in Figure 3. The peak of this curve indicates the corresponding T_g. In all the four plots the peak indicates the T_g of NR. This was due to the higher amount of NR in the blend. The T_g of NR in the control compound was found higher (more negative value) as compared with the experimental compounds. This also confirms the presence of higher amount of filler in NR phase in all the experimental compounds. From the plot it was also observed that tan δ above room temperature of all the three experimental compounds were lower compared with control.

Differential scanning calorimetric study

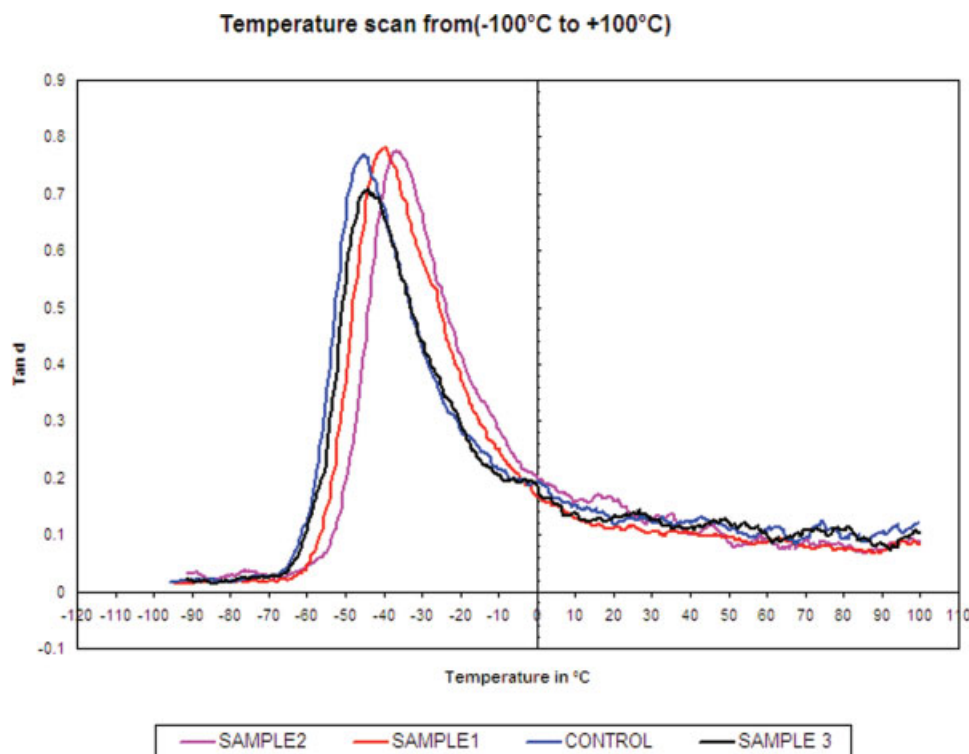The test result of the DSC study is shown in Table XVII.

Figure 3 Dynamic mechanical properties by DMA, VA4000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE XVII
DSC Data

Parameter	Control	Sample 1	Sample 2	Sample 3	100% BR	100% NR
T_g (°C)	−93/−55	−95/−52	−97/−51	−96/−54	−104	−61
Delta H (J/g) for crystalline melting of BR	0.216	0.811	1.061	0.964	43.2	–

In case of the control compound the NR and the BR was added together along with carbon black, whereas in case of all the experimental compounds most of the black was added with NR in the first master stage and BR was added in the second master. This may produce higher heterogeneous distribution of carbon black filler in the experimental compounds. The incorporation of black in a polymer shifts its T_g toward higher side as well as the crystallization temperature of BR is also affected.

The shift of T_g was found to be the highest in BR phase and lowest in NR phase in the control, whereas the shift of T_g of NR phase was found to be maximum in case of Sample 2. This may be due to the uneven distribution of carbon black in NR/BR phase. Higher amount of carbon black may be distributed in BR phase in the control than in others. The same type of observation was also found in the dynamic mechanical property study through VA 4000. From the Delta H value it was clearly seen that in the control compound crystallinity change was much more than other compounds.

CONCLUSIONS

Change in mixing sequence has direct impact on compound properties. This was confirmed in case of low filler–filler and high polymer–filler interaction as exhibited by the experimental compounds. Consequently, the dynamic mechanical properties of the experimental samples were also improved. The uneven distribution of the carbon black in the NR/BR phase was also advantageous for the improvement of dynamic mechanical properties of the experimental samples. The stress–strain, hardness, abrasion loss, as well rheometric properties did not change much because of change in mixing sequence.

References

1. McDonel, E. T.; Baranwal, K. C.; Andries, J. C. In Polymer Blends, Vol. 2; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1978; Chapter 19, p 264.
2. Roland, C. M. Rubber Chem Technol 1989, 62, 456.
3. Hess, W. M.; Herd, C. R.; Vegvari, P. C. Rubber Chem Technol 1993, 66, 329.
4. Corish, P. J. In Science and Technology of Rubber; Eirich, F. R., Ed.; Academic Press: New York, 1978; Chapter 12, p 543.
5. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer-Polymer Miscibility; Academic Press: New York, 1979; Chapter 2.
6. Herd, Ch. R.; Bomo, F.; Swartz, L. A. Kautsch Gummi Kunstst 1995, 48, 588.
7. Gent, A. N.; Zhang, L. Q. J Polym Sci Part B: Polym Phys 2001, 39, 811.
8. Costa, V. G.; Nunes, R. C. Eur Polym J 1994, 30, 1025.
9. Ultracki, L. A. Polymer Alloys and Blends: Thermodynamics and Rheology; Hanser: New York, 1990.
10. Brydson, J. A. In Rubber Materials and Their Compounds; Elsevier Science: New York, 1998; Chapter 4, p 69.
11. Boochathum, P.; Chiewnawin, S. Eur Polym J 2001, 37, 429.
12. Siqueira Filho, A. S.; Bo, M. C. Controle de Qualidade na Industria de Artefatos de Borracha; CNI: Rio de Janeiro, 1985.
13. Klei, B.; Koenig, J. L. Rubber Chem Technol 1997, 70, 231.
14. Hurston, D. J.; Song, M. J Appl Polym Sci 2000, 76, 1791.
15. Leutewiler, C. L. Borracha Atual 2001, 32, 34.
16. Freitas de Castro, D.; Martins, A. F.; Suarez, J. C. M.; Reis Nunes, R. C.; Visconte, L. L. Y. Kautsch Gummi Kunstst 2003, 56, 49.
17. Corish, P. J. Rubber Chem Technol 1967, 40, 324.
18. Sircar, A. K.; Lamond, T. G. Rubber Chem Technol 1973, 46, 178.
19. Payne, A. R. Rubber Plast Age 1961, 42, 963.
20. Coran, A. Y.; Donnet, J. B. Rubber Chem Technol 1992, 65, 973.
21. Sierpa, C. A.; Galan, C.; Gomez Fatou, J. M.; Ruiz Santa Quiteria, V. Rubber Chem Technol 1995, 2, 259.