CHAPTER – II

EXPERIMENTAL

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2.1 MATERIALS

Materials used in the present investigation are given in Table 2.1.

Table 2.1: Materials and specifications

Materials	Specification
Styrene butadiene rubber latex (23.5% Styrene content)	Reliance Ind. Ltd., India
Styrene butadiene rubber latex (40 % Styrene content)	Reliance Ind. Ltd., India
Sulfuric acid	Labort Fine Chem Pvt. Ltd., India
Styrenated phenol (SP) antioxidant	National Chemical, India
Polybutadiene rubber Cisamer 01	Reliance Ind. Ltd., India
Polybutadiene rubber, Neodymium catalyst (Synteca 44)	Synthos S. A., Poland
Industrial reference carbon black, IRB#9 (Standard Carbon Black)	Balentine Enterprises Inc., USA (Manufactured by Orion Engineered Carbon)
Carbon black N220	PCBL, India
N330 carbon black	PCBL, India
Zinc oxide pure	SD Fine-Chem Ltd., India
Stearic acid LR Grade	SD Fine-Chem Ltd., India
Zinc oxide	Silox India Pvt. Ltd., India
Stearic acid	Godrej, India
Antiozonant MC wax	Gujarat Paraffins, India
Antioxidant TMQ	NOCIL, India
Antioxidant 6PPD	NOCIL, India
Sulfur powder (98% extra pure)	LobaChemie Pvt. Ltd., India

Soluble sulfur	Jain Chemicals, India
Accelerator TBBS, N-ter-butyl-2-benzothiazole sulfenamide (97% pure)	Alfa Aeser by Thermo Fisher Scientific, India
Accelerator TBBS	Yaso Industries, India
Accelerator DPG	Yaso Industries, India
Accelerator CBS	NOCIL, India

2.2 PHYSICO-CHEMICAL CHARACTERIZATION OF OILS

The oils were characterized for flash point (ASTM D92), pour point (ASTM D97), kinematic viscosity (ASTM D445), refractive index (ASTM D1218) by Abbemat 300 Refractometer from Anton Paar and Fourier Transformed Infrared Spectroscopy (FTIR) Spectrum Two (ASTM D2702) Perkin Elmer was used for surface groups study.

2.2.1 Metal Content of Oils by ICP-OES

The oil samples were also characterized for metal contents using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) Optima 4300 DV from M/s Perkin Elmer using Charge-coupled device (CCD) detector. Oil sample (5-10 g) was taken in a platinum crucible, then sulfuric acid (3-4 mL) was added for digestion of oils to remove organic content by heating these samples on hot plate. Then the sample was heated @ 850°C for one h. The ash was diluted with demineralized water to make solution (4% w/w). This solution was tested using ICP-OES instrument to measure 25 metals at a time. Standard solution was run to get standard peak value for various metals. Metal content for experimental samples was calculated by software based on relative intensity of various peaks with respect to standard solution for different metals. This equipment can measure the metal content with accuracy level of 0.5 ppm. Transition metals are like poison to rubber compound as they drastically reduce the stress-strain properties after ageing in aerobic, anaerobic, oil and outdoor conditions[1]. Presence of these metals in high concentration affect the hot air ageing stress-strain properties adversely and as a result, service life of the product.

2.2.2 Measurement of Different Structural Groups in oils

Nuclear Magnetic Resonance (NMR) Spectrometer (Advance III^{TM} HD 400 from M/s Bruker, Switzerland) liquid was used for phase NMR to check various structural groups like aliphatic, olefinic and aromatic (Mono, di and poly). It was calculated as the distribution of proton present in different structural group in percentage.

2.3 E-SBR LATEX PREPARATION AND ITS CHARACTERIZATION

SBR latex was prepared using emulsion polymerization of styrene and butadiene monomer in 1:3 weight ratio for normal styrene content and 3:4 weight ratio for high styrene content rubbers. Free radical polymerization technique was used and reaction temperature was maintained between 0° to 20°C. Organic peroxide was used as initiator, rosin/fatty acid was used as emulsifier, mercaptan as chain modifier to control molecular weight, water was used as emulsifying media and hydroxylamine was used as short stop to achieve desired level of conversion.

SBR latex was characterized for solid content by acid coagulation and drying step. Then, further characterizations were made like Mooney viscosity using MV2000E from Alpha Technologies (ASTM D1646) and bound styrene content through refractive index by Abbemat 300 Refractometer from Anton Paar (ASTM D5775), Degradation study using Thermo Gravimetry Analyzer, TGA-Q50 from TA Instrument (ASTM D6370), Glass transition temperature using differential scanning calorimetry, DSC-Q20 from TA Instrument (ASTM E794), Gel permeation chromatography study for molecular weight and its distribution using GPC1260 Infinity from Agilent Technologies, etc. were determined.

2.4 SBR EXTENSION WITH OILS AT LABORATORY SCALE

SBR latex was extended with various oils and details are presented in Table 2.2.

Table 2.2: Various oil and their suppliers

S. No.	Source of oils	Name of oils	Supplier
1	**Petroleum**	Panoil C 160A, Distillate Aromatic Extract (DAE) oil	Panama Petrochem Ltd., India
2		Panoil 2500, Treated Distillate Aromatic Extract (TDAE) oil	Panama Petrochem Ltd., India
3		Elasto Supreme H, Residual Aromatic Extract (RAE) oil	Hindustan Petroleum Corporation Ltd., India
4		RPO, Naphthenic oil	Apar Industries Ltd., India
1	**Vegetable**	NO_2 (RQ, DECAS oil)	Jayant Agro-Organics Ltd., India
2		NO_6 (RBD Palmolein oil)	Satguru Oils Pvt. Ltd., India
3		NO_7 (Ground nut)	Local market
4		NO_8 (Soybean)	
5		NO_9 (Mustard)	
6		NO_10 (Coconut)	

Oil emulsion was prepared using oil and fatty soap in 1:1 ratio and heated with continuous stirring (250-350 rpm, 60°-90°C). Measured amount of this oil emulsion was mixed with SBR latex with continuous stirring at high speed (700-1200 rpm). The latex was then coagulated with sulfuric acid and salt mixture. Latex crumbs are separated from water and washed with demineralised water properly to remove acid. These rubber crumbs are dried in air oven and moisture removal was ensured to less than 0.5%. Dried rubber crumbs are passed on two roll mill to prepare proper sheet for further characterization.

2.5 PHYSICO-CHEMICAL CHARACTERIZATION OF OE-SBR’S

Total extractables (ASTM D5774) were measured using acetone and bound styrene content was measured using Abbemat 300 Refractometer Anton Paar (ASTM D5775).

OE-SBRs were characterized for density using bulk density Tester model RD3000 from M/s MonTech, Germany (ASTM D297), Mooney viscosity using MV2000E (ASTM D1646), moisture content using Halogen Moisture Analyzer, degradation study using Thermo Gravimetry Analyzer, TGA-Q50 and glass transition temperature (Tg) using Differential Scanning Calorimetry, DSC-Q20 were determined.

2.6 COMPOUND MIXING AND CHARACTERIZATION

2.6.1 ASTM Compound Mixing (Master batch)

Compound characterization was performed following ASTM for oil extended rubbers. Master batch mixing of rubber compound was carried out using a two-wing rotor laboratory Miniature Internal Mixer (MIM) of 350 mL capacity from Thermo Fisher Scientific. The formulation (as per ASTM D3185-2B) used for compound evaluation is given in Table 2.3.

Table 2.3: ASTM rubber compound recipe for master batch

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (23.5% styrene)	137.5
Carbon, IRB#9	68.75
Zinc oxide	3
Stearic acid	1

Master batch mixing was done setting the temperature control unit (TCU) at 70°C and rotor speed at 60 rpm for 6 min. The master batches were sheeted out in a laboratory two-roll mill for 6 passes at 2 mm nip gap and 2 passes at 0.8 mm nip gap. The dump temperature, mixing energy, maximum torque and final torque were measured for all the master batches.

2.6.2 PCR Tire Tread Compound Mixing

Master and final batch mixing of PCR tire tread compound was carried out using a two-wing rotor laboratory Miniature internal mixer (350 cc) from Thermo Fisher Scientific. The formulation used for compound evaluation are shown in Table 2.4.

Table 2.4: PCR tire tread compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (23.5% styrene)	96.25
Polybutadiene rubber Cisamer 01	30
Carbon black N220	70
Respective process oil	10
Zinc oxide	2.5
Stearic acid	1
Antiozonant MC wax	2
Antioxidant TMQ	1
Antioxidant 6PPD	1.5
Soluble sulfur	2
Accelerator TBBS	1.2
Accelerator DPG	0.2

Master batch mixing was done setting the Temperature Control Unit (TCU) at 90°C and rotor speed at 60 rpm for 5 min. Final batch mixing was done setting the TCU at 60°C and rotor speed at 30 rpm for 3 min. The master and final batches were sheeted out in a laboratory two-roll mill using standard procedure.

2.6.3 ASTM Compound Mixing (With curatives adjustment)

Mixing was carried out using a two-wing rotor laboratory Miniature internal mixer, MIM (350 cc) from M/s Thermo Fisher Scientific. Single stage mixing was done setting the Temperature Control Unit (TCU) at 60°C and rotor speed at 60 rpm for 9 min. The mixed batches were sheeted out in a laboratory two-roll mill using standard procedure. The formulations used for compound evaluation are given in Table 2.5.

Table 2.5: ASTM compound recipe (phr)

Ingredients	**Naphthenic**	**NO_2**	**NO_6**	**NO_7**	**NO_8**	**NO_9**	**NO_10**
OE-SBR (23.5% Styrene)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)
Carbon, IRB#9	68.75	68.75	68.75	68.75	68.75	68.75	68.75
Zinc oxide	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1
Soluble sulfur	1.75	2.19	1.75	2.10	2.01	2.01	1.75
Accelerator TBBS	1.38	1.73	1.38	1.66	1.59	1.59	1.38

Curatives were adjusted for vegetable oil extended E-SBR based formulations to achieve the close modulus with respected to naphthenic oil extended E-SBR formulation.

2.6.4 ASTM Gum Compound Mixing (High styrene content rubbers)

Mixing was carried out using a two-wing rotor laboratory Miniature internal mixer, MIM (350 cc) from Thermo Fisher Scientific. The formulation used for compound evaluation are tabulated in Table 2.6.

Table 2.6: ASTM gum compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (40 % styrene)	137.5 (100 rubber)
Zinc oxide	3
Stearic acid	1
Soluble sulfur	1.75
Accelerator TBBS	1.38

Single stage mixing was done setting the Temperature Control Unit (TCU) at 60°C and rotor speed at 60 rpm for 9 min. The mixed batches were sheeted out in a laboratory two-roll mill using standard procedure.

2.6.5 Motorcycle Tire Tread Compound Mixing

Master and final batch mixing was carried out using MIM. The formulation used for compound evaluation are given in Table 2.7.

Table 2.7: Motorcycle tire tread compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (40 % styrene)	89.375 (65 rubber)
Polybutadiene rubber, Neodymium catalyst	35
N330 carbon black	70
Respective process oil	3
Zinc oxide	4
Stearic acid	2
Antiozonant MC wax	1
Antioxidant TQ	1
Antioxidant 6PPD	1
Soluble sulfur	1.7
Accelerator CBS	1.2

Master batch mixing was done setting the Temperature Control Unit (TCU) at 90°C and rotor speed at 60 rpm for 5 min. Final batch mixing was done setting the TCU at 60°C and rotor speed at 30 rpm for 3 min. The master and final batches were sheeted out in a laboratory two-roll mill using standard procedure. Density of all the above mixed final batch filled compounds was checked using Compressed Volume Densimeter from Montec (ASTM D297).

2.7 CHARACTERIZATIONS OF UNCURED RUBBER COMPOUND

Bound rubber content was done by chemical method for master batch rubber compounds. Final compounds were characterized for processing parameters like Mooney viscosity (ASTM D1646), processing behaviour, filler dispersion and activation energy for flow (ASTM D6204). Cure characteristics (ASTM D5289) was evaluated by

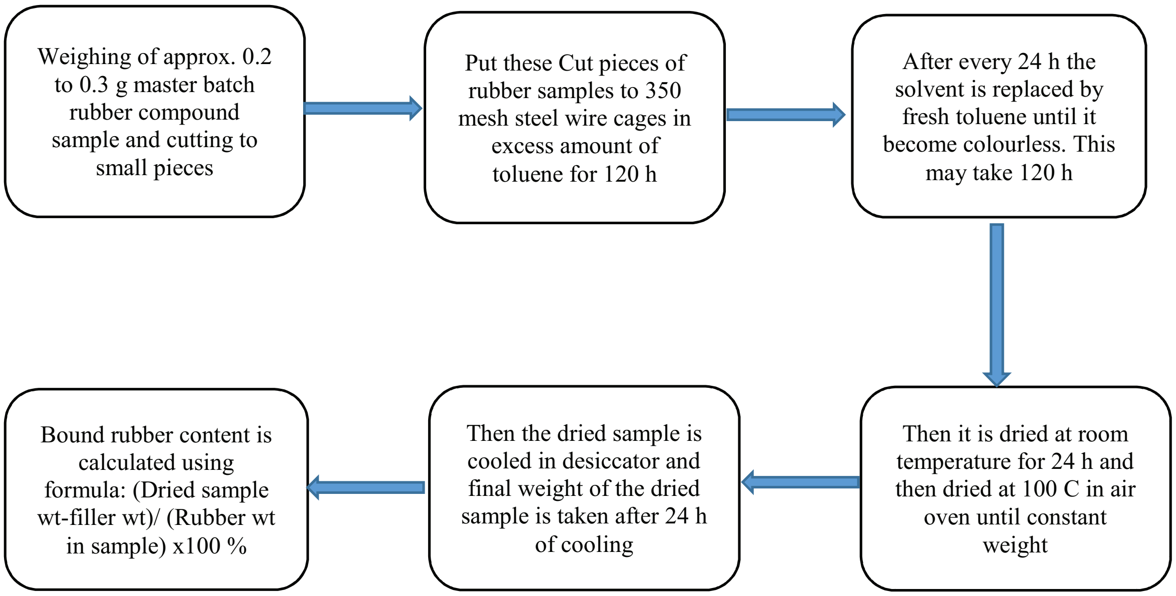
MDR2000 from M/s Alpha Technologies, USA at 160°C for 30 min for PCR, ASTM (curatives adjustment), motorcycle tire tread and ASTM gum compounds. Frequency sweep, strain sweep and temperature sweep tests were performed using RPA2000 from M/s Alpha Technologies, USA. RPA test conditions are reported in Table 2.8.

Table 2.8: RPA test conditions for various tests

Parameter	**Temperature (°C)**	**Strain (%)**	**Frequency (Hz)**
Flow behavior study (Power law index)			
Frequency sweep (compounded rubber)	100	14	0.05, 0.1, 0.2, 0.4, 0.9, 1.8, 3.7, 7.6, 15.6, 30, 31, 32
Filler dispersion			
Strain sweep (compounded rubber)	70	0.5, 1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 5, 1, 0.5	0.2
Activation energy study by Arrhenius equation			
Temperature sweep (Shear rate, 5.03 sec^{-1}) for compounded rubber	70, 80, 90, 100, 110, 120, 130	100	0.8
After cure (@160°C for tC90) properties by RPA			
Dynamic properties	40 and 70	5	10
Filler-filler interaction study (Payne effect) by strain sweep	70	0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, 25, 30, 40, 50	10

2.7.1 Bound Rubber Content Test

It is carried out master batch (without curatives) rubber compound to check polymer-filler interaction[2-4].



Around 0.2 to 0.3 g of sample was accurately weighed and cut to small pieces. It is then put to 350 mesh steel wire cages in excess amount of toluene for 120 h. After every 24 h, the solvent was changed until it became colourless. It is dried at room temperature for 24 h and then dried at 100°C in air oven until constant weight. It is then cooled in desiccator and final weight taken after 24 h. The bound rubber content (%) is calculated using the below equation (2.1).

$$\text{Bound rubber content (\%)} = \{(W_d - W_f)/ W_o\} \times 100 \qquad \dots (2.1)$$

Where,

W_d = Final weight of the dried sample in g,

W_f = Weight of the filler in the sample in g,

W_o = Weight of the rubber in the sample in g

When green rubber compound was exposed to toluene, some part of rubber was not extracted and it is known as bound rubber. Higher bound rubber content value indicates more polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement.

2.7.2 Mooney Viscosity

Mooney viscosity of rubber compounds was checked as ML(1+4)@100°C using Mooney Viscometer (MV2000E) from M/s Alpha Technologies, USA.

2.7.3 Frequency Sweep Test

The flow behaviour of rubber compound measured as power law index in frequency sweep test[5] as per Newton's power law. Power law index (n) close to zero or relative lower value means plastic nature of rubber compound and hence, better shear thinning (Flow behaviour) of rubber compound.

2.7.4 Strain Sweep Test

In strain sweep test, the temperature and frequency remained constant and strain changes, the filler networking or agglomeration of filler particles, which is controlled mainly by filler-filler interactions in a rubber compound. It was quantified from the strain dependence of the elastic modulus G'. Elastic modulus G' is expressed as MPa unit. The filler network was gradually destroyed on increasing the strain (at strains well below 100%). This resulted in a decrease in elastic modulus G' with strain amplitude. Payne effect was measured as difference between elastic modulus (G') at low and high strain and it indicated filler-filler interaction. It was measured for filled rubber compound only. Higher Payne effect means more filler-filler interaction, which is not desired in rubber compound. Generally, high filler loading compounds and silica filler-based compounds show high Payne effect value[5]. Strain sweep test was performed in reverse direction also, which means strain reached to highest level and then decreases with same trend. Elastic modulus G' was recorded in reverse sweep test also. Filler dispersion was calculated as retention of G' at low strain in reverse sweep to forward strain sweep.

2.7.5 Temperature Sweep Test

Activation energy of the rubber compound can be measured using temperature sweep test in RPA in which frequency and strain (shear rate) remained constant and temperature rises. Complex viscosity (η*) was measured at interval of 10°C. Normally test starts at 70°C and ends at 130°C. Activation energy can be calculated using the Arrhenius-Eyring formula[5]. Higher activation energy value means rubber compound need high energy for compound flow, which indicated poor processing.

2.7.6 Scanning Electron Microscopy (SEM) Study

Scanning Electron Microscope, Nova NanoSEM 650 from M/s FEI Co. was used to check carbon black dispersion. Images of master batch rubber compounds were captured at 40000X magnification.

2.8 CHARACTERIZATIONS OF CURED RUBBER COMPOUND

Uncured rubber compounds were vulcanized for various tests using compression molding press (LP3000) from M/s MonTech, Germany. Tensile slabs were molded at 160°C for tC90 + 2 min and other specimen were molded at 160°C for tC90 + 5 min as per ASTM D3182. Cured specimen were tested for parameters like stress-strain properties (ASTM D412) by UTM (Z005) from M/s Zwick, Germany, hardness (ASTM D2240) by Shore A Durometer from M/s Gibitre, Italy, Heat Build Up (HBU) by Goodrich Flexometer (EKT-2002GF) from M/s Ektrontec, Taiwan (ASTM D623) following chamber temperature as 50°C, test time 20 min and 7 Kg load, Abrasion loss (ASTM D5963) using DIN Abrasion tester from M/s Zwick, Germany with 10 N load on specimen and Akron angle abrasion tester GT7012-A from M/s Gotech Testing Machines Inc., Taiwan with 20° slip angle for 4000 cycles, Heat Build Up (HBU) by Goodrich Flexometer EKT-2002GF from M/s Ektrontec, Taiwan (ASTM D623) following chamber temperature as 50°C, test time 30 min and 7 Kg load, Rebound @30° and 70°C (ISO4662-2) using Rebound Resilience tester (2108RR-T) from M/s Ektrontec, Taiwan and glass transition temperature Tg using Differential Scanning Calorimetry (DSC-Q20) and Volume resistivity (ASTM D257) using High Resistance Meter (model 6517B) and Resistivity test fixture (model 8009) from M/s Keithley (A Tektronix company), US. Dynamic properties and Payne effect (ASTM D6601) were performed using RPA (test conditions are given in Table 2.8). Dynamic mechanical properties of cured rubber specimen were measured using DMA1000+ from M/s Metravib, France (ASTM D5992).

2.8.1 Reinforcement Index and Rubber-Filler Interaction Parameter

Reinforcement index was calculated using equation (2.2)[6-8]:

$$RI = M300/M100 \quad \dots (2.2)$$

where M300 is modulus of rubber compound at 300% elongation in MPa, and

M100 is modulus of rubber compound at 100% elongation in MPa.

Rubber-filler interaction parameter is the ratio of slope of stress-strain curve in relatively linear region (σ) and filler-filler networking factor (η), which is calculated as the ratio of elastic modulus at low (1%) and high (25%) strain. It was calculated using equation (2.3)[9,10]:

$$I = \sigma/\eta = [(M300-M100)/\lambda] / [G'@1\%/ G'@25\%] \quad \dots (2.3)$$

where λ is strain ratio, 2 to 4 measured over an elongation range of 100% -300%

$G'@1\%$ & $G'@25\%$ are storage moduli of rubber compound at 1% and 25% strain, respectively (in MPa).

2.8.2 Crosslink Density

Specimens were kept in toluene for 48 h and Swell index was measured using ASTM D3616. It was calculated as the ratio of swollen weight to original specimen weight. Volume fraction was measured by drying the swollen specimen in oven at 100°C for 2 h. It was calculated using equation (2.4)[11,12]:

$$V_r = [(D - FT)/\rho_r]/[(D - FT)/\rho_r + A_o/\rho_s] \quad \dots (2.4)$$

Where, D Weight of the de-swollen specimen

F is the Weight fraction of the insoluble non-rubber ingredients,

T = Original dry weight of the specimen,

A_o = Weight of solvent absorbed; it can be calculated as (S-T),

ρ_r = Density of the respective raw rubber, and

ρ_s = Density of the solvent (0.867 for toluene).

The cross-link density X of the rubber specimen was calculated using the Flory – Rehner relationship[13-17].

$$X = (-) [\ln (1-V_r) + V_r + \chi(V_r)^2] / [2 * \rho_r * V_s * (V_r)^{1/3}] \quad \ldots (2.5)$$

where X = Cross-link density (mol/ cm^3),

V_r = Volume fraction of the specimen,

χ = Rubber-solvent interaction parameter (0.31 for SBR-toluene),

ρ_r = Density of the respective raw rubber, and

V_s = Molar volume of solvent (106.3 for toluene).

2.8.3 Strain Sweep Test by RPA

In strain sweep test, in which temperature and frequency remained constant and strain changes, the filler networking or agglomeration of filler particles, which is controlled mainly by filler-filler interactions in a rubber compound, was quantified from the strain dependence of the elastic modulus G'. Elastic modulus G' is expressed as MPa unit. The filler network was gradually destroyed on increasing the strain (at strains well below 100%). This resulted in a decrease in elastic modulus G' with strain amplitude. Payne effect was measured as difference between elastic modulus (G') at low and high strain and it indicated filler-filler interaction. It measured for filled rubber compound only. Higher Payne effect means more filler-filler interaction, which is not desired in rubber compound. Generally, high filler loading compounds and silica filler-based compounds show high Payne effect value[18]. Strain sweep test is performed in reverse direction also, which means strain reached to highest level and then decreases with same trend. Elastic modulus G' is recorded in reverse sweep test also. Filler dispersion was calculated as retention of G’ in reverse sweep to forward strain sweep.

2.8.4 Dynamic Mechanical Properties by Dynamic Mechanical Analyzer (DMA)

Rectangular specimens (2 mm thickness, 10 mm width) were tested at 10 Hz frequency, 0.1% dynamic strain and temperature scan from -80° to +80°C. Elastic modulus, E′ and loss factor, tan δ were measured at 0°, 30° and 60°C temperatures. Dynamic Tg was calculated as the temperature value at peak tan δ for PCR tire tread compounds.

Rectangular specimens (2 mm thickness, 10 mm width) were tested at 10 Hz frequency, 1 % dynamic and 2 % static strain. Elastic modulus, E′ and loss factor, tan δ were measured at 0°, 30° and 60°C temperature, respectively for ASTM compound (curatives adjustment) and motorcycle tire tread compounds.

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