CHAPTER – III

RESULTS

CONTENTS

3.1 PHYSICO-CHEMICAL CHARACTERIZATION OF PETROLEUM AND VEGETABLE ORIGIN OILS

Test results for physico-chemical properties for oils are reported shown in Tables 3.1-3.3.

Table 3.1: Physico-chemical properties of oils

Parameter / Samples	Flash point (°C)	Pour point (°C)	Kinematic viscosity @100°C (cSt)	Refractive index @20°C
DAE oil	240	21	25.5	1.5672
TDAE oil	248	24	18.2	1.5398
RAE oil	235	15	52.5	1.5449
Naphthenic oil	228	-12	13.8	1.4853
NO_2 oil	290	-35	15.3	1.4828
NO_6 oil	325	9	10.0	1.4652
NO_7 oil	>300	-5	7.9	1.4689
NO_8 oil	>300	-10	8.0	1.4738
NO_9 oil	>300	-10	9.8	1.4729
NO_10 oil	292	18	5.5	1.4556

Table 3.2: Thermogravimetry analysis (TGA) of oils

Parameter / Sample	Degradation temperature (°C)	Ash content (%)	Volatile content (%)
DAE oil	376.0	0.02	0.16
TDAE oil	357.3	0.03	0.15
RAE oil	454.1	0.08	0.06
Naphthenic oil	394.9	0.00	0.16
NO_2 oil	433.0	0.06	0.12
NO_6 oil	432.9	0.04	0.03
NO_7 oil	430.1	0.10	0.01
NO_8 oil	427.0	0.13	0.02
NO_9 oil	430.1	0.08	0.31
NO_10 oil	403.9	0.02	0.06

Table 3.3: ICP-OES study of oils for metal contents

Parameter / Sample	Copper (ppm)	Iron (ppm)	Manganese (ppm)	Cobalt (ppm)	Molybdenum (ppm)
DAE oil	*	6	*	*	*
TDAE oil	*	8	*	*	*
RAE oil	*	5	*	*	*
Naphthenic oil	*	5	*	*	*
NO_2 oil	3	23	*	10	*
NO_6 oil	5	10	*	*	2
NO_7 oil	2	17	2	*	*
NO_8 oil	2	52	2	159	*
NO_9 oil	2	15	*	*	*
NO_10 oil	*	10	2	5	*

* not detected

Note: Ti, V, Cr, Zn, etc. were not detected in all these samples

Flash point more than 225°C is safer for rubber compound mixing and further processing for vegetable oil it was found greater than 290°C, which may be due to presence of triglyceride ester carbonyl groups in these oils. So, the rubbers extended with these vegetable oils are safe for processing on the shopfloor. Vegetable oils have lower pour point (< 20°C), which is good for handling them at shopfloor during oil extension stage because oils with higher pour point need heating for flow during their use. The samples NO_6 and NO_10 have shown higher pour point due to their saturated structure. Lower kinematic viscosity of oil indicated better flow ability during processing. The NO_6 to NO_10 oil samples have shown lower viscosity as compared to TDAE oil, so these oils will have less resistance for flow. Refractive index for vegetable oils was found to be comparable with naphthenic oil. The TDAE oil has shown higher refractive index, which is due to more aromatic content in this oil and it was found low for NO_6 and NO_10 samples due to low aromatic content in these oils. Aromatic content was found to be low in vegetable oils as confirmed by NMR study also.

Metal content values determined by ICP-OES were found less than 160 ppm for transition metals like copper, iron, manganese, cobalt, and for all oil samples. Titanium, vanadium, chromium and zinc were not detected in these oil samples. Presence of these metals in high concentrations affect the hot air ageing stress-strain properties adversely and in consequence, service life of the product. However, presence of these metals are found lower in vegetable oils so compound prepared with vegetable oil extended rubbers will have better ageing properties. FTIR spectra of oil samples are presented in Fig. 3.1.

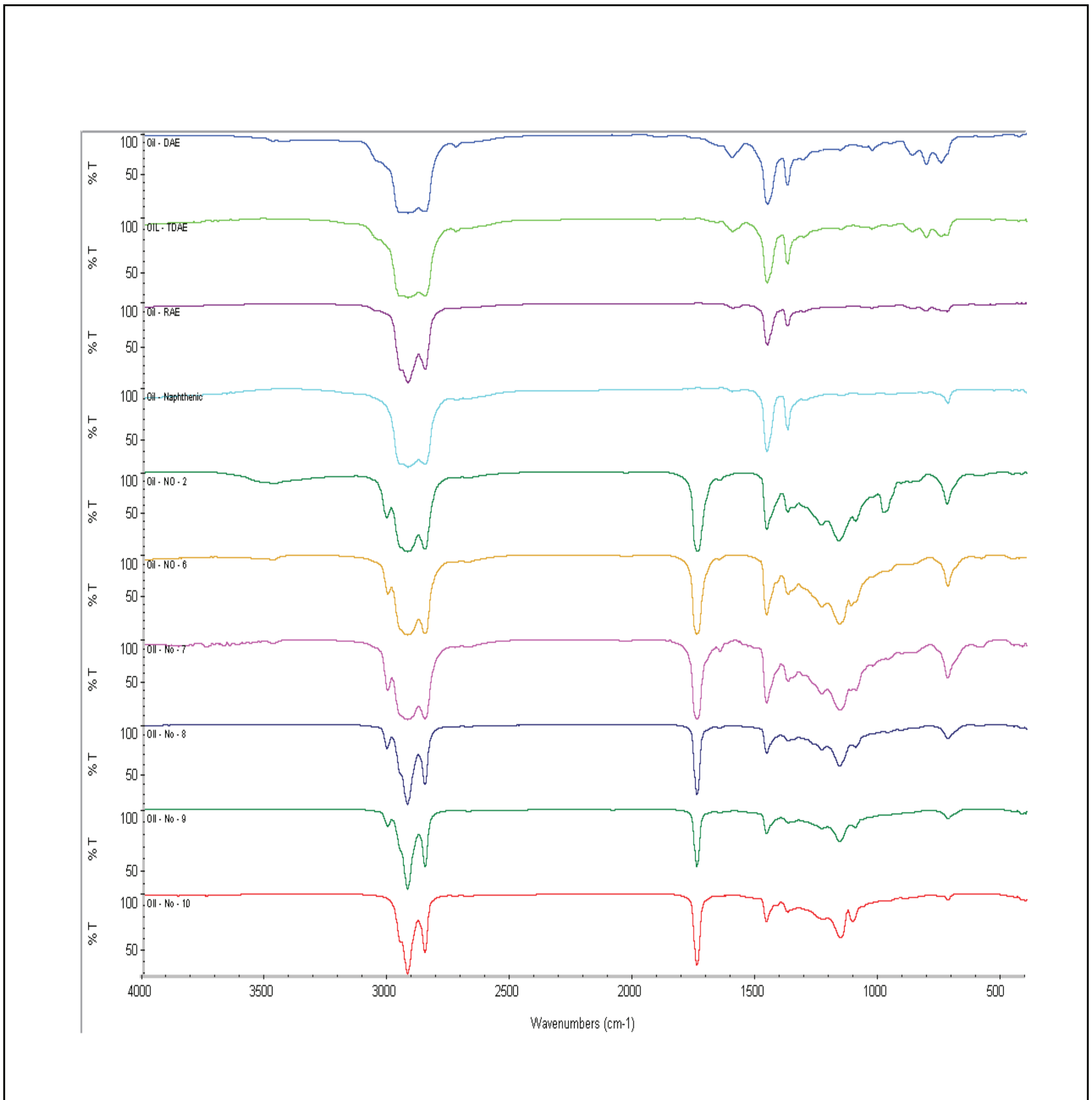

Fig. 3.1: FTIR spectra for oil samples

The DAE, TDAE, RAE and naphthenic oils show presence of weak aromatic C=C stretch (around 1600 cm^{-1}). Aliphatic CH_2 and CH_3 stretching (around 1375 and 1455 cm^{-1}) were also observed for these oils. The DAE and TDAE oils have shown peaks around 800 cm^{1} due to high aromatic content. Few additional peaks were observed for vegetable oils due to presence of additional functional groups. All vegetable oils show presence of triglyceride ester carbonyl groups (strong peak around 1745 cm^{-1}), hydrogen bonded C-O group (around 1100 and 1165 cm^{-1}) and acyl C-O group (around 1240 cm^{-1}), which may be due to presence of acidic groups. Aliphatic CH_2 group (around 725 and 1460 cm^{-1}), were also present in all vegetable oils. The C=C peak (around 1650 cm^{-1}) was missing in palm oil and coconut oil.

NMR data for oils are given in Fig. 3.2 and 3.3.

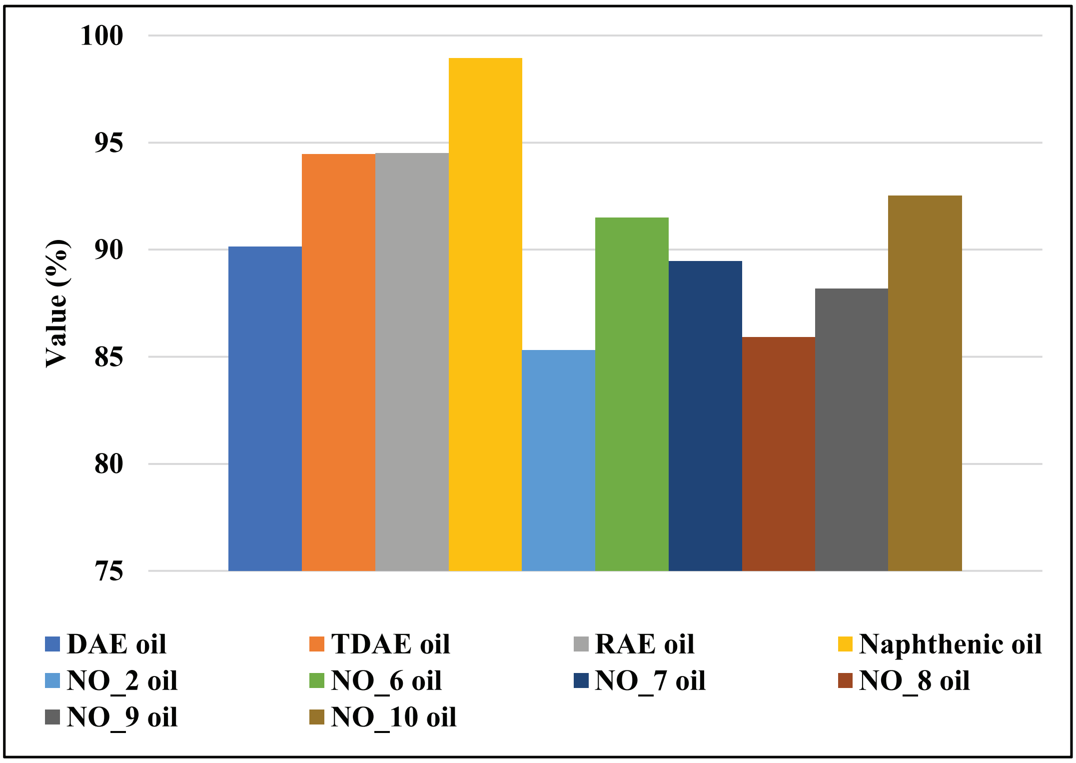

Fig. 3.2: Aliphatic proton content in detected by in oil samples

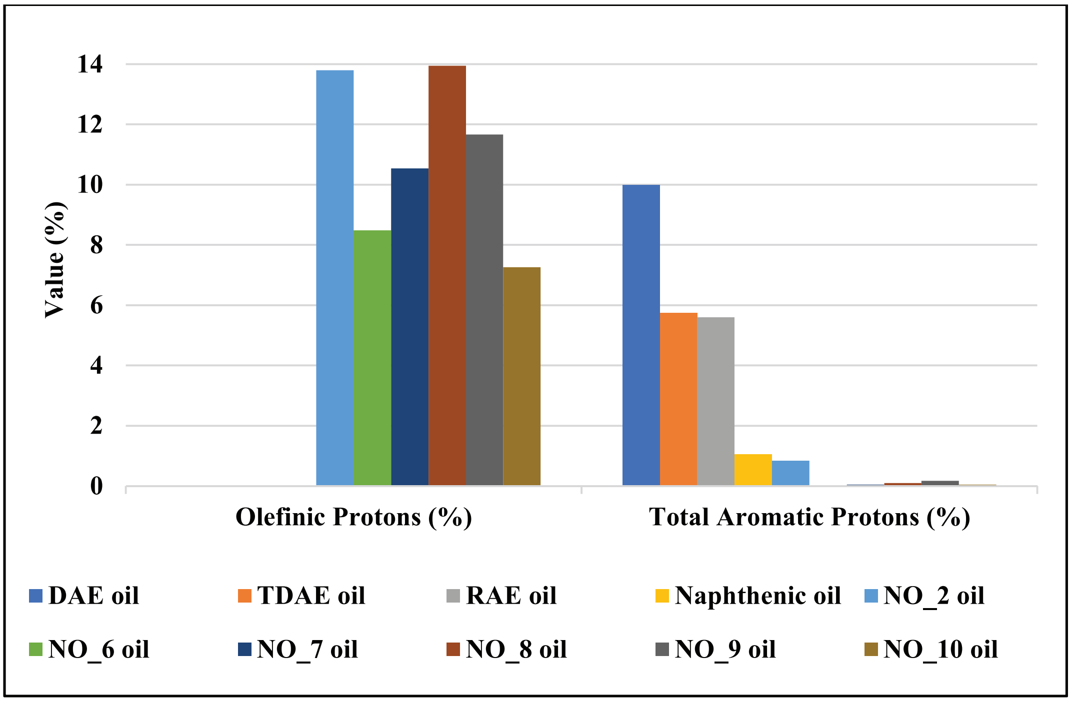

Fig. 3.3: Other structural groups detected by NMR in oil samples

All oil samples have aliphatic content more than 85% and all the vegetable oils have olefinic content more than 7%. The DAE, TDAE and RAE oils have aromatic content more than 5% (including poly aromatic content). This indicates that mineral oils have some PCA/PAH content, which may be carcinogenic for human. All vegetable oils have negligible aromatic content (< 1%). Hence, vegetable oils are safer to use in rubber industry to produce eco-friendly products.

3.2 PHYSICO-CHEMICAL CHARACTERIZATION OF STYRENE BUTADIENE RUBBER LATEX

3.2.1 Normal Styrene Content (23.5%) Latex

Test results for physico-chemical properties for styrene butadiene rubber latex is given in Table 3.4.

Table 3.4: Physico-chemical properties of styrene butadiene rubber latex (Normal styrene content)

Parameter	Value
Solid content (%)	19.9
Mooney viscosity (ML1+4) @100°C (MU)	106.2
Refractive index	1.5349
Bound styrene content (%)	23.9
Degradation temperature (°C)	465
Glass transition temperature (°C)	-53.4
Mn (g $mole^{-1}$)	1.9 lacs
Mw (g $mole^{-1}$)	8.0 lacs
Polydispersity index	4.2

Solid content of styrene butadiene rubber latex, Mooney viscosity, bound styrene content, glass transition temperature, molecular weight, molecular weight distribution and degradation, and temperature of coagulated dried latex sample were found within the specified range. This latex was used for oil extension and further study.

3.2.2 High Styrene Content (40%) Latex

Test results for physico-chemical properties of SBR latex are tabulated in Table 3.5.

Table 3.5: Physico-chemical properties of styrene butadiene rubber latex (High styrene content)

Parameter	Value
Solid content (%)	21.0
Mooney viscosity (MU)	127.7
Refractive index	1.5488
Bound styrene content (%)	39.4
Degradation temperature (°C)	405.4
Glass transition temperature (°C)	-31.8
Mn (g $mole^{-1}$)	2.0 lacs
Mw (g $mole^{-1}$)	7.7 lacs
Polydispersity index	3.8

All the properties of high styrene (40%) SBR latex sample were found within the specified range. This latex was used for oil extension and further study.

3.3 PHYSICO-CHEMICAL CHARACTERIZATION OF OIL EXTENDED STYRENE BUTADIENE RUBBERS

3.3.1 Normal Styrene Content (23.5%) SBRs

Vegetable oil-based SBRs were found to be light in color. So, these rubbers could be used for light color products. Physico-chemical properties of rubber samples are summarized in Tables 3.6 and 3.7.

Table 3.6: Physico-chemical properties of oil extended styrene butadiene rubber (Normal styrene content)

Parameter / Sample	Total extractables (%)	Bound styrene content (%)	Density (g cc^{-1})	Mooney viscosity (MU)	Moisture content (%)
S23.5_TDAE	32.8	24.0	0.945	50.4	0.13
S23.5_Naphthenic	31.1	24.0	0.923	45.3	0.10
S23.5_NO_2	32.1	23.9	0.939	44.7	0.19
S23.5_NO_6	30.9	24.1	0.933	46.4	0.09
S23.5_NO_7	34.3	23.2	0.938	45.5	0.15
S23.5_NO_8	35.4	23.0	0.936	44.1	0.12
S23.5_NO_9	30.7	24.2	0.934	43.2	0.14
S23.5_NO_10	35.8	23.4	0.940	48.2	0.18

Table 3.7: Physico-chemical properties of oil extended styrene butadiene rubber (Normal styrene content)

Sample / Parameter	Degradation temperature (°C)	Ash content (%)	Tg (°C)
S23.5_TDAE	456.3	0.42	-55.4
S23.5_Naphthenic	456.3	0.28	-56.7
S23.5_NO_2	435.5	0.30	-63.0
S23.5_NO_6	455.6	0.29	-58.0
S23.5_NO_7	449.4	0.06	-58.7
S23.5_NO_8	447.1	0.18	-62.3
S23.5_NO_9	439.4	0.18	-62.5
S23.5_NO_10	456.3	0.17	-56.2

Acetone extraction for SBRs prepared with vegetable oils were found to be comparable with petroleum oil-based rubbers, which indicates that proper oil is present in these rubbers, and this may be due to good compatibility of these oils with SBR. Bound styrene content was calculated through refractive index value, which was found comparable to these extracted SBR rubber samples. This indicates comparable composition of monomer for all SBR samples.

Density of OE SBRs were found to be in line with density of respective oil sample. Mooney viscosity was found to be higher for SBR prepared with TDAE and NO_10 oil and is within the range for all rubber samples. Variation in Mooney viscosity value may affect the processing behavior of rubber during compounding, calendaring, extrusion, etc. Moisture content was found less than 0.2%, which indicates that all rubber samples were dried properly. Higher moisture content may lead to poor processing and mechanical properties of rubber compounds. Degradation temperature and ash content were found comparable for all OE SBR samples. The NO_2, NO_8 and NO_9 oil extended SBRs have lower glass transition temperature, which may improve the abrasion and rolling resistance properties of the rubber compound based on these oils.

3.3.2 High Styrene Content (40%) SBRs

Physico-chemical properties of their rubber samples are given in Tables 3.8 and 3.9.

Table 3.8: Physico-chemical properties of oil extended styrene butadiene rubber (High styrene content)

Parameter / Sample	Total extractables (%)	Bound styrene content (%)	Density (g cc^{-1})	Mooney viscosity (MU)	Moisture content (%)
S40_DAE	33.7	40.5	0.979	62.3	0.13
S40_TDAE	32.3	40.4	0.962	61.7	0.14
S40_RAE	33.2	39.7	0.971	63.6	0.17
S40_Naphthenic	33.6	39.5	0.946	52.6	0.12
S40_NO_2	32.8	40.3	0.963	40.2	0.19
S40_NO_6	34.2	40.9	0.961	50.0	0.15
S40_NO_7	33.3	41.0	0.955	52.5	0.17
S40_NO_8	34.3	40.1	0.957	52.0	0.12
S40_NO_9	32.2	39.4	0.956	54.3	0.18
S40_NO_10	31.8	40.4	0.958	56.0	0.14

Table 3.9: Physico-chemical properties of oil extended styrene butadiene rubber (High styrene content)

Parameter / Sample	Degradation temperature (°C)	Ash content (%)	Tg (°C)
S40_DAE	394.6	0.25	-33.2
S40_TDAE	391.5	0.30	-38.4
S40_RAE	379.2	0.36	-31.5
S40_Naphthenic	386.9	0.37	-39.4
S40_NO_2	405.4	0.30	-48.8
S40_NO_6	413.9	0.28	-43.3
S40_NO_7	420.1	0.27	-47.8
S40_NO_8	416.2	0.31	-56.3
S40_NO_9	423.9	0.29	-49.5
S40_NO_10	389.2	0.24	-38.3

Acetone extraction for SBRs prepared with vegetable oils were found to be comparable with petroleum oil-based rubbers, which indicates that proper oil is present in these rubbers, and this may be due to good compatibility of these oils with SBR. Bound styrene content was calculated through refractive index value, which was found comparable within the specified range for these extracted SBR rubber samples. This indicates comparable composition of monomer for all SBR samples.

Mooney viscosity was found to be lower for S40_NO_2 sample and it was within the range for other samples. Moisture content was found less than 0.2 %, which means all rubber samples were dried properly. Degradation temperature was found in the range of 380° to 420°C in TGA test for all OE-SBRs. The S40_NO_2, S40_NO_6 to S40_NO_9 samples have lower Tg, which may improve the abrasion and rolling resistance properties of the rubber compound based on these OE-SBRs.

3.4 MIXING BEHAVIOUR DURING COMPOUND PREPARATION

3.4.1 ASTM Master Batch Recipe

Various mixing parameters like mixing energy, maximum torque and dump temperature are tabulated in Table 3.10.

Table 3.10: ASTM master batch mixing behaviour

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
ASTM_M_DAE	227.0	155.6	110.4	1.152
ASTM_M_TDAE	231.6	153.3	105.9	1.141
ASTM_M_RAE	235.1	155.8	113.5	1.145
ASTM_M_Naphthenic	236.3	156.6	105.5	1.126
ASTM_M_NO_2	210.6	138.1	107.8	1.135
ASTM_M_NO_6	209.6	141.6	107.3	1.130

Master rubber compound mixed using modified vegetable oils NO_2 and NO_6 based styrene butadiene rubbers exhibited around 8.5% less mixing energy, around 8.5% less mixing torque and around 11.5% less final torque. This may be due to lower Mooney viscosity of these rubber samples. Dump temperature for all the batches was found within the acceptable range. Batch weight after mixing was checked for all the mixed master batches and it was found within acceptable range. Density of all master batches were found related with the density of respective raw styrene butadiene rubber.

3.4.2 Passenger Car Radial Tire Tread Compound Recipe

Various mixing parameters including bound rubber content and density are presented in Tables 3.11 and 3.12 for master and final batches, respectively.

Table 3.11: PCR tire tread master batch mixing and characterization

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Bound rubber (%)
PCR_M_TDAE	213.2	153.6	129.5	27.2
PCR_M_Naphthenic	204.7	145.1	130.4	29.4
PCR_M_NO_2	211.7	142.8	129.7	31.9
PCR_M_NO_6	200.6	134.7	129.0	28.8
PCR_M_NO_7	198.8	141.9	129.3	30.0
PCR_M_NO_8	193.3	134.9	128.1	27.2
PCR_M_NO_9	202.7	136.4	128.7	28.5
PCR_M_NO_10	199.6	142.8	129.5	28.2

Table 3.12: PCR tire tread final batch mixing and characterization

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
PCR_F_TDAE	84.9	188.3	82.4	1.143
PCR_F_Naphthenic	75.5	160.0	84.3	1.130
PCR_F_NO_2	73.0	149.3	83.3	1.133
PCR_F_NO_6	75.3	160.0	84.6	1.126
PCR_F_NO_7	75.2	143.0	84.0	1.134
PCR_F_NO_8	73.9	141.3	83.5	1.135
PCR_F_NO_9	71.6	148.5	82.4	1.135
PCR_F_NO_10	77.8	161.0	84.5	1.137

Master and final batch compounds were mixed using NO_6 to NO_10 vegetable oil-based SBRs displayed less mixing energy as compared to TADE oil. Dump temperature was found comparable for all samples in both; master and final stage mixing. Higher bound rubber content value indicates higher polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement. Bound rubber was found to be comparable for all master compounds. Density of all final batches were found in line with the density of respective raw SBRs.

3.4.3 Motorcycle Tire Tread Compound Recipe

Various mixing parameters including bound rubber content and density are given in Tables 3.13 and 3.14 for master and final batches, respectively.

Table 3.13: Motorcycle tire tread master batch mixing and characterization

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Bound rubber (%)
MCT_M_DAE	203.3	186.3	145.7	19.8
MCT_M_TDAE	196.5	174.3	146.1	19.2
MCT_M_RAE	200.7	178.8	146.5	21.2
MCT_M_Naphthenic	198.5	171.2	143.3	19.6
MCT_M_NO_2	178.7	166.3	137.7	18.2
MCT_M_NO_6	178.0	156.3	140.7	20.2
MCT_M_NO_7	189.4	163.2	141.8	18.1
MCT_M_NO_8	183.3	160.7	140.9	18.2
MCT_M_NO_9	185.9	153.6	142.4	18.9
MCT_M_NO_10	184.0	162.7	140.4	19.5

Table 3.14: Motorcycle tire tread final batch mixing and characterization

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
MCT_F_DAE	59.6	116.1	114.0	1.176
MCT_F_TDAE	60.7	126.0	113.0	1.167
MCT_F_RAE	55.8	118.1	113.0	1.169
MCT_F_Naphthenic	57.4	130.2	111.0	1.152
MCT_F_NO_2	46.7	96.7	110.0	1.167
MCT_F_NO_6	50.0	103.7	111.3	1.153
MCT_F_NO_7	56.2	113.0	112.8	1.160
MCT_F_NO_8	53.7	111.4	113.4	1.162
MCT_F_NO_9	57.4	111.0	113.3	1.159
MCT_F_NO_10	53.2	115.7	112.8	1.161

Master rubber compound mixed using S40_NO_2 and S40_NO_6 show slightly less mixing energy for both; master and final stage as compared to compound prepared with petroleum oil based SBR. This may be due to lower Mooney viscosity of these rubber samples. Dump temperature was found comparable for all samples in both; master and final stage mixing. Higher bound rubber content value indicates more polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement. Bound rubber was found to be comparable for all master batch compounds. Density of all final batches were found in line with the density of respective raw SBRs.

3.5 RUBBER COMPOUND PROCESSING BEHAVIOUR

3.5.1 ASTM Recipe

Test results for master compounds like Mooney viscosity, power law index, dispersion, activation energy and bound rubber are tabulated in Table 3.15.

Table 3.15: ASTM master batch compound processing properties

Parameter / Sample	Mooney viscosity (ML1+4) @ 100°C (MU)	Power law index	Bound rubber (%)	Dispersion (%)	Activation energy, Eα (kCal mol^{-1} g^{-1})
ASTM_M_DAE	62.0	0.235	18.0	81.4	1409
ASTM_M_TDAE	59.6	0.239	17.9	83.3	1363
ASTM_M_RAE	66.2	0.235	19.8	82.7	1408
ASTM_M_Naphthenic	61.7	0.235	27.0	81.2	1100
ASTM_M_NO_2	52.5	0.231	28.7	79.8	1298
ASTM_M_NO_6	56.1	0.234	27.4	83.5	1249

Compounds prepared with NO_2 and NO_6 modified vegetable oil-based styrene butadiene rubber exhibited lower (around 12%) Mooney viscosity because these raw rubbers are also having low Mooney viscosity, comparable power law index, lower (around 15%), Payne effect (Fig. 3.4) and higher (around 55%) bound rubber content due to presence of various additional groups in vegetable oils, comparable filler dispersion and lower activation energy.

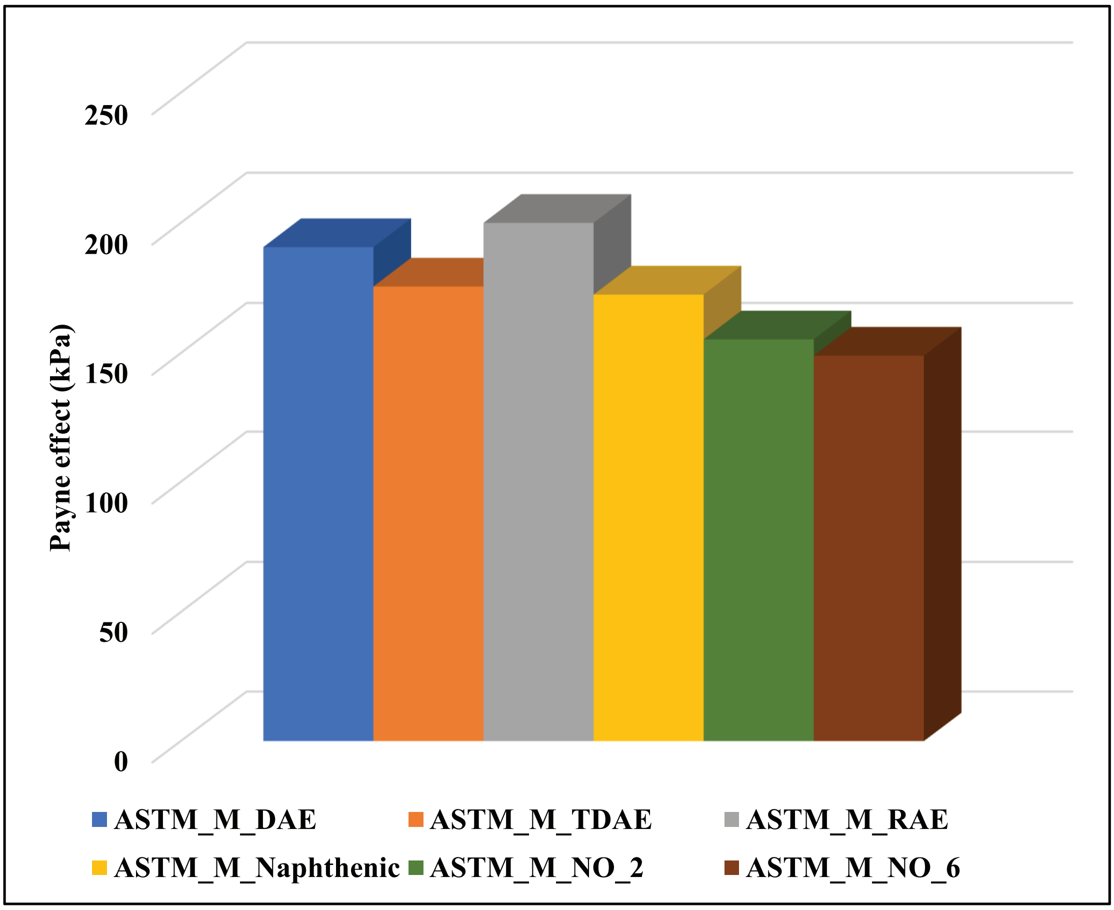

Fig. 3.4: RPA strain sweep test for ASTM master batch compound

This indicates comparable or slightly better processing properties for compounds prepared with modified vegetable oils-based styrene butadiene rubber as compared to compounds prepared with petroleum oil-based rubbers.

Carbon black dispersion was also measured through Scanning Electron Microscopy (SEM) analysis. SEM images for various rubber compound samples are presented in Fig. 3.5- 3.10.

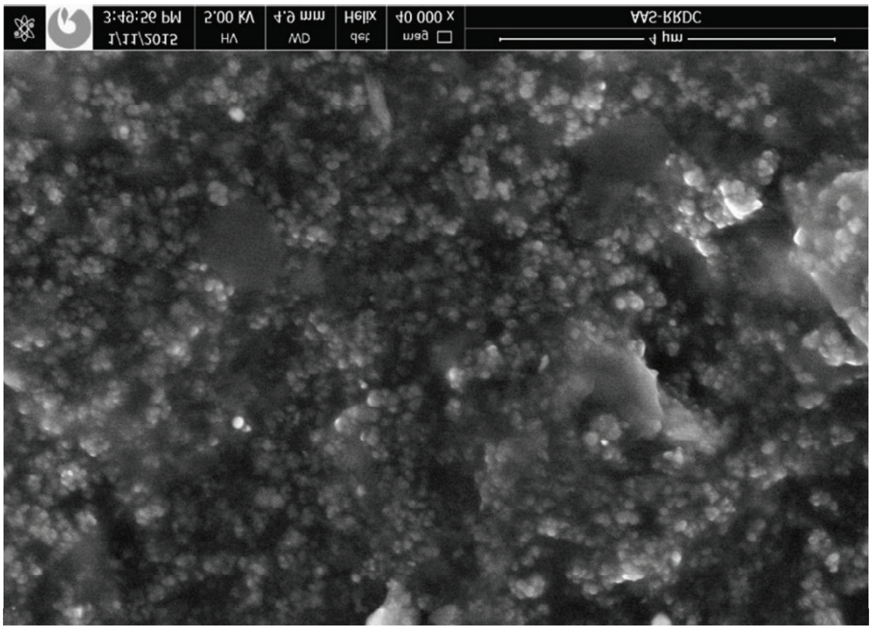

Fig. 3.5: SEM image (40000 X magnification) for DAE_ASTM master batch compound

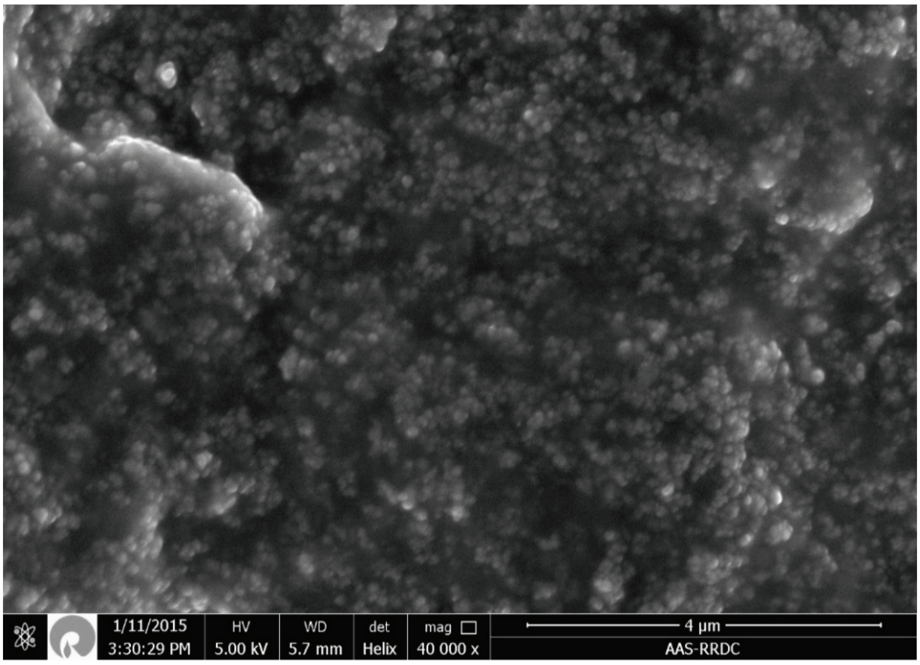

Fig. 3.6: SEM image (40000 X magnification) for TDAE_ASTM master batch compound

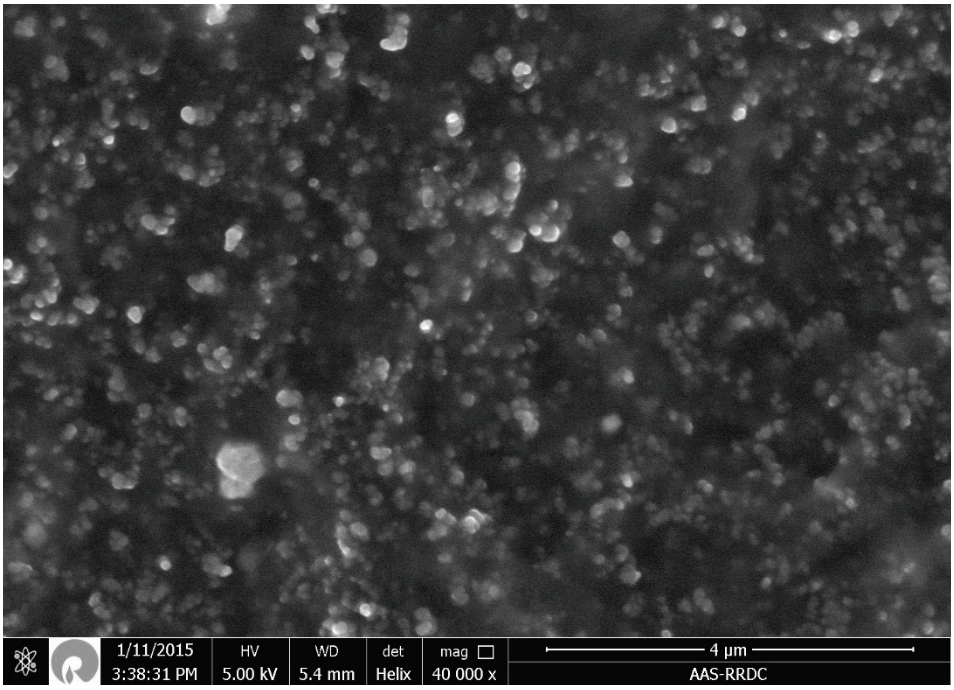

Fig. 3.7: SEM image (40000 X magnification) for RAE_ASTM master batch compound

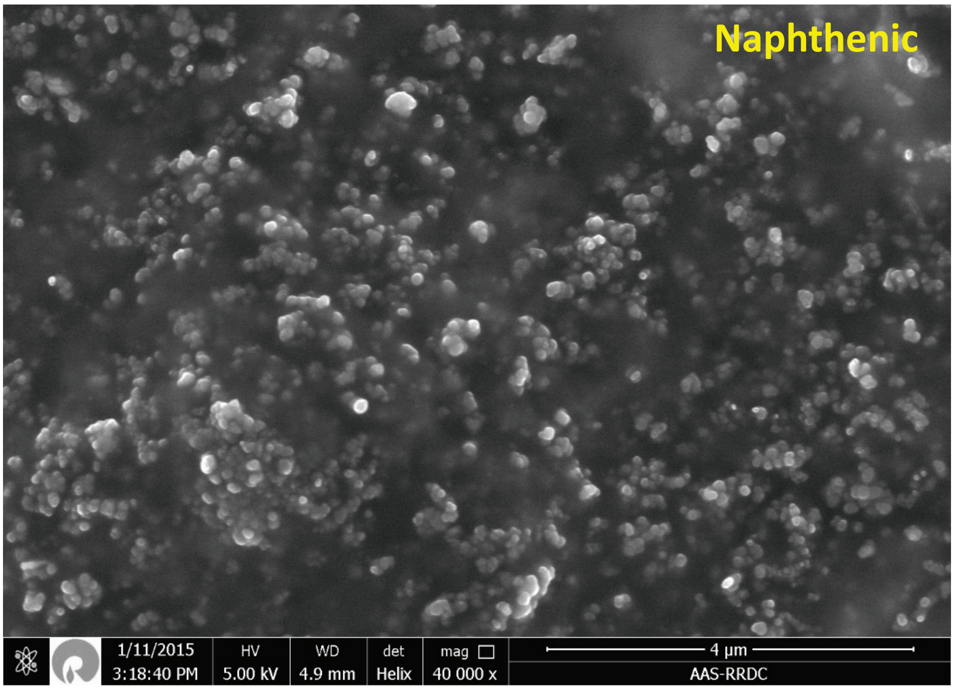

Fig. 3.8: SEM image (40000 X magnification) for Naphthenic_ ASTM master batch compound

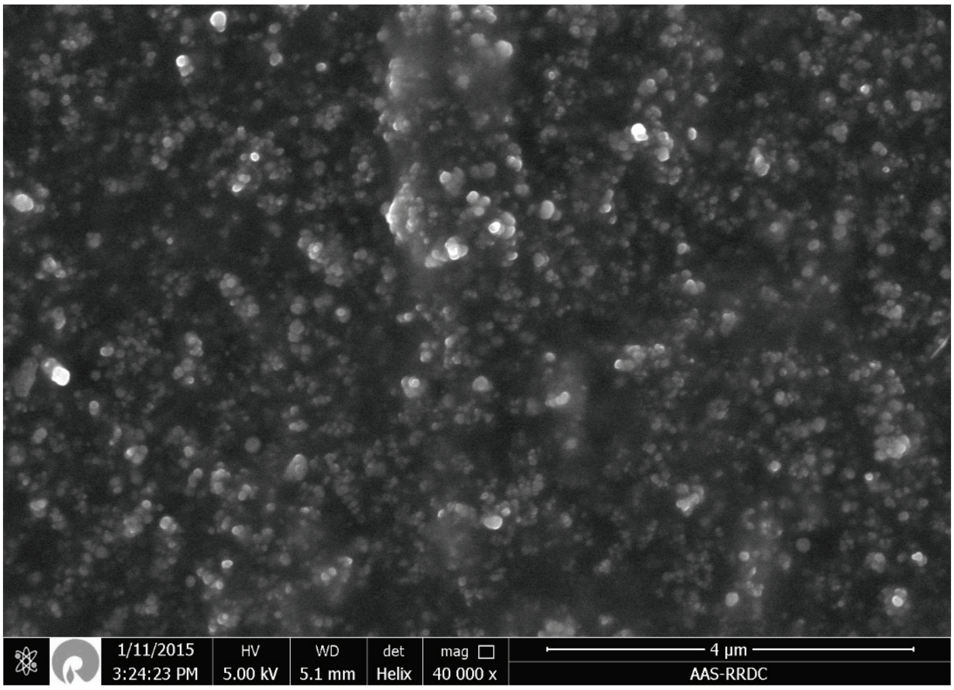

Fig. 3.9: SEM image (40000 X magnification) for NO2_ASTM master batch compound

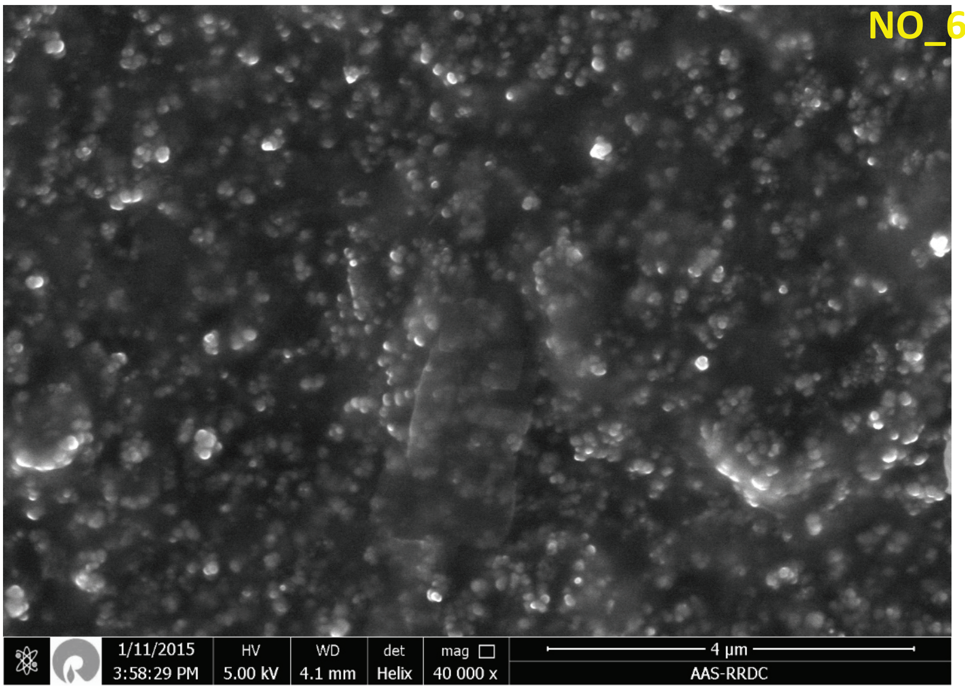

Fig. 3.10: SEM image (40000 X magnification) for NO6_ASTM master batch compound

Test results are showing comparable carbon black dispersion for all samples while analysing images captured for 10000X and 20000X magnification. However, some difference was observed while analysing the images captured at 40000X magnification. Carbon black aggregate size and inter-aggregate distance were found to be comparable for all the samples. This indicates that modified vegetable oil extended SBR based compounds have comparable properties with petroleum oil extended SBR based compounds for dispersion properties.

3.5.2 Passenger Car Radial Tire Tread Compound Recipe

Test results for final compounds like Mooney viscosity, power law index, dispersion, activation energy and rheometric properties are given in Tables 3.16 and 3.17.

Table 3.16: PCR tire tread final batch compound processing properties

Parameter / Sample	Mooney viscosity (MU)	Power law index	Filler dispersion (%)	Activation energy, Eα (kCal mol^{-1} g^{-1})
PCR_F_TDAE	55.4	0.202	53.0	3248
PCR_F_Naphthenic	56.7	0.187	67.3	2805
PCR_F_NO_2	55.8	0.180	65.4	2853
PCR_F_NO_6	54.6	0.167	61.5	2954
PCR_F_NO_7	54.7	0.189	57.0	2841
PCR_F_NO_8	54.2	0.192	63.0	2785
PCR_F_NO_9	51.9	0.190	57.7	2870
PCR_F_NO_10	57.5	0.179	64.2	2669

Table 3.17: PCR tire tread compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC50 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
PCR_F_TDAE	2.44	10.30	4.32	2.64	6.44	14.99	7.86	8.1
PCR_F_Naphthenic	2.61	8.61	4.27	2.05	6.32	15.29	6.00	7.6
PCR_F_NO_2	2.56	8.27	4.20	1.93	6.10	14.82	5.71	7.8
PCR_F_NO_6	2.51	9.57	4.22	2.28	6.46	15.36	7.06	7.6
PCR_F_NO_7	2.65	8.79	4.26	2.25	6.21	14.59	6.14	8.1
PCR_F_NO_8	2.36	7.74	4.09	1.82	5.92	14.31	5.38	8.0
PCR_F_NO_9	2.46	7.70	4.15	2.08	5.90	14.13	5.24	8.3
PCR_F_NO_10	2.75	10.14	3.96	2.14	6.05	14.34	7.39	8.2

* Cure rate = 100/(tC90 -t C10)

Mooney viscosity was found comparable for all compounds. Power law index (n) close to zero or relative lower value, while means plastic nature of rubber compound and hence, better shear thinning (Flow behavior) of rubber compound. Higher activation energy value means rubber compound need high energy for compound flow, which indicates poor processing. Compounds prepared with vegetable oil-based SBRs displayed lower power law index, lower activation energy and higher filler dispersion as compared to compound prepared with TDAE oil extended SBR. This indicates better processing properties for compounds prepared with vegetable oils-based SBRs. Compounds prepared with naphthenic oil and vegetable oil based SBR show comparable processing properties. Compound prepared with NO_6 and NO_10 vegetable oil-based SBRs have comparable rheometric properties with respect to TDAE oil. Compound prepared with NO_2 and NO_7 to NO_9 vegetable oil-based SBRs exhibited less delta torque value as compared to TDAE oil. This may be due to presence of more olefinic content as indicated by NMR of these oils.

3.5.3 ASTM Compound Mixing (With curatives adjustment)

Rheometric properties are shown in Table 3.18.

Table 3.18: ASTM compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	Scorch safety time, tS2 (min)	tC10 (min)	tC50 (min)	Optimum cure time, tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
ASTM Naphthenic	2.50	11.83	4.53	2.81	6.28	13.00	9.33	9.8
ASTM_NO_2	1.95	11.94	4.16	3.42	5.57	10.43	9.99	14.3
ASTM_NO_6	1.94	11.77	4.95	3.29	6.93	13.98	9.83	9.4
ASTM_NO_7	2.56	12.54	3.60	2.32	4.97	10.01	9.98	13.0
ASTM_NO_8	2.66	11.91	3.59	2.26	4.97	10.47	9.25	12.2
ASTM_NO_9	2.41	11.87	3.50	2.17	4.95	10.30	9.46	12.3
ASTM_NO_10	2.07	12.26	4.02	2.78	5.97	12.38	10.19	10.4

*Cure rate = 100/(tC90 - tC10)

Compounds prepared with vegetable oil-based SBRs have comparable delta torque value with respect to naphthenic oil. Lower delta torque and modulus were observed for compounds based on few vegetable oils (like NO_2, NO_7, NO_8 and NO_9) extended SBRs, when similar dosage of curatives was used. This is due to presence of more olefinic content in these vegetable oils. For better comparison of rubber or any other ingredients in standard recipe, it is better to match compound torque/modulus first by adjusting filler, oil and curatives dosage. So, higher dosage (15 to 25%) of curatives (sulfur and accelerator) was used for compounds prepared with vegetable oil-based SBRs (except NO_6 and NO_10) to achieve similar delta torque value. These compounds show higher cure rate index due to use of higher curatives. The NO_6 and NO_10 vegetable oil extended SBRs do not need additional curatives due to relatively higher saturation with respect to other vegetable oils.

Vegetable oils contain unsaturated fatty acids, which may affect the cure characteristics and mechanical properties of filled compounds as these free acids took part in vulcanization. Most of the vegetable origin oils are rich in oleic and linoleic acids such as sesame, rapeseed, sunflower, soybean and peanut oils, linseed oil is most unsaturated vegetable oil with presence of oleic, linoleic, and linolenic acids Coconut oil is most saturated vegetable oil, which contains very less oleic and linoleic acids. It contains mainly palmitic, stearic, lauric and myristic acids. Palm oil has both; saturated and unsaturated carbon chains due to presence of palmitic acid and oleic acid. Ratio of unsaturated to saturated acid content is very high for castor oil and it is very low for coconut oil. Palm oil has this ratio slightly higher with respect to coconut oil. Groundnut, soybean and mustard oil has the moderate ratio[1-7].

3.5.4 ASTM Gum Compound Recipe (High styrene only)

Test results for rheometric properties are given in Table 3.19.

Table 3.19: ASTM gum compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
Gum_DAE	0.79	4.68	15.62	11.07	23.28	3.89	8.2
Gum_TDAE	0.78	5.19	14.00	10.83	25.85	4.41	6.7
Gum_RAE	0.81	4.60	18.36	12.75	27.57	3.79	6.7
Gum_Naphthenic	0.67	4.35	21.36	14.68	31.63	3.68	5.9
Gum_NO_2	0.19	2.12	8.67	4.82	17.00	1.93	8.2
Gum_NO_6	0.64	4.00	21.30	13.54	30.54	3.36	5.9
Gum_NO_7	0.46	3.29	23.04	11.12	29.05	2.83	5.6
Gum_NO_8	0.24	2.36	8.43	4.88	19.65	2.12	6.8
Gum_NO_9	0.51	3.28	18.34	8.42	22.72	2.77	7.0
Gum_NO_10	0.56	4.44	18.91	12.80	29.33	3.88	6.0

* Cure rate = 100/ (tC90 - tC10)

Compounds prepared with S40_NO_6 and S40_NO_10 have shown rheometric properties almost comparable with naphthenic oil. Compounds prepared with S40_NO_2 and S40_NO_7 to S40_NO_9 have less delta torque value, which may be due to presence of more olefinic content as a indicated by NMR of these oils.

3.5.5 Motorcycle Tire Tread Compound Recipe

Test results for final batch uncured compounds are presented in Tables 3.20 to 3.21.

Table 3.20: Motorcycle tire tread final batch compound processing properties

Parameter / Sample	Mooney viscosity (MU)	Power law index	Activation energy, Eα (kCal mol^{-1} g^{-1})
MCT_F_DAE	70	0.187	2444
MCT_F_TDAE	67	0.194	2434
MCT_F_RAE	66	0.191	2550
MCT_F Naphthenic	60	0.190	2419
MCT_F_NO_2	53	0.198	2596
MCT_F_NO_6	57	0.194	2273
MCT_F_NO_7	64	0.188	2349
MCT_F_NO_8	63	0.185	2201
MCT_F_NO_9	65	0.187	2301
MCT_F_NO_10	64	0.185	2257

Table 3.21: Motorcycle tire tread compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
MCT_F_DAE	2.70	13.31	5.08	4.27	10.81	10.61	15.3
MCT_F_TDAE	2.56	13.46	5.45	4.51	12.07	10.90	13.2
MCT_F_RAE	2.55	12.87	5.59	4.67	11.79	10.32	14.0
MCT_F Naphthenic	2.35	12.37	5.23	4.20	11.50	10.02	13.7
MCT_F_NO_2	2.08	9.67	4.76	3.70	10.69	7.59	14.3
MCT_F_NO_6	2.31	11.37	5.09	3.89	10.41	9.06	15.3
MCT_F_NO_7	2.61	10.73	4.80	3.52	10.82	8.12	13.7
MCT_F_NO_8	2.51	10.67	4.76	3.48	10.54	8.16	14.2
MCT_F_NO_9	2.53	11.04	4.74	3.49	10.75	8.51	13.8
MCT_F_NO_10	2.56	13.19	4.67	3.70	11.18	10.63	13.4

* Cure rate = 100/ (tC90 - tC10)

All the compounds have shown Mooney viscosity in line with respective raw OE-SBRs Mooney viscosity. 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. Power law index was found to be comparable for all compounds. Higher activation energy means rubber compound need high energy for compound flow, which indicates poor processing. Compounds based on S40_NO_6 to S40_NO_10 have shown lower activation energy as compared to compound prepared with petroleum oil extended SBR. This may be due to absence of aromatic content in these vegetable oils. Refractive index[8] and nuclear magnetic resonance (NMR) data indicates the presence of aromatic content in oil samples. Rheometric properties for motorcycle tire tread compounds were found in line with gum compounds.

3.6 VULCANIZATE PROPERTIES

3.6.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for stress-strain including hardness are in Table 3.22.

Table 3.22: PCR tire tread compound stress-strain properties

Parameter / Sample	M100 (MPa)	M200 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)
PCR_F_TDAE	2.3	6.3	11.3	21.2	494	60
PCR_F_ Naphthenic	1.5	4.3	8.5	18.9	536	53
PCR_F_NO_2	1.7	5.0	9.3	18.9	500	53
PCR_F_NO_6	1.9	5.7	11.1	18.9	444	55
PCR_F_NO_7	1.7	4.7	9.1	18.9	521	56
PCR_F_NO_8	1.3	3.5	7.0	18.9	603	51
PCR_F_NO_9	1.4	3.8	7.4	19.1	597	53
PCR_F_NO_10	1.9	5.6	10.9	18.6	427	57

Reinforcement index and rubber-filler interaction parameter are given in Table 3.23

Table 3.23: PCR tire tread compound reinforcement index and rubber-filler interaction parameter

Parameter / Sample	RI (M300/M100)	M300-M100 (MPa)	G′@1%/ G′@25%	I (MPa)
PCR_F_TDAE	4.9	9.0	2.315	1.94
PCR_F_Naphthenic	5.7	7.0	1.993	1.76
PCR_F_NO_2	5.5	7.6	1.922	1.98
PCR_F_NO_6	5.8	9.2	1.946	2.36
PCR_F_NO_7	5.4	7.4	2.015	1.84
PCR_F_NO_8	5.4	5.7	2.013	1.42
PCR_F_NO_9	5.3	6.0	1.934	1.55
PCR_F_NO_10	5.7	9.0	1.884	2.39

Swell index, Volume fraction and crosslink density and glass transition temperature are given in Table 3.24.

Table 3.24: PCR tire tread compound crosslink density and glass transition temperature

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink density X 10^4 (mol cm^{-3})	Tg (°C)
PCR_F_TDAE	2.24	0.266	1.68	-50.2
PCR_F_Naphthenic	2.37	0.248	1.45	-52.1
PCR_F_NO_2	2.41	0.242	1.38	-57.3
PCR_F_NO_6	2.24	0.268	1.70	-54.2
PCR_F_NO_7	2.31	0.256	1.54	-51.8
PCR_F_NO_8	2.54	0.225	1.18	-56.4
PCR_F_NO_9	2.49	0.231	1.24	-57.9
PCR_F_NO_10	2.20	0.277	1.83	-51.6

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have shown similar (within experimental error) static modulus as compared to TDAE oil. Vulcanizates prepared with vegetable oil-based SBRs have shown slightly less tensile strength and less hardness, which may be due to less crosslink density. Vulcanizate prepared with NO_8 and NO_9 have lowest modulus and hardness due to lowest crosslink density and lowest delta torque. However, crosslink density may be increased by adjustment of curatives type and dosage level. Tg of all the vulcanizates were found to be in line with respective OE SBR.

3.6.2 ASTM Compound Mixing (With curatives adjustment)

Test results for stress-strain including hardness and reinforcement index are given in Table 3.25.

Table 3.25: ASTM compound stress-strain

Parameter / Sample	M100 (MPa)	M200 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300 /M100)
ASTM_Naphthenic	1.8	5.1	9.8	21.4	540	54	5.4
ASTM_NO_2	1.9	5.5	10.0	20.2	532	56	5.3
ASTM_NO_6	1.9	5.7	10.9	19.7	467	54	5.7
ASTM_NO_7	1.8	5.2	9.7	19.7	510	55	5.4
ASTM_NO_8	1.8	4.9	9.4	19.2	505	55	5.2
ASTM_NO_9	1.8	5.0	9.7	20.4	513	53	5.4
ASTM_NO_10	1.9	5.6	10.8	18.8	458	56	5.7

Swell index volume fraction and crosslink density are shown in Table 3.26.

Table 3.26: ASTM compound crosslink density

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink Density X 10^4 (mol cm^{-3})
ASTM_ Naphthenic	1.92	0.327	2.59
ASTM_NO_2	1.93	0.327	2.55
ASTM_NO_6	1.92	0.330	2.62
ASTM_NO_7	1.93	0.326	2.52
ASTM_NO_8	2.00	0.314	2.33
ASTM_NO_9	1.98	0.315	2.36
ASTM_NO_10	1.88	0.332	2.65

Vulcanizates prepared with vegetable oil based SBRs have comparable static modulus value with respect to naphthenic oil. This may be due to matching of the delta torque value for all the compounds. Tensile strength, elongation at break and hardness were found to be comparable for all compounds. Reinforcement index was found to be slightly high for NO_6 and NO_10 oil extended SBR based compounds. This may be due to relatively high rubber-filler interaction for these oil-based rubbers. Crosslink density was found slightly low for NO_8 and NO_9 and slightly high for NO_6 and NO_10 oil extended SBR based compounds. This may be due to relatively less unsaturation to saturation ratio which helps in tighter crosslinking.

3.6.3 ASTM Gum Compound Recipe (High styrene only)

Test results for stress-strain including hardness and reinforcement index are shown in Table 3.27.

Table 3.27: ASTM gum compound stress-strain properties

Parameter / Sample	M100 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300/ M100)
Gum_DAE	0.6	1.7	2.7	395	31	2.8
Gum_TDAE	0.7	2.2	2.3	309	36	3.1
Gum_RAE	0.6	1.6	3.2	458	32	2.7
Gum_Naphthenic	0.6	1.6	2.5	409	29	2.7
Gum_NO_2	0.3	0.6	1.1	512	19	2.0
Gum_NO_6	0.5	1.4	2.0	444	27	2.8
Gum_NO_7	0.4	1.0	2.1	512	24	2.5
Gum_NO_8	0.3	0.6	1.6	610	20	2.0
Gum_NO_9	0.5	1.1	2.2	494	22	2.2
Gum_NO_10	0.6	1.8	2.3	366	27	3.0

Swell index volume fraction and crosslink density data are shown in Table 3.28.

Table 3.28: ASTM gum compound crosslink density

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink density X 10^5 (mol cm^{-3})
Gum_DAE	4.33	0.160	5.68
Gum_ DAE	3.83	0.191	8.16
Gum_ RAE	4.38	0.161	5.82
Gum_ Naphthenic	4.47	0.162	6.05
Gum_NO_2	7.16	0.100	2.36
Gum_NO_6	5.05	0.143	4.64
Gum_NO_7	5.51	0.127	3.72
Gum_NO_8	6.77	0.101	2.44
Gum_NO_9	5.63	0.126	3.68
Gum_NO_10	4.56	0.155	5.43

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have similar (within experimental error) static modulus as compared to naphthenic oil. Higher unsaturated to saturated acid content ratio may affect the crosslink density adversely. Due to this, vulcanizate prepared with NO_2 has lowest crosslink density and lowest delta torque. This results in lowest modulus and hardness of this compound. Gum compound study was also made to check the effect of various oils (in absence of carbon black) on crosslink density.

3.6.4 Motorcycle Tire Tread Compound Recipe

Test results for stress-strain including hardness and reinforcement index are reported shown in Table 3.29

Table 3.29: Motorcycle tire tread compound stress-strain properties

Sample \ Parameter	M100 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300 /M100)
MCT_F_DAE	2.0	10.1	20.5	530	60	5.1
MCT_F_TDAE	2.0	10.2	20.7	537	60	5.1
MCT_F_RAE	2.0	10.0	20.7	536	59	5.0
MCT_F_ Naphthenic	1.9	10.5	19.6	489	58	5.5
MCT_F_NO_2	1.3	6.3	18.9	707	52	4.9
MCT_F_NO_6	1.9	10.1	19.9	549	55	5.3
MCT_F_NO_7	1.6	8.4	18.6	568	53	5.3
MCT_F_NO_8	1.4	7.2	20.4	670	53	5.1
MCT_F_NO_9	1.6	8.4	21.4	640	54	5.3
MCT_F_NO_10	1.9	10.3	19.0	479	57	5.4

Swell index, volume fraction and crosslink density data are exhibited in Table 3.30.

Table 3.30: Motorcycle tire tread vulcanizate crosslink density

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink density X 10^4 (mol cm^{-3})
MCT_F_DAE	2.43	0.234	1.29
MCT_F_TDAE	2.52	0.233	1.27
MCT_F_RAE	2.46	0.233	1.27
MCT_F_Naphthenic	2.53	0.230	1.24
MCT_F_NO_2	3.20	0.168	0.66
MCT_F_NO_6	2.64	0.209	1.01
MCT_F_NO_7	2.80	0.197	0.90
MCT_F_NO_8	3.03	0.174	0.71
MCT_F_NO_9	3.08	0.172	0.69
MCT_F_NO_10	2.70	0.213	1.05

Modulus and hardness values for motorcycle tire tread vulcanizates were found in line with gum vulcanizates. Crosslink density for motorcycle tire tread batches were found in line with crosslink density of respective gum batches.

3.7 PERFORMANCE

3.7.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for heat build up, abrasion loss and rebound resilience shown in Table 3.31.

Table 3.31: PCR tire tread compound performance properties

Parameter / Sample	HBU (°C)	Abrasion (mm^3)	Rebound (%) at 30°C	Rebound (%) at 70°C
PCR_F_TDAE	18.9	97	34.9	44.5
PCR_F_ Naphthenic	22.5	98	36.4	45.9
PCR_F_NO_2	23.6	76	36.1	45.4
PCR_F_NO_6	18.5	92	36.2	46.2
PCR_F_NO_7	23.5	105	34.0	43.5
PCR_F_NO_8	27.5	92	32.3	41.9
PCR_F_NO_9	27.0	82	36.1	46.4
PCR_F_NO_10	18.2	98	37.0	46.2

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have less heat generation, which may be due to high crosslink density, high reinforcement index and high rubber-filler interaction parameter. Higher heat generation in rubber compound during dynamic application may lead to fast rubber degradation and deteriorate service life of the product. So, lower heat generation is better for product service life. The NO_2, NO_6, NO_8 and NO_9 oil extended SBR based vulcanizates have less abrasion loss as compared to vulcanizate prepared with TDAE oil extended SBR due to lower Tg value of these vulcanizates. Rebound resilience values measured at

30° and 70°C were found to be lowest for NO_8 oil extended SBR based vulcanizate. This may be due to lowest crosslink density and lowest rubber-filler interaction parameter for this compound. Other all vulcanizates have comparable rebound value.

3.7.2 ASTM Compound Mixing (With curatives adjustment)

Test results for angle abrasion loss and rebound resilience are presented shown in Fig. 3.11 and 3.12, respectively.

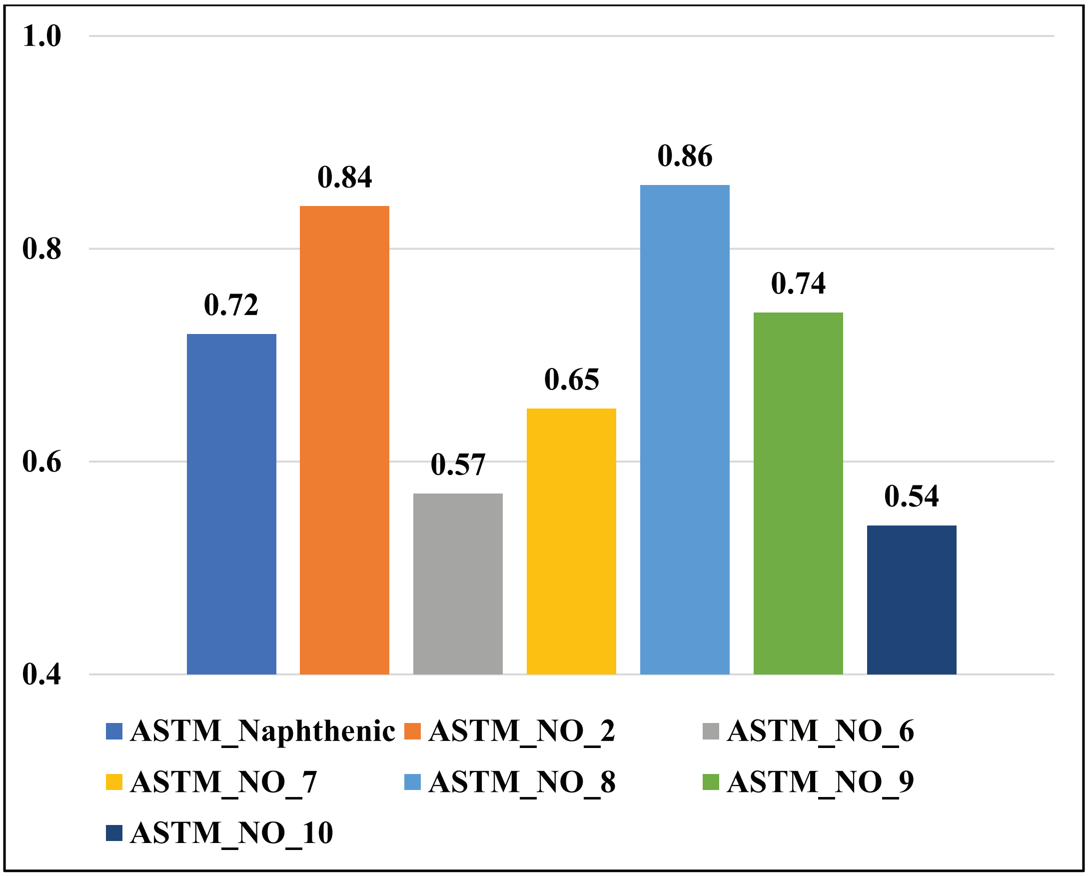

Fig. 3.11: Angle abrasion loss (g) by Akron tester (20° slip angle, 4000 cycles) for ASTM compounds

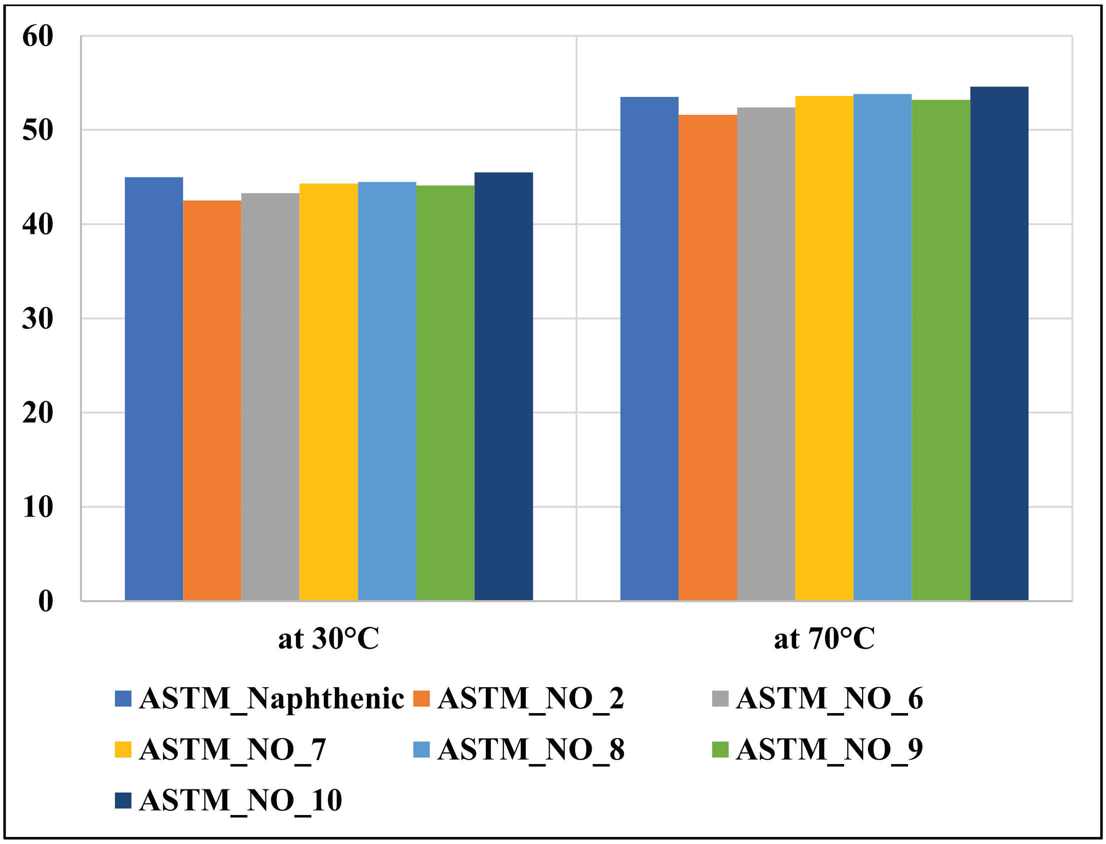

Fig. 3.12: Rebound resilience (%) for ASTM compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have less abrasion loss as compared to naphthenic oil, which may be due to slightly high crosslink density, slightly high reinforcement index and high rubber-filler interaction parameter (Fig. 3.13).

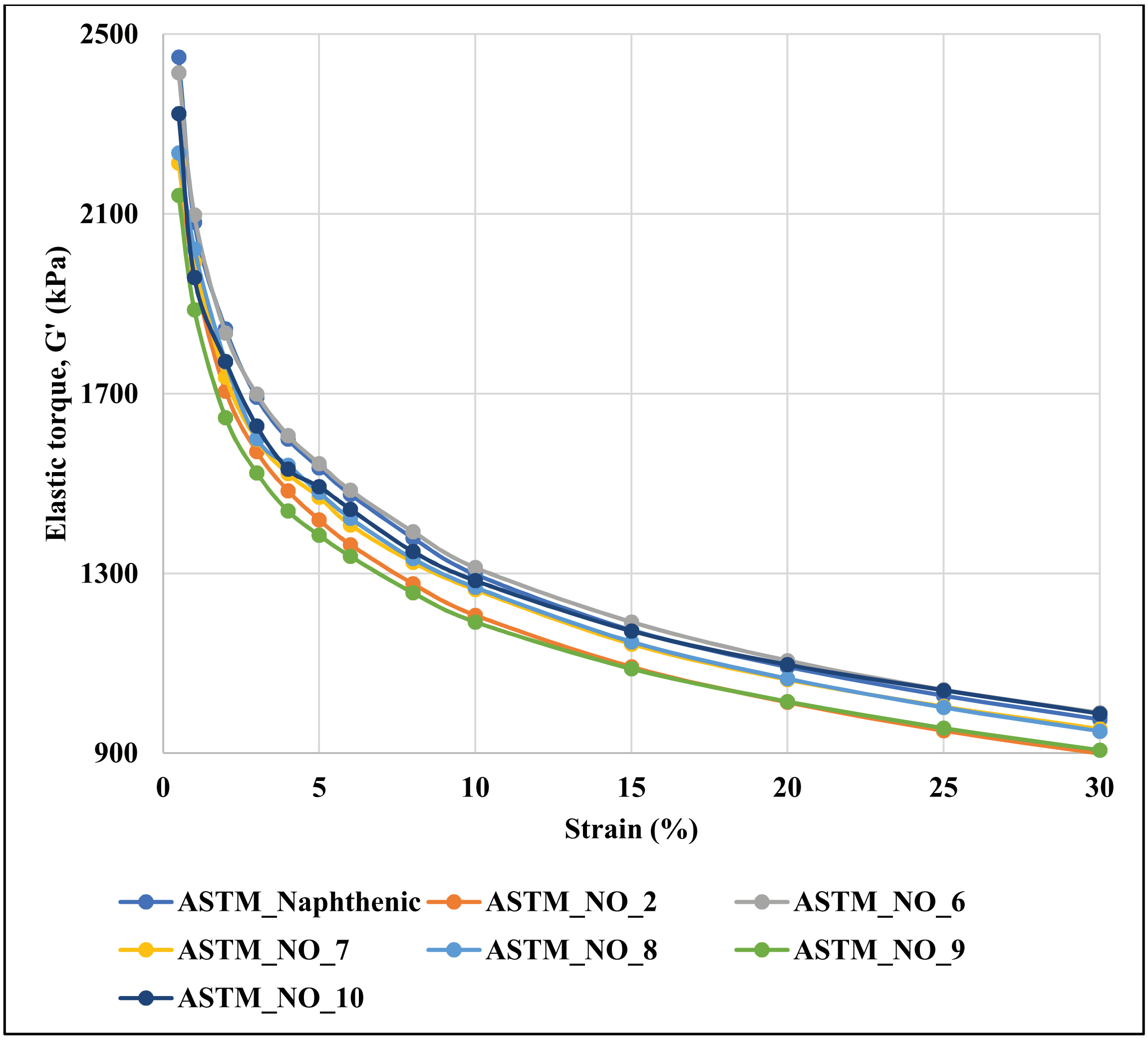

Fig. 3.13: Strain sweep test by RPA for final batch ASTM compounds @70°C (after cure)

These rubbers may be used for motorcycle tire application due to less abrasion loss in angle abrader because motorcycle tire needs frequent turns while in use. Rebound resilience values measured at 30° and 70°C were found to be comparable for all the compounds. This is due to matching of modulus of all rubber compounds. This indicated that all rubbers have almost similar elastic and viscus components, which may result in comparable traction and rolling resistance.

3.7.3 Motorcycle Tire Tread Compound Recipe

Test results for DIN and Akron abrasion loss, heat build-up (HBU) and rebound resilience @30° and 70°C are given in Table 3.32.

Table 3.32: Motorcycle tire tread compound performance properties

Parameter	DIN abrasion (mm^3)	Akron abrasion (mm^3)	Heat build up (°C)		Rebound resilience (%)	
			Surface	Centre	@30°C	@70°C
MCT_F_DAE	72	334	32.0	110	34.0	43.0
MCT_F_TDAE	70	291	29.3	107	35.7	46.2
MCT_F_RAE	73	288	27.1	101	34.9	45.1
MCT_F_ Naphthenic	67	565	25.5	99	36.0	47.1
MCT_F_NO_2	72	716	49.1	133	35.9	47.2
MCT_F_NO_6	68	313	32.0	106	38.2	46.5
MCT_F_NO_7	74	528	42.2	116	37.6	47.2
MCT_F_NO_8	72	669	47.2	120	37.8	47.1
MCT_F_NO_9	68	648	36.3	109	38.0	47.1
MCT_F_NO_10	70	266	33.6	104	37.8	46.8

DIN abrasion was found to be comparable for all compounds. However, Akron test at high severity condition displayed different observation. Vulcanizates prepared with all vegetable oils extended SBR (expect S40_NO_6 and S40_NO_10) have high abrasion loss and high heat generation. This may be due to low crosslink density of these compounds. Rebound resilience was found comparable for all compounds. Tg results are shown in Fig. 3.14.

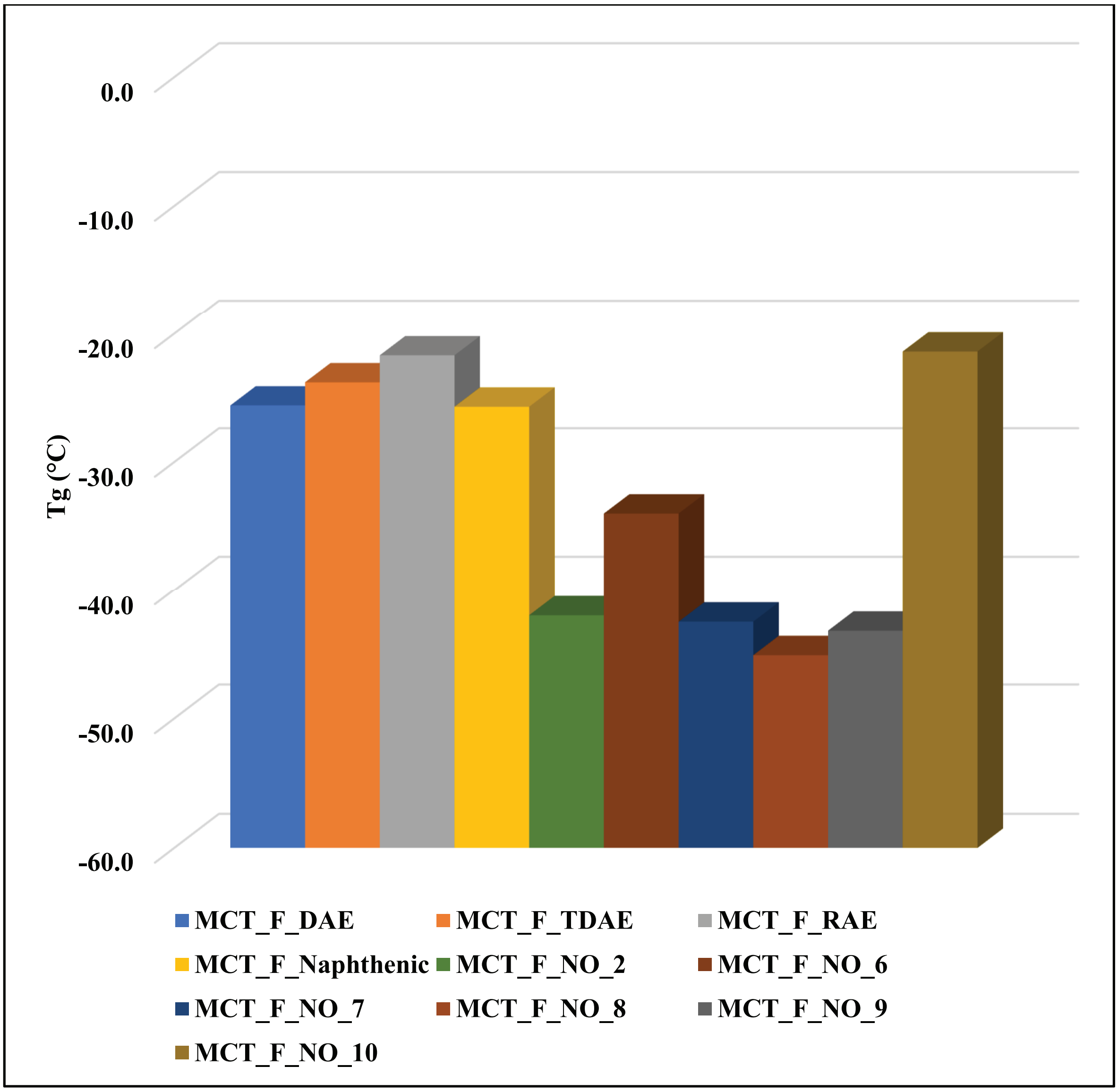

Fig. 3.14: Glass transition temperature (Tg) for motorcycle tire tread compounds

Tg of all the vulcanizates were found in line with raw rubber Tg. All vegetable oil extended SBR based vulcanizates except (S40_NO_10) have lower Tg. Despite low Tg value, vulcanizates prepared with S40_NO_2, S40_NO_7, S40_NO_8 and S40_NO_9 have high abrasion loss due to less crosslink density. Carbon dispersion was checked for cure specimen using volume resistivity measurement. Lower resistivity indicates better carbon black dispersion in rubber matrix. Test results are reported in Fig. 3.15.

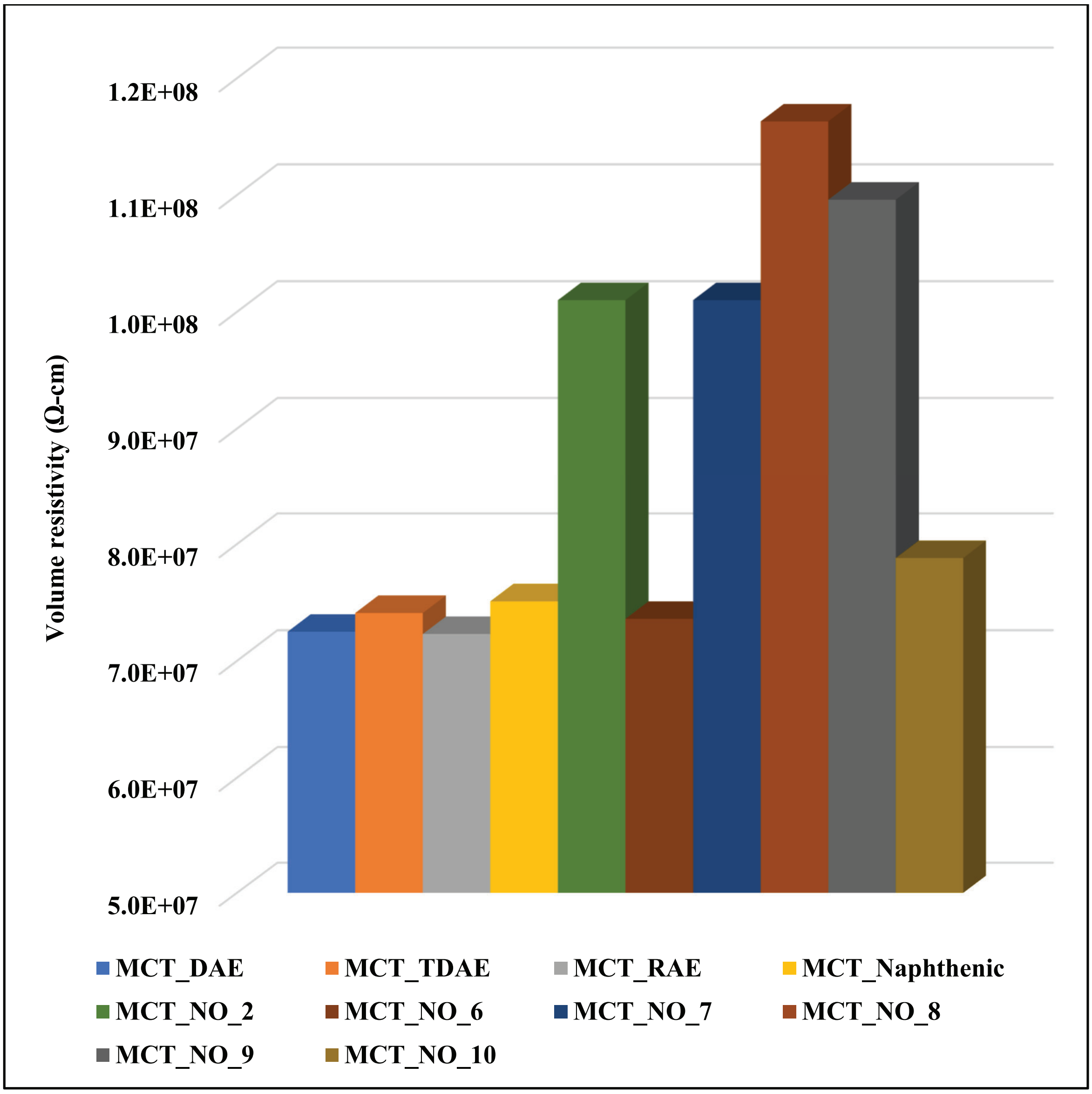

Fig. 3.15: Volume resistivity for motorcycle tire tread compound

Volume resistivity for compounds prepared with S40_NO_6 and S40_NO_10 was found comparable with petroleum oil. Poor carbon black dispersion for vulcanizates prepared with vegetable oils extended SBR (expect S40_NO_6 and S40_NO_10) may be due to for deterioration in various properties like high abrasion loss, high heat generation and lower modulus.

3.8 DYNAMIC PROPERTIES AND FILLER-FILLER NETWORK STUDY BY RPA

3.8.1 Passenger Car Radial Tire Tread Compound Recipe

Dynamic properties are presented in Table 3.33.

Table 3.33: PCR tire tread compound dynamic properties by RPA

Parameter / Sample	G′@40°C (kPa)	G′@70°C (kPa)	Tan δ@ 40°C	Tan δ@ 70°C
PCR_F_TDAE	2127	1540	0.28	0.23
PCR_F_ Naphthenic	1941	1330	0.25	0.20
PCR_F_NO_2	1846	1268	0.24	0.20
PCR_F_NO_6	1988	1403	0.24	0.19
PCR_F_NO_7	1963	1366	0.24	0.20
PCR_F_NO_8	1811	1180	0.27	0.22
PCR_F_NO_9	1757	1191	0.25	0.21
PCR_F_NO_10	2032	1482	0.23	0.17

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have comparable elastic modulus as compared to TDAE oil. Payne effect (after cure) is given in Fig. 3.16.

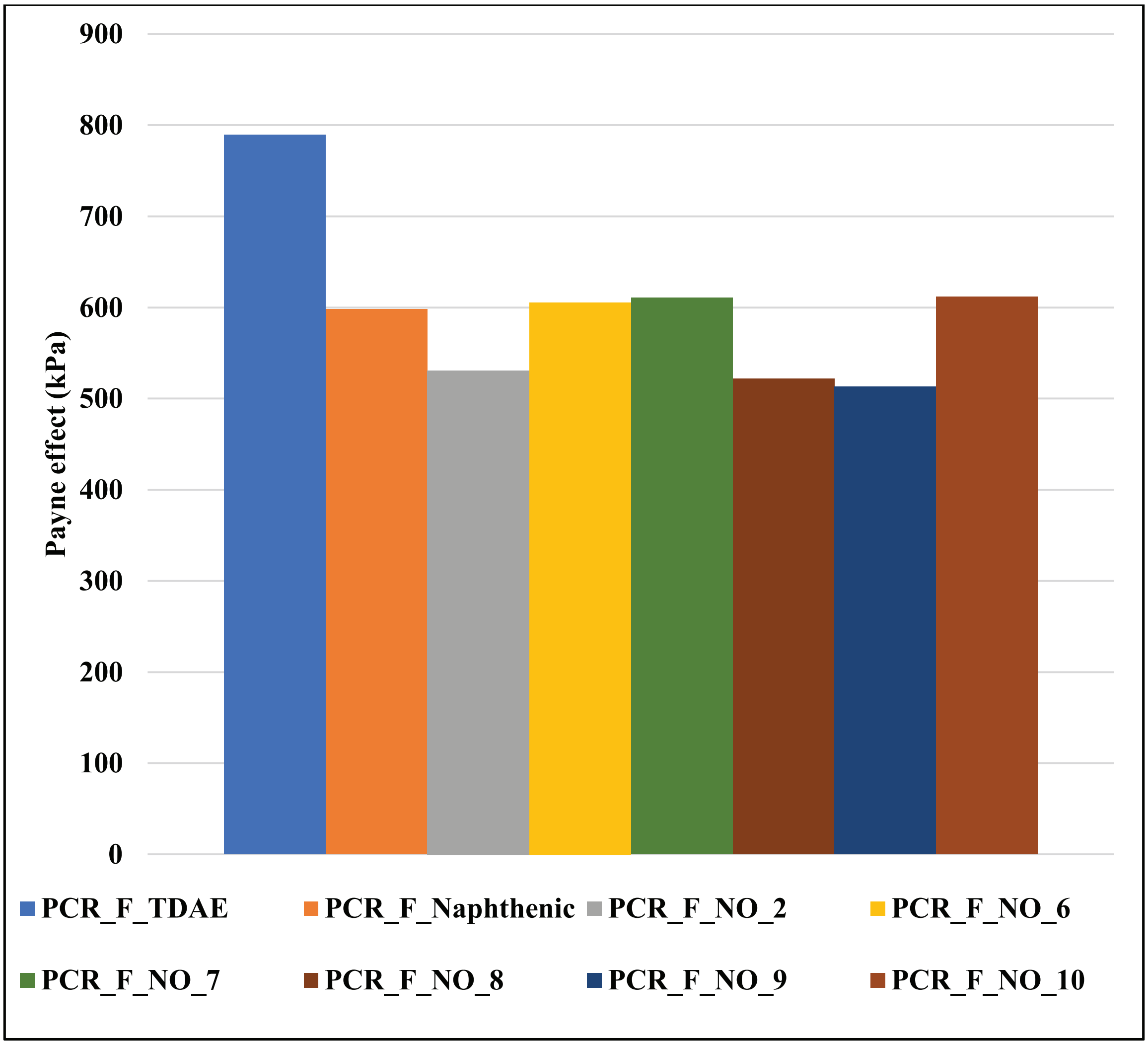

Fig. 3.16: RPA strain sweep test for final batch compound @70°C (after cure) for PCR tire tread compounds

Higher Payne effect means more filler-filler interaction. Generally high filler loading compounds and silica filler-based compounds show high Payne effect value[9]. Compounds prepared with vegetable oil-based SBRs have shown lower Payne effect (due to high polymer-filler interaction) as compared to TDAE oil

3.8.2 ASTM Compound Mixing (With curatives adjustment)

Dynamic properties and Payne effect are reported in Table 3.34.

Table 3.34: ASTM compound dynamic properties by RPA

Sample \ Parameter	G′@40°C (kPa)	G′@70°C (kPa)	Tan δ@ 40°C	Tan δ@ 70°C	Payne effect, ΔG□ (kPa)
ASTM_Naphthenic	1986	1522	0.24	0.19	1107
ASTM_NO_2	1998	1423	0.26	0.22	1065
ASTM_NO_6	2167	1546	0.23	0.19	980
ASTM_NO_7	2083	1469	0.24	0.21	1039
ASTM_NO_8	2098	1470	0.24	0.21	1073
ASTM_NO_9	1970	1387	0.25	0.21	1008
ASTM_NO_10	2110	1483	0.23	0.18	971

All the compounds have comparable dynamic properties. Elastic torque, G’ vs strain (after cure) in strain sweep test is shown in Fig. 3.17.

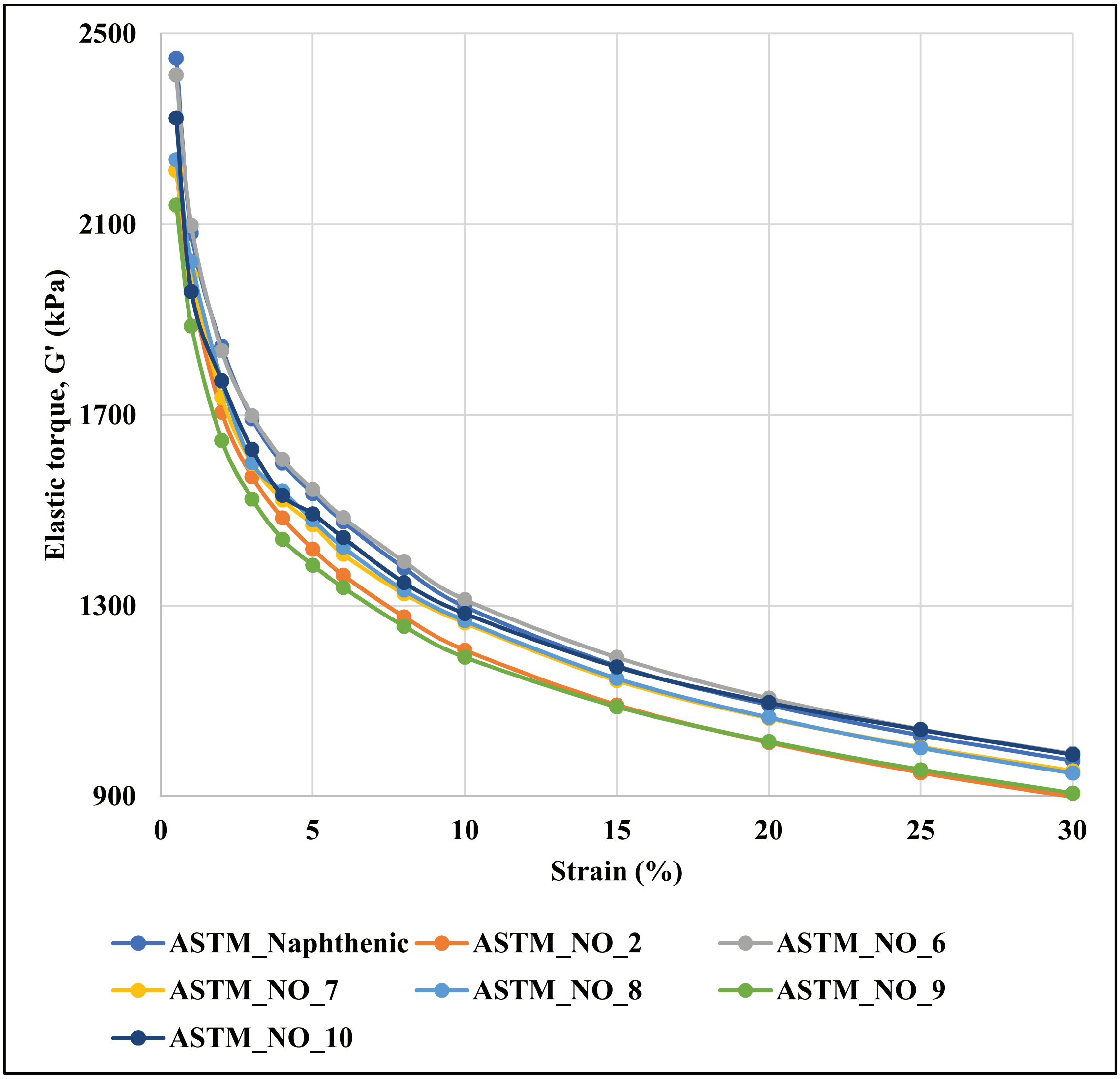

Fig. 3.17: Strain sweep test by RPA for final batch ASTM compounds @70°C (after cure)

Higher Payne effect means more filler-filler interaction. Compounds prepared with NO_6 and NO_10 vegetable oil-based SBRs have lower Payne effect (due to high rubber-filler interaction) as compared to naphthenic oil. High polymer-filler interaction helps in improvement of various mechanical and dynamic-mechanical properties. This rubber-filler interaction was improved due to presence of additional functional groups in the vegetable oils.

Motorcycle Tire Tread Compound Recipe

Dynamic properties are tabulated in Table 3.35.

Table 3.35: Motorcycle tire tread compound dynamic properties by RPA

Parameter / Sample	G′@40°C (kPa)	Tan δ @40°C	G′@70°C (kPa)	Tan δ @70°C
MCT_F_DAE	2754	0.34	1968	0.29
MCT_F_TDAE	2620	0.31	1873	0.27
MCT_F_RAE	2563	0.32	1828	0.27
MCT_F_Naphthenic	2410	0.29	1725	0.25
MCT_F_NO_2	2127	0.34	1378	0.33
MCT_F_NO_6	2383	0.31	1705	0.29
MCT_F_NO_7	1820	0.29	1291	0.28
MCT_F_NO_8	2113	0.31	1402	0.31
MCT_F_NO_9	2115	0.31	1441	0.30
MCT_F_NO_10	2395	0.28	1735	0.25

Compounds prepared with S40_NO_6 and S40_NO_10 have comparable dynamic modulus @ 40° and 70°C with naphthenic oil. This may be due to comparable maximum torque of these rubber compounds. Payne effect is presented in Fig. 3.18.

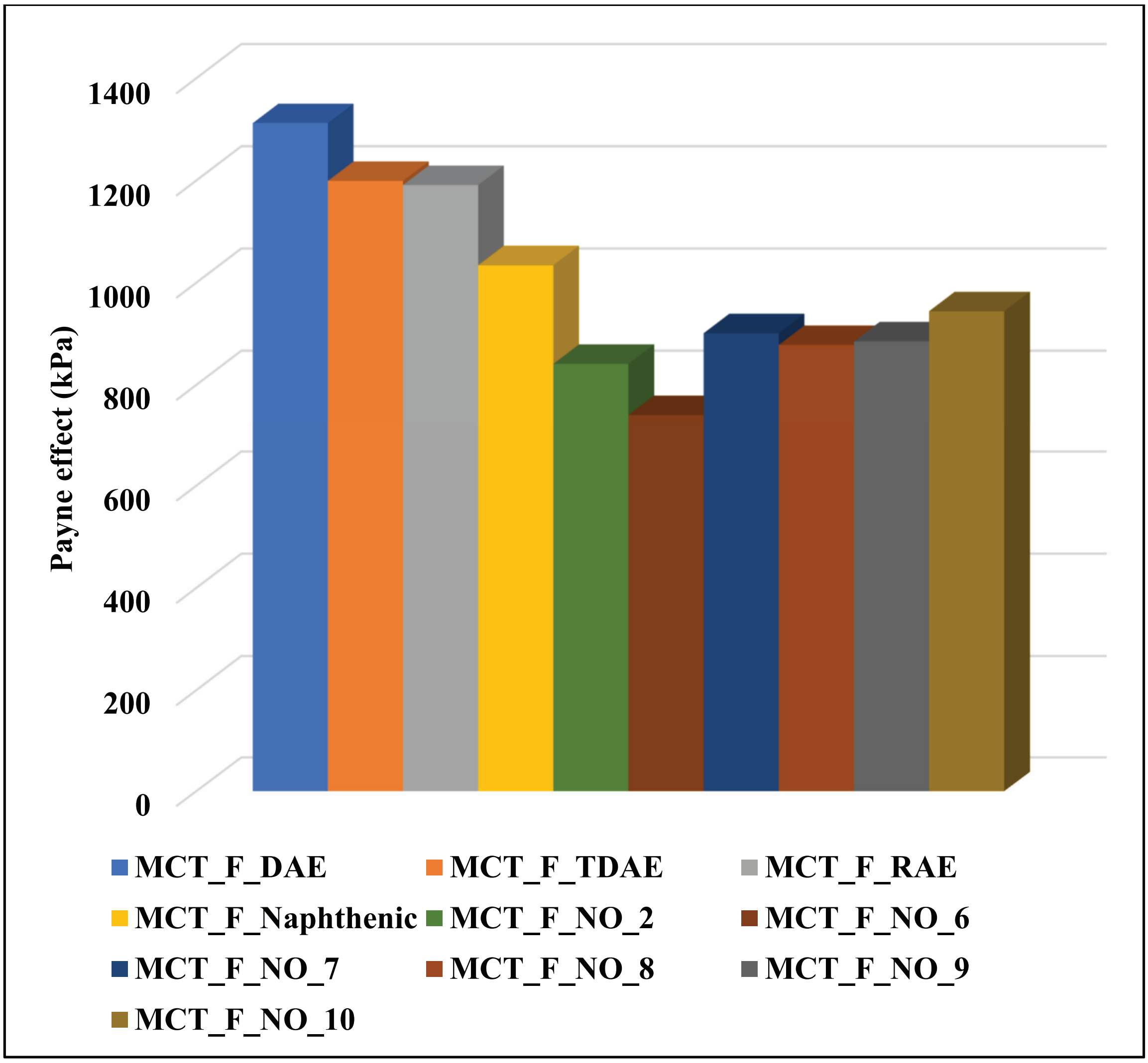

Fig. 3.18: RPA strain sweep test for final batch compound @70°C (after cure) for motorcycle tire tread compounds

Higher Payne effect means more filler-filler interaction[9]. Compounds based on vegetable oil extended SBR have lower Payne effect as compared to petroleum oil. Lower filler-filler interaction for these compounds may be due to presence of few additional functional groups in vegetable oils like triglyceride, ester, carbonyl, hydrogen bonded C-O, and acyl C-O. These groups may form bonds with surface groups present on carbon black, which resulted in more polymer-filler interaction and less filler-filler interaction.

3.9 DYNAMIC PROPERTIES BY DMA

3.9.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for elastic modulus and tan δ are given in Table 3.36 and presented in Fig. 3.19.

Table 3.36: PCR tire tread compound dynamic properties measured by DMA

Parameters / Sample	E′@0°C (MPa)	E′@30°C (MPa)	E′@60°C (MPa)	Tan δ @0°C	Tan δ @30°C	Tan δ @60°C	Tg (°C)
PCR_F_TDAE	58.0	27.0	17.2	0.28	0.17	0.15	-24.7
PCR_F_Naphthenic	62.9	21.4	14.1	0.19	0.18	0.17	-31.3
PCR_F_NO_2	38.7	19.5	13.0	0.21	0.18	0.16	-36.2
PCR_F_NO_6	98.9	37.5	17.1	0.26	0.18	0.15	-30.2
PCR_F_NO_7	35.9	19.2	13.0	0.19	0.19	0.19	-30.4
PCR_F_NO_8	35.0	18.4	11.3	0.22	0.20	0.20	-35.9
PCR_F_NO_9	33.7	18.4	12.0	0.20	0.17	0.17	-35.8
PCR_F_NO_10	96.9	36.8	14.4	0.23	0.18	0.14	-25.9

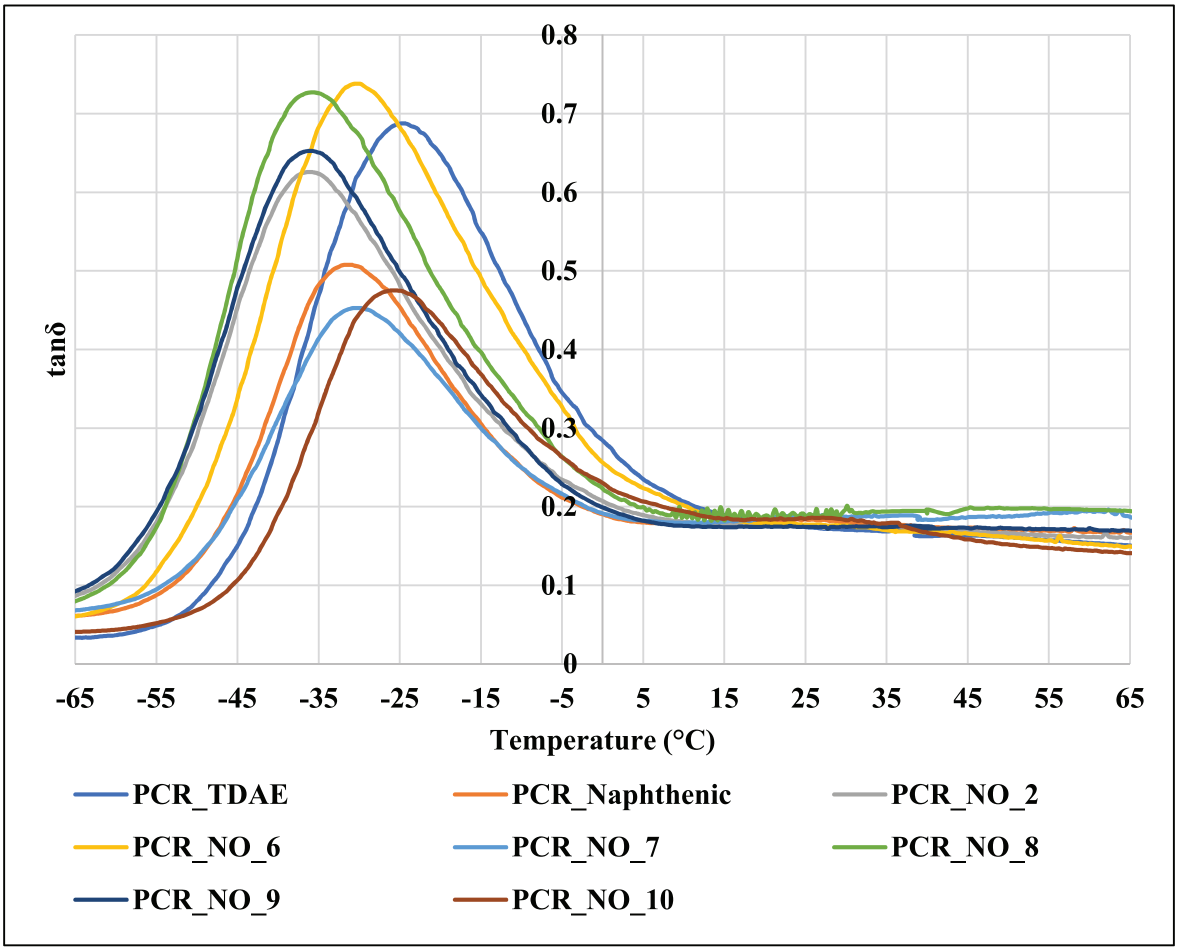

Fig. 3.19: DMA temperature sweep test for PCR tire tread compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBR's have higher elastic modulus, which may be due to high rubber-filler interaction parameter.

Lower tan δ values is desired @ 60°C, which correlates with rolling resistance. Higher tan δ values are desired at 0° and 30°C, which correlate with wet and dry traction, respectively. Vulcanizates prepared with NO_6 and NO_10 vegetable oils extended SBRs have comparable tan δ value at 0°, 30° and 60°C as compared to TDAE oil. This indicates comparable performance for these vulcanizates like dry & wet tractions and rolling resistance. Vulcanizates prepared with NO_7 and NO_8 vegetable oil extended SBRs have slightly higher tan δ value at 30°, which indicates better dry traction for these vulcanizates. Dynamic Tg of all the vulcanizates were found in line with Tg of respective OE SBRs.

3.9.2 ASTM Compound Mixing (With curatives adjustment)

Rubber compounds are visco-elastic in nature. Hence, they release energy in the form of heat under deformation. This heat dissipation affects the tire traction and rolling resistance. It is very important to balance fuel economy and safety of cars. These requirements are related with rolling resistance and traction of tread compounds with respect to tire. The Tanδ is the ratio of viscous and elastic component of rubber compound. Lower tan δ values is desired @ 60°C, which correlates with rolling resistance. Higher tan δ values are desired at 0° and 30°C, which correlate with wet and dry traction, respectively. Due to this contradictory requirement, it is very difficult to achieve improvement in both: rolling resistance and traction at the same time[10,11].

Test results for elastic modulus and tan δ are presented in Fig. 3.20 and 3.21, respectively.

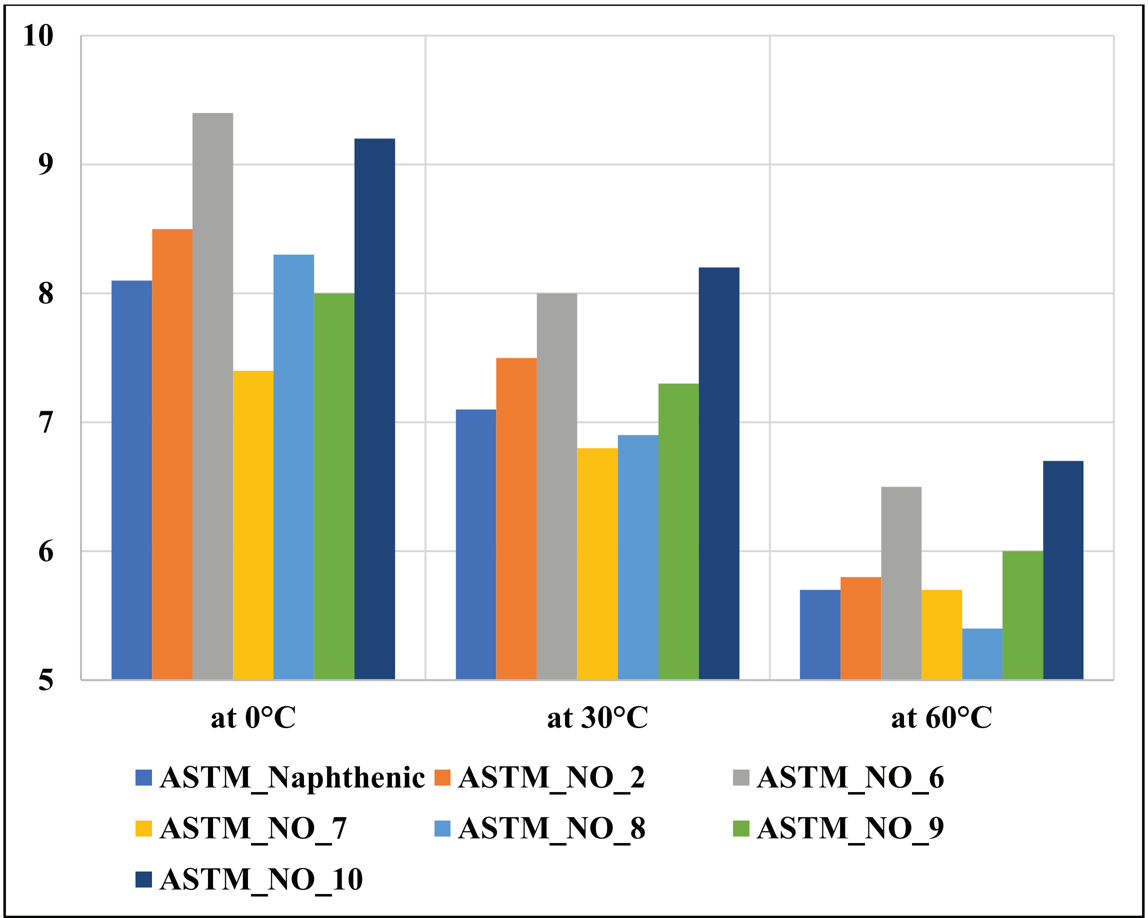

Fig. 3.20: Elastic modulus, E′ (MPa) measured by DMA for ASTM compounds

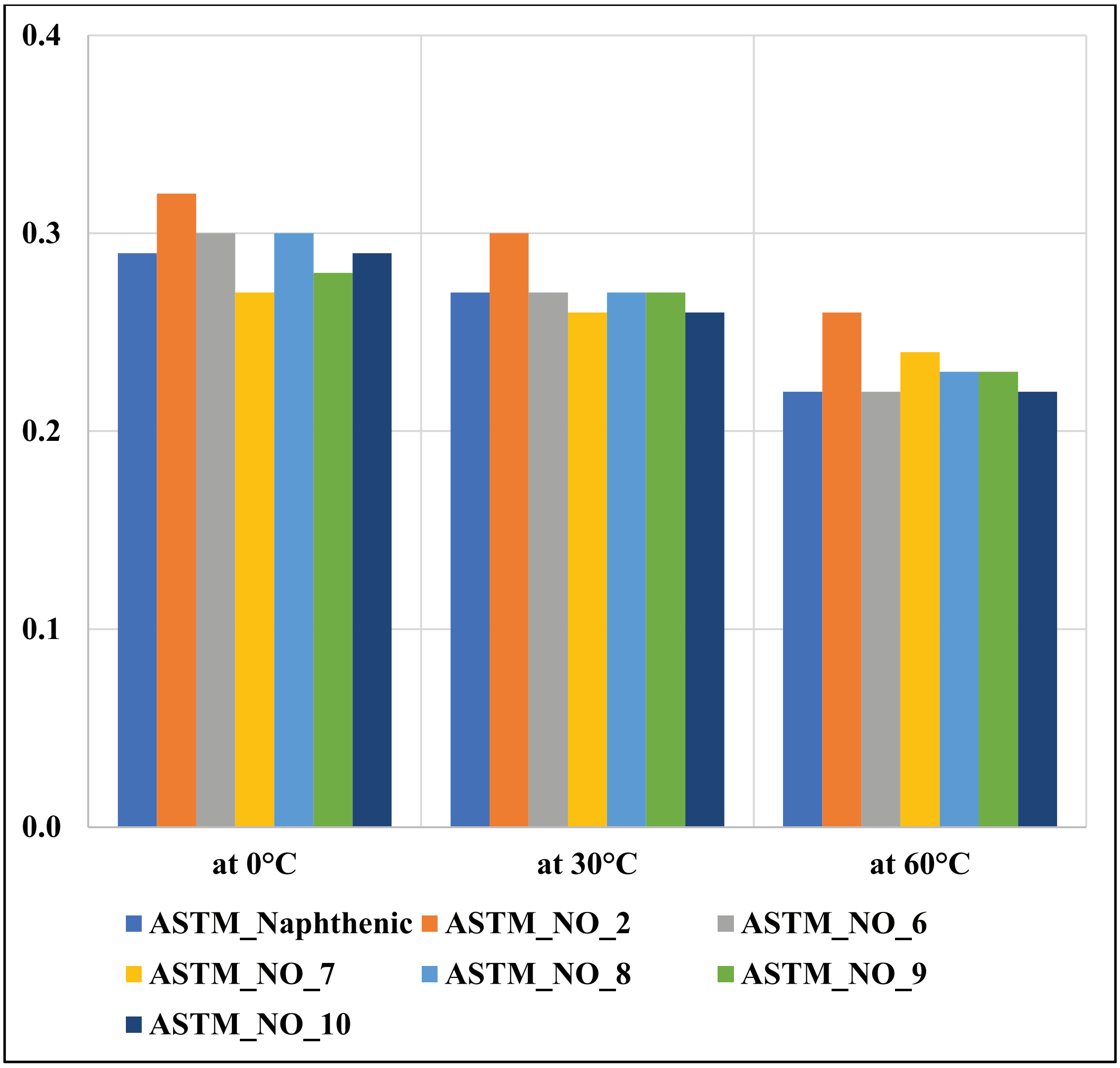

Fig. 3.21: Loss factor, tan δ for ASTM compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have slightly higher elastic modulus, which may be due to high rubber-filler interaction parameter. Vulcanizates prepared with NO_6 and NO_10 vegetable oil extended SBRs have comparable tan δ value at 0°, 30° and 60°C as compared to naphthenic oil. This indicates comparable performance for these vulcanizates like dry and wet traction and rolling resistance.

3.9.3 Motorcycle Tire Tread Compound Recipe

Test results are shown in Table 3.37.

Table 3.37: Motorcycle tire tread compound dynamic mechanical properties measured by DMA

Parameter / Sample	tan δ @0°C	tan δ @30°C	tan δ @60°C
MCT_F_DAE	0.39	0.37	0.28
MCT_F_TDAE	0.36	0.33	0.24
MCT_F_RAE	0.40	0.35	0.27
MCT_F_Naphthenic	0.35	0.32	0.23
MCT_F_NO_2	0.36	0.33	0.24
MCT_F_NO_6	0.32	0.29	0.23
MCT_F_NO_7	0.33	0.31	0.25
MCT_F_NO_8	0.34	0.31	0.25
MCT_F_NO_9	0.36	0.31	0.25
MCT_F_NO_10	0.34	0.30	0.23

Dynamic mechanical properties (tan δ) measured at 0°, 30° and 60°C indicate about wet traction, dry traction and rolling resistance properties of tire, respectively. Vulcanizates prepared with S40_NO_6 and S40_NO_10 have lower tan δ @60°C as compared to vulcanizate prepared with S40_DAE. This indicates better rolling resistance for these vulcanizates. This may be due to lower filler-filler interaction in these vulcanizates.

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