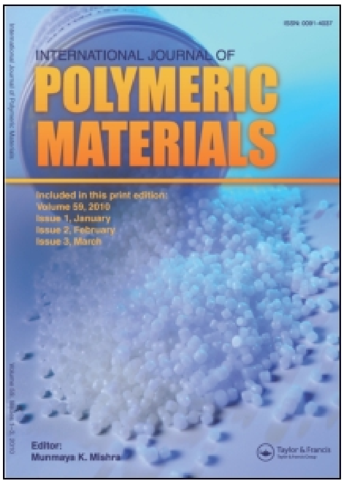

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A Correlation Between Micro and Macro Structure of High Cis-Polybutadiene and its Performance in Tyre Compound

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A Correlation Between Micro and Macro Structure of High Cis-Polybutadiene and its Performance in Tyre Compound

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High cis-polybutadiene from twelve different sources synthesised by using Ziegler Natta catalyst system based on four different metals viz. Co, Nd, Ni and Ti was studied. Raw polymers were characterised by measuring cis and trans content, vinyl content, branching index, molecular weight, molecular weight distribution, glass transition and melting temperatures, Mooney and delta Mooney values and Mooney relaxation behaviour. Performance of the polymer in compound was evaluated in truck and light truck tyre tread and sidewall compounds as well as in ASTM formulation. Extrusion characteristics of the truck tread compound were determined by Brabender Plasticorder. Stress-strain properties (unaged & aged), dynamic mechanical properties, abrasion loss, resilience and heat build up characteristics were measured. A correlation between micro and macro structure and optimum performance of polybutadiene was established.

Keywords: Polybutadiene; cis content; tread compound; branching index and Mooney relaxation.

INTRODUCTION

Automobile industries are coming up with vehicles having increased speed, fuel efficiency, braking efficiency, comfort, etc. Accordingly the tyres to cope up with these requirements are demanded. This demand is fulfilled by enhanced tyre design and using new improved compounds. As a consequence compounders are looking for more and more selective and specialty rubbers which will provide desired properties for different components of tyres. One of the mostly used rubbers in automobile tyre is high cis-polybutadiene (BR). This rubber is used in blends with natural rubber and styrene butadiene rubber in many components, such as sidewall, tread, rim chafer strips, etc. The advantages of using polybutadiene are improved wear and cut resistance, resilience, hysteresis, ozone resistance, low temperature flexibility and low heat development under dynamic stress.

At present commercial polybutadienes are usually produced by solution process using Ziegler Natta type catalyst system based on metal organic complexes (e.g. Co, Nd, Ni, Ti, etc.). The micro & macro structure namely cis & trans content, molecular weight, molecular weight distribution, branching of polymer chain, etc. depend on the catalyst system used. These are again responsible for overall performance of the rubber. So it is absolutely necessary to select right type of polybutadiene to have compound with improved performance.

The importance of cis content in solution BR was reported by Vohwinkel [1]. Comparative studies on BR of different catalytic origins were reported by various researchers [2 – 4]. Colombo, *et al.* studied tyre performance using a new high cis-polybutadiene [5]. However, the information which correlates micro and macro structure of BR with performance of tyre compounds in current literature is inadequate. This investigation is an endeavour to establish a correlation between catalyst type (which is responsible for producing BR having different micro and macro structure) and overall performance of the BR in truck and light truck tyre compounds as well as in ASTM formulation.

EXPERIMENTAL

Materials

Polybutadiene used were commercial ones, synthesised by using Ziegler Natta catalyst system based on cobalt, neodymium, nickel and titanium. All other ingredients used in this study were from standard sources. In this study BR_1—BR_6 were based on Co catalyst, BR_7—BR_9 on Nd, BR_{10}—BR_{11} Ni and BR_{12} were based on Ti catalyst systems.

Procedure

Characterisation of raw rubber

Macro structure (cis and vinyl content) was determined by a Perkin Elmer model 1760 FTR spectrometer and calculated according to Morero method [6].

The branching index, G was evaluated according to Drott-Mendelson method [7]. This is defined as the ratio between the experimental intrinsic viscosity and the theoretical one obtained from GPC chromatograms assuming all molecules to be linear.

Molecular weight and molecular weight distribution were measured by a Multipore-Waters model 712 Wisp (Lichrogel columns array : PS 400000, PS 40000, PS 400, PS 40) and using the following Mark-Houwink constants:

$K = 0.000457: \quad \alpha = 0.693.$

Melting temperature, T_m and glass transition temperature, T_g were measured by differential scanning calorimetry method using a DSC 30 model Mettler calorimeter.
Mooney value was determined as per ASTM D1646 and delta Mooney was measured at 100°C by a Monsanto Mooney viscometer MV2000E.

Mooney relaxation

The Mooney relaxation for the raw rubber was measured subsequent to the measurement of Mooney value by stopping the rotor immediately after the test time is complete. Depending on the elasticity of the polymer, the torque decreases more or less rapidly. The ratio of the torque after 30 *s* stop to the Mooney value at a time of 1 + 4 min (in %) is the Mooney relaxation, M_R [8,9].

Mixing

Mixing of compounding ingredients with rubber was carried out in a laboratory banbury of chamber volume 1.5 litre.

Extrusion behaviour

Extrusion behaviour of the truck tyre tread compound was studied by using a Brabender Plasticorder (Model PL 2000 – 3). The die used was a round capillary having diameter of 5 mm, screw speed was kept constant at 30 RPM and temperature of extrusion was 90°C. Diameter of the extrudate was measured at the exit of the capillary by an opto-electronic rod thickness tester (supplied by Brabender OHG, Germany). Extrudate swell presented here is the ratio of diameter of the extrudate, d_e to the diameter of the capillary die, d_c.

Testing

Stress-strain properties of the vulcanizates were measured using a Zwick Universal Testing machine (model 1445) in accordance with ASTM D 412 and D 624 at a cross head speed of 500 mm/min.

Abrasion loss was determined as per DIN 53416.

Loss tangent, tan δ of the vulcanizates was measured by using a Dynamic Viscometer, Rheovibron model DDV–III–C.

Resilience was determined by a Resilo-tester according to ASTM D 2632.

Fatigue to failure properties were determined by a Monsanto Fatigue to Failure Tester at an extension of 100%. Heat build up was measured using a Martin's ball fatigue tester at ambient temperature under 15 Kg load after 1950 revolutions.

RESULTS AND DISCUSSION

Micro and macro structure

Micro structure of twelve polybutadiene rubbers is presented in Table I. The table show that the 1, 4-cis content is comparable for Co and Nd based BR, but it is slightly lower for Ni based BR and lowest value is observed for Ti-BR. The 1, 2-vinyl content is maximum for Ti-BR followed by Ni, Co and Nd-BR (Tab. I). The lowest vinyl content of BR indicates that Nd-BR have got the highest stereoregularity in the polymer chains. The branching index, G which is a measure of polymer chain linearity i.e. G values close to one means linear polymer whereas the lower the G values higher is the macromolecular

TABLE I
Micro structure of BR

BR type	*Cis content (%)*	*Vinyl content (%)*	*Branching index*
BR_1	97.3	1.3	0.75
BR_2	97.2	1.4	0.71
BR_3	97.2	1.3	0.75
BR_4	97.4	1.1	0.88
BR_5	97.3	0.9	0.70
BR_6	97.0	1.5	0.90
BR_7	97.5	0.8	0.96
BR_8	96.3	0.4	0.92
BR_9	97.6	0.8	0.98
BR_{10}	96.6	1.2	0.71
BR_{11}	96.3	2.0	0.80
BR_{12}	91.6	3.9	0.91

branching. It is clear from the table that chain linearity is maximum for Nd catalyst based BR followed by Ti, Co and Ni.

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Polybutadiene synthesised by using Ni catalyst system is having broadest molecular weight distribution (MWD) followed by the BR based on Nd, Co and Ti catalyst systems. The highest molecular weight (M_w) is observed for Nd based BR (except BR_6 which is a Co—BR) followed by Ni, Co and Ti-BR (Tab. II). M_w and MWD play important roles to the mechanical properties and processing behaviour of an elastomer [10, 11]. An elastomer with broad MWD generally shows good processing behaviour but Nd based BR inspite of their broad MWD offer processing difficulties like higher black incorporation time. Higher M_w and branching index of Nd based BR probably outweigh the advantages of broad MWD.

GLASS TRANSITION TEMPERATURE, T_g AND MELTING TEMPERATURE, T_m

T_g and T_m values are comparable for all the BR used in this study (shown in Tab. II). It may be noted that T_g is strongly related to wear and traction properties of an elastomer [12].

TABLE II
Macro Structure of BR

BR type	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w/M_n	T_g(°C)	T_m(°C)
BR_1	321	125	2.57	−100.0	−8.4
BR_2	303	108	2.81	−100.1	−8.2
BR_3	318	131	2.43	−100.9	−7.3
BR_4	309	113	2.73	−101.0	−7.1
BR_5	338	156	2.17	−101.2	−7.3
BR_6	458	125	3.66	−101.1	−8.3
BR_7	412	99	4.16	−100.8	−6.2
BR_8	353	186	2.10	−102.1	−8.6
BR_9	381	103	3.70	−101.3	−5.9
BR_{10}	368	86	4.28	−100.1	−8.0
BR_{11}	347	87	3.99	−100.1	−8.6
BR_{12}	337	126	2.67	−101.2	*

*-Does not crystallize

MOONEY AND DELTA MOONEY VALUES

Mooney value of all the BR studied is comparable but delta Mooney is slightly lower for Nd—BR than that of the others (Tab. III). Lower delta Mooney value indicates lower branching of the polymer chains. This observation is corroborated with the higher values of branching index of Nd—BR (Tab. I).

MOONEY RELAXATION

Mooney relaxation is a measure of the elasticity of a polymer. Smaller the value of M_R, lower is the elastic characteristic and better is its processing behaviour [10 – 12]. The stress relaxation testing can be used for processability quality control test for synthetic rubber since this test is relatively quick than the other rheological tests. The values of M_R are tabulated in Table III. There is a considerable variation in the value of M_R for Co-BR though there is no such variation observed in the processability of these BR. For other types of BR, M_R values were very close for a particular catalyst type. It is to be noted that there is a correlation between the values of delta Mooney and M_R i.e. if delta Mooney is high for a particular BR M_R is also high for that BR e.g. BR_2. A similar observation was also reported by other researcher [13].

EXTRUSION BEHAVIOUR

Extrudate swell of the truck tread compound does not show noticeable difference for the BR having different catalytic origins (Tab. IV). Extrusion rate for this compound also maintained similar behaviour. The extrudate surface was found smooth for all the BR except Nd—BR. This may be because of higher M_w of this type of BR. These observations clearly indicate that extrudate swell and extrusion rate do not depend on the catalyst system but nature of the extrudate surface does get affected by the same.

VULCANIZATE PROPERTIES

As shown in Figure 1 resilience property of the vulcanizates in ASTM formulation is comparable for all the BR used here.

It has been established by several scientists that loss tangent of tread compounds at 50 – 100°C is directly proportional to the rolling resistance

TABLE III
Mooney Values of BR

BR type	ML_{1+4}@ 100°C	ΔMooney	M_R
BR_1	46	8	9.0
BR_2	44	11	14.0
BR_3	45	7	7.5
BR_4	42	8	11.0
BR_5	47	6	4.5
BR_6	48	8	11.0
BR_7	46	5	7.5
BR_8	50	6	5.0
BR_9	42	5	8.0
BR_{10}	42	6	10.0
BR_{11}	44	7	9.0
BR_{12}	44	6	5.0

M_R is Mooney Relaxation

TABLE IV
Formulations

Ingredients	*Truck tread*	*Lt. Truck tread*	*Sidewall*
NR	40	–	70
BR	60	30	30
SBR	–	70	–
Black	60	65	45
Curing System	CV	CV	CV

NR-Natural rubber
BR-Polybutadiene rubber
SBR-Styrene butadiene rubber
CV-Conventional vulcanization

[14, 15]. The loss tangent values (tan δ) at 11 Hz and at three different temperatures viz., 25°, 50° and 75°C of the vulcanizates of ASTM and tread compound are presented in Figures 2 & 3. In the case of tread compound Ni (BR_{10} & BR_{11}) and Ti (BR_{12}) based BR have highest loss tangent value followed by Co and Nd based BR at all the temperatures studied. The trend remained similar also for the ASTM vulcanizates. It is clear from the figures that there is a systematic drop in the loss tangent value as the temperature increases. This may be due to the increase in the mobility of polymer chain with increase in temperature which reduces the resistance to molecular motion [16].

Stress-strain properties of the vulcanizates of truck tyre tread compound are tabulated in Table V. It is clear from the table that modulus at 300% elongation is higher for Co—BR than the other type of BR. The trend

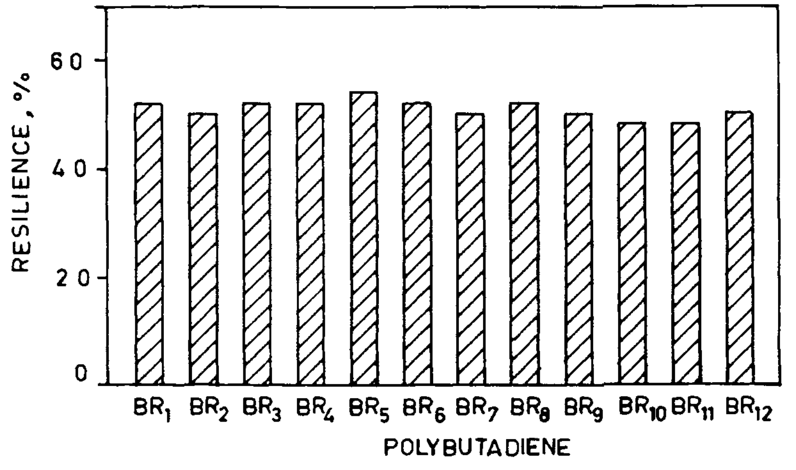

FIGURE 1 Rebound resilience values of the vulcanizates of ASTM formulation.

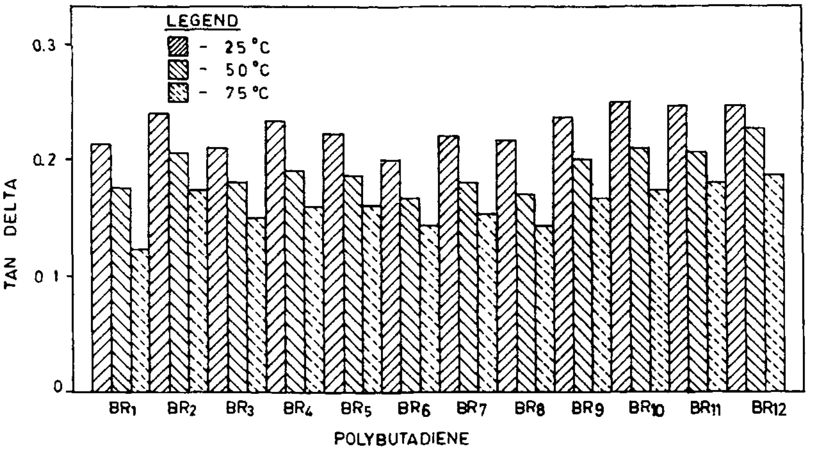

FIGURE 2 Tangent delta values of the vulcanizates of ASTM formulation.

remained similar after aging for 4 weeks at 70°C. In the case of tensile strength (T. S.) unaged values are comparable for all the BR but Co—BR show slightly higher T. S. than that of the other types of BR after aging for 3 days at 105°C and 70°C. Elongation at break and tear resistance properties are comparable before and after aging for all the BR used here. Retention of physical properties are important for tyre compounds from the service life point of view. Higher the retention better is the service life.

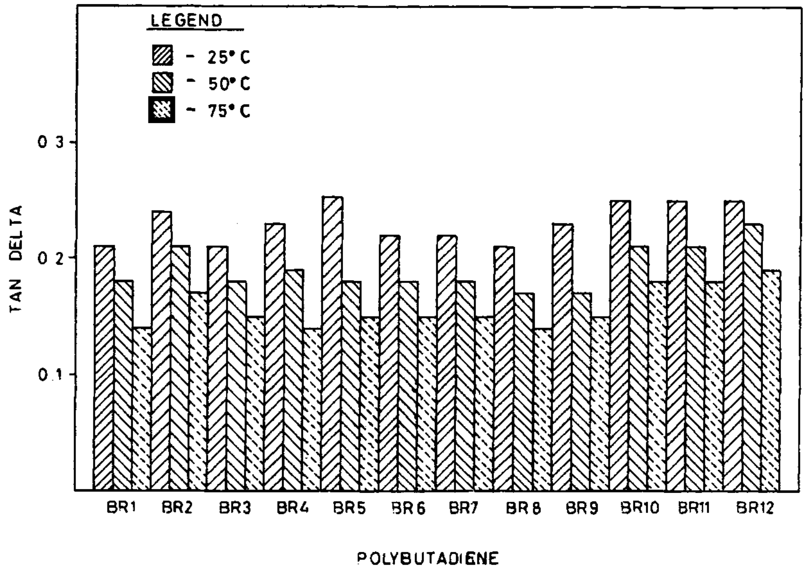

FIGURE 3 Tangent delta values of the vulcanizates of truck tread compound.

Abrasion loss which is one of the most important properties for tread compound when investigated in light truck tread formulation all the BR showed a comparable value except BR_{10} (Ni—BR) which showed highest loss but BR_{12} (Ti—BR) the lowest value (Fig. 4). The same for the truck tread showed a comparable abrasion loss for all the BR studied here. The abrasion

TABLE V
Extrusion Behaviour of Truck Tread Compound

BR type	*Extrudate Swell* (d_e/d_c)	*Extrusion Rate* (m/s)	*Nature of Extrudate Surface*
BR_1	1.23	0.016	Smooth
BR_2	1.25	0.016	Smooth
BR_3	1.23	0.016	Smooth
BR_4	1.24	0.016	Smooth
BR_5	1.23	0.015	Smooth
BR_6	1.24	0.016	Smooth
BR_7	1.22	0.016	Sharkskin like surface
BR_8	1.25	0.016	Rough
BR_9	1.24	0.015	Rough
BR_{10}	1.18	0.013	Smooth
BR_{11}	1.20	0.016	Smooth
BR_{12}	1.20	0.018	Smooth

TABLE VI
Stress-strain Properties of Truck Tread Compound

BR type	*Modulus at 300 % Elongation (MPa)*			*Tensile Strength (MPa)*			*Elongation at Break (%)*			*Tear Resistance (N/mm)*		
BR_1	9.5	-	13.2 (139)	19.6	9.5 (48)	17.6 (90)	525	225 (43)	400 (76)	78	20 (26)	41 (53)
BR_2	8.6	-	12.5 (145)	18.9	9.9 (52)	16.5 (87)	550	225 (41)	400 (73)	64	19 (30)	52 (81)
BR_3	9.6	-	13.4 (140)	19.5	10.3 (53)	17.6 (90)	525	225 (43)	400 (76)	78	20 (26)	40 (51)
BR_4	9.5	-	13.7 (144)	19.6	9.8 (50)	16.6 (85)	525	200 (38)	350 (67)	65	20 (31)	42 (65)
BR_5	9.1	-	12.9 (142)	20.7	9.6 (46)	17.5 (85)	575	225 (39)	400 (70)	51	20 (39)	40 (78)
BR_6	9.3	-	13.2 (142)	19.8	10.0 (51)	17.3 (87)	510	220 (43)	390 (76)	65	22 (34)	41 (65)
BR_7	8.1	-	11.7 (114)	18.8	9.6 (51)	15.7 (84)	575	250 (43)	375 (65)	68	21 (31)	41 (60)
BR_8	8.4	-	11.7 (139)	19.0	9.6 (51)	16.5 (87)	550	250 (45)	400 (73)	52	19 (37)	40 (77)
BR_9	8.2	-	11.8 (144)	18.7	9.5 (51)	15.9 (85)	580	245 (42)	380 (66)	70	22 (31)	43 (61)
BR_{10}	7.6	-	11.1 (146)	18.7	9.0 (48)	16.1 (86)	600	225 (38)	400 (67)	61	18 (30)	53 (87)
BR_{11}	8.7	-	11.9 (137)	19.5	10.2 (52)	15.4 (79)	575	250 (43)	350 (61)	66	29 (44)	47 (71)
BR_{12}	6.9	-	11.6 (168)	19.1	9.9 (51)	16.3 (85)	625	225 (36)	400 (64)	76	20 (26)	38 (50)

For each property the second and third columns indicate the values aged for 3 days at 105 °C and for 4 weeks at 70 °C, respectively. The figure within the parenthesis indicates per cent retention of the property

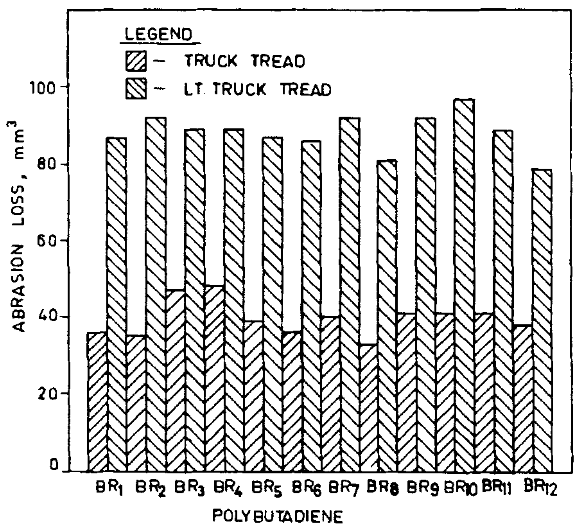

FIGURE 4 Abrasion loss values of Truck and light Truck tread compounds.

process can be described as detachment of rubber particles from the bulk due to catastrophic tearing of the rubber surface [17].

Fatigue to failure behaviour of the vulcanizates of truck tread, light truck tread and sidewall compounds is presented in Figure 5. The figure shows that truck tread with Co—BR fatigue property is better than that of the other except BR_3 (a Co—BR) which required minimum cycles to fail. In the case of light truck tread, Ti—BR (BR_2) required maximum cycles to fail followed by Co, Ni and Nd—BR. But in sidewall compound Nd—BR showed maximum (BR_7) and minimum (BR_8) fatigue resistance property but for other types of BR it is comparable. There are reports available in literature which state that BR based on Nd catalyst systems has got improved fatigue properties over the other catalyst based BR [5, 18]. This observation was not reflected in the present study.

Heat build up values of truck tread compound are shown in Figure 6. This shows that the temperature development varies from 57°–66 °C, where lower

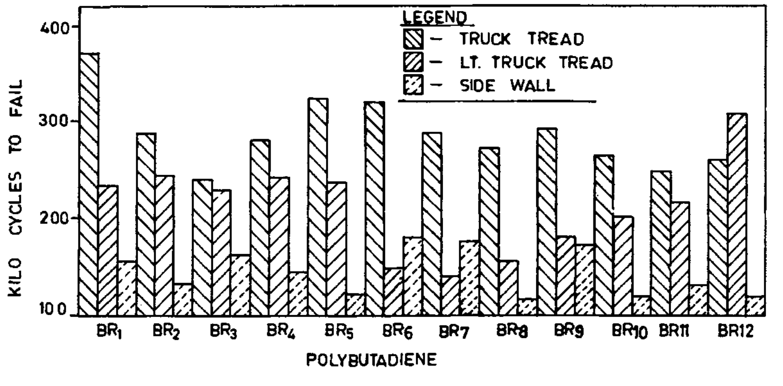

FIGURE 5 Monsanto fatigue to failure values.

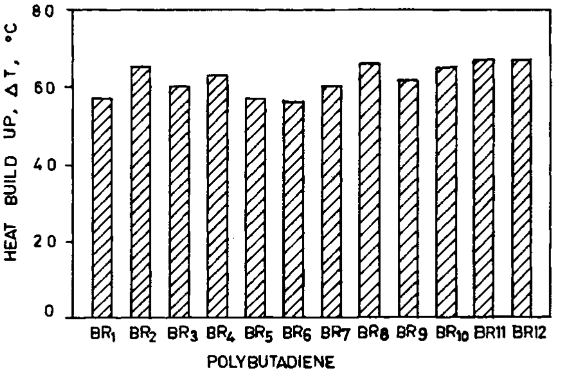

FIGURE 6 Heat build up values of the tread compound in Martin's ball fatigue test.

values are observed for Nd and Co—BR but the higher are for Ni and Ti—BR. Heat development and effect of dynamic stress on the vulcanizate play an important role towards the performance and life of a tyre. Particularly Martin's ball technique in which heat development takes place because of shearing and compression of the sample which exactly simulate the service conditions of tread compounds.

CONCLUSIONS

The 1,4 cis content of polybutadienes synthesised by using Co & Nd catalyst systems is found to be higher than that of Ni—BR and Ti—BR.

The order of stereoregularity is as follows:

Nd—BR > Ti—BR > Ni—BR > Co—BR.

The broadest MWD is found for Ni—BR followed by Nd, Co and Ti—BR.

Mooney value is comparable for all the BR used in this study. Delta Mooney and Mooney relaxation values are higher for few Co—BR and Ti—BR than the other type of BR.

Extrudate swell and extrusion rate are almost same for all the BR used here. Nd—BR showed rough extrudate surface whereas other types of BR showed smooth surface.

The highest loss tangent value is observed for Ni—BR and Ti—BR followed by Co and Nd based BR.

Unaged stress-strain properties are better for Co based BR than that of the others. The same after hot air aging are comparable.

Abrasion loss is found to be comparable for all the BR studied. Co—BR showed better fatigue properties and a comparable heat development.

The polybutadiene based on Co catalyst system showed balanced processing and physical properties in tyre compounds as well as in ASTM formulation.

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