

# Effect of tread polymer structure on tyre performance\*

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A history of the development of tread rubbers is summarized with emphasis on the importance of macrostructure and the glass transition temperature of the polymer for the best balance of properties. Fundamental differences in structure and properties between emulsion and solution SBR are then presented. Finally, the effect of micro- and macrostructure of solution rubbers on the performance characteristics of tread materials is discussed based on tyre performance data.

(Keywords: tread polymers; solution SBR; linear molecular weight; polymer  $T_g$ ; tyre rolling loss; tyre traction; tyre wear)

## INTRODUCTION

The first large-scale synthetic tread rubber was developed during World War II under the responsibility of the US Government-sponsored Rubber Reserve Company. The 'hot' emulsion styrene-butadiene rubber (SBR) polymerized at 50°C was highly branched and contained a very-low-molecular-weight fraction. A significant improvement in abrasion resistance was achieved when the polymerization temperature was reduced to 5–10°C by the use of a 'redox' catalyst system. The lower polymerization temperature suppressed branching reactions and resulted in the formation of a higher-molecular-weight SBR without the very-low-molecular-weight fraction. The 'cold' SBR improved the abrasion resistance of the resulting tread compounds and thereafter was used almost exclusively in tyre manufacturing. A further improvement in the abrasion resistance and traction relationship of tread rubbers was reported when solution SBRs were developed using alkyllithium catalysts<sup>1</sup>. Because of the 'living' nature and very limited branching reactions from the lithium catalyst, an elastomer with very high primary-chain molecular weight and narrow molecular-weight distribution was obtained. The high primary-chain molecular weight also contributed to reduced hysteresis.

In the mid 1970s when low-rolling-loss tyres became important for automobile fuel efficiency, several elastomers made by the lithium catalyst were claimed as an ideal tread rubber. Some authors have claimed that a specific microstructure is responsible for the low hysteresis<sup>2</sup> and some have claimed that macrostructure is responsible for this<sup>3</sup>. Some modified elastomers<sup>4,5</sup> also reduced the hysteresis of the compounds, presumably by preventing the network formation of carbon black. These modified systems resulted in increased interaction between the polymer and black.

When we review the history of tread rubber development, we notice that each time the primary-chain

molecular weight of an elastomer was increased, the tread performance was improved. It is not a coincidence that almost all tread rubbers claimed to be 'ideal' are based on alkyllithium catalysts which provide a high primary-chain molecular weight.

In this paper, we first investigated fundamental structure and physical property differences between an emulsion and a solution SBR. Then we tried to identify the sources of these differences. Finally we investigated the effect of micro- and macrostructure of solution rubbers on the performance characteristics of tread compounds based on tyre test data.

## EXPERIMENTAL

Our investigation included the following procedures.

Polymer characterization studies utilized gel permeation chromatography, dilute solution viscosity (DSV), Mooney viscosity, infra-red for microstructure analysis, and differential scanning calorimetry for the determination of onset glass transition temperature.

Compounds for laboratory properties were prepared in either a CW Brabender or BR Banbury mixer. Compounds for preparing treads for tyre testing were mixed in a size 1D Banbury. Standard laboratory testing procedures were utilized for evaluating compounded stocks: Mooney viscosity—ASTM D1646; curing characteristics—ASTM D2084; stress-strain—ASTM D412; tear strength—like ASTM D624; ball rebound—like ASTM D2632; dynamic hysteresis—MTS model 830 tester or Dynastat Mechanical Spectrometer; Young's bending modulus (YMI)—ASTM D797; wet traction—British Portable Skid Tester (BPST); and abrasion test—Pico Abrader per ASTM D2228.

Treads for radial tyres were made by a sheet lamination technique to the specified shape. These were applied during the conventional tyre building process. For certain aspects of this study P195/75R14 tyres were studied. A major focus of the programme was to evaluate the effect of a variety of tread polymer microstructure variations on the tyre performance of P175/80R13 all-season radial

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**Table 1** Structure of emulsion and solution SBRs

	Emulsion SBR	Solution SBR
Styrene content (%)	25	18
1,2 content (%)	16	13
Cis-1,4 content (%)	10	33
Trans-1,4 content	70	54
$M_n$ ( $\times 10^{-3}$ )	88	105
$M_w$ ( $\times 10^{-3}$ )	411	345
DSV (dl g <sup>-1</sup> )	1.8	1.8
$T_g$ (°C)	-55	-75
ML/4/100°C	50	57

tyres. Rolling loss was determined by the four-point SAE J1269 procedure. At least four tyres of each tread composition were tested. Clayton twin-roll rolling loss was also measured. The smaller-diameter drum of this test is more sensitive to tread stock variations. The averages of peak and slide traction properties were measured according to ASTM E274 procedures using the skid trailer. Wet traction properties are reported for 0.3 coefficient concrete at 32 km h<sup>-1</sup>. Dry traction was measured on 0.8 coefficient asphalt at 64 km h<sup>-1</sup>. Three-way multi-section tyres were built for wear determination. A common control section was included on each tyre. A moderate wear test was conducted at Fort Stockton, Texas. Tyres were rotated to all positions of a three-car group during the 38 000 km test. Each tyre saw every position twice during the test procedure.

## RESULTS AND DISCUSSIONS

### Fundamental difference between emulsion and solution SBR

Gelation in diene polymerization occurs when one crosslink point per weight-average degree of polymerization of the primary chain is reached. The term 'primary chain' is defined as the original polymer chain formed before any crosslinking reactions occur.

In the emulsion polymerization of SBR, the crosslinking reaction is quite prevalent. Therefore, the primary chain molecular weight of emulsion SBR should be regulated by using a chain transfer agent to reduce crosslinking reactions. The concentration of crosslinked units in the total polymerized units increases with increasing polymerization temperature. Morton *et al.*<sup>6</sup> determined the weight-average degree of polymerization of primary chains at the gel point for the emulsion polymerization of butadiene at different temperatures. From their results, the maximum primary chain molecular weight of hot and cold emulsion SBR can be calculated. The maximum molecular weights of the primary chains are increased tenfold by reducing the polymerization temperature from 50°C (hot SBR) to 5°C (cold SBR). The number-average molecular weight of a commercial cold SBR is typically 90 000 to 175 000.

In contrast, the primary-chain molecular weight of solution SBR by an anionic lithium catalyst can be increased to a very high value without gelation even at relatively high polymerization temperature. A number-average molecular weight of 150 000 to 250 000 is not unusual for commercial solution SBRs. In the laboratory, molecular weights of 500 000 to 1 000 000 can even be achieved.

Another difference between emulsion and solution SBR is in the content of rubber hydrocarbon. The emulsion SBR contains only about 90% rubber hydrocarbon owing to a large amount of residues, while solution SBR contains close to 100% rubber hydrocarbon.

These differences in composition and macrostructure between emulsion and solution SBRs contribute to their physical properties as a tread material. *Tables 1* and *2* summarize the differences between emulsion and solution SBRs in micro- and macrostructure and the physical properties of resulting tread compounds from these commercial polymers. Some of the noticeable differences in physical properties include the cure rate, hysteresis, tensile and tear strength. Solution SBR is faster-curing than emulsion SBR. However, the emulsion SBR is higher in tensile and tear strength than solution SBR. Solution SBR has much lower hysteresis than emulsion SBR, as shown by the steel-ball rebound.

In order quantitatively to analyse the contribution of the macrostructure to the difference in physical properties between emulsion and solution SBR, a series of solution SBRs was prepared with a relatively narrow molecular-weight distribution and minimum degree of branching. Then the solution SBRs were artificially branched by means of ionizing radiation. In this manner, a variety of macrostructures were generated starting from a linear chain. *Table 3* summarizes the micro- and macrostructures of these solution SBRs along with those of emulsion SBR. Some solution SBRs in *Table 3* are very similar in macrostructure to that of emulsion SBR.

These polymers were compounded in a standard formulation (*Table 4*) and their physical properties were evaluated. The hysteresis of the compounds is shown in terms of steel-ball rebound at 66°C in *Figures 1, 2* and *3* as a function of macrostructure and Mooney viscosity of the SBR. As shown in *Figure 1*, the rebound values showed a good correlation with the number-average molecular weight,  $M_n$ , of the SBR used in the compounds. However, the correlation of rebound was very poor with the weight-average molecular weight,  $M_w$ , and with the Mooney viscosity of the polymer. These results clearly indicate that a specific macrostructural parameter of the polymer is very important for the hysteretic property of the resulting compounds and that the Mooney viscosity cannot be used as a criterion. Noting that the hysteresis of the compounds decreased with increasing number-average molecular weight of the polymer and also that the number-average molecular weight does not increase significantly with random branching, the primary chain molecular weight is considered as a key parameter of

**Table 2** Compound properties of emulsion and solution SBRs

	Emulsion SBR	Solution SBR
Polymer ML/4/100°C	50	57
Compound ML/4/100°C	57	66
Rheometer (150°C)		
Scorch time (min)	15	15
Optimum cure (min)	39	26
Ring tensile (23°C)		
Tensile strength (MPa)	25.5	21.4
Elongation (%)	405	315
Hot ring tear (kN m <sup>-1</sup> )	61.3	39.4
Rebound (%)		
23°C	48	61
100°C	65	74

Table 3 Summary of macro- and microstructure of SBRs

Polymer	Symbol	Irradiation (Mrad)	Styrene content (%)	1,2 content (%)	$M_n$ ( $\times 10^{-3}$ )	$M_w$ ( $\times 10^{-3}$ )	Dilute solution viscosity ( $\text{dl g}^{-1}$ )	Mooney viscosity (ML/4/100°C)
A	$\triangle$		25	20	76	91	0.84	—
A	$\blacktriangle$	3.9	25	20	92	324	1.32	22
A	$\blacktriangle$	5.0	25	20	101	434	1.96	41
B	$\square$		25	20	79	103	0.98	6
B	$\blacksquare$	2.1	25	20	97	211	1.18	20
B	$\blacksquare$	2.65	25	20	107	308	1.38	29
C	$\nabla$		31	20	89	144	1.11	16
C	$\blacktriangledown$	1.4	31	20	102	242	1.31	29
C	$\blacktriangledown$	2.5	31	20	112	454	1.67	47
D	$\circ$		25	20	147	231	1.46	34
S1502	$\times$		25	18	88	411	—	50

Table 4 Standard tread formulation

Polymer	100
N339	45
ZnO	3
Stearic acid	2
Wax	3
Sulphur	1.4
TBBS	1.4
MBT	0.2

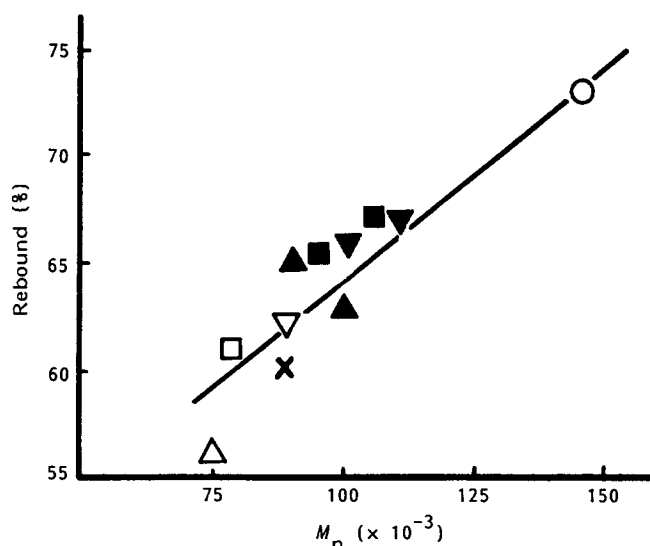


Figure 1 Steel-ball rebound at 66°C vs. number-average molecular weight for linear and branched solution SBRs compared with emulsion SBR

polymer macrostructure for the hysteresis of the resulting compounds. These results agree with the findings reported by Takao *et al.*<sup>3</sup>, which demonstrated the importance of long-chain-end concentration for the hysteresis of the compounds. Another important finding from this study was that the rebound value of the compound from emulsion SBR was significantly lower than that of solution SBRs with similar macrostructure, as shown in Figures 1, 2 and 3.

As discussed earlier, emulsion SBR is different from solution SBR in the degree of branching and also in the amount of non-rubber hydrocarbon, namely soap residue. In order to study the effect of soap residue, the

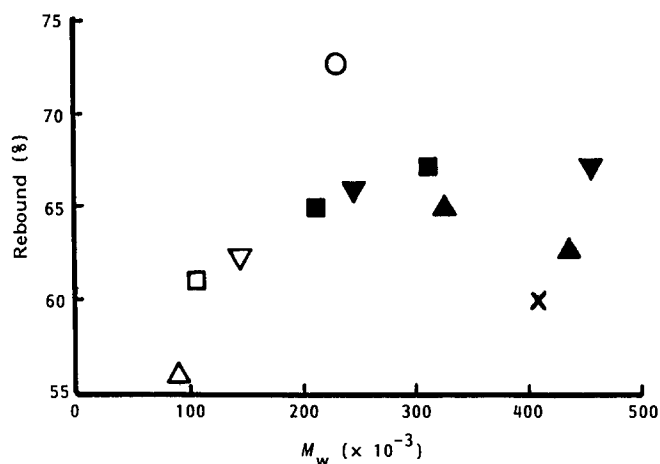


Figure 2 Steel-ball rebound at 66°C vs. weight-average molecular weight for linear and branched solution SBRs compared with emulsion SBR

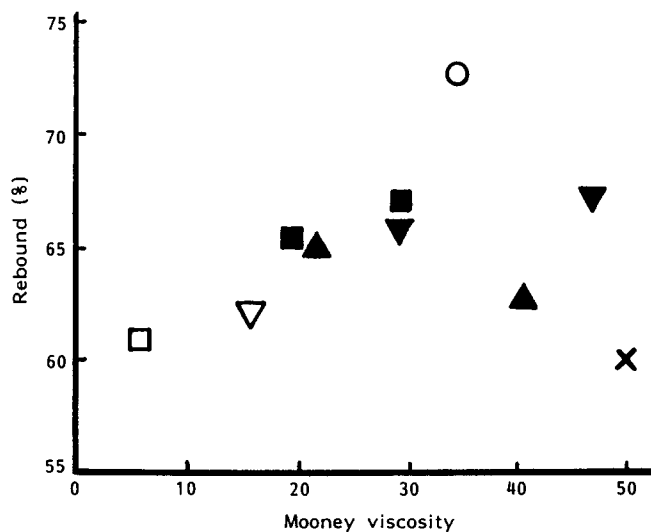
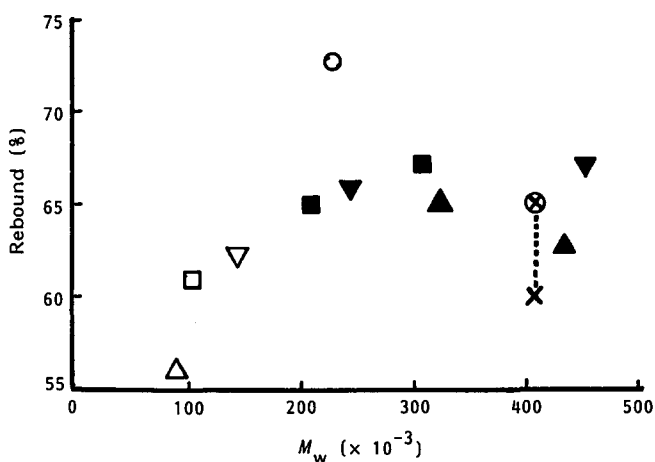


Figure 3 Steel-ball rebound at 66°C vs. Mooney viscosity for linear and branched solution SBRs compared with emulsion SBR

emulsion SBR was extracted with a toluene/ethanol mixed solvent for removal of the soap residue. The extracted emulsion SBR was compared with the original emulsion SBR in the standard formulation. The extracted emulsion SBR showed very similar behaviour to solution

**Table 5** Compound properties of emulsion SBR (before and after removal of residue)

	S1502	S1502 extracted
Extract (%)	7	1
Compound ML/4/100°C	57	66
Rheometer		
Scorch time (min)	15	17
Optimum cure (min)	39	33
Ring tensile (23°C)		
Tensile strength (MPa)	25.5	20.7
Elongation (%)	405	335
Hot ring tear (kNm <sup>-1</sup> )	61.3	39.4
Rebound (%)		
23°C	48	57
100°C	65	69


**Figure 4** Effect of extracting polymerization residues from emulsion SBR on steel-ball rebound

SBR (Tables 2 and 5). That is, the cure rate was increased, the hysteresis and tear strength were reduced, and Mooney viscosity was increased. As can be seen in Figure 4, the extracted emulsion SBR now shows the same level of hysteresis as that of branched solution SBRs.

This study showed that the high hysteresis of emulsion SBR is caused by its macrostructure, primarily by the low primary chain molecular weight and high degree of branching, and also by the residues, which exist in an amount of 5–10% in the rubber. However, these residues also contribute positively to better processability and higher tear strength of emulsion SBR.

#### Effect of tread polymer structures on tyre performance

The effect of polymer structure on the performance characteristics of tread compounds was also investigated based on actual tyre test data. The effect of polymer macrostructure on tread stock and tyre properties is shown in Table 6 for medium-vinyl polybutadiene (PBD) tread stocks. The beneficial effect of higher molecular weight, in equal formulation, on laboratory hysteresis and tyre rolling loss is evident. The laboratory abrasion data also confirm that higher molecular weight is preferred for improved wear resistance.

The data summarized in Table 7 are for a series of polybutadienes of increasing vinyl content. All were made to nominally the same Mooney viscosity. In spite of best

efforts, the macrostructures of these polymers were slightly different. The polymer in example D was lower in  $M_n$  and broader in molecular-weight distribution than that in example H. The polymer in example C had the highest  $M_n$ . The traction properties of tread stocks from these polymers were consistent with the glass transition temperature ( $T_g$ ) of the polymer or compound YMI value, which are dependent on vinyl content. On the other hand, rolling loss and wear resistance were not necessarily in line with increasing polymer  $T_g$ . Compounds featuring polymers D and H are equal for wear and rolling-loss performance, with the higher- $T_g$  compound containing polymer H being favoured for traction performance. The higher molecular weight,  $M_n$ , of polymer H compared with polymer D is suggested as the reason for this behaviour. In addition to the  $T_g$  of the polymer, its macrostructure is seen to have a dominant role in rolling-loss and tyre-wear resistance.

**Table 6** Effect of tread polymer macrostructure on properties (formulation: 100 polymer, 63 N339, 37.5 aromatic oil)

Example	1	2
Polymer properties		
$M_n$ ( $\times 10^{-3}$ )	165	210
ML/4/100°C	48	98
1,2 content (%)	42	36
$T_g$ (°C)	-74	-80
Stock properties		
ML/4/100°C	42	66
YMI (°C)	-48	-52
BPST (CF $\times 100$ )	37	35
Rebound (%) (100°C)	66	70
Pico abrasion rating <sup>a</sup>	100	108
Tyre performance (P195/75R14)		
Wet traction performance <sup>a</sup>	100	100
Dry traction performance <sup>a</sup>	100	100
Rolling-loss performance <sup>a</sup>		
drum	100	105
twin-roll	100	120

<sup>a</sup> High number is best

**Table 7** Influence of tread polymer micro/macrostructure on properties

Example	C	D	H
Polymer properties			
$M_n$ ( $\times 10^{-3}$ )	223	178	208
$M_w/M_n$	1.5	2.1	1.8
ML/4/100°C	95	103	99
1,2 content	11	49	59
$T_g$ (°C)	-91	-60	-49
Stock properties			
ML/4/100°C	87	64	59
YMI (°C)	-80	-52	-42
BPST (CF $\times 100$ )	33	38	42
Rebound (%) (100°C)	70	59	61
Pico abrasion rating <sup>a</sup>	100	52	47
Tyre properties (P175/80R13)			
Wet traction performance <sup>a</sup>	100	119	130
Dry traction performance <sup>a</sup>	100	112	114
Rolling-loss performance <sup>a</sup>			
drum	100	93	93
twin-roll	100	80	79
Wear performance <sup>a</sup>	100	87	87

<sup>a</sup> High number is best

Table 8 Polymers used in treads for tyre tests

Polymer	Symbol	Composition		$T_g$ (°C)	$M_n$ ( $\times 10^{-3}$ )	$M_w/M_n$	Mooney viscosity ( )
		1,2 (%)	Sty. (%)				
A	○	12	28	-65 (OE)	212	1.9	44 (OE)
C	●	11	0	-91	223	1.5	95
D	■	49	0	-60	178	2.1	103
G	×	19	25	-52 (OE)	175	2.8	45 (OE)
H	▲	59	0	-49	208	1.8	99
I	▲	51	16	-44	205	2.1	93
J	□	16	38	-53 (OE)	247	1.8	93 (OE)
Q	▽	25	45	-41	174	2.1	104

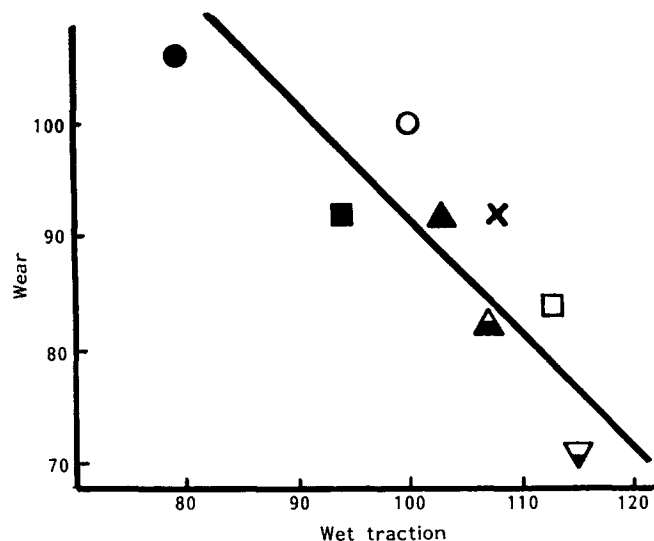


Figure 5 Wear vs. wet traction performance of various tread polymer structures. Solid symbols—vinyl PBDs. Open symbols—low-vinyl SBRs. Semi-solid symbols—medium-vinyl SBRs. Cross—emulsion SBR

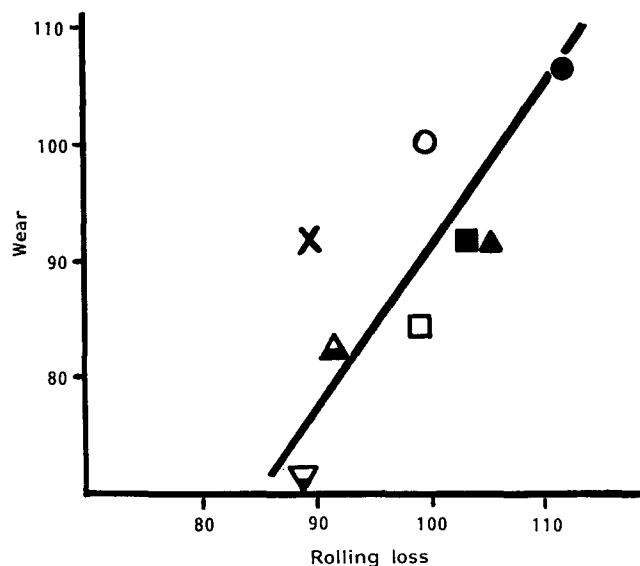


Figure 6 Wear vs. rolling-loss performance of various tread polymer structures. Solid symbols—vinyl PBDs. Open symbols—low-vinyl SBRs. Semi-solid symbols—medium-vinyl SBRs. Cross—emulsion SBR

In an attempt to analyse the effect of the type of microstructure on tyre performance, a series of polymers with nominally similar Mooney viscosity, but differing in vinyl and styrene (Sty) contents, was prepared. They were the three solution vinyl PBDs previously discussed, two low-vinyl solution SBRs, two medium-vinyl solution SBRs and for comparison purposes an emulsion SBR was included. The polymer properties are summarized in Table 8. As noted in the table, some polymers contained aromatic oil. Therefore, the glass transition temperature and the Mooney viscosity are the values for the oil-extended polymers. All the polymers described in Table 8 were evaluated in the same formulation listed in Table 6, which included 37.5 phr oil total (phr = parts per hundred parts rubber).

Tyre performance results are given in Figures 5, 6, 7 and 8. Tyre performance properties in these figures are presented relative to polymer A, a solution SBR that is assigned a rank of 100. For all tyre performance properties, i.e. wear, traction and rolling loss, a high rank is desired. The statistical analysis of these test results indicates that in order for two examples to be different at a 90% level of confidence, they should differ by at least 2% in rolling loss, 3% in dry traction, 6% in wet traction and 6% in wear.

The typical inverse relationship between wear and wet traction is evident in Figure 5. There does not appear to

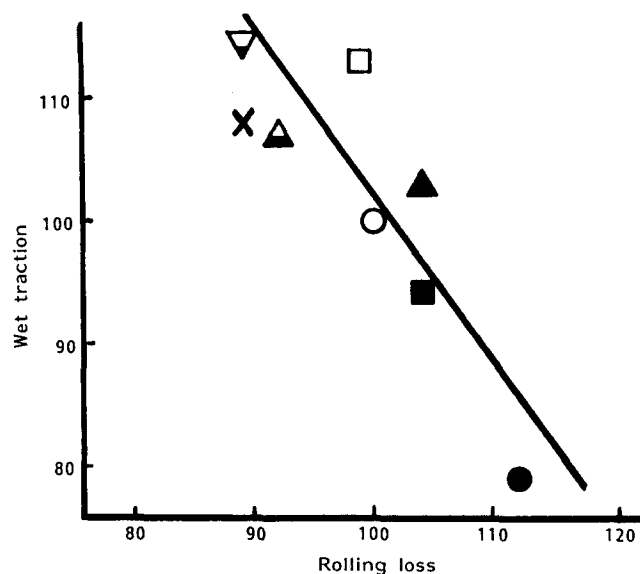


Figure 7 Wet traction vs. rolling-loss performance of various tread polymer structures. Solid symbols—vinyl PBDs. Open symbols—low-vinyl SBRs. Semi-solid symbols—medium-vinyl SBRs. Cross—emulsion SBR

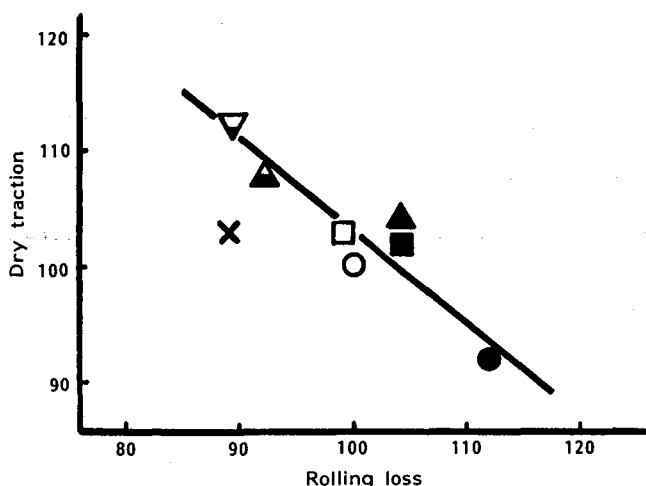


Figure 8 Dry traction vs. rolling-loss performance of various tread polymer structures. Solid symbols—vinyl PBDs. Open symbols—low-vinyl SBRs. Semi-solid symbols—medium-vinyl SBRs. Cross—emulsion SBR

be any particular microstructure that is definitely favoured. The improvement in wet traction with increasing vinyl or styrene composition (i.e. higher  $T_g$ ) is at the expense of tyre wear. As previously noted, the benefit of higher molecular weight is seen by comparing the equivalent wear and rolling-loss performance of polymers H and D. The performance of emulsion SBR as a tread rubber is also shown for comparison in the attached graphs. In particular, the rolling-loss disadvantage of emulsion SBR is apparent when compared with a solution polymer of comparable wear and traction behaviour as shown in Figures 6, 7 and 8.

The findings of Aggarwal *et al.*<sup>2</sup> suggest that vinyl structure is preferred over styrene structure for low-hysteresis compounds. Because polymer macrostructure was not specified in that study, its contribution to hysteresis was not considered. The higher polymerization temperature and technique, described for preparing the low-vinyl solution SBR, probably resulted in lower

primary-chain molecular weight than the vinyl polymers, which in turn increased the hysteresis of the polymer.

Where a vinyl BR and solution SBR are of approximately equal  $T_g$  (polymer H vs. polymer J) and the vinyl composition shows a slight rolling-loss and wear advantage, the solution SBR is observed to have a distinct wet traction advantage as seen from Figures 5 and 7. It is important to consider all aspects of tyre performance when advocating the advantages of certain tread polymer characteristics.

## CONCLUSIONS

It has been found that the linear molecular weight or molecular weight of a primary chain is the key parameter of polymer macrostructure that determines the hysteretic properties of compounded stocks.

The high hysteresis of emulsion SBR is caused by its macrostructure, i.e. its low primary-chain molecular weight and high degree of branching. In addition, the soap residue in emulsion SBR also contributes to high hysteresis. The high primary-chain molecular weight of solution SBRs provides a favourable balance of rolling-loss, traction and wear performance when utilized as tread polymers.

## ACKNOWLEDGEMENT

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