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OF COMMERCIAL POLYMERS*

**STRUCTURE AND PHYSICAL PROPERTIES
OF HIGH-VINYL POLYBUTADIENE
RUBBERS AND THEIR BLENDS**

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Structure and physical properties of high-vinyl polybutadiene rubbers and their blends

ABSTRACT: Some physical properties of high-vinyl polybutadiene rubber prepared with an alkyl lithium catalyst system were studied in regard to their micro- and macro-molecular structures. It was found that high-vinyl polybutadiene rubbers show characteristic features in the critical properties for tire tread such as rolling resistance and wet skid resistance: (1) High-vinyl polybutadiene rubbers show high rebound resilience at high temperatures despite the high glass transition temperature. (2) High-vinyl polybutadiene rubbers show the highest value of wet skid resistance at approximately 70% vinyl content. (3) The blends of high-vinyl polybutadiene rubbers with high cis-1,4-polybutadiene, and with high cis-1,4-polyisoprene rubber exhibit an excellent balance of rebound resilience and wet skid resistance. The compatibility for these blends series was also discussed. Finally, it is concluded that high-vinyl polybutadiene rubbers with 70% vinyl content, and its blend compounds are suitable tire materials for low fuel consumption, because of the excellent balance of low rolling resistance and high wet grip.

INTRODUCTION

In the first half of the '70s, European synthetic rubber producers tried to produce medium vinyl polybutadiene rubbers as an alternative of conventional styrene-butadiene rubber, because of the shortage of styrene monomer supply (ref. 1). After that, new requirements to endow low rolling resistance and high wet skid resistance for passenger-car tires appeared particularly in the US from the viewpoints of low fuel consumption and of safety car driving.

It has been believed (ref. 2) that the above mentioned critical properties of passenger-car tire rubbers are closely related to the glass transition temperature T_g of the rubber. According to the careful studies on the structure-property relationship for polybutadiene rubbers having various micro- and macro-molecular structure, however, it has been found that T_g is not the sole decisive factor. Polybutadiene rubbers with high-vinyl contents (abbreviated as V-BR hereafter) exhibit both the low heat build-up and high wet skid resistance. This implies that V-BR is well suited for passenger-car tire treads. Polybutadiene rubber with 70% vinyl content was produced as the first commercialized rubber for passenger-car tire by NIPPON ZEON CO., LTD. in 1980, aiming at the low rolling resistance and high wet traction.

This report describes the relationships between micro- and macro-structure and physical/mechanical properties for high-vinyl polybutadiene rubbers and their blends. All the experiments have been done by NIPPON ZEON Co., Ltd. and the excavation of data and discussions have been made by Sub Group meeting in JAPAN of IUPAC Working Party IV-2-1.

EXPERIMENTAL

Materials

Polybutadiene rubber samples with various vinyl contents were prepared by polymerizing 1,3-butadiene in hexane or benzene with a n-butyl lithium catalyst in combination with diglyme (diethylene glycol dimethyl ether) at 40 °C. The molecular characteristics of the polybutadiene samples are shown in Tables 1 and 2. Commercially available high cis-1,4-polybutadiene (Nipol BR-1220), high cis-1,4-polyisoprene (Nipol IR-2200), natural rubber (RSS#3), and emulsion polymerized styrene-butadiene rubber (Nipol SBR-1502) were used for preparing blend samples and for a comparison of results. These

raw rubbers were mixed with carbon black and other ingredients by a labo-mixer of Banbury type and an open roll, and were press-cured for preparing test specimens. The test formulation is shown in Table 3.

TABLE 1. Mooney viscosity and molecular characteristics (molecular weight and molecular weight distribution) of the polybutadiene samples having various vinyl contents.

Vinyl Cont. (%)	Mooney Vis.		GPC - LALLS		
	ML ₁₊₄	100 °C	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	M _w /M _n
55.0	11		1.02	1.06	1.04
58.8	50		1.72	1.91	1.11
70.1	45		1.54	3.18	2.06
71.8	50		1.73	3.78	2.18
67.0	113		2.28	2.51	1.10
79.3	16		1.14	1.25	1.10
69.3	17		0.932	1.19	1.28
69.7	33		1.42	3.04	2.13
78.0	74		1.69	2.35	1.40

TABLE 2. Polybutadiene samples having different molecular weight distributions (M_w/M_n), but having almost constant Mooney viscosity and vinyl contents. These samples are used for to investigate effect of the molecular weight distribution on the mechanical properties.

Vinyl Cont. (%)	Mooney Vis.		GPC - LALLS		
	ML ₁₊₄	100 °C	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	M _w /M _n
70.7	47		2.02	2.17	1.08
72.8	49		1.04	2.43	2.33
72.4	60		1.65	8.09	4.90
71.7	47		2.56	13.3	5.21

TABLE 3. Recipe for preparing the test specimens of valcanizates.

Polymer	100
Carbon Black (HAF)	50
High Aromatic Oil	5
Zinc Oxide	3
Stearic Acid	2
Sulfur	1 2
Accelerator MSA	0.8 2

Measurements

The microstructure of polybutadiene samples was determined by IR spectra and ¹³C-NMR spectra. IR spectra were obtained with a HITACHI (Model 260-30) spectrometer at 0.5% sample solution. The microstructure was evaluated by the following equations using Morero's absorption coefficients (ref. 3).

$$\begin{aligned} \text{Vinyl} &= 3.745 D_{910\text{cm}^{-1}} - 0.07 D_{730\text{cm}^{-1}} \\ \text{Cis} &= 17.459 D_{730\text{cm}^{-1}} - 0.151 D_{910\text{cm}^{-1}} \\ \text{Trans} &= 4.292 D_{965\text{cm}^{-1}} - 0.454 D_{730\text{cm}^{-1}} - 0.129 D_{910\text{cm}^{-1}} \end{aligned} \quad (1)$$

¹³C-NMR spectra were obtained with a NIPPON DENSHI (Model FX-100) spectrometer for 7% solution in deuterio-chloroform at room temperature. Other measuring conditions are 25 MHz, 45 ° pulse (7 microsec), 10 sec repetition time and sweep width of 400 Hz. The vinyl contents of the samples were calculated from the peak intensities in 132 ~ 128 ppm region and those at 143 and 114 ppm. These peaks are assigned to the unsaturated carbon of 1,4-bond and of vinyl group, respectively (refs. 4, 5). The ¹³C-NMR spectrum of 45.7% vinyl polybutadiene is shown in Fig.1.

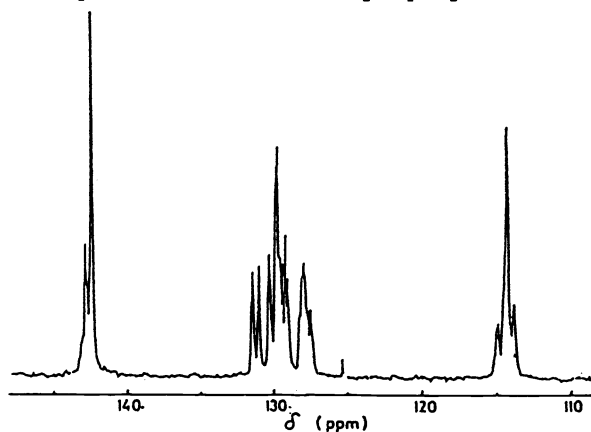


Fig. 1 ¹³C-NMR spectrum of polybutadiene rubber of 45.7 % vinyl content.

The molecular weight and its distribution were measured at room temperature, by use of a JASCO GPC equipped with a differential refractometer connected to a TOYO SODA (Model LS-8) low angle laser light scattering photometer (LALLS). Concentration of sample solution was 0.1 % in chloroform. The columns used were SHODEX-M80A x 2, and the flow rate was 1 ml/min.

The fractional molecular weight M_i of each elution volume count can be obtained from the following equation:

$$h_i^{LS}/h_i^{RI} = (k_2K/k_1) M_i \quad (2)$$

where (k_2K/k_1) is a constant relating to the instrument constant and the polymer-solvent system, h_i^{LS} and h_i^{RI} denote the scattering intensity of LALLS and the amplitude of differential refractometer record, respectively.

The number-average molecular weight M_n and the weight-average molecular weight M_w were calculated from the following equations, respectively:

$$M_n = \sum W_i / \sum (W_i / M_i) \quad (3)$$

$$M_w = \sum (W_i M_i) / \sum W_i, \quad (W_i = h_i^{RI} / \sum h_i^{RI}) \quad (4)$$

As a measure of molecular weight distribution, M_w/M_n was used.

Glass transition temperatures T_g of various V-BR samples and their blends were measured with a DAINI SEIKOSHA (Model SSC/560) differential scanning calorimeter (DSC).

Temperature dispersions of mechanical viscoelasticity were measured with an IWAMOTO VES-S spectrometer over a wide range of temperature (-110 ~ 0 °C). The measurements were performed at +0.2 % extensional strain amplitude superimposed on 10 % static strain at the frequency of 100 Hz.

Rebound resilience was measured using a DUNLOP tripsometer at a temperature range of 17 ~ 83 °C. Wet skid resistance was measured at room temperature using a STANLEY LONDON portable skid tester with a safety walk track. Heat build-up was measured by a GOODRICH flexometer at 100 °C (25 lb load, 17.5 % stroke, and 1,800 rpm).

A JEM-7A model electron microscope was used for observing the phase structures of blends using ultra-thin sections of osmium tetroxide stained samples.

RESULTS AND DISCUSSION

Microstructure and glass transition temperature

Vinyl contents estimated from ^{13}C -NMR are plotted against those estimated from IR for various polybutadiene samples in Fig. 2. It can be seen that correlation of the two methods becomes worse at high vinyl contents showing that the IR method provides higher value than the NMR method.

Relations between the glass transition temperature measured by DSC and the vinyl contents measured by IR and NMR methods are shown in Fig. 3. The data by IR method (Δ) show a deviation in the high vinyl (> 60 %) region. On the other hand, the plots of T_g against vinyl contents measured by NMR method (\circ) seem to make a smooth curve as is seen in Fig. 3. We may conclude that the NMR method is better than the IR method to evaluate vinyl content. The solid line in Fig. 3 shows calculated T_g values by the following Gordon-Taylor equation, using T_g values of samples having 12 and 78 % vinyl contents.

$$T_g = [T_{g1} + (KT_{g2} - T_{g1})V_2] / [1 + (K - 1)V_2] \quad (5)$$

where K , the ratio of expansion coefficients is assumed to be 0.5.

Mechanical and thermal properties

The mechanical and thermal properties characterizing practical performance of rubber vulcanizates are plotted against vinyl content in Figs. 4 to 6. (The level of SBR-1502 is shown in each figure.) Fig. 4 shows the relationship between the rebound resilience at room temperature and the vinyl content.

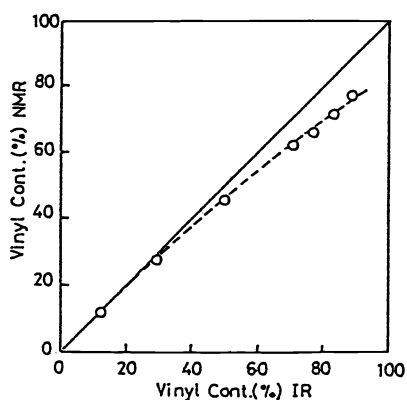


Fig. 2 Comparison of vinyl contents of polybutadiene samples evaluated from IR and ^{13}C -NMR.

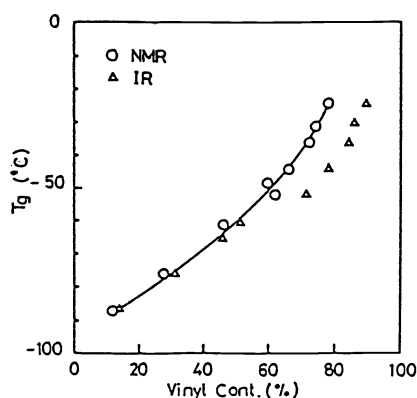


Fig. 3 Glass transition temperature plotted against vinyl content measured by IR (Δ) and ^{13}C -NMR (\circ). The solid line represents a theoretical curve calculated by Gordon-Taylor equation, using T_g values of two samples of 12 % and 78 % vinyl contents (NMR method).

The rebound resilience decreases with increasing vinyl content, in other words, with increasing T_g (see Fig. 3). Fig. 5 shows that the wet skid resistance increases with the increase of vinyl content. The heat build-up measured by a GOODRICH flexometer shows a decreasing tendency with the increase of vinyl content, as shown in Fig. 6. It has been considered that the rubber with higher T_g shows higher heat build-up (ref. 2). However, Fig. 6 shows that rubber with higher T_g shows a lower heat build-up in the case of V-BR.

Both the rebound resilience and the heat build-up are considered to be the properties correlated with dynamic loss factor of the rubbers. Figs. 4 and 6 exhibit quite opposite results with the increase of the vinyl content. This contradiction on vinyl content (and also T_g) dependences of rebound resilience and heat build-up would be due to the difference in the measuring temperatures between the two methods. Namely, the rebound resilience was measured at room temperature, but the heat build-up was measured at 100 °C with cyclic deformation (1,800 rpm) under 25 lb pre-load.

More detailed study on the effect of molecular structure on physical properties was made. The samples employed here are listed in Table 1. As is seen in this table, the vinyl content and the molecular weight (M_w) were varied from 55 % to 80 % and from 1×10^5 to 4×10^5 , respectively. Mooney viscosity (ML_{1+4} , 100 °C) which can be considered as a measure of molecular weight, was varied from 11 to 113. On the other hands, molecular weight distribution (M_w / M_n) was maintained within a relatively narrow range ($M_w / M_n = 1 \sim 2$). From the results for the samples of $M_w / M_n < 2$ in Table 1, the following experimental equation was derived for the relation between Mooney viscosity (ML_{1+4}) and molecular weight (M_w).

$$ML_{1+4} = 2.89 \times 10^{-10} M_w^{2.1} \quad (6)$$

Fig. 7 shows the rebound resilience levels of various V-BR at room temperature (17 °C) on the map of Mooney viscosity against vinyl content. It is clear from this figure that the rebound resilience of V-BR at room temperature (17 °C) predominantly depends on the vinyl content, but hardly depends on the Mooney viscosity. Contrary, the rebound resilience of the same samples measured at a higher temperature (80 °C) is much less dependent on the vinyl content as shown in Fig. 8. This type of behavior has never been known for other rubber materials, and seems to be one of characteristic features of V-BR.

In Fig. 9, the heat build-up levels decrease with the increase of vinyl content and Mooney viscosity. This tendency of high vinyl polybutadiene rubbers on the heat build-up is quite opposite to that of other rubbers generally known so far.

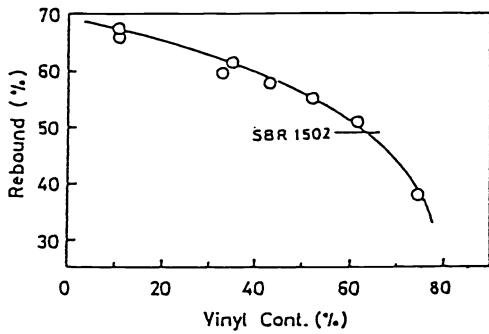


Fig. 4 Rebound resilience measured at room temperature plotted against vinyl content of polybutadiene rubbers. The level of rebound resilience of styrene-butadiene rubber (SBR 1502) is shown in the figure.

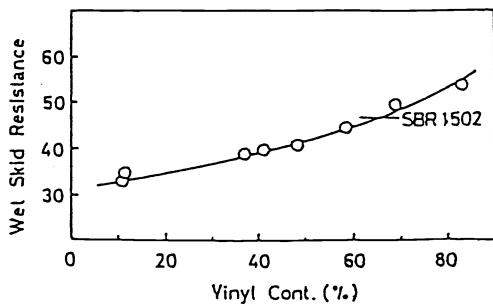


Fig. 5 Wet skid resistance measured at room temperature plotted against vinyl content of polybutadiene rubbers. The samples are the same as those in Fig. 4

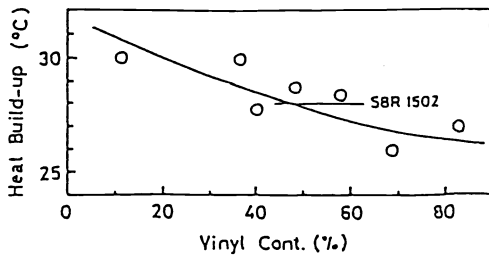


Fig. 6 Relationship between heat build-up measured at 100 °C and vinyl content of polybutadiene rubbers.

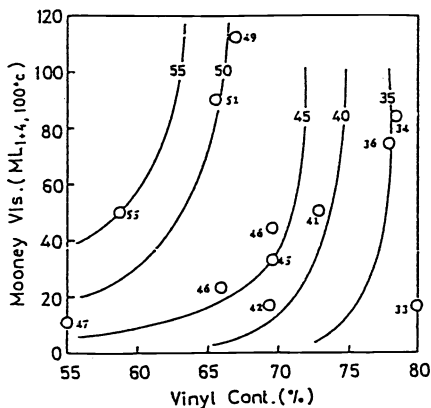


Fig. 7 Rebound resilience levels of various V-BR samples at 17 °C expressed as function of Mooney viscosity and vinyl content.

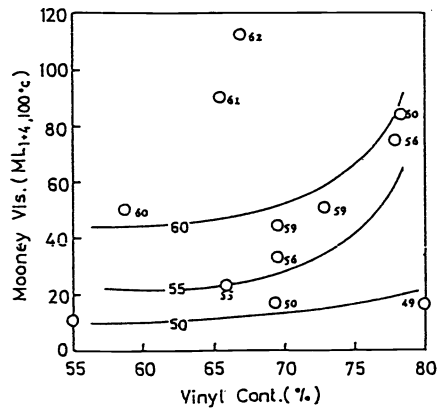


Fig. 8 Rebound resilience levels of the same samples as in Fig. 7 at 82 °C expressed as function of Mooney viscosity and vinyl content.

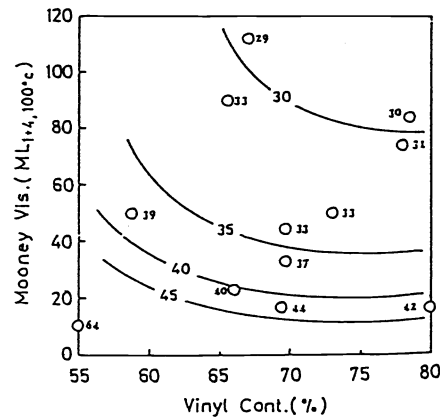


Fig. 9 Heat build-up levels of various V-BR samples measured by GOODRICH flexometer at 100 °C expressed as function of Mooney viscosity and vinyl content.

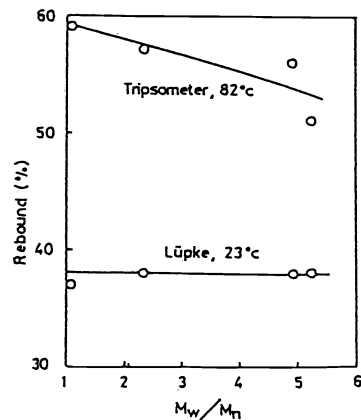


Fig. 10 Effect of molecular weight distribution (M_w/M_n) on rebound resilience at different temperatures, 23 °C (Luepke) and 82 °C (DUNLOP tripsometer).

The effect of the molecular weight distribution on the rebound resilience was examined by use of the samples, whose Mooney viscosity and molecular weight distribution are shown in Table 2. M_w/M_n was varied from 1.08 to 5.21 with little changes in the vinyl content and Mooney viscosity. Samples with a variety of MWD were prepared by blending.

The effects of M_w/M_n on the rebound resilience at 23 °C and 82 °C are shown in Fig. 10, which shows that so far as the vinyl content remains unchanged, M_w/M_n does not affect the rebound resilience at room temperature (23 °C), but considerably affects it at higher temperature (82 °C).

Through the experimental results of Figs. 7 to 10, it can be concluded that the rebound resilience of V-BR at around room temperature is not affected by macro-molecular quantities such as M_w , M_w/M_n and ML, but is dominantly affected by micro-molecular structure such as vinyl content. On the contrary, the rebound resilience at higher temperature than 60 °C is affected by macro-molecular quantities, and is less affected by micro-structures. This phenomena might be explained by considering the difference between the measuring temperature and T_g . The facts means that the high-vinyl polybutadiene rubbers are acceptable as low rolling resistance tire tread materials, in spite of their high T_g values.

Wet skid resistance

Next, we describe the relation between the molecular structures of the polybutadiene rubbers and the wet skid resistance, which is another important property of tire rubber for passenger-car. Relationship between the wet skid resistance and the glass transition temperature T_g is shown in Fig. 11 for several types of rubbers. It is seen that the wet skid resistance reaches the highest value at T_g of around -30 °C. In the case of V-BR, the rubber with approximately 70 % vinyl content has the T_g corresponding to the highest value. This is a new fact which needs more consideration. According to the theoretical and experimental approaches to wet grip performance of tire by Bond et al. (ref.6), the total frictional force F_t generated at the tire-road surface interface under wet sliding conditions can be approximated by:

$$F_t = F_a + F_{mh} \quad (7)$$

where F_a is the frictional force due to the tread adhesion component, and F_{mh} is the frictional force due to the tread micro-hysteresis component under sliding conditions and is believed to be proportional to the loss factor. Thus, the important parameter relating to the wet skid resistance of tread rubbers is the loss factor at appropriate frequency and temperature. It has been considered (ref. 6) that very high frequency deformation (50 kHz to 1 MHz) are generated at tire-road surface interface by the road surface microtexture (10^{-5} to 10^{-4} m).

Considering the well known time (frequency) - temperature superposition principle, the reason why the wet skid resistance reaches the highest value at the T_g range (-40 ° to -20 °C) can be understood. The mechanical loss factor of a rubber reaches the maximum value at the temperature range of $T_g + 10$ ° to 20 °C when the viscoelastic properties are measured at the frequency of 100 Hz (see Figs. 18 and 19). Therefore, if the temperature dependence of the viscoelastic properties of V-BR with a T_g around -40 ° to -20 °C is measured at a frequency range of 50 kHz to 1MHz, corresponding to the wet skid condition, the maximum value of the mechanical loss factor will be seen at around room temperature.

Commercially available high-vinyl polybutadiene rubber Nipol BR-1240 (NIPPON ZEON CO.,LTD.) has the vinyl content of about 70 % and T_g at -35 °C.

Blends

We studied the characteristics of V-BR/C-BR and V-BR/IR blends, based on the above mentioned results. The relationship between the rebound resilience at room temperature (23 °C) and the wet skid resistance of the blend series compared with the conventional SBR/C-BR blends is shown in Fig. 12. SBR/C-BR series show a linear relationship with a minus slope, but V-BR/C-BR and V-BR/IR blend series show relationships given by the curves convex upward. Consequently, V-BR/C-BR and V-BR/IR blends reveal a good balance of these two properties shifted to practically desirable direction (high rebound and high wet skid resistance) for tire application.

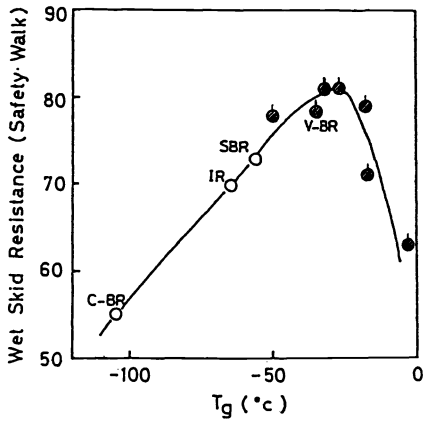


Fig. 11 Relation between wet skid resistance and T_g on several types of general-purpose rubbers (C-BR, IR, SBR) and various V-BR (●).

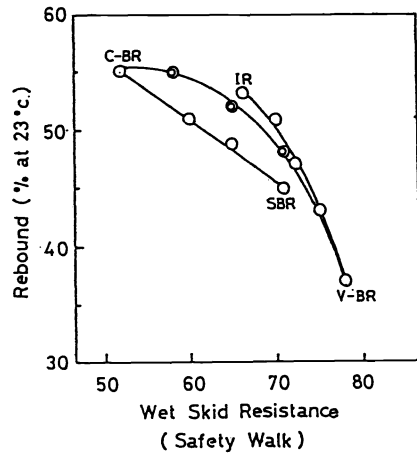


Fig. 12 Relations between rebound resilience at room temperature (23 °C) and wet skid resistance of two series of V-BR/IR and V-BR/C-BR, as compared with conventional SBR/C-BR. The composition of blend series shown are 75/25, 50/50 and 25/75 for V-BR/IR and V-BR/C-BR (●), and 70/30 and 50/50 for SBR/C-BR.

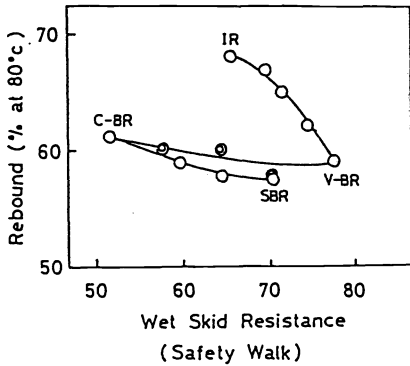


Fig. 13 Relation between rebound resilience at 80 °C and wet skid resistance for the same blend series used in Fig. 12.

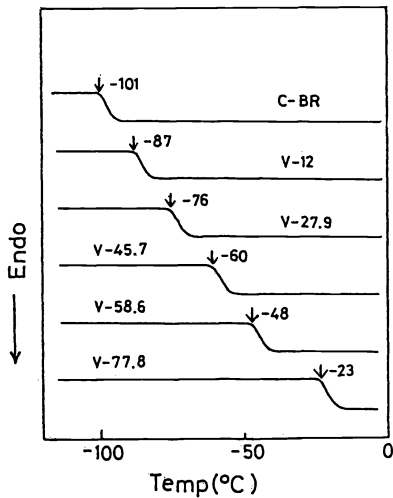


Fig. 14 DSC curves of polybutadiene rubbers having various vinyl contents. T_g for each sample in °C is shown by the arrow and numeral.

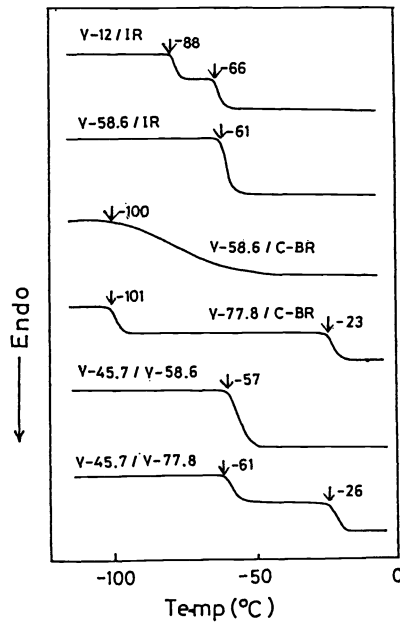


Fig. 15 DSC curves of 50/50 blends of V-BR/C-BR, V-BR/IR, and V-BR/V-BR series.

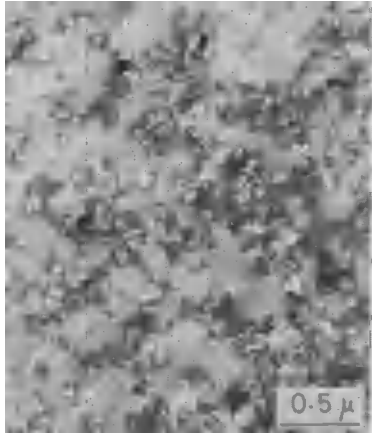


Fig. 20 Electron micrograph
of 70 % vinyl-BR/C-BR blend.

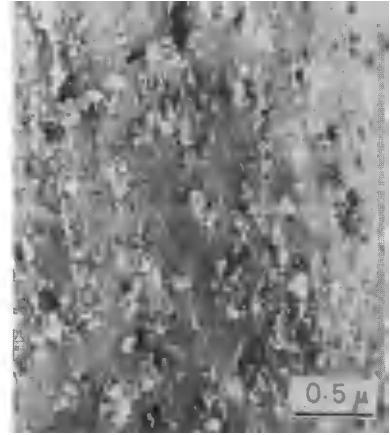


Fig.21 Electron micrograph
of 70 % vinyl-BR/IR blend.

Fig. 13 shows the relationship between the rebound resilience at 80 °C and the wet skid resistance. It can be seen that tire of V-BR/IR blend shows a remarkably lower rolling resistance (high rebound) and high wet grip than the conventional SBR/C-BR blend tire.

Compatibility

The glass transition temperature, and the temperature dependence of viscoelastic properties of the rubbers were measured to study the compatibility of the blends series. Systematic DSC curves of polybutadiene rubbers with various vinyl contents are shown in Fig. 14. The glass transition temperatures used in Fig. 3 were evaluated from this figure. Fig. 15 shows the DSC curves of 50/50 blends of V-BR/C-BR, V-BR/IR, and V-BR/V-BR series.

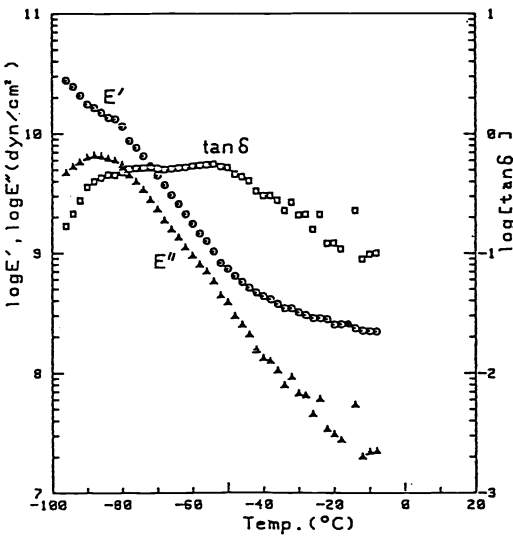


Fig. 16 Temperature dispersion of dynamic viscoelastic functions E' , E'' , and $\tan \delta$ for 50/50 blend of 58.6 % vinyl-BR/C-BR at 100 Hz.

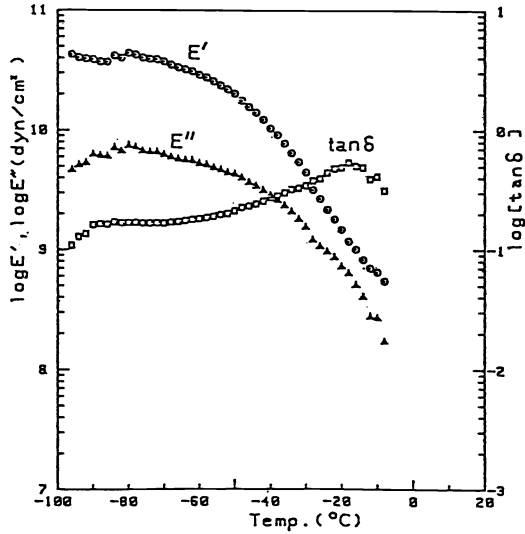


Fig. 17 Temperature dispersion of dynamic viscoelastic functions E' , E'' , and $\tan \delta$ for 50/50 blend of 77.8 % vinyl-BR/C-BR at 100 Hz.

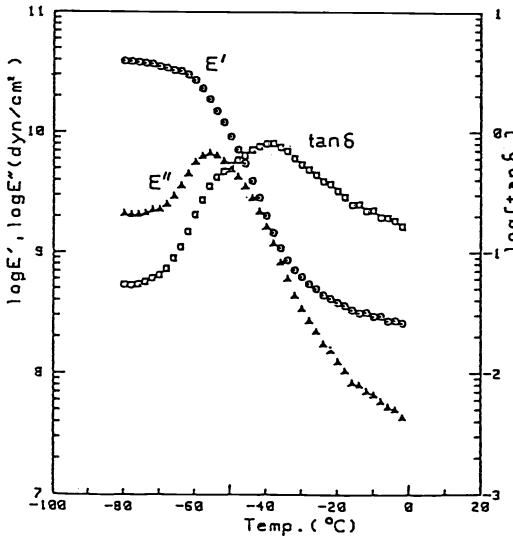


Fig. 18 Temperature dispersion of dynamic viscoelastic functions E' , E'' , and $\tan \delta$ for 50/50 blend of 45.7 % vinyl-BR/58.6 % vinyl-BR at 100 Hz.

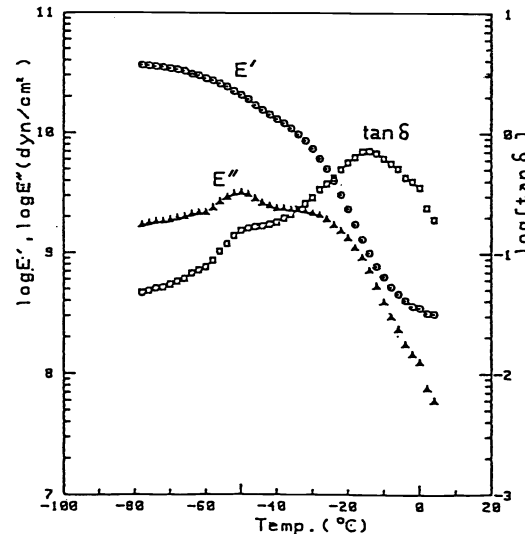


Fig. 19 Temperature dispersion of dynamic viscoelastic functions E' , E'' , and $\tan \delta$ for 50/50 blend of 45.7 % vinyl-BR/77.8 % vinyl-BR at 100 Hz.

The temperature dependence of dynamic viscoelastic properties for 50/50 blends of V-BR/C-BR are shown in Figs. 16 and 17. Results on 50/50 blends of V-BR/V-BR with different vinyl contents are shown in Figs. 18 and 19. Taking a look at both DSC and viscoelastic properties carefully, it can be seen that the 45.5 % vinyl BR is compatible with 58.6 % vinyl BR, while it is incompatible with 77.8 % vinyl BR. This compatibility of polybutadiene rubbers with various vinyl contents has been examined with a contrast microscope in greater detail by Nishi et al. (ref. 7). These results were also confirmed by electron microscope observations.

Fig. 20 shows an electron micrograph of V-BR/C-BR blend. The micro-hetero phase structure of the order of around 0.5 μm is observed as an evidence of incompatible blend series. In this micrograph, the dark parts show the C-BR phase stained by osmium tetroxide. On the other hand, V-BR/IR blend as indicated in Fig. 21 shows homogeneous phase suggesting a compatible series. Another feature observed in these figures is that most of the carbon black particles are present in the C-BR phase. These heterogeneous structural features of V-BR/C-BR blend are considered to be related to some physical properties of vulcanizates.

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