

# A STUDY ON THE YIELD STRENGTH OF SBR RAW RUBBER

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## ABSTRACT

The relationship between intrinsic viscosity  $[\eta]$  and yield strength  $[\sigma_y]$  of SBR-1500 raw rubber was studied. It was found that the critical molecular weight for yielding varied with temperature. The critical yield temperature of SBR-1500 is 18°C, which is equivalent to transition temperature  $T'_{II}$  as determined by linear expansion. The transition temperature  $T'_{II}$  of SBR increased with styrene content in the sample.

In our previous papers<sup>[1, 2]</sup>, we have reported the relationship between yield strength and intrinsic viscosity, the additivity of yield strength, the activation energy of yielding and the critical molecular weight ( $M_c$ ) of nature rubber, *cis*-1,4-polybutadiene (Ln-PB) and polyisoprene (Ln-PI) prepared with lanthanide catalyst, as well as the mechanism of yielding. In the present paper, random copolymers of styrene and butadiene (SBR) were studied. They differ from the above-mentioned homopolymers in the following aspects: (1) SBR does not crystallize under stress; therefore, it is advantageous to study the yield phenomena in a wider temperature range. (2) The mechanism of yielding can be further understood by observing the effect of comonomer content on  $T'_{II}$ .

## EXPERIMENTAL

### 1. Samples

Three samples of SBR were used in this work, the microstructure and origin of which are

Table 1 Origin and microstructure of samples

| Sample   | Origin of sample                       | Composition (%) |           | Microstructure (%) |     |
|----------|----------------------------------------|-----------------|-----------|--------------------|-----|
|          |                                        | styrene         | butadiene | <i>cis</i> -1,4    | 1,2 |
| SBR-A    | Jilin Institute of Chemical Technology | 7.7             | 92.3      | 74.3               | 18  |
| SBR-1500 | Japan                                  | 23.5            | 76.5      | 7                  | 16  |
| SBR-B    | Jilin Institute of Chemical Technology | 47.0            | 53.0      | 40.9               | 12  |

shown in Tab. 1.

Samples of different molecular weight were obtained by milling SBR-1500. Intrinsic viscosity in toluene was determined at 30°C<sup>[3]</sup>. The microstructure of samples A and B were determined by <sup>13</sup>C-NMR.

## 2. Sample preparation and experimental methods

Details on sample preparation have been reported previously<sup>[2]</sup>. Uniaxial tensile test was performed on an electronic tensile tester (Model DL-1000B, Changchun 2nd Material Testing Machine Works) at eight different temperatures in the range of -75 to 50°C. Nominal yield strength was calculated from cross-section of unstrained samples. Transition temperature was determined by linear dilatometer on samples of 40×50×1 mm<sup>3</sup> at a heating rate of 1.5°C/min.

## RESULTS AND DISCUSSION

### 1. Relationship between $\sigma_y$ and $[\eta]$ of SBR-1500

Uniaxial tensile test was carried out at 25°C. Using least square method, a linear relationship between  $\sigma_y$  and  $[\eta]$  can be expressed as:

$$[\eta] = 0.54\sigma_y + 0.36 \quad (1)$$

It indicates that chains of the rubber begin to entangle only when  $[\eta]$  is greater than 0.36, below which the rubber does not show any elasticity and  $\sigma_y$  is zero. The Mark-Houwink equation<sup>[3]</sup> of SBR-1500 in toluene is:

$$[\eta] = 5.44 \times 10^{-4} M_n^{0.68} \quad (2)$$

When  $\sigma_y$  approaches zero, the intrinsic viscosity will be 0.36 dl/g. As calculated from equation (2), the molecular weight at which entanglement appears, defined as the critical yield molecular weight,  $M_c$ , is  $1.9 \times 10^4$ , beyond which rubber elasticity would develop. The linear relationship between  $\sigma_y$  and  $[\eta]$  not only exists in homopolymers such as Ln-PB, Ln-PI and NR, but is also observed in copolymer SBR. Thus, this relationship is characteristic of rubbers (Fig. 1).

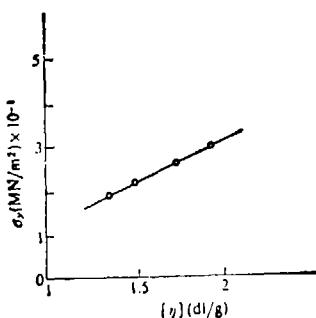


Fig. 1 Relationship between  $\sigma_y$  and  $[\eta]$  at 25°C

## 2. Additivity of yield strengths

According to polymer dilute solution theory,  $[\eta]$  is additive, i.e.

$$[\eta] = \sum_{i=1}^n [\eta]_i \bar{W}_i \quad (3)$$

where  $\bar{W}_i$  is the weight-fraction of  $i$ -th component. From the linear relationship between  $\sigma_y$  and  $[\eta]$  in equation (1)<sup>(2)</sup>, the yield strength should be additive also, namely

$$\sigma_y = \sum_{i=1}^n \sigma_{y_i} \bar{W}_i \quad (4)$$

This relationship also holds for SBR as shown in Fig. 2.

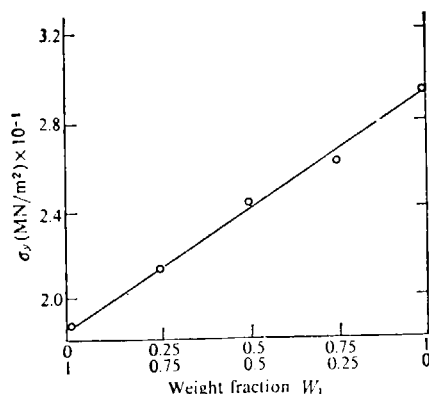


Fig. 2 Additivity of yield strength of SBR-1500

## 3. Temperature dependence of $\sigma_y$

### (1) Stress-strain curves

It is known in the literature<sup>(4)</sup> that there are five different forms of stress-strain curves of polymers—soft and weak, hard and brittle, hard and strong, soft and tough, and hard and tough. When SBR-1500 was subjected to strain at eight selected temperatures from 17 to  $-75^\circ\text{C}$ , the above-mentioned five types of stress-strain curves were all observed as shown in Fig. 3. The stress-strain behaviour of SBR-1500 changes with temperature—hard and brittle at  $-75^\circ\text{C}$ , hard and strong at  $-70^\circ\text{C}$ , and soft and tough at temperatures above  $T_g$ .

### (2) Yield activation energy

An inflection point is seen in the plot of  $\sigma_y$  against  $1/T$ , as shown in Fig. 4. This point corresponds to the glass transition temperature  $T_g$  at which pronounced change in yield strength occurs. The  $T_g$  detected by stress-strain method is  $-69^\circ\text{C}$ , which is lower than the  $T_g$  determined by linear dilatometer ( $-52^\circ\text{C}$ ). This difference may be attributed to the fact that under the action of external force the movement of segments becomes easier, leading to a lower  $T_g$ . Thus the value of  $T_g$  is dependent on the method of determination. The yield activation energy  $\Delta E_y$  above  $T_g$  calculated according to Arrhenius' equation,

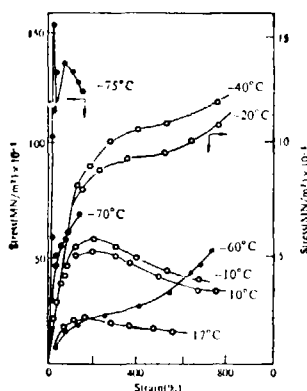
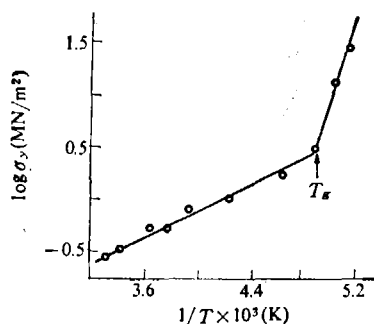


Fig. 3 Effect of temperature on stress-strain curve

Fig. 4 Relationship between  $\log \sigma_y$  and  $1/T$ 

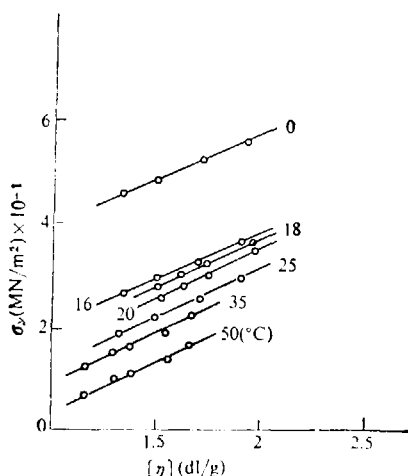
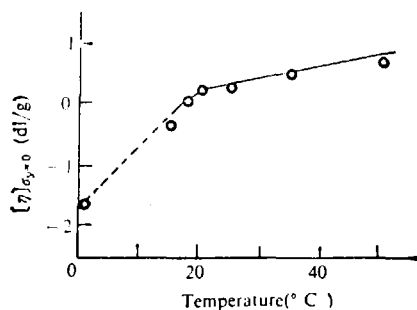
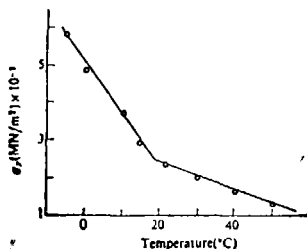
$\sigma_y = A^{-\Delta E_y/RT}$ , is  $31.09 \times 10^3$  J/mol. It has the same order of magnitude as those published in the literature for the activation energy of entanglement<sup>[1, 51]</sup>. The activation energy below  $T_g$  is  $16.23 \times 10^3$  J/mol, which is larger than that in the rubbery state. All the above results indicate that the mechanism of yielding is quite different at temperatures above and below  $T_g$ .

(3) The relationship between critical yield molecular weight and temperature

The linear relationship between  $\sigma_y$  and  $[\eta]$  holds true at 50, 35, 20, 18, 17 and  $0^\circ\text{C}$  (Fig. 5) as well as at  $25^\circ\text{C}$  (Fig. 1). Thus a general equation can be written as:

$$[\eta] = A\sigma_y + C \quad (5)$$

Where  $A$  is the slope which is almost independent of temperature in the temperature range from  $25$  to  $50^\circ\text{C}$  and  $C$  the intercept in a plot of  $[\eta]$  vs.  $\sigma_y$ . It implies that the higher the temperature is, the higher the value of  $C$ . At a temperature of  $18^\circ\text{C}$ , the value of the slope deviates only a little but the intercept changes drastically. It seems that  $M_e$  is more sensitive to temperature. The critical yield temperature, at which  $M_e$  approaches zero, is  $18^\circ\text{C}$  for SBR-1500 (Fig. 6). It is suggested that critical yield temperature is related to the interaction of phenyl groups to form physical entanglements and is closely related to  $T'_n$ . At temperature below  $18^\circ\text{C}$ ,  $M_e$  shows negative values. It takes only a mathematical meaning at present

Fig. 5 Relationship between  $\sigma_y$  and  $[\eta]$ Fig. 6 Relationship between  $M_c$  and temperatureFig. 7 Relationship between  $\delta_y$  and  $T$ 

but the physical explanation is still obscure.

#### (4) Change of $\sigma_y$ in the region of critical yield temperature

As suggested above, the critical yield temperature for SBR-1500 (18°C) is related to the interaction of phenyl groups in SBR. Obviously, with change in interaction of phenyl groups around the critical yielding temperature, both the yield strength and molecular weight between entanglement of the sample (containing 23.5% styrene) will also change. In Fig. 7, an abrupt change in  $\sigma_y$  with temperature is seen at 18°C, which is just the same as the critical

temperature. This suggested that the change of  $\sigma_y$  at 18°C is related to the interaction of phenyl groups. In order to clarify this point, the relationship between transitions and styrene content of SBR was investigated using linear dilatometer as follows:

#### 4. Transitions of SBR

##### (1) The glass transition

The  $T_g$  of random copolymers follows Fox's formula:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where  $T_{g1}$  and  $T_{g2}$  are the glass temperatures of components 1 and 2, respectively, and  $W_1$  and  $W_2$  are the corresponding weight fractions in the copolymer. The glass temperatures of three samples of SBR determined by linear dilatometer are very close to those calculated by the above equation (Tab. 2). All the three samples show single  $T_g$  only, so these polymers

Table 2 Values of  $T_g$ ,  $T'_{II}$  and  $T'_{II}/T_g$  for three samples of SBR

| Sample   | Styrene content (%) | $T_g$ (K)<br>(Expt'l) | $T_g$ (K)<br>(Calc'd) | $T'_{II}$ | $T'_{II}/T_g$ |
|----------|---------------------|-----------------------|-----------------------|-----------|---------------|
| SBR-A    | 7.7                 | 199                   | 198                   | 263       | 1.32          |
| SBR-1500 | 23.5                | 221                   | 215                   | 292       | 1.32          |
| SBR-B    | 47.0                | 250                   | 247                   | 327       | 1.31          |

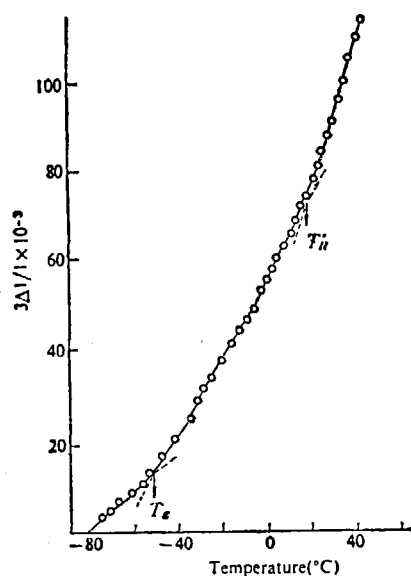


Fig. 8 Linear expansion curve of SBR-1500

are random copolymers. It is well known that styrene content influences the flexibility of the segments and the cohesive energy density of these copolymers.

(2) The  $T'_{ii}$  transition

$T'_{ii}$  transition is a transition through which the state of polymer changes from one flow state to another. The ratio of  $T'_{ii}$  to  $T_g$  is 1.31 for polystyrene<sup>[6]</sup>, but it has not yet been studied for SBR. In Tab. 2 were listed the  $T'_{ii}$  transition of three samples of SBR, as well as the ratio of  $T'_{ii}/T_g$ .

The values of  $T'_{ii}$  vary with the styrene content in SBR, but the ratio  $T'_{ii}/T_g$  is almost a constant. For SBR-1500, the transition temperature  $T'_{ii}$  is 18°C (Fig. 8), which is the same as the critical yielding temperature. This coincidence can be related to the interaction of phenyl groups.

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