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# Studies on Polymer Blends: Blending Methods for Natural Rubber and Styrene-Butadiene Rubber

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## Synopsis

The relations between the properties and the blend ratios of natural rubber (NR) and styrene-butadiene rubber (SBR) blends were studied in comparison with four blending methods. The relations between the properties of unvulcanized and vulcanized blends and the blend ratios of blends prepared by means of solution blending, latex blending, roll blending, and Banbury mixer blending were studied. In practice, such rubber blending methods as roll blending are more effective for obtaining uniform blends than Banbury mixer blending the latter. In roll blending, it is more effective to blend NR and SBR by way of a master-batch in which the ingredients are compounded beforehand than to blend raw rubber. In solution and latex blending, very uniform blends are easily obtained. It was found, however, that the properties of NR/SBR blends prepared carefully showed a direct relation to their blend ratios, regardless of blending method used.


## INTRODUCTION

Many studies on blending of rubber polymers have been reported,[1-7] but few studies have been reported in detail. In earlier studies, relations between the properties and blend ratios showed a maximum or minimum even in the blends of NR/SBR which are similar to one another in their properties.[4,5] The results however, varied considerably.

Recently, blends of rubber and plastics such as ABS resin have been developed.[8-11] Basic studies of such blends have been carried out in order to relate theory with technology. The results indicate that the blends even of polymer components which are similar to one another in their properties, are not homogeneous but only microheterogeneous.[12]

In the present study, the relations between the properties and the blend ratios of natural rubber (NR) and styrene-butadiene rubber (SBR) blends prepared by means of four methods, i.e., solution blending, latex blending, roll blending, and Banbury mixer blending, were studied.

It was found that, even in practical blending methods such as roll and careful Banbury mixer blending the properties of blends did not show any anomalous behavior, i.e., maximum or minimum points versus blend ratios, but showed a straight line. It is more effective to blend by roll blending

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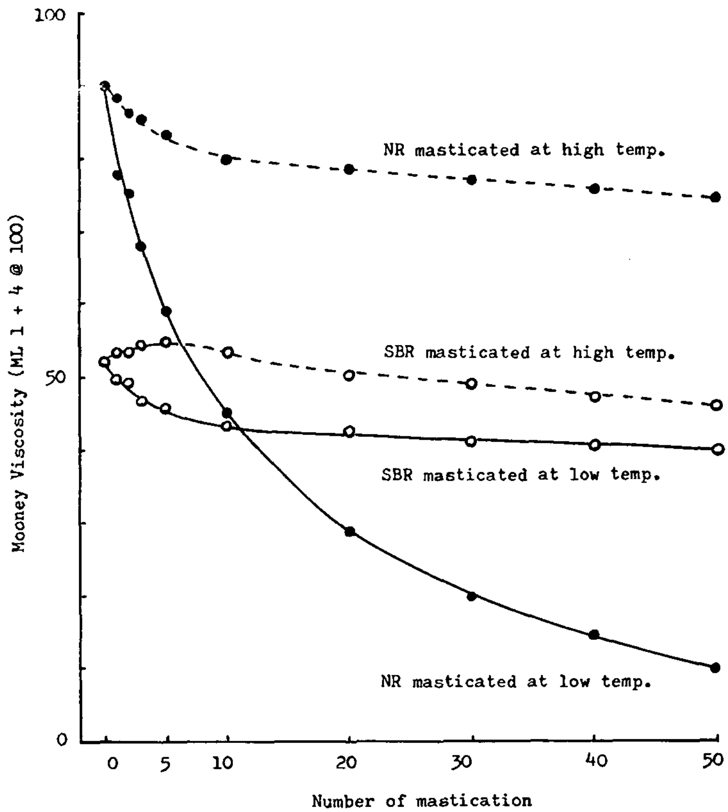


Fig. 1. Mooney viscosity vs. number of mastication cycles of NR and SBR for various mastication temperatures.

than by Banbury mixer blending in order to prepare the uniform blends, so it is desirable to treat by roll after blending by Banbury mixer. Furthermore, in roll blending it is more effective for uniform blends to blend mutual masterbatches than to blend the raw NR and SBR. With solution blending and latex blending, which are expected to give more uniform blends than mechanical methods such as roll blending and Banbury mixer blending, the properties of blends show apparently a straight-line relationship versus the blend ratios.

The results indicate that the properties of NR/SBR blends showed a straight line versus the blend ratios.

## EXPERIMENTAL

### Samples Used

Polymers used were NR (pale crepe) and SBR JSR #1502, manufactured by Japan Synthetic Rubber Co., Ltd., and the compounding ingredients

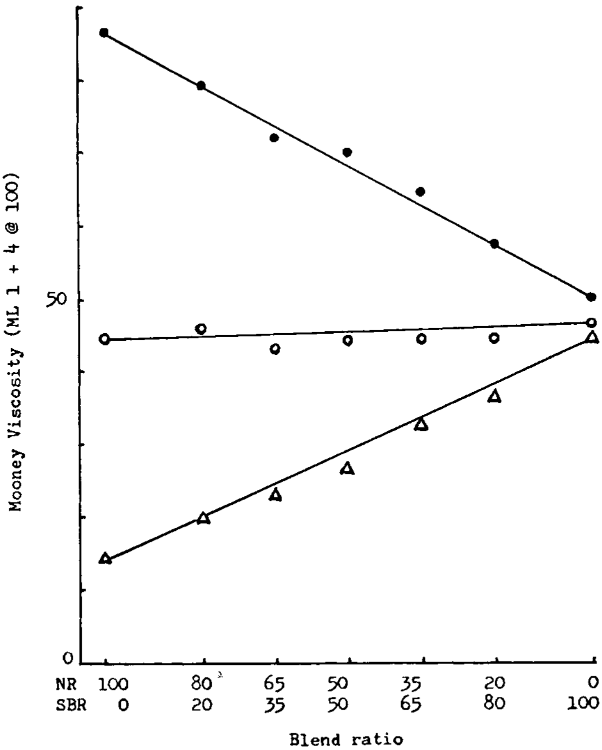


Fig. 2. Mooney viscosity vs. blend ratio of NR/SBR blends in low-temperature mastication at various numbers of mastication cycles: (Δ) 6 mastications; (O) 11 mastications; (●) 16 mastications.

used were commercially available ones. The blend ratios of NR/SBR examined were 100/0, 80/20, 65/35, 50/50, 35/65, 20/80 and 0/100 (by weight).

## Blending Methods

**Roll Blending.** The test roll used was 8 × 12 in., the speed of revolution of the roll was 25 rpm, and the ratio of revolution was 1:1. The roll temperature was maintained at 50–60°C. (low-temperature method) or at 120–130°C. (high-temperature method). This blending method as a raw rubber method, that is, with NR and SBR masticated individually and then compounding ingredients added, was compared with the masterbatch method, that is, blending at previously compounded NR and SBR.

**Banbury Mixer Blending.** NR and SBR weighed at blend ratios described were put together into a type B Banbury mixer and blended. The optimum volume of batch was 1 liter, the revolution ratio of the rotors was 77:101 rpm, and the pressure was 2.3–2.8 kg./cm.[2].

**Solution Blending.** The 5% solutions in toluene of NR and SBR were blended at the blending ratios described with effective stirring. The blend solutions were poured into methanol with vigorous agitation, and then blended rubbers were obtained through coprecipitation.

**Latex Blending.** The latex used contained parts of soap and 1.25 parts of antioxidant and was diluted into 21.5% DRC. The blend latex was prepared by blending NR latex and SBR latex at the blend ratios described. Creaming was carried out by adding brine to the blend latex. Then a coagulum of blend latex was prepared by means of coagulation with 0.2% $H_2SO_4$. The samples of blend rubber were prepared by washing and drying of the coagulum.

## Recipe and Vulcanization

The recipe used in the present experiments is shown in Table I. The ingredients of this recipe were so adjusted as to make curing time of NR and SBR component of blends agree. Compounding was carried out by roll mixing at 50–60°C. Vulcanization was by the press vulcanization method; the temperature was 141°C., and the optimum cure time was determined.

TABLE I
Recipe

| Component | Parts | | | | | | |
|---|---|---|---|---|---|---|---|
| NR | 100 | 80 | 65 | 50 | 35 | 20 | 0 |
| SBR | 0 | 20 | 35 | 50 | 65 | 80 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Sulfur | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Benzothiazyl disulfide | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Tetramethylthiuram disulfide | 0 | 0.04 | 0.07 | 0.10 | 0.13 | 0.16 | 0.20 |
| Diethylene glycol | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Hard clay | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

## Physical Properties

On varying the blending ratio and method of blending, the Mooney viscosity, mill shrinkage, and tensile properties of blend rubber, compounded rubber, and vulcanized rubber were measured. The conditions of these tests were as shown below.

**Mooney Viscosity.** The ML-4 value was obtained after preheating for 1 min. at 100°C. by use of a large rotor, 4 min. after commencement of measurement.

**Mill Shrinkage.** The shrinkage ratio of sheets of blend rubber compounded was determined as

$$\text{Shrinkage ratio} = [(l_0 - l) \times 100/l_0]$$

where $l_0$ is the original length between two marks on the surface of sheetings, $l$ is the length after 24 hr. at room temperature.

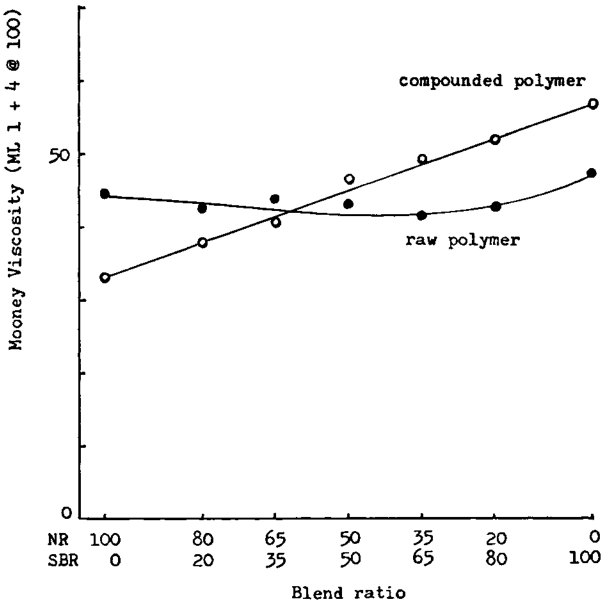


Fig. 3. Mooney viscosity vs. blend ratio for roll blending at low temperature by the raw rubber method.

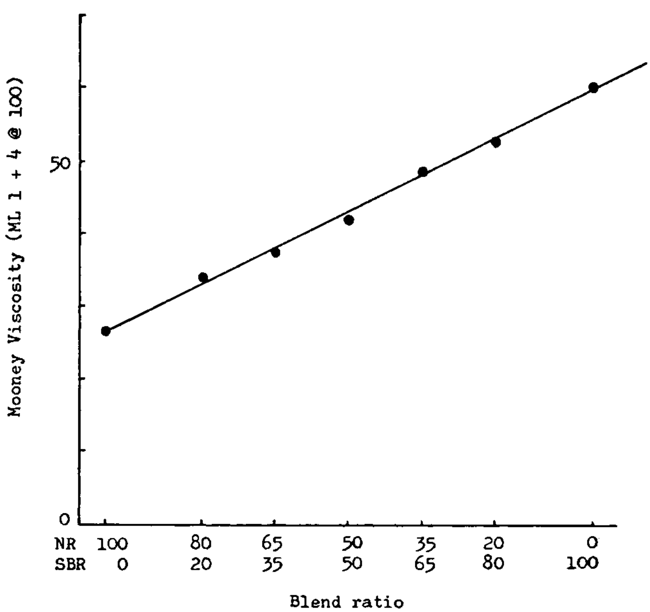


Fig. 4. Mooney viscosity vs. blend ratio in roll blending at low temperature by the masterbatch method.

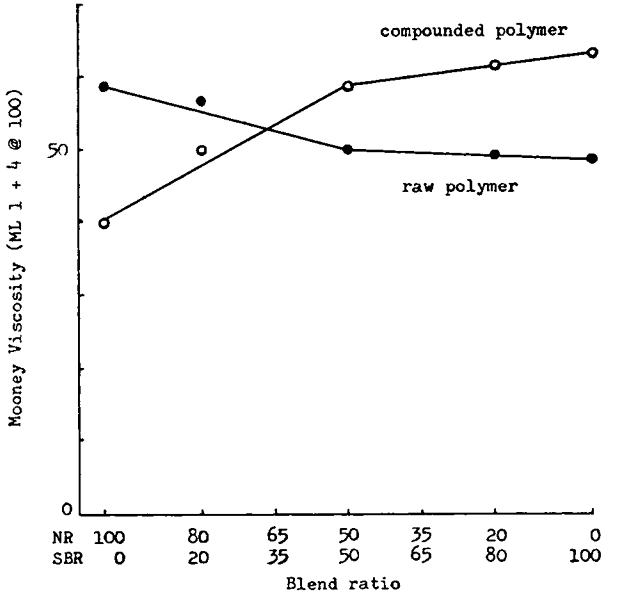


Fig. 5. Mooney viscosity vs. blend ratio in Banbury mixer blending.

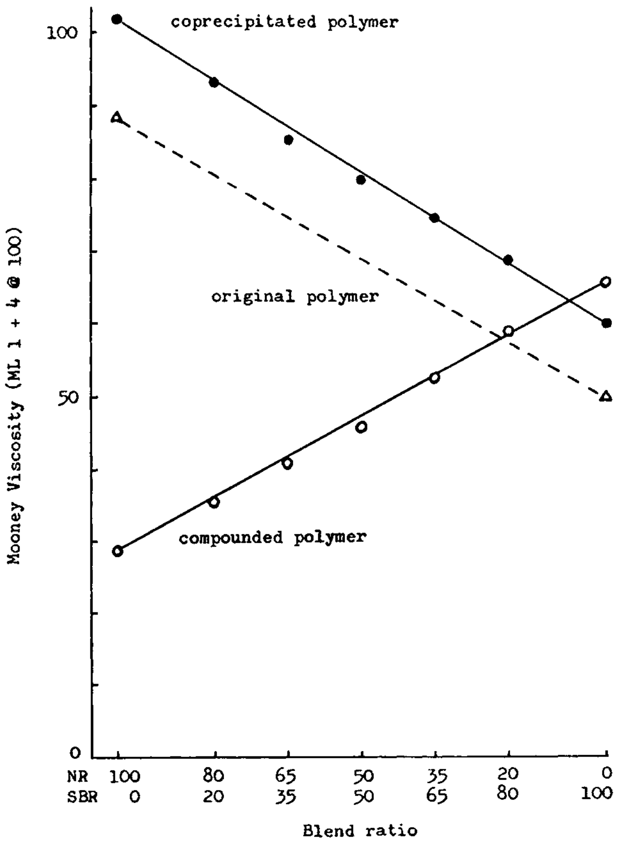


Fig. 6. Mooney viscosity vs. blend ratio in solution blending.

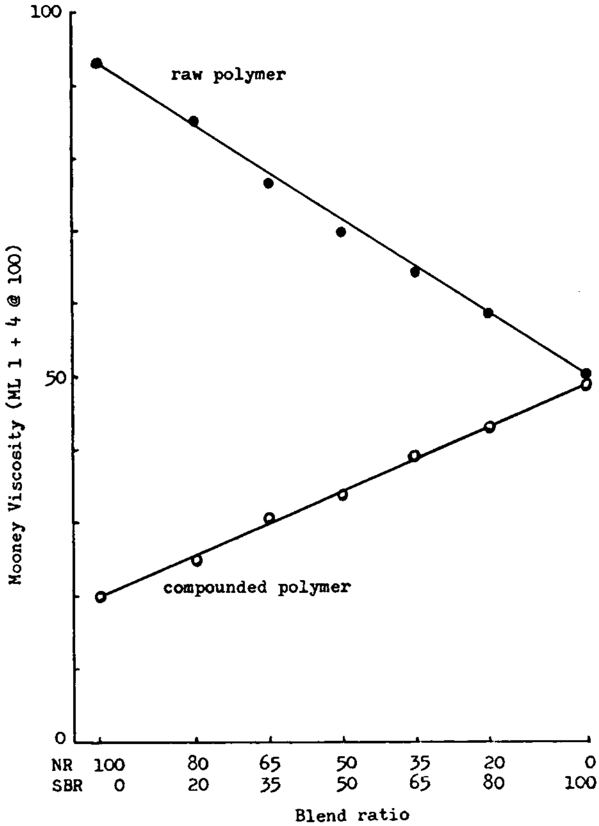


Fig. 7. Mooney viscosity vs. blend ratio in latex blending.

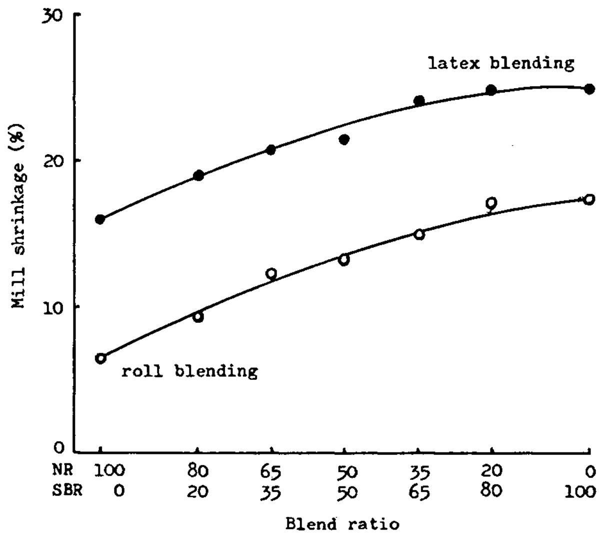


Fig. 8. Mill shrinkage vs. blend ratio of compounded polymer in latex and roll blending methods.

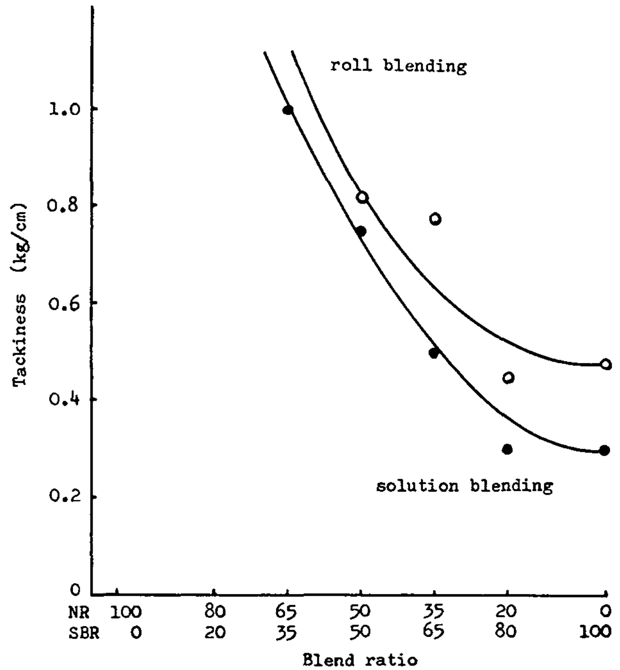


Fig. 9. Tackiness vs. blend ratio of compounded blends for roll and solution blending methods.

**Tensile Properties.** The tensile properties, hardness, and other properties were measured by the usual methods.

## RESULTS AND DISCUSSION

### Effect of Mastication of Raw Rubber

In this study, as compounding was carried out by roll mixing in every blending method, the properties of all blends are affected by the breakdown of polymer caused by roll milling. Therefore, the effect of mastication of raw rubber was studied.

The relations between Mooney viscosity and number of mastications are shown in Figure 1. The mastication was carried out at low (50–60°C.) and high (120–130°C.) temperatures.

At high temperature, the Mooney values of NR decrease gradually, while those of SBR increase slightly in the initial stage and then remain almost unchanged. At low temperature, the Mooney values of NR decrease markedly, while those of SBR decrease slightly in the initial stage then remain about the same. Therefore the Mooney viscosities of NR and SBR are reversed after about 10 mastication cycles. This is expected on the basis of previous studies of mastication of NR and SBR.[13]

The relations between Mooney viscosity and blend ratio of NR/SBR

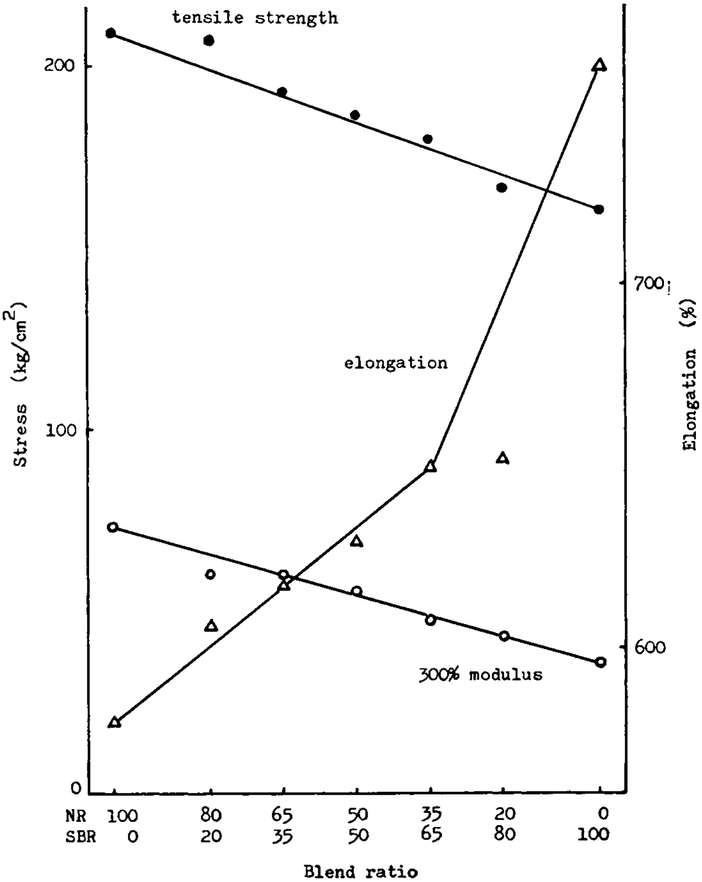


Fig. 10. Tensile properties of vulcanizates vs. blend ratio in roll blending by the raw rubber method.

blends for varying number of cycles masticated at low temperature are shown in Figure 2. For low or high numbers of mastication cycles, i.e., 6 or 16, respectively, the Mooney viscosities change linearly with blend ratios, while with 11 mastication cycles the Mooney viscosities do not change, being independent of the blend ratios. This fact shows that in low-temperature mastication the curves of Mooney viscosities of NR intersect those for SBR at a point corresponding to about 10 mastication cycles.

Therefore, in the following experiments the mastications of NR/SBR blends were carried out under these conditions in which the Mooney viscosity is independent of the blend ratios.

## Comparison of Blending Methods

In roll blending, the masterbatch method was easier and more practical for obtaining NR/SBR blends than the raw rubber method.

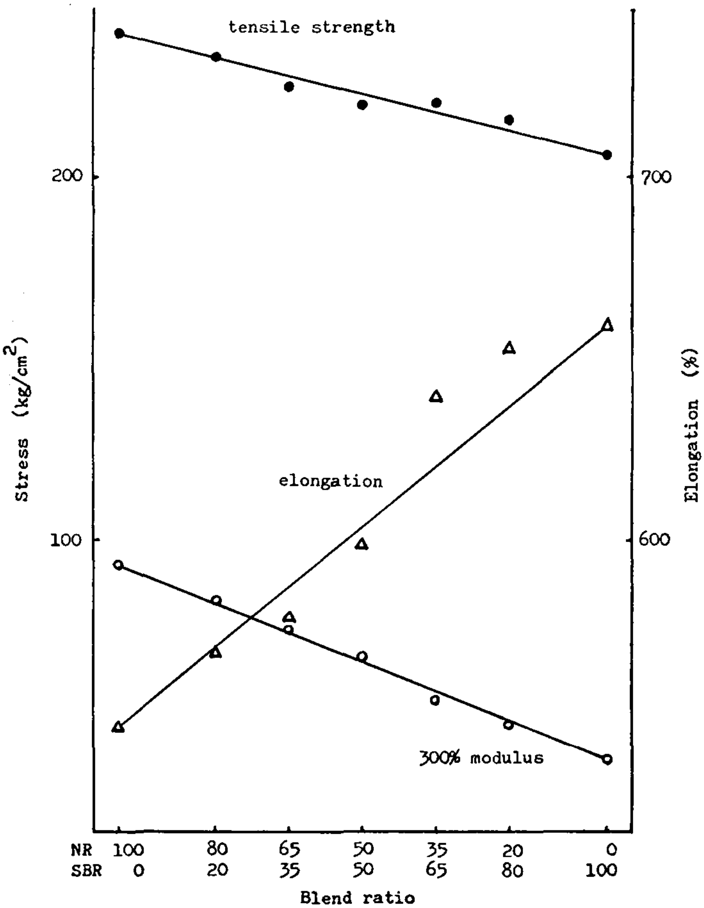


Fig. 11. Tensile properties of vulcanizates vs. blend ratio in roll blending by the masterbatch method.

Banbury mixer blending was a simple and easy method for blending NR and SBR, but it was difficult to obtain smooth sheets of blends, so roll mixing process was required after Banbury mixing.

The solution blending and latex blending were effective methods. However, they are not practical for manufacturing.

## Properties of Compounded Blends

The relations between Mooney viscosity and blend ratios of NR/SBR blends are shown in Figures 3–7.

In the roll blending method, the Mooney viscosities show a line as relation to the blend ratios. The relations described are more plainly shown in the blends after addition of compounding ingredients. Furthermore, the masterbatch method shows more apparent straight line than the raw rubber method.

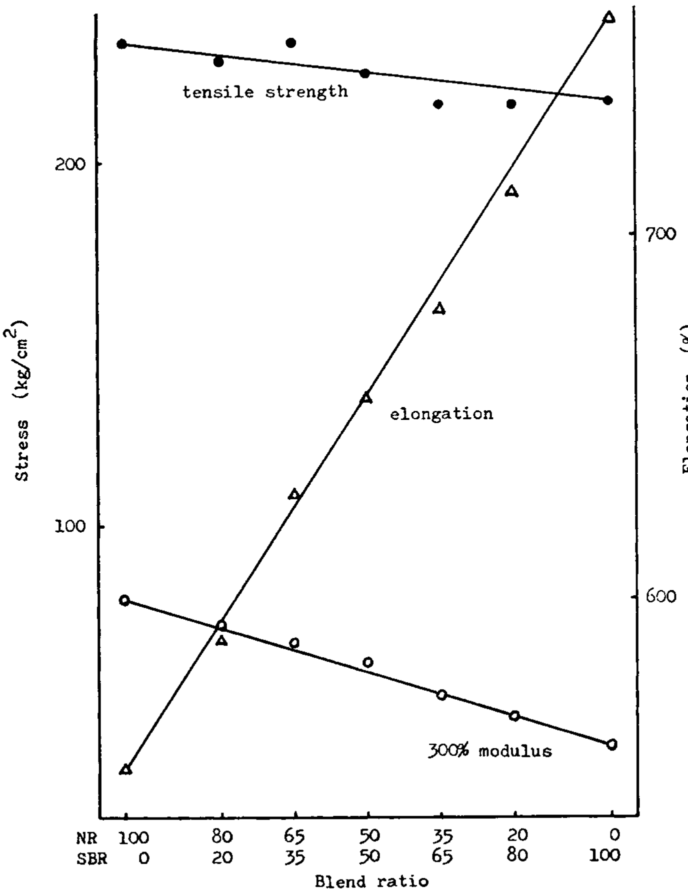


Fig. 12. Tensile properties of vulcanizates vs. blend ratio in Banbury mixer blending.

In Banbury mixer blending, the plots of Mooney viscosity versus blend ratios show more scatter than those in roll blending. With compounding on the roll into blends, however, the scatter of the plots apparently decreases.

In solution blending and latex blending, straight-line relationships of the Mooney viscosity and blend ratios are clearly shown. These follow the equation:

$$M_{ns} = C_n M_n + C_s M_s$$

where $M_{ns}$ is Mooney viscosity of the NR/SBR blend, $C_n$ and $C_s$ are concentrations of NR and SBR, respectively, and $M_n$ and $M_s$ are Mooney viscosity of NR and SBR components, respectively.

Figure 6 shows that the raw rubbers obtained by coprecipitation from solution have higher Mooney viscosities than the original rubbers. An explanation for this may be that the low molecular weight rubbers and/or

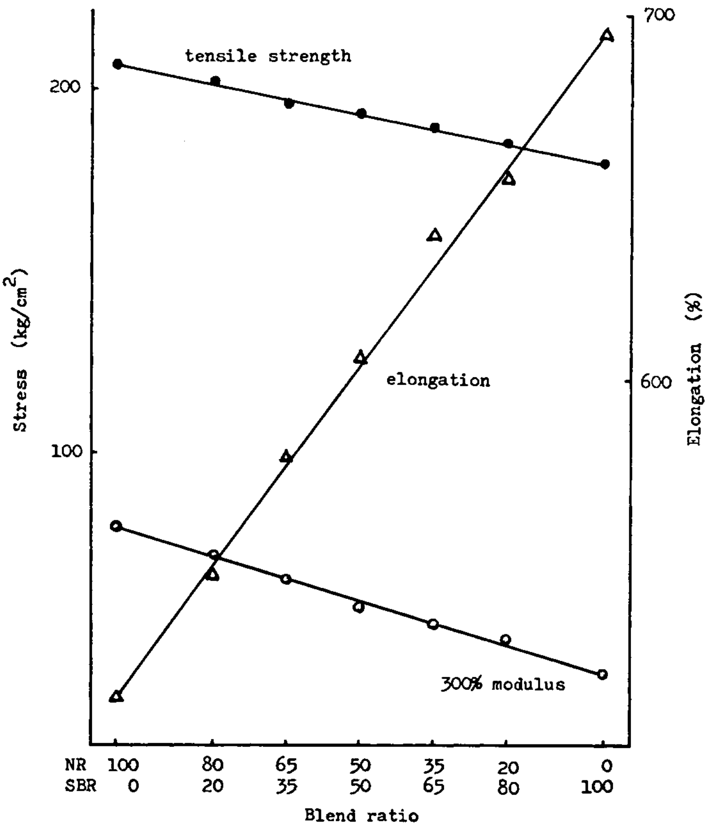


Fig. 13. Tensile properties of vulcanizates vs. blend ratio in solution blending.

nonrubber materials (low molecular materials) are extracted with methanol on precipitating from solution.

The change of Mooney viscosities of blends versus blend ratios shows a change on addition of compounding ingredients, that is, before compounding the Mooney values of NR-rich blends are higher than those of SBR-rich ones, while after compounding the Mooney values of NR-rich blends are lower. On the other hand, the Mooney values of SBR-rich blends are nearly constant. It is considered that NR is being broken down through compounding on the roll, but SBR is not. Such a conclusion would suggest that the behavior of NR and SBR in NR/SBR blends are independent of one another in compounding on roll.

The mill shrinkage and the tackiness of sheeting versus blend ratios are shown in Figures 8 and 9, respectively. Both properties show a straight-line relationship versus blend ratios.

## Tensile Properties of Vulcanizates

The relations between the properties and blend ratios of the vulcanizates of NR/SBR blends are shown in Figures 10–14.

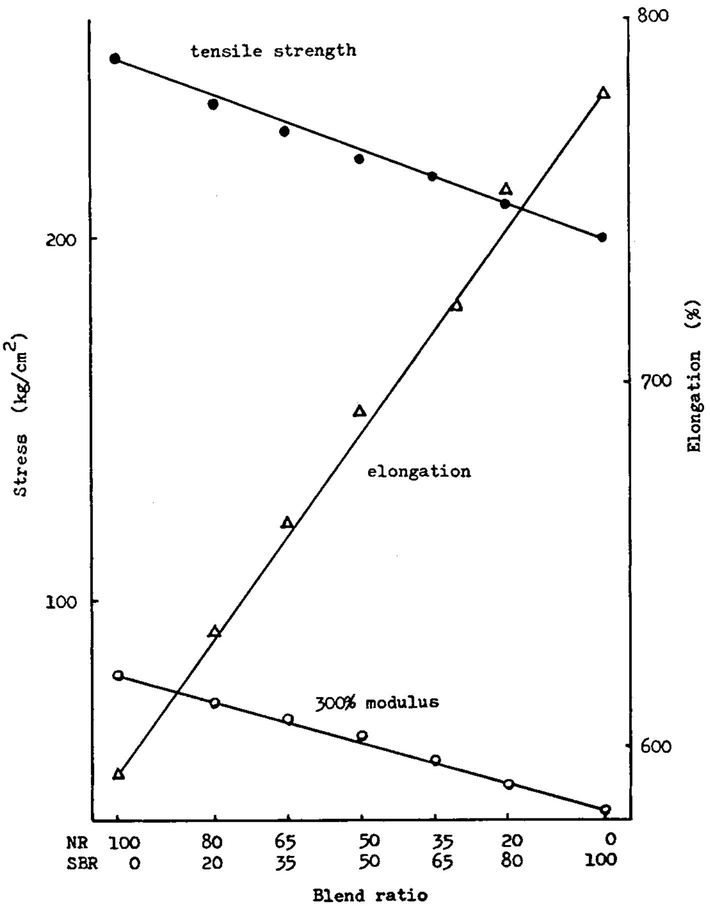


Fig. 14. Tensile properties of vulcanizates vs. blend ratio in latex blending.

In roll blending, the properties of blends obtained by the masterbatch method show more clearly a straight line relationship than those obtained by raw rubber method. The blends undergoing Banbury mixer blending also show the same tendency after compounding. Solution and latex blending clearly show, of course, the linearity in the relations of the properties and blend ratios of NR/SBR blends.

Thus, it was found that in the blends of NR and SBR which were similar to one another in their properties, the plots of the properties of blends showed a straight line versus blend ratios, independent of the method of blending.

## Uniformity of Blends

The masterbatch method in roll blending was found to be a practical blending method with which it was easy to obtain uniform blends. The uniformity of the blends so obtained was studied by observing the change of specific gravity of blends. The results are shown in Figure 15.

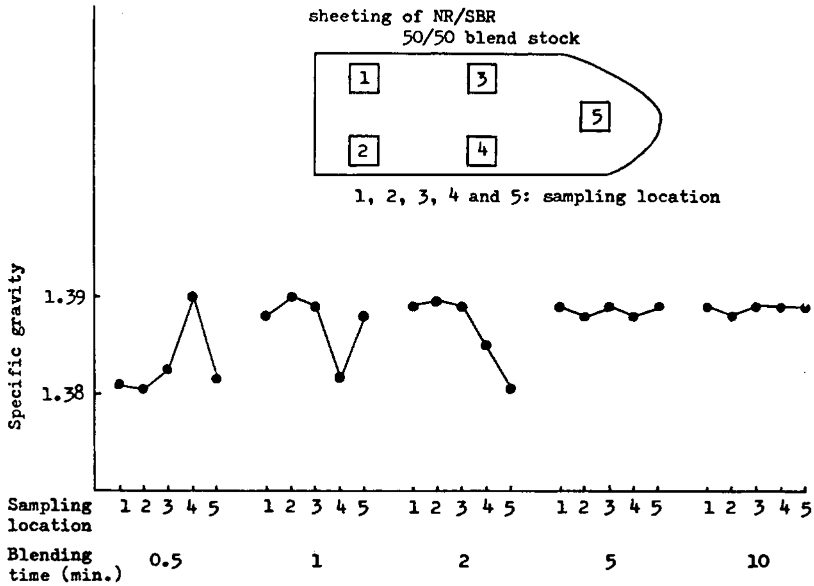


Fig. 15. Scatter of specific gravity vs. blending time data for NR/SBR blend stock subjected to roll blending by the masterbatch method.

The masterbatches of NR and SBR compounds were blended at an equal blend ratio (50/50). Sheets were obtained after blending for 0.5, 1, 2, 5, and 10 min., and then the specimens for measuring specific gravity were taken at various locations (described in Figure 15) on the sheetings.

The specific gravity data show scatter at each location for specimens blended for less than 2 min. from starting of blending. The scatter, however, decreases at blending times of 5 min. or more. This indicates that in these blends the uniform blends could be obtained in about 5 min. blending time.

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## Résumé

Les relations entre les propriétés et les rapports de mélange de caoutchouc naturel et de caoutchouc styrène–butadiène ont été étudiées en comparant quatre méthodes de mélanges. C'est ainsi que l'on a étudié les relations entre les propriétés de vulcanisats de mélanges et de mélanges non-vulcanisés, de mélanges dans différents rapports qui ont été préparés soit par mélange en solution soit sous forme de latex, soit sous forme de calendrage, soit via un mélangeur de Banbury. Parmi les méthodes pratiques de mélange des caoutchoucs telle que le mélange par calendrage ou par mélangeur de Banbury, le premier est plus effectif pour obtenir des mélanges uniformes que le second. Dans le calendrage, il est plus effectif de mélanger le caoutchouc naturel et le copolymère styrène–butadiène-caoutchouc au départ d'une grande cuve qui contient au départ les différents ingrédients plutôt que mélanger le caoutchouc brut. Dans les mélanges par solution ou par latex, on obtient des mélanges très uniformes qui peuvent être aisément réalisés comme prévu. On a trouvé toutefois que les propriétés de ces mélanges caoutchouc naturel/caoutchouc styrène–butadiène préparés avec précaution, montraient une ligne droite en fonction des rapports du mélange indépendamment des méthodes de préparation de ces mélanges.

## Zusammenfassung

Die Beziehungen zwischen den Eigenschaften und dem Mischungsverhältnis von Naturkautschuk (NR)- und Styrol–Butadien-Kautschuk (SBR)-Mischungen wurde für vier Mischungsverfahren untersucht. Es wurden die Beziehungen zwischen den Eigenschaften von nicht vulkanisierten und vulkanisierten Mischungen und Mischungsverhältnissen von Mischungen, welche durch Mischung aus Lösung, durch Latexmischung, Kalandermischung und Mischung im Banbury Mischer hergestellt worden waren, untersucht. Von den früher verwendeten Kautschukmischungsmethoden wie Kalandermischung und Banbury Mischer-Mischung ist die erstere zur Gewinnung einheitlicher Mischung wirksamer als die letztere. Bei der Kalande mischung ist es besser, NR und SBR als "Master"-Ansatz mit den vorher zugesetzten Füllstoffen zu mischen als den Rohgummi zu mischen. Bei der Lösungs- und Latexmischung können wie erwartet leicht einheitliche Mischungen erhalten werden. Es wurde aber festgestellt, dass die Eigenschaften der unter den entsprechenden Vorsichtsmassnahmen hergestellten NR-SBR-Mischungen unabhängig von den Mischungsverfahren eine geradlinige Abhängigkeit ihrer Eigenschaften vom Mischungsverhältnis aufwiesen.

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