

Studies on Polymer Blends. III. Butadiene-Acrylonitrile Copolymer and Polybutadiene-Polyacrylonitrile Blend

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Synopsis

The properties of butadiene-acrylonitrile copolymers were compared with those of polybutadiene-polyacrylonitrile blends. Also, the properties of copolymers having an acrylonitrile unit content of about 30% were compared with those of polymer blends having the same acrylonitrile unit content, i.e., NBR-NBR, polybutadiene-NBR, and polyacrylonitrile-NBR, having different acrylonitrile unit contents. These blends were prepared by roll blending and the vulcanizates were prepared by sulfur cure. The properties of the copolymers were markedly different from those of the blends, that is, in the blends the properties showed a linear relationship with their blending ratios, while in the copolymers the properties showed a curvilinear relationship. In the cases of the polymer blends having a constant acrylonitrile unit content, those blends which were prepared by blending two polymers having similar acrylonitrile unit contents showed better properties than the ones having very different acrylonitrile unit contents.

INTRODUCTION

Recently, the consumption of butadiene-acrylonitrile rubber (NBR) has increased by special use in the rubber industry. However, only a few studies have been made of its basic properties, as in the case of butadiene-styrene rubber.¹ In the cases of butadiene-styrene polymer systems, studies of the blending method and of the comparison of the properties of copolymers and blends have been presented by the authors.^{2,3}

In this study, the properties of butadiene-acrylonitrile copolymers were compared with those of polybutadiene-polyacrylonitrile blends and other blends. In the butadiene-acrylonitrile copolymer composition, it was difficult to obtain homogeneous copolymers having acrylonitrile unit contents of more than 50-60% because of the monomer reactivity ratio. The copolymers, used, therefore, were NBRs having acrylonitrile unit contents of about 10, 20, 30, 40, and 50%. The blends used were prepared by roll blending and consisted of four systems, i.e., polybutadiene-polyacrylonitrile,

NBR-NBR, polybutadiene-NBR, and polyacrylonitrile-NBR blends. The NBR-NBR blends were studied in order to clarify the effect of the distribution of the acrylonitrile unit content in the butadiene-acrylonitrile polymer systems. The polybutadiene-NBR and the polyacrylonitrile-NBR blends were studied for the cases where the acrylonitrile unit content of one NBR was zero in the NBR-NBR blends and where the butadiene unit content of one NBR was zero.

From the results, it was found that in the blends the properties showed a linear relationship with their blending ratios, while in the copolymers the properties showed a curvilinear relationship. In the blends, the blends which were prepared by blending two polymers having acrylonitrile unit contents close to one another showed better properties than ones having acrylonitrile unit contents which were very different. Polyacrylonitrile does not soften under the conditions of roll blending and is not compatible with polybutadiene and with butadiene-acrylonitrile copolymers, so that it was very difficult to blend polyacrylonitrile with the polymers. The difficulty of blending polyacrylonitrile was improved by adding a plasticizer or solvent such as dioctyl phthalate or dimethylformamide, but the homogeneity of the blends was not improved.

EXPERIMENTAL

Materials

The butadiene-acrylonitrile copolymers and the polybutadiene used were prepared by emulsion polymerization at low temperature in the pilot plant of the Japanese Geon Co. Ltd. They are shown in Table I. The polyacrylonitrile and the compounding ingredients used were commercially available ones.

Characterization of Starting Material

The specific gravities, intrinsic viscosities, refractive indices, acrylonitrile contents, and Mooney viscosities of the starting material polymers were determined.

TABLE I
Properties of Starting Material Polymers

Polymer No.	Specific gravity	Intrinsic viscosity (in toluene)	Refractive index	Acrylonitrile unit content, %
1	0.911	1.55	1.5158	0
2	0.938	1.20	1.5149	10.4
3	0.968	0.86	1.5143	27.9
4	0.986	0.82	1.5142	32.1
5	1.001	0.90*	1.5138	40.3
6	1.032	0.62*	1.5051	48.8

* In methyl ethyl ketone.

Specific Gravity. The specimens were hot-pressed at 120°C under 150 kg/cm² for 10 min to make them uniform and smooth, then weighed in air and in ethanol at 25 ± 0.5°C. The specific gravities were calculated from

$$D = D_0M/(M - M')$$

where D and D_0 are the specific gravities of the specimens and of ethanol, respectively, and M and M' are the weights of the specimens in air and in ethanol, respectively.

Intrinsic Viscosity. The polymers having butadiene unit contents of more than 60% were purified by precipitation from toluene solution with methanol, and ones having butadiene unit contents of less than 60% were purified by precipitation from methyl ethyl ketone solution in methanol. The purified polymers were dissolved in toluene or methyl ethyl ketone, then the solutions were used for determining the intrinsic viscosities at 25°C.

Refractive Index. The refractive indices of the polymers were measured by the usual method.

Acrylonitrile Content. The Kjeldahl analytical method was used.

Mooney Viscosity. The specimens were preheated for 1 min, then their viscosities were measured after 4 min at 100°C by means of a large rotator.

Blending, Compounding, and Vulcanization

The blending of the polymers and the mixing of the compounding ingredients were carried out on a laboratory roll mill at a roll temperature of about 40°C. The starting material polymers were masticated for several minutes, then the compounding ingredients were added in the order stearic acid, zinc oxide, accelerator, and sulfur. The recipe for the compounding is shown in Table II. The vulcanization was carried out with sulfur by means of a hot press at 150°C.

TABLE II
Compounding Recipe

	Parts
Polymer	100
Stearic acid	0.5
Zinc oxide	25.0
Sulfur	1.5
Accelerator CZ	1.5

Characterization of Green Stocks and Vulcanizates

The Mooney viscosity, Mooney scorch time, tensile properties, hardness, rebound, compression set, and oil resistance were measured.

Mooney Viscosity. The specimens were preheated for 1 min, then the viscosities were measured after 4 min by means of a large rotator at 100°C.

Mooney Scorch Time. The specimens were preheated for 1 min, then the scorch times at five point up were measured with a small rotator at 120°C.

Mill Shrinkage. The shrinkage ratios of the sheets of the stocks were measured. The shrinkage ratio is given by the following formula:

$$\text{Mill shrinkage (\%)} = (150 - L)100/150$$

where 150 is the length (in centimeters) between two lines marked on the surface of the sheet just after sheeting and L is the length between the two lines after 1 hr at room temperature.

Rebound. The rebound elasticities were measured by a Lüpke type apparatus.

Oil Resistance. The swelling of the samples immersed in ASTM #3 oil at 70°C was measured.

The other properties were measured by the usual testing methods.

RESULTS AND DISCUSSION

Properties of Initial Polymers

The properties of the polybutadiene and the butadiene-acrylonitrile copolymers used are shown in Table I. The specific gravities of the polymers increased linearly with increasing content of acrylonitrile units. Their refractive indices showed a tendency to decrease linearly. Their intrinsic viscosities decreased linearly with increasing content of acrylonitrile units.

Properties of Butadiene-Acrylonitrile Copolymers and Polybutadiene-Polyacrylonitrile Blends

The blending of the polymers and the mixing of the compounding ingredients were carried out on a laboratory roll mill at a roll temperature of about 40°C. The processing of both the copolymers and the blends tended to become difficult as the acrylonitrile unit contents decreased. The blending of polybutadiene with polyacrylonitrile was very difficult. The polyacrylonitrile were blended as a fine powder and as a powder swollen with dioctyl phthalate (plasticizer), and it was found that in the cases of such polybutadiene-polyacrylonitrile blends which had no compatibility with one another, the swelling of the polyacrylonitrile with plasticizer improved the processability for blending.

The Mooney values of the copolymers and of the blends are shown in Figure 1. In the copolymers, Mooney viscosities of both the starting materials and the stocks decreased as the acrylonitrile unit contents of the copolymers increased. This tendency was in agreement with the decrease in the intrinsic viscosities of the copolymers used. The Mooney scorch times

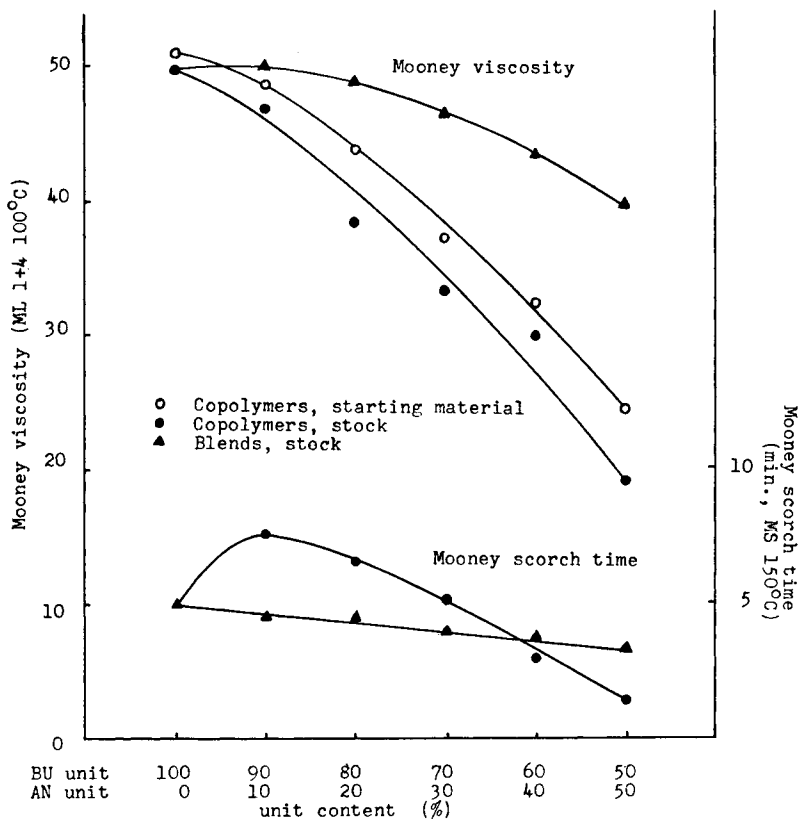


Fig. 1. Comparison of Mooney values for the polymers and of stocks with those for the polybutadiene-polyacrylonitrile blends.

of the copolymers showed a tendency to shorten as their acrylonitrile unit contents increased. In the blends, the tendency of the Mooney values was similar to those of the copolymers, but the degree of the change was not so marked as in the cases of the copolymers.

Properties of the Vulcanizates of Copolymers and Polybutadiene-Polyacrylonitrile Blends

The hardness and the tensile properties of the vulcanizates are shown in Figure 2. In the copolymers, the hardness of the vulcanizates was independent of the acrylonitrile unit contents, while in the blends, the hardness increased as the acrylonitrile unit contents increased, except in the cases of those blends containing plasticizer which did not show any change. In the copolymers, the tensile strengths and the elongations showed a curvilinear relationship, while in the blends they showed a linear relationship. But in the cases of the blends containing a plasticizer the elongations increased linearly with increasing acrylonitrile unit contents.

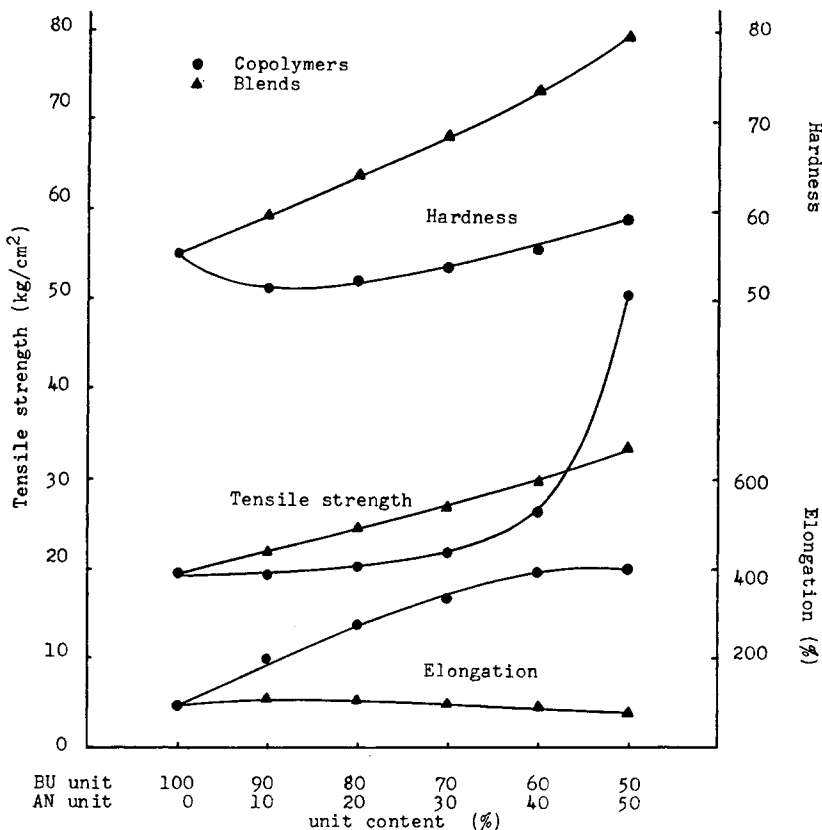


Fig. 2. Comparison of hardness and tensile properties of the vulcanizates of the copolymers with those for the polybutadiene-polyacrylonitrile blends.

The rebound and the compression set of the vulcanizates are shown in Figure 3. In the copolymers, the rebounds decreased markedly and curvilinearly, while in the blends they decreased slightly and linearly with increasing acrylonitrile unit contents. In the copolymers, the compression sets were not so much affected by the acrylonitrile unit contents and were of a rather lower level. In the blends, the compression sets increased linearly with increasing acrylonitrile unit contents.

The oil resistances of the vulcanizates are shown in Figure 4. In the copolymers, the oil resistances were improved by addition of acrylonitrile units but were independent of their acrylonitrile unit contents. In the blends, the oil resistances increased linearly with increase in their acrylonitrile unit contents. The extent of the increase in the oil resistance of the blends, however, was lower than for the copolymers.

The properties of the butadiene-acrylonitrile copolymers showed a curvilinear relationship versus their acrylonitrile unit contents. This

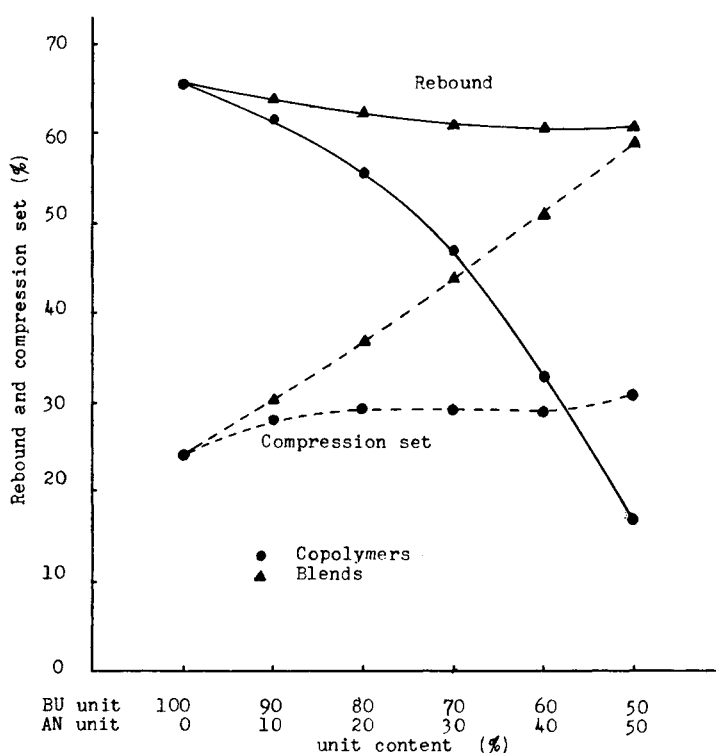


Fig. 3. Comparison of rebound and compression set of the vulcanizates of the copolymers with those for the polybutadiene-polyacrylonitrile blends.

tendency is the same as that shown by butadiene-styrene copolymers.² In the blends, the properties showed a linear relationship versus their acrylonitrile unit contents. There was no compatibility between the polybutadiene and the polyacrylonitrile. In addition, the polyacrylonitrile did not soften under the conditions of the roll milling. The polyacrylonitrile, therefore, was probably dispersed in the polybutadiene heterogeneously like an inert filler.

From the results, it was found that the properties of the copolymers were affected by their monomer unit components, while in the blends the properties were affected by the intermolecular force of polyacrylonitrile. It was also found that in the process of blending the polyacrylonitrile into the polybutadiene, it was made easier by swelling it with a plasticizer such as dioctyl phthalate. The state of the blend, however, was not improved.

Properties of the NBR Blends Having Different Acrylonitrile Unit Contents

In order to clarify the effect of the distribution of the acrylonitrile units in the blends, the properties of the blends which were prepared by blending two butadiene-acrylonitrile copolymers (NBR) having different acryloni-

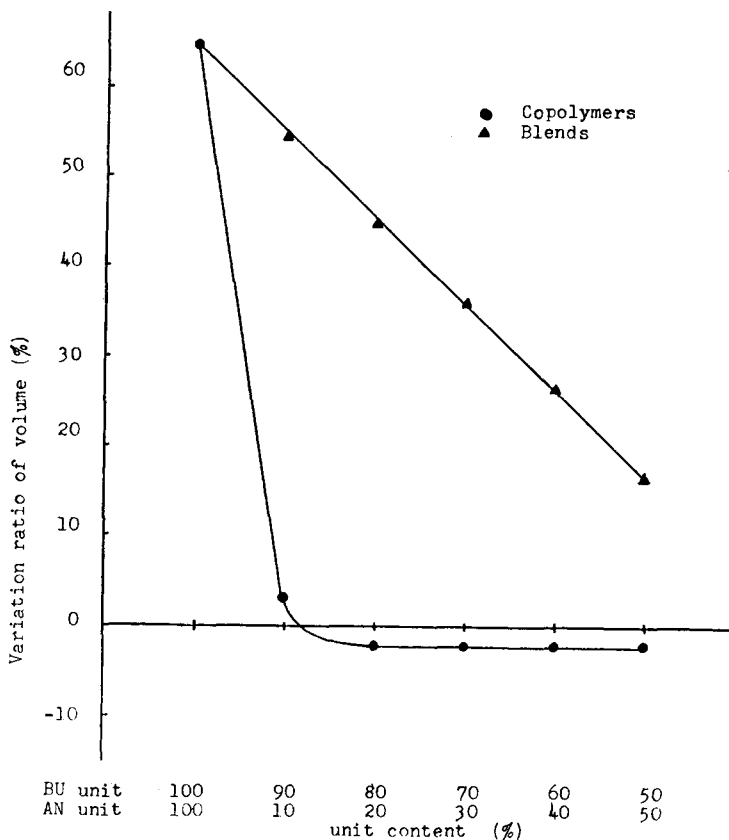


Fig. 4. Comparison of oil resistance of the vulcanizates of the copolymers with those for the polybutadiene-polyacrylonitrile blends.

trile unit contents were compared with those of a copolymer having the same acrylonitrile unit content.

The blends which had an acrylonitrile unit content of about 30% were prepared by means of blending two NBR copolymers having different acrylonitrile unit contents. These blends, NBR copolymers, and blending ratios are shown in Table III, and the recipe for the compounding of these blends is shown in Table IV.

The hardnesses, the tensile properties, and the oil resistances of the vulcanizates of the NBR-NBR blends are shown in Figure 5. The hardness and the moduli of the vulcanizates increased as the distribution of their acrylonitrile unit contents became broad, while the tensile strength, the elongation, and the oil resistance decreased.

In the cases of the blends of two NBR copolymers having different acrylonitrile unit contents, the NBR of higher acrylonitrile content showed such a strong intermolecular force because of its polarity due to $-\text{C}\equiv\text{N}$ that its compatibility with the NBR of lower acrylonitrile content

TABLE III
 Copolymers and Blend Ratios

Blend no.	AN unit content of one copolymer	AN unit content of the other copolymer	Blend ratio
1	32	28	1:1
2	32	20	5:1
3	40	20	1:1
4	48	20	5:9

decreased. In the case of blends which consisted of two NBR copolymers of similar acrylonitrile unit contents, their compatibility with one another did not decrease, and uniform blends were easily obtained. It seems, therefore, that even in blends having similar acrylonitrile unit contents, the

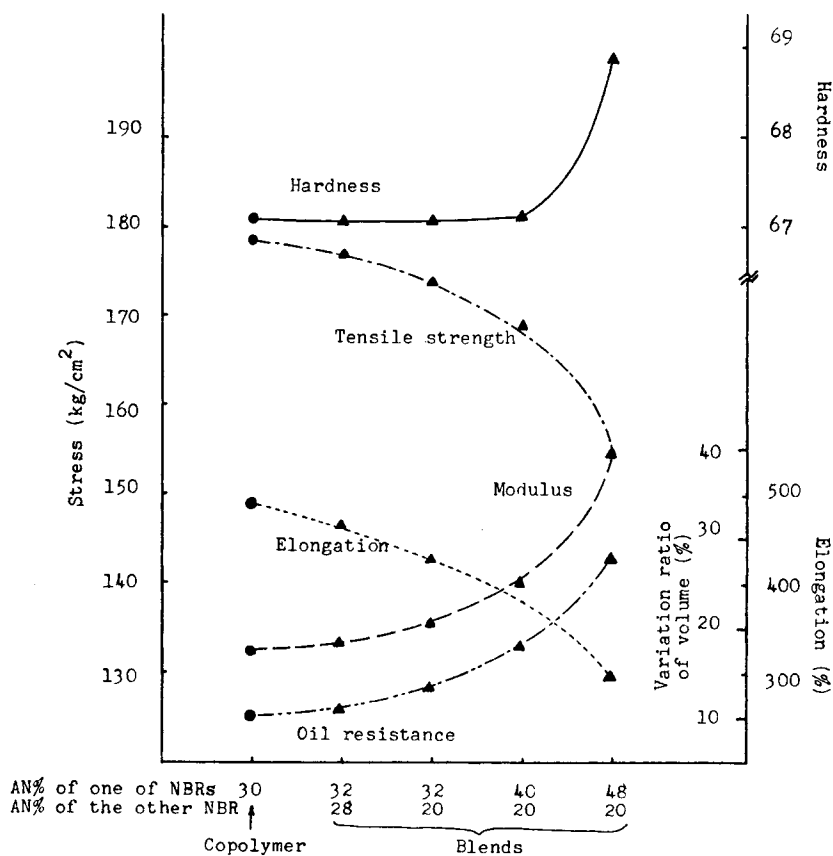


Fig. 5. Comparison of hardness, tensile properties, and oil resistance of the vulcanizates of the copolymers with those for the NBR-NBR blends.

TABLE IV
Recipe for NBR-NBR Blends

	Parts
Polymer	100
Zinc oxide	5.0
Sulfur	1.5
Stearic acid	1.0
Carbon black SRF	65.0
Dioctyl phthalate	15.0
Accelerator TS	0.4

broader the distribution of the monomer units, the poorer the properties of the blends.

Properties of Blends of NBR with Polybutadiene

In blends of two NBR copolymers of different acrylonitrile unit contents, for cases where the acrylonitrile unit content of one of the pair was zero, a

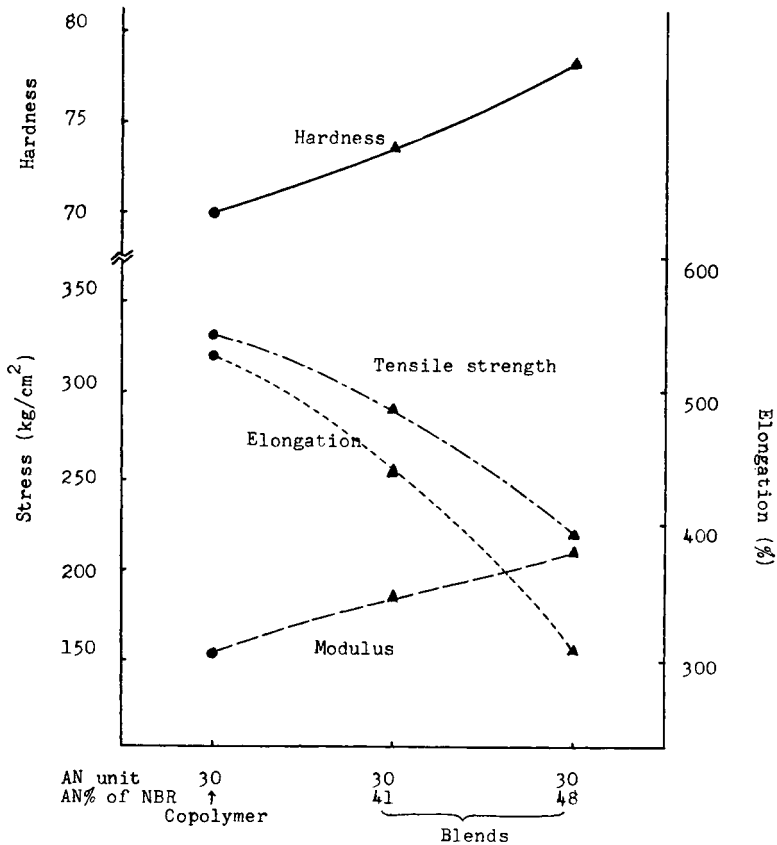


Fig. 6. Comparison of hardness and the tensile properties of the vulcanizates of the copolymers with those for the polybutadiene-NBR blends.

TABLE V
Recipe for Polybutadiene-NBR Blends

	Parts
Polymer	100.0
Zinc oxide	5.0
Sulfur	1.5
Stearic acid	1.5
Carbon black	45.0
Accelerator DM	1.5
Accelerator D	0.5
Antioxidant D	1.0

polybutadiene was used. The acrylonitrile unit contents of the NBR copolymers used were 41 and 48%. These NBRs were blended with polybutadiene on a roll mill in order to obtain blends having an acrylonitrile unit content of about 30%, and the properties of the blends were compared with those of a copolymer having the same acrylonitrile unit content. The recipe for the blends is shown in Table V.

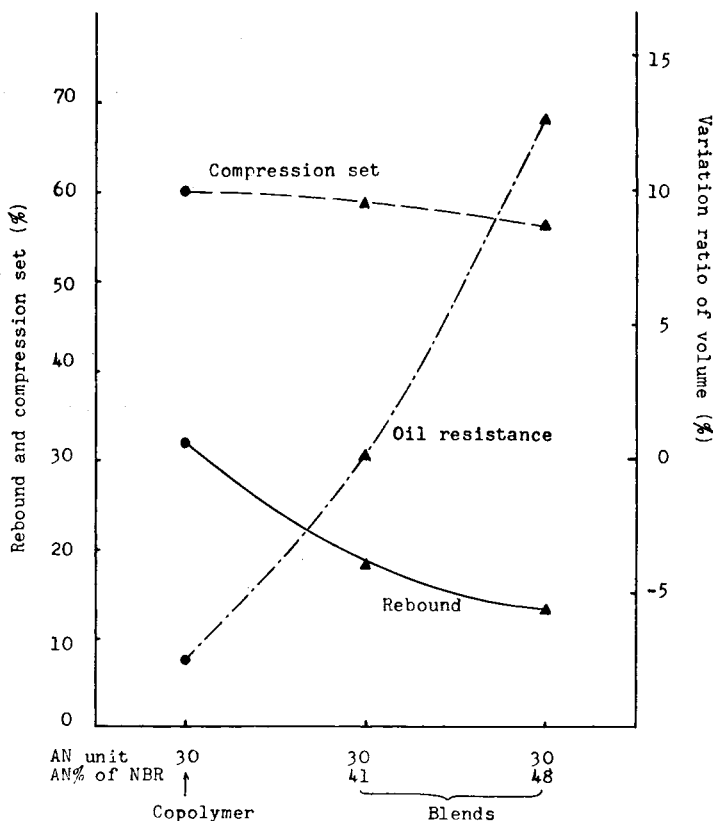


Fig. 7. Comparison of rebounds, compression sets, and oil resistances of the vulcanizates of the copolymers with those for the polybutadiene-NBR blends.

The properties of the vulcanizates of polybutadiene-NBR blends are shown in Figures 6 and 7. The properties show the same tendency as the NBR-NBR blends, i.e., the properties of the blends having a broad distribution of acrylonitrile unit content are poorer than those of blends having a narrow distribution.

Properties of Blends of NBR with Polyacrylonitrile

As the opposite case to the blends of NBR with polybutadiene, the blends of NBR with polyacrylonitrile were studied. The blending of NBR with polyacrylonitrile was carried out on a roll mill, but uniform blends were not obtained, because the compatibility of polyacrylonitrile with NBR was not good.

In this section, therefore, polyacrylonitrile was swollen with dimethylformamide, and then it was blended with NBR. The acrylonitrile unit content of the NBR was 49%. The blending was carried out on a laboratory roll mill at 160°C, and then the dimethylformamide was evaporated on the roll mill.

The roll blending of the polyacrylonitrile containing dimethylformamide was a little easier than that of polymer without it. Also, the polyacrylonitrile blends containing dimethylformamide were more uniform than those without dimethylformamide. Thus polyacrylonitrile containing dimethylformamide had a reinforcing effect on the blends, but the polyacrylonitrile without dimethylformamide did not.

It was found that the properties of the polymer blends were markedly affected by the uniformity of the blends.

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