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Anisotropic Shrinkage of Injection-Molded Rubber

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Synopsis

The anisotropic characteristics of injection-molded flat rubber sheets were investigated. The shrinkage and mechanical properties were measured in two directions: parallel and perpendicular to the flow direction. The results showed that (1) the shrinkage in the parallel direction is larger than that in the perpendicular direction, (2) such anisotropic shrinkage increases with the increase of vulcanization temperature and flow distance, (3) similar anisotropy was also noticed in 300% modulus, tensile strength, and elongation. Two kinds of orientation, "shear orientation" and "expanded orientation," were observed. The former occurs by plug flow, and the latter by the expansion of the materials. The shrinkage was independent of the expanded orientation but was strongly associated with the shear orientation, while the mechanical properties were affected by the expanded orientation.

INTRODUCTION

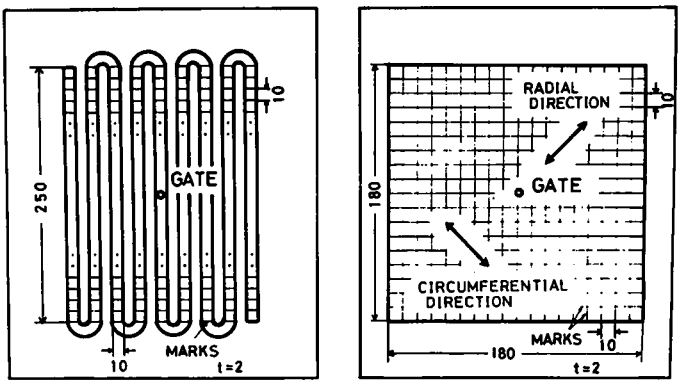
It has been pointed out that thin injection-moldings of rubber and plastics possess considerable anisotropy. These anisotropic characteristics of injection-molded thermoplastic materials have been studied,[1,2] but the reports dealing with rubber are very few. In the injection-molding of rubber in general, it is well known that shrinkage is more than that of compression molding. However, no detailed research has been made on the cause of the shrinkage and on the relation between shrinkage and molding conditions.

Therefore, studies were made on the effects of the shrinkage depending on the flow distance, vulcanization temperature, and injection pressure. Attempts were also made to elucidate the anisotropic characteristics; the shrinkage of the vulcanizates was measured, and stress–strain curve, tensile strength, and elongation were also studied with the specimens cut in parallel and perpendicular to the flow direction from these vulcanized sheets.

EXPERIMENTAL

Test Equipment and Procedure

The molding of the specimens was carried out by a 5-oz rubber injection molding machine made by Nagoya Rubber Co., Ltd. Two test mold designs are illustrated in Figure 1. The mold cavities are 2 mm in depth.



(A) BELT TYPE SPECIMEN (B) FLAT SHEET SPECIMEN

Fig. 1. Mold design.

Such cavities are convenient for testing the shrinkage and physical properties. The gates are located at the center of each cavity. In order to measure the shrinkage of molded test specimens, lines were lightly marked at every 10 mm on the surface of the molds.

Commercial grades of SBR, EPDM, CR (chloroprene rubber), and NR (natural rubber) were used. Each compound was adjusted to the same hardness of 60 degrees in Shore A. Molding conditions were the following: injection pressure, 200–1200 kg/cm^2; barrel temperature, 80°C; mold temperature, 140–180°C; vulcanization time, 0.5–16 min.

Measurement of Shrinkage

The dimensions of the mold and molded specimens were measured at 20°C with a traveling microscope having an accuracy of 0.001 mm. Total shrinkage was calculated from the equation

$$\text{shrinkage rate} = \frac{L_m - L_s}{L_m} \times 100$$

where L_s = length of the molded specimen at 20°C, and L_m = length of the mold at 20°C.

The shrinkage measurements of the belt-type specimens were made in the flow direction, and those of the flat sheets were made in two directions: parallel (radial direction) and perpendicular (circumferential direction) to the direction of the flow.

Measurement of Anisotropy of Mechanical Properties

The test specimens shown in Figure 1b were cut at 0° (radial direction), 45°, and 90° (circumferential direction) against the flow direction at 60-mm distances from the gate. A stress–strain curve, tensile strength, and elongation were obtained by using a Shopper tensile tester.

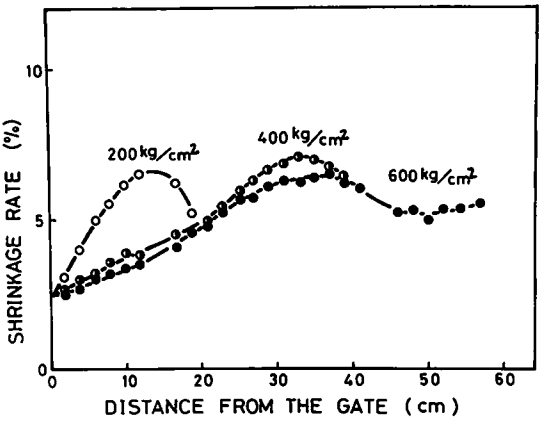


Fig. 2. Flow distance vs. shrinkage rate of belt-type natural rubber specimen (vulcanization temp. 180°C, vulcanization time 0.5 min).

RESULTS

Effects of Flow Distance and Vulcanization Temperature on Shrinkage

Effects of the flow distance from the gate and injection pressure on the shrinkage of the belt-type vulcanizate are shown in Figure 2. Figure 3 shows the relation between mold temperature and shrinkage of the same belt-type specimens. The shrinkage in the flow direction increases with increase in the distance from the gate, reaches a maximum, and then decreases gradually. However, such a tendency weakens at 160°C and is not observed at all at 140°C. At 140°C, the flow distance did not affect the shrinkage, as shown in Figure 3.

Generally, the shrinkage tends to decrease with increase in injection pressure and decrease in vulcanization temperature. However, shrinkage rate is about 2.5% at a position close to the gate at every temperature.

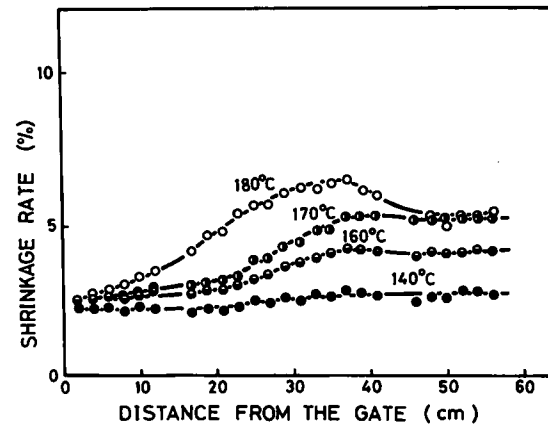


Fig. 3. Vulcanization temperature vs. shrinkage rate.

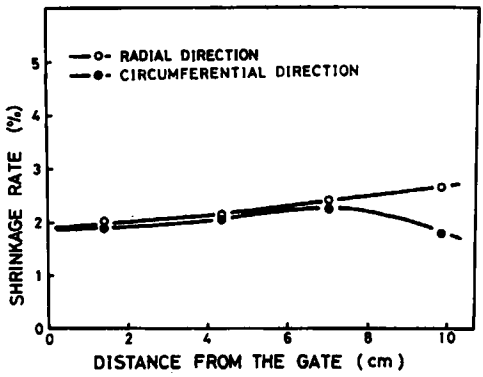


Fig. 4. Flow distance vs. shrinkage rate of natural rubber flat-sheet specimens (vulcanization temp. 160°C, vulcanization time 10 min).

Anisotropy of Shrinkage

Figures 4 and 5 show the dependence of the shrinkage of the flow distance from the gate of the flat sheets vulcanized at 160°C and 180°C. These figures show that:

1. The shrinkage in the radial direction is larger than that in the circumferential direction.
2. This anisotropy of the shrinkage increases with vulcanization temperature.
3. The anisotropic character becomes pronounced with increase in flow distance, since the shrinkage in the radial direction increases with the distance from the gate, while that in the circumferential direction decreases after the passage of a maximum point.

Studies were made on the relation between the shrinkage and the nature of polymers such as SBR, NBR, CR, EPDM, and NR. The degrees of the shrinkage in these polymers plotted versus the flow distance are shown in Figure 6. The shrinkage of NBR is larger than that of any other material.

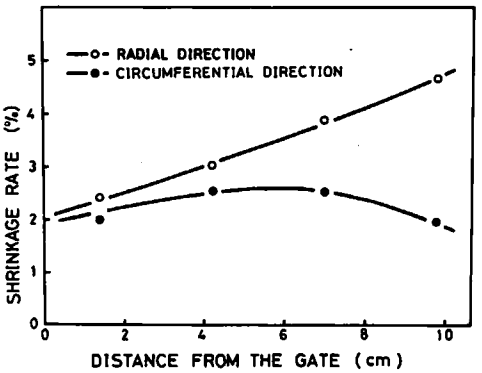


Fig. 5. Flow distance vs. shrinkage rate of natural rubber flat-sheet specimens (vulcanization temp. 180°C, vulcanization time 3 min).

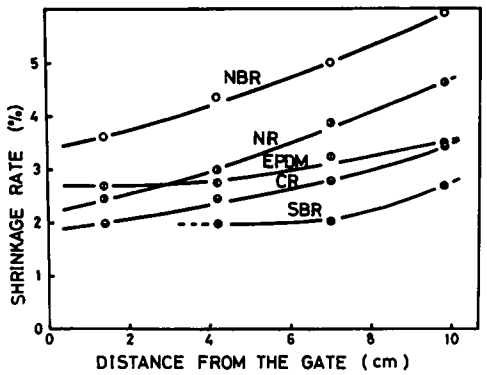


Fig. 6. Shrinkage of various polymers (radial direction, vulcanization temp. 180°C).

Anisotropy of Mechanical Properties

Effects of mechanical properties for the angle between the flow direction and stretch direction are presented in Figure 7. These results indicate that:

1. The 300% modulus in the circumferential direction is larger than that in the radial direction.

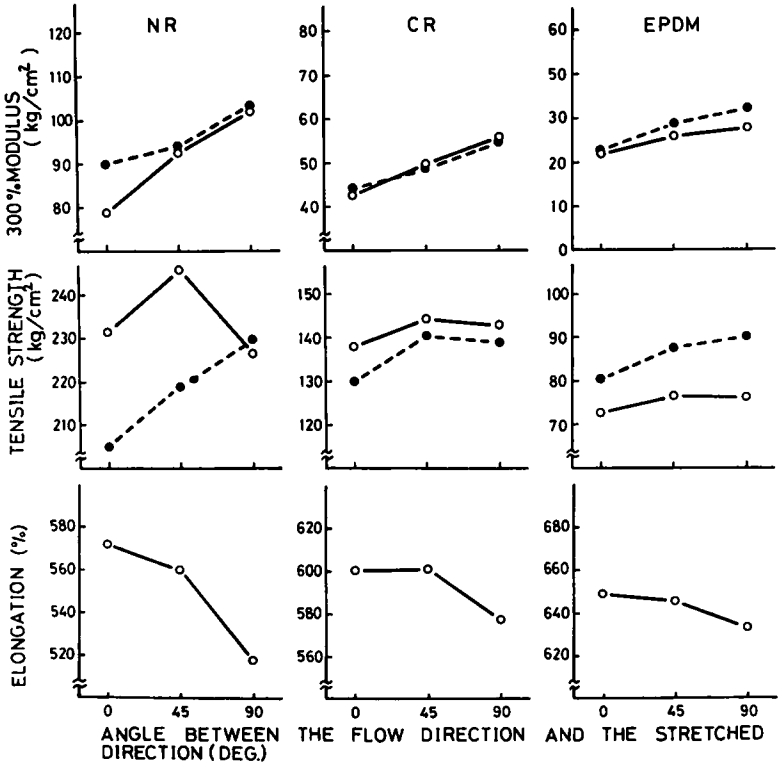


Fig. 7. Anisotropy of mechanical properties (vulcanization temp. 160°C (—O—) and 180°C (– –O– –).

2. The anisotropy of the 300% modulus barely depends upon the vulcanization temperature.

3. The tensile strength in the circumferential direction is higher than that in radial direction.

4. The elongation in the circumferential direction is less than that in radial direction.

DISCUSSION

Effects of Shrinkage

The shrinkage rate of the compression-molded rubber was measured and compared with that of the injection-molded rubber. It can be understood from Figure 8 that temperature dependence of the shrinkage in injection molding is more significant than that in compression molding. The relation between temperature and shrinkage rate in compression molding is plotted on a straight line. When this straight line is extrapolated to room temperature, the shrinkage rate becomes approximately zero. Therefore, the major factor of shrinkage in compression molding is attributed to the thermal contraction in volume.

In injection molding, however, the shrinkage increases rapidly as vulcanization temperature rises. Therefore, the shrinkage cannot be explained by the thermal contraction only. It may be understood that the increase of shrinkage in the flow direction is caused by orientation of rubber molecule that occurred during the forward flow in one direction. This orientation may be noticed in the electron-microscopic photograph shown in Figure 9. This photograph illustrates orientation of spindle-shape calcium carbonate particles mixed into the rubber. It was recognized that calcium carbonate particles were noticeably orientated in the flow direction at 0.1 mm inside the surface. However, such orientation showed reduction with lowering of vulcanization temperature.

In the case of flat sheets, it was observed that the degree of shrinkage varied with flow direction. It was also found that the shrinkage in the

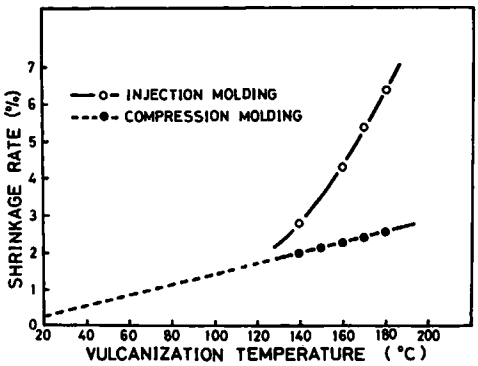


Fig. 8. Difference of shrinkage between compression and injection molding.

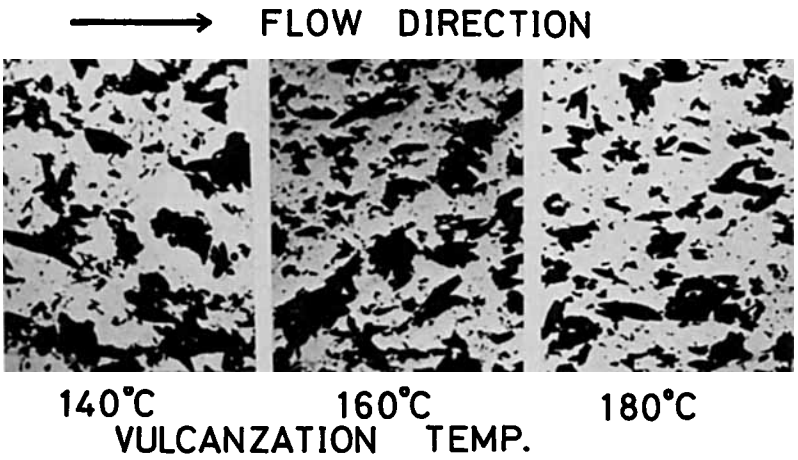


Fig. 9. Electron-microscopic pictures showing the state of filler orientation (1,500×).

radial direction increased with increase in flow distance and vulcanization temperature in all cases. This increase is attributable to the same reason as that of the belt-type specimen. The decrease in shrinkage in the circumferential direction cannot be explained by this mechanism.

Therefore, several tests were carried out in order to examine the flow behavior in the cavity. The orientation of the chopped thin metal wires mixed into the rubber was observed. Photographs were taken with soft x-rays after the specimens were sliced into thin films. Figure 10a shows the cross section of a surface portion and Figure 10b, that of the center portion. The thin metal pieces in the center portion are oriented in the same direction perpendicular to the flow direction, while the pieces are oriented in two directions in the surface portion. A similar result in fiber-reinforced nylon 66 has been found by Karpov.[3]

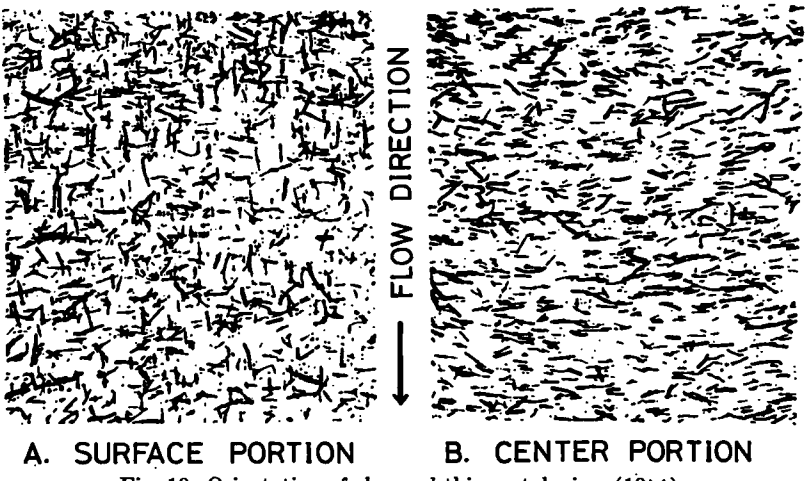


Fig. 10. Orientation of chopped thin metal wires (10×).

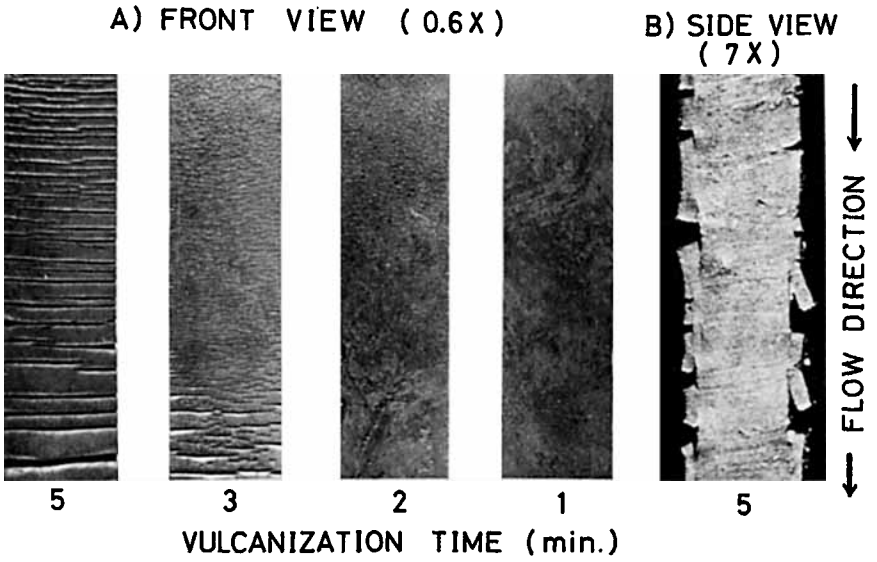


Fig. 11. Cracks formed when tensile strain of 400% was imposed for 5 min on specimen cut parallel to the flow direction.

One more interesting phenomenon, as illustrated in Figure 11, was found in injection-molded flat natural rubber sheets cured at 180°C. When a tensile strain of 400% was imposed for 5 min on a specimen cut in paralle- to the flow direction (radial direction), cracks similar to ozone cracks appeared on the surface and grew in the direction perpendicular to the direcl tion of extension. However, no cracks appeared in the specimen cut perpendicular to the flow direction. This photograph shows that (1) the number of cracks increases with increase in vulcanization time, (2) the cracks become larger and deeper with increase in flow distance, (3) the size of the cracks decreases as the number of cracks increases.

Woebcken[4] found two kinds of orientation; one is the so-called "shear orientation" which depends upon plug flow, the other is "expanded orientation" which occurs according to the expansion of the material. "Shear orientation" can be explained by Figure 12a, which shows a profile of plug flow. Molecules at the surface portion are arranged in parallel to the stream. Since the velocity of the molecules at the center of the stream is

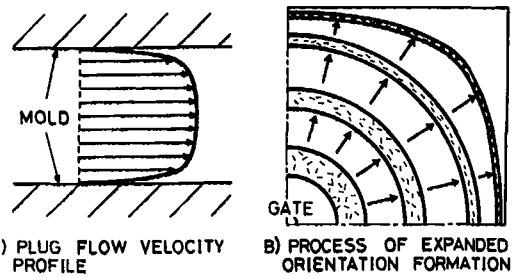


Fig. 12. Two flow models.

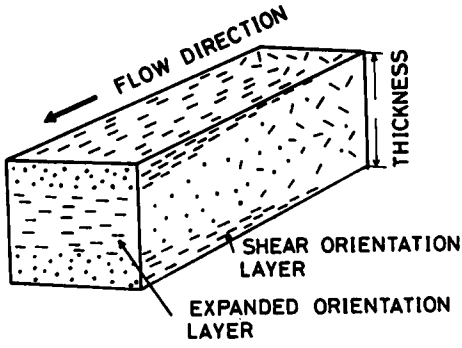


Fig. 13. Profile of two orientations.

uniform, molecules are not oriented in the single stream as in the belt-type specimen. But another orientation, as shown in Figure 12b, which is caused by the expansion of material, must be considered in the case of flat sheets. This kind of orientation is called "expanded orientation."

The two directions of the thin metal wires indicated in Figure 10 depend upon these two different types of orientation, and the profiles of these orientations are shown in Figure 13. It is likely that the shrinkage in the flow direction is not due to the expanded orientation but mainly to the shear orientation. The reason is as follows: High temperature or long flow distance makes the rubber compound close to the wall scorch, and these scorched molecules are stretched by the shear force. These stretched molecules tend to shrink because of their own elastic energy.

It may be appropriate to study the effects of scorched and stretched molecules on shrinkage. Therefore, a "double vulcanization" was made to demonstrate this theory. Specimens were vulcanized at first at 120°C for 18 min, 21 min, 25 min, or 30 min and again vulcanized at 170°C for 10 min after being stretched by 50%. The shrinkage calculated according to the following equation is shown in Table I:

$$\text{shrinkage rate} = L_{ss}/L_{se}$$

where L_{ss} = specimen length after the second vulcanization, and L_{se} = extended specimen length. The data indicate that the degree of shrinkage

TABLE I
Shrinkage Obtained From the Second Vulcanization[a]

Extention rate, %	Shrinkage, %			
	18 min	21 min	25 min	30 min
50	10	17	41	40
100	20	25	40	40
150	13	27	33	33
200	20	32	37	40

[a] Second vulcanization, 10 min at 170°C; first vulcanization shown in Table subheadings (18, 21, 25, or 30 min).

TABLE II
Reaction Rate versus Shrinkage

Polymer	Reaction rate constant k, mm	Shrinkage at 10 cm, %	Increase in shrinkage per flow distance, %/cm
NBR	2.2	5.9	0.26
NR	0.33	4.6	0.26
CR	0.18	3.4	0.14
SBR	0.13	2.7	0.08

increases with increase in the first vulcanization time. It is of interest that the tendency of the shrinkage found in this experiment is similar to that of the injection-molded rubber. It is very important whether the orientation occurs during or before vulcanization. If it occurs during vulcanization, orientation affects the shrinkage; however, if it occurs before vulcanization, the shrinkage will not be influenced by this orientation.

The shrinkage is independent of the expanded orientation, because the temperature in the center portion is not so high as to cause the vulcanization during the flow.

The reaction rate constant k of the vulcanization obtained from the oscillating disk rheometer[5] was studied in order to examine whether the shrinkage depends upon the vulcanization rate or not. The results are given in Table II. These data suggest that the shrinkage increases with increase in vulcanization rate. The tendency becomes evident with the increase in flow distance.

Effects of Mechanical Properties

As described above, it has been shown that the 300% modulus in the perpendicular direction to the flow direction is larger than that in the parallel direction. The same results have been obtained in tensile strength. However, the tendency of tensile strength is not so clear as the 300% modulus. Opposite characteristics have been found in elongation; elongation in the perpendicular direction to the flow direction is less than that in the parallel direction. From these results, the mechanical properties are evidently affected by the expanded orientation. Expanded orientation layers are usually thicker than the shear orientation layers, as observed in Figure 11b.

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