

## Transition Behavior of Polychloroprene and Polychloroprene/Styrene-Butadiene Blends

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This paper reports crystallization and glass transition studies on various commercial polychloroprenes. It is known, of course, that many polychloroprenes crystallize readily, and that this factor must be considered is selecting such polymers for low-temperature service.<sup>1,2,3</sup> However, much of the data on melting temperatures and crystallization rates included here have not previously been given.

The polychloroprenes studied include Neoprenes W, WRT, GN, and GRT in both unvulcanized and vulcanized states. In addition, blends of the W-type polymers with SBR-1500 were included to show the effect of a noncrystallizable rubber on the transition properties. The data were determined dilatometrically. Melting temperatures of the unvulcanized, unstressed polychloroprenes varied from 36 to 43°C., and the crystallites showed a maximum rate of growth at about -5°C. It was found that blending of SBR-1500 with Neoprenes W and WRT retards the rate and extent of crystallization slightly, but has very little effect on the melting or optimum crystallization temperatures.

### EXPERIMENTAL

Dilatometric techniques described by Bekkedahl<sup>4</sup> were followed in this work. The capillary tubing of the dilatometers had an i.d. of about 2 mm., and was of the precision-bore type supplied by the Fischer and Porter Company, Hatsboro, Pennsylvania. The bore volume of this tubing was found to be constant within  $\pm 0.0001$  ml./mm. over its entire length, and since this degree of precision falls within experimental error, it was unnecessary to correct the volume of the confining fluid for variations in the bore.

Each raw polymer sample was first pressed into a  $6 \times 6 \times 0.075$ -in. sheet for 15 min. at 120-135°C. This procedure removed nearly all of the air and rendered the sample transparent, so that any re-

maining air bubbles could easily be detected and excluded from the sample used. It was necessary to handle the samples as small pieces, because the polymers were so tacky that large strips or chunks could not be pushed into the dilatometer bulb without entrapping large amounts of air. Therefore, the de-aerated samples were cut into small cubes and about 5 to 7 g. were charged into the dilatometers with tweezers. Silicone oils General Electric SF (81)-40 and Dow Corning 510/50 were used as confining fluids. These oils have no swelling effect on the polymers as determined by a three-month swell test at room temperature. It was determined experimentally that the linear expansivity coefficient of these oils is constant from 25 to -100°C. Each dilatometer was cleared of air under vacuum, and was considered to be properly evacuated if the oil meniscus changed no more than 1 mm. between atmospheric pressure and full vacuum. Meniscus and reference heights for the dilatometer were measured to  $\pm 0.01$  cm.

Long-term exposures at low temperature were carried out in a cold bar patterned after a device originally described by Mooney and Wolstenholme.<sup>5</sup> This consists of 16 separate cold baths operating between 0 and -60°C., controlled by the temperature gradient between a water bath at 0°C. and a Dry Ice bath at -72°C. With this cold bar, temperatures were maintained within  $\pm 1^\circ\text{C}$ . for months at a time. Dewar flask baths were used in cooling or warming samples for transition data. Cooling was done at a rate of 0.5°C. per minute, with the temperature held constant at each 5-degree interval for 10 minutes before measuring volume change. For melting transitions, samples were first crystallized for about 2 weeks at 15°C., and then warmed at about 1°C. per hour for 6 hours every day with the temperature held constant overnight. Temperatures were measured to  $\pm 0.1^\circ\text{C}$ . by means of thermocouples and calibrated mercury thermometers.

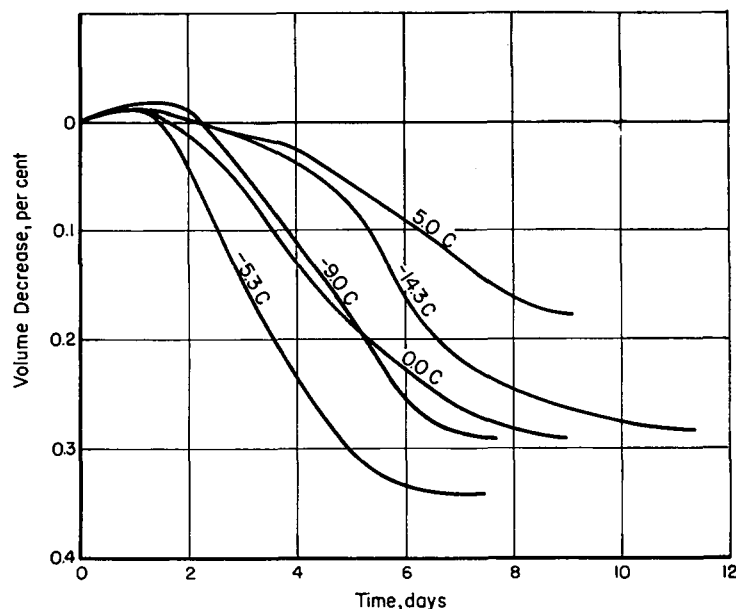


Fig. 1. Volume-time relation of Neoprene WRT.

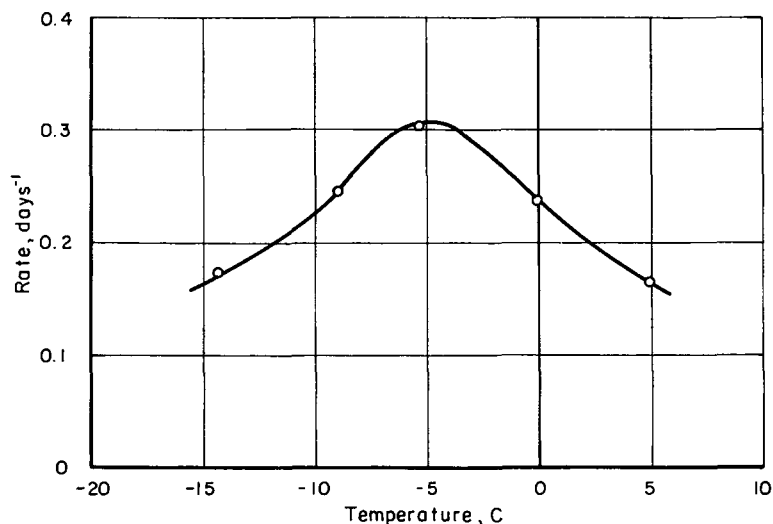


Fig. 2. Crystallization rate of Neoprene WRT.

### RESULTS

Among the commercial neoprenes available today, Types AC and AD crystallize the fastest, requiring but a few hours at room temperature. These types are used in quick-freezing cements to take advantage of the strength provided by their crystallinity. Among the general purpose types, Neoprene W requires about 10 hours at a low temperature to reach maximum crystallinity. In contrast, the crystallization-resistant type WRT requires about six days to reach an equilibrium degree of crystallization at the optimum temperature. Currently, Neoprene WRT is recommended

for low temperature service.<sup>2</sup> This material is thought to be a copolymer, consisting predominately of chloroprene but containing sufficient quantity of a comonomer to disrupt the structural regularity of the polymer, thus reducing its tendency to crystallize. The typical volume decrease due to crystallinity in type WRT is shown in Figure 1. It appears that type WRT crystallizes most rapidly at about  $-5^{\circ}\text{C}$ . This is confirmed by plotting the reciprocal of the half-times of crystallization at each temperature, as in Figure 2. This same optimum temperature was found for Neoprene W, and there is every

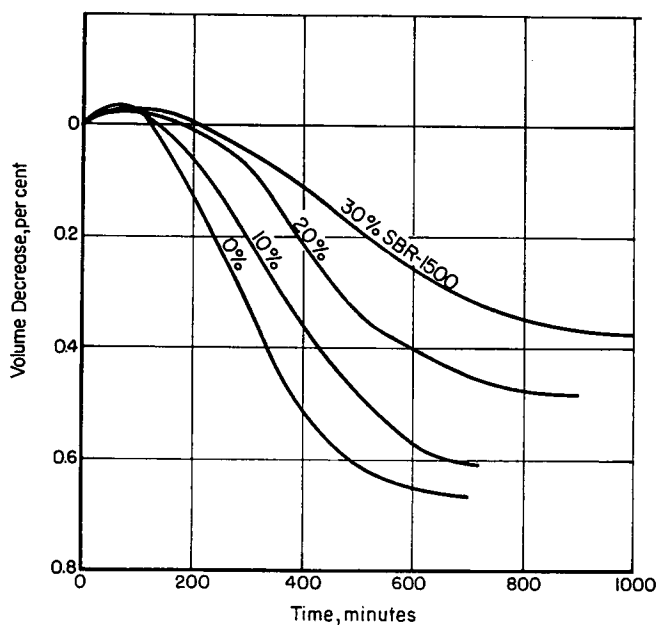


Fig. 3. Volume-time relation of Neoprene W/SBR-1500 blends at  $-5.0^{\circ}\text{C}$ .

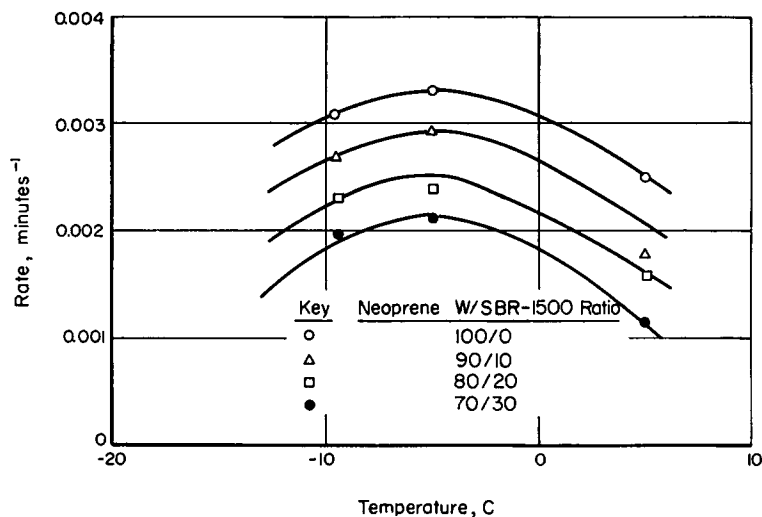


Fig. 4. Crystallization rate of Neoprene W/SBR-1500 blends.

reason to believe that other neoprenes also crystallize most rapidly at about this same temperature. This is expected because the crystallization and melting temperatures of a polymer appear to be a function of the structure of the crystallizing portion of the molecule. Other efforts to improve the crystallization resistance of neoprenes have also involved copolymerization. This is illustrated by type RT in which the second monomer is styrene. This material was shown to crystallize to a smaller degree during storage than the general purpose types.<sup>1</sup> Another example is Neoprene Q which is a

copolymer of chloroprene and acrylonitrile. During the present work, no evidence of crystallization was found in this raw polymer after storage in a dilatometer for more than 400 days at  $-10^{\circ}\text{C}$ . Neither of these two neoprenes are now listed as being commercially available.

Another suggested means of reducing the tendency of general purpose neoprenes to stiffen and embrittle at low temperature involves mechanical blending with another polymer.<sup>6</sup> This method was also investigated dilatometrically. The above reference<sup>6</sup> recommends in particular blends of

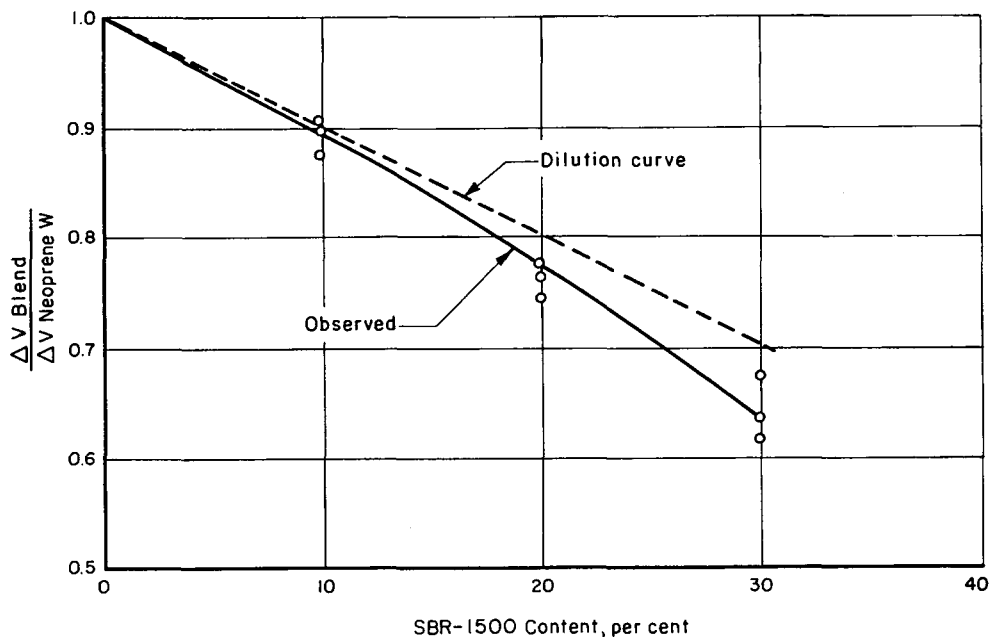


Fig. 5. Crystallization volume change of Neoprene W: effect of SBR-1500.

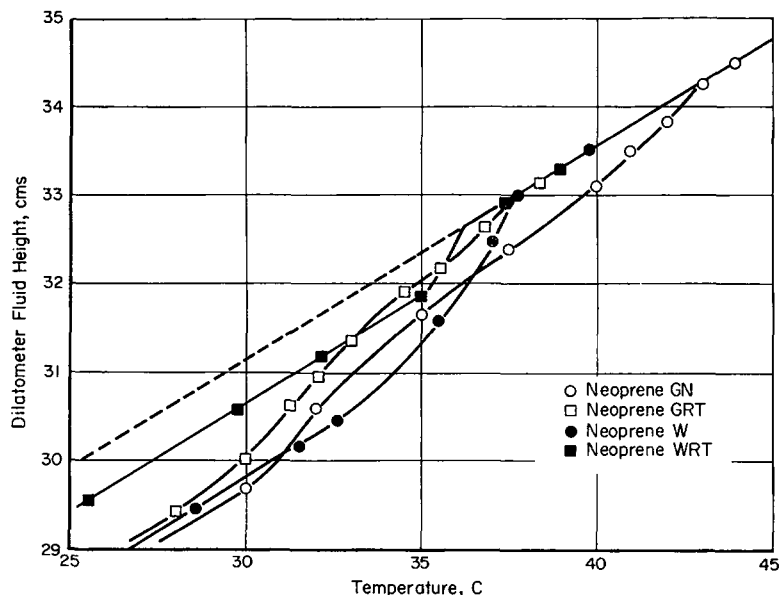


Fig. 6. Melting curves for various Neoprenes.

natural, styrene-butadiene, and polybutadiene rubbers with Neoprene type WRT. In the present work, blends of SBR-1500 with Neoprene W, rather than type WRT, were studied since the W-type crystallizes much more rapidly than WRT. This can be seen in Figure 3, which shows that type W crystallizes to its maximum extent at  $-5^{\circ}\text{C}$ . in about 600 minutes, which is about 14 times faster than WRT. Figure 3 also illustrates the retarding

action of SBR-1500 on both the rate and degree of crystallization of Neoprene W. The blends were also crystallized at other temperatures, and these results are plotted as rate curves in Figure 4. It is apparent that polymer blending has little, if any, influence on the optimum crystallization temperature of Neoprene W. However, the rate of crystallization is reduced. About 10 hours are required for an equilibrium volume decrease of the un-

modified Neoprene W, whereas almost 17 hours are required for a 70/30 blend with SBR-1500. The question arises as to whether the added styrene-butadiene rubber has any real effect in reducing the extent of crystallization of Neoprene W or if this is not a simple result of dilution. Therefore, the ratio of the volume decrease due to crystallinity of the blend to the volume decrease for Neoprene W is plotted as shown in Figure 5. Dilution of the polychloroprene by the noncrystallizable SBR-1500 accounts for most of the reduction in crystallinity. But in addition, it can be seen that the ultimate degree of crystallization of the Neoprene W is reduced somewhat, probably due to the mechanical interference of the SBR polymer with ordering of the polychloroprene molecules. It is possible that even this effect would be removed by a slow, continued crystallization. It would be expected that the decrease in overall crystallinity of blends with SBR or similar polymers would be accompanied by a loss in oil resistance.

In addition to the above information, it was the purpose of this work to obtain melting temperatures for the more common polychloroprenes so that these data could be used in studying the effect of compounding variables or of external forces on crystallization of these materials. Crystallized samples of the various neoprenes were melted slowly over a period of about 10 days so as to approach the thermodynamic melting temperature. The observed melting curves, shown in Figure 6, have been superimposed on a single line representing the amorphous polymers, to aid comparison. Values obtained for  $T_m$  are listed in Table I.

TABLE I  
Melting Temperatures of Neoprenes

Polymer	$T_m$ , °C.
Neoprene GN	43
Neoprene GRT	38
Neoprene W	38
Neoprene WRT	36

The data for the Neoprene W/SBR-1500 blends are not shown. These blends all melted at 38°C. and differed from the pure type W only in their lower degree of crystallization. Thus the blending had no effect on  $T_m$ . The curve for the 70/30 Neoprene W/SBR-1500 blend was very similar in appearance to the curve for Neoprene WRT, except for the difference in melting temperature of 2°C. between these two materials.

The effect of vulcanization on any polymer is generally to lower the rate of crystallinity, and, to a lesser extent, the final degree of crystallinity. When the polymer is stored at low temperature under no stress, the reduced molecular freedom resulting from crosslinking may prevent ordering altogether. For example, a Neoprene WRT gum vulcanizate was stored near -6°C. for more than 450 days in a dilatometer, and showed no evidence of crystallinity. On the other hand, vulcanization produced no readily observable effect on the glass transition temperature. Gum vulcanizates as well as unvulcanized samples of Types GN, GRT, W, and WRT all had glass transition temperatures close to -45°C.

The presence of another polymer, such as styrene-butadiene rubber, causes a definite change in the glass transition of neoprene, as shown in Table II for type WRT.

TABLE II  
Glass Transition and Brittle Temperatures of Neoprene WRT/SBR-1500 Vulcanizates

SBR-1500 content, %	$T_g$ , °C.	$T_b$ , °C. <sup>5</sup>
0	-45	-40
10	-47	-45
20	-49	-55
30	-50	-60

The same  $T_g$  values were also found for equivalent unvulcanized blends of Neoprene W and SBR rubber. In these mixtures, the SBR rubber has a lower  $T_g$  than the neoprene and acts as a plasticizer in lowering the  $T_g$  of the blend. It is interesting also to compare the glass transition temperatures of the various blends with brittle temperatures as reported in the literature.<sup>6</sup> The blends compared in Table II have similar recipes, except the  $T_b$  data are for a carbon black stock. It is usually expected that  $T_b$  will be higher than  $T_g$  for a given elastomer. However, this rule obviously does not apply to the polymer blends studied in this work. Different values would be expected from these two methods, since one is a static and the other a dynamic test. As the amount of SBR-1500 (or other low-temperature polymer) in the blend approaches 50% it is expected that two values of  $T_g$  would be observed, lying near the  $T_g$  values of the pure polymers, while  $T_b$  would steadily decrease, approaching the brittle temperature of the component having the lower  $T_g$ . This illustrates that  $T_g$  values must be

used cautiously in estimating low-temperature performance, particularly where polymer blends are concerned.

In summary, the data given in this paper are intended to serve as a base line in studying the effect of various factors on the crystallinity of neoprene. It can be seen that vulcanization greatly inhibits crystallization as long as the polymer is free from stress. However, there are no quantitative data available to show the effect of stress on crystallization behavior. Further work on the interrelationships of stress, temperature, and crystallinity is needed.

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#### Synopsis

Dilatometric studies have been carried out to determine crystallization and glass transition data for various unvulcanized and vulcanized polychloroprenes and polychloroprene/styrene-butadiene blends. The maximum rate of crystallization of both unvulcanized polychloroprene and

the blends occurred near  $-5^{\circ}\text{C}$ . Melting temperatures of the polychloroprenes ranged from  $36$  to  $43^{\circ}\text{C}$ . The glass transition temperature of all polychloroprenes studied was near  $-45^{\circ}\text{C}$ ., and this was lowered to  $-50^{\circ}\text{C}$ . with the addition of 30 pph of SBR-1500. The added SBR polymer retarded the rate and ultimate degree of crystallization somewhat.

#### Résumé

On a suivi dilatométriquement les mesures de cristallisation et de transition vitreuse dans le cas de nombreux polychloroprènes vulcanisés et non-vulcanisés de même que des produits styrène-butadiène/polychloroprène. La vitesse maximum de cristallisation du polychloroprène non-vulcanisés et de ces derniers produits se situe vers  $-5^{\circ}\text{C}$ . Les températures de fusion des polychloroprènes varient de  $36$  à  $43^{\circ}\text{C}$ . La température de transition vitreuse de tous les polychloroprènes étudiés était environ  $-45^{\circ}\text{C}$ , et celle-ci était abaissée à  $-50^{\circ}\text{C}$  par addition de 30 pph de SBR-1500. Le polymère additionné de SBR possède une vitesse de cristallisation et un taux final de cristallinité quelque peu plus faibles.

#### Zusammenfassung

Dilatometrische Untersuchungen wurden zur Bestimmung von Kristallisations- und Glasumwandlungsgrößen für verschiedene unvulkanisierte und vulkanisierte Polychloroprene und Polychloropren/Styrol-butadienmischungen ausgeführt. Die Maximalgeschwindigkeit der Kristallisation trat sowohl bei unvulkanisiertem Polychloropren als auch bei den Mischungen im Gebiete um  $-5^{\circ}\text{C}$  auf. Die Schmelztemperaturen der Polychloroprene lagen zwischen  $36$  und  $43^{\circ}\text{C}$ . Die Glasumwandlungstemperatur aller untersuchten Polychloroprene betrug etwa  $-45^{\circ}\text{C}$  und wurde durch Zusatz von 30 Teilen SBR-1500 auf 100 Teile auf  $-50^{\circ}\text{C}$  erniedrigt. Das zugesetzte SBR-Polymer setzte die Kristallisationsgeschwindigkeit und den Endwert des Kristallisationsgrades etwas herab.

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