

# The Effects of Degree of Mixing on the Properties of Filled Elastomers

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## Synopsis

A new technique has been established for improving the degree of mixing of the filler in an elastomer matrix. This technique includes a unique heating and cooling mixing procedure in conjunction with surface modification of the carbon black and proper choices of polymers. The heating cycle is for decreasing the microvoid concentration and for enhancing polymer-filler adhesion. The cooling cycle is for improving the degree of mixing of the filler. Experimental data obtained from several polychloroprene systems strongly substantiate the new mixing technique. The results clearly show that a good degree of mixing obtained using the foregoing mixing technique can indeed enhance the mechanical and permeability properties of filled elastomers.

## INTRODUCTION

Elastomers are a very important class of material for engineering applications. This is because of their unique mechanical properties, such as elastic behavior at very large deformation, energy absorbing capability, etc. Examples of automotive applications using elastomers are tires, hoses, mounts, and seals. However, due to the complexity of filled elastomer systems, the design of elastomer compositions for achieving the required properties is very difficult. For example, the tensile strength and ultimate elongation of a given elastomer formulation depend very much on the mixing processes used. In other words, the properties of a given elastomer formulation depend on the degree of mixing of the filler. The degree of mixing is defined as the extent of homogeneity for the dispersion of a given filler in the polymer matrix. So far no methods exist to deal with the effects of degree of mixing on the properties of filled elastomers. Therefore, trial and error methods are still used in designing elastomer compositions for achieving the required properties.

The purpose of this work is, therefore, to establish a mixing technique based on the effects of composition and processing on the degree of mixing of the filler. This mixing technique will then be used to improve the properties of filled elastomers in engineering applications. In order to achieve the foregoing purpose, we have to examine the variables that affect the degree of mixing of the filler.

As has just been mentioned, mechanically mixing elastomer ingredients can lead to different properties. This is because the dispersion of the ingredients within the elastomer matrix depends on the mixing time period. As an example, Figure 1 shows the cryogenically fractured surface of an acrylonitrile-butadiene copolymer (Hycar 1032, Goodrich) reinforced using N330 carbon black at a volume fraction of 20%. The acrylonitrile-butadiene copolymers were mixed

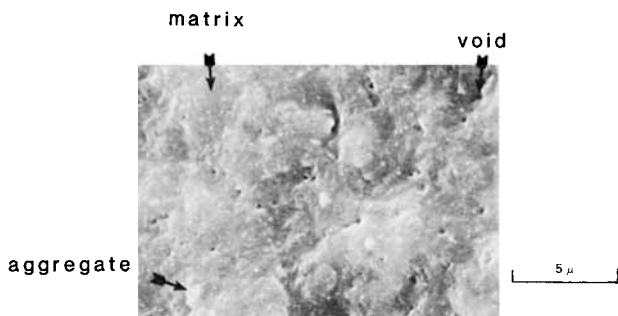


Fig. 1. Cryogenically fractured surface of a butadiene-acrylonitrile rubber filled with N330 carbon black (volume fraction = 20%).

for 7 min using a 1135 g Banbury internal mixer. It is clearly shown in Figure 1 that at least three key components exist in a filled elastomer system. They are the rubber matrix, the polymer-filler aggregates, and the closed-cell microvoids. The voids are in the order of  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  mm.

In order to improve the properties of filled elastomers, decreasing the aggregate size and the void concentration is needed. Two methods are used to decrease the size of polymer-filler aggregates. These are (1) increase the local shear stresses of the matrix in order to break down the aggregates and (2) optimize the adhesion characteristics to improve the degree of dispersion of the filler.

For a given deformation, increasing the shear stresses can be accomplished by increasing the modulus of elastomer. Using composition variables, increasing the modulus of elastomer is accomplished by choosing rubber with a high molecular weight. This is because the modulus of a rubber is a function of its shear viscosity,<sup>1</sup> which increases at high molecular weight. Using processing variables, increasing the modulus of elastomer is accomplished by decreasing the mixing temperature through the use of a cooling mixing cycle.

Surface modification of the filler is a method used for optimizing the adhesion characteristics. The optimized adhesion interaction between the polymer and the filler should have intermediate values, since a very strong adhesion interaction hinders the mobility of the filler particle, while a very weak adhesion interaction decreases the reinforcement by the filler particle.

The effects of voids and fillers on mechanical properties of filled polymers were discussed by Chow.<sup>2</sup> Reduction of the microvoid concentration in the polymer matrix can be accomplished by increasing the mixing temperature through a heating mixing cycle. When the mixing temperature is increased, it will decrease the viscosity (and equivalently the modulus) of the polymer matrix.<sup>3</sup> Consequently, the critical stress for microvoid propagation will also decrease. As a result, the microvoids can be easily squeezed out of the polymer system. The foregoing methods are summarized in Table I. In the forthcoming sections, we will discuss the experimental work which was designed and conducted based on these new methods for achieving good mixing.

## EXPERIMENTAL

**Materials.** The rubber used in this study was polychloroprene (Neoprene W, DuPont). The fillers consisted of two types of carbon black, N330 and at-

TABLE I  
Methods for Achieving Good Mixing for Elastomers

	Method	Design
Optimize the polymer-filler adhesion	chemically modify the filler surface	elastomer
Increase the modulus of the gum	choose rubber with high molecular weight	compositions
Increase the modulus of the gum	cooling mixing cycle	mixing processes
Decrease the microvoid concentration	heating mixing cycle	

trited N330.<sup>4,5</sup> The attrition process of the carbon black was performed by first oven heating at 150°C for 24 h, and then ball milling at 125–225°C for 48 h. The amount of the carbon black put into the ball mill container was about one third of the volume of the container.<sup>6</sup> The polychloroprene compositions used in this study are shown in Table II.

**Sample Preparation.** Since there are four methods involved as shown in Table I, this implies that we can have a total of 15 combinative procedures for enhancing the degree of mixing of the filler. In this report, we will discuss only one of the combinative procedures and compare it with a commonly used procedure. The commonly used procedure consists of mixing the N330 carbon black into polychloroprene compositions for 7 min at mixing temperatures ranging from 30°C to 110°C.

In our new mixing method we used attrited N330 carbon black in conjunction with the heating and cooling mixing cycles to prepare the polychloroprene compositions. Polychloroprene with the same molecular weight distribution was used. The steps and conditions for this new mixing procedure are summarized in Table III. In this mixing procedure, we used two heating cycles and two cooling cycles. The cooling cycle is for enhancing carbon black dispersion. The heating cycle is for decreasing microvoid concentration. The mixing temperatures shown in Table III were chosen to be 10°C and 100°C. These temperatures are the temperatures for the chill water and the steam used for the two-roll mill and the Banbury internal mixer.

TABLE II  
Compositions of Polychloroprene Used

Polychloroprene rubber	
Ingredients	(phr) <sup>a</sup>
Polychloroprene (neoprene W)	100
Filler <sup>b</sup>	30
MgO	4
ZnO	5
Stearic acid	0.5
Ethylene thiourea	0.7
Sulfur	0.5

<sup>a</sup> phr = parts per 100 parts of rubber.

<sup>b</sup> N330 carbon black is used for common polychloroprene, and attrited N330 carbon black is used for GMR polychloroprene.

TABLE III  
The Cyclic Mixing Procedure

Mixing step	Time period (min)	Temp (°C)
1. Mixing of polymer	2	30
2. First cooling cycle for mixing polymer and carbon black	4	10
3. First heating cycle for mixing polymer and carbon black	4	100
4. Second cooling cycle for mixing polymer and carbon black	3	10
5. Second heating cycle for mixing polymer and carbon black	3	100
6. Low temperature mixing of oil and curatives with the elastomers	1	30

Both the cyclically mixed and the conventionally mixed polychloroprene compositions were performed using a 152.4 mm × 304.8 mm two roll mill and also using a Banbury (1135 g) internal mixer. The temperatures of the elastomer composition were higher during the Banbury mixing than the two-roll mill mixing. The temperatures for the two-roll mixing were controlled to be very close to the mixing temperatures described in Table III and Figure 2. In this report we will only discuss the experimental results for the polychloroprene mixed using the two-roll mill. To prepare standard slabs the curing temperature was 160°C, and the curing time was 25 min. The thicknesses of the slabs were in the range of 2.45 mm to 1.84 mm. Testing specimens were prepared by die cutting.

**Test Procedures.** Uniaxial tensile tests were conducted at room temperature using an Instron tensile machine. The crosshead speed chosen was 508 mm/min (20 in./min), which corresponds to an initial strain rate of 0.33 s<sup>-1</sup>. The dynamic modulus properties were measured using the Dynamic Mechanical Analyzer (DMA, DuPont 990) with a heating rate of 5°C/min. Fatigue tests were conducted using a DeMattia fatigue tester at a vibrational frequency of 5 Hz and an initial strain of 75%. Cryogenically fractured surfaces were obtained at -198.5°C and examined by a scanning electron microscope (ISI-DS130). The permeability was measured at 93.3°C using a Linde volumetric permeability cell in which Freon-22 was used with a pressure of 50 psig. The permeability was then calculated by the following equation<sup>7</sup>:

$$P = (q \cdot t)/(A \cdot \Delta p) \quad (1)$$

where  $P$  = permeability of Freon-22 through polychloroprene membrane,  $q$  = volume flow rate of Freon-22,  $t$  = thickness of polychloroprene membrane,  $A$  = cross-sectional area of polychloroprene membrane,  $\Delta p$  = pressure difference of Freon-22 across polychloroprene membrane. The permanent set was obtained by stretching the rubber specimen up to 300% and then unloading and relaxing

TABLE IV  
Changes in the Properties of Carbon Black after Attrition<sup>6</sup>

Properties	Before attrition	After attrition
Particle Size (Å)	260	150
pH	8.1	3.4
Critical surface energy of wetting ( $\gamma_c$ ) (dyn/cm)	40	32.6
Extent of interaction	1.509	1.368
Solid/liquid surface energy ( $\gamma_{sl}$ ) (dyn/cm)	43.1	34.1

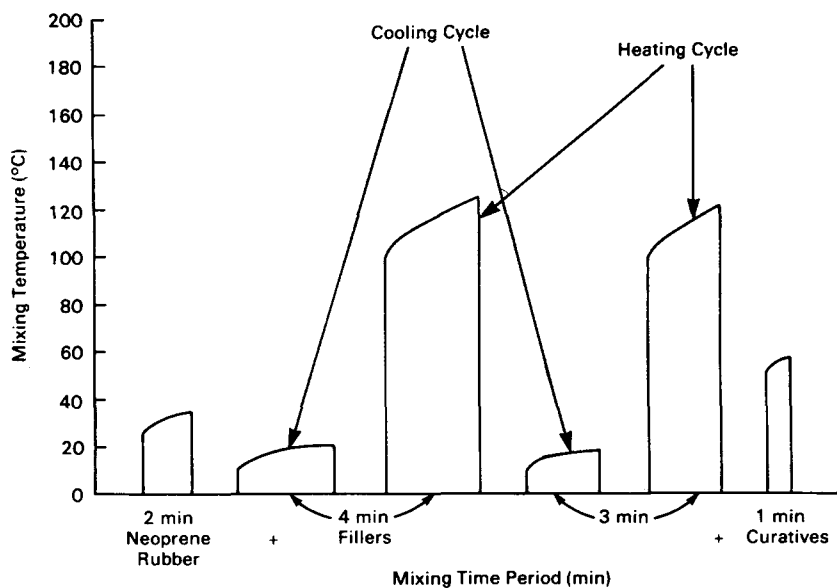


Fig. 2. Mixing temperatures on a two-roll mixer using the cyclic mixing procedure.

the specimen for 24 h. The hysteresis was obtained from stress-strain curves measured on the Instron between 0% to 100% strain.

## RESULTS AND DISCUSSION

**Effects of Attrition on the Properties of Carbon Black.** The average particle size of the N330 carbon black, as obtained from scanning electron microscope measurements, and the pH values of its slurry in water before and after the attrition process were measured and are summarized in Table IV. Contact angle measurements were conducted at room temperature using a filler column method.<sup>6,8,9</sup> The wetting liquids used in this study were decane, benzyl alcohol, aniline, formamide, and water. The experimental data of contact angle and liquid/vapor surface energy were then analyzed using a new equation of state for adhesion<sup>6</sup> and are shown in Figure 3. From this figure the critical surface energy of wetting,  $\gamma_c$ , and the extent of interaction,  $b$ , were determined for each carbon black. The solid/vapor surface energy of each carbon black,  $\gamma_{SV}$ , was then calculated using the following equation<sup>6</sup>:

$$\gamma_{SV} = \gamma_c b \cdot \exp(1/b - 1) \quad (2)$$

The results of  $b$ ,  $\gamma_c$ , and  $\gamma_{SV}$  are also shown in Table V.

The attrition process not only decreases the solid/vapor surface energy  $\gamma_{SV}$  but also decreased the average particle size of the carbon black and the pH value of its slurry. The low value of pH after attrition indicate the occurrence of oxidation reactions on the black surface.<sup>5</sup> It has been shown that the adhesion characteristics for N330-filled polychloroprene are quite different from that for attrited N330-filled polychloroprene.<sup>6</sup> Several determined adhesion properties of the two polychloroprene systems are summarized in Table V. Based on the values of work of adhesion shown in Table V, we concluded that the polymer-

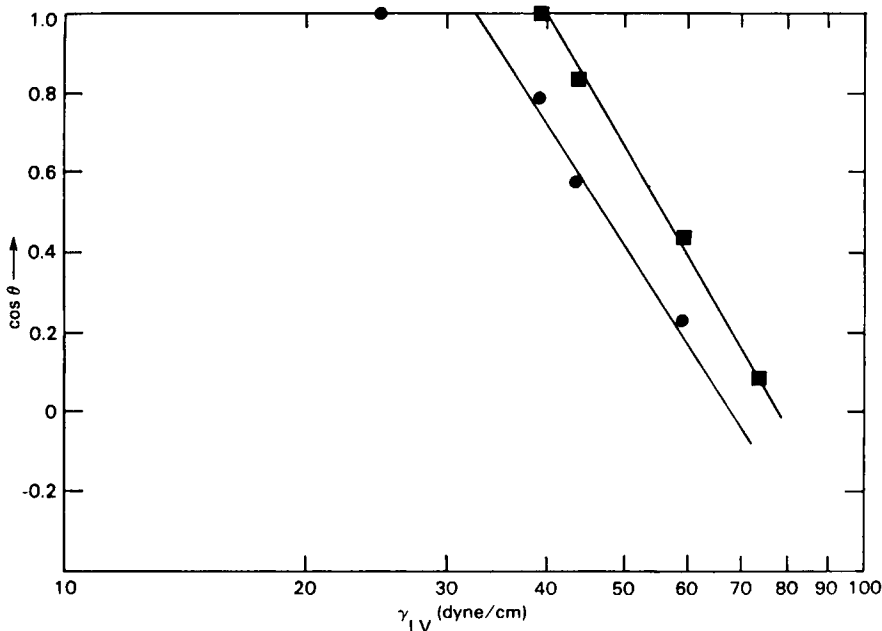


Fig. 3  $\cos \theta$  vs.  $\gamma_{LV}$  for the attrited and nonattrited carbon blacks: (■) N330;  $\gamma_c = 40.0$  dyn/cm and  $b = 1.509$ ; (●) attrited N330;  $\gamma_c = 32.6$  dyn/cm and  $b = 1.368$ .

filler interaction for N330-filled polychloroprene is higher than that for attrited-N330-filled polychloroprene. The values of Harkins spreading coefficient  $\lambda_{LS}$  also indicate that spreading of polymer chains on the surface of N330 carbon black is more complete than that in the case of the attrited N330 carbon black. These findings indicate that the attrited carbon black particles can easily penetrate into the polymer matrix and, thereby, disperse homogeneously in the elastomer system.

TABLE V  
Adhesion Properties of N330 and Attrited N330 Filled Polychloroprene (CR)<sup>6</sup>

Properties	CR-N330	CR-A330
Extent of interaction (b)	1.04	0.99
Surface energy of filler $\left(\frac{\gamma_{SV}}{\gamma_{LV}}\right)$	1.30	1.03
Polymer-filler interfacial tension ( $\gamma_{LS}$ ) <sup>a</sup>	0.272	0.274
Work of adhesion ( $W_A$ ) <sup>a</sup>	76.01	67.03
Harkin's spreading coefficient ( $\lambda_{LS}$ ) <sup>a</sup>	9.63	0.63
Work of adhesion $\left(\frac{W_A}{\gamma_{LV}}\right)$	2.29	2.01

<sup>a</sup> The unit is dyn/cm.

**Morphology of the Cryogenically Fractured Surface.** The cryogenically fractured surfaces of both the cyclically mixed polychloroprene and the conventionally mixed polychloroprene are shown in Figure 4. The improvement in the degree of mixing for the cyclically mixed polychloroprene over the conventionally mixed polychloroprene is quite obvious. The conventionally mixed polychloroprene contains many microvoids with the size ranging from  $10^{-3}$  to  $2 \times 10^{-4}$  mm. The average density of the conventionally mixed polychloroprene is  $1.410 \text{ g/cm}^3$ . On the other hand, the microvoid concentration of the cyclically mixed polychloroprene is very much reduced, and the density of the rubber is  $1.475 \text{ g/cm}^3$ . The average size of the microvoid of the cyclically mixed polychloroprene, which is less than  $2 \times 10^{-4}$  mm, is considerably smaller than that of the conventionally mixed polychloroprene.

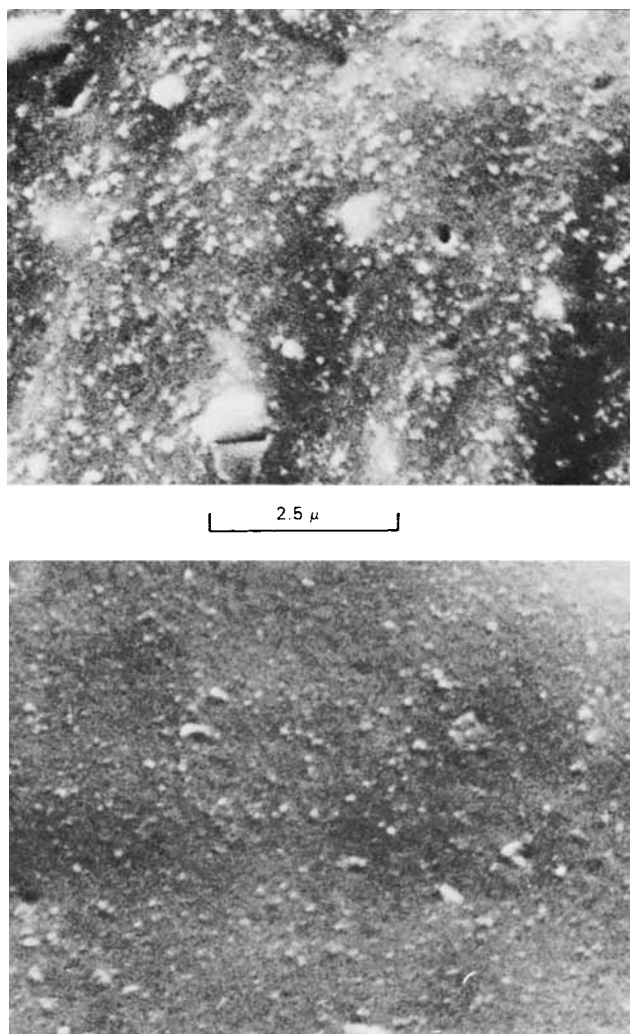


Fig. 4. Cryogenically fractured surfaces for both the conventionally mixed (top) and the cyclically mixed (bottom) polychloroprene compositions.

It is also important to note that the average size of the carbon black aggregate in the cyclically mixed polychloroprene is much smaller than that in the conventionally mixed polychloroprene. Moreover, the dispersion of the carbon black agglomerate in the cyclically mixed polychloroprene is also more homogeneous. The improvement in the degree of mixing is also evidenced by the morphology of the fractured surfaces formed by crack propagation. The fractured surface for the conventionally mixed polychloroprene is very wavy and hilly in comparison with a flat surface for the cyclically mixed polychloroprene. This is because the crack always propagates through the weakest spots inside the elastomer system. In the case of good degree of mixing, there exists no preferential path for crack propagation in the elastomer, and, consequently, the fractured surface is flat. Contrary to the above, crack propagation in the case of poor degree of mixing is through the weakest spots. This results in the wavy and hilly fractured surface observed for the conventionally mixed polychloroprene.

From the morphological results, the mixing methods established in this work can indeed improve the degree of mixing of the filler in an elastomer matrix. In the next section, we will show to what extent a good degree of mixing can improve the properties of filled elastomers.

**Mechanical and Permeability Properties.** Useful mechanical properties of elastomers include tensile strength, ultimate elongation, fatigue life, permanent set, and hysteresis. Permeability properties, in conjunction with mechanical properties, are key criteria used by engineers to select elastomer materials. For example, a long fatigue life is a criterion for designing good mounts; long fatigue life, low permanent set, and low hysteresis are criteria for designing energy-saving tires; and low permanent set and low permeability are criteria for designing superior hoses.

As a result of the improvement in the degree of mixing of filled elastomers, the Freon permeability properties and mechanical properties, which include static and dynamic properties, are improved. The experimental results for both polychloroprene systems are summarized in Table VI. It is important to note that all properties of the cyclically mixed polychloroprene are superior to those of the conventionally mixed polychloroprene. The improvements in the cyclically

TABLE VI  
Comparison of the Properties at Room Temperature of Carbon Black Reinforced  
Polychloroprene Obtained by the Two Mixing Methods

Property	Cyclic mixing <sup>a</sup>	Conventional mixing <sup>b</sup>	Percent improvement (%) <sup>c</sup>
Tensile strength (MPa)	23.8	19.9	18.6
Ultimate elongation (%)	390	285	36.8
Fatigue life (cycle)	151,360	109,000	38.8
Permanent set (%)	0.90	3.25	72.3
Hysteresis at 100% elongation and room temperature	9.8	11.8	16.9
Freon-22 Permeability (cm <sup>4</sup> /s · dyn)	$7.03 \times 10^{-13}$	$7.821 \times 10^{-13}$	10.1

<sup>a</sup> Attrited N330 filled polychloroprene.

<sup>b</sup> N330 filled polychloroprene.

<sup>c</sup> Percent improvement (%) =  $[(a - b)/b] \times 100\%$ , where  $a$  = cyclic mixing and  $b$  = conventional mixing.



mixed polychloroprene are realized by a better filler dispersion and less void concentration than for the conventionally mixed polychloroprene.

Perhaps the most important improvement is obtained in the case of the dynamic modulus properties at low temperatures. Figure 5 shows the DMA results of both polychloroprenes. The glass transition temperature for each case is  $-37^{\circ}\text{C}$ . However, the temperature sensitivities of the storage modulus of the two systems are quite different. The storage modulus of the conventionally mixed polychloroprene remains constant down to  $40^{\circ}\text{C}$ , and then gradually increases as the temperature decreases and the polymer approaches the glassy state. The storage modulus of the cyclically mixed polychloroprene remains constant down to  $-10^{\circ}\text{C}$ , and then sharply increases to its glassy state value as the temperature decreases. In other words, through better mixing, the polychloroprene investigated has better low temperature properties and less temperature sensitivity. A possible explanation for the difference in the temperature sensitivities is the difference in the distribution functions of the effective chain lengths of the two systems. We believe that these experimental results have never been reported in the literature.

**Some Remarks on the Mixing Procedures.** In this work we have estab-

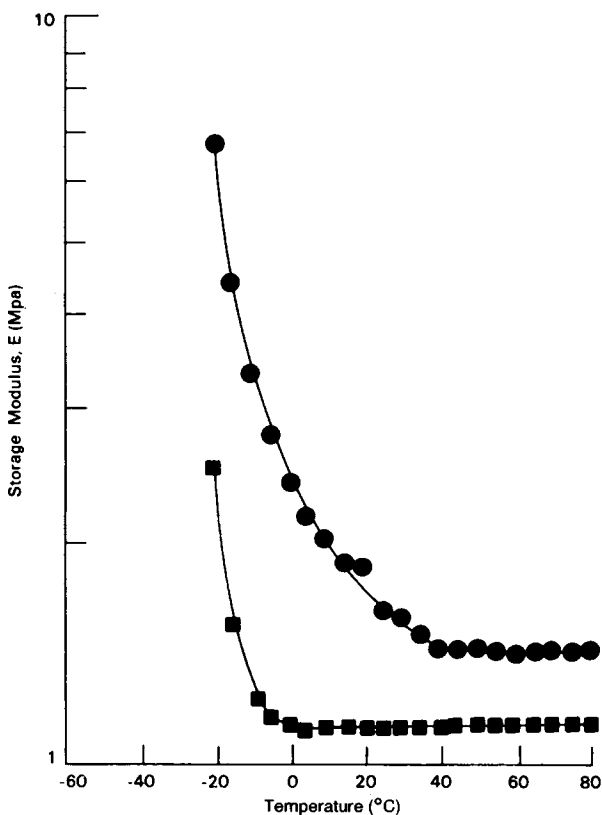


Fig. 5. Storage modulus as a function of temperature for both the conventionally mixed (●) and the cyclically mixed (■) polychloroprene compositions.

lished a cyclic heating-cooling method for mixing elastomer ingredients. Using this method, in conjunction with proper selections of carbon black, good dispersion of the filler and hence improved properties of the elastomer have been achieved. Certainly, it is very important to differentiate the effect of mixing conditions from that of chemical modifications of the filler on the physical properties of a given filled elastomer. For example, earlier study conducted by Gessler<sup>4,10</sup> indicated that heat-treated butyl rubber, in conjunction with attrited carbon black, also showed improved physical properties. In order to achieve the optimum physical properties of filled elastomers, optimization of the mixing temperatures and selections of polymers and fillers with different adhesion characteristics should be considered for further investigation of this mixing procedure.

### SUMMARY AND CONCLUSIONS

A cyclic cooling-heating mixing procedure has been developed for improving the degree of mixing of the filler in polymer matrix. Experimental results show that, for a given elastomer formulation, a good degree of mixing will enhance the properties of filled elastomers.

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