

Mill Processability of *cis*-1,4-Polybutadienes and Deformational Characteristics

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ABSTRACT: Mill behavior was examined with gum rubbers and carbon black-filled compounds of different types of *cis*-1,4-polybutadiene. The rubbers were Ti-, Nd-, and Co-polymerized polymers. The Co-polymerized rubber contained crystalline particles of 1,2-polybutadiene. The carbon black was 50 phr N330. Photographs of the samples on the mill were taken after milling for 2 min. The mill behaviors were classified according to the four regions of Tokita and White. Behavior at loading, stickiness, and mill shrinkage were evaluated qualitatively to interpret mill behavior with aid of the deformational data of previous publications. The Ti-rubber, containing relatively short branches and exhibiting a strain-softening, was in Region III. The Nd-rubbers, containing relatively long branches and exhibiting a strain-hardening, tended to go to Region IV, because the degree of branching was low. The Co-rubbers containing crystalline particles were in Region II, even though they gave strain-softening since they had a high modulus because of the presence of the particles. An overriding effect on the mill behavior appeared to come from how high the modulus of the gum rubber was at the milling condition. Both the gum rubber and the corresponding compound were in the same region of the mill processability. The strain-induced crystallization occurred only when the compounds were under tension on the mill, i.e., Region II. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1995–2001, 1997

INTRODUCTION

The first systematic interpretation of mill behavior was advanced by Tokita and White.^{1,2} In brief, there are four regions of mill processability: When a gum rubber is first put on the mill, it does not go into the mill easily if it is too stiff, and when forced into the gap, it crumbles into pieces (Region I). When the temperature of the rubber is increased, it becomes more easily deformable and forms an elastic band around the roll without breaking (Region II). At still higher temperature,

the band changes from the front roll to the back roll on a differential speed mill. Also, the band loses tightness, tears easily, and sags (Region III). At even higher temperature, the material forms a uniform band around the roll, but the band is sticky and not as elastic as that at the lower temperature (Region IV).

The above mill behavior was later interpreted in terms of the viscoelastic and failure behavior,³ namely, the excessive stiffness at Region I means that the modulus is too high, the rubber being close to the glass–rubber transition. It crumbles to pieces because the failure strain is small. In Region II, the rubber is in the rubbery region, the modulus is not as high as that in Region I, and the rubber is elastic and gives a large deformation without break. When the rubber approaches from the rubbery region to the flow region, Region III, the dominance of the elastic behavior is taken over by the dominance of the vis-

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Table I Samples

Sample	Catalyst	<i>cis</i> -1,4 (%)	1,2-Vinyl (%)	$M_w^a \times 10^{-4}$	$M_n^a \times 10^{-4}$	M_v^b	SPB ^c (Wt %)
BUNA CB11 ^d	Ti	93	4	51	12	47	—
BUNA CB22 ^d	Nd	98	1	53	20.5	63	—
BUNA CB23 ^d	Nd	98	1	51.5	15	51	—
BUNA CB24 ^d	Nd	98	1	66.5	12	44	—
VCR309 ^e	Co	—	—	45.9	17.1	39	9
VCR412 ^e	Co	—	—	45.1	18.8	45	12
VCR617 ^e	Co	—	—	46.2	17.6	63	17
VCR512 ^e	Co	—	—	44.2	15.5	43	12

Data supplied by the manufacturers.

^a Data by GPC; molecular weights are not absolute but relative values based on the hydrodynamically equivalent volume of polystyrene standards. The data of VCRs represent the matrix polymer only.

^b Moony viscosity.

^c The amount of syndiotactic 1,2-polybutadiene crystalline particle.

^d Registered trademark of BayerAG.

^e Registered trademark of UBE Industries.

ous behavior. At this point, the modulus is not high enough to maintain the tight band; also, the band loses strength. Therefore, the band sags and is torn easily. When the rubber is in the flow region, Region IV, it becomes sticky like a polymer melt. The band is held on the roll by the stickiness rather than by the elastic force. As apparent from the above discussion, the four regions of the mill behavior may be simulated by conducting large deformation and failure measurements over the range of temperature and deformation corresponding to the conditions of the mill operation.³

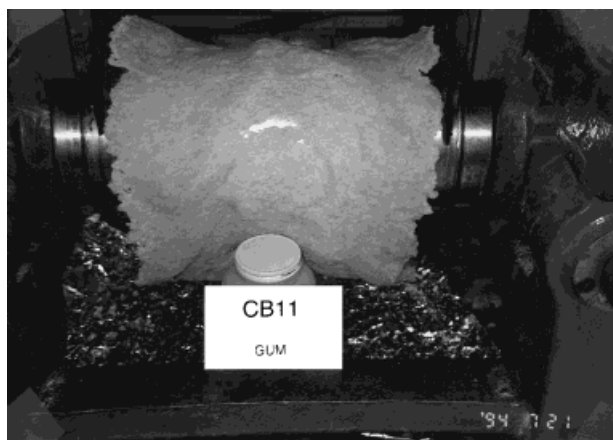
When a gum rubber is charged into a mill at room temperature, if it is in Region I, the mill operator must recharge the broken pieces again and again until the rubber becomes warm enough to be in Region II. The operation is very cumbersome. The usual treatment in the case is to open the mill gap very wide, which reduces the deformation rate. Lowering the deformation rate and increasing the temperature, as is well known, have the same effect on the material; they follow the principle of the time-temperature correspondence, here in a qualitative sense. Thus, the breaking of the rubber becomes less severe at the wider mill gap.

If the milling starts in Region II, the rubber may stay in this region throughout the milling if it possesses a wide rubbery region; on the other hand, if the rubbery region is very narrow, it may move from Region II to III or even to Region IV as the temperature of the rubber increases.

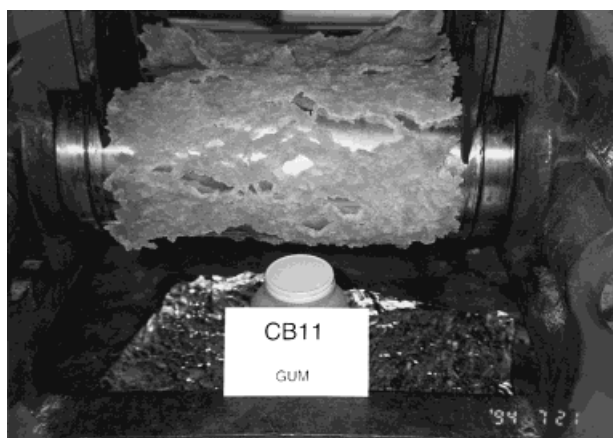
Because the mill behavior is, in general, a mechanical behavior, the same argument must be

applicable to gum rubbers and mixed compounds. However, it does not necessarily mean that when a gum rubber is in Region II the compound made from it must be in Region II also. Rather, in this study, we wished to find the relation between gum rubbers and their compounds with respect to their mill behavior and their deformational (also failure) behavior.

cis-1,4-Polybutadiene is one of the major commercial rubbers. It is usually blended with other rubbers such as NR or SBR because it does not have good processability. It is a soft rubber which tends to go into Region III of the mill processability. To overcome the weakness, many modified polybutadienes have been developed. Such rubbers have structural variations including molecular weight, molecular weight distribution, long branch content, branch pattern, and dispersed crystalline particles. These structures have significant influence on the deformational behavior. This means that deformational measurements may be used for analyzing these structures and for interpreting the mill processability. Although the mill processability is one of the most commonly used techniques for screening of the gum rubbers, systematic interpretation is seldom given. Bruzzone et al.⁴ compared the mill processability of four *cis*-1,4-polybutadienes and corresponding carbon black compounds. The results were rated only in terms of good, fair, or bad. Without reference to the regions of mill processability, it is difficult to tell in what way the mill processability was different. Also, the important structural variables, e.g., the degree and relative



(a)



(b)

Figure 1 (a) Photograph of CB11 gum rubber on the mill. (b) Photograph of CB11 gum rubber on the mill.

length of branching, were not included. In general, there has been no work relating the structural variables of gum rubbers of *cis*-1,4-polybutadiene and their deformational behavior to the four regions of mill processability. In this work, we examined *cis*-1,4-polybutadienes from different sources and explained the differences in mill behavior in terms of the deformational behavior and the structural variables.

EXPERIMENTAL

Samples

The gum rubber samples used are listed in Table I. They may be classified into three groups:

1. Ti-polymerized rubber, CB11, is the most

branched. However, branches are relatively short. The rubber gives strain-softening and strain-induced crystallization upon stretching.⁵

2. Nd-polymerized rubbers, CB22, 23, and 24, have low degrees of branching compared to CB11. However, the branches are longer; they are long enough to give a "constrained" entanglement. It results in strain-hardening when the degree of branching is relatively high, i.e., CB22 and 23. They did not give strain-induced crystallization. The least branched rubber, CB24, gave neither softening nor hardening,⁵ but gave strain-induced crystallization.
3. Co-polymerized rubbers, VCR309, 412, 617, and 512, contain dispersed crystalline particles of 1,2-polybutadiene.⁶ The first three have different amounts of the particles in the same matrix rubber. The matrix rubber of VCR512 has more long branches than that of VCR412. The crystalline particles are made up of a block copolymer of *cis*-1,4- and 1,2-butadiene.⁶ The crystalline particles cause strain-softening. The extent of strain-softening is lessened in VCR512 because the branching of the matrix is long enough to give the "constrained" entanglement resulting in strain-hardening. All VCRs gave strain-induced crystallization.⁷

The compounds were made from these rubbers with 50 phr N330 carbon black from Cabot.

Mixing and Milling

A Banbury-type internal mixer with a 250 cc capacity was used for mixing the compounds. The

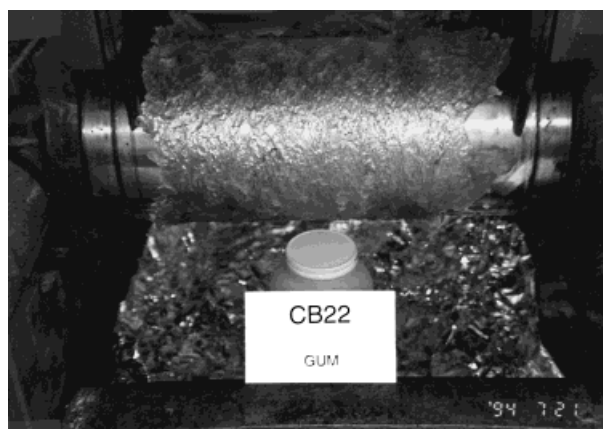


Figure 2 Photograph of CB22 gum rubber on the mill.



Figure 3 Photograph of CB23 gum rubber on the mill.

fill factor was 0.7 and the rotor speed was 100 rpm. After mastication of the rubber for 1 min, carbon black was added over a period of 1 min. After an additional 2 min, the compound was dumped. All dumped compounds were crumbly and a small amount of the free filler remained. After dumping, compounds were immediately milled with a 6-in. two-roll mill in order to develop further mixing and to observe mill processability. Photographs of the rubber on the mill were taken after milling for 2 min. The speed of the fast roll was 28 rpm and the friction ratio was 1 : 1.26.

RESULTS

When CB11 gum was loaded on the mill, it broke into many pieces, which required recharging. The process was repeated several times until a band was formed. The band was loose and sagging as shown

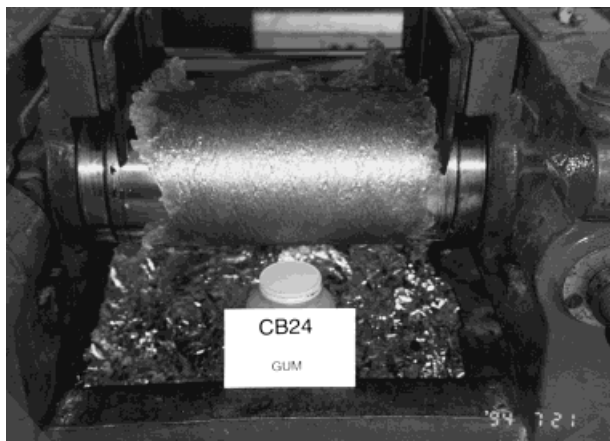


Figure 4 Photograph of CB24 gum rubber on the mill.

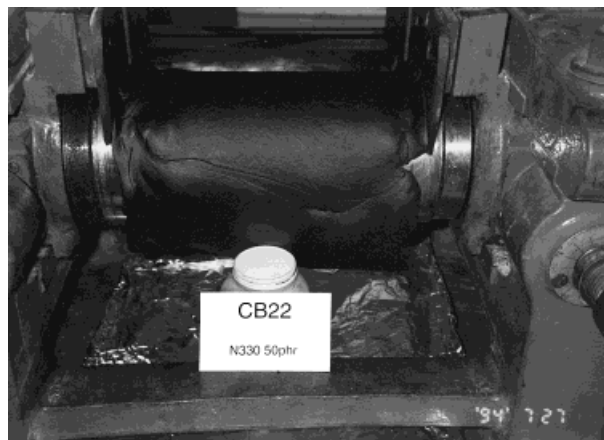


Figure 5 Photograph of CB22 carbon black-filled compound on the mill.

in Figure 1(a). After taking the photograph, the band was pushed up against the roll in an attempt to make a tight band. The band sagged again if not pushed up and tore at many places as shown in Figure 1(b). The CB11 compound did not make a band and crumbled after passing through the mill; therefore, no photograph is shown. With CB22, CB23, and CB24, the gum rubbers formed bands immediately after loading. The bands are as shown in Figures 2–4. The surface of CB22 had a rough texture, that of CB24 was smooth, and that of CB23 was intermediate. The stickiness was observed with all three, but the least with CB22, more with 23, and the most with 24. When the band was cut and the sheet was pulled, CB22 was most elastic, giving a large mill-shrinkage. The elasticity decreased in the order from 22 through 23 to 24. The CB22, 23, and 24 compounds made smooth bands, which were loose on the mill and sagging somewhat (Fig. 5).

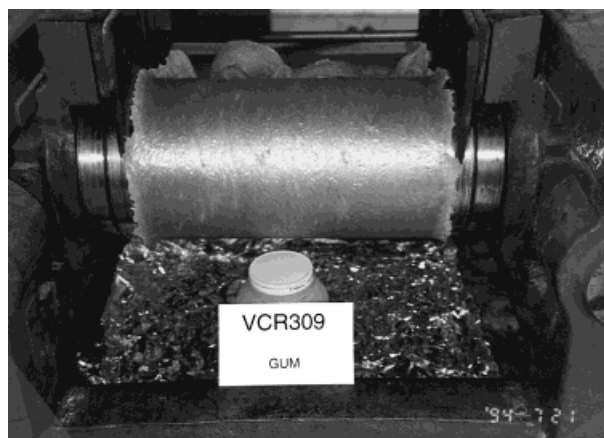


Figure 6 Photograph of VCR309 gum rubber on the mill.

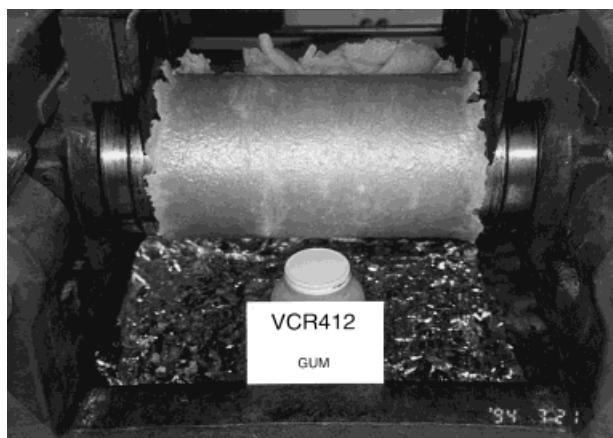


Figure 7 Photograph of VCR412 gum rubber on the mill.

VCR309, VCR412, and VCR617 made smooth bands immediately after charging as shown in Figures 6–8. For VCR512, although it did not break into pieces, the band sagged. When it was pushed against the roll, the band was torn (Fig. 9), but the tearing was not extensive as that in the case of CB11. The bands were not sticky; when the sheet was cut and pulled out, there was no appreciable elastic tension. The VCR309, 412, 617, and 512 compounds made tight bands, of which 412 and 617 had a slight tear (Fig. 10).

DISCUSSION

Although CB11 gum broke into many pieces on charging, it is not likely in Region I, because the rubber is not stiff, and when the band was formed

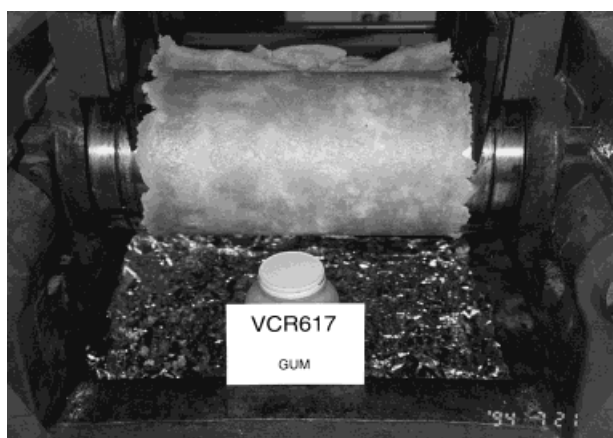


Figure 8 Photograph of VCR617 gum rubber on the mill.

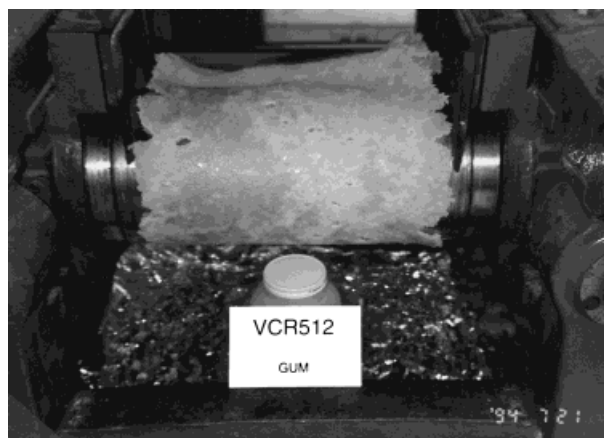


Figure 9 Photograph of VCR512 gum rubber on the mill.

eventually, it behaved more like in Region III. If it had been in Region I, it would have moved to Region II eventually. As shown in Figure 11, CB11 gum has a rather high rate-dependence. (For other CB rubbers, refer to the original articles.⁵) From the principle of time–temperature correspondence, we also expect a relatively high temperature dependence. This was already observed in the dynamic measurement,⁵ where this rubber had highest values of the temperature-shift factor, α_T . When the rate decreased, the strain at break decreased significantly, meaning that when the temperature increases, the strain at break decreases also, going into Region III. The high-temperature dependence comes from the high degree of branching. The nature of the difficulties in milling of CB11 gum rubber and its compound are from the same origin. Although CB11 gum rubber gave strain-induced crystallization in

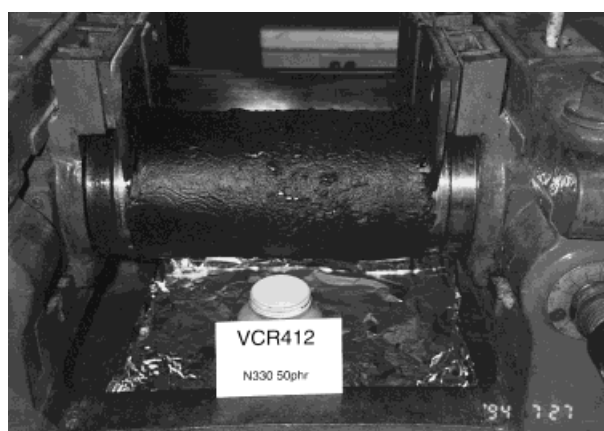


Figure 10 Photograph of VCR412 carbon black-filled compound on the mill.

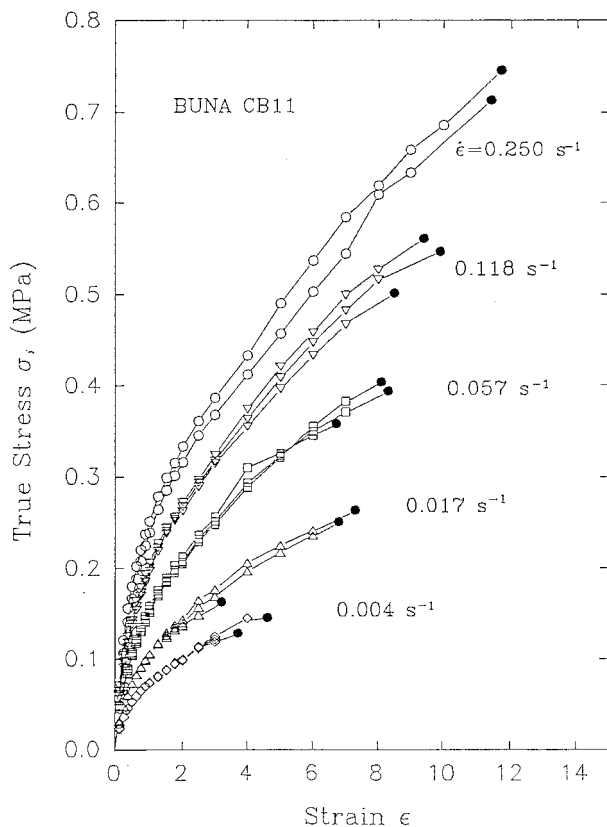


Figure 11 Tensile stress-strain curves of CB11 gum rubber.

tensile tests, it did not help processability. When the rubber is in Region III, there is insufficient tension to cause the crystallization.

The stickiness of gum rubbers, CB22, 23, and 24, indicates that they were in Region IV on the mill. When the carbon black was added, stickiness was no longer observed. Because the stickiness was the reason for forming a band in Region IV, the compound became loose from the surface of the roll. Also, in Region IV, there is insufficient tension to cause strain-induced crystallization for CB24, which crystallizes in a tensile test.

With VCR309, 412, 617, and 512, the gum rubbers were in Region II, bordering toward Region III, exhibiting slight sagging and tearing in some cases but not sticky. Consequently, the compounds made tight bands, but showed slight tearing. VCR512 gum showed a relatively large rate-dependence in the stress-strain measurement compared to those of other VCRs. This is similar to the behavior of CB11 as compared to the other CB rubbers. It implies the higher-temperature dependence as well. This explains the fact that VCR512 tends to move toward Region III as the rubber becomes warmer

on the mill. This is seen as a slight sagging and a slight tearing (Fig. 9), whereas no sagging or tearing occurred with other VCRs.

In contrasting three types of gum rubbers, which are represented by CB11, CB22, and VCR412, a clear-cut differentiation may be made about their mill behavior. CB11 was in Region III, CB22 type was in Region IV, and VCR412 type was in Region II. This ordering is related to the modulus level at the very low frequency region in the dynamic shear measurements.^{5,7} The lower-frequency region of the data represent the higher temperature behavior, which is encountered in milling. Evidently, the added crystalline particles are most effective in raising the modulus at the low frequency as shown with VCR rubbers. A degree of branching is more effective than is a relative length of branching with respect to the modulus level, CB11 vs. CB22. However, if a sticky band, Region IV, is preferred over a sagging band, Region III, CB22 is said to be easier for milling than is CB11.

Among the three Nd-polymerized rubbers, CB22 had the highest degree of branching, followed by 23, and CB24 was the least branched. Because branching makes rubber more elastic, it explains the roughest texture and least stickiness of CB22 among the three. CB22 was most elastic when pulled from the mill and showed a large mill shrinkage. The difference in CB23 and 24 may be explained similarly on the basis of the difference of the degree of branching.

Concerning VCR309, 412, and 617, there was no significant difference in mill behavior among these gum rubbers and also among their compounds, meaning that, within the present variation in the amount of the crystalline particles, no difference was detected in the milling. In detail, however, a significant number of white spots appeared in the band of VCR617, a little in that of VCR412, and none in that of VCR309 (Figs. 6–8). The white spots gradually disappeared when the sheets were removed from the mill and left to relax. The white spots appear to be the strain-induced crystalline domains.

Previously, it was noticed with the matrix rubber⁷ that in the presence of the larger amount of the crystalline particles there was an indication of more strain-induced crystallization. Among the samples that we examined, the three rubbers of the VCR series were the only ones which gave an indication of strain-induced crystallization in milling. This means that in order for the gum rubber and the compound to have strain-induced

crystallization during milling the material must be under sufficient tension, i.e., Region II.

The mill behavior of the compounds with respect to the four regions of processability was readily explained from the mill behavior of the matrix rubber. Within the structural variables investigated in this study, both the gum rubber and the corresponding compounds were in the same region of mill processability.

CONCLUSION

Mill behavior among Ti-polymerized, Nd-polymerized, and Co-polymerized (containing crystalline particles) rubbers were classified in accordance with the four regions of mill processability of Tokita and White. Ti-rubber was in Region III, Nd-rubbers were in Region IV, and Co-rubbers were in Region II. The compound behavior reflected the behavior of the gum rubbers as described above.

The most significant structural variables were branching and the dispersed crystalline particles. A high degree of branching tended to decrease the elongation at break significantly, when temperature went up on the mill. This brought Ti-rubber to Region III. On the other hand, a low degree of branching of Nd-rubbers, even though the branches were very long, tended to bring this rubber into

Region IV, which was not as good a processing region as Region II.

The dispersed crystalline particles in Co-rubbers brought them into Region II. A larger amount of the crystalline particles provided a higher degree of strain-induced crystallization. It appeared that only when the rubber was in Region II was there a sufficient tension to give strain-induced crystallization on the mill.

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