Effect of Fillers and Rubber Structures on Tensile Behavior of Filled, Unvulcanized Compounds of *cis*-1,4-Polybutadienes

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ABSTRACT: The effect of fillers and the structure of matrix rubbers on the tensile stress–strain behavior were examined with unvulcanized compounds of *cis*-1,4-polybutadiene. The matrix rubbers were CB11, CB22, and VCR412, which had been studied previously. The fillers were two different carbon blacks (N110 and N330) and silica. The tensile modulus was found to be separable into the time-dependent and strain-dependent functions. The time dependence was represented with a universal form, the observed time being reduced with the extension ratio. The strain-dependent function was affected by material variables. The function indicated a strain-softening tendency. The extent of softening is related to the softening or hardening observed with the unfilled matrix rubbers, which are in turn related to the length and degree of branching and to the presence of crystalline particles of 1,2-polybutadiene. However, carbon black evidently accentuates the softening tendency. Also, poorer dispersion results in higher softening. The silica-filled compound had a poor dispersion. With the addition of a coupling agent, the dispersion improved but the compound behaved like it was crosslinked. The strain-induced crystallization previously observed with CB11 and VCR412 gum rubbers (but not with CB22) appears as significant differences of the moduli of the compounds. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1445–1453, 1997

Key words: fillers; rubber structures; tensile behavior; filled unvulcanized compounds; *cis*-1,4-polybutadiene

INTRODUCTION

Tensile stress–strain measurements have been one of the standard methods for characterizing rubber vulcanizates.[1] The tensile moduli at certain strains and the failure data are usually used for characterizing the properties of the vulcanizates. They are also used to interpret the network structure and reinforcement mechanisms.[2] However, the use of tensile stress–strain measurements for characterizing filled but unvulcanized compounds have been rather limited. In fact, viscoelastic studies with unvulcanized rubber compounds are rare. Arai and Ferry[3] made shear measurements of carbon black filled compounds including *cis*-1,4-polybutadiene, but only at small deformations.

The viscoelastic work relating the properties of various grades of gum rubbers to those of the corresponding compounds was reported before for nitrile butadiene rubbers (NBRs).[4] The present work was motivated by a similar interest in *cis*-1,4-polybutadienes.

It is known that *cis*-1,4-polybutadiene tends to be soft and is difficult to mill. This behavior is different from that of gum rubbers like styrene BR (SBR) and NBR. In the previous articles[5,6] of

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Table I Samples

Sample Designation	Catalyst	Type (*cis* Content)	Mooney Viscosity of Gum	Filler Loading (phr)
BUNA CB11[a]	Ti	*cis*-BR (93%)	47	N110[b] 50 N330[b] 50
BUNA CB22[a]	Nd	*cis*-BR (98%)	63	N110[b] 50 N330[b] 50 VN3[c] 56 VN3[c] 56/Si 69[d] 5.6
VCR412[e]	Co	*cis*-BR (91%) and SPB[f]	45	N110[b] 50 N330[b] 50

[a] Registered trademark of Bayer AG.
[b] Produced by Cabot.
[c] Silica produced by Degussa.
[d] Coupling agent produced by Degussa. Bis(3-[triethoxisilyl]propyl)tetrasulfane.
[e] Registered trademark of UBE Industry.
[f] Crystalline particles made up of block copolymer of *cis*-1,4- and *syn*-1,2-polybutadiene.

this series, the effect of long branching and dispersed crystalline particles on the deformational behavior were investigated with various grades of *cis*-1,4-polybutadiene. At large deformation the long branches introduced strain softening for some rubbers and hardening for others. These differences were explained with a relative branch length, that is, strain softening for shorter branches and strain hardening for longer branches. The presence of the crystalline particles introduced strain softening and the mechanism was interpreted to be the same as the effect of shorter branches, which in this case are the *cis*-1,4-polybutadiene branches attached on the surface of the crystalline particles. With the emulsion polymerized SBR and NBR some grades exhibited strain hardening but strain softening was never observed.

Building on the knowledge of the gum rubber behavior, we wish to extend our investigation to the filled compounds made from the above-mentioned rubbers. The method of the investigation is an examination of the tensile stress–strain data to see if the tensile modulus is separable to the time-dependent and strain-dependent functions. As will be explained later, the time dependence is in a universal form and only the strain dependence is affected by material variables. The effect of different fillers on the above behavior will also be examined.

Characterization Methods

In general, the tensile data being nonlinear, tensile stress σ and strain ε may be presented as modulus E, which depends upon time t and strain as

$$\sigma/\varepsilon = E(t, \varepsilon) \qquad (1)$$

When time and strain are separable, eq. (1) may be written as[7]

$$\sigma/\varepsilon = F(t)\phi(\varepsilon) \qquad (2)$$

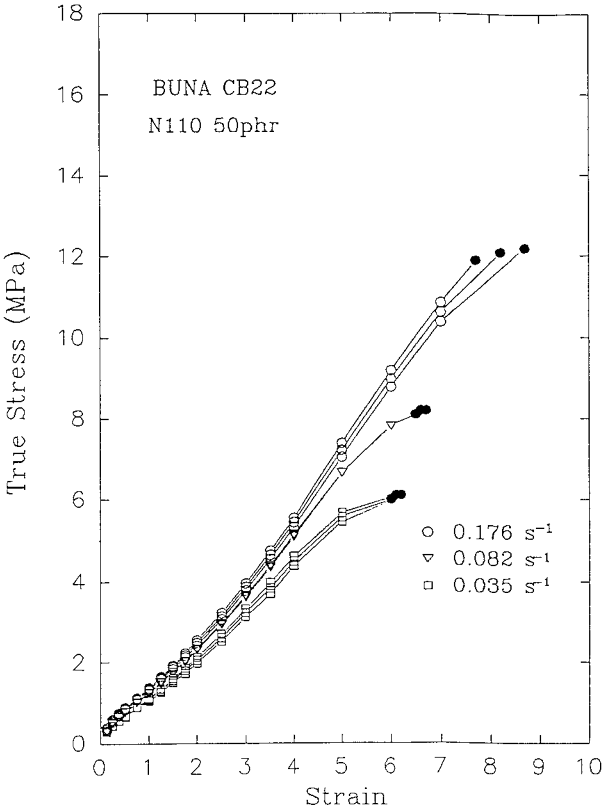

Figure 1 Tensile stress–strain curves of CB22 compound with carbon black N110.

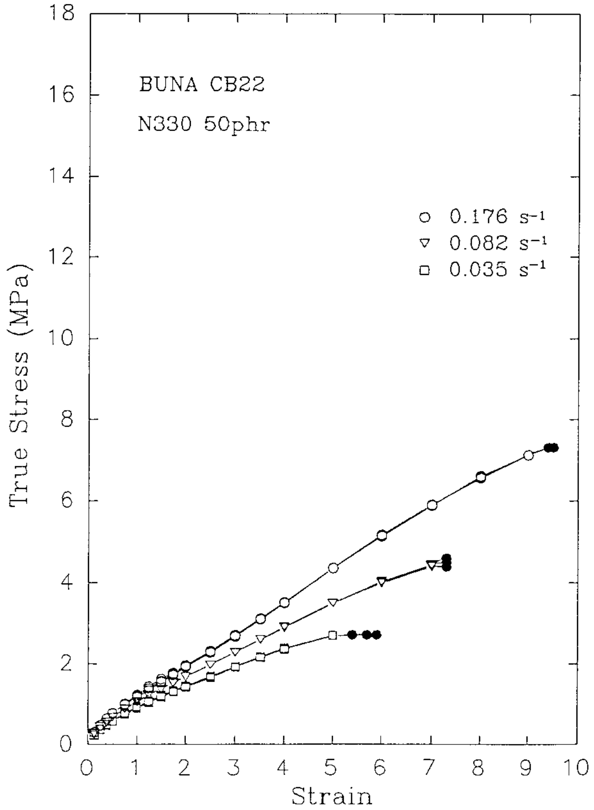

Figure 2 Tensile stress–strain curves of CB22 compound with carbon black N330.

where $F(t)$ and $\phi(\varepsilon)$ are functions of time and strain, respectively, and $\phi(\varepsilon) \rightarrow 1$ at $\varepsilon = 0$. Therefore, this equation offers a means of linearizing the nonlinear data. However, the use of this representation in relating the polymer structure to its elongational behavior has not been demonstrated.

In the previous study[8] a different linearization scheme was used to relate the structure to behavior,

$$\sigma/\varepsilon = E(\alpha t) \qquad (3)$$

where α is the extension ratio,

$$\alpha = \varepsilon + 1 \qquad (4)$$

Therefore, it is a universal constant. When eq. (3) is applicable, plots of log $E(t, \varepsilon)$ against log t at fixed values of ε may be shifted along the time axis by the magnitude of α to form a master curve. Because α approaches unity as ε approaches zero, this is also a linearization scheme. The direction of the shift with the increasing strain is the same as that with the increasing temperature in the time–temperature correspondence. This treatment recognizes a similarity between the effect of thermal activation and that of mechanical activation on the "material time."[9] A number of gum rubbers are shown to obey this linearization scheme (strain–time correspondence). They are, in general, gel-free polymers or polymers containing microgels (a crosslinked particle). However, a rubber containing macrogel (extensively branched giant molecule) and a crosslinked-network rubber do not obey the scheme; for the former an additional modulus shift is necessary,[10]

$$\sigma/\varepsilon = E(\alpha t)\Gamma(\alpha) \qquad (5)$$

where $\Gamma(\alpha)$ is the modulus shift factor. When the macrogel is present, $\Gamma(\alpha) > 1$, indicating strain hardening.

EXPERIMENTAL

Sample

Samples of gum rubbers and fillers used for the compounds are listed in Table I. These gum rub-

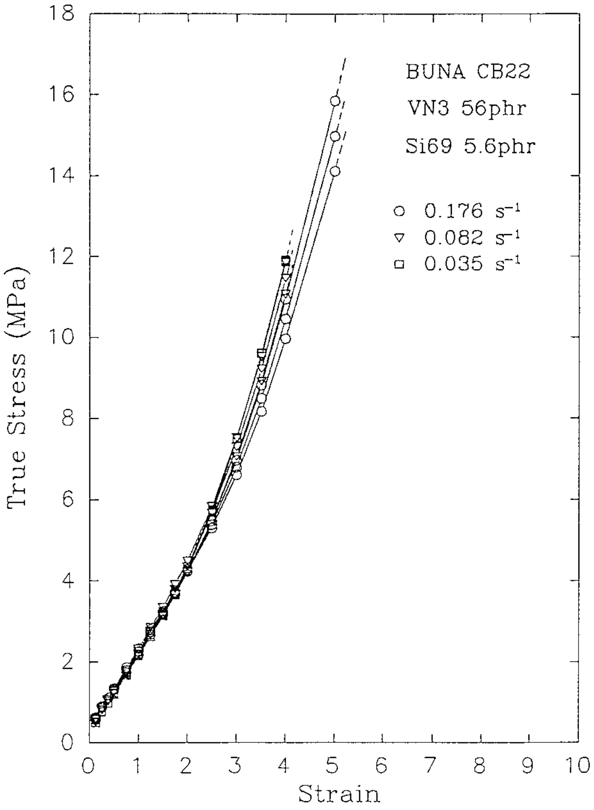

Figure 3 Tensile stress–strain curves of CB22 compound with silica and coupling agent.

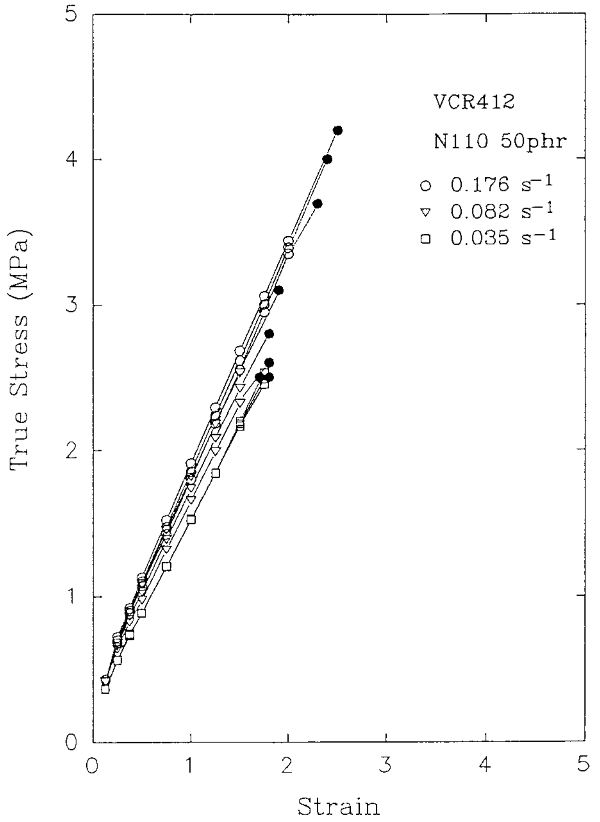

Figure 4 Tensile stress–strain curves of VCR412 compound with carbon black N110.

bers were chosen from eight previously studied samples, which represented three different groups. They were Ti-, Nd-, and Co-polymerized polymers. The Ti-polymerized CB11 had a higher degree of branching but the branches were relatively short, causing strain softening. Nd-polymerized CB22 had a lower degree of branching than that of CB11, but the branches were relatively long and exhibited strain hardening. The Co-polymerized VCR412 contained 12% crystalline particles made from a block copolymer of *cis*-1,4- and -1,2-polybutadiene.[11] The particles produced strain softening. The *cis*-1,4 branches attached to the surface of the particles were relatively short and facilitated the elongation.

The amount of silica was adjusted to make its volume equal to the volume of 50-phr carbon black by taking account of the density difference.

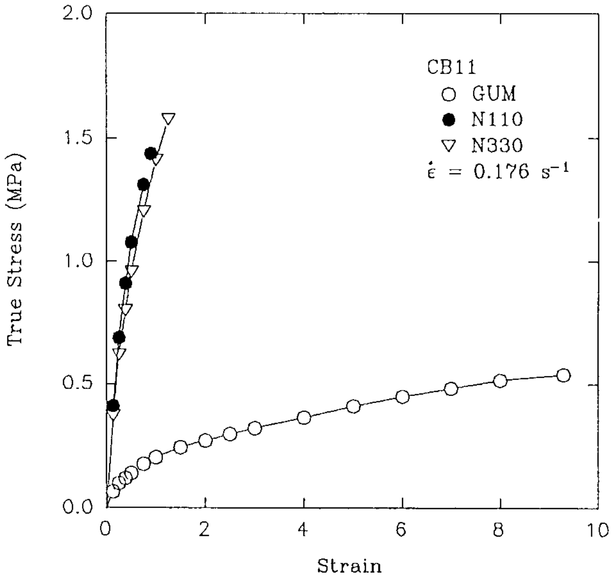

Figure 5 Comparison of tensile stress–strain curves of gum rubber and compounds of CB11.

Mixing

A Banbury-type internal mixer with a 250-mL capacity was used. The fill factor was 0.7 and the rotor speed was 100 rpm. First the mixer was cleaned with gum rubber. Then fresh rubber was charged and masticated for 1 min. At this time half of the carbon black was added over a period of 1 min. After an additional 30 s of mixing the rest of the carbon black was added. After mixing another 2 min, the compound was dumped. For mixing of silica, one-third was added every minute. After an additional 4 min of mixing the compound was dumped. The coupling agent was added with the second addition of silica. All

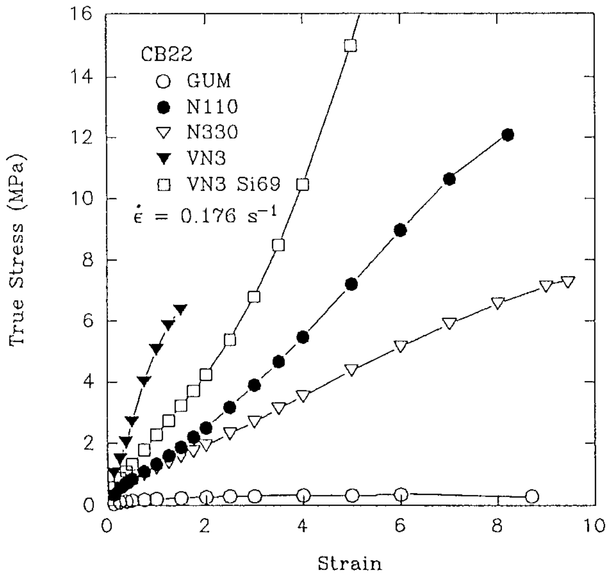

Figure 6 Comparison of tensile stress–strain curves of gum rubber and compounds of CB22.

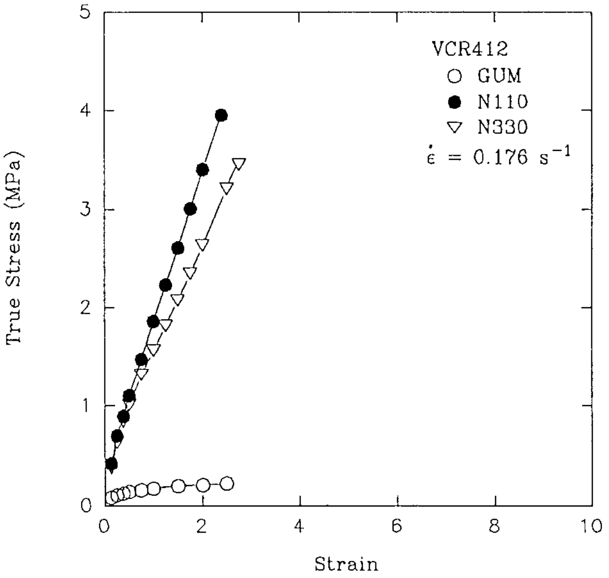

Figure 7 Comparison of tensile stress–strain curves of gum rubber and compounds of VCR412.

dumped compounds were crumbly and a small amount of the free filler remained.

The dumped compounds were milled and sheeted with a 6-in. two roll mill to develop further mixing and to observe mill behavior of the compounds. All compounds were pressed at 140°C for 10 min for preparing tensile specimens.

Tensile Measurement

Tensile measurements were performed with a Monsanto Tensometer 500. The strip chart recorder recorded force against time. The force was measured with a 45-kg load cell. The extent of deformation was measured by recording with a videocamera. The measurements were performed at room temperature with deformation rates of 0.035, 0.082, and 0.176 s^{-1}.

RESULT AND DISCUSSION

Examples of stress–strain curves at various deformation rates are shown in Figures 1–4 where the stress is the true stress, assuming incompressibility of the compounds. The data of the same symbol show reproducibility of the measurement, which was within ±3%. It was smaller compared to that of the gum rubbers: ±15%. The stress–strain curves of the carbon black compounds include failure data shown by filled circles. The silica-filled compound of CB22 with coupling agent was very stiff and the specimen slipped out of the grips at the high elongation. With this compound the stress decreased slightly with the increasing deformation rate at the large deformation. This may be the error resulting from slipping. However, the silica-filled compound without the coupling agent and the carbon black filled compounds showed the increase of stress with increasing deformation rate.

In Figures 5–7 stress–strain curves of gum rubbers and their filled compounds are compared. The stresses for all compounds are greatly increased by the filler. The gum rubbers of CB11 and CB22 showed a similar elongation at break. However, the elongation at break of the CB11 compound was considerably reduced in the presence of carbon black whereas that of the CB22 compound was unaltered. From our previous work[5] CB11 was known to have a higher degree of branching than CB22, but the branches of the former were found to be relatively short whereas those of the latter were found to be long. The more branched rubber is known generally to have a higher affinity to carbon black. This together with the shortness of the branches may be the cause

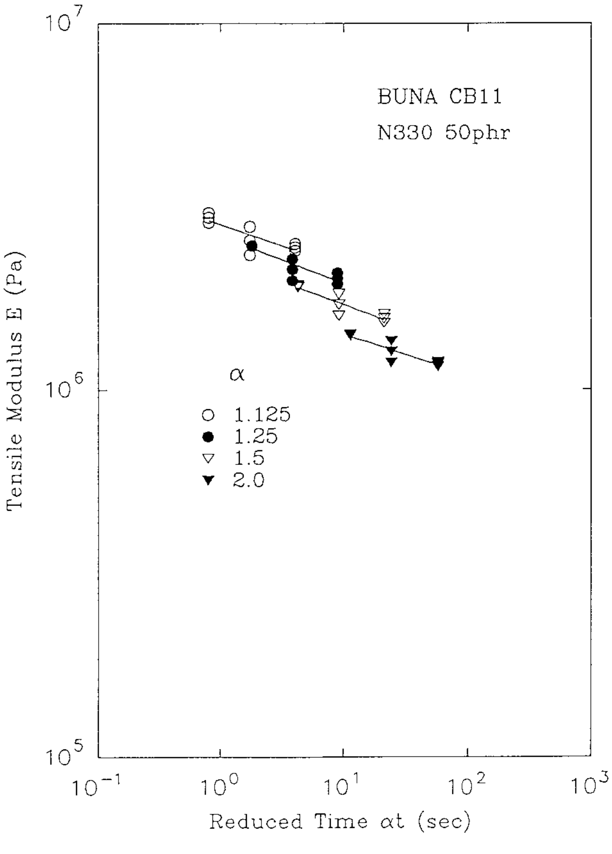

Figure 8 Tensile modulus as a function of reduced time at fixed extension ratios for CB11.

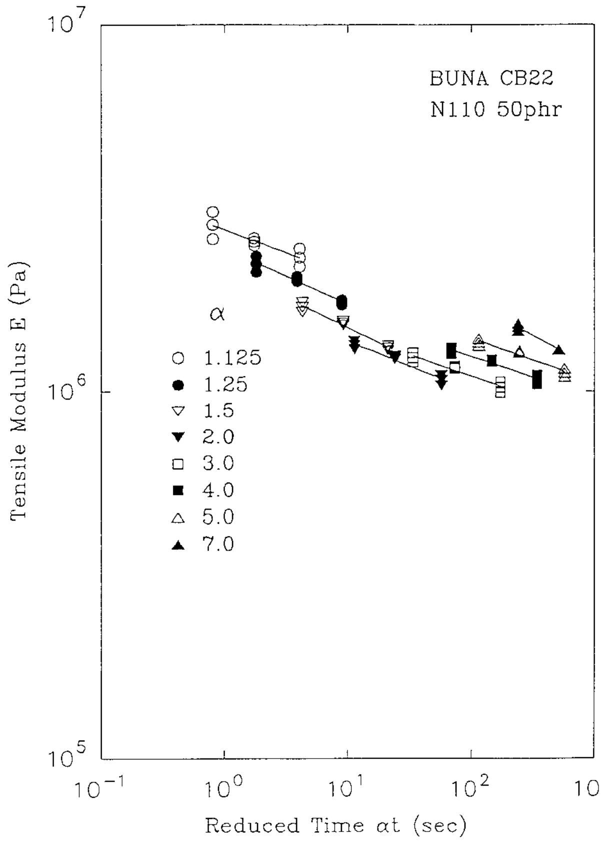

Figure 9 Tensile modulus as a function of reduced time at fixed extension ratios for CB22.

of the reduced elongation at break of the CB11 compound. On the other hand, long branches are known to aid the retention of elongation at break upon loading with carbon black,[12] the fact that accounts for the above-mentioned behavior of the CB22 compound.

Gum VCR412 has a much lower strain at break compared to CB11 and CB22. The matrix rubber of VCR412 is not significantly different from that of CB22, except for the crystalline particles. Therefore, the crystalline particles must be affecting the decrease of strain at break. The addition of carbon blacks does not decrease the strain at break. In this respect it is similar to the CB22.

Referring to Figure 6, the silica-filled compound without the coupling agent shows the highest modulus. This is because of the poor dispersion of the filler.[13] The compound with silica and the coupling agent show lower modulus because of a better dispersion. This compound behaves like a crosslinked network; the stress rise indicates limited extensibility. The coupling agent is known to sometimes give premature crosslinking during compounding.[14] The carbon black filled compounds show lower modulus than those of silica-filled compounds because of the better dispersion. The compounds with smaller particles of carbon black (N110) show higher modulus than that with larger particles (N330); the better reinforcement from smaller particles is well recognized.

Figures 8 and 9 show modulus as a function of reduced time [eq. (3)]. The lines connect the data at the same strain. The parallel lines at different strains were obtained. Master curves after application of the modulus shift, eq. (5), are shown in Figures 10 and 11. With all compounds the master curves were obtained after the time and the modulus shift. As shown in Figures 12–14, the direction of the modulus shift was that of strain softening for all compounds. The different behavior of the gum rubbers CB11 and CB22 (i.e., strain softening vs. strain hardening[5]) is apparently carried over to the difference in the behavior of the corresponding compounds; that is, the initial strain softening of the CB11 compounds is much higher than that of the CB22 compounds. Also, the softening trends were reversed at the higher elongation in the CB22 compounds (Fig. 13), indicating the strain hardening of the matrix rubber. The

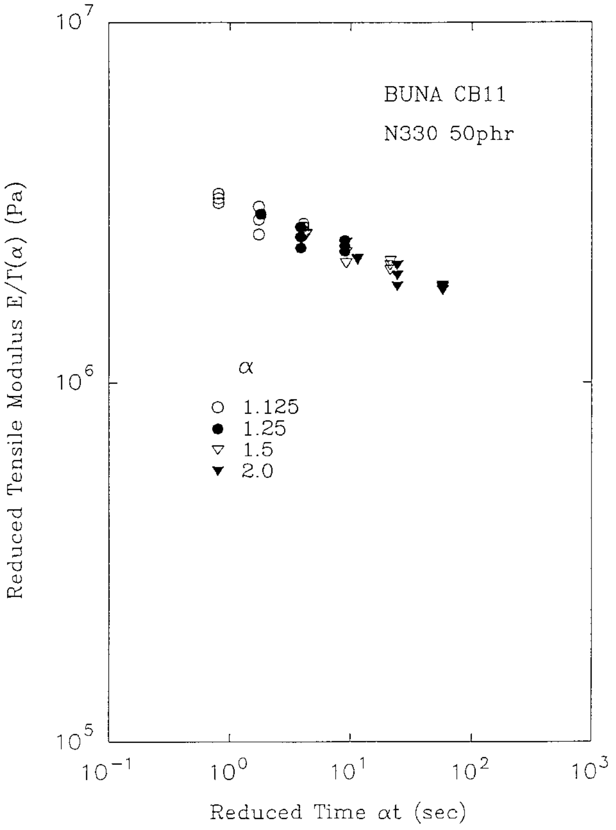

Figure 10 Reduced tensile modulus as a function of reduced time for CB11.

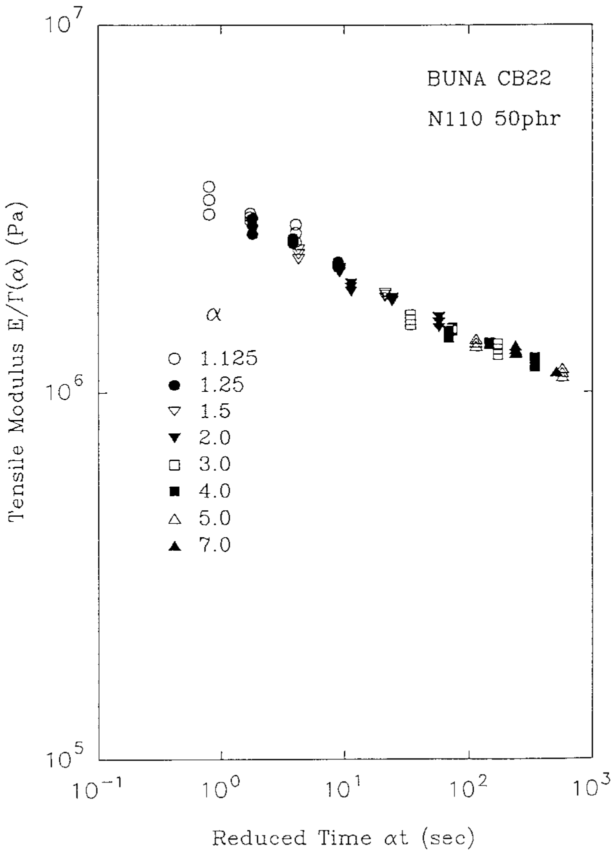

Figure 11 Reduced tensile modulus as a function of reduced time for CB22.

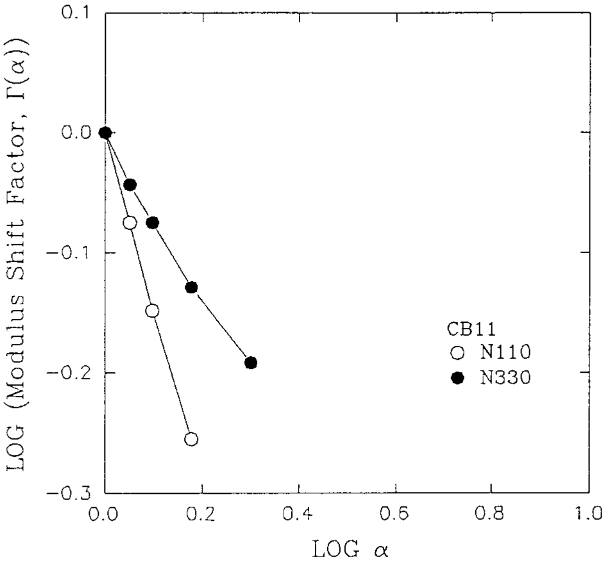

Figure 12 Modulus shift factors as a function of extension ratio for CB11 compounds, indicating degree of strain softening.

carbon black filled compounds with N110 compared to those with N330 show a larger degree of strain softening for CB11 and CB22 but not for VCR412. The carbon black N110 is more difficult to disperse than the N330. The compounds exhibiting a greater degree of strain softening, when other variables are unchanged, have relatively poor dispersion of the filler. VCR412 was the easiest to handle on the mill when either of the carbon blacks was incorporated. This accounts for the same degree of strain softening for N110 and N330. On the other hand, if we compare CB22 and VCR412 compounds with carbon black N330 (Figs. 13, 14), the CB22 compound shows much less strain softening than the VCR412 compound does. The difference must come from the difference of the behaviors of the matrix rubbers: CB22 produces strain hardening and VCR412 strain softening. These rubbers with N110 show the same degree of strain softening. As mentioned before, the explanation is a poor dispersion of N110 in CB22, a fact that resulted in substantial strain softening.

The effect of silica on strain softening is larger than that of carbon black. This is because of the poorer dispersion of silica compared to that of carbon black. Because of the poor dispersion of the silica and anomalous crosslinking due to the coupling agent, no further comment can be made for the silica-filled compounds.

Whereas the extent and the manner of the strain softening provides useful information on

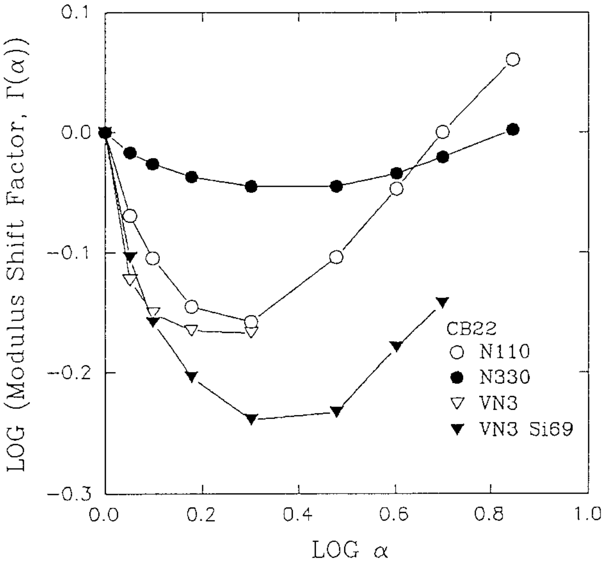

Figure 13 Modulus shift factors as a function of extension ratio for CB22 compounds, indicating degree of strain softening.

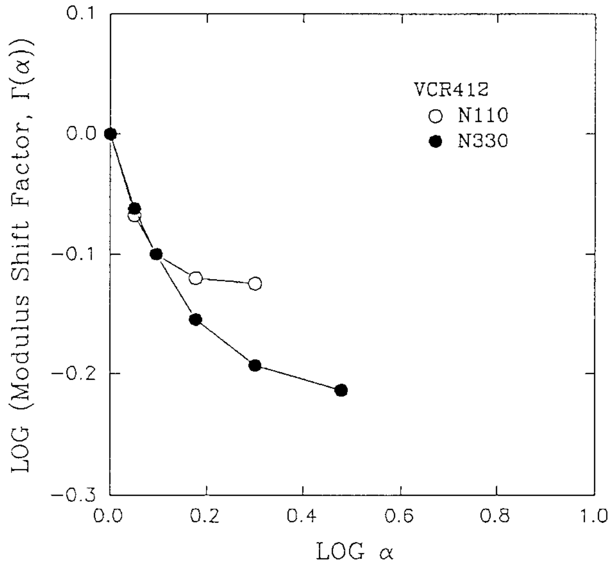

Figure 14 Modulus shift factors as a function of extension ratio for VCR412 compounds, indicating degree of strain softening.

the effect of fillers and that of the structure of matrix rubbers, the data are taken relative to the moduli at the infinitesimal strain. Therefore, the absolute magnitude of moduli must also be examined. The data in Table II indicate clearly that the moduli of CB22 compounds are significantly lower than those of CB11 and VCR412 at all strain rates. In the previous observations[5,6] with gum rubbers, CB22 did not give a noticeable strain-induced crystallization while CB11 and VCR412 clearly indicated crystallization. Therefore, the above differences in the compound moduli are attributable to the difference in the ease of strain-induced crystallization of the matrix rubbers.

CONCLUSION

Tensile stress–strain measurements were shown to be very effective for characterizing the carbon black filled compounds of *cis*-1,4-polybutadienes chosen from three groups of different origins. We noted large differences in the values of the elongation to break, which were shown with both N110 and N330 carbon blacks. The differences were explained on the basis of the relative length of the branches and the presence of the crystalline particles in one of the rubbers.

The separability of the time and strain worked with the data. After applying the time shift of the strain–time correspondence and the modulus shift, we found strain-softening behavior for all the compounds. However, the extent of the strain softening was different among them. This was related to the behavior of the matrix rubber as well as the differences in the degree of dispersion of the carbon black; poorer dispersion gives more softening. With one compound at the higher elongation the extent of the strain softening decreased or even pointed toward strain hardening. The matrix rubber of this compound exhibited strain hardening whereas two other matrix rubbers gave strain softening. This indicated that the structure of the matrix rubber had a significant effect on the elongational behavior of the compound.

There were significant differences in the compound moduli, indicating the differences in the ease of strain-induced crystallization of matrix rubbers.

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Table II Tensile Modulus of Compounds

	CB11			CB22			VCR412		
	M50	M100	M200	M50	M100	M200	M50	M100	M200
$\dot{\varepsilon} = 0.176\ s^{-1}$									
N110	1.08	—	—	0.85	1.34	2.48	1.10	1.86	3.40
N330	0.96	1.41	—	0.76	1.19	1.93	1.01	1.57	2.64
$\dot{\varepsilon} = 0.082\ s^{-1}$									
N110	1.03	—	—	0.77	1.24	2.33	1.03	1.74	—
N330	0.85	1.27	—	0.66	1.05	1.67	0.87	1.36	2.36
$\dot{\varepsilon} = 0.035\ s^{-1}$									
N110	0.92	—	—	0.66	1.08	2.06	0.89	1.53	—
N330	0.88	1.18	—	0.57	0.91	1.43	0.82	1.33	2.27

M50, M100, and M200 are the modulus (in MPa) at 50, 100, and 200% strain.

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