Studying the Storage Maturation of Freshly Mixed Rubber Compounds and Its Effects on Processing Properties

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SYNOPSIS

Experiments were performed to study the variation upon storage at room temperature of both the bound rubber and the rheological properties of filled rubber compounds, prepared either with high cis-1,4 polybutadiene or with natural rubber and various levels of a reinforcing carbon black. It was found that the bound rubber and the rheological properties vary upon storage according to a two-stage model. Depending on the chemical nature of the rubber, several hundred hours storage are necessary before constant properties are measured. These variations are related to changes occuring in the rubber-black morphology of the compounds. Large strain rheological tests are most sensitive to storage maturation which suggests an explanation for well-known hardening effects observed on the factory floor. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

When an elastomer and a reinforcing filler (i.e., carbon black) are mixed, the interactions are so strong that a good solvent of the rubber can only extract a portion from the compounds. The remaining fraction of elastomer is called "bound rubber." Known for years,[1] this concept has been extensively studied as one of the major factors in carbon black reinforcement.[2-6] The possible relationship between bound rubber and the processing behavior of uncured compounds is a relatively recent concern[6] and it has been demonstrated that, whatever the rubber nature, bound rubber evolves during a storage period of approximately 1 month at room temperature, before reaching a constant value.[7] If, indeed, bound rubber is a key component in controlling the flow behavior of rubber compounds, it can be expected that this storage maturation process goes along with similar changes in rheological properties, thus explaining the well-known hardening effect of compounds on storage, as observed on the factory floor.

The aims of the reported work were to study the variations of both the bound rubber and the rheological properties of a series of natural rubber and high cis-polybutadiene compounds with various levels of HAF carbon black, over a storage period of several weeks at room temperature. Extensive use of a new dynamic tester for rubber has been made and original testing techniques have been developed.

EXPERIMENTAL

Test Materials and Compounds

Compounds were prepared in an internal mixer with SMR 60CV natural rubber and high cis-1,4-polybutadiene with different levels of N330 carbon black. The formulations and the mixing procedure are given in Tables I and II. After dump, the compounds were sheeted off on a roll-mill and stored at room temperature under a plastic cover. Samples for bound rubber measurements and rheological tests were taken at various intervals during 3 months.

Bound Rubber Measurements

Bound rubber (BR) was measured according to a technique previously described,[7] using toluene as the

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Table I   Formulations

Compound	BR 30	BR 50	BR 70	NR 30	NR 50	NR 70
Neocis BR 40[a]	100	100	100	—	—	—
SMR 60 CV[b]	—	—	—	100	100	100
N330 black	30	50	70	30	50	70
Rhenogran ZnO 80[c]	6.25	6.25	6.25	6.25	6.25	6.25
Stearic acid	2	2	2	2	2	2
Dutrex R729[d]	5	5	5	5	5	5
Anox HB antioxidant[e]	2	2	2	2	2	2

[a] 98% cis-1,4-polybutadiene; $ML_{(1+4)}$ 100°C = 43; EniChem Elastomeri.
[b] Natural rubber; premasticated to $ML_{(1+4)}$ 100°C = 44.
[c] Polymer-bound ZnO (80%); Rhein Chemie.
[d] Aromatic oil; Shell Chemical Co.
[e] Polymerized trimethyldihydroquinolin; EniChem Synthesis.

solvent. Essentially, around 0.5 g of the sample was cut in small pieces and introduced in a steel wire basket previously weighed; the basket was suspended in 150 mL toluene under stirring for 72 h at room temperature. Then, the basket was slowly removed from the solvent and dried a few hours at room temperature, then for 24 h under vacuum at 40°C. Complete drying was checked by a constant final weight. The amount of BR (in % of initial rubber content of the compound) is calculated from

$$BR(\%) = 100 \times \frac{(m_{init} - m_{bask}) - \dfrac{CPD}{100}(m_{init} - m_{end})}{(m_{init} - m_{bask})}$$

where CPD is the total formulation (in phr); m_{init},

Table II   Mixing Conditions

Internal mixer (Banbury type): Pomini 4.3 L

Mixing conditions	
Rotor speed	60 rpm
Start temperature	30°C
Ram pressure	3 bar
Cooling water	Full

Mixing Procedure

Operation	Power Reading (MJ)
• Add all ingredients, then rubber	0
• Dump	3

the initial weight (basket + unextracted sample); m_{bask}, the empty basket weight; and m_{end}, the final weight (basket + extracted sample), dried.

Rheological Measurements

Mooney tests were performed at 100°C according to a standard procedure (ASTM D1646—Test method for rubber-viscosity and vulcanization characteristics [Mooney Viscometer]).

The new dynamic strain tester for (uncured) rubbers designed by Monsanto, i.e., the Rubber Process Analyzer 2000 (RPA),[8] was extensively used to perform various tests as described below. This instrument is essentially a moving die rheometer with frequency and strain sweep capabilities at selected temperatures. Figure 1 schematically describes the reciprocal cones test cavity with grooved dies to prevent slippage. The cavity has a diameter of 20.625 mm and the angle between the cones is 0.125 rad; the cavity volume is 4.5 cm^3. The instrument is fully monitored by a computer, thus allowing complex testing procedures to be programmed in the following ranges: frequency, 0.21–209.44 rad/s; strain, 0–90° (depending on ω); and temperature, 40–200°C.

The lower die of the RPA2000 is oscillating and moved sinusoidally by a special drive motor over selected ranges of strain and frequency. The upper die is connected to a torque transducer, separately calibrated with a torsion spring. The sinusoidal strain on the rubber produces a corresponding signal: in fact, the complex dynamic torque that is separated into inphase and 90° out-of-phase components. The corresponding elastic $G'(\omega)$ and viscous $G''(\omega)$ moduli are calculated from the torque measurements
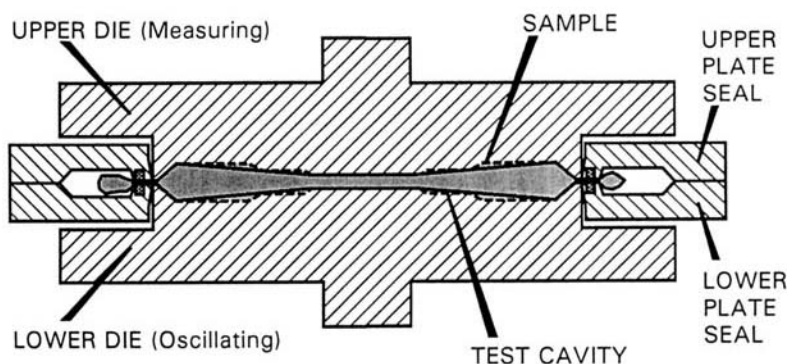
MONSANTO RPA 2000 - Rubber Process Analyzer
Dynamic strain tester for rubbery materials

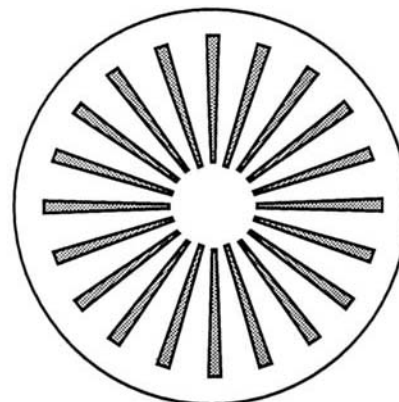## Cross-section of test cavity

Grooved dies

Figure 1   Schematic description of the measuring gap of the Monsanto Rubber Process Analyzer RPA 2000.

and the appropriate shape factor. Test data can be stored on a diskette and retrieved in spreadsheet software for further handling.

RESULTS

Bound Rubber and Mooney Viscosity

Tables III and IV give the Mooney test results [i.e., initial peak value and $ML_{(1+4)}$] and the BR data as measured at different times after dump (i.e., from 24 h up to 3 months after compounding). At 100°C, some compounds with 70 phr carbon black were so viscous that the capabilities of the viscometer were exceeded.

As can be seen, both the Mooney viscosity and the BR readily evolve during the maturation period. As already observed with a series of other compounds,[7] the BR is steadily increasing with the square root of time until a plateau is reached. Therefore, a two-stage variation model can well fit the data, as shown in Figures 2 and 3. As can be seen, the occurrence of the plateau seems to depend

Table III   Mooney Visocisty; $ML_{(1+4)}$ at 100°C

	Peak	$ML_{(1+4)}$	Peak	$ML_{(1+4)}$	Peak	$ML_{(1+4)}$	Peak	$ML_{(1+4)}$
	Time After Dump							
	24 h		168 h		696 h		1752 h	
BR 30	67.2	52.6	71.1	54.5	73.2	55.0	74.8	55.7
BR 50	114.7	77.9	121.4	79.9	127.8	82.1	132.5	83.2
BR 70	a	a	a	a	a	a	a	a
	24 h		168 h		696 h		1512 h	
NR 30	57.7	41.3	67.3	43.1	62.7	44.0	65.5	43.3
NR 50	82.2	54.4	89.3	56.0	94.1	57.1	102.6	56.8
NR 70	174.2	96.1	198.5	98.0	a	a	196.8[b]	99.9[b]

[a] Data outside instrument scale.
[b] Extrapolated from measurements at higher temperature.

Table IV   Bound Rubber Data

Compound	Filler Volume Fraction[a]	BR (%) Time After Dumping			
		24 h	168 h	696 h	2208 h
BR 30	0.312	7.28	9.41	10.06	10.66
BR 50	0.430	13.63	14.62	15.23	15.93
BR 70	0.514	17.64	19.71	20.46	21.30
		24 h	168 h	696 h	2040 h
NR 30	0.316	10.98	13.31	18.84	21.36
NR 50	0.435	16.66	21.23	26.68	28.25
NR 70	0.518	20.24	25.67	30.35	32.03

[a] The following specific gravity data were used to calculate the volume fractions—NR: 0.92 g/cm^3; BR: 0.90; N330 black: 1.80; Rhenogran ZnO 80: 2.90; stearic acid: 0.92; oil: 0.98; anox: 1.10.

mainly on the rubber nature, with no significant effect of the filler level. With the BR compounds, the plateau is reached within 300 h, and with the natural rubber (NR) compounds, within 600 h.

Figure 4 shows the effect of storage on Mooney viscosity; the occurrence of a plateau (i.e., constant viscosity reached after a certain period) is clearly seen. Note that in order to complete the viscosity data, the missing results [i.e., $ML_{(1+4)}$ 100°C > 100] were estimated. For the 70 phr N330-filled BR compounds, the Guth and Gold relationship[9]—as modified by White and Crowder to consider the effective volume fraction of the filler[10]—was used to calculate the likely viscosity data (at any given storage time t) from

$$ML_{[\ ]}(t) = ML_0(t) \times [1 + 2.5$$
$$\times \phi_{eff}(t) + 14.1 \times \phi_{eff}^2(t)]$$

where $ML_{[\ ]}$ is the viscosity at a given filler fraction, and ML_0, the (unknown) viscosity at a zero filler

BOUND RUBBER MATURATION (at room Temperature)
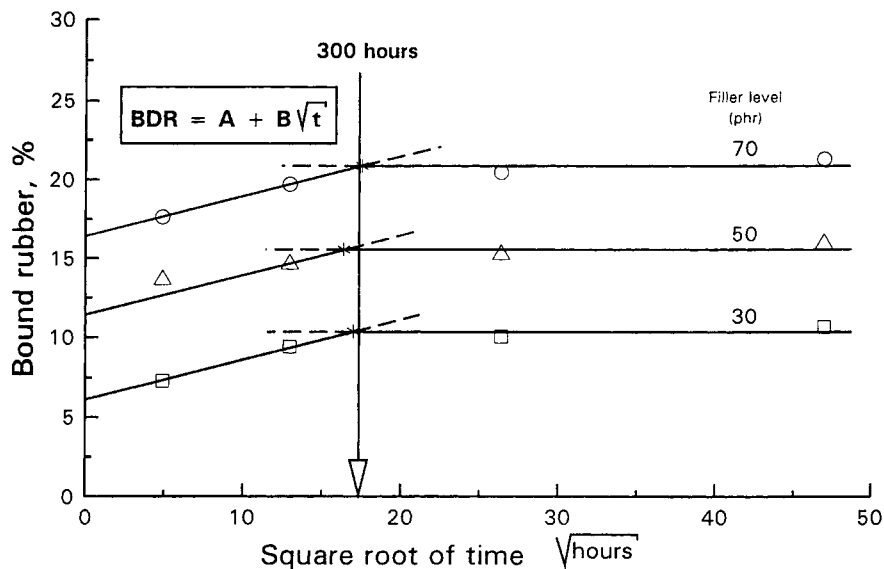### Cpd : High Cis Polybutadiene/N330 carbon black

Figure 2   Two-stage maturation process of BR, as observed with the polybutadiene compounds.

BOUND RUBBER MATURATION (at room Temperature)

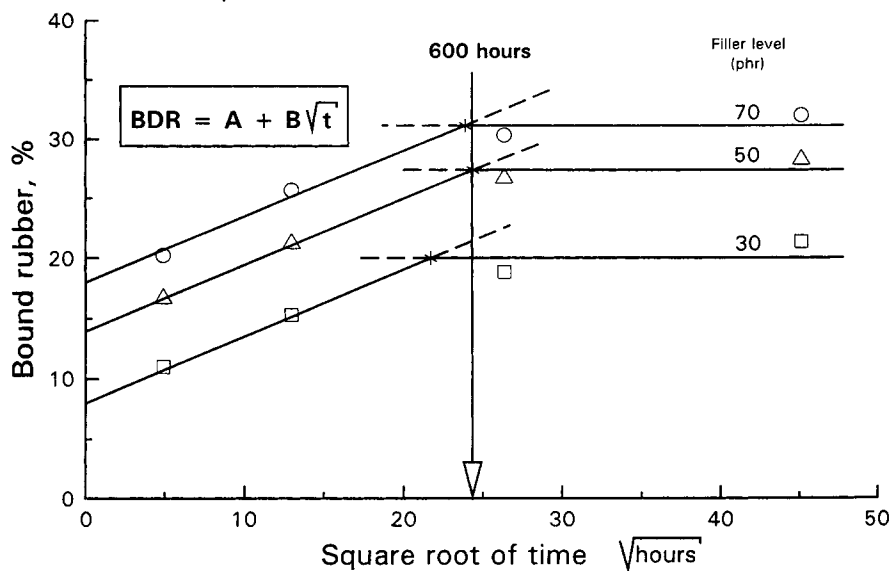### Cpd : Natural Rubber/N330 carbon black

Figure 3   Two-stage maturation process of BR, as observed with the NR compounds.

fraction. ϕ_{eff} is the effective filler volume fraction, as can be obtained when knowing the BR content:

$$\phi_{eff} = \phi_{black} + \frac{\rho \times BR}{100}$$

where ϕ_{black} is the filler volume fraction; BR, the measured bound rubber (in % of initial rubber), and ρ, the specific gravity of the gum elastomer. To estimate the viscosity of the 70 phr BR compounds, average ML_0 were obtained from the data with the

STORAGE EFFECT ON VISCOSITY
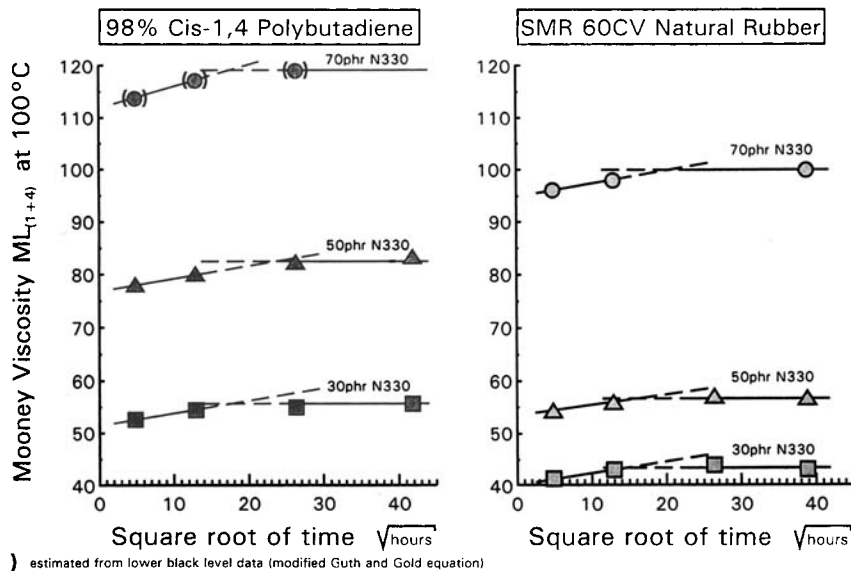
(Compounds stored at room temperature)

Figure 4   Effect of storage at room temperature on Mooney viscosity of polybutadiene and NR compounds.

Table V Estimating the Mooney Viscosity of 70 phr BR Compound

Storage Time (h)	BR 30		BR 50			BR 70	
	ϕ_{eff} (t)	ML_0 (t)	ϕ_{eff} (t)	ML_0 (t)	Mean $\overline{ML}_0$ (t)	ϕ_{eff} (t)	Estimated $ML_{(1+4)}$
24	0.378	13.31	0.553	11.65	12.48	0.673	113.0
168	0.397	12.94	0.562	11.66	12.30	0.691	116.4
696	0.403	12.82	0.567	11.81	12.31	0.698	118.4

30 and 50 phr compounds, using the equation above. Table V gives details about this estimation procedure. The Mooney data of the 70 phr NR compound after 1512 h storage were derived by extrapolation from measurements at higher temperatures and applying the Arrhenius equation, i.e.:

$$ML_T = ML_{T_0} \times e^{-E_a(1/T - 1/T_0)/R}$$

where the temperatures are expressed in K and E_a is the apparent activation energy as obtained from least-square fitting of the experimental data.

Figure 5 compares the effect of storage on both the Mooney viscosity and the BR. As can be seen, there is a relationship between the storage time effect on the two properties, but the nature of the elastomer as well as the actual filler level are significant parameters. The BR is definitively more sensitive to storage time than is the Mooney vis-

cosity. However, it must be underlined that the Mooney test itself does have a "mixing" component associated with the rotor motion within the sample; consequently, the rubber–filler morphology[6,11] is somewhat altered by the test and it is therefore quite remarkable that the $ML_{(1+4)}$ is, nevertheless, found evolving with time. Because it represents the immediate response of the rubber–black network at the beginning of the test, the initial Mooney peak is quite logically exhibiting a stronger dependence on the storage time. Consequently, nearly linear relationships are obtained when plotting the Mooney peak vs. BR (Fig. 6). Bound rubber, as well as the Mooney peak, do directly address the rubber–filler interactions that are likely to evolve during storage.

Dynamic Tests

RPA dynamic test results vs. storage time are given in Table VI, in terms of elastic G' and viscous G''
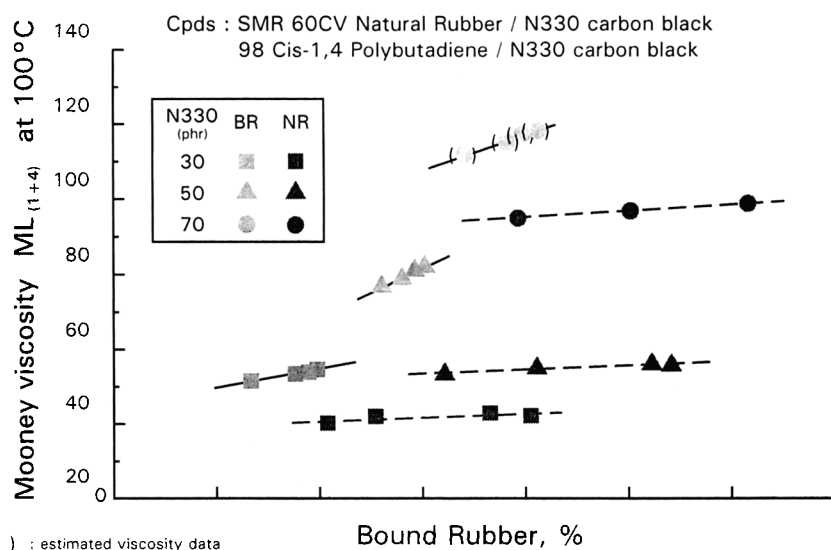

Figure 5 Plot of Mooney viscosity vs. BR content of polybutadiene and NR compounds with various levels of HAF carbon black.

MOONEY PEAK vs BOUND RUBBER
Effect of storage time at room temperature
Cpds : SMR 60CV Natural Rubber / N330 carbon black
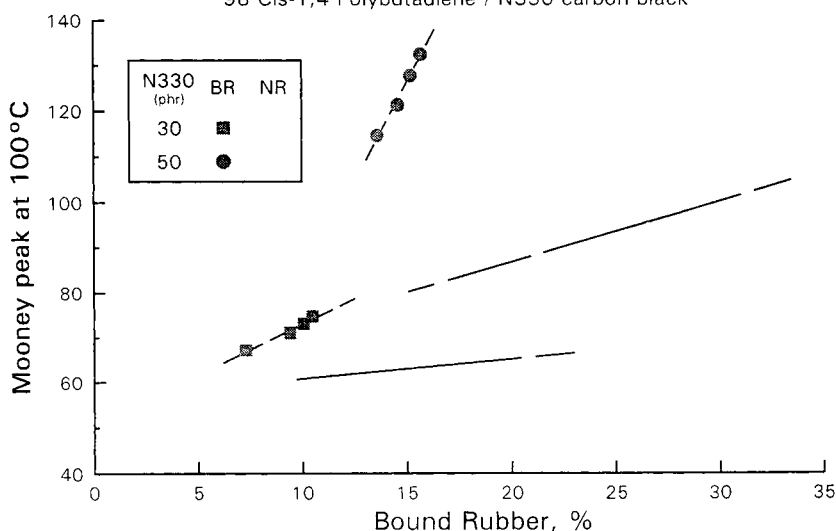98 Cis-1,4 Polybutadiene / N330 carbon black

Figure 6 Plot of Mooney peak vs. BR content of polybutadiene and NR compounds with different levels of HAF carbon black.

moduli at a fixed frequency of 10.47 rad/s and two strain levels, 1.0° and 10.0°.

As can be seen, marginal changes, if any, in G' and G'' are unexpectedly observed with the 30 phr carbon black compounds, whatever the dynamic strain. As the filler level increases, significant vari-

Table VI   Monsanto RPA 2000 Test Results

	Strain							
	1.0°		10.0°		1.0°		10.0°	
	G' (kPa)	G'' (kPa)	G' (kPa)	G'' (kPa)	G' (kPa)	G'' (kPa)	G' (kPa)	G'' (kPa)
Storage Time (h)	NEOCIS BR 40 30 phr N330				SMR 60 CV 30 phr N330			
24	207	134	186	122	149	81	136	71
168	205	133	185	122	152	78	134	69
696	205	131	186	121	153	79	135	70
	NEOCIS BR 40 50 phr N330				SMR 60 CV 50 phr N330			
24	336	205	263	168	208	119	171	97
168	344	206	267	169	212	119	170	96
696	349	208	272	171	217	121	172	95
	NEOCIS BR 40 70 phr N330				SMR 60 CV 70 phr N330			
24	815	393	463	270	417	250	262	158
168	852	404	486	278	445	255	268	158
696	894	420	506	285	454	255	274	160

STORAGE EFFECT ON DYNAMIC PROPERTIES
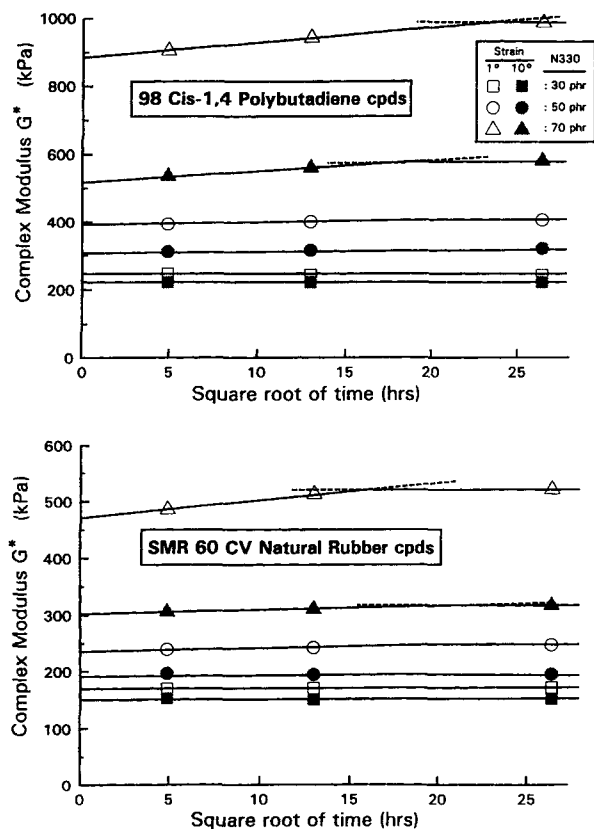Monsanto RPA at 100°C; Freq. = 10.47 rad/s

Figure 7   Effect of storage on dynamic properties of polybutadiene and NR compounds with various levels of HAF carbon black.

ations on storage are, however, observed on G' and G''. Since with the RPA the values for G' and G'' are actually calculated from a Fourier transform of the complex modulus,[8] it make sense to study the storage effect of the complex modulus [i.e., $G^*_{(\omega,\gamma)} = \sqrt{G'^2_{(\omega,\gamma)} + G''^2_{(\omega,\gamma)}}$] rather than the split elastic and viscous moduli. As illustrated in Figure 7, a two-stage evolution is readily seen on G^* with the 70 phr black compounds only, whatever the strain level. With lower black levels, variations upon storage of the dynamic properties (at least as measured with the RPA under the selected conditions) are likely to exist but within the limits of test sensitivity. When a two-stage model can be fit to experimental data, linear relationships are demonstrated between the elastic modulus and the BR of a given compound, as illustrated in Figure 8 with the 50 phr black BR compound and the 70 phr black NR compound.

DISCUSSION

In a previous work, a two-stage maturation effect on BR was observed with a range of rubber compounds and it was hypothesized that a parallel evolution in processing properties should be observed during storage.[7] The data presented above essentially confirm this hypothesis, but it is striking that the storage effect on processing properties is more apparent with a low steady shear flow test (i.e., Mooney; $\dot{\gamma} \approx 1.5 \text{ s}^{-1}$) than with a medium dynamic

STORAGE EVOLUTION OF G' vs BOUND RUBBER
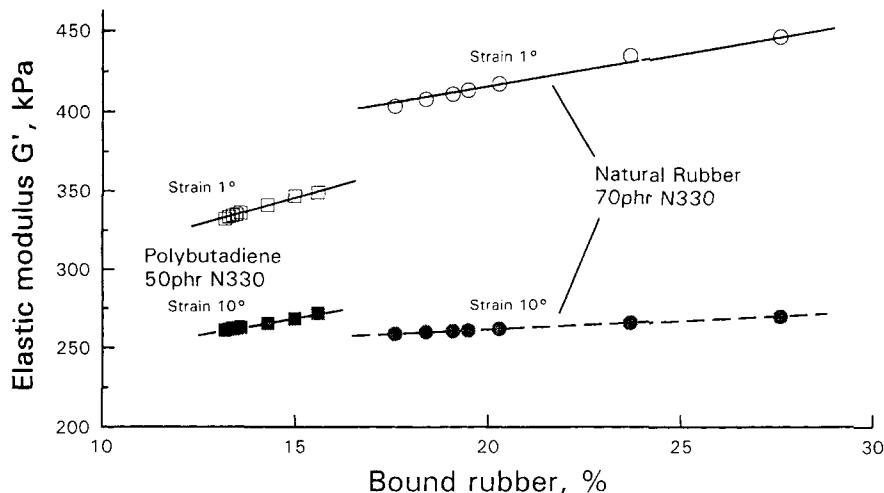2 Stages modelised maturation effects

Figure 8   Two-stage modelized effect of storage on the elastic modulus of polybutadiene and NR compounds with different levels of HAF carbon black.

MOONEY VISCOSITY AND EFFECTIVE FILLER VOLUME FRACTION
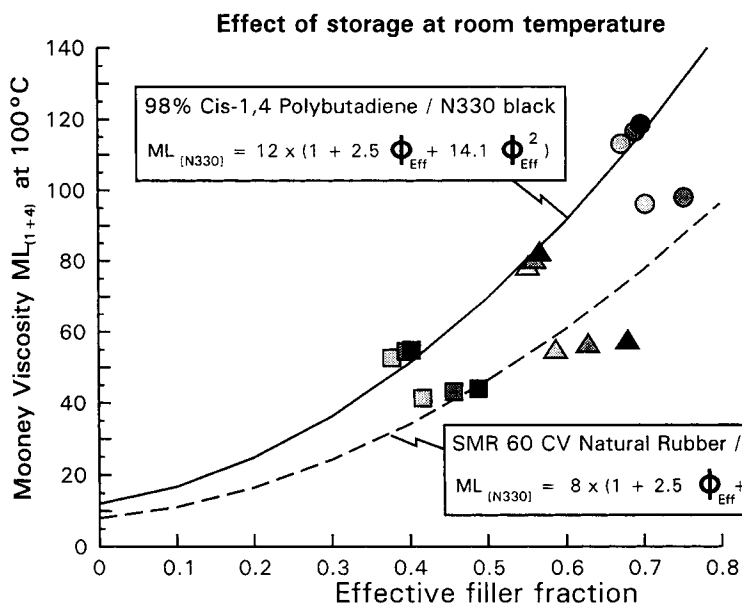### Effect of storage at room temperature

Figure 9 Mooney viscosity vs. effective filler volume fraction of polybutadiene and NR compounds, with the effect of storage at room temperature.

shear test (i.e., RPA; $\omega = 10.47$ rad/s). It is obvious that the BR is not the sole parameter that can influence the hardening of rubber compounds on storage, but it is worth underlining that the higher the filler content the stronger is the storage effect and the stronger the relationship between the processing property and the BR.

The chemical nature of the rubber is surely an important parameter of the observed effects. Generally, the processing properties of polybutadiene compounds evolve faster than does the BR on storage, and the reverse is observed with NR compounds. This might be related to differences in macromolecular flexibility of the two elastomers, but other investigation techniques (e.g., solid NMR) would be needed to study this point.

It is interesting to analyze the combined influence of filler level and storage time by modeling first the black concentration effect. Therefore, the experimental data have been treated in order to fit the modified Guth and Gold equation,[9,10] i.e.:

$$Prop_{cpd} = Prop_{gum} \times (1 + 2.5 \times \Phi_{Eff} + 14.1 \times \Phi_{Eff}^2)$$

where $Prop_{cpd}$ is the property of the compound; $Prop_{gum}$, the property of the gum elastomer; and Φ_{Eff}, the effective filler volume fraction.

The effective filler volume fraction after a given storage period can readily be calculated from the actual filler volume fraction and the measured BR,

but it is clear that the property considered for the elastomer must concern a (gum) material having a shear history comparable to the elastomer portion within the compound. This is obviously very difficult to assess and, therefore, the above equation has been directly fitted to the data; in other words, $Prop_{Gum}$ is the only adjusted parameter of the fitting.

Figure 9 compares the experimental Mooney viscosity data with the modified Guth and Gold fitting. As can be seen, the fit is excellent with the polybutadiene compound and acceptable with the NR compounds. The same approach gives very bad results with the dynamic properties at low strain, but good results at higher strain, as illustrated in Figures 10 and 11.

From a rheological point of view, the Mooney test (steady shear) has very little in common with the RPA test (dynamic shear), but it is worth noting that the latter gives a good fit with the modified Guth and Gold equation *only* when high deformation is considered. It seems, thus, that, for a relationship to be clearly seen between the BR variation and the change in processing properties upon storage, it is necessary to have "large" strain. In other words, one must consider rheological flows large enough to destroy, or at least to affect, the rubber–filler morphology of the compound. It could also be argued that there is hardly a "flow" in a (rotational) dynamic test since the material is sinusoidally strained in a closed geometry around an equilibrium position.
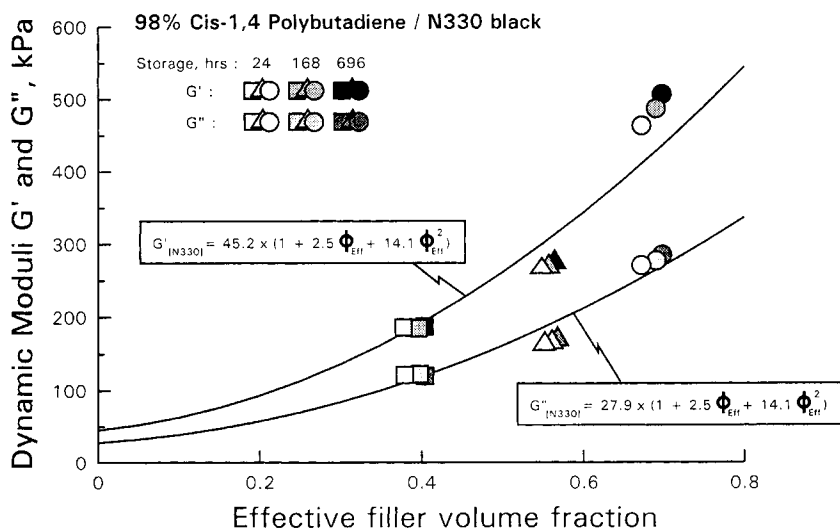
Figure 10 Dynamic moduli vs. effective filler volume fraction of polybutadiene compounds, with the effect of storage at room temperature.

Over a given test duration, the total strain is therefore essentially zero in the dynamic mode, whereas it is obviously positive and large in the shear mode, particularly with rotational devices.

So, the higher the total strain considered, the larger the effects resulting from modification of the rubber–filler interaction. In agreement with electron microscopy evidence, the morphological model considered for (carbon black) filled rubber compounds describes two levels of BR: tightly and loosely.[6] It is conceivable that the tightly BR can play a role in the rheological properties only if the strain is large
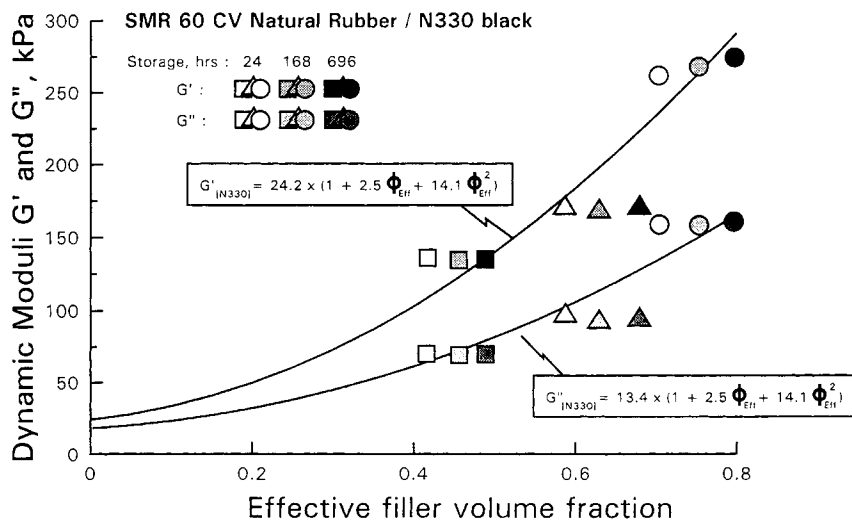

Figure 11 Dynamic moduli vs. effective filler volume fraction of NR compounds, with the effect of storage at room temperature.

enough. Because the relationship between the rheological properties and the BR do clearly appear when large total strain tests are considered, one would conclude that, upon storage, it is the tightly BR that is modified rather than the loosely BR fraction. Additional work is needed to confirm this hypothesis.

CONCLUSIONS

The relationships between the variation upon storage of bound rubber (BR) and processing properties has been studied with polybutadiene and a natural rubber (NR) compound with various filler levels. It has been found that the two-stage model previously established for BR,[7] i.e.,

$$\text{Property} = A + B \times \sqrt{t} \qquad \text{for } t < t_{\text{stabil}}.$$

$$\text{Property} = \text{constant} \qquad \text{for } t > t_{\text{stabil}}.$$

does apply to processing properties. High-strain rheological tests are, however, more sensitive to the maturation effect, which would indicate that similar effects are to be expected in factory processing.

The differences between steady-shear and dynamic-shear variations upon storage could indicate that the tightly BR rather than the loosely BR is modified during the early storage period after mixing.

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