Advanced Torsional Dynamic Methods to Study the Morphology of Uncured Filled Rubber Compounds

JEAN L. LEBLANC, MARIE CARTAULT

Polymer Rheology and Processing, Université Pierre and Marie Curie, Paris VI, France

ABSTRACT: Uncured compounds of SBR1500 with various levels of silica were studied using a torsional dynamic tester (rubber process analyzer; RPA). Silica-filled compounds were prepared with the appropriate amounts (8.2%) of silane, i.e., bis(3-triethoxysilylpropyl)tetrasulfane (TESPT). A carbon black-filled compound was also studied for comparison. Strain sweep tests at constant frequency show that filled rubber materials exhibit either no or limited linear viscoelastic domain. Frequency sweep tests were performed either at the lowest strain amplitude or within the linear range at several temperatures; results were treated through time–temperature superposition in order to yield G' and G'' master curves at the reference temperature of 100°C. Special test procedures were applied that are known to give interesting information about the morphology of complex polymer systems: the morphology damaging test (MDT) and the damaged morphology recovery test (DMRT). Results obtained are discussed with respect to the likely morphology of carbon black and silica-filled rubber compounds. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2093–2104, 2001

Key words: rubber compounds; SBR; carbon black; silica; dynamic moduli; methods

INTRODUCTION

Filled rubber compounds are a class of complex polymer systems that exhibit singular flow properties whose control is an essential factor in efficient processing and hence the development of optimum properties in cured parts. Strong flow anisotropy, severe shear thinning, and nonlinear viscoelastic behavior, as well as reduced elastic effects (e.g., extrudate swell) with increasing filler content, are typical properties of such systems, whose origin is currently assigned to their particular morphology, as it results from strong interactions between the filler particles and the elastomer.[1] Elastomer–filler interactions can be studied by a number of methods—either direct methods such as solid nuclear magnetic resonance (NMR), or indirect methods such as bound rubber assessment. Certain rheological techniques are also interesting because they provide information that can be considered with respect to processing and/or technological conditions.

For long carbon blacks of appropriate size and structure have been used as reinforcing materials in rubber compounds. Although strong interactions between the filler and the polymer have been recognized as the main source of the reinforcing effect, the true physical nature of carbon black–rubber interactions was also demonstrated.[2,3] With silica, the reinforcing effect is also obtained with the appropriate size and structure but, in addition, interactions between the elastomer and the particles have to be promoted by chemical means, essentially by using silanes that first react with silanol groups on the particles surface, then with rubber chains. This two-step

Table I   Test Samples

| Silica-Filled Compounds | | Carbon Black-Filled Compound | |
Ingredient	phr	Ingredient	phr
SBR 1500	100	SBR 1500	100
VN3 silica	30, 40, 50	N330 carbon black	50
Zinc oxide	5	Zinc oxide	5
Stearic acid	3	Stearic acid	3
Processing oil	5	Processing oil	5
Antidegradants	2	Antidegradants	2
TESPT[a]	2.4, 3.3, 4.1		

[a] Bis(3-triethoxysilylpropyl)tetrasulfane.

chemistry has to be carefully controlled, the former step occurring during the mixing operation, the latter during vulcanization.[4] It follows that while a tridimensional morphology involving filler particles and bounded rubber chains likely exists in both carbon black and silica-filled compounds, subtle differences are expected between both type of systems because carbon black–rubber interactions are essentially of physical nature, while chemistry plays the key role with silica.

The aims of this article are to investigate some advanced testing methods using a torsional dynamic tester, in order to obtain (indirect) information about the morphology of carbon black and silica-filled rubber compounds, with the ultimate objective of understanding the basic differences between both types of reinforcing filler.

EXPERIMENTAL

Test Materials

SBR1500 compounds with different levels and silica and the appropriate content of silane were prepared and kindly supplied by DEGUSSA (Germany), according to the formulations described in Table I. Bis(3-triethoxysilylpropyl)tetrasulfane [TESPT] was used in proportion with silica level, in the ratio 8.2 phr TESPT ($\rho = 1.095$ g/cm^3) for 100 phr silica ($\rho = 2.2$ g/cm^3), and the mixing procedure was conducted in order to activate the rubber–filler-promoting action of the silane. For comparison, a 50-phr carbon black-filled compound was prepared in our laboratory using a 1.5-L Banbury-type mixer and an upside-down mixing procedure, in such a manner that the batch received ~1800 MJ/m^3 mixing energy. All compounds were sheeted off on open mill and

stored at room temperature under black plastic cover.

After several months storage at room temperature under dark plastic coverage, compounds were tested for bound rubber (BdR), using an extraction kinetic method developed in our laboratory,[5] which yielded results given in Table II. A coherent gel was always obtained, indicating thus the full development of the rubber–carbon black or rubber–silica (silane-treated) morphology.

Test Equipment

The RPA is a torsional dynamic instrument, developed by Alpha Technologies to test highly viscous materials such a filled rubber compounds.[6,7] It consists essentially of a biconical test chamber with grooved dies to prevent slippage. The lower die can be oscillated in torsion at controlled strain and frequency. The torque measuring system is fixed on the upper die and calibrated with a torsion spring. The temperature controlled system is highly sophisticated with a resolution to the nearest 0.1°C. The test cavity is maintained closed through the application of a pressure of 4 MPa. The instrument is fully monitored by a controlling computer (PC) with the capability to combined pre-programmed test sequences in any order.

Table II   Bound Rubber Measurements

Silica (phr)	Silane (phr)	BdR (%)	Carbon Black (phr)	BdR (%)
30	2.4	11.1	50	22.4
40	3.3	22.1		
50	4.1	30.9		

Test Methods

Carbon black and silica–SBR compounds were tested with the RPA, using a number a test techniques, from simple strain and frequency sweeps at different temperatures to more sophisticated procedures, especially designed for complex polymer systems.[8] Two such test procedures are particularly interesting for uncured filled rubber compounds: the morphology damaging test (MDT) and the damaged morphology recovery test (DMRT). The former consists in a sequence of alternatively low strain test (e.g., at 0.5° angle, i.e., 7%) and increasingly higher strain test (e.g., 1.0, 1.5, 2.0, 5.0, 10.0, 20.0°,···); the low strain test measures the evolution—if any—of the dynamic properties after the application of an increasingly larger strain amplitude The latter procedure consists of first measuring the dynamic properties at low strain (generally 0.5°) then applying a large strain to damage the rubber-filler morphology, and subsequently repeating the low strain measurement at various intervals. Because such test techniques imply that the material remains in the test cavity under 4-MPa pressure for quite a long time, it is necessary to consider possible modulus changes under static pressure. This is achieved by repeating at various times a dynamic modulus measurement at low strain amplitude (0.5°) and constant frequency (6.28 rad/s), while maintaining the sample in the closed cavity under constant temperature.

RESULTS AND DISCUSSION

Strain Sweep Tests

The RPA applies a nearly sinusoidal strain (i.e., the input signal) on the sample maintained in the closed biconical cavity. Providing the tested viscoelastic material responds linearly, the recorded torque (i.e., the output signal) is also sinusoidal but out-of-phase by an angle δ, depending on the viscous character of the material. In fact, the phase angle is not actually measured and the complex torque $S^*(t, \omega)$ is first treated in such a manner that during one cycle several discrete values are read with respect to equal periods on the time scale. For any complex (sinusoidal) torque, one has

$$S(t) = S^*\sin(\omega t + \delta) = S'\sin(\omega t) + S''\cos(\omega t)$$

and through discrete Fourier transform the selected values of $S(t)$ with their locations are used to calculate S', S'', and the phase angle δ, by considering the following equalities:

$$S^* = \sqrt{S'^2 + S''^2} \qquad \text{and} \qquad \delta = \tan^{-1}\frac{S''}{S'}$$

The dynamic shear moduli are obtained using a shape factor for the considered test gap:

$$B = \frac{2\pi R^3}{3\phi}$$

where R and ϕ are, respectively, the radius of the cavity (20.625 mm) and the angle between the two conical dies (0.125 radian), and the following relationships:

$$G^* = \frac{S^*}{B\gamma} \qquad G' = \frac{S^*\cos\delta}{B\gamma} \qquad G'' = \frac{S^*\sin\delta}{B\gamma}$$

where γ is the strain angle. The shape factor is a textbook relationship for a cone-and-plate gap with a free spherical boundary for the test sample. Any possible effects due to the closed cavity is thus considered negligible or at least within the limits of test repeatability (found to be ~5%).

Strain sweep test results at $T = 100°C$ are given in Table III in terms of complex modulus G^* and tan δ at $\omega = 6.28$ rad/s.

As expected, the complex modulus increases with filler content and, at constant silica loading, remains within 5% up to a limiting strain angle that depends to some extent on filler quantity. At very low strain, silica-filled SBR compounds thus exhibit a linear viscoelastic region, that is clearly seen when drawing 3D maps of G' and G'' vs. strain and silica content (Fig. 1); all compounds exhibit a linear viscoelastic region when γ is ~<1° (i.e., 14% deformation). The expected increase in modulus with filler level is also clearly observed. The same tests at 80°C and 120°C show also that <1° strain angle, a linear viscoelastic behavior is observed.

Within the RPA strain range, the SBR compound filled with 50 phr carbon black does not exhibit any linear viscoelastic region. Figure 2 shows that both G' and G'' are decreasing with increasing strain amplitude. Test repeatability margins (i.e., 5%) as indicated on G' data clearly show that even at <0.1° strain angle, dynamic moduli suffer from a significant strain effect.

Table III   RPA–Strain Sweep Test at 100°C and ω = 6.28 rad/s

VN3 Silica, phr:	30		40		50		—	
TESPT, phr:	2.4		3.3		4.1		—	
N330 Black, phr:	—		—		—		50	
Strain (deg)	G^* (kPA)	Tan δ	G^* (kPa)	Tan δ	G^* (kPa)	Tan δ	G^* (kPa)	Tan δ
0.05	226.0	0.445	261.5	0.375	401.6	0.320	465.93	0.566
0.10	218.1	0.396	266.4	0.385	407.6	0.337	421.84	0.589
0.20	219.8	0.392	266.4	0.385	392.6	0.345	360.49	0.609
0.50	214.4	0.413	257.0	0.390	366.9	0.361	289.93	0.634
1.00	205.3	0.425	241.7	0.413	335.1	0.391	246.48	0.647
2.00	186.2	0.464	214.6	0.456	282.8	0.455	204.70	0.697
5.00	138.0	0.618	153.2	0.619	185.3	0.659	145.97	0.920
10.00	90.9	0.915	98.1	0.913	113.8	0.959	102.28	1.258
20.00	54.3	1.568	57.2	1.500	64.9	1.427	68.86	1.799

Frequency Sweep Tests

Frequency sweep tests were performed on all silica compounds at 80°, 100°, and 120°C, using a strain angle of 0.1°, i.e., essentially in the linear viscoelastic region of the materials. As expected, the higher the temperature, the lower the moduli, and the time–temperature superposition technique applies well as illustrated in Figure 3, where G' and G'' master curves at 100°C are given for the compound with 50 phr silica. Despite some scatter on G'' data in the terminal region, the superposition is excellent and yields dynamic moduli curves over 3.5 decades of frequency. As can be seen, the viscous modulus is significantly
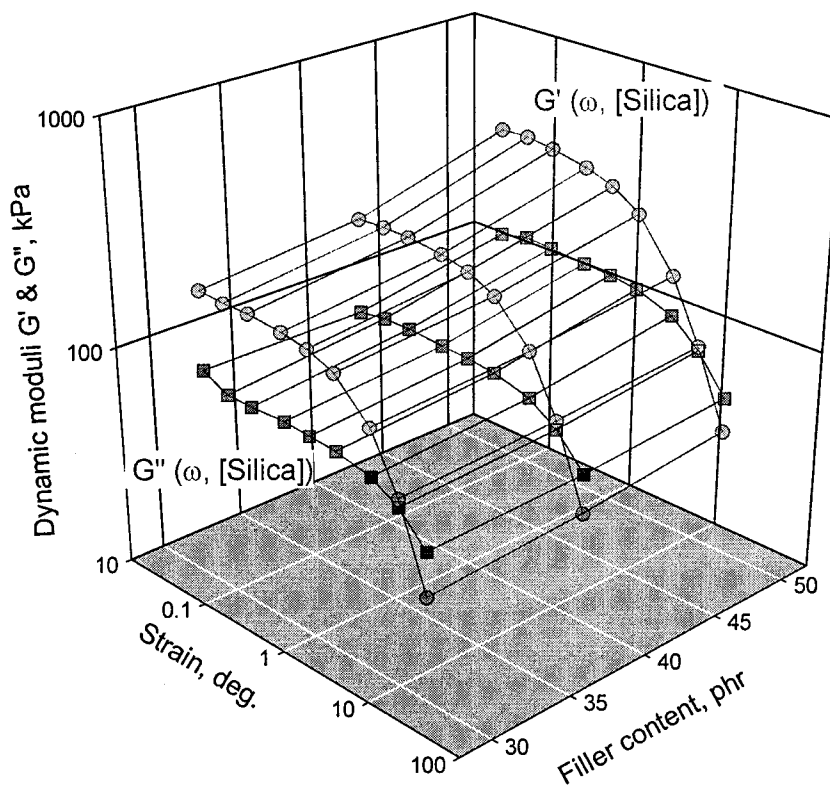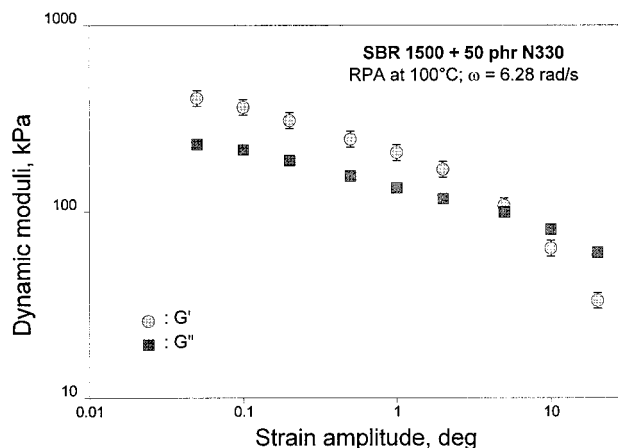

Figure 1   Elastic moduli of SBR-silica compounds.

Figure 2 Rubber process analyzer (RPA) strain sweep test on carbon black-filled SBR compound.

lower than the elastic modulus, clearly reflecting the high elastic nature of this uncured silica–silane compound.

The effect of silica content on dynamic moduli master curves at 100°C is shown in Figure 4. As can be seen, at <40 phr, the filler content effect is relatively moderate on G' and practically not significant on G''. Above 40 phr, i.e., near the so-called percolation level, adding 10 more parts of silica shift upward both moduli curves by some 150% at $\omega = 0.01$ rad/s and around 60% at $\omega = 1$ rad/s. The corresponding fitted G^* and tan δ master curves are given in Table IV.

It is interesting to analyze the dynamic properties of silica-filled compounds with respect to bound rubber. As shown in Figure 5, there is a clear but nonlinear relationship between G^* and
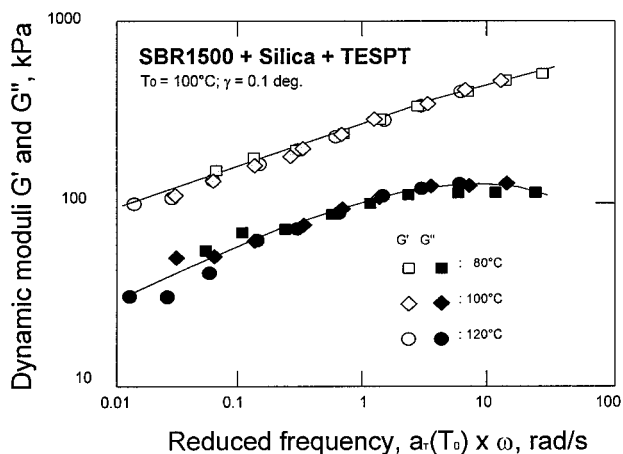

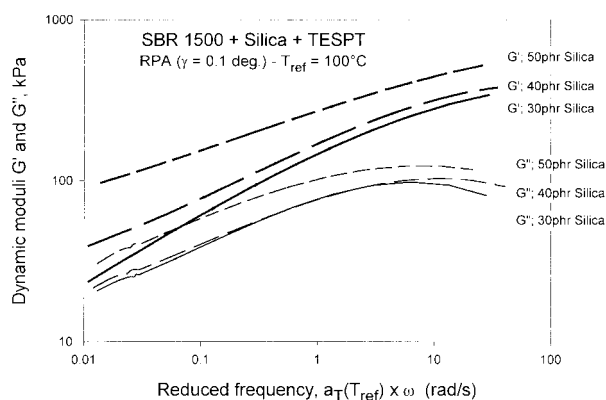**Figure 3** Dynamic moduli master curves at 100°C;5-phr silica-SBR compound.

Figure 4 Dynamic moduli master curves at 100°C for silica-filled compounds.

BdR , while tan δ decreases with higher bound rubber level in a near linear manner. This suggests that, within the linear viscoelastic domain of uncured silica-filled SBR compounds, the elastic component rather than the viscous one, is affected by increasing filler content.

Figure 5 suggests an analysis of the effect of silica content on dynamic properties in terms of effective filler content Φ_{eff}, i.e., to consider the addition of bound rubber (and silane) to silica content to give the overall filler loading, and to apply a Guth–Gold-type equation through nonlinear regression, i.e.:

$$G_{\mathrm{cpd}} = G_{\mathrm{gum}} \times (1 + a \times \Phi_{\mathrm{eff}} + b \times \Phi_{\mathrm{eff}}^2)$$

Figure 6 shows such an analysis, using data given in Table V. As can be seen, while quadratic modeling of the effect of effective filler content on dynamic moduli is satisfactory, the nonlinear fitting gives a and b parameters that are quite different from those obtained through the Guth–Gold approach ($a = 2.5$ and $b = 14.1$, respectively). If one considers that the first parameter (i.e., 2.5) reflects the filler volume effect and the second (i.e., 14.1) accounts for additional effects involving interactions between complex silane treated silica-bound rubber units, the comparison with the values obtained by our experimental fitting suggests that the dynamic properties of uncured silica-filled compounds are controlled by a complex silica + silane + bound rubber network.

Morphology Damaging Test

Typical results of the morphology damaging test are shown in Figure 7. As explained in the section on Test Methods, the test consists in damaging

**Table IV   Complex Modulus Master Curves $G*(\omega = 6.28$ rad/s) at 100°C for Silica-Filled SBR Compounds**

VN3 Silica, phr:	30		40		50	
TESPT, phr:	2.4		3.3		4.1	
Frequency (rad/s)	$G*$ kPa	tan δ	$G*$ kPa	tan δ	$G*$ kPa	tan δ
0.01	29.6	0.852	44.0	0.534	95.0	0.311
0.03	44.9	0.713	59.4	0.533	122.0	0.348
0.1	72.1	0.633	87.1	0.521	164.2	0.379
0.3	109.3	0.584	125.6	0.495	216.2	0.390
1	164.9	0.527	185.2	0.451	288.8	0.376
3	226.1	0.453	253.4	0.397	367.2	0.340
10	295.7	0.344	331.8	0.326	460.1	0.278
30	351.0	0.233	386.5	0.258	542.0	0.211

the rubber-filler morphology with dynamic strain of increasing severity whilst observing the damage through low strain tests. Conveniently, the results are analyzed in terms of low strain modulus vs. previous strain difference, i.e., the large damaging strain applied minus the low measuring strain (0.5°). As can be seen, significant losses in modulus are observed, which can be attributed to changes in the rubber-filler morphology upon increasingly larger strains. With the highly filled sample (50-phr silica), the curve plateaus out when the previous strain difference reaches 10°. With lower silica levels, an upturn is observed, i.e., the modulus passes through a minimum value then increases (slightly) as the previous

strain difference increases. This likely reflects some recovery effects of the rubber matrix.

Damaged Morphology Recovery Test

Figure 8 is an example of the early recovery behavior observed on the 50 phr silica SBR compound after a 5° (i.e., 69.8%) damaging strain has been applied (at $\omega = 6.28$ rad/s). The recovery is studied through modulus measurements at γ = 0.5° and $\omega = 6.28$ rad/s performed at various intervals. Temperature is maintained at 100°C during the whole experiment that typically lasts more than 4000 s (~1 h.). The test protocol is such that although the damaging strain is typically in
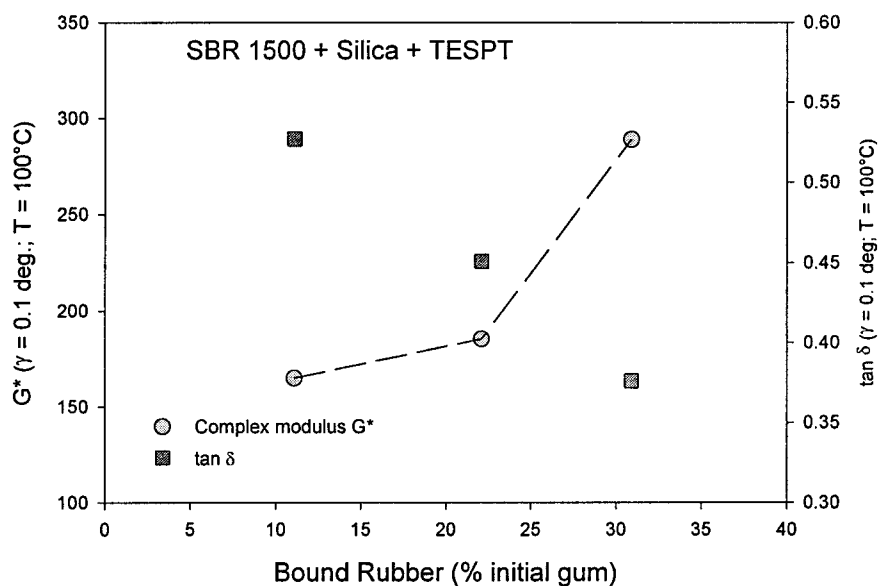
Figure 5   Dynamic properties of silica-filled SBR compounds versus bound rubber.
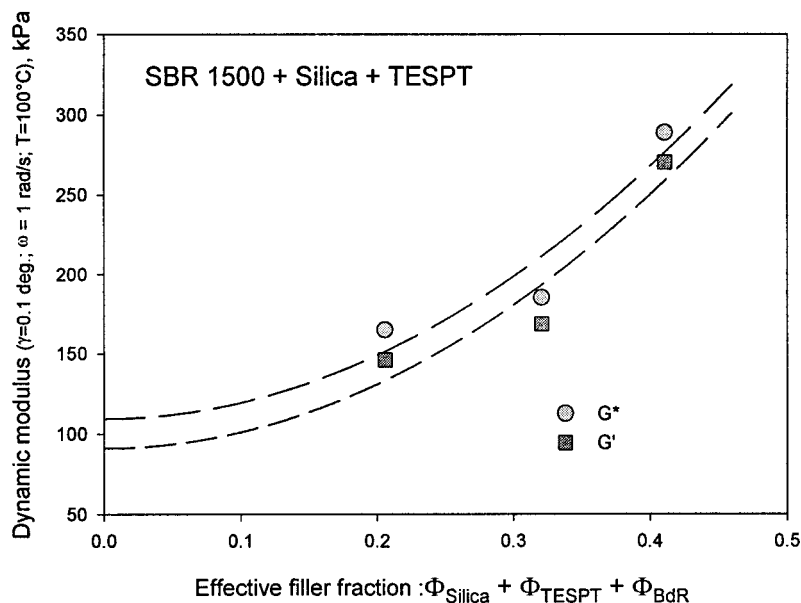
Figure 6 Dynamic moduli versus effective filler fraction.

the nonlinear region, the recovery is observed through dynamic tests performed in the linear viscoelastic region.

The recovery behavior of the 50 phr silica-filled and 50 phr carbon black-filled compounds was studied after damaging strains of different magnitudes. Results are given in Tables VI and VII.

An intriguing aspect of such results is the fact that, providing the damaging strain is small, the recovering modulus becomes higher than what was measured before damaging the rubber-filled morphology. Because during the test, the material is maintained in RPA cavity for quite a long time under high pressure (4 MPa) and temperature (100°C), a kind of accelerated storage maturation effect was suspected, in line with bound rubber variations upon storage previously studied.[9]

To document this point, tests were performed by repeating, after various dwell times, dynamic modulus measurements at low strain amplitude (0.5°) and constant frequency (6.28 rad/s), while maintaining the sample in the cavity under constant temperature and pressure. The results are given in Table VIII.

As can be seen, the viscous modulus G'' measurement is marginally affected by maintaining the sample under high pressure and temperature. There is however a significant shift of the dynamic modulus G' that can simply be fitted with the following equation:

$$G'(t) = A + B \times \ln(t + t_0)$$

No particular meaning is assigned to fit parameters, but obviously the quantity $A + B \times \ln(t_0)$

Table V Analyzing Silica Effect on Dynamic Moduli

			$G_{cpd} = G_{gum} \times (1 + a \times \Phi_{eff} + b \times \Phi_{eff}^2)$	
Φ_{Silica}	Φ_{TESPT}	Φ_{BdR}	G^* (kPa)	G' (kPa)
0.1006	0.0162	0.0890	$G_{gum} = 109.46$	$G_{gum} = 91.14$
0.1290	0.0214	0.1704	$a = 1.2 \times 10^{-7}$	$a = 7.8 \times 10^{-8}$
0.1554	0.0256	0.2297	$b = 9.03$	$b = 10.89$

Specific gravity used in calculating ingredient fractions (g/cm³): SBR, 0.92; VN3, 2.2; ZnO, 5.57; stearic acid, 0.92; oil, 0.98; antidegradants, 1.17 and 1.08; TESPT, 1.095.
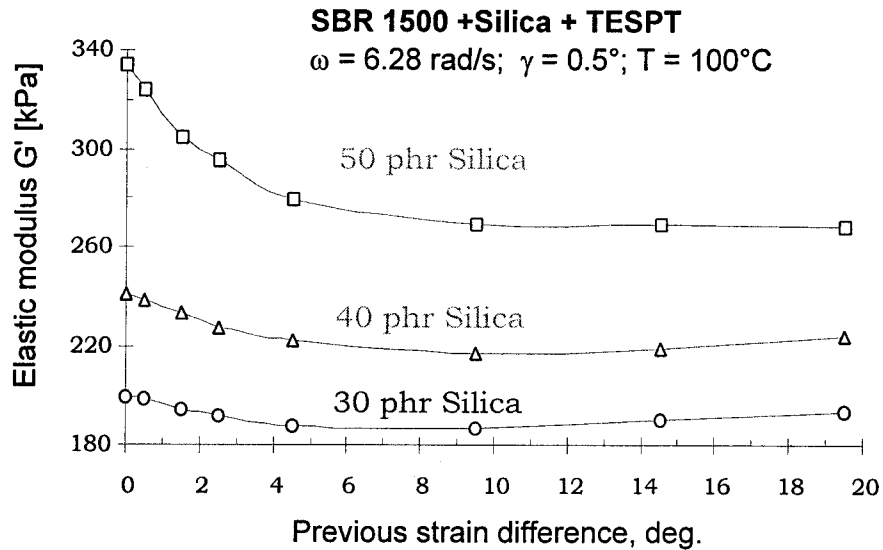
Figure 7 Dynamically damaging the morphology of SBR-silica compounds.

corresponds to the instant dynamic modulus that would be measured at time zero, B expressed the rate of variation of the modulus and t_0 is the time after which a significant rise in G' is observed. As can be seen through the parameters values given in Figures 9 and 10, the nature of the filler affects the modulus shift. For instance, a significant shift occurs sooner with the silica compound (cf. t_0), but the variation is steeper with the carbon black compound (cf. B). Such data allow us to correct the DMRT results by simply subtracting the G' shift from the data presented in Tables VI and

VII. The importance of the correction is illustrated in Figure 11 using DMRT data on the silica compound with a damaging strain of 1°.

Damaged morphology recovery test results corrected for modulus shift under pressure are given in Figures 12 and 13 for the silica- and carbon black-filled compounds, respectively. A similar pattern is obtained: a small (~3–4%) but nearly permanent loss in G' providing the damaging strain is small (i.e., 1°) for both types of filler, and larger losses when the damaging strain is 5° and higher, but with a trend to recover in the long
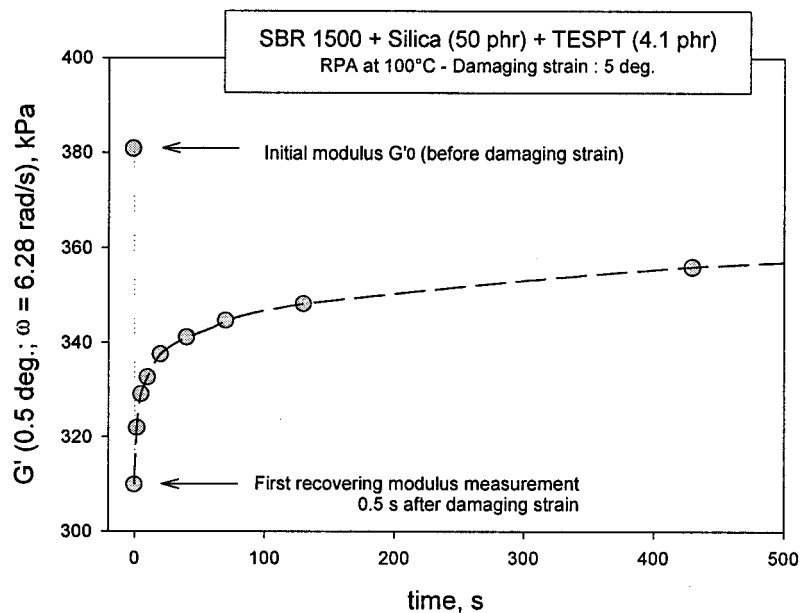

Figure 8 Morphology damage recovery test; typical recovery behavior.

Table VI   Damaged Morphology Recovery Tests on 50-phr Silica SBR Compound–RPA at 100°C

Initial $G'0$ (0.5 deg; 6.28 rad/s)	376.4	380.8	377.2	380.2
Damaging Strain, deg:	1.0	5.0	10.0	20.0
Time (s)	$G'(t)$ (kPa)	$G'(t)$ (kPa)	$G'(t)$ (kPa)	$G'(t)$ (kPa)
0[a]	365.70	309.89	301.43	289.19
2	371.05	321.94	317.50	303.73
5	373.35	329.03	322.09	309.08
10	376.41	332.58	325.91	314.44
20	377.94	337.54	329.74	317.50
40	381.00	341.09	332.80	320.56
70	381.76	344.64	335.86	323.62
130	384.82	348.18	340.45	327.44
430	390.18	355.99	346.57	333.56
1030	395.53	361.66	352.69	339.68
2230	399.36	368.04	359.57	344.27
4030	404.71	374.42	365.70	350.39

[a] Modulus recovery measurement starts 0.5 s after damaging strain (at $\omega = 6.28$ rad/s).

Table VII   Damaged Morphology Recovery Tests on 50-phr Carbon Black SBR Compound–RPA at 100°C

Initial $G'0$ (0.5 deg; 6.28 rad/s)	250.9	258.6	260.9	264.7
Damaging Strain, deg:	1.0	5.0	10.0	20.0
Time (s)	$G'(t)$ (kPa)	$G'(t)$ (kPa)	$G'(t)$ (kPa)	$G'(t)$ (kPa)
0[a]	240.23	206.56	192.79	188.97
2	243.29	218.04	204.27	198.15
5	244.82	221.87	208.86	203.50
10	244.82	224.93	211.92	207.33
20	246.35	227.99	214.98	211.15
40	247.88	231.81	218.80	213.45
70	249.41	234.11	224.16	218.04
130	253.23	237.93	227.22	220.34
430	257.82	246.35	234.11	230.28
1030	264.71	251.70	242.52	237.17
2230	270.06	260.12	249.41	245.58
4030	274.65	265.47	257.06	254.00

[a] Modulus recovery measurement starts 0.5 s after damaging strain (at $\omega = 6.28$ rad/s).

Table VIII   Dynamic Moduli Shift With Time When Maintaining Sample Under 4-MPa Pressure at $T = 100$°C [RPA − $\gamma = 0.5$ deg; $\omega = 6.28$ rad/s]

Time (s)	SBR + Silica (50 phr) + Silane (4.1 phr)		SBR + Carbon Black (50 phr)	
	$G'(t)$ (kPa)	$G''(t)$ (kPa)	$G'(t)$ (kPa)	$G''(t)$ (kPa)
0.5	347.33	112.46	237.93	156.84
2.5	350.39	113.23	237.93	156.07
5.5	352.69	113.23	240.99	156.07
10.5	356.51	112.46	241.76	156.07
20.5	357.28	112.46	243.29	154.54
40.5	359.57	112.46	244.05	155.31
70.5	361.87	112.46	245.58	155.31
130.5	364.16	112.46	247.88	155.31
430.5	371.05	113.23	255.53	158.37
1030.5	375.64	113.23	259.35	159.90
2230.5	382.53	114.76	265.47	162.19
4030.5	386.35	114.76	270.06	165.25

term. The recovery is, however, clearly slower for the silica compound, suggesting that damage to the silica–rubber network are likely to have a permanent character.

The damaged morphology recovery test was first designed to study uncured carbon black-filled rubber compounds with the hypothesis that such materials develop a complex morphology with two essential features: complex rubber-filler entities with connective filaments.[8] Recent studies by solid NMR are strongly supporting this hypothesis.[10,11] The resulting soft tridimensional network[12] is expected to be sensitive to large damaging strains, but with capabilities to recover, owing to the essential physical nature of the rubber–carbon black interaction. Indeed, at a given temperature, bound rubber reflects an adsorption–desorption equilibrium of polymer segments on appropriate sites on filler particles. Applying a sufficiently large strain temporary displaces this equilibrium towards desorption, with a subsequent return to the initial state.

The above results show that silica-filled compounds likely develop a similar morphology but, because the interaction with the rubber is chemical in nature, (essentially owing to silanization), there are limits to the analogy. For instance, one should consider the possibility of permanent damages through large strains, as suggested by the
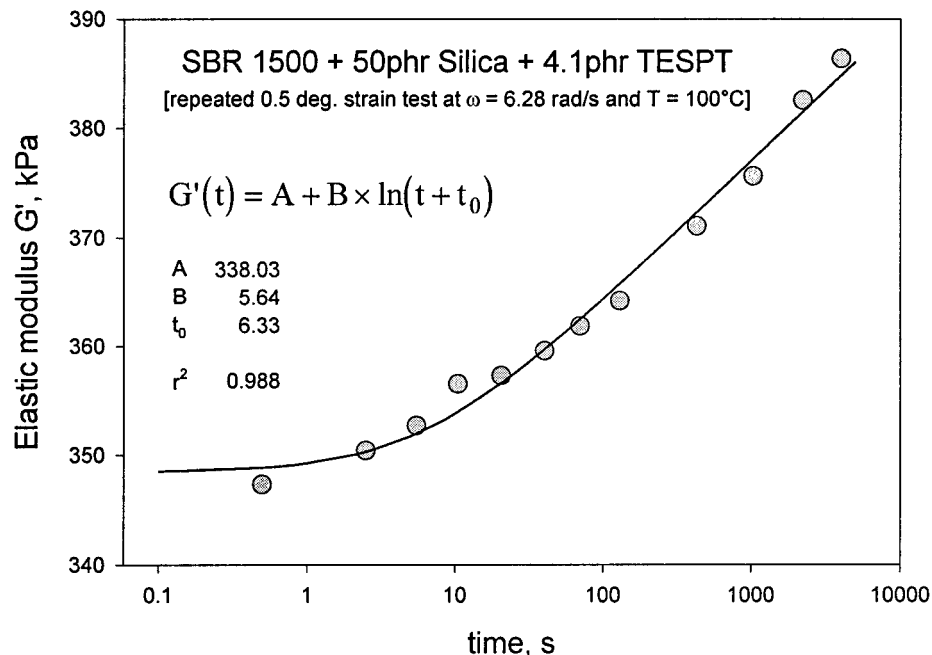
Figure 9 Dynamic modulus shift under 4-MPa pressure at 100°C. Silica-filled compound.

slower recovery behavior seen when comparing Figures 12 and 13.

CONCLUSIONS

Modern torsional dynamic testers offer interesting possibilities for the study of complex polymer systems such as filled rubber compounds. In addition to frequency and strain sweeps that are test procedures common to many commercial instruments, special techniques can be designed whose basic principle is either to observe the effect of progressively higher strains on subsequent low strain dynamic test or to study how low strain
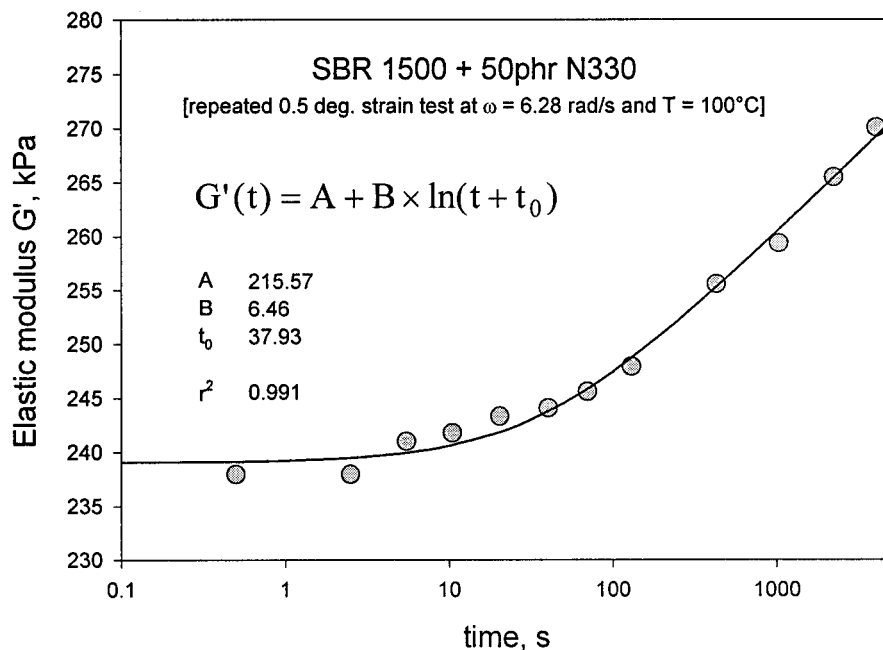

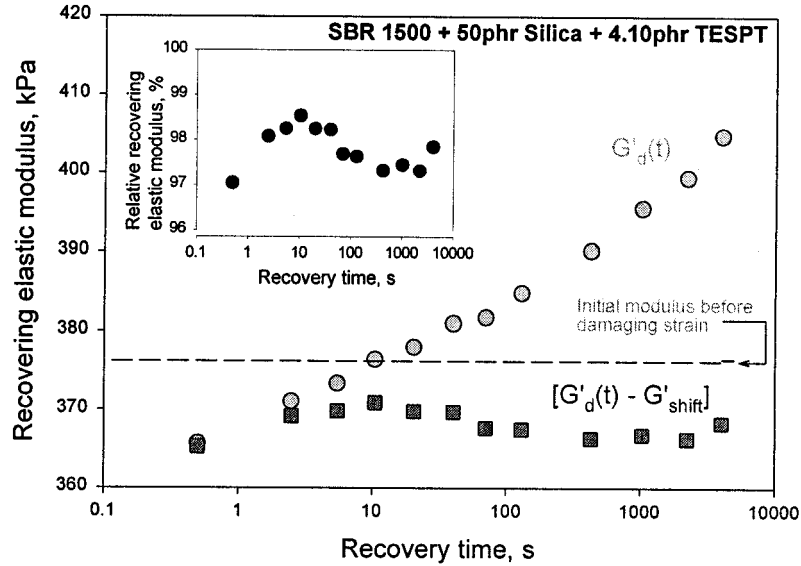**Figure 10** Dynamic modulus shift under 4-MPa pressure at 100°C. Carbon black-filled compound.

Figure 11 Damaged morphology recovery test (DMRT) corrected for G' shift under pressure and temperature. DMRT at $\gamma = 0.5$ deg and $\omega = 6.28$ rad/s.

dynamic modulus recovers with time after a large strain has been applied.

Such advanced techniques have been used to study uncured silica (silane treated)-filled SBR compounds in comparison with carbon black-

filled compounds. Significant differences have been found that are believed to reflect the particular nature of the filler. For instance, while 50 phr carbon black-filled SBR does not exhibit a linear viscoelastic domain, the corresponding
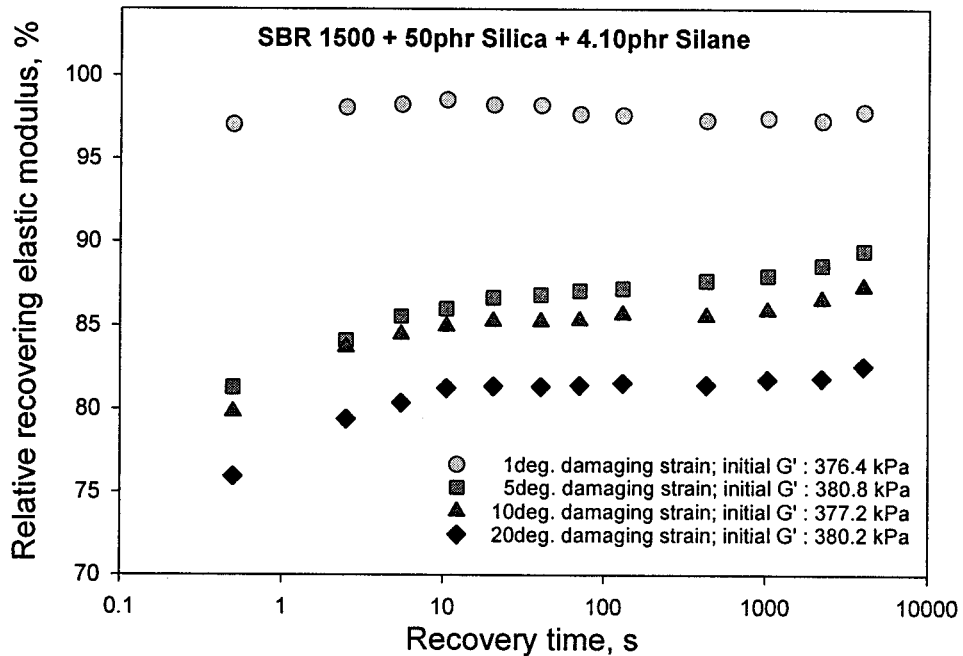

Figure 12 Damaged morphology recovery test results on silica-filled SBR compound. Rubber process analyzer (RPA) at 100°C corrected for G' shift under pressure and temperature.
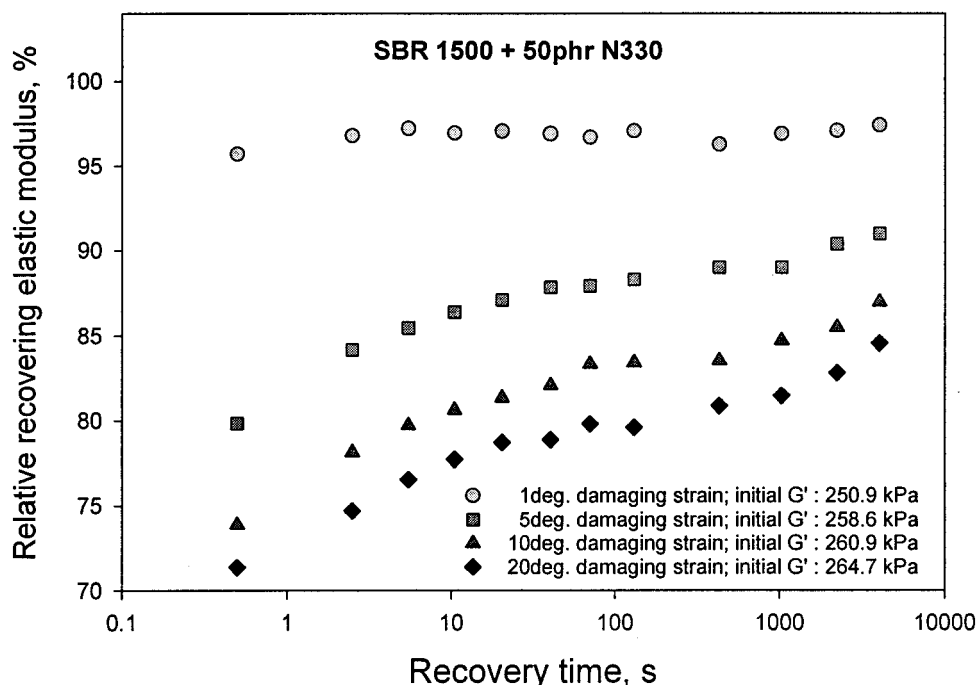
Figure 13 Damaged morphology recovery test results on carbon black-filled compound. Rubber process analyzer (RPA) at 100°C corrected for G' shift under pressure and temperature.

silica-filled material shows a linear plateau up to dynamic strain of 1° (14% deformation). The size of the linear plateau increases as silica level decreases.

One of the most intriguing aspects of the results reported is the observation of a dynamic modulus shift (increase) when the material is maintained in the cavity of the tester for long period. Owing to the design and principle of the torsional dynamic tester used, the material is strained in a closed cavity under 4 MPa pressure. With filled rubber, this results in a slight increase in G' that is likely due to pressure–temperature variations in filler–rubber interaction. The effect is qualitatively the same for silica and carbon black but differing in magnitude and must be considered when analyzing the results of damaged morphology recovery tests.

Damaged morphology recovery tests show significant difference between silica- and carbon black-filled materials that are likely reflecting the different origins of rubber–filler interaction of both fillers—essentially a physical interaction for carbon black, and dominated by (silanization) chemistry for silica. Further works, with other techniques, are necessary to fully understand such differences.

REFERENCES

1. Leblanc, J. L. Eur Rubber J 1989, 171, 93.
2. Sircar, A. K.; Voet, A. Rubber Chem Technol 1970, 43, 973.
3. Wang, M.-J.; Wolff, S.; Tan, E. H. Rubber Chem Technol 1993, 66, 178.
4. Wolff, S. Rubb. Chem Technol 1996, 69, 325.
5. Leblanc, J. L.; Stragliati, B. J Appl Polym Sci 1997, 63, 959.
6. Pawslowski, H.; Dick, J. Rubber World 1992, 206(3), 35.
7. Pawslowski, H.; Barker, B.; King, D. Measurement of the viscoelastic properties of elastomers with a new dynamic mechanical rheological tester; Belgian PRI, International Conference, Leuven, Belgium; April 19, 1994
8. Leblanc, J. L. Kautch Gummi Kunstst 1996, 49, 258.
9. Leblanc, J. L.; Barrès, C. In Rubber Division Meeting, Am Chem Soc Chicago, Illinois April 13–16, 1999, paper 70.
10. Litvinov, V. M.; Steeman, P. A. M. Macromolecules 1999, 3225, 8476.
11. Leblanc, J. L. Prog Rubber Plast Technol 1994,10, 112, for a pictorial representation of such a morphology.
12. Yatsuyanagi, F.; Kaidou, H.; Ito, M. Rubber Chem Technol 1999, 72, 657.