

Nonlinear Dynamic Behavior of Rubber Compounds: Construction of Dynamic Moduli Generalized Master Curves

THEONIS RICCÒ and ALESSANDRO PEGORETTI*

*University of Trento
Department of Materials Engineering
Via Mesiano 77, 38050 Trento, Italy*

The nonlinear dynamic behavior of a vulcanized rubber compound employed in the production of tires was investigated. The values of the dynamic storage modulus, E' , and the loss factor, $\tan\delta$, were measured at different frequencies, temperatures and strain amplitudes. Data were subsequently analyzed and treated by an empirical method of frequency-temperature-deformation reduction that provided for E' and $\tan\delta$, respectively, a single master curve and the frequency-temperature and frequency-deformation shift factors. The E' trend, extrapolated at higher strain amplitudes on the basis of the master curves, resulted in good agreement with E' values obtained from direct experimental measurements.

INTRODUCTION

The dynamic behaviors of rubber components, such as suspension dampers and tire treads, are strictly related to the thermo-mechanical behaviors of the materials of which they are constituted. Generally, these materials consist of vulcanized elastomeric compounds, filled with carbon black and other additives according to formulations suitably optimized for the final applications (1). The dynamic and thermal behavior of such materials is mostly determined by their viscoelastic nature that causes energy dissipation, and consequent heating, within the material under dynamic loading. These hysteric effects, as well as the material stiffness, depend on temperature and frequency of the applied load. In linear conditions this behavior is usually described in terms of the complex dynamic modulus $E^* = E' + iE''$, being E' and E'' the conservative and the loss component ($E'' = E' \tan\delta$, with δ the out-of-phase angle), respectively, dependent only on temperature and frequency of the applied load (2). The determination of $E'(\nu, T)$ and $E''(\nu, T)$ in wide ranges of frequency is usually obtained by empirical

frequency-temperature reduction of experimental data obtained at different temperatures in a small range of frequency (2). This procedure allows the determination of the empirical frequency-temperature horizontal shift-factor, $a_1^{T_0}(T)$, as well.

Because of the high content of carbon black usually incorporated within the compounds, the dynamic behavior of these materials is markedly nonlinear (3–10), so depending also on the deformation amplitude the material undergoes. Nonlinear characteristics of the material response to dynamic inputs are generally found from very low levels of strain amplitude (8, 10). In particular, E' is found to decrease by increasing strain amplitude till it attains a plateau level for sufficiently high strain levels, such behavior being attributed to disruption of the filler agglomeration network caused by strain. Further, $\tan\delta$ is found to increase by increasing strain amplitude and to reach a maximum that is attained approximately at strain levels where the storage modulus begins to level off (8–10). These nonlinearity effects can condition the behavior of rubber components, such as tire treads or suspension dampers and hence the dynamics of the whole vehicle. Thus, in problems concerning the dynamic simulation of those rubber components co-responsible for vehicle dynamics, it is important to dispose of a database for dynamic moduli with varying frequency, temperature, and strain amplitude.

In the present work the characterization of the nonlinear dynamic behavior of a rubber compound used in the production of tires is performed over a wide

* Corresponding author:
Dr. Alessandro Pegoretti
Department of Materials Engineering
University of Trento
Via Mesiano 77, 38050 Trento, Italy
Tel +39-0461-882413
Fax +39-0461-881977
E-mail Alessandro.Pegoretti@ing.unitn.it

range of frequency and temperature. Generalized master curves, $E'(\nu, T_0, \varepsilon_0)$ and $\tan\delta(\nu, T_0, \varepsilon_0)$ were obtained by adopting an empirical approach of frequency-temperature-deformation reduction. The dependence of the frequency-temperature and frequency-deformation shift factors on temperature and strain amplitude, respectively, was also determined. The data obtained appear suitable to be handled in the dynamic simulation and modeling of rubber components (11).

EXPERIMENTAL

The material studied, consisting of a vulcanized rubber compound containing carbon black and other additives, was kindly supplied by Pirelli S.p.A. (Milan, Italy) in the form of cylinders, with 17.5 mm diameter and 24.7 mm height, and of 1.9 mm thick sheets. The elastomeric phase was based on a SBR/polybutadiene rubber compound and the carbon black content was about 50 phr. More detailed information about the composition of the elastomeric compound was not directly available from the manufacturer.

Dynamic tests were carried out on $40 \times 5 \times 1.9$ mm³ strip specimens, cut from the sheets, by a Dynamic Mechanical Thermal Analyzer from Polymer Laboratories Ltd. (U.K.), which can perform dynamic tests by scanning temperature and frequency simultaneously. The tests were carried out in tensile mode at various levels of the strain amplitude, i.e. 0.2%, 0.5%, 0.7%, and 1.4%. Tests were performed at five different frequencies, 0.3, 1, 3, 10, 30 Hz by scanning temperature in the range from -100°C to $+100^\circ\text{C}$, at a heating rate of $0.4^\circ\text{C}/\text{min}$.

Room temperature cyclic tension-compression tests at low frequency (0.1 Hz) were also carried out on the cylindrical test-pieces by a 4502 Instron machine for different strain amplitudes in the range between 0.3% and 8%. The two bases of the rubber cylinders were joined by a cyanacrylic adhesive to two aluminum blocks that were connected to the jaws of the machine.

RESULTS AND DISCUSSION

Experimental data of the conservative modulus, E' , and the loss factor $\tan\delta$ ($\tan\delta = E''/E'$), were obtained by DMTA for the different frequencies and strain amplitude by scanning temperature. At the strain amplitude of 0.2%, data for E' and $\tan\delta$ are reported in Figs. 1a and 1b, respectively, at various frequencies as a function of temperature.

For each level of the strain amplitude, the cross plots of the curves such as those of Fig. 1 allowed the construction of a series of isothermal curves for E' and $\tan\delta$ as a function of frequency in the range between 0.3 and 30 Hz. The results of E' at 0.2% strain amplitude are shown in Fig. 2. The data were then reduced according to the frequency-temperature superposition approach to obtain master curves of dynamic storage modulus E' at a reference temperature of

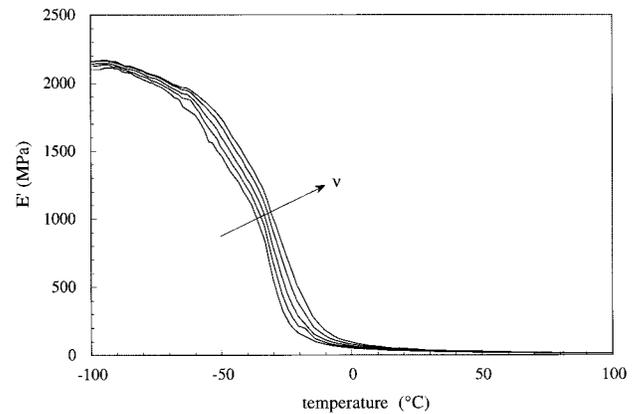


Fig. 1a. Dynamic storage modulus, E' , as a function of temperature, for a strain amplitude of 0.2% at various frequencies (0.3, 1, 3, 10, 30 Hz).

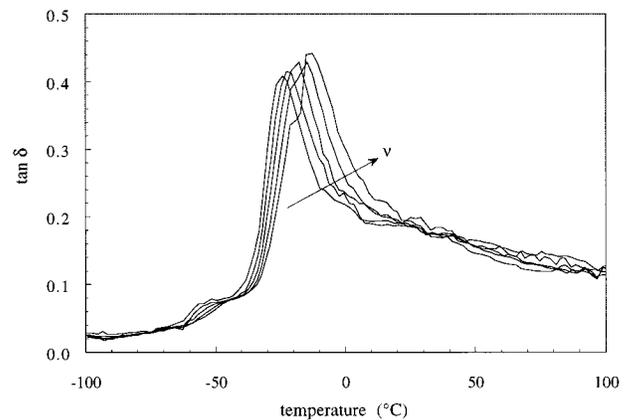


Fig. 1b. Dynamic loss factor, $\tan\delta$, as a function of temperature, for a strain amplitude of 0.2% at various frequencies (0.3, 1, 3, 10, 30 Hz).

-20°C , the same procedure being applied separately to each set of isometric (isostrain) data. Each experimental value of the modulus E' in the rubber-like region was previously reduced by the rubber elasticity factor T/T_0 . Then, the isothermal curves were shifted horizontally to best superposition. The procedure provided an empirical determination of the shift factor $a_T^{\pm 0}(T)$. At each level of the strain amplitude, the shift factor obtained was used to shift the isothermal curves of $\tan\delta$. Strictly, the frequency-temperature reduction performed can be questionable because of possible thermorheological complexity of the material examined. Indeed, thermorheological complexity has been observed for filled rubbers (12, 13), mainly associated to the transition zone (13). In fact, temperature might change the strength of filler-filler and filler-matrix interaction, so that decreasing temperature could not be equivalent to increasing frequency.

The isometric master curves of E' and $\tan\delta$ at -20°C are shown in Figs. 3a and b, respectively. The curves

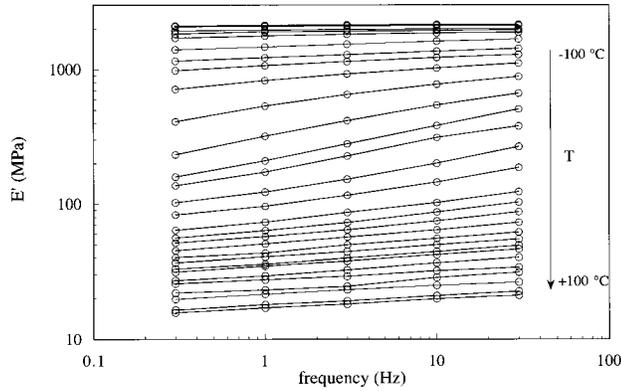


Fig. 2. Isothermal storage modulus values as a function of frequency, for a strain amplitude of 0.2%.

extend over a frequency range between 10^{-10} and 10^{10} Hz and show the viscoelastic transition between 10^{-2} and 10^2 Hz. The nonlinear effects are clearly shown by the decrease of the rubbery plateau level of E' (low frequency region), and the increase of the level of $\tan\delta$ in the same frequency range, by increasing strain amplitude. Nonlinear effects are not appreciable in the glass-like region. The isometric master curves obtained for $\tan\delta$ show that the viscoelastic transition shifts to lower frequencies by increasing strain amplitude, which seems to point out the viscoelastic feature of the nonlinear effects. The result observed could be attributed to strain-induced volume changes at rubber filler/interface in agreement with the hypothesis that in filled rubbers, polymer chains at carbon-black interface have reduced segmental mobility (14, 15). The shift factors $a_{T_0}^T(T)$ obtained for the master curves at the different strain amplitudes were very similar and showed different behavior above and below -20°C . In particular, above -20°C they agree with the Williams-Landel-Ferry (WLF) model (2), as shown in Fig. 4. This plot provides the values $C1 = 19.2$ and $C2 = 99.1$ for the constants to introduce in the following, well-known, WLF equation:

$$\log a_{T_0}^T = \frac{-C1(T - T_0)}{C2 + T - T_0} \quad (1)$$

The results of E' and $\tan\delta$, shown in Fig. 3a and 3b, respectively, were further reduced to generalized master curves by shifting the isometric curves so as to superpose them to the isometric curve at 0.2% strain amplitude. For $\tan\delta$ the shifting was tentatively performed so as to superpose the maxima of the curves at various strains, whereas for E' the superposition was limited to the data relative to the rubber-like region (portion of the curves at frequencies up to the flex point) where the nonlinearity effects are clearly appreciable. A good superposition was obtained by performing both a horizontal and a vertical shift of the curves. The generalized master curves for E' and $\tan\delta$ are shown in Fig 5a and 5b, and the experimental

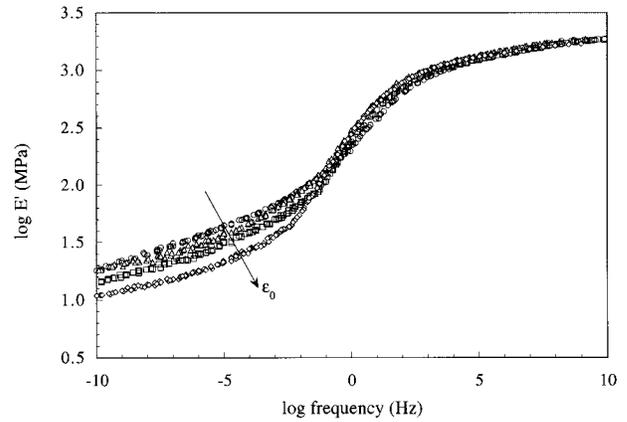


Fig. 3a. Storage modulus master curves for strain amplitudes of (O) 0.2%, (Δ) 0.5%, (□) 0.7%, (◇) 1.4% referred to a temperature $T_0 = -20^\circ\text{C}$.

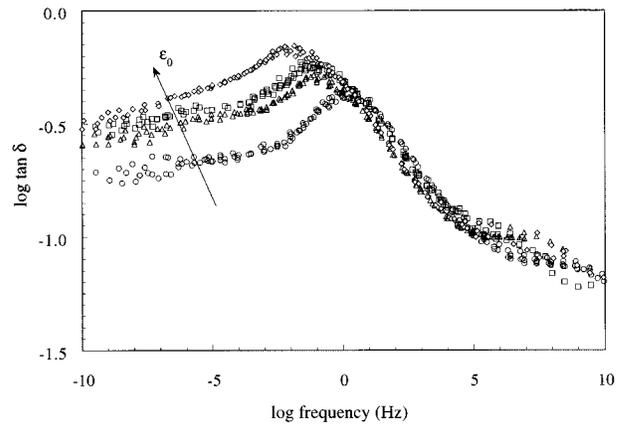


Fig. 3b. Loss factor master curves referred to a temperature $T_0 = -20^\circ\text{C}$. Symbols as in Figure 3a.

horizontal $b_{\epsilon_0}^{\epsilon}$ and vertical $c_{\epsilon_0}^{\epsilon}$ shift factors are reported in Figs. 6 and 7, respectively. Both for E' and $\tan\delta$ the horizontal shift factors have the same sign and then move the isometric curves in the same direction along the frequency axis, as expected. In particular, curves at higher strain amplitudes must be shifted to higher frequencies (shorter times) to superpose the reference curve at 0.2% strain amplitude. Results of strain-reduced complex modulus, previously attempted over a more limited range of frequency, did not provide any horizontal shift both for E' and E'' (16). The extent of the horizontal shift of the curve at 1.2% strain amplitude with respect to the reference curve is about two decades of frequency. The vertical shifts for E' and $\tan\delta$ are of opposite sign to account for the lowering of E' and increasing of $\tan\delta$ with increasing strain amplitude.

The analysis performed suggests that from a master curve $E'(\nu, T_0, \epsilon_0)$ at a given temperature and strain

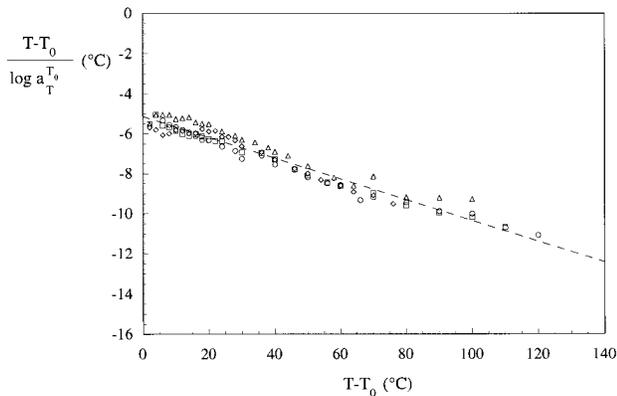


Fig. 4. Frequency-temperature horizontal shift factors referred to a temperature $T_0 = -20$ °C. Symbols as in Figure 3a.

amplitude, if the three shift factors $a_{T_0}^T(T)$, $b_{\varepsilon_0}^{\varepsilon}(\varepsilon)$ and $c_{\varepsilon_0}^{\varepsilon}(\varepsilon)$ are known, it is possible to obtain E' data in wide ranges of temperature and strain amplitude, at least within the range of strain amplitude where this approach can be applied. The same considerations hold for $\tan\delta$.

On the basis of the results obtained, the nonlinear behavior of dynamic modulus E' can be described by the following equation:

$$E'(v, T, \varepsilon) = \frac{T/T_0 E'(v^*, T_0, \varepsilon_0)}{c_{\varepsilon_0}^{\varepsilon}} \quad (2)$$

where $v^* = v a_{T_0}^T b_{\varepsilon_0}^{\varepsilon}$

Figure 8 shows data of E' as a function of strain amplitude up to 8% obtained from tests performed at 0.1 Hz by the Instron machine. E' is found to decrease by increasing strain amplitude and seems to begin to level off at about 8% strain amplitude. In this plot, data of E' , evaluated according to the generalized master curve approach (Eq 2), are also reported. The values of $b_{\varepsilon_0}^{\varepsilon}$ and $c_{\varepsilon_0}^{\varepsilon}$ at strain higher than those experimentally determined were evaluated by fitting the experimental values of $b_{\varepsilon_0}^{\varepsilon}$ and $c_{\varepsilon_0}^{\varepsilon}$ with a proper function and considering the extrapolated values at the strain levels of interest. Notwithstanding the difference between E' values measured with the two different testing approaches, tension-tension on strips and tension-compression on cylindrical specimens, the E' trend as a function of applied strain amplitude appears in good agreement with those obtained according to Eq 2, thus supporting the reliability of the generalized master curve approach. Moreover, it has to be considered that the dispersion band of the generalized master curve data reported in Fig. 5a is of the same order of the discrepancy between moduli compared on Fig. 8.

It is worth noting that the strain-reduction approach was recently applied by some authors to describe the nonlinear viscoelastic response of amorphous glassy polymers (17–19) and also of semicrystalline polymers above T_g , such as high and medium density polyethylene (20, 21). Even in this last case, the authors found

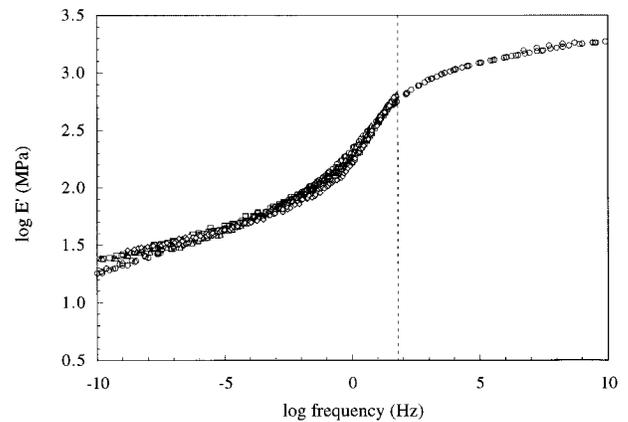


Fig. 5a. Generalized storage modulus master curve referred to a strain amplitude $\varepsilon_0 = 0.2\%$ and a temperature $T_0 = -20$ °C. Symbols as in Figure 3a.

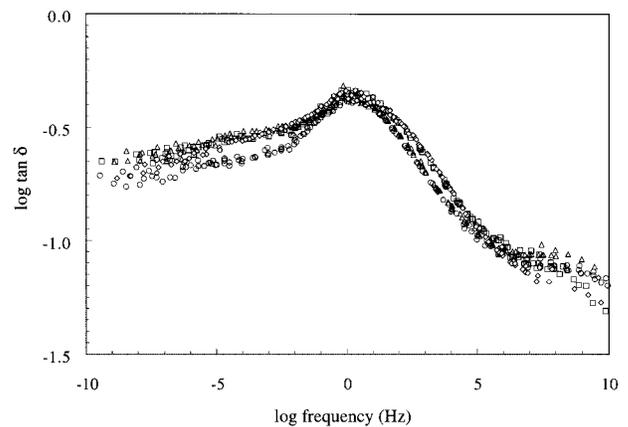


Fig. 5b. Generalized loss factor modulus master curve referred to a strain amplitude $\varepsilon_0 = 0.2\%$ and a temperature $T_0 = -20$ °C. Symbols as in Figure 3a.

that short-term creep data at different stresses can be reduced to a single master curve by shifting the isometric curves both vertically and horizontally, the horizontal shift being attributed to stress-induced change of free volume. Though the theoretical implications concerning the construction of dynamic moduli generalized master curves for filled rubbers need further investigation, the approach can be extremely useful for obtaining data for modeling the dynamic and thermal behaviors of rubber components for engineering applications, where the characterization of dynamic moduli in wide ranges of frequency, temperature and strain amplitude is necessary. Further, in simulation problems the data can be easily handled via computer through the use of Eq 2.

CONCLUSIONS

In this work, the nonlinear effects on the dynamic behavior of a filled vulcanized rubber compound were studied. The values of the storage modulus and loss

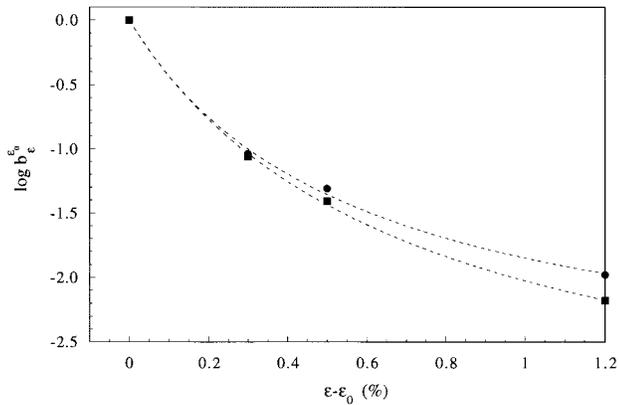


Fig. 6. Frequency-deformation horizontal shift factors for (●) storage modulus and (■) loss factor.

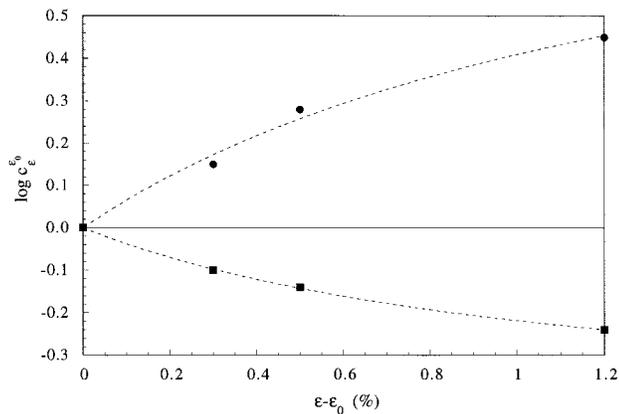


Fig. 7. Frequency-deformation vertical shift factors for (●) storage modulus and (■) loss factor.

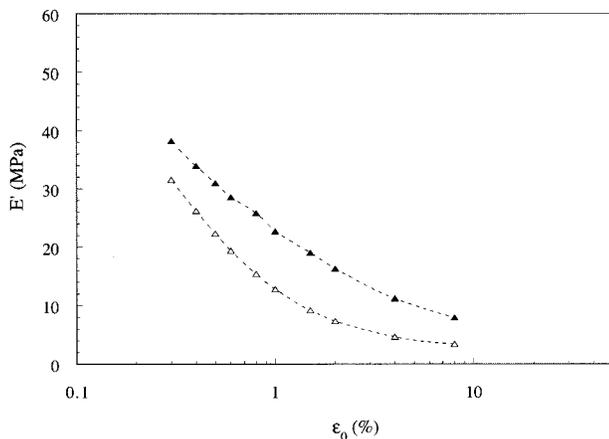


Fig. 8. Storage modulus (▲) from direct measurements, and (△) from generalized master curve extrapolation.

factor were experimentally determined by dynamic mechanical thermal analysis at various frequencies, temperatures and strain amplitudes. Subsequently, the data were analyzed by an empirical method of frequency-temperature-deformation reduction. The analysis provided a single master curve for E' and $\tan\delta$ together with the frequency-temperature horizontal shift factor, $a_T^{T_0}(T)$, and frequency-deformation horizontal, $b_{\epsilon_0}^{\epsilon_0}(\epsilon)$, and vertical, $c_{\epsilon_0}^{\epsilon_0}(\epsilon)$, shift factors.

Storage modulus extrapolated at higher strain amplitudes resulted in reasonable agreement with direct experimental measurements.

The construction of dynamic moduli generalized master curves can be seen as an extremely useful method to provide data for modeling the dynamic and thermal behaviors of rubber components for engineering applications.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Alfeo Tecchiolli for his contribution to the experimental work and discussion of results. Pirelli S.p.A. (Milan, Italy) is kindly acknowledged for providing the rubber compound.

REFERENCES

1. W. W. Barbin and M. B. Rodgers in *Science and Technology of Rubber*, Chapter 9, J. E. Mark, B. Erman, F. R. Eirich, eds., Academic Press Inc., San Diego Calif., (1994).
2. J. D. Ferry, *Viscoelastic Properties of Polymers*, J. Wiley & Sons Inc., New York (1980).
3. S. D. Geham, D. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.*, **33**, 1032 (1941).
4. W. P. Fletcher and A. N. Gent, *Trans. IRI*, **26**, 45 (1950).
5. W. F. Fletcher and A. N. Gent, *Trans. IRI*, **29**, 266 (1953).
6. A. R. Payne, *J. Appl. Polym. Sci.*, **6**, 57 (1962).
7. A. R. Payne, *ibidem*, **8**, 266 (1964).
8. A. R. Payne and R. E. Whittaker, *Rubb. Chem. Technol.*, **44**, 340 (1971).
9. G. Kraus, *Angew. Makromol. Chemie*, **60/61**, 215 (1977).
10. C. M. Roland and G. F. Lee, *Rubb. Chem. Technol.*, **63**, 554 (1990).
11. D. Cambiaghi, D. Vetturi, A. Pegoretti, and T. Ricco, *Res Mechanica*, submitted.
12. B. Duperray and J. L. Leblanc, *Kautschuk Gummi Kunst.*, **35**, 298 (1982).
13. P. G. Santangelo and C. M. Roland, *Macromolecules*, **31**, 3715 (1998).
14. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, p. 55-56, Elsevier Publ. Co., Amsterdam (1978).
15. F. Yatsuyanagi, H. Kaidou, and M. Ito, in *Proc. ACS Rubber Division Meeting*, paper 14, Nashville, Tenn. (Sept. 29-Oct. 2, 1998).
16. R. E. Martin and S. C. Malguarnera, *J. Elast. Plast.*, **13**, 139 (1981).
17. J. M. Crissmann and G. B. McKenna, *J. Polym. Sci.: Part B: Polym Phys.*, **25**, 1667 (1987).
18. J. M. Crissmann and G. B. McKenna, *ibidem*, **28**, 1463 (1990).
19. P. Meriani, R. Frassine, M. Rink, and A. Pavan, *Polym. Eng. Sci.*, **36**, 2750 (1996).
20. C. F. Popelar, C. H. Popelar, and V. H. Kenner, *ibidem*, **30**, 577 (1990).
21. A. Bakker and J. Lai, *Polymer*, **36**, 93 (1995).