# Dynamic Mechanical Characterization of Tire Cord Dip Films

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## Synopsis

Various dip films with different amounts of F/R resins, polybutadiene latex, styrene/butadiene/vinyl pyridine terpolymer latex, and/or with carboxylated butadiene latex were prepared on a Teflon-coated hot plate by spraying the properly formulated dip mixes using a Binks air gun. These dip films were cured at 300°F in hot air oven between two Teflon plates. A DDV-IIC Rheovibron instrument was used to measure elastic modulus ($E'$), loss modulus ($E''$), and tan $\delta$ ($E''/E'$) of different dip films. Dip films with higher F/R resin (11 vs. 7%) concentration gave higher tan $\delta$ values which peaked between −20 and −30°C. Films with higher resin concentrations were also found stiffer (higher $E'$), if all other ingredients of the films were identical. Dip films, where more than 40% of the film ingredient was polybutadiene, showed a phase-separated glass transition temperature for polybutadiene between −60 and −90°C. Films, with 40% polybutadiene and 7.0% F/R resin and the rest of the ingredients being styrene/butadiene/vinyl pyridine and other additives such as wax, silanes, etc., gave two distinct glass transition temperatures: one between −60 and −80°C for polybutadiene and the other for complex between F/R resin and vinyl pyridine around −20 and −30°C. Tire cords coated with dip mixtures of lower tan $\delta$ values in the −20 to +20°C range gave better fatigue performance in the Gristmill tire test at room temperature. Tire cords coated with dip mixtures containing 40% polybutadiene and 7.0% F/R resin exhibited phase separated two distinct glass transition peaks in the temperature ranges of −60–−90°C and −20–−30°C. Films of the above formulations showed low modulus and high elongations. Cords coated with the above dip mixtures gave good fatigue performance in the Firestone cold wheel test at −50°C. It so happens that, in this temperature range of −30–−60°C, the above phase-separated dip films go through a minimum damping value and, therefore, give superior tire performance.

## INTRODUCTION

The mechanism of fatigue failure of cords in tires has been extensively discussed in the literature.[1-8] Many complex mechanisms have been presented to explain the fatigue behavior of tire cords in running tires. Organic, inorganic, and metallic cords fail following different mechanisms. A simplistic summary of the opposing views on this subject can be given in the following statements. One school of researchers suggest that cords in tires lose their strengths linearly with use mileage. Other researchers believe that tire cords do not get progressively weak during service but fail suddenly by an undefined catastrophic process. These views, though 20 years old, are still prevalent in discussing the mechanism of fatigue failure of organic cords under ambient conditions.

In fiber glass tire cords, the mechanism of fatigue failure becomes more complex. The inherent brittle nature of glass filaments makes the cords more susceptible to self-destruction by fretting and abrasion. Normally, single filament properties of fiber glass are reduced when these fibers are fabricated as

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strands or yarns. The excellent flex life of fine single filament drops when combined as a tire cord. A combination of elastomeric materials, formaldehyde/ resorcinol resins, and silane coupling agents have been used by the tire and the fiber manufacturing industries to improve the flex properties of fiber glass tire cords.

Various fatigue tests have been used in the literature[9] to screen the cord properties. The Mallory tube fatigue test, the Goodrich disk fatigue test, the Firestone compression fatigue test, the Dunlop fatigue test, the Demattia flex tester, and many others have been developed in different research laboratories for screening properties of tire cord candidates for different end use.

As is the case in a complex human body, one medicine cannot be prescribed for all diseases; similarly, in a complex tire structure, one laboratory test can not simulate all service conditions of a running tire. Therefore, it is logical for researchers to develop different tests and simulate different service conditions to screen different cord candidates. It should be very clear to those who are knowledgeable in the field of tire science that any laboratory test can only be used as a screening tool and not as a substitute for tire testing.

## EXPERIMENTAL

### Sample Preparation

The dip mixtures were formulated following the dip mixing specifications. These were, then sprayed on a Teflon-coated hot plate using a Binks air gun. Dip mixtures were atomized at 40 psi pressure and were sprayed uniformly on the hot Teflon plate. Eighty to 100 passes were made over the plate to develop a film thickness of 15–20 mils. Temperature of the Teflon plate was maintained between 140 and 160°C. These films were then cured between two Teflon-coated steel plates in a hot press at 300°F and 1500 psi. pressure for 1 min. The ideal thickness of the cured films were targeted to be 10–15 mils. Samples, used in DDV IIC Rheovibron, were 2.5–3.0 cm long, 5.0 mm wide, and 10–15 mil thick. Films thinner than 10 mils and thicker than 20 mils were discarded.

### Rheovibron Viscoelastometer

This instrument (DDV IIC) is manufactured by the Toyo Baldwin Company Ltd. There are newer, computerized versions of this instrument available now which are much easier to calibrate and generate reproducible data. At the time when this work was done, we conducted our research using DDV IIC. The principle on which this instrument works is simple and is briefly described here. In this instrument, when a tensile or compressive sinusoidal strain is applied on one end of the specimen, sinusoidal stress arises at its other end. From the phase angle between stress and strain and the absolute values of stress and strain, tan $\delta$ (hysteresis) and complex modulus of elasticity ($E^*$) are deduced. The complex modulus is related to the elastic modulus ($E'$) and loss modulus ($E''$) as follows:

$$E^* = E' + iE'', \quad \text{where } i = \sqrt{-1}$$

$$\tan\delta = E''/E', \quad \text{where } \delta \text{ is the phase angle between stress and strain}$$

DDV IIC Rheovibron was available to us at Fiber Glass Research Center of PPG. In this instrument, the oscillations were generated at 3.5, 11.0, 35.0, or 110 Hz on the sample by a built-in oscillator which was amplified by a power amplifier. Sinusoidal stress produced at the other end of the sample was detected by a stress gauge. Using the appropriate expressions, the elastic modulus ($E'$), loss modulus ($E''$), and tan $\delta$ were calculated at a specified frequency and as a function of temperature (range −100–200°C). In Rheovibron, the sample is subjected to very small strains (less than 0.1%) and, therefore, masking effects of large nonlinear rupture strains of cured dip films get eliminated.

### Calculations

Oscillating displacement = $S \cdot A \cdot N \cdot 10^{-3}$ cm and dynamic force = $10^4$ dyn $\cdot 10^3/D \cdot N$, where $S$ = sample cross section area (cm$^2$), $A$ = amplitude factor (given in the table), $N$ = table value of tan $\delta$ range, $D$ = dynamic force dial reading, $K$ = modulus error constant, and $L$ = sample length (cm). Complex modulus = $E^* = 2 \times 1/\text{ADK} \times L/S \times 10^9$ dyn/cm$^2$, elastic modulus = $E'$ = $E^* \cos \delta$, loss modulus = $E'' = E^* \sin \delta$, and $\tan \delta = E''/E'$.

### Description of Gristmill Test

The Gristmill tire test,[10] run by ARA, measures the compression fatigue resistance of belt cords of belted tires. A major portion of the stress on tires, running in circular laps, is applied on the outside shoulder of the tire where belt cord breakage is most likely to occur. Cord breaks in each tire belt (top and bottom) are totalled and expressed as breaks/m of belt length. The ambient Gristmill test conditions are given below:

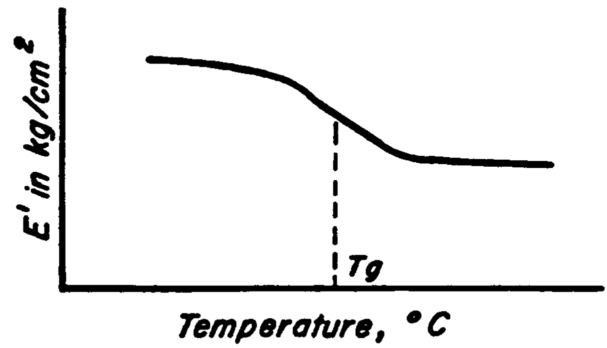
1. Diameter of lap = 85 ft
2. 100 laps at 15 mph in clockwise direction followed by 100 laps in counterclock wise direction
3. Initial inflation pressure = 24 psi
4. Load = 100% rated by Tire and Rim Association at 24 psi
5. Front fixed position mounting
6. Cord breaks/m of belt were checked after 1600 laps

### Description of Firestone Cold Wheel Test

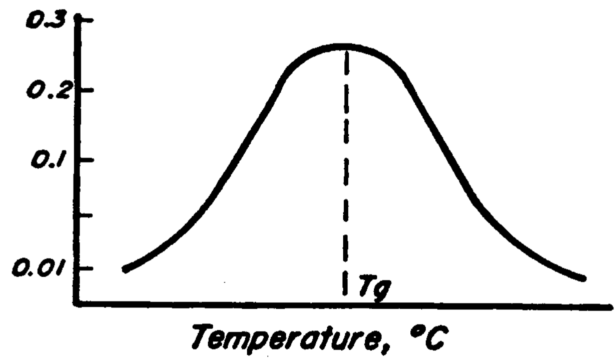
The Firestone indoor cold wheel test[11] is run on tires after they are cooled to −50°C. These cooled tires are immediately mounted on a loaded wheel and run for 25 min. This constitutes one cycle. Cycles are added to report durability of running tires and tests are run until distortion in the running tire structure occurs. If the running tire completes 25 cycles successfully, then it is removed from the indoor testing wheel. The tested tire is then stripped and the belts are rated. Zero rating is no cord failure and rating 5 is for the excessive cord breakage. If the tire is removed after 25 cycles with no failure, it is then rated as RNF (removed with no failure).

## RESULTS AND DISCUSSION

Dynamic mechanical properties on cured dip films were obtained by Rheovibron (DDV-IIC) between −100 and 30°C at 110 HZ sinusoidal frequency. In these dynamic spectral measurements, the elastic moduli ($E'$) is the reflection of elastic stiffness of a material under test. Normally for the polymeric materials, if elastic modulus is plotted against temperature on a semilog graph paper, the typical $E'$ vs. temperature curve will look as shown below:




The tan $\delta$ or hysteresis curves in such dynamic spectral measurements, generally looks like the one shown below:




tan $\delta$ value is the ratio of loss modulus and elastic modulus ($E''/E'$). The loss modulus is the fraction of the total stored stress lost per cycle in cyclic sinusoidal deformation. The elastic moduli and tan $\delta$ spectra for the five dip films, whose formulations are given in Table I, are shown in Figures 1–5. The top curve in each figure is the plot of $E'$ and the bottom curve in each figure is the plot of tan $\delta$ against temperature. The units for $E'$ are shown on the left-hand vertical axis (↑) and the units for tan $\delta$ are shown on the right hand vertical axis (↑) in each figure.

From Table I it is clear that dip films A, B, and C contained 11% F/R resin in which F/R ratio was 1.5. Formulation A contained higher percent of neoprene than formulation B. Formulation C did not contain any neoprene at all. Since Gristmill tire tests are run at ambient temperatures, the tan $\delta$ values of the

TABLE I
Dip Film Formulations

| Ingredients | A | B | C | D | E |
|---|---|---|---|---|---|
| Polybutadiene (%) | 24.2 | 24.2 | — | 46.0 | 59.3 |
| Carboxylated polybutadiene (%) | — | — | 36.7 | — | — |
| Styrene/butadiene/vinyl pyridine ter polymer (%) | 45.1 | 36.9 | 47.8 | 42.4 | 31.7 |
| Neoprene (%) | 17.7 | 10.7 | — | — | — |
| F/R resin (%) | 11.0 | 11.0 | 11.0 | 7.0 | 7.0 |
| Other ingredients (wax, antioxidants, silane, etc.) (%) | 2.0 | 1.9 | 4.5 | 4.6 | 7.4 |
| F/R ratio | 1.5 | 1.5 | 1.5 | 1.1 | 1.0 |

above dip films between −20 and +20°C were chosen to examine if a correlation exists between the film hysteresis (tan $\delta$) of cured films and the Gristmill cord breaks/m in belts of tested tires. The cords (K 15 1/3) coated with dips shown in formulations A, B, and C were tested in Gristmill test at ambient temperatures. These test results along with the dip film tan $\delta$ values of the corresponding films in the −20–+20°C temperature range are given in Table II.

The cord coated with dip film showing maximum hysteresis (A), gave maximum breaks/m and the one coated with dip film showing the least hysteresis (C), gave minimum breaks/m of the tire belt. Thus, there appears to be a correlation between the dip film dynamic hysteresis (tan $\delta$) and Gristmill tire cord performance.

An additional review of the formulations of different dip films in Table I and a review of their elastic moduli and tan $\delta$ curves indicate that these formulations are not only different in resin ratios and resin contents, but are also different in having different combinations of polymeric latices. Dip films A and B, for example, contained neoprene which others did not. These were the two films which showed higher tan $\delta$ values in the −30–+20°C temperature range. They also showed higher rigidity ($E'$) in the low temperature range (−80– −100°C). Films which contained less than 40% polybutadiene showed either a broad, high damping tan $\delta$ peak in the −20–−30°C temperature range or showed weak shoulders in the lower temperature regions (−60–−100°C). Transitions in these lower temperature regions are attributed to phase separated polybutadiene. Their absence or their weak presence in dip films A–C indicate

TABLE II
Correlation between Gristmill Tire Test and Hysteresis of Dip Films

| Identification of dip films | Gristmill tire test, 400 laps (breaks/m) | Hysteresis (tan $\delta$) at temperatures (°C) | | | | |
|---|---|---|---|---|---|---|
| | | −20 | −10 | 0 | +10 | +20 |
| A | 63.5 | 0.40 | 0.21 | 0.23 | 0.09 | 0.05 |
| B | 37.0 | 0.26 | 0.21 | 0.08 | 0.09 | 0.02 |
| C | 1.1 | 0.13 | 0.07 | 0.05 | 0.04 | — |

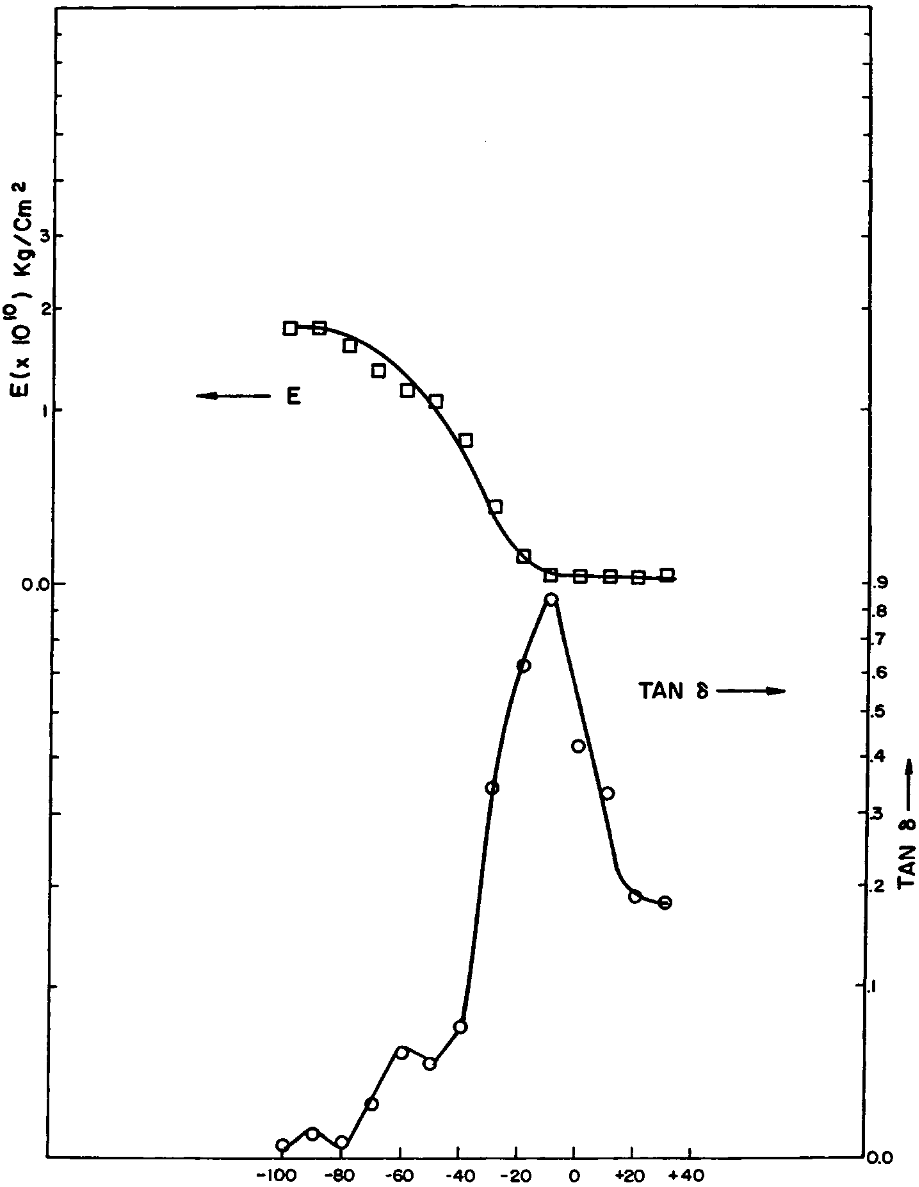



Fig. 1. Elastic modulus tan δ dip, film A.

that polymeric segments of different functionality are probably interacting with each other and are compatibilizing with each other. This results in a diffused and broadened transition peak with multiple weak shoulders.

**Firestone Indoor Cold Wheel Test.** Various tire cord combinations, coated with dips similar to formulations D and E in Table I, were run in radial tires on the Firestone cold wheel tests at −50°C. Most of the dips containing more than 40% polybutadiene and 7.0% F/R resin in which F/R ratio was kept 1.0

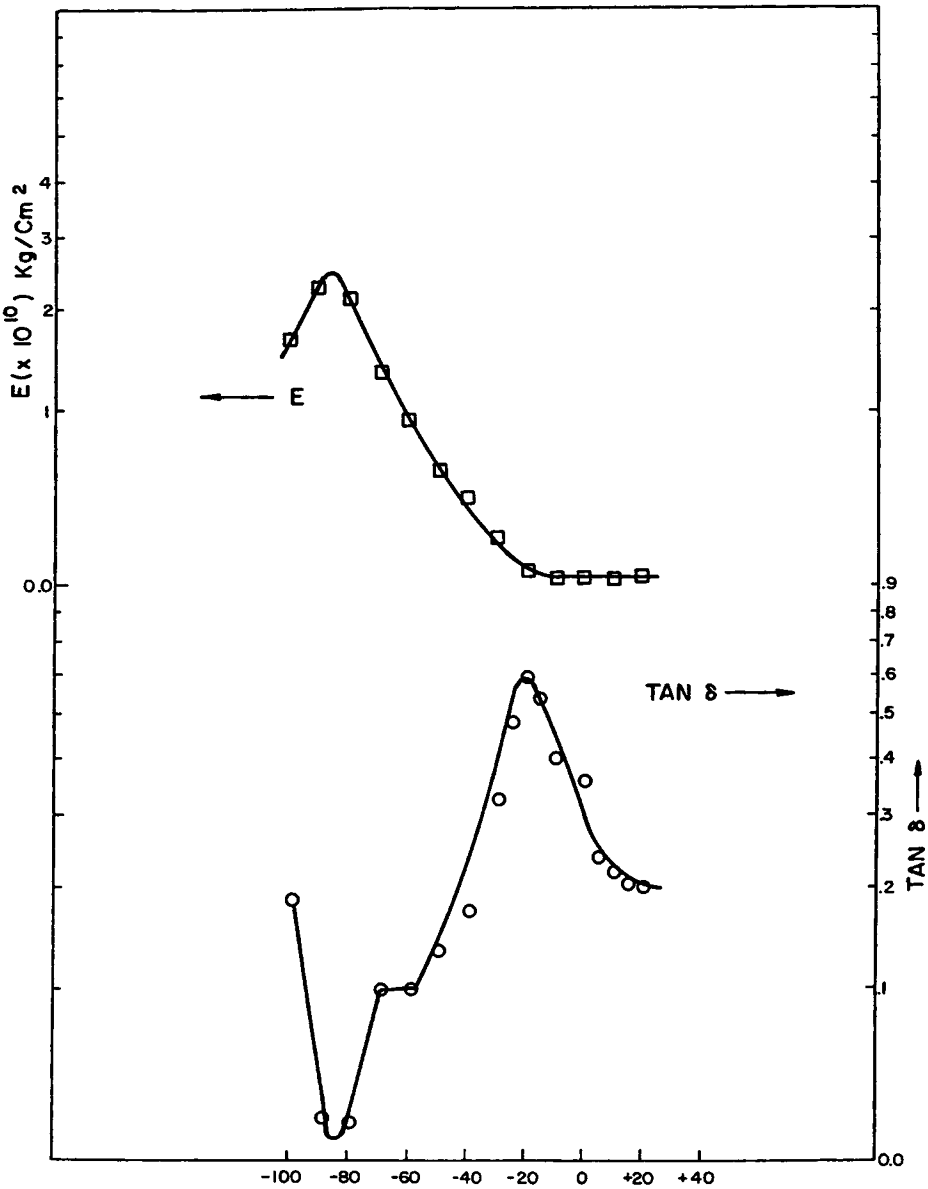



Fig. 2. Elastic modulus tan δ dip, film B.

or below 1.0, passed the 25 cycle Firestone cold wheel test with no cord breakage. Of course, the cords (K 15 1/3) coated with these two specific dips, D and E, are shown here as typical examples which also passed the 25 cycle test in flying colors (RNF). Films of this category showed two distinct transition peaks, one between −60 and −100°C for polybutadiene and the other between −20 and −30°C for vinyl pyridine–F/R resin complex. The lower temperature (−75°C) peak transition tan δ values for these films ranged between 0.2 and 0.4 and the

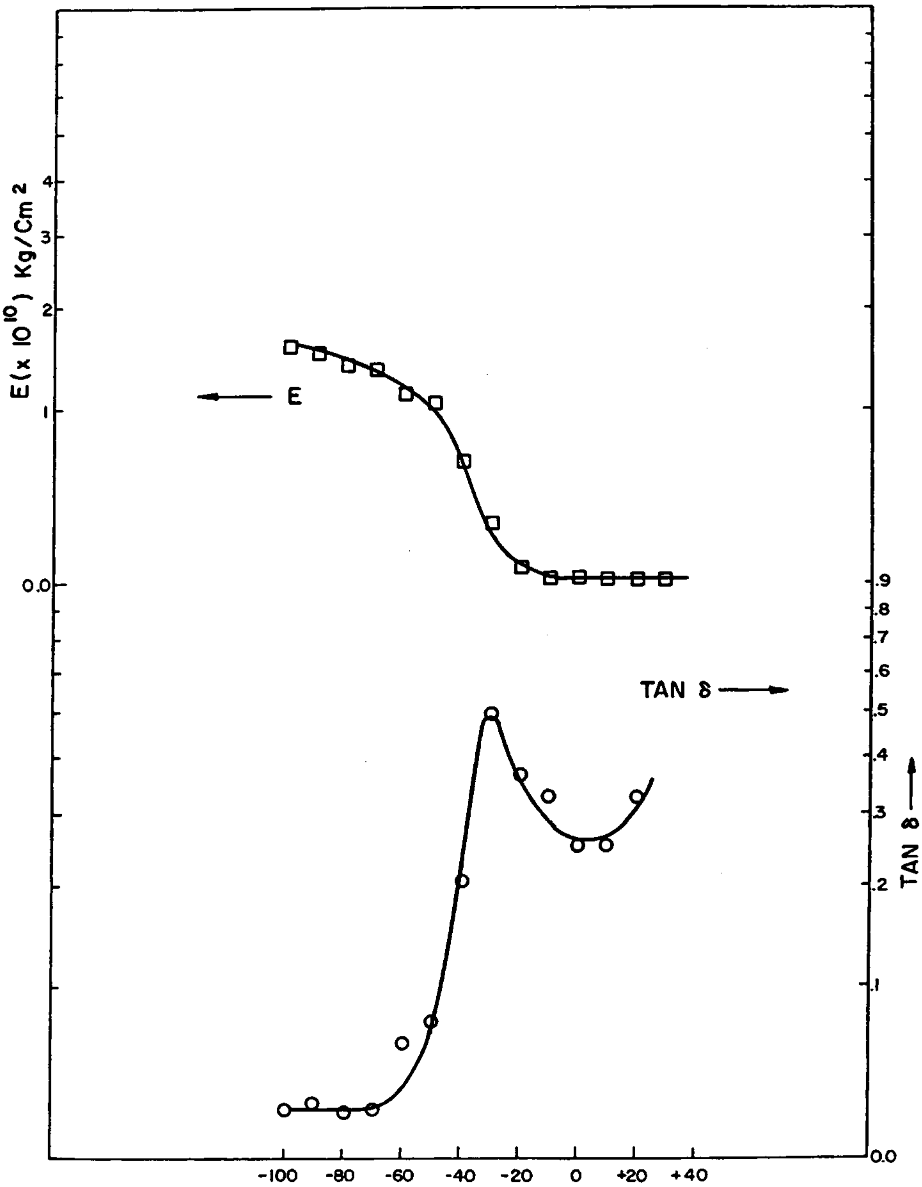



Fig. 3. Elastic modulus tan δ dip, film C.

peak tan δ values at −20°C ranged between 0.3 and 0.5. In contrast, the peak tan δ values of dip films A and B in this temperature region, ranged between 0.7 and 0.9. In the temperature range at which this wheel test is run (−50°C), the tan δ values of the coating dip films turned out to be even lower than the values mentioned above. This is because, between −60 and −30°C, the films in question go through a minima.

Thus, it is concluded from the data in this publication that the selection of types of polymeric latices in a dip formulation, their amounts in the dip, the

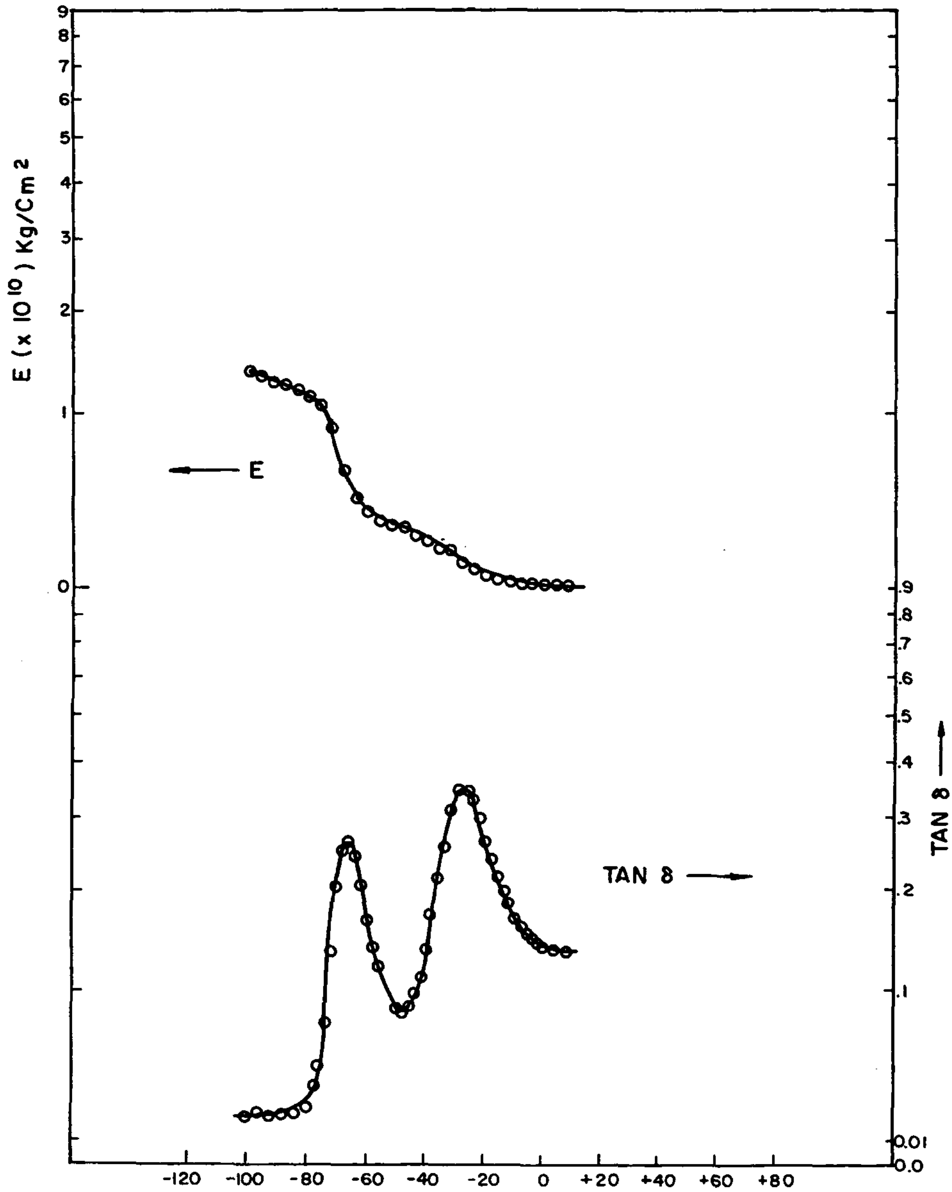



Fig. 4. Elastic modulus tan δ dip, film D.

amount of F/R resin in the dip, the F/R ratio in the dip and presence of special additives such as wax and silanes, all play a very important role in controlling the elastic moduli and the damping properties (tan δ) of the tire cord dip films. It is also concluded from the data presented in this publication that if fiber glass tire cord yarns had flexible size, then a good directive indication of the cord's fatigue properties can be obtained from the dynamic mechanical properties of the dip films. The fact that a correlation between the dynamic me-

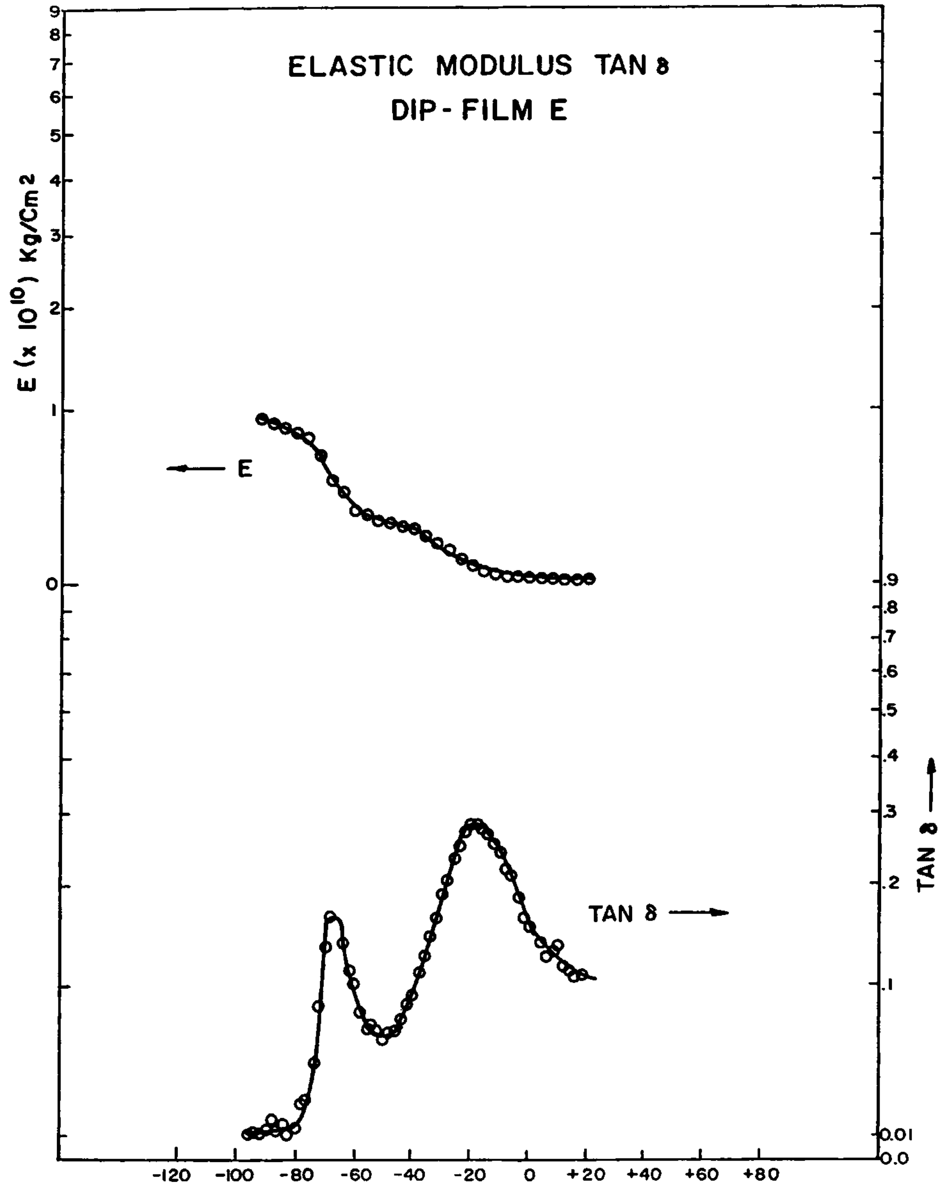



Fig. 5. Elastic modulus tan δ dip, film E.

chanical properties of the dip films and their tire fatigue performance has been shown, it does not mean that the dynamic mechanical properties of dip films should be considered as a substitute for final tire testing. However, these properties can certainly be used as screening tools for candidate selection.

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## References

1. J. F. Steckel, et al., *Polym. Eng. Sci.,* **27,** 1121–1127 (1987).

2. A. Prakash, et al., *Rubber World,* **196**(May), 36–38, 40–43 (1987).

3. J. M. Holt, *Wire J. Int.,* **18**(Oct.), 62–77 (1985).

4. D. K. Kim, et al., *International Conference on Fatigue, Corrosion Cracking, Fracture Mechanics and Failure Analysis,* LASM, Metal Park, Ohio, Dec. 1985.

5. R. A. Fleming and D. I. Livingston, *Tire Reinforcement and Tire Performance,* ASTM, Philadelphia, 1979, p. 332.

6. D. C. Prevorsek, et al., *Rubber Chem. Technol.,* **44**(1), 271–293 (1971).

7. S. K. Clark, Ed., *Mechanics of Pneumatic Tires,* NBS Monograph 122, Natl. Bur. Stand., Gaithersburg, MD, 1971, pp. 307–398, pp. 446–471.

8. J. Matsui and T. Takeyama, *Rubber Chem. Technol.,* **42,** 194 (1969).

9. Reference 8, p. 198

10. M. M. Girgis, U.S. Pat. 4,476,191 (1984).

11. M. M. Girgis, U.S. Pat. 4,434,208 (1984).

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