Viscoelastic Properties of Tire Cords

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Synopsis

The viscoelastic properties of commercial rayon, nylon 66, and poly(ethylene terephthalate) tire cords have been investigated by dynamic mechanical techniques using the Vibron viscoelastometer DDV-II. The effect of temperature, humidity, and geometric structure on the viscoelastic response has been determined for the tire cord assemblies. Subsequently, the underlying mechanisms and the polymer and fiber structural factors which influence them are discussed. Also, the consequences of the cord properties on tire hysteretic characteristics are discussed. This enables tires to be designed to meet specific service requirements. Characterization of materials in this way is becoming more important, particularly as the performance demands on tires become more stringent.

INTRODUCTION

Organic fibers have dominated the pneumatic tire reinforcement field for many years. In general, these fibers were engineered for textile applications and subsequently developed for pneumatic tire usage. The most useful textile fibers are linear high polymers with a moderate degree of crystallinity and a high degree of molecular orientation. Both in processing and service, textile composites have to withstand a wide variety of stresses and strains[1] over wide ranges of temperature and humidity. As the performance demands on tires become increasingly more stringent, there is a need for the development of other reinforcement materials[2,3] such as steel and fiber glass. However, other than physical requirements,[4] there are other factors[5] which influence the market for tires and tire fibers.

As previously discussed by the author,[6] the theory of linear viscoelasticity has been extensively studied in relation to amorphous polymers, and more recently to semicrystalline polymers.[7,8] Most investigations of viscoelastic behavior of fibers have been carried out by either stress relaxation or creep measurements.

Even though techniques for making dynamic mechanical measurements have been well established, few publications have appeared in the literature on their application to fiber assemblies. Butterworth et al.[9] have studied the mechanisms of tire cords embedded in an elastomer composite, under dynamic conditions comparable to those experienced in actual tires. Zorowski et al.[10] established the mechanism of propagation of high-frequency small-amplitude strain waves in continuous filament twisted yarns of dacron, nylon, acetate, and viscose. These experiments using a sonic-velocity pulse-propagation technique concluded

that viscous dissipation was negligible. This work was extended by Zorowski et al.[11] to include low-frequency deformations where dissipation processes could no longer be neglected. Meredith[12] has presented some dynamic mechanical properties of various types of fiber assemblies under different experimental conditions such as changing applied static strain. The relationship between the viscoelastic properties and dye diffusion behavior of various fibers has enabled the mechanisms involved to be ascertained.[13–15] More recently, Murayama et al.[16] have carried out dynamic loss energy measurements of tire cord adhesion to rubber.

This paper presents the results of a study of the viscoelastic properties of three different types of tire cord. The effect of temperature, humidity, and geometric structure on the viscoelastic response of the tire cord assemblies is investigated. Such a study has been shown by the author[17] to be pertinent to the energy losses experienced by pneumatic tire carcasses and to be essential to tire cord characterization to meet tire performance requirements.

EXPERIMENTAL

The effective viscoelastic properties of continuous-filament tire cords of various materials were determined as a function of temperature, humidity, and changes in geometric structure.

Viscoelastic properties of the various tire cords were determined on a direct-reading dynamic viscoelastometer, the Rheovibron Model DDV-II,[6] developed by the Toyo Measuring Instrument Co. Ltd. The Vibron applies a sinusoidal tensile strain to the sample and uses two transducers to determine both the complex dynamic modulus E^* and tan δ. From these parameters, the storage modulus E' and the loss modulus E'' can be calculated.

The dynamic and static strains applied to the samples were comparable to those experienced by tire cords in service.[6] The temperature range over which the properties were determined was 20°C to 160°C, at a frequency of 110 Hz which was considered appropriate for the tests. All tire cords were adhesive-dipped with RFL which facilitated testing and was considered more appropriate to the study. The study was divided into two parts, as detailed in the following.

Effect of Humidity

The tire cords used in the investigation of the effect of temperature and humidity on the viscoelastic properties are tabulated in Table I.

Study of the viscoelastic properties of the tire cords was carried out in an atmosphere containing 2.3 mg of water per liter of air, and also in an atmosphere of 9.4 mg/l. moisture content. These values for moisture content of air are equivalent to a relative humidity of 10% and 45%, respectively, at a temperature

TABLE I
Characteristics of the Various Tire Cords Used

Cord	Tex
Viscose rayon	122/2
Nylon 66	93/2
Poly(ethylene terephthalate) (PET)	144/3

TABLE II
Physical Characteristics of the Viscose Rayon Tire Cords

Cord sample	Tex	Twist per m	
		S	Z
1	183/3	276	276
2	183/2	472	472
3	122/2	531	531

of 24°C. The moisture content of the atmosphere was obtained by passing dry air through a saturated solution of an appropriate salt at 24°C and circulating it through the chamber containing the sample.

The moisture content of the tire cords when heated in atmospheres of differing moisture content was investigated by means of the Perkin-Elmer TGS-1 thermobalance with a heating rate of 0.07°C/sec. The moisture contents of the atmospheres used were the same as those used for the dynamic measurements above. The moisture content of the atmosphere was calculated by passing the air that is circulated through the sample chamber, through magnesium perchlorate and measuring the weight change due to moisture pickup. In all cases, samples were dried prior to testing and then placed in an atmosphere of the specified humidity and allowed to approach equilibrium from the dry side.

Effect of Geometric Structure

To determine the effect of changes in the geometric structure of the tire cords, only rayon was used. The characteristics of the cords used in the investigation are tabulated in Table II.

RESULTS

Effect of Temperature

Figures 1 and 2 show E', E'', and tan δ as functions of temperature for the three types of tire cord with an atmosphere containing 9.4 mg/l. of water. From Figure 1, the storage modulus for rayon is 40% higher than PET, and 60% higher than nylon at 25°C. At 150°C, E' for rayon has dropped by 40%, while PET remains virtually unchanged until about 135°C, where it decreases rapidly. Nylon decreases the most over the temperature range, with two inflections.

The loss modulus E'', shown in Figure 1, is a measure of the energy dissipated per cycle.[17] It is considerably lower for nylon than for the other two cords, over the temperature range investigated. PET is 50% lower than rayon for moderate temperatures and rises rapidly to a maximum, in excess of that of rayon, at a temperature of 135°C. The loss modulus for rayon remains fairly constant, and nylon has two moderate peaks at 50°C and 120°C.

In Figure 2, the loss factor follows a similar trend to that of the loss modulus. However, the maximum values of the loss factors for nylon and PET are more significant and are displaced to higher temperatures.

Influence of Moisture Content

With an atmosphere of 2.3 mg/l., some of the viscoelastic properties as a function of temperature change slightly (Fig. 3) when compared to those at 9.4 mg/l.
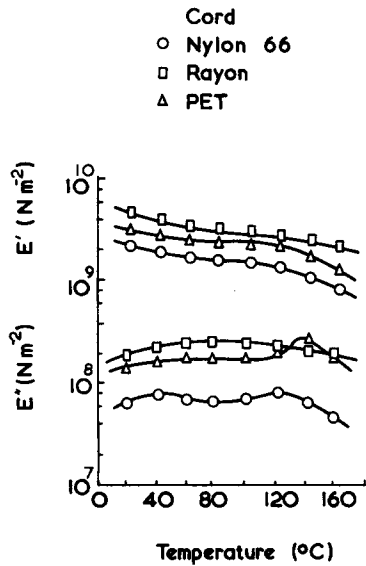
Cord
O Nylon 66
□ Rayon
△ PET

Fig. 1. Storage modulus E' and loss modulus E'' as a function of temperature for the various tire cords in an atmosphere of 9.4 mg/l. water content.
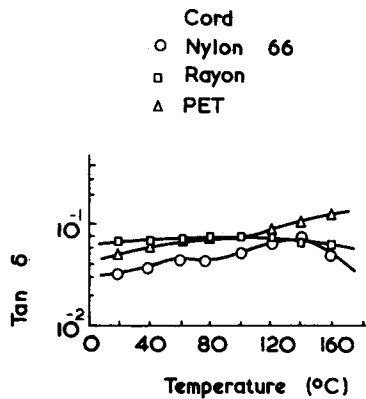
Cord
O Nylon 66
□ Rayon
△ PET

Fig. 2. Tan δ as a function of temperature for the various tire cords in an atmosphere of 9.4 mg/l. water content.

atmosphere. The general shape and value of E' for nylon and PET shows no appreciable change from that at 9.4 mg/l. atmosphere; on the other hand, the shape of the curve for rayon has altered and the values of E' are lower.

The loss modulus E'' is affected slightly by the change in moisture content. The reduced moisture content results in a consistently higher value of E'' for nylon. However, for rayon, a reduced moisture content gives a consistently lower value for E''. In the case of PET, E'' values are slightly less up to 120°C with the lower moisture content, but similar above this temperature. In general, these curves were displaced to higher temperatures by approximately 2°C and 8°C for PET and nylon, respectively, with decreasing humidity of the environment. It should be noted that an experimental frequency of 110 Hz causes an upward shift of the transitions of approximately 15°C relative to static measurements.

TABLE III
Percentage Moisture Content of the Fibers at the Two Experimental Humidities

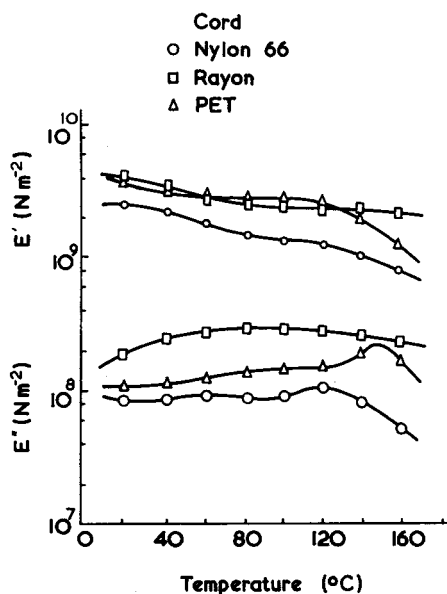| Cord	Water content, %	
	2.3 mg/l.	9.4 mg/l.
PET	0.3	0.5
Nylon 66	1.0	2.5
Rayon	4.5	9.2

Fig. 3. Storage modulus E' and loss modulus E'' as a function of temperature for the various tire cords in an atmosphere of 2.3 mg/l. water content.

From the work carried out with the thermobalance, it was found that most of the moisture of absorption had been driven off at a temperature of 90°C for PET, 110°C for nylon, and 130°C for rayon. The moisture content of each tire cord for the two humidities, at 25°C, is given in Table III. The water content is given in terms of percentage by weight.

Effect of Geometric Structure

The effect of twist on the storage and loss moduli of rayon tire cord is shown in Figure 4. It can be seen that as the degree of twist increases, E' goes through a minimum value at about 394 tpm. The magnitude of E' at room temperature is slightly larger for small degrees of twist than for high degrees of twist. However, E' falls rapidly with increasing temperature at low twist, but is hardly affected at high values of twist. Hence, as the temperature is increased, the minimum value of E' is displaced to lower degrees of twist.

As the degree of twist increases, the loss modulus generally decreases, as shown in Figure 4. The magnitude of E'' is virtually independent of the degree of twist up to about 378 tpm. Further increase in the degree of twist increases the loss modulus rapidly. Similarly to the storage modulus, E'' becomes independent of temperature at higher degrees of twist.
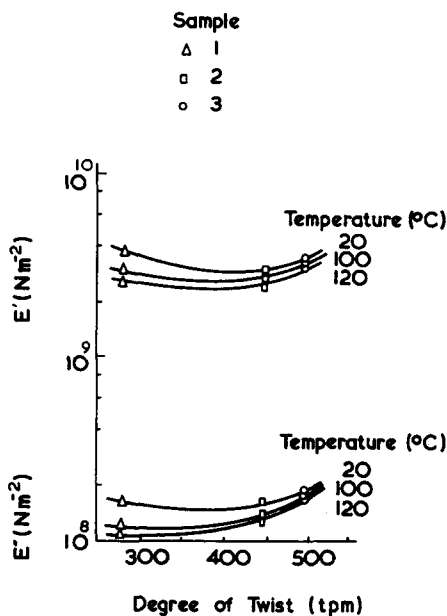
Sample

△   1
□   2
○   3

Fig. 4. Storage modulus E' and loss modulus E'' as a function of the degree of twist at various temperatures for viscose rayon tire cord.

Sample

△   1
□   2
○   3

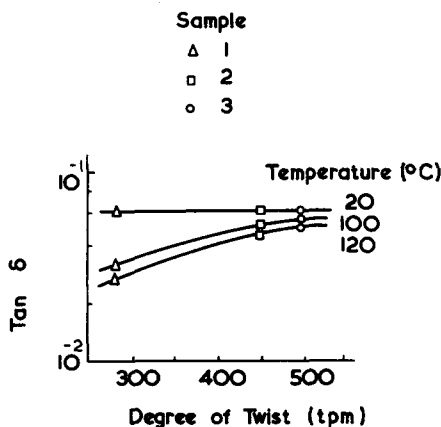Fig. 5. Tan δ as a function of the degree of twist at various temperatures for viscose rayon tire cord.

Figure 5, showing the loss factor tan δ, is very interesting. At room temperature, tan δ is independent of the degree of twist, but becomes more sensitive to it as the temperature increases, particularly at low degrees of twist. As the degree of twist increases, the isothermal curves asymptotically approach a limiting value of 0.062, which corresponds to tan δ at room temperature.

DISCUSSION

Even though the cross-sectional area of some of the cords whose properties were compared was not the same, these differences were taken into account by the modulus calculation.

As the temperature increased for nylon, E'' was seen to pass through two moderate peaks, one at 50°C and the other at 120°C. The transition at 50°C has been attributed to the motion of the chain segments in the amorphous phase of the semicrystalline fiber. At temperatures between this second-order transition temperature and 120°C, only the chain segments in the amorphous phase are mobile, while those in the crystalline phase remain immobile and exert a reinforcing action on the molecular system. This second-order transition at 50°C corresponds to the T_g of the noncrystalline polymer.[18] The transition occurring at 120°C results from torsional and rotational motion in the crystalline regions. The final sharp decrease in the modulus at temperatures above 120°C indicates the onset of melting of the crystalline phase.

Increasing the degree of crystallinity of a semicrystalline polymer results in a decrease in the magnitude of E'' peak for the second-order transition temperature, causing it to eventually become difficult to locate. The presence of the peak at 50°C in oriented nylon indicates the presence of undrawn or amorphous material, thus illustrating the semicrystalline nature of nylon tire cord. However, the clarity of maxima in E'' may be obscured by other mechanisms of energy loss due to the interaction between the fiber filaments, which will be discussed in more detail later.

Over the temperature range investigated, only the transition due to the molecular motion occurring in the crystalline phase was observed for the PET cord. The loss modulus for rayon did not appreciably change with temperature, but formed a gentle maximum peak extending over the entire experimental temperature range of Figure 1. This most probably corresponds with the reported[12] minor peak for rayon at approximately 90°C, as distinct from the normal T_g.

Determination of the molecular mechanisms that govern the physical properties of fiber systems as a function of temperature is complicated by the thermal shrinkage experienced by drawn fibers. Ribnick has shown that thermal shrinkage of nylon 66[19] and PET[20] is due to a recrystallization process. The mechanism by which this recrystallization proceeds[21] is that the polymer chains contract from the extended configuration at relatively low temperatures into folded chains at high temperatures. These folded chains, corresponding to the thermal shrinkage of the fibers, form into new folded crystallites.[22] Measurements of the tensile strength and thermal shrinkage of rayon tire cords[23] have indicated that there is a decrease in hydrogen bonding in the crystalline region. These molecular mechanisms would modify the response of the polymeric system and influence the viscoelastic properties, which can be inferred from the results presented in Figures 1 and 2.

Influence of Moisture

Water absorbed by fibers can influence the viscoelastic properties of such fibers. As can be seen from Figure 3, where the curves tended to be displaced to low temperatures with increasing water content, in this context water acts as a plasticizer. The way in which water influences the segmental mobility of fibers has been examined by Lynch et al.[24] Due to the small physical size and strong polarizability of water molecules, they have the ability to penetrate the polymeric system and to modify the internal electric fields within the fiber. In this way, the response of the molecular system is perturbed. Mechanisms by which

water absorption takes place in fibers have been adequately discussed in the literature.[25]

The tabulated values of Table III for the equilibrium moisture content of the fibers is in good agreement with published results[15,26] when they are reduced to the same relative humidity levels.

Meredith[12] has shown that for a particular temperature, rayon and nylon go through a maximum value in E'' as the relative humidity increases. As shown in Table III, the water absorption was less for PET, and hence the loss modulus was little affected. The E'' peaks for PET and nylon were found to shift at the approximate rate of 10°C/% water and 5°C/% water, respectively. While the rate determined for the temperature shift of PET is in agreement with that of Dumbleton et al.,[15] the rate for nylon was only $1/3$ of that reported by Howard et al.[27]

When the temperature had reached the value determined by the thermo-balance, where all the "free" water had been evaporated from the fiber, the visco-elastic properties for PET were independent of the relative humidity of the environment. This indicates that the moisture history does not significantly affect the viscoelastic response of the fiber at elevated temperatures. Because of this, recrystallization does not seem to be adversely affected by the water content. The relatively high temperature required to remove the moisture from viscose rayon was most probably due to the high affinity of the hydroxyl groups for water.

Effect of Geometric Structure

The effect of geometric structure on the dynamic mechanical properties of rayon have been described in the results section. In considering what mechanisms are operating, it is important to note that the Vibron viscoelastometer applies a dynamic tensile strain to the sample, thus giving rise to the following considerations.

For twisted continuous filament yarns, small strain waves are propagated as one-dimensional longitudinal plane waves. As the waves propagate through the viscoelastic material, in addition to internal viscous damping, energy is also dissipated owing to the physical geometry of the fiber assembly. The mechanism by which this energy dissipation takes place is by Coulomb friction[11] between filaments which move relative to each other. This relative motion is due to the variations in the local helix angle as the strain wave propagates along the yarn. The angle of the helix formed by the plies of cord assembly is a function of the degree of twist.

With the Coulomb friction mechanism operating, it would be expected that the energy dissipated in this manner would increase as the degree of twist. This phenomenon of increasing energy loss with the degree of twist is generally true, as shown in Figure 4. From the results presented in Figures 4 and 5, it is apparent that the Coulomb friction mechanism is virtually insignificant between the plies as indicated by sample 1 with three plies, when compared with the others with two plies. The large dependence of the viscoelastic properties on temperature at the low degrees of twist appears to be due to the viscoelastic properties of the polymeric system being dominant at the low degrees of twist, whereas at higher degrees of twist the Coulomb effect becomes dominant. As

the degree of twist decreases, the measured viscoelastic properties approach those of the polymeric system.

This mechanism of Coulomb friction most probably contributed to the diffusion of the transition peaks observed in Figures 1 and 2. Estimating the degree of crystallinity of fibers from such results is then difficult, but relative comparisons are possible for samples tested under identical conditions.

CONCLUSIONS

From a previous analysis presented by the author,[17] the energy loss experienced by the cord system in the carcass of a passenger tire is proportional to E''. This makes the choice of tire cord used depend, among other things, on the magnitude of E''. The loss modulus was found to be least for nylon, followed by PET, and greatest for rayon.

The effect of different reinforcing cord material in the carcass has been further investigated[28] by determining the mechanical mobility of tires on the University of Birmingham's test rig.[29] In the case of rayon and nylon, little difference was observed in the flexural resonant frequencies for the two types of tires. However, as expected from the viscoelastic measurements, the rayon tire provides more damping than nylon.

When a tire cord becomes hot, the storage modulus decreases and the rate of creep increases. These combined factors give rise to the phenomenon known as "flat spotting."[30] This manifests itself as a thumping sensation which the occupants of a vehicle experience when it is initially driven after standing for a length of time following a long run. This phenomenon can be reduced if the peak in E'' can be displaced to higher temperatures. Such is the case when PET tire cords are used in preference to nylon, as they do not experience "flat spotting." However, with later developments of nylon tire cord, the phenomenon of "flat spotting" with nylon is now not as prominent as it was in the past.

The use of PET as a tire reinforcement has become established in passenger tires, but has not been used to any significant extent in truck tires. From the character of the E'' curve for PET, at moderate speeds the heat generation would be tolerable, and less than for rayon. But at high speed, and hence higher temperatures, PET cord generates more heat, as indicated in the rapid rise in E'' in the range of 110° to 135°C, than the other two cords studied. At these higher temperatures, PET fibers suffer from degradation and loss of strength. This is also the reason why PET has been slow to penetrate the truck tire market, as these run at inherently higher temperatures.

Hence, the temperature at which the loss modulus is a maximum is an important property of PET cord. Thus, the heat generation characteristics of PET cord could be significantly improved if the magnitude of the E'' maximum could be reduced or displaced significantly to higher temperatures.

Atmospheric humidity affects the cords in different ways, with greatest effect being at lower temperatures, as would be expected. A higher moisture content results in higher E'' for rayon, and lower for nylon and PET under certain conditions. From the results presented, it appears that in the cases of rayon and nylon, there would be no adverse effect if the cords experienced a moderate moisture pickup during processing.

Unfortunately, changes in the geometric structure for increased storage modulus were also accompanied by an increase in loss modulus. Hence, determination of the geometric structure most suitable for a particular tire design would have to be a compromise between the desired properties. At room temperature, three-ply cords have a high storage modulus and a relatively low loss modulus, however, the storage modulus falls rapidly. Cords consisting of two plies with a high degree of twist are less dependent on temperature and more stable for tire design.

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