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Dynamic Loss Energy Measurement of Tire Cord Adhesion to Rubber

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Synopsis

The dynamic loss energy measurements for characterizing adhesion using Vibron DDV-II have been applied to the tire cord–rubber composite system, and the relationships between these dynamic measurements and static adhesion test (H-block pull test and strip peeling test) were also investigated. Tested samples were the commercial nylon 66 tire cord and poly(ethylene terephthalate) tire cord with two adhesive systems. The degree of adhesion (adhesion factor) was obtained as the energy dissipation at the tire cord-to-rubber interface as measured by dynamic testing. It was shown that energy dissipation is increased at the filament–matrix interface when the composite is subjected to continuous cyclic loading if a condition of poor adhesion exists. The test was based upon the separation of the total energy dissipation in a composite under cyclic loading into a portion associated with viscous properties of the constituent materials and a second portion resulting from the lack of perfect bonding in the interfacial regions. The strip peeling measurement of adhesion exhibited an approximately linear correlation with the dynamic loss energy measurement of adhesion. The dynamic energy loss measurement is suggested as a potential source of information on the rheological characteristics of the interfacial region of bonding.

INTRODUCTION

In a previous study[1] of the bonding characterization in reinforced composites it was found that energy is dissipated at the filament-matrix interface when the composite is subjected to continuous cyclic loading if a condition of poor adhesion exists. Also a theory has been developed which permits the separation of the total energy dissipation in a composite system under cyclic loading into a portion associated with the viscous properties of the constituent materials themselves and that resulting from the lack of perfect adhesion at the filament–matrix interface. This provides a mechanism for quantitatively characterizing degree of adhesion by means of a dynamic test using instruments like the Vibron DDV-II on composite systems of a variety of materials.

Since, theoretically, this dynamic loss energy measurement for characterizing adhesion should also apply to other composite systems, the tire cord–rubber system was studied by this procedure, and the relationships between these dynamic measurements and static adhesion test (H-block pull test[2] and strip peeling test[3]) were also investigated.

EXPERIMENTAL

Dynamic Adhesion Test by Loss Energy Measurements

The dynamic viscoelastometer (Vibron) built by Toyo Measuring Instrument Company was used. The Vibron applies a sinusoidal tensile strain to one end of a sample and measures the stress response at the other end. The instrument uses two transducers to read directly the absolute dynamic modulus $|E^*|$ (the ratio of maximum stress amplitude to maximum strain amplitude) and the phase angle δ between stress and strain. From these two quantities, the real part E' and imaginary part E'' of the complex dynamic tensile modulus E^* can be calculated.

The principle of this direct reading method and the instruments are described in detail by Takayanagi.[4] This principle is extended to the dynamic mechanical analysis on the bicomponent system for determining the energy dissipation ($\tan \delta$) due to poor adhesion. The details of these analyses are given by Zorowski and Murayama,[1] who obtain the following relations:

$$\tan \delta_{\text{adh}} = \tan \delta_{\text{exp}} - \tan \delta_s \qquad (1)$$

$$\tan \delta_s = \frac{\tan \delta_f E_f V_f + \tan \delta_m E_m V_m}{E_m V_m + E_f V_f} \qquad (2)$$

where $\tan \delta_{\text{adh}}$ = internal energy dissipation due to poor adhesion, $\tan \delta_{\text{exp}}$ = measured effective loss tangent for composite (cord–rubber), $\tan \delta_s$ = effective loss tangent for composite with perfect adhesion, $\tan \delta_f$ = filament (cord) loss tangent, E_f = filament modulus, V_f = filament volume fraction, $\tan \delta_m$ = matrix (rubber) loss tangent, E_m = matrix modulus, and V_m = matrix volume fraction. (The moduli E_f and E_m refer to the storage (E') part of the dynamic response.[1])

By measuring the total system energy dissipation in terms of $\tan \delta$ and knowing $\tan \delta$ and the dynamic moduli of the components as well as the volume fraction composition, the dissipation due to the poor interface adhesion can be determined. Dynamic measurements of the internal energy dissipation of the adhesive-dipped tire cords and tire cord–rubber blocks, 0.5 × 5 cm and about 0.1 cm thick, were made at a frequency of 11 Hz with a strain amplitude of 0.5%. Samples were heated at 1°C/min in a nitrogen atmosphere under relaxed conditions. Measurements of the tensile modulus E and loss tangent $\tan \delta$ were made at 10° or 20°C increments.

Samples were allowed to equilibrate at temperature for 15 min before measurements were made.

Test Sample Preparation

In order to examine the relation between dynamic energy loss measurements and the H-block pull test or the strip peeling test, portions of H-blocks and strips were utilized in the dynamic test. The commercial tire cords were nylon 66 twisted into a two-ply, 840-denier-per-ply with 12-turns-per-inch Z-twist in singles and a 12-turns-per-inch S-twist in the ply (6 denier per filament); and poly(ethylene terephthalate) (PET) twisted into a two-ply, 1000-denier-per-ply with 12-turns-per-inch Z-twist in singles and a 12-turns-per-inch S-twist in the ply (5 denier per filament). The cord was dipped through a bath of adhesive and passed through a drying oven at 165°C and then into an electrically heated circulating hot-air oven for 1- to 3-min cures at constant length. The dry add-on of adhesive was approximately 5%.

The cured cord was tested for static adhesion at 120°C in the H-pull test as described in ASTM D-2138-67, with the exception that $^3/_{16}$ in. rather than $^1/_4$ in. of cord was pulled from rubber.[2] The peeling adhesion of 1-in. by 6-in. strips of a cord rubber composite were tested at 120°C. The construction of these strip adhesion samples was described by Brownlee.[3]

The two plies of cord are parallel, and the strips are pulled at 12 in./min at a 180° angle and the peel force averaged for a 2-in. length of peel. The plies are built with the closest possible spacing of cords. The thickness of the skim stock between plies was 15 to 20 mils.

The rubber used in the H-blocks and strips was a commercial skim stock. Mooney scorch time (5-point rise/135°C) was 13.5 min; Monsanto rheograph indicated a cure time of 20 min at 153°C. The H-block and strip pad mold surfaces were subjected to 500 lb/in.^{2} in a Pasadena hydraulic press Model Q-230 at 300°F for 25 min during vulcanization.

Pull loads listed in the tables are average values from eight H-blocks. Errors are stated as 95% confidence intervals. Peeling loads are average values from five strips from a single mold. The strip peeling loads exhibited a maximum average deviation from the mean of ± 2 lb.

The H-7 dip consisted of 82 ml of H-7 adhesive (Imperial Chemical Industries Ltd.), 50 ml of Gen-Tac Latex (General Tire & Rubber Company, poly(vinylpyridine–styrene–butadiene) latex, 41 wt-% solids), and 73 ml deionized water.

A standard RFL dip was prepared by dissolving 5.5 g of resorcinol in 116 ml water containing 0.15 g sodium hydroxide. To this solution, 8.1 g of 37 wt-% aqueous formaldehyde was added, and the solution was stirred for 5 min. This resin master solution was allowed to age for 6 hr at 75–78°F. The 133 g resin master was added to a dispersion of 122.0 g Gen-Tac and 30.0 g deionized water, and the resulting dispersion was mixed for 15 minutes. The RFL dip was used within 72 hr.

Cords used in H-blocks dipped in the H-7 adhesive were cured at 230°C for 3 min and those in the RFL adhesive, at 220°C for 1 min. The PET cords utilized in strip tests were dipped in RFL and cured at 230°C for 3 min, while the Nylon 66 cord dipped in RFL was cured at 210°C for 3 min.

Two of the PET cords used in strip testing had received surface treatments in electrical discharges to increase their adhesion to RFL. These surface treatments did not alter the bulk properties of these two cords.

The composite blocks for dynamic testing (0.5 × 5 cm and 0.1 cm thick) were cut from static test samples. The composite from the H-block sample contained a single centered cord composing 4% to 6% volume fraction of the sample. The composite from the strip sample contained 7 ends of parallel cords composing 28% to 32% volume fraction of the sample.

RESULTS AND DISCUSSION

The dynamic modulus (E_m) and the internal friction (tan δ_m) of the vulcanized skim stock rubber used for test samples are shown in Figure 1. The dynamic moduli (E_f) and loss tangent (tan δ_f) of the dipped cords (nylon 66, RFL, 210°C; and PET, H-7, 230°C) as a function of temperature at 0% R.H. are shown in Figure 2.

The internal friction of both dipped textile cords shows the α-transition peak which is connected with the so-called glass transition in which polymer chain segments acquire considerable mobility. The values of tan δ were higher than those of yarns in the temperature range 25°C to 100°C.[5,6] This difference indicates that the twist geometry and the surface coating of adhesive on the cord influenced the energy dissipation in the system. Figure 3 shows the loss tangent (tan δ_{exp}) of dipped cord–rubber samples from H-blocks as a function of temperature at 0% R.H. The internal friction of dipped nylon 66 (RFL, 220°C) or PET (RFL, 230°C) cord–rubber composites exhibit the α-transition peak. The tan δ values of these samples were higher than those of the dipped cords. These differences reflect the

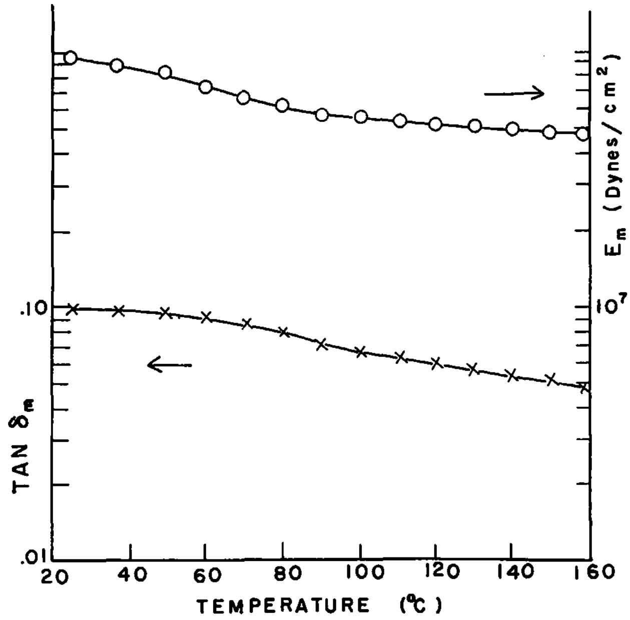

Fig. 1. Dynamic modulus (E_m) and internal friction (tan δ_m) of vulcanized skim stock rubber.

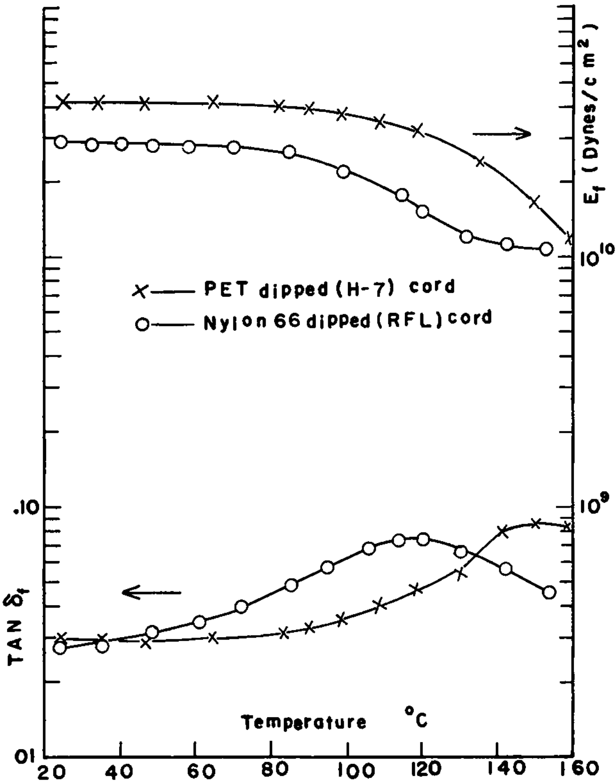

Fig. 2. Dynamic moduli (E_f) and loss tangent (tan δ_f) of nylon 66 and PET dipped cords.

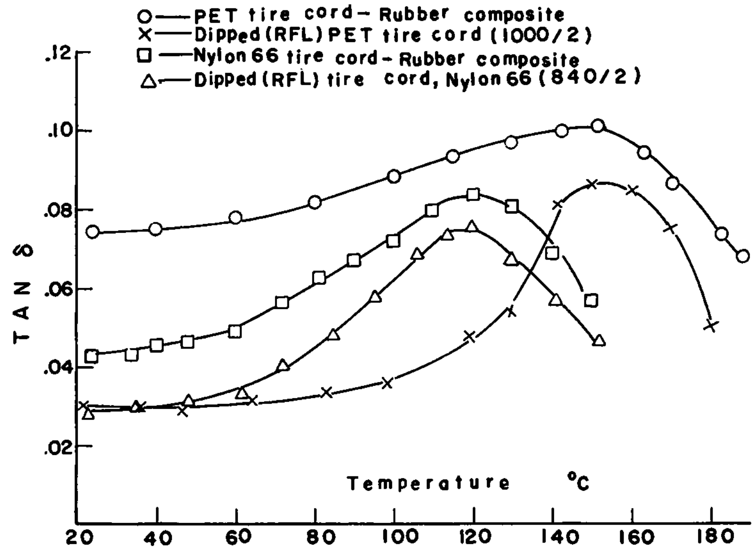

Fig. 3. Loss tangent (tan δ_{exp}) of dipped cord-rubber composites (nylon 66, PET).

TABLE I. Adhesion of Tire Cord to Rubber at Room Temperature[a]

Tire cord	Dynamic moduli, dynes/cm^2		Internal friction			Adhesion factor	H-block pull load, lb
	E_f $\times 10^{10}$	E_c $\times 10^{9}$	$\tan \delta_f$ $\times 10^{-3}$	$\tan \delta_s$ $\times 10^{-3}$	$\tan \delta_{exp}$ $\times 10^{-3}$	$\tan \delta_{adh}$ $\times 10^{-3}$	
Nylon 66 (840/2)							
No adhesive	2.15	0.99	55.0	58.5	108.7	50.2	7.8 ± 0.3
H-7 adhesive	2.26	1.23	65.0	68.1	86.3	18.2	23.6 ± 1.3
RFL adhesive	2.13	1.24	65.0	69.2	81.7	12.5	17.3 ± 1.0
PET (1000/2)							
No adhesive	4.25	1.82	25.0	27.2	84.2	57.0	9.5 ± 0.1
H-7 adhesive	4.50	2.15	33.0	36.2	74.4	38.2	21.0 ± 1.8
RFL adhesive	4.42	2.16	32.1	34.7	80.9	46.2	16.9 ± 1.0

[a] Rubber: $E_m = 9.3 \times 10^7$ dynes/cm^2; $\tan \delta_m = 0.095$; $V_f = 4\% \backsim 6\%$.

TABLE II. Dynamic Loss Energy Measurements and Strip Adhesion Test at 120°C[a]

Tire cord	Dynamic moduli, dynes/cm^2		Internal friction			Adhesion factor	Strip adhesion peeling load, lb
	E_f $\times 10^{10}$	E_c $\times 10^{10}$	$\tan \delta_f$ $\times 10^{-3}$	$\tan \delta_s$ $\times 10^{-3}$	$\tan \delta_{exp}$ $\times 10^{-3}$	$\tan \delta_{adh}$ $\times 10^{-3}$	
Nylon 66 (840/2)	2.50	0.75	65.2	58.6	77.1	18.5	18.3
PET (1000/2) (untreated)	3.82	1.23	43.3	43.6	98.6	55.0	3.0
PET (1000/2) (surface treatment I)	4.62.	1.05	30.2	31.0	61.1	30.1	17.5
PET (1000/2) (surface treatment II)	4.23	1.18	40.5	41.4	80.1	38.7	11.2

[a] Rubber: $E_m = 5.4 \times 10^7$ dynes/cm^2; $\tan \delta_m = 0.60$; $V_f = 28\% \sim 32\%$.

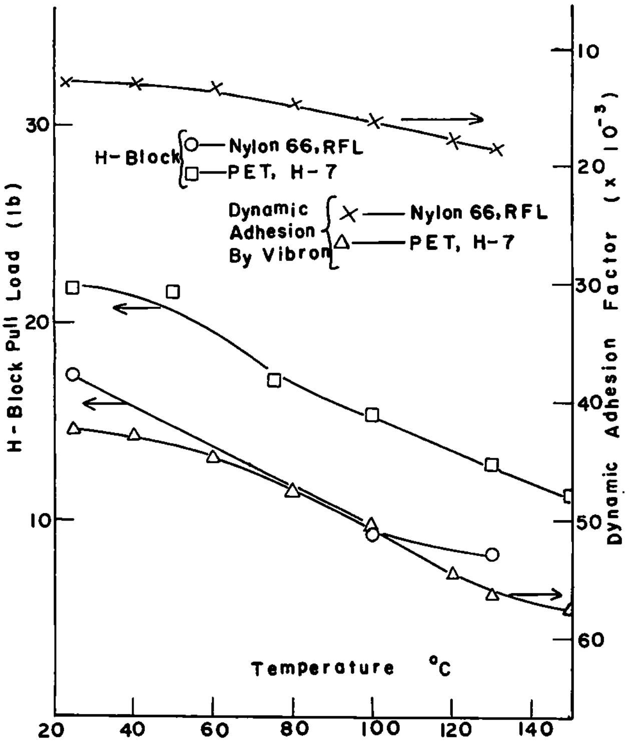

Fig. 4. Adhesion factor (tan δ_{adh}) and H-block pull load of nylon 66 and PET cord–rubber composites as functions of temperature.

energy dissipation of rubber and the degree of adhesion. The measured values of the system damping (dipped cord–rubber), tan δ_{exp}, for these samples at room temperature are listed in Table I along with the system dynamic modulus, E_c; moduli of dipped cord, E_f; loss tangent of dipped cord, tan δ_f; energy dissipation with perfect adhesion, tan δ_s; and interface dissipation due to lack of perfect adhesion, tan δ_{adh}.

The results of the H-block pull test are listed in Table I. The adhesion factors (tan δ_{adh}) of nylon 66 and PET tire cords without adhesives were very high (50.2 ~ 57.0$\times 10^{-3}$) and pull loads of these samples were low (7.8 ~ 9.5 lb). These higher values of tan δ_{adh} are associated with the case of bonding of cord to rubber without an adhesive.

It should be noted that for the nylon 66 and PET cords bound to rubber by RFL, the H-block pull loads were very similar: 17.3 and 16.9 lb, respectively. However, the tan δ_{adh} value for the nylon sample was much smaller than the tan δ_{adh} value for the PET sample. This difference may be related to the unsatisfactory performance of RFL adhesive in PET-reinforced tire building.[7] The static H-block and strip test may not be particularly sensitive to the rheological properties of the bonded interface, while the dynamic loss energy measurement may potentially yield informa-

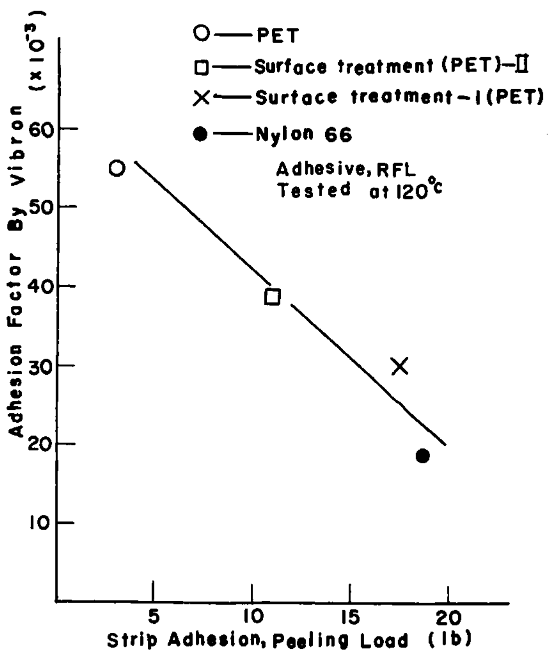

Fig. 5. Relationship between strip adhesion peeling load and adhesion factor (tan δ_{adh}) from Vibron testing.

tion on the rheological characteristics of the interfacial region of bonding. Kaelble has proposed that the bonding state of an adhesive can be rheologically distinguished from the holding state.[8]

In Figure 4, the similar response of adhesion factor (tan δ_{adh}) and H-block pull load of nylon 66 and PET cord–rubber composites to temperature is shown. The degree of adhesion was reduced with increasing temperature to similar extents in both measurements. There appears to be a reasonable correlation between the two tests.

The peeling loads of strip adhesion test and dynamic mechanical properties of four different tire cords and cord–rubber composites are summarized in Table II. These properties were measured at 120°C. From these results, the energy dissipation at the tire cord-to-rubber interface (adhesion factor) was obtained and listed in Table II. Figure 5 illustrates the relationship of strip peeling load to the adhesion factor from Vibron tests. As expected, samples with higher peeling loads show lower values of energy dissipation at the interface (tan δ_{adh}). These results indicate an approximately linear correlation between the strip peeling measurement and dynamic loss energy measurement of adhesion, and illustrate the improvement of adhesion of PET to rubber with RFL obtainable by surface modification of the PET.

It has been recognized that static measurements of adhesion between dipped tire cord and rubber may not reflect the performance of the adhesive system under dynamic testing conditions. Although an adhesive may yield a high initial strip peeling load, after dynamic testing under conditions simulating tire running, the bonding of this adhesive may deteriorate more rapidly than that of an adhesive with a lower initial strip peeling load. The separation of the total energy dissipation in a composite under cyclic loading into a portion associated with the viscous properties of the constituent materials and a second portion resulting from lack of perfect bonding in the filament-matrix interface may potentially be used to examine the performance of adhesives under dynamic conditions and the relationship between interfacial rheology and performance of adhesives under dynamic conditions.

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