Evaluation of Cord/Rubber Adhesion by a New Fatigue Test Method

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ABSTRACT: Polymer adhesion and its evaluation are important from academic and industrial points of view. Today cords are used to reinforce rubber in various products. Cord–rubber adhesion can be evaluated using static and dynamic methods. The static methods are commonly used for qualification of raw materials. These methods are not suitable for prediction of durability of the cord/rubber system in real conditions. The dynamic adhesion tests (e.g., fatigue method) involve some important parameters to simulate the real conditions of cord/rubber composite usage. So they produce reliable results in comparison with static adhesion results. Increase in temperature of cord/rubber system occurs during utilization of product. Adhesion usually decreases with increasing temperature. So the static adhesion test (e.g., H-pull test) results that are measured in the ambient temperature (23 ± 2°C) cannot be considered as the composite's performance in the utilization condition. Although heat build up occurs in the test samples during the fatigue test procedure, but this is not enough to illustrate the decreasing effect of the increased temperature on the results. The authors produced a heat chamber to improve the dynamic test. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2488–2494, 2006

Key words: fatigue; cord/rubber interfacial interactions; RFL adhesive

INTRODUCTION

Today, cords are used to reinforce various rubber products like tires.[1] Interfacial adhesion strength between the cord and the rubber matrix is of major importance in durability and performance of the tire.[2,3] Thus the final properties of complex polymer systems (e.g., polymer blends and composites) depend on the strength of polymer/polymer and polymer/reinforcement interfaces.[4]

Several types of the cords have been used in tires as reinforcement, such as rayon, nylon 6 and 66, and polyester. Because of the vast use of poly(ethylene terephthalate) (PET) cords in passenger tires, many researches concentrate their interests to increase PET/rubber adhesion.

To improve PET/rubber adhesion, an adhesive usually is used on the PET. The cord and rubber reactive groups and surface properties are different, so to increase the interfacial bonding, following materials can be used:

1. materials which readily react with the cord or have affinity to it
2. materials which display high reactivity to the rubber or are highly compatible with it.[5–15]

In 1935, resorcinol formaldehyde latex (RFL) was found as a very good choice to increase the adhesion between the above-mentioned systems. The resin functional groups bond to the cord (hydrogen bonds) and functional groups of the latex part (styrene–butadiene–vinyl pyridine) bond chemically to the rubber. This is schematically shown in Figure 1.

To improve the interfacial bonding of this kind of systems, the adhesion strength must be primarily evaluated. Different test methods, static or dynamic, are used for adhesion evaluation. The static and quasistatic tests, such as the H-pull (H-adhesion) test, peel and wedge-cleavage test, are not suitable to predict the durability of the system in the real conditions. The H-pull test is commonly used to determine the cord/rubber adhesion but the results are not accurate and are not reliable for evaluation of cord/rubber performance in tires.[16] This test is used in research studies and industries for material selection.

Many authors have reported the evaluation of adhesion between the cord and rubber in the static condition.[4–15] A few numbers of researchers have evaluated adhesion at dynamic condition.[16] In the dynamic test (e.g., fatigue test), adhesion is affected by some factors.

Some of the important parameters that have negative effect on the interfacial adhesion are: the temperature, humidity, oxygen, and ozone.[1]

In the present study, the static and dynamic adhesions of the cord/rubber system were evaluated in a wide temperature range, to simulate the running of tire.

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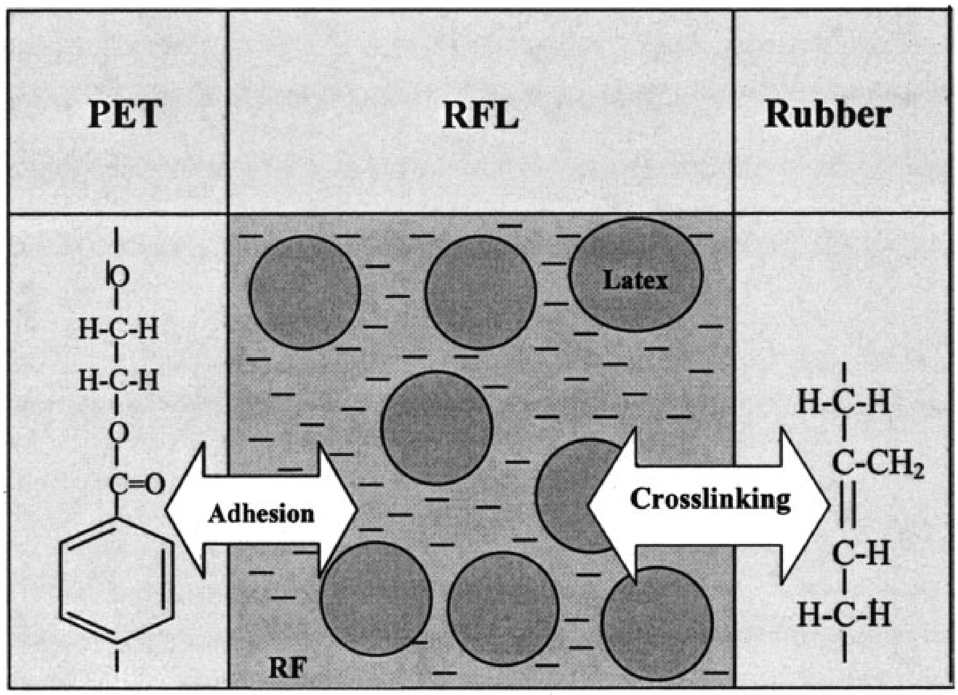

Figure 1 Interfacial interaction between PET-cord, RFL, and rubber.

EXPERIMENTAL

Raw materials

A NR/SBR rubber compound was prepared and its composition has been shown in Table I. It was used in all adhesion tests.[17,18]

RFL coated N6, N66, and PET cords (from Iranian Kian Kordsa Co.) were used in the static and dynamic tests.

Test apparatus

Static adhesion (tensile strength) was evaluated by a Monsanto 500 tester, at an elongation rate of 120 mm/min. The maximum force per area unit (N/m^2) required to remove the cord from rubber was evaluated at different temperatures.

Dynamic adhesion was evaluated by Monsanto fatigue tester.

TABLE I
Rubber Composition[a]

Compound	phr
NR (standard Malaysian rubber)	45
SBR	55
ZnO	5
Stearic acid	1.5
Carbon black 330	35
Carbon black 550	35
Antioxidant (4010)	3
Oil (aromatic oil 840)	15
TMTD (tetramethyl thiuram disulfide)	0.7
MBT (2-mercapto benzo thiazole)	2.2
S (sulfur)	1.45
Total	198.85

[a] Vulcanizing temperature, 150°C; vulcanizing time, 20 min; hardness (Shore A), 75.

Test procedure

Static adhesion

The RFL-coated cords were embedded between two rubber sheets in a die. The system was vulcanized at 150°C and 35 Mpa for about 20 min (Fig. 2). Then the H-shaped samples were cut from these cured sheets (Fig. 3). These were performed according to the ASTM D4776.[19]

To evaluate cord/rubber adhesion by Monsanto 500 apparatus, a cord grip (Fig. 4) was prepared to hold rubber part. It is fixed by lower fixtures of tensile strength tester. The upper holder of tensile strength tester holds H-sample's cord and rubber parts together. So, when it moves up, the cord is removed from lower rubber part (Fig. 5).

Also, to study the effect of temperature on cord/rubber H-adhesion, the samples were heated in an oven for 15 min, and then tested in the ambient temperature, within 15 s after going out of oven.[20]

Dynamic adhesion

The H-shaped samples, which were made with extended cord parts, were used for the fatigue evalua-

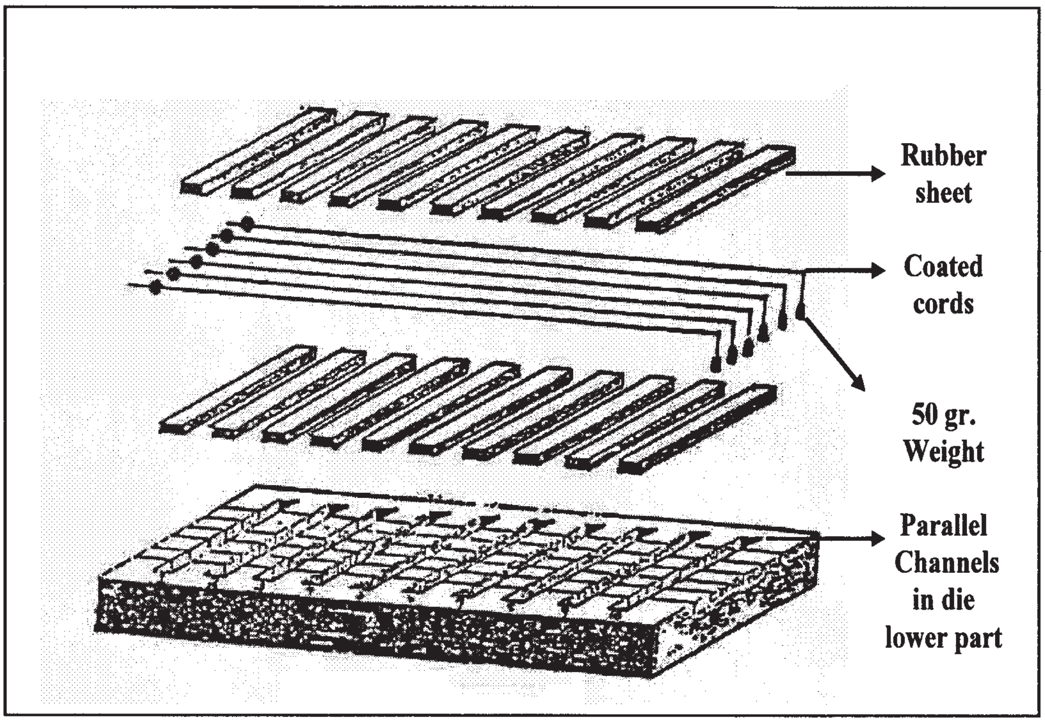

Figure 2 H-Adhesion test die and sample manufacturing (ASTM D4776).

tion. One rubbery column of test sample (Fig. 3) was fixed using the lower fixture of the fatigue tester.

The upper part was connected to a mobile clamp. It introduces a cyclic stress to cord/rubber joint (Fig. 6). The minimum distance between lower and upper clamps is equal to the cord length. When upper clamp moves upward, the spring is stretched. This movement tends to stretch the cord/rubber joint up to 1 mm, alternatively. But, it is assumed that cord is not stretched.

The cyclic stress is continued until the joint became tired (or removal of cord from rubbery matrix). The numbers of cyclic movements that cord/rubber joint undergo is proposed as fatigue resistance.[16]

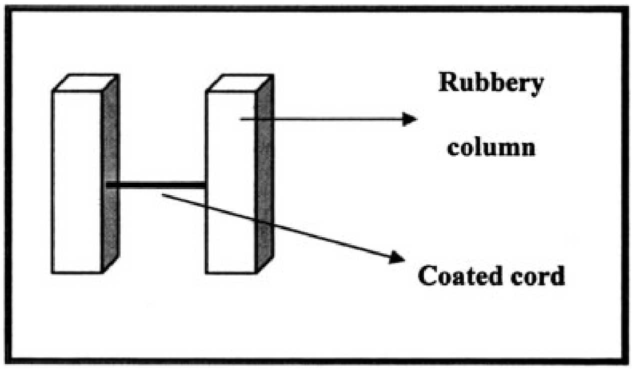

Figure 3 H-shaped sample of H-Pull test method (ASTM D4776).

To study the effect of temperature on dynamic adhesion results, a heat chamber was produced and installed on the fatigue tester (Fig. 7). The H-samples were tested in this unit in the dynamic condition at the elevated test temperatures also.

The temperature is increased in the heat chamber by heating plates. The heating plates are connected to a thermostat by a wire-type thermocouple to fix the temperature in test space.

RESULTS AND DISCUSSIONS

Static adhesion

The static adhesion of the cord/rubber systems were tested at the temperatures of 25, 50, 100, 125, and 170°C. The results are shown in Figure 8.

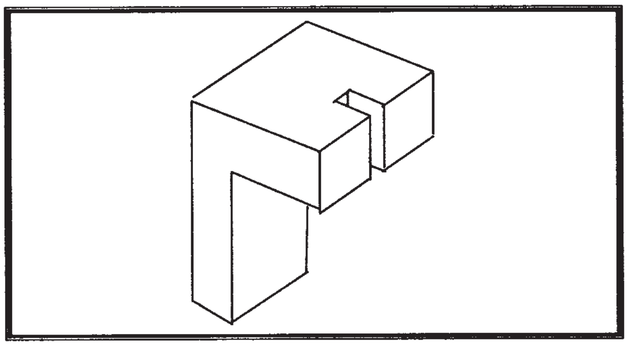

Figure 4 Schematic design of cord grip in H-adhesion test.

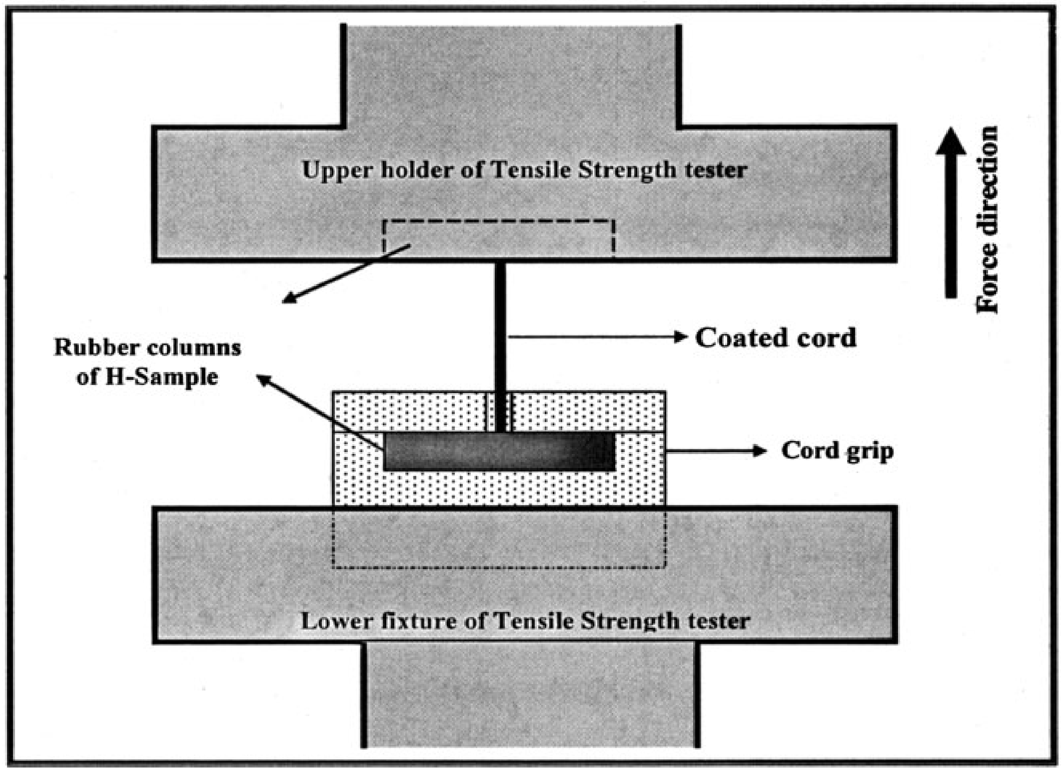

Figure 5 Evaluation of H-adhesion using the tensile strength tester.

For the PET/rubber system, the increase in temperature causes an initial sharp decrease in the adhesion (about 65%). The adhesion experiences a plateau region up to 125°C. Above 125°C, the system experiences increasing adhesion.

The decrease in adhesion is due to bond cleavage/scission at elevated temperatures. The plateau region at the temperature range of 50–100°C can be attributed to the interfacial covalent bonds that are stable at these temperature ranges.

The increase in the adhesion strength (at temperatures of 125–170°C) can be due to crosslinking of adhesive's latex and rubber. The new bonds are made at the temperatures higher than vulcanization temperature.

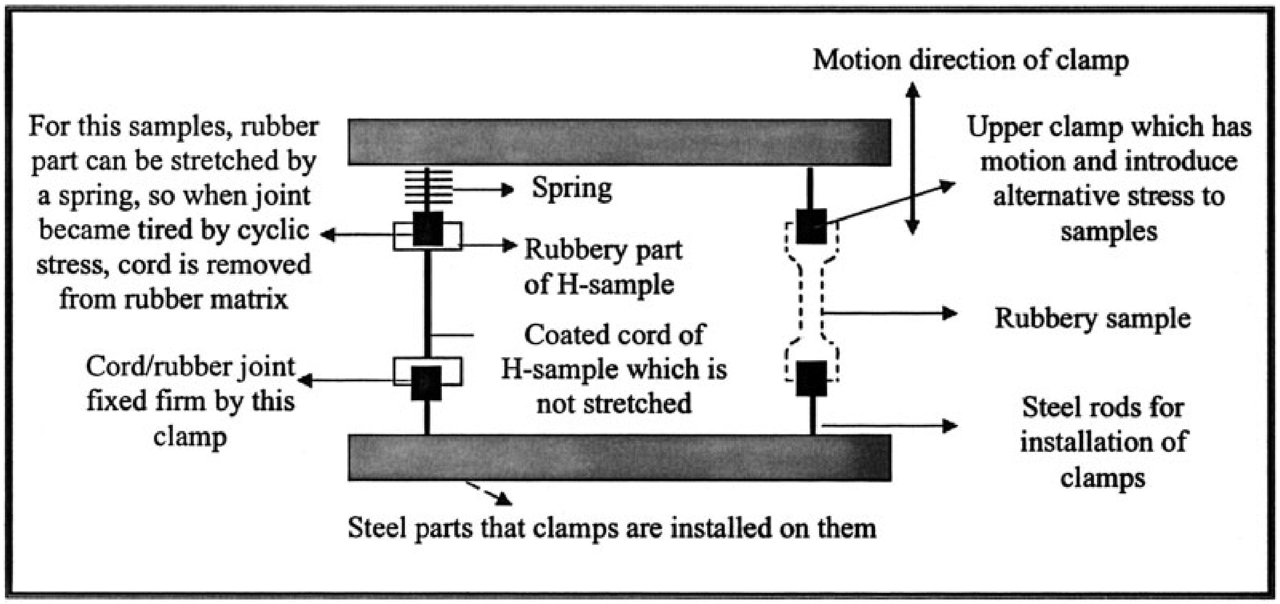

Figure 6 Schematic image of fatigue testing on H- and rubber samples in comparison with fatigue test on dumbbell samples.

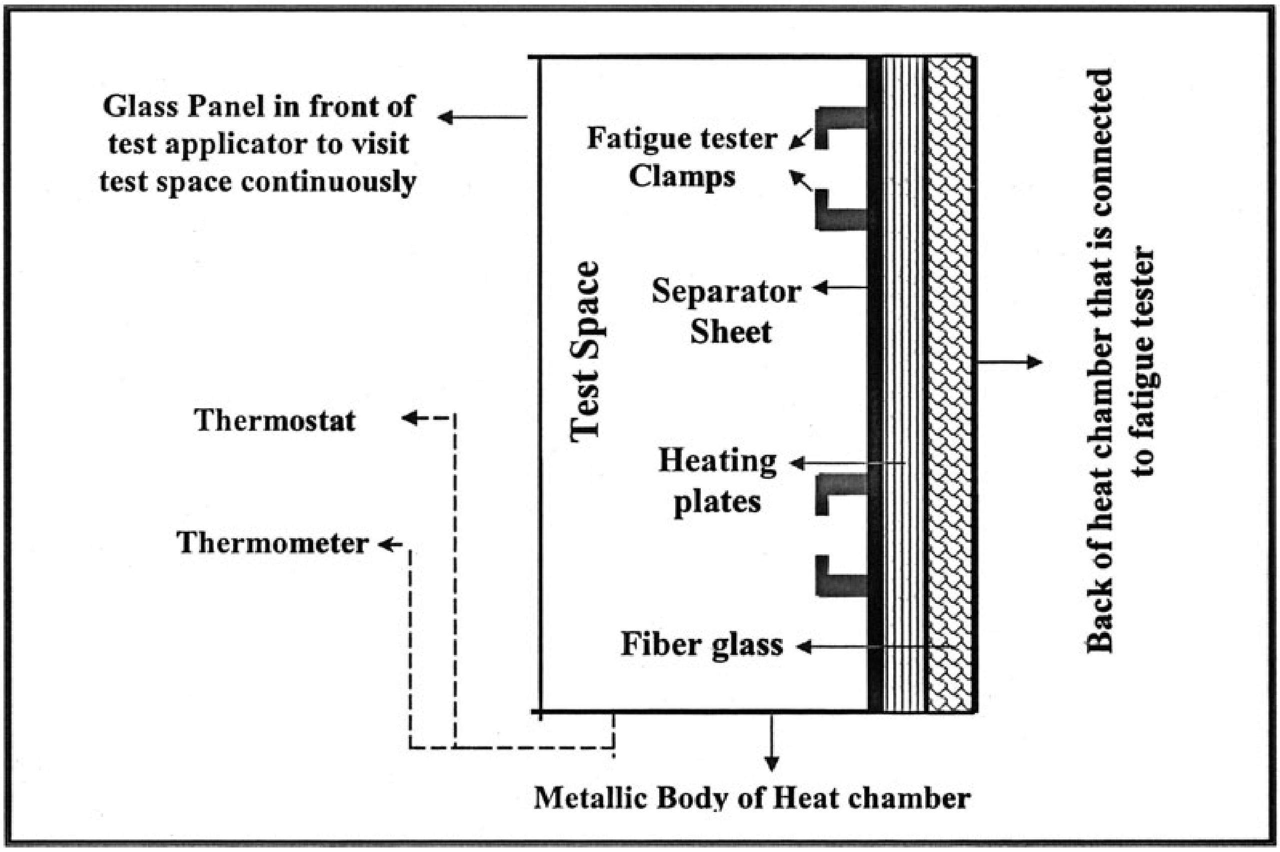

Figure 7 Cross section of heat chamber that was installed on fatigue tester.

The temperature dependences of H-adhesion test results are evident from this curve. It can be seen that the data obtained by this method cannot be used to evaluate the performance of the cord/rubber system.

Figure 8 also shows the effect of temperature on N66 and N6 cords/rubber adhesion. The N66/rubber adhesion decreases (in the temperature range of 25–100°C) alike that of the PET/rubber system. Surprisingly, the N6/rubber system has different behavior at temperature range of 25–50°C.

The adhesion is constant at 25–50°C. It can be attributed to type of produced interfacial interactions between N6 and rubber at vulcanization temperature of 150°C. When vulcanizing temperature is suitable, more stable bonds are produced between cord and rubber. These bonds are not broken by increasing test temperature. When vulcanizing temperature is not

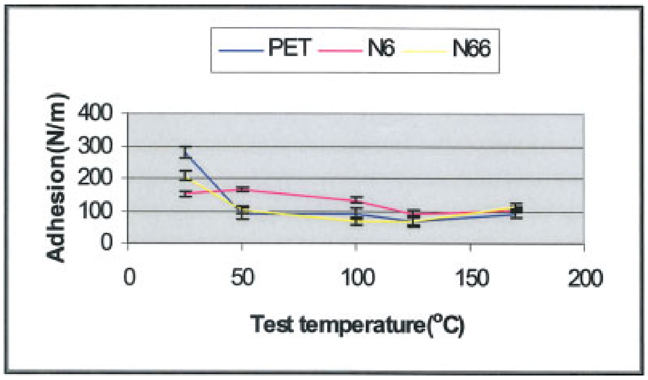

Figure 8 Changes in adhesion of different cord/rubber systems at different test temperatures (vulcanized at 150°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

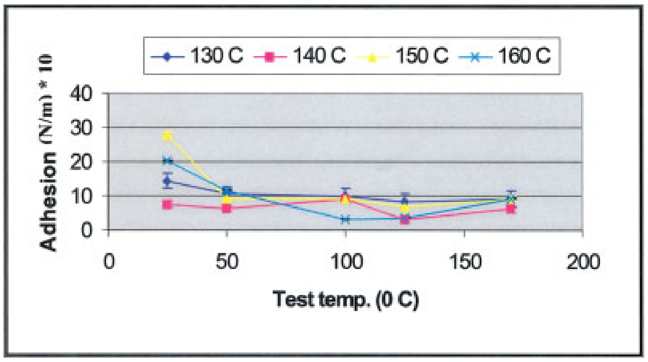

Figure 9 Changes in adhesion of PET/rubber at different curing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Cord/Rubber Dynamic Adhesion (Fatigue) Results at 25°C

Cord type	Dynamic adhesion (number of cycles)	H-adhesion (N/m)
PET	1703	280
N66	1750	220
N6	5833	150

suitable, labile bonds (such as hydrogen bonds) are produced further at interface. They are broken by increasing test temperature. In temperature range of 100–170°C, behavior becomes similar to that of the previous systems.

Figure 9 shows adhesion behavior of the PET/rubber systems that were vulcanized at 130, 140, 150, and 160°C.

Dynamic adhesion

Table II shows results of the fatigue tests of the H-shaped samples. This was done in Monsanto fatigue tester. The trend of adhesion in the dynamic test is in contrast with that in the H-adhesion test. So, it can be concluded that the static adhesion results in the ambient temperature are not responsible for prediction of the cord/rubber durability. Also N6 and N66 cords have better adhesion than PET cords in the dynamic condition at this temperature.

Figure 10 shows results of the fatigue tests of the PET-cord/rubber samples at the elevated temperatures. It is seen that the dynamic adhesion (fatigue) is decreased with increasing temperature. The H-adhesion data are equal in the temperature range of 50–100°C. It is evident that the H-adhesion results can not be used to predict cord/rubber adhesion strength in real conditions.

Figure 11 shows the temperature dependence of the fatigue results. The unitless dynamic adhesion can be estimated by the Weibull model equation

$$G_D = a - b \times e^{-c\,(T)^d} \qquad (1)$$

Where G_D is dynamic adhesion (fatigue) and T is test temperature. The values of a, b, c, and d, which are unitless constants, are equal to 1834.3, 1786.3, 8054.9, and −2.5, respectively.

CONCLUSIONS

The temperature dependence of the cord/rubber adhesion was studied. Different cords were used to prepare test specimens. The H-adhesion and dynamic adhesion tests were carried out on these systems.

The PET cords had the best H-adhesion. But at real conditions (and in industry), PET/rubber adhesion is weaker than adhesion between N6 or N66 and rubber. So, it is concluded that H-adhesion test could not predict the cord/rubber system durability. Also, it was concluded that the weaker interfacial bonds are produced further at unsuitable vulcanizing temperature. These labile bonds are broken at elevated test temperatures.

The dynamic adhesion results have an inverse trend in comparison to the H-adhesion (at 25°C). PET cords had lower adhesion strength in comparison to N6 and

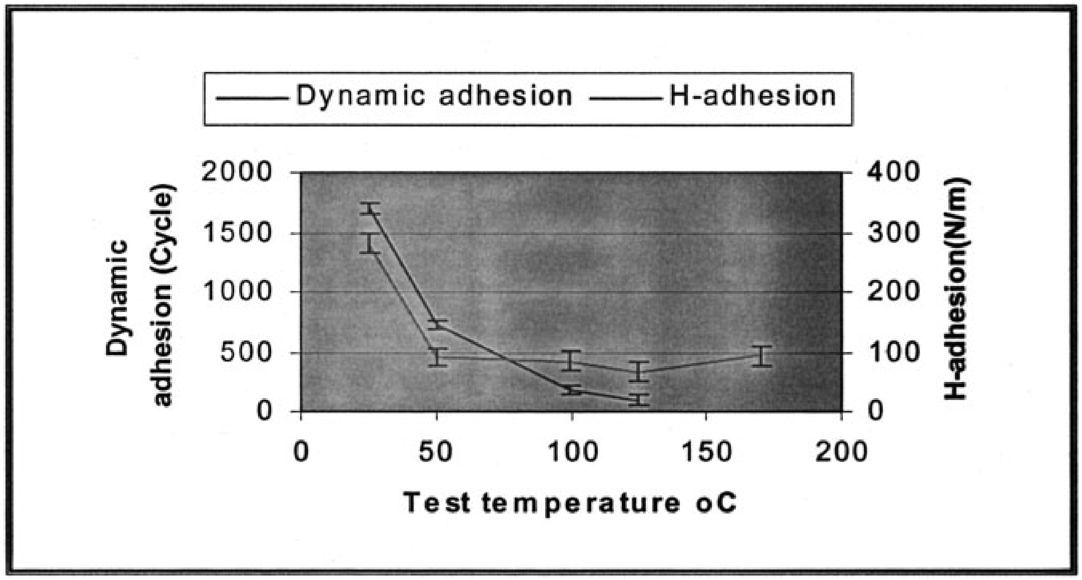

Figure 10 Changes in adhesion of PET/rubber at different test temperatures.

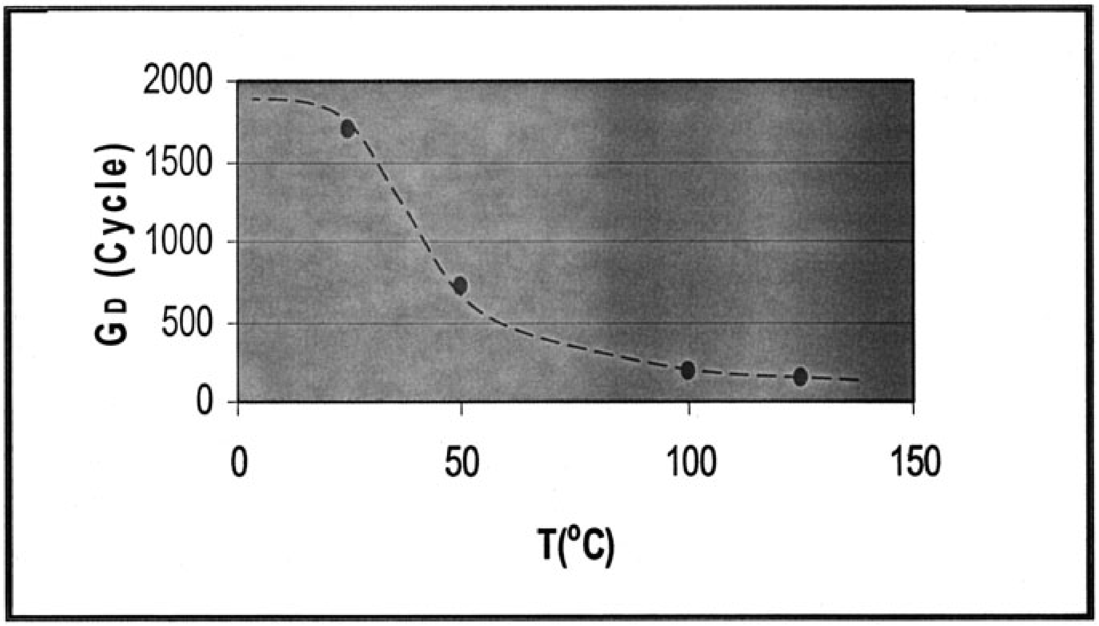

Figure 11 Decreasing trend of dynamic adhesion of PET/rubber at different test temperatures.

N66 cords. These results were predicted for PET/rubber adhesion.[6–10]

Authors believe that this is due to bond breakage of the polyester chains because of cyclic stress. They installed a heat chamber on fatigue tester to produce more reliable results.

Also, it was found that the fatigue results have a correlation with temperature. A mathematical equation was proposed for estimation of fatigue from testing temperature.

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