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The Effect of Temperature on Interfacial Interactions of Cord-RFL-rubber System

Masoud Jamshidi, Faramarz Afshar Taromi*, Naser Mohammadi

Polymer Engineering Department, Amir Kabir University of Technology, P.O. Box: 15875/4413
Tehran, I.R. Iran

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ABSTRACT

Today cords are used generally for reinforcing rubber compounds. To increase interfacial adhesion of cords to rubber, they are coated by an adhesive (usually RFL (resorcinol-formaldehyde-latex) base). These composites are used in many industries such as tyre and belt industries. Adhesion strength between the cord and rubber determines durability and performance of composites. In a recent paper, temperature which is an effective factor in cord/rubber adhesion decrease, was reported to be used for determination of interfacial interactions breakage instead of traditional methods such as swelling method and load of static/ dynamic forces. For this purpose adhesion has been measured in a wide range of temperatures (25-170^{o}C). Stable/labile interactions ratios are evaluated from adhesion-temperature curves as well. Also authors have compared the adhesion of different cords(N6, N66 and PET) to rubber and have determined the best vulcanization temperature for them.

Key Words:
H-adhesion;
RFL;
cord to rubber adhesion;
interfacial interactions.

(*)To whom correspondence should be addressed.
E-mail: afshar@cic.aut.ac.ir

INTRODUCTION

Polymer adhesion and its evaluation are important from the both academic and industrial points of view [1]. One of the most important industries of interest to this aspect is rubber industry. It is well known that different fibres and cords are used as rubber reinforcement in various products such as tyres, belts, hoses, and diaphragms, etc. [2].

The interfacial adhesion strength between the cord and rubber matrix is the major determinant of the performance characteristics of products.

Therefore, to achieve improved adhesion, generally a polar adhesive is used between a polar cord and a non-polar rubber [3,4]. Resorcinol-formaldehyde-latex (RFL) is the preferred adhesive since 1935 for cord/rubber adhesion promotion. No other resin has replaced the RF resin and no other latex has replaced 2-vinylpyridine-butadiene-styrene(15:70:15 wt%) latex as the components in adhesive dip recipes. These aqueous dips have the advantage of low viscosity and thus good wetting properties, but after curing they change to an insoluble system. The latex gives the adhesive necessary flexibility and reactivity to rubber, while the RF resin provides the desired heat and fatigue resistance by forming a 3-dimensional network [5-15].

The RFL solutions were originally introduced for rayon cords and the bonding can be ascribed to the reaction of rayon hydroxyl groups and RF methylol groups. Similarly, the functional groups of nylon can undergo reaction with these methylol groups, although physical forces resulting from interpenetration and interlocking of the RF resin with the fibre can be an adhesion factor. The low level of reactive functional groups in poly(ethylene terephthalate)(PET) leads to an unacceptable adhesion when standard RFL dips are used on PET. So some different methods are utilized for producing satisfactory adhesion between the PET and rubber. Nevertheless, because of good cost-quality balance of PET cords, they are usually used more than other cords.

Many authors have studied the adhesion strength and some of the evaluated cord/rubber adhesion in 1 or 2 temperatures higher than ambient temperature[6,9-10,16-18].

In recent papers the temperature dependency of adhesion strength is studied in a wide region by H-adhesion test method that is outfitted by a heat stage. In this case, a decrease in adhesion through a decrease in curve, can be ascribed as the breakage of labile bonds. In fact this method can be utilized as a new method in determining stable/labile interfacial interactions ratio instead of swelling method of Shmurak [19-20] and surface analyzing methods. Also, the best vulcanizing temperature in different cords is determined and the cords adhesion to rubber are compared with each another.

EXPERIMENTAL

Materials

Rubber Compound

A similar rubber compound is used in this study and its formulation is given in Table 1. Materials weighed and mixed in an internal mixer and rolled in a roll mill. Finally the rubber compound became a sheet with about 1.5 mm thickness.

Latex

Styrene-butadiene-2-vinylpyridine latex of Bayer Company (Pyratex 241).

RF Resin

Waterborne resorcinol/formaldehyde resin of Bayer Company (Vulcador H).

Adhesive

Resorcinol-formaldehyde latex adhesive of Kordsa Co. is used in this study. Typical formulation is given in Table 2.

Adhesion Measurement Samples

At first, rubber parts(sheets with about 1.5 mm thickness) are placed in channels of stainless steel die (Figure 1). Then coated cords are vertically embedded on rubber. The cords are stretched by 50 g weights. Rubber

Table 1. Rubber compound formulation [12-13,18].

Compound	Weight (g)	Wt (%)
NR(standard Malaysian rubber)	45	22
SBR	55	26.5
ZnO	5	2.4
Stearic acid	1.5	0.7
Carbon black 330	35	17
Carbon black 550	35	17
Antioxidant (4010)	3	1.5
Oil(aromatic oil 840)	15	7.3
TMTD	7	3.4
MBT	1	0.5
DM	1	0.5
S	1.5	0.5
total	205	0.7
Vulcanizing temperature (^{o}C)	165	100
Vulcanizing time (min)	3	-
Hardness (Shore A)	75	-

Table 2. Typical one stage RFL adhesive formulation [12-13,15-16,18].

RF Solution	weight (g)	Wt (%)
Resorcinol	11.0	11.0
Formaldehyde	6.0	16.2
Sodium hydroxide	0.3	3.0
Soft water	-	235.8
(maturation: 25°C, 6 h)	17.3	266.0
Final dip solution	Dry part	Wet part
RF solution	17.3	266.0
Latex	100	250.0
Ammonium hydroxide	-	11.3
Soft water	-	59.2
(maturation: 25 °C, 20 h)	117.3	586.5

Usually adhesion promoter is applied to this formulation.

parts are placed on the mentioned parts, in channels. Samples are vulcanized at 130-160°C, for 20 min. They are cut into H-shape samples (Figure 2). Every adhesion data that are reported in figures are average of three data, on the other hand all tests are repeated 3 times.

Adhesion Test Apparatus

Static adhesion was evaluated by a Monsanto 500 tensile strength tester, at the rate of elongation of 120 mm/min. Test samples are tested at 25°C, 50°C, 100°C, 125°C and 170°C.

Surface Characterization

RFL Adhesive film and cords were surface analyzed by a BOMEM, Canada ATR-IR instrument.

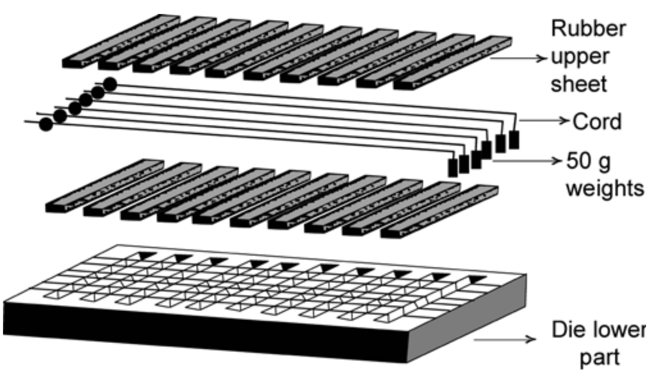

Figure 1. H-Adhesion test die and sample manufacturing ASTM D4776.

RESULTS AND DISCUSSION

Adhesion Results

For the purpose of comparison between the static adhesion of different cords and to study the effects of curing and test temperature on adhesion, H-shape samples were prepared and tested statically (Figures 3-5). In accordance to our expectation, the adhesion decreases with increasing test temperature, in all cords. A big fall in adhesion occurred with increasing temperature from 025°C to 50°C. It can be attributed to destructive effects

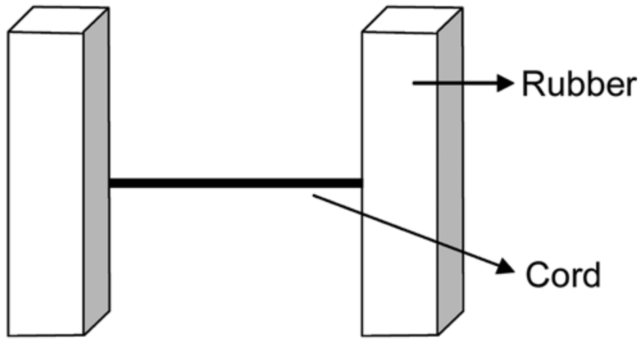

Figure 2. H-Adhesion test sample(ASTM D4776).

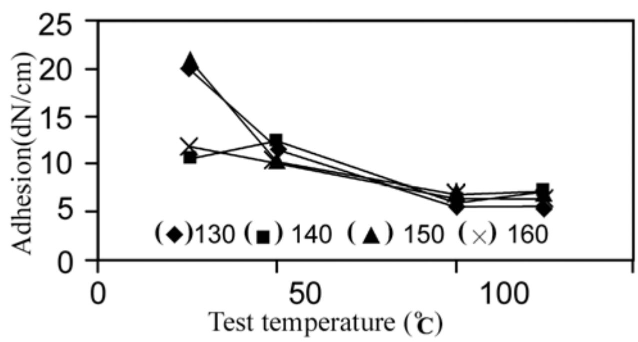

Figure 3. Adhesion of N66 cord to rubber at different temperatures.

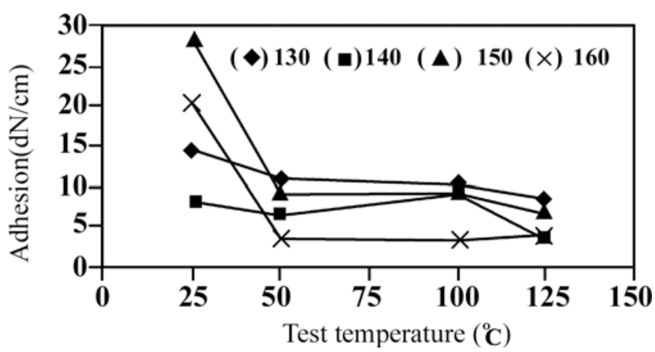

Figure 4. Adhesion of PET cord to rubber at different temperatures.

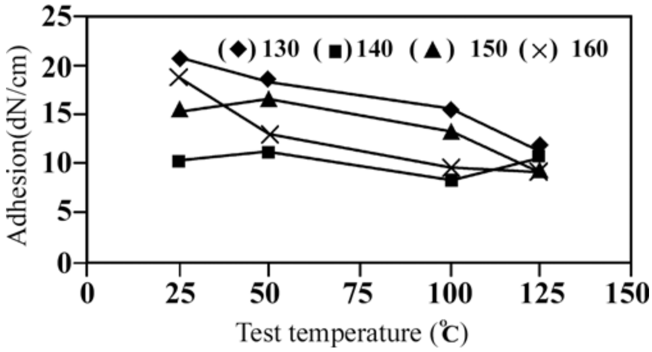

Figure 5. Adhesion of N6 cord to rubber at different temperatures.

of temperature on interfacial interactions of cord-RFL-rubber system. It seems that temperature acts as a dynamic factor in interfacial bonds breakage, i.e. the labile bonds are broken with increasing in temperature.

After this adhesion fall, the curve slope decreases because the labile bonds break with initial small stresses arising from increased temperature. Increasing in temperature leads to breaking weaker bonds, until all of them break. At this point, only stable (covalence or chemical) bonds remain. Therefore, minimum points in Figures 3-5 can be attributed to the amount of stable bonds. Table 3 shows cords/rubber stable/labile interactions ratio for different vulcanization temperatures.

An increasing trend is seen after 125°C in all cords, adhesions that is not shown in these figures. It can be considered that some new strong bonds have been created in a temperature higher than vulcanizing temperature. In fact, this shows that after curing cross-linking is not complete, so some potential reactive zones still exist. Also, comparison of vulcanization temperatures of the cords can show the best curing condition.

N6 and N66 cords show the better adhesion properties at vulcanizing temperature of 130 and 150°C, especially at ambient temperature. But N6 shows uniform behaviour at different test temperatures. Also the amount of ambient adhesion of N6 at curing temperature of 150°C is a test operating error.

PET Cord shows better adhesion than N6 and N66 cords that it does not match to what we have known from literature review. This occurs because of the chemical treatment of PET surface with epoxy active materials during spinning.

Table 3. Interfacial interaction amount in different cord/rubber systems.

Vulcanizing temperature (°C)	130	140	150	160
Bond type / Cord type	Stable/labile bonds ratio			
PET	1.39	0.72	0.31	0.19
N66	0.37	0.90	0.32	1.11
N6	1.16	2.88	1.28	0.92

Heat Aging

The effect of heat aging on N6, N66 and PET H-shape

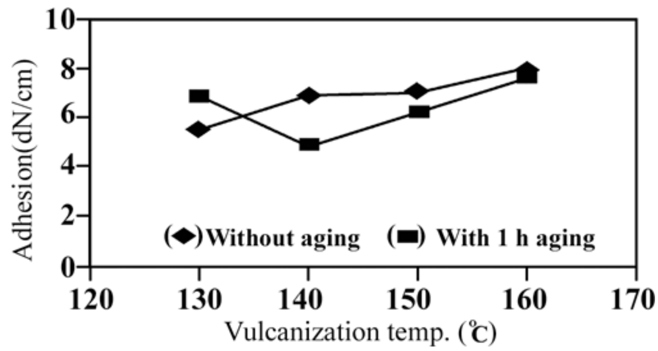

Figure 6. Aging of N66 cord-rubber adhesion at 125°C for 1 h.

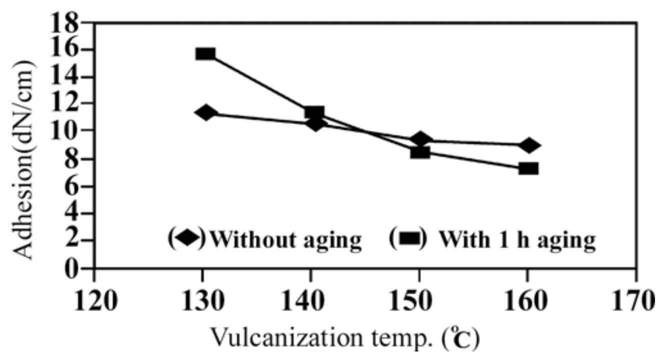

Figure 7. Aging of N6 cord-rubber adhesion at 125°C for 1 h.

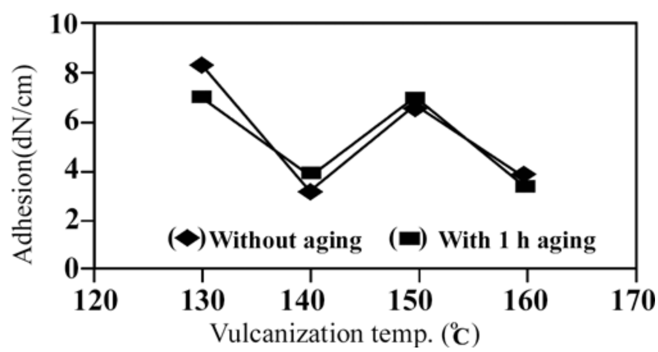

Figure 8. Aging effect on PET-rubber sample adhesion at 125°C for 1 h.

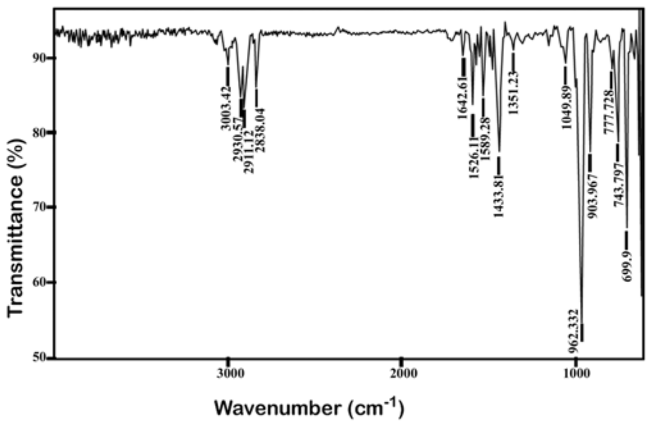

Figure 9. ATR-IR Analysis results of RFL film.

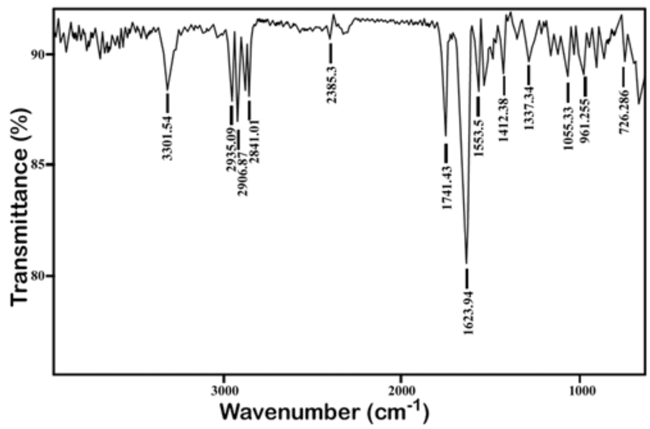

Figure 12. ATR-IR Analysis results of N66 cord

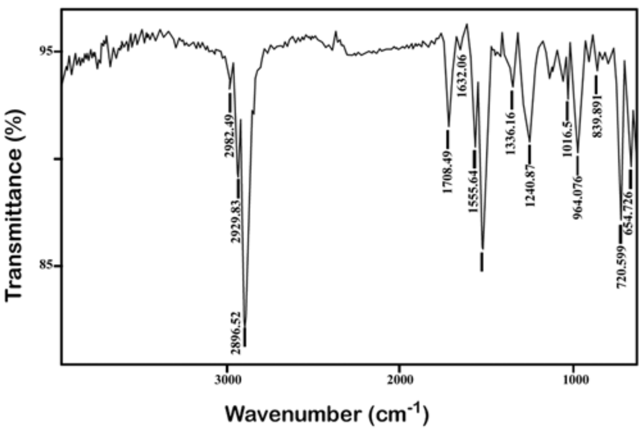

Figure 10. ATR-IR Analysis results of coated PET cord.

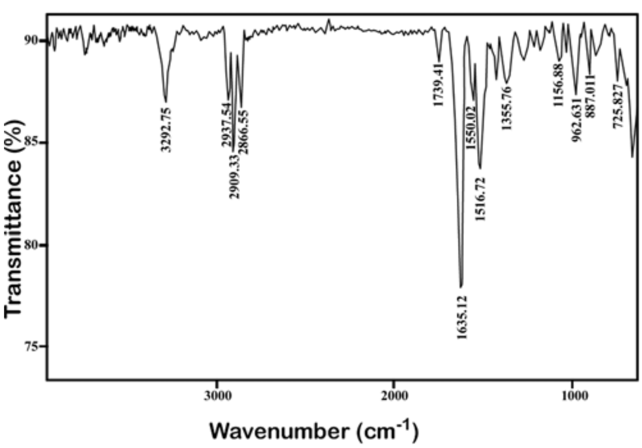

Figure 11. ATR-IR Analysis results of N6 cord.

samples were studied by aging vulcanized samples at 125°C(test temperature) for 1 h. In some vulcanizing temperatures, the better results can be seen after aging (Figures 6-8).

Usually adhesion must decrease with heat aging, so when this is not occurred, it can be considered that vulcanization temperature was not enough. On the other hand where the non-aged samples curve is high than the other, this region can be considered as a suitable vulcanizing temperature.

Cords and RFL Surface Characteristics

ATR-IR Analysis of N6 and N66 cords, RFL coated PET cord and RFL film are presented in Figures 9-12. ATR-IR Analysis of RFL film confirms the presence of aromatic rings, alkenes, ethers and aldehydes, etc. So adhesive has non-saturated zones for reaction with rubber.

Also RFL coated PET shows the same absorption bonds, but it does not show -OH absorption either. Absorption bonds of aldehyde and ether (respectively, at 1708.49 and about 1100 cm-1) are stronger in this figure from what is shown in RFL.

ATR-IR Analysis of N6 and N66 cords show the same absorption bonds of amine/amide, aldehyde/ketone, ether and alcohol groups. So they can chemically react with methylol groups of RFL adhesive.

CONCLUSION

The effect of temperature on the interfacial interaction and determination of stable and labile bond quantities were examined in the interface of N6, N66 and PET cords with NR/SBR rubber compound. In all cord-rubber systems increasing in test temperature leads to decrease in adhesion. This is mainly attributed to breaking of hydrogen bonds and London interactions. Decreasing in adhesion is stopped at a minimum point that can be considered as stable bonding amount. So stable/labile interactions ratio are evaluated from curves.

It seems that vulcanizing temperature of 150ºC is the best vulcanizing temperature for all cords.

ATR-IR Analysis of RFL does not show -OH absorption bond(3200-3600 cm^{-1}), and it can be attributed to migration of polar zones into the bulk of film and non-polar groups to surface as the ATR-IR analysis of RFL coated PET confirms it. It seems that polar sites migrate to cord surface from the adhesive bulk when cord/rubber system is heated until vulcanization.

Usually dynamic tests are used to predict the behaviour of reinforced rubbers in real condition. Therefore, to approach this purpose by H-adhesion test method, a heating stage can be added to test procedure to simulate it with real condition.

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