Journal Fluorine Chemistry, 20 (1982) 827–831
Received: October 15, 1981

PRELIMINARY NOTE

ADHESION OF FLUORINATED POLYESTER CORD TO RUBBER

D. D. DIXON, M. E. FORD and W. M. SMITH

Air Products and Chemicals, P.O. Box 538, Allentown, PA 18105 (U.S.A.)

SUMMARY

Surface fluorination of polyester cord increases adhesion of the cord to rubber fivefold. Fluorinated polyester fabric retains the high tensile strength necessary for efficient reinforcement of rubber tires.

Reinforcement of rubber tires by incorporation of synthetic fibers is a fundamental principle of tire design [1]. Development and maximization of adhesion between the reinforcing element and the body of the rubber article is a key concern of high performance reinforced rubber technology [1-4]. Extensively investigated approaches toward this goal include selection of the appropriate tire cord material and chemical adhesive system [1]. Owing to its combination of desired properties: high modulus, low elongation, dimensional stability, and superior fatigue resistance, polyester cord finds significant and expanding utilization in this application. While polyester tire cord has experienced favorable market acceptance, limited adhesion to rubber has been recognized as a shortcoming [1]. This property may derive from the lack of hydrophilic groups in the polyester structure. Successful techniques to overcome this problem have centered on 'double dip' methods. In these, polyester tire cords are functionalized by coating with a reactive monomer (toluene diisocyanate, an ethylene urea) or polymer (polyethylene oxide) prior to bonding with a resorcinol - formaldehyde latex (RFL) adhesive.

0022-1139/82/0000-0000/$02.75

We wish to report that fluorination of polyester tire cord constitutes a simple, rapid procedure by which RFL-promoted bonding of the cord to rubber is substantially improved. Exposure of polyester cord to 0.05 to 1.0 volume percent of fluorine in nitrogen gas prior to RFL treatment typically increases adhesion of the cord to rubber by a factor of five (Table 1).

Surface fluorination of polyester cord is readily effected. A general procedure consists of wrapping polyester cord in a single layer around a perforated copper cylinder. The sample is inserted into a two liter monel reactor, and the reactor closed and purged with nitrogen. Evacuation of the reactor, introduction of fluorine-containing reaction gas for 5 to 60 seconds, and subsequent evacuation and purging of the reactor with nitrogen provide fluorinated tire cord. Treatment of polyester cord with fluorine-nitrogen mixtures in this manner is preferably carried out within the temperature range of $15^{o}C$ to $25^{o}C$. At lower temperatures, longer reaction times are required to obtain the improved levels of tire cord adhesion shown in Table 1. At temperatures in excess of $30^{o}C$, this process occurs rapidly with poor selectivity; the polyester fiber is fluorinated throughout. Exclusion of oxygen and employment of low fluorine levels are vital to success of the technique. Under these conditions, very little degradation of tensile strength accompanies fluorination of polyester cord and subsequent RFL treatment (See Tables 1 and 2 for additional experimental data.)

Identification and investigation of the mechanism by which surface fluorination increases the adhesive properties of poly(ethylene terephthalate) fibers are in progress. However, some initial observations can be made. During fluorination of poly(ethylene terephthalate), preferential attack of fluorine at ethylene units on the surface of the polyester fibers is known to generate carboxylic acid functionality [5]. At low fluorine levels, carboxylic acid groups are distributed randomly over the surface of the fiber. Under the alkaline conditions of RFL treatment, surface carboxylate groups may bond in polar or covalent fashion to the RFL coating. Interaction of fluorine-induced surface functionality, such as carboxylate groups, with the RFL adhesive may thus account for the enhanced adhesions of fluorinated polyester cord to rubber compositions However, use of fluorine levels or reaction temperatures in excess of those reported here leads to extensive chain scission throughout the polyester fiber. The severe and immediate degradation of highly fluorinated poly-

TABLE 1

Effect of fluorination on adhesion of polyester cord to rubber [a]

Fluorine Level[b]	Reaction Pressure (atm)[c]	Reaction Time (sec)	Adhesion of Polyester Cord (lbs, pull force)[d]			
			Untreated[e]	Fluorinated[f]	RFL Treated[g]	Fluorinated/RFL Treated[h]
0.05	0.5	5	3.8	4.4	10.5	16.0
0.05	1.0	5	3.8	4.2	10.5	20.5
0.05	1.0	30	3.8	4.9	10.5	17.5
0.05	1.0	60	3.8	5.2	10.5	15.0
0.5	1.0	5	3.8	3.9	10.5	20.0
0.5	1.0	30	3.8	3.6	10.5	21.0
1.0	1.0	5	3.8	3.4	10.5	20.5

(a) Celanese T-800-1000/2 polyester tire cord was used in all experiments.

(b) Volume percent of fluorine included in the carrier gas.

(c) Pressure of the fluorine/nitrogen mixture.

(d) Evaluated according to ASTM D-2138-62T; all values are $\pm$ 0.1 lbs, pull force.

(e) Adhesion to rubber of polyester cord which has been neither fluorinated nor RFL treated.

(f) Adhesion to rubber of fluorinated polyester cord.

(g) Adhesion to rubber of RFL-treated polyester cord.

(h) Adhesion to rubber of polyester cord which has been (1) fluorinated and (2) RFL treated.

TABLE 2

Effect of fluorination on tensile strength of polyester cord [a]

Fluorine Level[b]	Reaction Pressure (atm)[c]	Reaction Time (sec)	Cord Tensile Strength (in-lbs)[d] Untreated[e]	Fluorinated[f]	RFL Treated[g]	Fluorinated/RFL Treated[h]
0.05	0.5	5	34.8	33.5	33.5	31.0
o.o5	1.0	5	34.8	34.0	33.5	31.5
0.05	1.0	30	34.8	34.8	33.5	30.5
0.05	1.0	60	34.8	34.4	33.5	32.0
0.5	1.0	5	34.8	34.0	33.5	31.0
0.5	1.0	30	34.8	33.3	33.5	31.0
1.0	1.0	5	34.8	34.2	33.5	30.0

(a) Celanese T-800-1000/2 polyester tire cord was used in all experiments; cord diameter is 0.020 *inch*.

(b) Volume percent of fluorine included in the nitrogen carrier gas.

(c) Pressure of the fluorine/nitrogen mixture.

(d) Evaluated according to ASTM D-412 and ASTM D-2240; all values are ± 0.1 lbs, pull force.

(e) Tensile strength of polyester cord which has been niether fluorinated nor RFL-treated.

(f) Tensile strength of fluorinated polyester cord.

(g) Tensile strength of RFL-treated polyester cord

(h) Tensile strength of polyester cord which has been (1) fluorinated and (2) RFL-treated.

ester cord (tensile strength declines to 50-60% of its original level) obviates its utility as a tire reinforcement.

Owing to the dramatic rise in price of petrochemical fuels since 1973, recent trends in tire development and manufacture have emphasized increased fuel economy. Reduction of tire weight is one approach by which greater economy of operation has been pursued [6]. For example, replacement of a two-ply fabric-reinforced tire body with a single-ply construction yields a 4-6% reduction in tire weight [6]. Fluorine-enhanced adhesion of polyester cord to rubber tires will facilitate this trend, since lesser amounts of polyester will be required for tire reinforcement. Moreover, extension of this procedure to fabrication of other polyester reinforced rubber articles, such as conveyor belts and power transmission belts, may expand the utility of polyester cord and provide higher performance rubber products.

1 T. Takeyama and J. Matsui, Rubber Chem. Technol., Rubber Rev., 42 (1969) 159.
2 Y. Iyengar, J. Appl. Polym. Sci., 13, (1969) 353.
3 Y. Iyengar, J. Appl. Polym. Sci., 15, (1971) 267.
4 Y. Iyengar, J. Appl. Polym. Sci., 19, (1975) 855.
5 L. J. Hayes and D. D. Dixon, J. Fluorine Chem., 10 (1977) 1.
6 R. B. Knill, Chemtech, (1981) 698.