Evaluation of Adhesion Characteristics of Nylon-6 Tire Cord to Natural Rubber

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Synopsis

The adhesion characteristics of Nylon-6 cords to rubber matrix, using Resorcinol Formaldehyde Latex (RFL) solution, were evaluated at various conditions. The heat-setting studies of RFL-dipped cords in the temperature range of 180–210°C showed a loss in tensile properties. However, a minimum in the loss was observed when a pretension load was given to the cords. Percent shrinkage of RFL-dipped cords increased with the increase in temperature of heat setting. Adhesion behavior of Nylon-6 cords to rubber matrix showed some improvement under relaxed conditions in the entire temperature range studied. With the application of suitable tension to cord, adhesion behavior can be made constant. This has been attributed to the higher extent of shrinkage of cords under relaxed conditions providing greater cord surface area. This in turn, leads to increased cord to rubber matrix.

INTRODUCTION

The interfacial adhesion strength between the cord and rubber matrix is the major determinant of the performance characteristics of an automobile tire. In the case of Nylon-6 tire cords, the polar cord shows poor adhesion to the nonpolar rubber matrix, generally used in tires. To improve the adhesion between these two dissimilar surfaces, tire cords are dipped into a resorcinol-formaldehyde latex (RFL) so as to form a coating. The resin part adheres to the nylon cord whereas the latex part helps bonding with rubber matrix. The increase in the adhesion depends upon various conditions used during the dipping process.[1]

The present study has been aimed toward evaluation of the effect of certain parameters on adhesion in Nylon-6 tire cord–natural rubber system.

EXPERIMENTAL

Materials:

Two Nylon-6 cords having almost similar mechanical characteristics were obtained from different manufacturers. These had been characterized by a study reported earlier.[2]

Masticated natural rubber, supplied by Modi Rubber Limited, India, was used for adhesion studies.

Present address: *Garware Nylons, Pune, India. †Modi Rubber Limited, Modipuram, Meerut, U.P., India.

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Dip Pick-up Studies

Dipping of nylon cords was carried out for 10 sec in resorcinol-formaldehyde-latex (RFL) solution. The excess solution was removed in a padding mangle (at 4.5 kg/cm^2 pressure). The dipped cords were dried in an air oven at 145°C for two minutes, at constant length. Dip pick-up was calculated using ASTM procedure.[3] The sample was dissolved in formic acid. After filtering off, the residue was dried to a constant weight. Pick-up was obtained from the following relationship:

$$\% \text{ Dip pick-up} = \frac{R}{S - R} \times 100$$

where R is the weight of the residue and S is the weight of specimen.

Tensile Studies

Tensile measurements for cords were carried out on "Instron" Tensile Tester 1112, using the following conditions:

Gauge length	—25 cm
Full scale load	—50 kg
Chart speed	—200 mm/min
Cross-head speed	—200 mm/min
Temperature	—20 ± 2°C
Relative humidity	—65%

Adhesion Studies

Static adhesion test on cord rubber composite was carried out according to ASTM procedure.[4] Cords were kept perpendicular to the rubber strip forming the shape H followed by curing at 134°C.

RESULTS AND DISCUSSION

Two Nylon-6 cords having almost similar inherent mechanical properties (Table I) were evaluated for their adhesion with rubber matrix. Our earlier[2] studies on heat treatment of nylon cords have shown that sample A retains most of its strength characteristics on heat treatment at 200°C for 16 h, whereas sample C loses its strength by about 52% during similar treatment

TABLE I
Physical Properties of Nylon-6 Cords

				Tenacity (gpd)	
Sample code	Twist ply (TPI)	Denier	Modulus (gpd)	Before heat treatment	After heat treatment at 200°C for 16 h
A	8.3	2881.88	26.5	7.53	5.57
C	8.7	2900.57	27.0	7.23	3.45

TABLE II
Dip Pick-up and Static Adhesion Strength of Nylon-6 Cords

Sample code	Dip pick-up (%)	Static adhesion (kg/5 mm)
A	3.9	1.62
C	4.1	1.67

(Table I). The reasons for such a difference were attributed to the difference in molecular weight and its distribution in the two samples. Sample A has higher molecular weight and lower shape factor value than that of C and hence retains strength better during heating at 200°C. However, sample C has the highest shape factor value[2] among four samples studied earlier, suggesting a broadening in the molecular weight distribution of the polymer. Furthermore, the molecular weight is also much lower than sample A. Hence, these two structural changes in the cord may be responsible for strength loss of 52% in the parent sample. In the present study, these two samples have been chosen to find whether the molecular weight parameters have an effect on adhesion characteristics of the tire cords to natural rubber.

The dipping of cord samples in RFL solution was carried out at 20°C for ten seconds followed by drying at 145°C for two minutes at a constant length. The heat setting of RFL-dipped cords was studied at three temperatures, viz., 180, 200, and 210°C for 30 and 90 sec, respectively. The drying of cords was carried out at a temperature of 145°C which is very close to the maximum crystallization temperature of Nylon-6.[5] Hence, such a treatment should lead to the formation of more perfect crystallites, and a better ordered sample. A subsequent heat treatment at elevated temperature would, thus, introduce less effective structural changes in comparison to that in the parent sample.

Percent pick-up and adhesion values of cords before heat treatment, but after drying at 145°C for two min have been presented in Table II. It can be seen from the results that both the samples have similar dip pick-up values. The adhesion strength of both the cords to rubber is also almost similar.

The effect of subsequent heat treatment on tensile properties at elevated temperature has been presented in Tables III to V. In general, tensile

TABLE III
Tenacity of the Dipped-Cords after Heat Setting at Various Conditions

		Tenacity (gpd)						
		Treated cords						
		180°C		200°C		210°C		
Sample code	Tension (kg)	30 sec	90 sec	30 sec	90 sec	30 sec	90 sec	Untreated cord
A	0.0	6.55	6.52	6.21	6.13	5.97	5.89	7.52
	2.2	6.91	6.90	6.88	6.85	6.55	6.49	—
C	0.0	5.64	5.64	5.28	5.25	4.90	4.82	7.22
	2.2	6.66	6.62	6.62	6.61	6.59	6.59	—

TABLE IV
Initial Modulus of Dipped-Cords after Heat Setting at Various Conditions

Sample code	Tension (kg)	Initial modulus (gpd) Treated cord 180°C 30 sec	180°C 90 sec	200°C 30 sec	200°C 90 sec	210°C 30 sec	210°C 90 sec	Untreated cord
A	0.0	27.65	27.85	28.13	28.19	29.16	29.56	26.5
	2.2	26.98	26.97	27.01	27.13	27.19	27.23	—
C	0.0	28.69	28.70	28.99	28.96	29.93	30.03	27.0
	2.2	27.64	27.68	27.73	27.74	27.92	27.99	—

properties of dipped and heat-set cords show a decrease with increasing temperature. However, the loss in strength is minimum with the application of pretension load. It seems that the use of tension during heat treatment restricts the mobility of the polymer chains in the amorphous region. Hence, the orientation of molecular chains does not alter to any appreciable extent.[6]

Shrinkage behavior of the two Nylon-6 cords at various temperatures has been presented in Table VI. With the increase in temperature, an increase in percent shrinkage was observed. Buchanan and Dumbleton[7] have also reported an increase in percent shrinkage with the increase in temperature of annealing. This should essentially be due to the increased mobility of structural units resulting in more relief of localized internal stresses which in turn is followed by the folding of molecular chains in the amorphous region.[8]

Tension tends to align the molecular chains of a polymer in the amorphous region. Hence, the external stress would be distributed more evenly among the structural elements. On the other hand, folding of chains could be minimized at higher tension load.[9] These factors would, thus tend to reduce the effect of temperature in decreasing the strength characteristics of cords.

The effect of heat treatment on adhesion at elevated temperature has been presented in Table VII. The results show that with the increase in time of treatment, adhesion characteristics do not show any appreciable change. However, with the increase in temperature under relaxed conditions, slight

TABLE V
Percent Elongation of the Dipped-Cords after Heat Setting at Various Conditions

Sample code	Tension (kg)	Percent elongation Treated cord 180°C 30 sec	180°C 90 sec	200°C 30 sec	200°C 90 sec	210°C 30 sec	210°C 90 sec	Untreated cord
A	0.0	39.40	39.53	39.83	39.93	40.32	40.68	31.2
	2.2	33.86	33.84	33.90	33.92	34.02	34.12	—
C	0.0	40.68	40.68	40.68	41.00	41.52	41.79	31.96
	2.2	34.40	34.54	34.60	34.69	34.68	34.73	—

TABLE VI
Shrinkage of Nylon-6 Cords (with Pretreatment at 145°C for 2 min at Constant Length) after Heat Setting at Various Conditions

		Percent shrinkage					
		180°C		200°C		210°C	
Cord	Tension (kg)	30 sec	90 sec	30 sec	90 sec	30 sec	90 sec
A	0.0	7.90	8.11	9.41	10.59	10.4	11.49
	0.5	1.59	1.79	1.60	2.10	1.95	3.12
	1.7	—	—	—	—	—	—
	2.2	—	—	—	—	—	—
C	0.0	8.00	8.59	9.30	9.99	10.8	12.09
	0.5	1.50	1.74	1.60	1.82	1.90	2.68
	1.7	—	—	—	—	—	—
	2.2	—	—	—	—	—	—

improvement in adhesion was observed. Adhesion strength characteristics are essentially a function of the extent of cross-linking reaction taking place in the system. The solubility parameter value of nylon ($\delta = 16$) is quite close to that of resorcinol ($\delta = 15.9$), indicating the thermodynamic compatibility of the nylon cord and adhesive.[10] Hence, the cross-linking reaction of RFL solution proceeds with the embedding of Nylon-6 cord in the cross-linked matrix. From the results it appears that the cross-linking is incomplete at the curing temperature of 180°C up to a time period of 90 sec and continues so at a temperature of 210°C. Iyenger[1] carried out the adhesion studies in Nylon-6 cord-rubber system, using the dip-curing temperature in the range of 270–410°F (132–210°C) with an exposure time of 80 sec. He found that the adhesion initially increases rapidly with the increasing temperature, but attains a maximum value at 410°F (210°C). Our studies with the RFL curing temperature in the range of 180–210°C are well in agreement with those observed by Iyenger.[1]

The adhesion of cord to rubber matrix did not show any improvement when curing was carried out under tension. One of the obvious reasons may be that at zero tension, percent shrinkage in cords increases with the increase in temperature (Table VI). This necessarily leads to a higher surface area of the

TABLE VII
Static Adhesion Strength of Dipped-Cords after Heat Setting at Various Conditions

		Static adhesion (kg/25 mm)					
		180°C		200°C		210°C	
Sample code	Tension (kg)	30 sec	90 sec	30 sec	90 sec	30 sec	90 sec
A	0.0	2.20	2.26	2.23	2.25	2.34	2.94
	2.2	2.01	2.00	2.00	1.99	1.99	2.00
C	0.0	2.14	2.19	2.22	2.23	2.25	2.38
	2.2	1.71	1.79	1.80	1.82	1.99	1.99

cord. The higher the surface area, the more amenable becomes the structure for diffusion of RFL solution into the cord.[11] Furthermore, the contact area between the cord and rubber also increases which, in turn, is reflected in improved adhesion characteristics.[12] With the application of tension, restrictions to the mobility of polymeric chains in the amorphous regions are imposed. When the tension to the cord is high enough to prevent any shrinkage, surface area of the cord is not affected. Consequently, it does not show any substantial improvement in the adhesion. This behavior has been observed when a pretension load of 2.2 kg was applied to the cord (Table VI). From the results it appears that heat setting of RFL-dipped tire cord at 210°C for 30 sec under relaxed conditions can give rise to better adhesion characteristics of Nylon-6 tire cords to rubber.

References

1. Y. Iyenger, *J. Appl. Polym. Sci.*, **13**, 353 (1969).
2. A. K. Mukherjee, B. D. Gupta, S. G. Kulkarni, D. S. Chauhan, and S. N. Chakravarty, *J. Appl. Polym. Sci.*, **30**, 4417–4429 (1985).
3. ASTM, D855, Volume 7.01, 173 (1985).
4. ASTM, D 2138, Vol. 9.01, 557 (1985).
5. B. B. Burnett and W. F. McDevit, *J. Appl. Phys.*, **28(10)**, 1101 (1957).
6. Y. Y. Choi and J. K. Suh, *Hanguh Sumyu Konghukhoe Chi*, **19(1)**, 1 (1982).
7. D. R. Buchanan and J. H. Dumbleton, *J. Polym. Sci.*, **A(2)**, **7**, 113 (1969).
8. D. E. Bosley, *J. Polym. Sci., Part C*, **20**, 77 (1967).
9. W. O. Statton, J. L. Koenig, and M. Hannon, *J. Appl. Phys.*, **41**, 4291 (1970).
10. Y. Iyengar and D. E. Erickson, *J. Appl. Polym. Sci.*, **11**, 2311 (1967).
11. B. D. Gupta, Ph.D. thesis, IIT Delhi (1984).
12. R. L. Patrick, *Treatise on Adhesion and Adhesives*, Vol. 1, Marcel Dekker, Inc., New York, 1967, p. 119.

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