

# Studies on Rubber-to-Nylon Tire Cord Bonding

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**ABSTRACT:** Nylon tire cord (1680/2) was dipped in different adhesives based on resorcinol formaldehyde resin and latex (RFL) and was bonded to natural rubber-based compounds. The resin-rubber ratio in the RFL adhesive was optimized. The variation of pull-through load was studied by varying the drying and curing temperature of the dipped nylon tire cord. RFL adhesive based on vinylpyridine latex was found to have better rubber-to-nylon tire cord bonding, compared with the one based on natural rubber latex. Addition of a formaldehyde donor into the RFL adhesive/rubber compound improves adhesion. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 1197–1202, 1999

**Key words:** nylon tire cord; rubber to tire cord bonding; resorcinol formaldehyde resin; VP latex; NR latex

## INTRODUCTION

Adequately bonded rubber-textile combinations form the basis of many heavy duty “mechanical rubber products,” notably tires and belts. When fabric materials (such as nylon, vinylon, rayon, or polyester fibers) are used as reinforcing items for articles (such as pneumatic tires, belts, air cushions, hoses, or rubber vibration insulators), it is necessary to bond rubber compounds to this synthetic fabric materials.

Rubber cement adhesives have been used preferably in the belt and coated fabric industries. A heavy responsibility of the rubber textile bonding depends on the adhesive component, an optimum adhesion that binds up the surface of textile and rubber together without appreciably stiffening or tendering the fiber and without affecting the vulcanization characteristics of the rubber. If latex alone is used as an adhesive, good rubber-to-textile bonding cannot be obtained because of lack of active groups in the latex and weak tensile prop-

erties of the adhesive coating film. Several thermosetting resins were used for this purpose. Phenol formaldehyde,<sup>1</sup> urea formaldehyde,<sup>2</sup> aniline formaldehyde,<sup>3</sup> ketone formaldehyde,<sup>2</sup> and resorcinol formaldehyde (RF) resins were patented. Among them, RF resin was chosen to be used as an aqueous adhesive incorporated into latex because of its superior adhesion and ease of processing.<sup>4</sup> Thus, the RF latex adhesive (known as the RFL adhesive) was used to meet the requirements of model tires and received wide acceptance.

Rubber-to-textile adhesion can also be achieved by the addition of bonding agents to the rubber compounds so that the adhesive treatment of the textile can, to some extent, be avoided. Isocyanate derivatives have been used for this purpose,<sup>5</sup> but more a widely accepted combination is RF donors.<sup>6</sup>

In this article, we report on the preparation of RF resin and its use as a bonding agent. For cord dipping, drying, and curing, a dipping unit was designed and fabricated. The dipping unit consists of two drying zones and a curing zone. The temperature of each zone can be varied from 30° to 210°C. The length of each zone is 33.33 cm. The cords were dipped, dried, cured, and wound on a

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**Table I Formulation of NR Compounds for Bonding (phr)**

Ingredients	1	2	3	4	5	6	7	8	9	10	11	12
NR	100	100	100	100	100	100	100	100	100	100	100	100
HAF black	40	40	40	40	40	40	40	40	40	40	40	40
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
Wood rosin	5	5	5	5	5	5	5	5	5	5	5	5
Vulkanox 4020 <sup>a</sup>	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS <sup>b</sup>	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MOR <sup>c</sup>	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Hexamethylene-tetramine	—	0.5	1.0	1.5	2.0	2.5	—	—	—	—	—	—
Paraformaldehyde	—	—	—	—	—	—	0.4	0.4	0.4	0.4	0.4	0.4
RF resin I <sup>d</sup>	—	—	—	—	—	—	—	0.2	0.4	0.6	0.8	1.0
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
$T_{10}$ min <sup>e</sup>	1.8	2.0	2.1	1.9	1.9	1.8	7.0	6.9	10.7	6.6	6.2	6.1
$T_{90}$ min <sup>f</sup>	14.1	12.0	10.6	9.4	9.0	8.2	15.1	18.9	21.1	19.0	18.6	17.6

<sup>a</sup> *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine.

<sup>b</sup> Polymerized 1,2-dihydro-2,2,4-trimethylquinoline.

<sup>c</sup> 2-(Morpholiniothio) benzthiazole.

<sup>d</sup> RF resin prepared by method I.

<sup>e</sup> Scorch time, time for attaining 10% of the maximum torque.

<sup>f</sup> Optimum cure time, time for attaining 90% of the maximum torque.

pulley. The effect of resin concentration, type of polymer, temperature of drying, curing, etc., were evaluated. The pull-through load was also determined after 1 week of storage of the RFL adhesives.

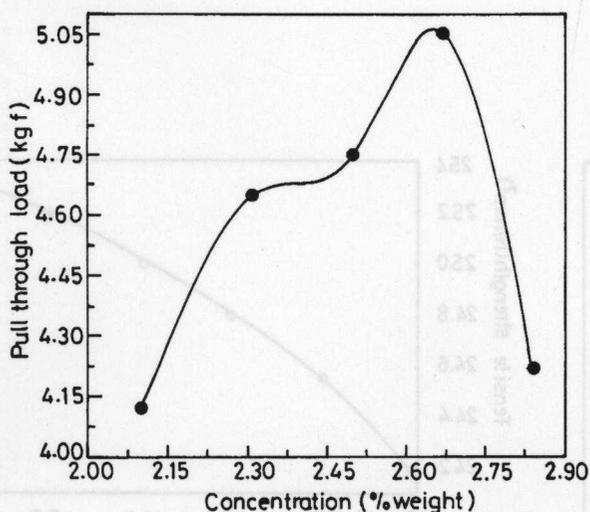
## EXPERIMENTAL

The nylon cord used for dipping studies was 1680/2, supplied by SRF Ltd. (Madras, India). The lattices used were vinylpyridine (butadiene, 70%; styrene, 15%; vinylpyridine, 15%) and natural rubber (NR; 60% centrifuged latex). The elastomer used for bonding studies was natural rubber [ISNR-5 ML (1+4) 100°C-82]. The compounding ingredients (*viz.* zinc oxide, stearic acid, HAF black, wood rosin, antioxidants, accelerators, sulfur, hexamethylenetetramine, paraformaldehyde, resorcinol, and formaldehyde) were commercial grade. The RF resin used for the preparation of the RFL adhesive was prepared in the laboratory by two methods. In method I, the ratio of resorcinol to formaldehyde was 2 : 1 (RF resin I); and, in method II (commercial method), the ratio was 1 : 2 (RF resin II).

NR was mixed with other compounding ingredients according to the formulations given in Table I [ASTM D 3182 (1982)]. The optimum cure

time,  $T_{90}$  min (the time required to reach 90% of the maximum torque), and scorch time,  $T_{10}$  min (time required to reach 10% of the maximum torque), of the compound shown in Table I, were determined using a Goettfert Elastograph model 67.85, according to ASTM D 1648 (1981). In compounds 2–6, the amount of hexamethylenetetramine is varied in increments of 0.5 phr (phr = per hundred rubber). In compounds 7–12, the amount of RF resin I is varied by 0.2 phr, keeping the amount of paraformaldehyde constant at 0.4 phr. Dipped cords were bonded with the rubber compounds, and the pull-through load was determined by the H-adhesion test. The H-test was designed to measure the force required to pull a cord in the direction of its axis from a strip of rubber in which the ends of the cords are embedded as per the ASTM D 2138 (1983).

RFL adhesives, with varying amounts of RF resin, were prepared using NR latex (NR latex), as well as vinylpyridine terpolymer latex (VP latex). RF resin I was dried, and a 7.5% solution of the dried resin was prepared in distilled water. RFL adhesives A, B, C, D, and E contain 7, 8, 9, 10, and 11 mL, respectively, of the previously described RF resin I solution mixed with 8 mL NR latex and 10 mL distilled water. The RFL adhesive, based on RF resin I, was matured for a period of 20 h. RFL adhesive F contains RF resin



**Figure 1** Variation of pull-through load with RF resin I to rubber ratio in the NR latex-based RFL adhesive.

II mixed with NR latex and distilled. RF resin II, based on RFL adhesive, was matured for a period of 4 h.

The 1680/2 nylon cord was dipped in different RFL adhesives A–F. The effect of a formaldehyde donor, hexamethylenetetramine, in the rubber compound was studied by varying its amount from 0 to 2.5 phr. The optimum resin-rubber ratio in NR latex and the amount of the hexamethylenetetramine in the rubber compound were determined.

The NR latex in the previously described RFL adhesives was replaced by VP latex to get RFL adhesives I–N. A maturation time of 20 h was given for adhesives I–M, a maturation time of 4 h was given for adhesive N. Studies were repeated with cord 1680/2.

To study the effect of drying and curing temperature on bonding, the drying temperature varied from 140° to 160°C, and the curing temperature varied from 180° to 200°C using the cord 1680/2.

The effect of donor concentration on bonding was also studied by adding a combination of paraformaldehyde and RF resin I into the rubber compound. The concentration of the paraformaldehyde in the compound was kept constant, and RF resin I concentration varied from 0 to 1 phr. Also, the concentration of paraformaldehyde was varied from 0 to 3 phr in the RFL adhesive keeping the concentration of the RF resin I constant.

Compounds 1–12 were compression-molded up to their respective optimum cure times at 150°C

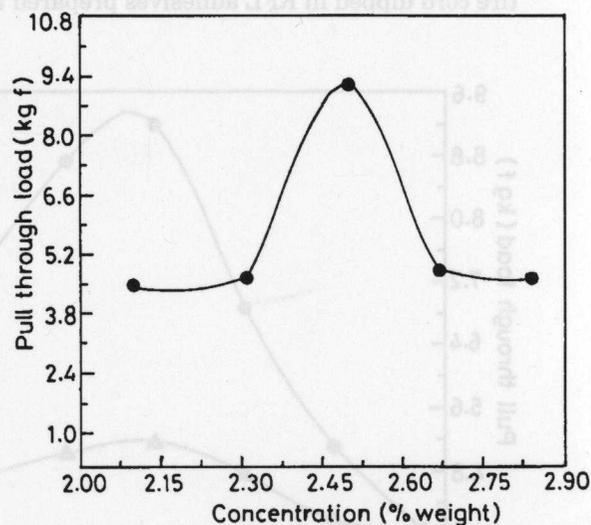
in a laboratory hydraulic press. The tensile strength of these vulcanizates were determined according to ASTM D 412 (1980) using dumbbell-shaped specimens on a Zwick Universal Testing Machine model 1445.

The pull-through load of the above RFL adhesives were measured after aging for a period of 7 days at 30°C.

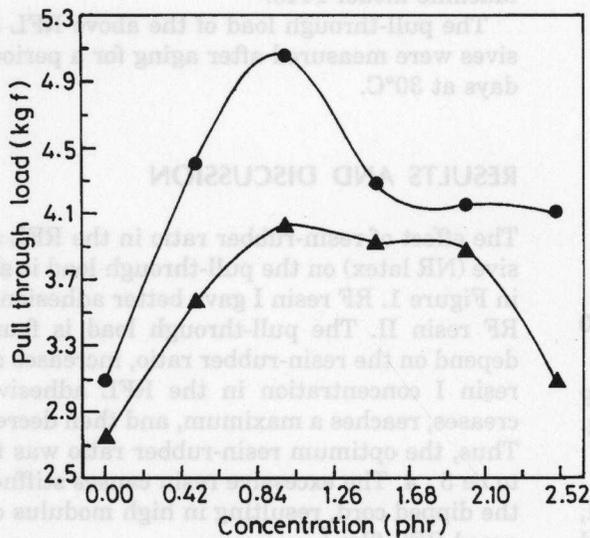
## RESULTS AND DISCUSSION

The effect of resin-rubber ratio in the RFL adhesive (NR latex) on the pull-through load is shown in Figure 1. RF resin I gave better adhesion than RF resin II. The pull-through load is found to depend on the resin-rubber ratio, increases as RF resin I concentration in the RFL adhesive increases, reaches a maximum, and then decreases. Thus, the optimum resin-rubber ratio was found to be 5 : 4. The excessive resin causes stiffness of the dipped cord, resulting in high modulus of the cured RFL film.<sup>7</sup>

When the NR latex was replaced by the VP latex in the RFL adhesive, there was a tremendous increase in the pull-through load (as shown in Fig. 2). This may be due to the exceptionally high stability and polarity of this latex. The optimum resin-rubber ratio was found to be 9 : 8. Thus, it is found that the amount of RF resin I required for VP latex is lower than that required for NR latex. This may be due to the higher po-



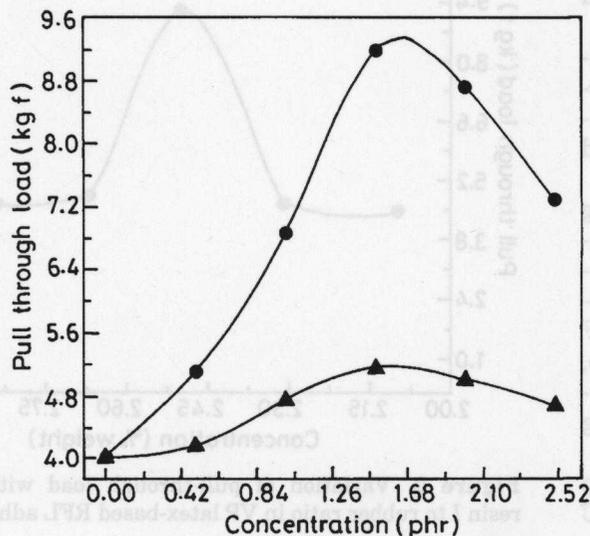
**Figure 2** Variation of pull-through load with RF resin I to rubber ratio in VP latex-based RFL adhesive.



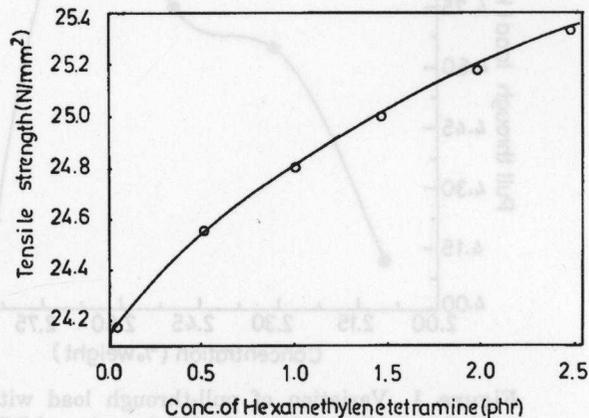
**Figure 3** Variation of pull-through load with hexamethylenetetramine in rubber compound. (●) NR latex/RF resin I-based RFL adhesive. (▲) NR latex/RF resin II-based RFL adhesive.

larity of VP latex, compared with NR latex; also, the pH of the two latex differs.

Figures 3 and 4 show the effect of concentration of hexamethylenetetramine in the rubber compound on the pull-through load for the nylon tire cord dipped in RFL adhesives prepared using



**Figure 4** Variation of pull-through load with hexamethylenetetramine in rubber compound. (●) VP latex/RF resin I-based RFL adhesive. (▲) VP latex/RF resin II-based RFL adhesive.



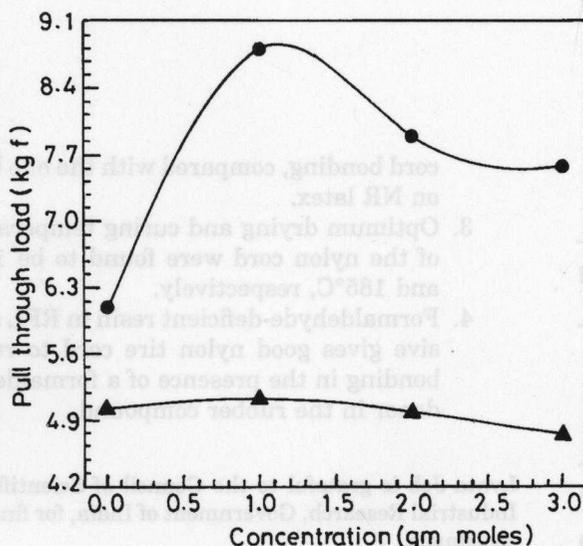
**Figure 5** Variation of tensile strength with concentration of hexamethylenetetramine in the rubber compound.

RF resin I and RF resin II. The optimum amount is found to be 1 phr when NR latex was used in the RFL adhesive (as shown in Fig. 3). When VP latex was used, the optimum concentration was found to be 1.5 phr as shown in Figure 4. This difference in the dependence of adhesion on the copolymer composition may be due to the change of miscibility with the rubber compound, rigidity of the adhesive film, and contribution of covulcanization sites to adhesion.<sup>7-9</sup> The tensile strength of the rubber compounds with the change in the concentration of hexamethylenetetramine is shown in Figure 5. There is a slight increase in the tensile strength when the concentration of the hexamethylenetetramine is increased. This slight increase may not effect the pull-through load of the dipped cord.

Table II shows the variation in the pull-through load with temperature of drying and curing of the nylon tire cord dipped in RFL adhesive. As the temperature increases, the pull-through load increases, reaches a maximum, and then de-

**Table II** Variation of Pull-Through Load with Drying and Curing Temperature

Drying Temperature (°C)	Curing Temperature (°C)	Pull-Through Load (kg f)
140	180	8.15
145	185	9.18
150	190	9.07
155	195	8.77
160	200	8.59

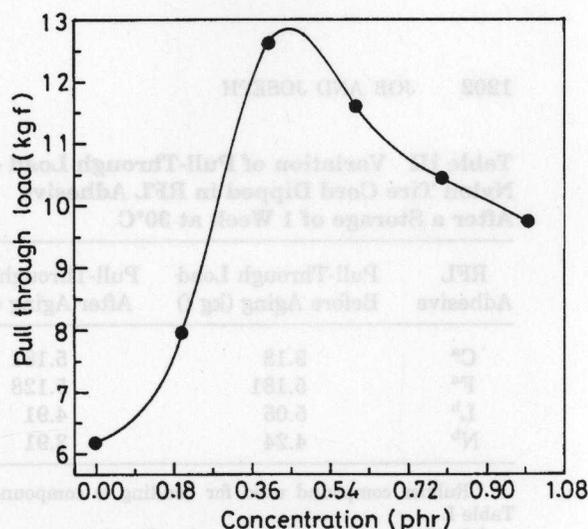


**Figure 6** Variation of pull-through load with donor (paraformaldehyde) in the RFL adhesive. (●) VP latex. (△) NR latex.

creases. This may be due to the highly crosslinked structure formed in the RFL adhesive at optimum heat treatment resulting in a strong interaction with the textile. Weak heat treatment causes the RFL coating to have inferior tensile properties, and there is a lack of interaction with the textile. Strong treatment impairs compatibility with rubber. Both over and under heat treatment cause inferior bonding to textiles.

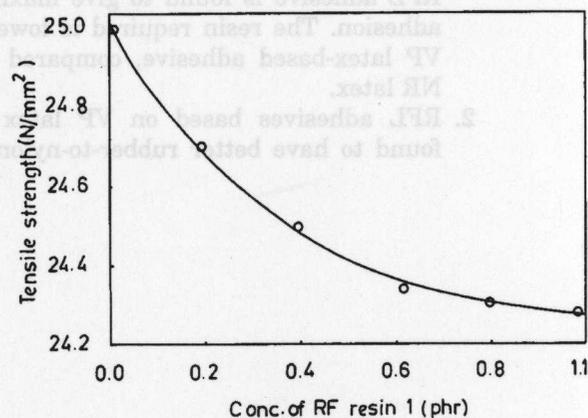
The effect of a donor into the RFL adhesive and the rubber compound is shown in Figures 6 and 7. As the concentration of the donor paraformaldehyde, in the RFL adhesive increases, the pull-through load is found to decrease. The optimum result was obtained when the concentration of paraformaldehyde was 1 mol. Paraformaldehyde is soluble in cold water and is slowly liberated from formaldehyde. This formaldehyde reacts with RF resin in the RFL adhesive. The viscosity of the matured RF solution varies with the RF ratio. It has been reported that, in RF solutions containing two or more moles of formaldehyde per mole of resorcinol, sudden viscosity change occurs at a certain aging time. Ultimately, they geled.<sup>10</sup> It was found that, when the concentration of formaldehyde was decreased, the change of viscosity was depressed.<sup>9,11,12</sup>

When RF resin I and paraformaldehyde were added into the rubber compound, the pull-through load was found to increase with an increase in the RF resin concentration, reaches a



**Figure 7** Variation of pull-through load with donor (RF resin I) in the rubber compound.

maximum, and then decreases (as shown in Fig. 7). The amount of paraformaldehyde was kept constant (0.4 phr). The strength of adhesion was found to be maximum at 0.4 phr of the RF resin. On heating, the paraformaldehyde releases the formaldehyde that reacts with the RF resin to form the methylol group that may react with the active hydrogen of the fiber. A possible ionic interaction or chemical reaction between the RF resin and the rubber compound might have also taken place.<sup>7,11,13,14</sup> The variation of tensile strength with concentration of the RF resin I is shown in Figure 8. There is a slight reduction in the tensile strength as the concentration of the



**Figure 8** Variation of tensile strength with concentration of RF resin I in the rubber compound.

**Table III Variation of Pull-Through Load of Nylon Tire Cord Dipped in RFL Adhesive After a Storage of 1 Week at 30°C**

RFL Adhesive	Pull-Through Load Before Aging (kg f)	Pull-Through Load After Aging (kg f)
C <sup>a</sup>	9.18	5.181
F <sup>a</sup>	5.181	5.128
L <sup>b</sup>	5.05	4.91
N <sup>b</sup>	4.24	3.91

<sup>a</sup> Rubber compound used for bonding is compound 4 in Table I.

<sup>b</sup> Rubber compound used for bonding is compound 3 in Table I.

RF resin I increases, which may not effect the pull-through load of the RFL dipped cord.

Table I shows the scorch time and cure time of compounds containing RF resin I and paraformaldehyde. As the quantity of resin and paraformaldehyde increases, there is only a marginal change in both scorch time and cure time.

Table III shows a decrease in the pull-through load after 1 week of storage at 30°C. This is due to the loss in stability of the RFL adhesive because of the limited pot life of the RFL adhesive.<sup>15</sup>

## CONCLUSIONS

1. An optimum concentration of resin in the RFL adhesive is found to give maximum adhesion. The resin required is lower for VP latex-based adhesive, compared with NR latex.
2. RFL adhesives based on VP latex was found to have better rubber-to-nylon tire

cord bonding, compared with the one based on NR latex.

3. Optimum drying and curing temperatures of the nylon cord were found to be 145°C and 185°C, respectively.
4. Formaldehyde-deficient resin in RFL adhesive gives good nylon tire cord to rubber bonding in the presence of a formaldehyde donor in the rubber compound.

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