

# Bonding of Vulcanized Rubber to Polyester Cord Using RFL Adhesives Modified with Chlororesorcinolic Resin

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**ABSTRACT:** A typical resorcinol/formaldehyde/latex (RFL) adhesive and two modified versions were used to bond a tire body stock (NR/SBR/BR blend) to polyethylene terephthalate (PET) cord. Modifications contained a commercial chlorophenol/resorcinol condensate or a lab-prepared chlororesorcinol/resorcinol condensate (CRA). Standard H-test specimens were prepared by embedding adhesive-coated, heat-treated cords into the rubber and then

vulcanizing. The effect of heat treatment time and overcure on pull-out adhesion was studied. Overcure conditions were used to simulate long service. Pull-out forces increased with longer heat treatment and decreased with overcure. The CRA-modified adhesive gave the highest pull-out forces after overcure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1993–1996, 2004

## INTRODUCTION

Resorcinol/formaldehyde/latex (RFL) adhesives<sup>1–9</sup> and modified versions have been used to bond nylon and polyester cord to rubber in composite structures, such as tires. A typical RFL adhesive suitable for bonding nylon cord to sulfur-vulcanized tire body stocks (TBS) is given in Table I. This adhesive contains two thermodynamically incompatible components: (1) a resorcinol/formaldehyde condensate (hard phase) and (2) a styrene/butadiene/vinyl pyridine (15/70/15) terpolymer (soft phase) latex. The former provides strong bonding to the cord, while the latter covulcanizes with the rubber. The vinyl pyridine comonomer improves the cohesive strength of the adhesive itself—by increasing the interphase adhesion between the hard and soft phases.

In practice, an adhesive is applied by dipping cord into the adhesive and then subjecting the coated cord to a brief heat treatment. The adhesive dries, the RF further reacts, and good bonding between the adhesive and cord develops. Next, a ply is made by covering the cord with rubber in an extrusion or calendaring operation.

Although the adhesive in Table I gives durable bonding between nylon and TBS, the formulation has not been found to give durable bonding between greige polyester cord and TBS. Rather, with polyester, two approaches<sup>8,9</sup> have been used: (1) a two-step method: polyethylene terephthalate (PET) is “adhesively activated” with a proprietary finish (e.g., isocyanate or epoxide) and then a conventional RFL (like that in Table I) can be employed; or (2) a one-step method: the RFL is modified by the addition of an agent such as Denabond K, an oligomeric chlorophenol/resorcinol condensate. The

modified adhesive is used commercially for bonding greige PET to TBS.<sup>10</sup> The one-step method is preferred because it eliminates a process step.

The use of Denabond K as an agent to promote bonding to polyester can be rationalized by considering the interaction between small molecules with chlorine functionality and those with ester functionality. Properties from two areas of physical chemistry provide useful insight: (1) heats of mixing  $\Delta H_m$  and (2) vapor pressures  $p_v$  above mixtures. Although both properties manifest from the interaction of small molecules in solution, this information may, nonetheless, be applicable to adhesion science, as briefly discussed below.

The *Handbook of Heats of Mixing*<sup>11</sup> is a tome that gives  $\Delta H_m$  for a great many combinations of organic liquids. When two nonfunctional, hydrocarbon liquids are mixed,  $\Delta H_m$  is always positive. This indicates a greater interaction energy between molecules of the same kind than between dissimilar ones, i.e., “cohesion is favored over adhesion.” Indeed, this is usually the case even when functional organic liquids are mixed. However, occasionally, even when no chemical reaction occurs,  $\Delta H_m$  is negative—a circumstance that indicates a strong, specific interaction between different molecules. An example is tetrachloroethane and ethyl acetate, which, when mixed 50/50, have a  $\Delta H_m = -2545$  J/mol. Another indication of the strong interaction between these liquids is a large negative deviation from Raoult’s law. A mixture of these two liquids exhibits a vapor pressure that is much less than sum of the product of the mole fraction times the vapor pressure of each component. The abnormally low  $p_v$  of this mixture is due to the strong interaction of dissimilar liquid molecules, which inhibits their entering the gas phase.

Thus, the specific interaction measurable when ester and chlorine functional liquids are mixed may explain the effectiveness of Denabond K as an agent to in-

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TABLE I  
RFL Adhesive Formulation

Materials	Dry part (g)	Wet part (g)
Resorcinol formaldehyde condensate (70% solution)	4.44	6.35
Sodium hydroxide	0.35	0.35
Formalin (37% formaldehyde)	0.36	0.96
Distilled water	—	70.00
Rubber latex (41% solids)	25.62	62.50
Total	30.77	140.16

crease adhesion to PET. A liquid that strongly interacts with PET will diffuse into the fiber—thereby enhancing adhesion.

In this paper, we discuss the synthesis of a chlororesorcinol/resorcinol condensate and its use to modify an RFL adhesive for bonding PET to a tire body stock. Standard H-test specimens were prepared by embedding adhesive-coated, heat-treated cords into the rubber and then vulcanizing. Pull-out forces are compared to those obtained with a simple RFL adhesive and one modified with Denabond K.

## EXPERIMENTAL

### Materials

#### Rubber compound

Masterbatch, a blend of NR/SBR/BR prepared by Specialty Tire of America (Table II); *N-t*-butyl-2-benzothiazolesulfenamide (TBBS; Santocure NS, Flexsys America L.P.); 2-(4-morpholiniothio)benzothiazole (MBS; Santocure MOR, Flexsys America L.P.); and sulfur (Crystex HS OT 20, Flexsys America L.P.) were used. The final rubber compound was prepared on a mill, using the masterbatch in Table II plus 2.65 phr of sulfur, 0.75 phr of TBBS, and 0.60 phr of MBS.

#### Fiber

Greige PET cord, 1300 denier, two ply with  $9.7 \times 9.7$  turns per inch, diameter 0.8 mm (Allied-Signal Inc.) was used.

#### Adhesive components

Resorcinol/formaldehyde condensate (70% in water), Penacolite R-2200 (Indspec Chemical Corp.); resorcinol; 4-chlororesorcinol; formalin (37% formaldehyde in water); sodium hydroxide; and aqueous ammonium hydroxide, 28%  $\text{NH}_3$  (all from Aldrich Chemical); chlorophenol/formaldehyde condensate (20% in water) (DK), (Denabond K; Nagase and Co., Ltd., Osaka Dyestuff); rubber latex, 41% solids, Pliocord VP106, styrene/butadiene/vinyl pyridine (15/70/15) (Goodyear Tire and Rubber Company); and distilled water were used.

The designations used in this study are defined as follows. The first letter indicates the type of base adhesive. R signifies RFL. Subsequent letters designate the additive used to modify the base RFL. DK refers to the chlorophenol condensate (Denabond K), and CRA refers to the chlororesorcinol condensate prepared in our laboratory. The numbers after the letters are the (solids) ratio of DK or CRA to RFL.

## EXPERIMENTAL PROCEDURES

### Chlororesorcinol condensate (CRA) preparation

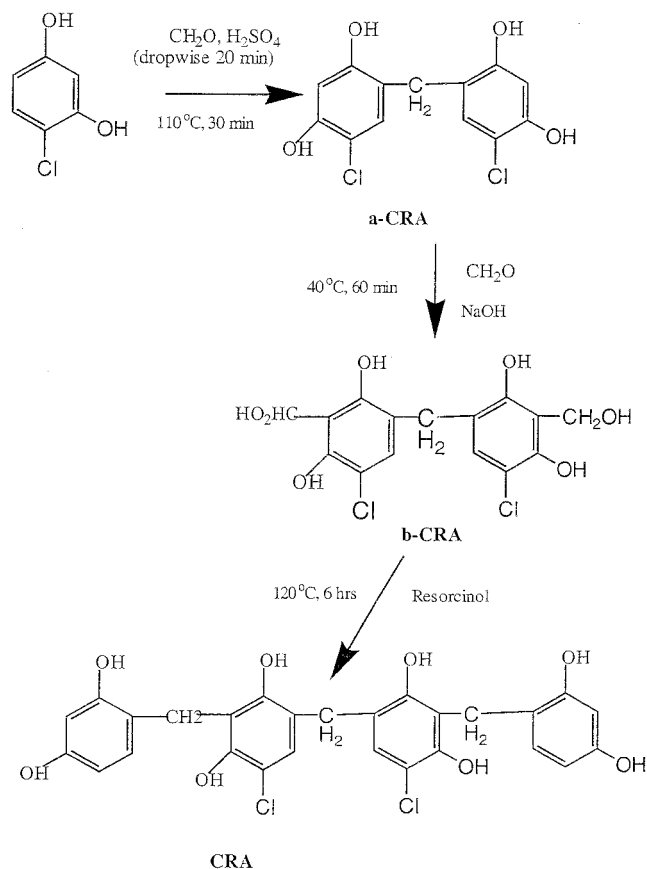
Chlororesorcinol (43.5 g (0.3 mol)) and 0.1 g of sulfuric acid (18.4 mol/L) were added and refluxed in a three-neck bottle in an oil bath under continuous stirring. Reflux temperature was 110–120°C (melting point of chlororesorcinol, 106°C). Formalin (12.16 g (0.15 mol)) was added dropwise to the refluxing mixture over about 20 min. The reaction mixture was refluxed for 30 min at 110°C, giving “a-CRA.” The reaction mixture was then cooled to 40°C, and 70 mL of 1,4 dioxane and 1.4 g of sodium hydroxide in 10 mL of water were added. This mixture was then refluxed, and 13.78 g (0.17 mol) of formalin was added dropwise over 20 min. The reaction mixture was refluxed for 60 min, affording “b-CRA.” Next, 18.87 g (0.17 mol) of resorcinol in 30 mL of water was added to the mixture and refluxed at 120°C for 6 h. The mixture was poured into water to precipitate and washed with hot water three times to dissolve unreacted resorcinol and formaldehyde. The product was dried in vacuum at 30°C for 24 h and was designated CRA. The reaction scheme is given in Figure 1. Percent yield, the weight of CRA divided by the total weight of reactants, was about 75–80%. To make a 20% chlororesorcinol condensate solution, 30 g of CRA was dissolved in 120 g of ammonium hydroxide solution.

### Preparation of adhesive dipping solutions

The RFL adhesive is shown in Table I. After mixing, it was allowed to mature for 20 h at RT before use. To prepare a modified RFL formulation, an additive (DK or CRA) solution (20%) was mixed into the matured

TABLE II  
Tire Body Stock Masterbatch

Materials	Amount (phr)
SMR 20	62.0
SBR 1778	14.0
EBR 8419	24.0
ZnO	3.2
Stearic acid	1.8
Flectol H	0.9
N 650	46
LX 782	3.7
Stanplast 2000	7.6



**Figure 1** Reaction scheme for the synthesis of CRA chlororesorcinol/resorcinol condensate.

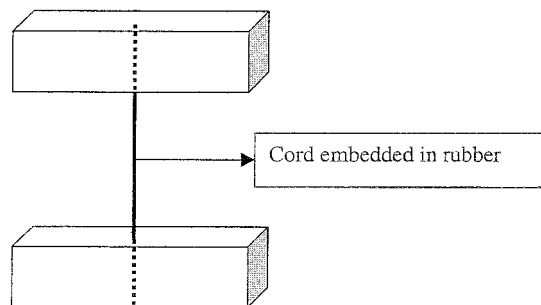
RFL and left for 1 h before use. Modified adhesives are shown in Table III. The concentration of modifier used was that recommended by Nagase and Co. to optimize adhesion to PET with Denabond K.

### H-test specimens

Greige PET cord was dipped into an adhesive solution for 1 min. The coated cord was then treated in an oven at  $233^\circ\text{C}$  for a specified time before preparing test specimens according to ASTM D4776-95a. Samples then were vulcanized for 18.5 min at  $160^\circ\text{C}$ . Figure 2 shows an H-specimen, which was tested at a separation rate of 305 mm/min until cord pull-out. Maximum pull-out forces are reported.

**TABLE III**  
Modified RFL Adhesives

Modified RFL	Amount (g)		
	RFL Solution	DK Solution (20%)	CRA Solution (20%)
RDK0.6	140.16	93.75	—
RCRA0.6	140.16	—	93.75



**Figure 2** H-test specimen.

### Overcure

Some specimens, after the regular cure (18.5 min at  $160^\circ\text{C}$ ), were then overcured (90 min at  $170^\circ\text{C}$ ) to simulate tire service. Six specimens were used in each case and the average results determined.

## RESULTS AND DISCUSSION

### Characterization of chlororesorcinol/resorcinol condensate

Figure 3 shows the FTIR spectrum of CRA. The peak at  $2861\text{ cm}^{-1}$  is due to C-H stretching of methylene groups,  $-\text{CH}_2-$  or  $-\text{CH}_2\text{O}-$ ,<sup>11</sup> indicating the reaction between chlororesorcinol and formaldehyde. The peak at approximately  $975\text{ cm}^{-1}$  indicates reaction between resorcinol and the chlororesorcinol derivative (b-CRA). These results are consistent with those of Chow<sup>12</sup> who reported that PRF (phenol/resorcinol/formaldehyde) resins with resorcinol contents greater than 5% exhibit a strong band at  $960\text{ cm}^{-1}$ . These bands are assigned to in-plane bending modes of hydrogen atoms in the 1,3-substituted benzene ring.

### Pull-out testing

Figure 4 shows the effect of cord heat treatment (before specimen preparation) and overcure (after normal vulcanization) on pull-out forces using the three adhesives (RFL, chlorophenol condensate-modified (RDK0.6), and chlororesorcinol condensate-modified (RCRA0.6)). Curves labeled with the suffix (O) are results for specimens that, after the normal cure at  $160^\circ\text{C}$  for 18.5 min, were then subjected to  $170^\circ\text{C}$  for 90 min (i.e., overcure) before pull-out testing. Overcuring, an anaerobic aging process, has been used to accelerate and simulate degradation of bonding during long-term tire service.<sup>6</sup>

Even though simple RFL adhesives do not provide durable bonding in PET tire body plies, Figure 4, nonetheless, shows that pull-out forces are high initially, if heat treatment is sufficient. With the RFL, pull-out forces  $P$  increase to a plateau of about 170 N when heat treatment times are 3 min or more. For comparison, the pull-out force of an RFL-coated cord

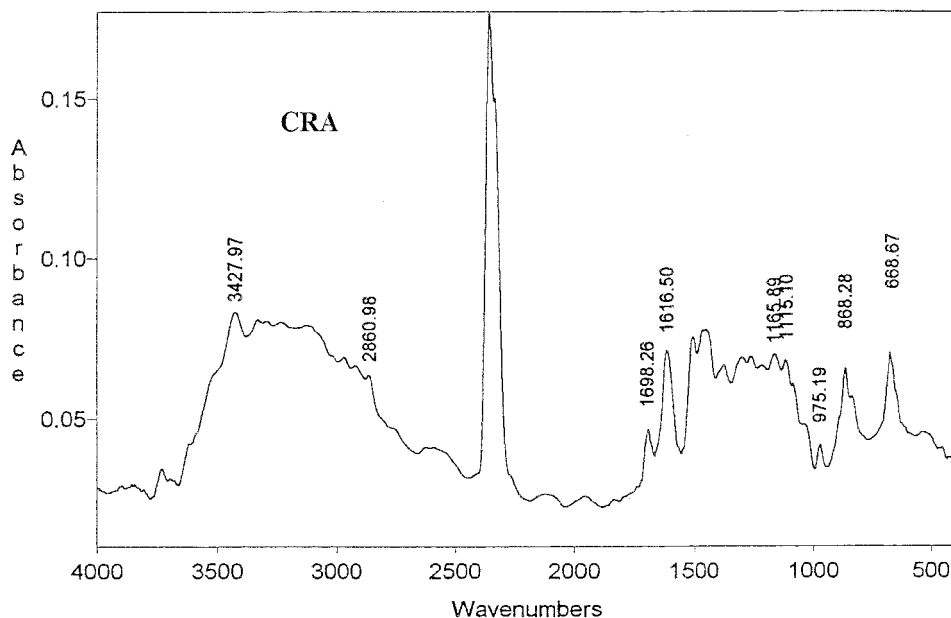


Figure 3 FTIR spectrum of CRA.

without heat treatment is about 66 N, and greige PET cord (no adhesive) gives a pull-out force of about 20 N, a result that agrees with Darwish et al.'s study (20–22 N).<sup>2</sup> Overcure causes a marked decrease in  $P$  to only about 70 N for the RFL-coated cords. This is consistent with the poor durability in service of PET/TBS bonding with simple RFL adhesives.

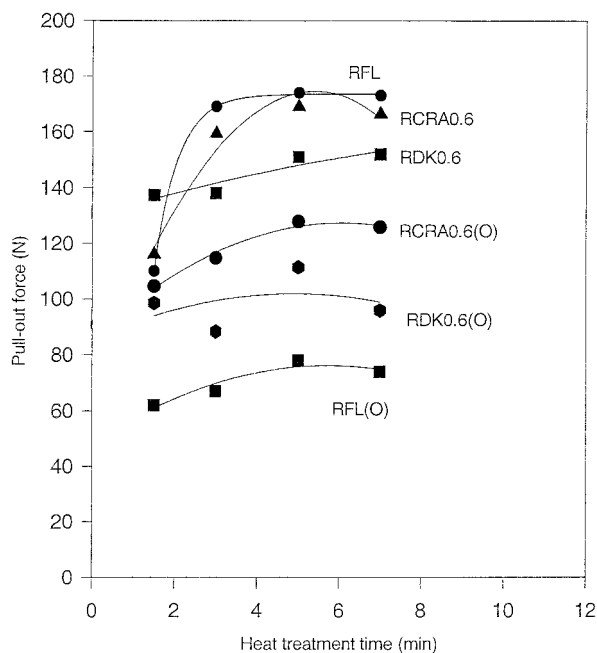


Figure 4 Pull-out forces for the three adhesives. Dipped PET cords were subjected to heat treatment at 233°C before building test specimens and curing normally at 160°C for 18.5 min. Curves labeled with the suffix (O) are results for specimens that, after normal cure, were subjected to 170°C for 90 min (i.e., overcure) before pull-out testing.

After normal cure, the adhesive modified with Denabond K (RDK0–6) gives the highest  $P$  at the shortest heat treatment time of 2 min. However,  $P$  after 7 min of heat treatment is less than that with the RFL. The advantage of DK, and apparently why it is commercially viable, can be seen from the results after overcure, when the DK-modified adhesive is superior to the RFL.

Finally, we consider the RFL that has been modified with the chlororesorcinol condensate prepared in our lab. RCRA0.6 gives pull-out forces after normal cure that increase with heat treatment time in a way similar to that of the RFL adhesive, but, after overcure, RCRA0.6 exhibits nearly twice the  $P$  of the overcured specimens made with the RFL. Furthermore, the CRA-modified adhesive gives values of  $P$  that significantly exceed those found—both initially and upon overcure—with the Denabond K.

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