Adhesion of Kevlar Aramid Cords to Rubber

Y. IYENGAR, *E.I. du Pont de Nemours & Company, Inc., Textile Fibers Department, Wilmington, Delaware 19898*

Synopsis

Adhesion development to Kevlar aramid yarn is discussed in relation to polymer characteristics and parameters of molecular structure that determine specific or entropic interactions with adhesives. The effects of rubber compounding variables on adhesion of Kevlar tire cords treated with epoxy/RFL adhesives were determined using the single-cord pull-out and 2-ply peel adhesion tests, which differ in sensitivity to physical properties (stiffness) of the rubber compound. Kevlar adhesion was unaffected by changes in the curing system (e.g., sulfur level, type of sulfenamide accelerator) used in a high-modulus tire belt compound. Methylene donor/acceptor-type bonding agents in the compound improved the adhesion initially and after exposure of dipped cords to ozone. RFL modifications (e.g., use of preformed versus *in situ* RF resins) improved adhesion. Effects of rubber compounds and adhesives on adhesion are discussed in relation to their chemical and physical characteristics. Lastly, two types of adhesive systems were developed for bonding Kevlar to high-modulus nitrile and neoprene compounds used in hoses. The simpler system involves curing an aqueous epoxy dip and then applying an air-drying, solvent-based cement (polyisocyanate). The other consists of curing two aqueous dips (epoxy/RFL with latex modification).

INTRODUCTION

The exceptionally high strength, excellent dimensional stability, and high-temperature durability of Kevlar aramid yarn make it attractive for reinforcement in critical in-rubber applications such as tires and high-pressure hoses. Good adhesion to rubber is a key requirement in most of the in-rubber applications. However, adhesion development to Kevlar aramid is hindered by the same polymer or yarn characteristics that are responsible for its outstanding mechanical properties of this para-oriented aromatic polyamide. Wilfong and Zimmerman[1] discussed fiber structural factors that control the main tire yarn property criteria. While the excellent high-temperature modulus of aramid is related to its very high glass transition temperature ($T_g > 300°C$), adhesion development is facilitated when T_g is below the temperatures normally used for bonding (i.e., adhesive curing), as is the case with nylon and polyester ($T_g < 100°C$). The effect of T_g on adhesion development was illustrated[2] in the case of another aramid yarn, Nomex, when adhesion to rubber began to increase rapidly as the bonding temperature approached the T_g (~270°C). The high crystallinity and amorphous region orientation needed for the high strength and low shrinkage of aramid also impede adhesion development. Previous work[3] showed improved adhesion of nylon monofilaments after steam treatment, which reduced the amorphous orientation of the surface layer. The aromatic structure of the aramid responsible for the chain rigidity sterically hinders the availability of the hydrogen bonding amide groups beneficial for adhesion development. Adhesion is influenced by parameters of molecular structure that determine specific (e.g., chemical, H bonding) or entropic interaction with adhesives. Adhesion of polyester cords has been explained[4] by entropic interactions involving thermodynamic compatibility.

Journal of Applied Polymer Science, Vol. 22, 801–812 (1978)
© 1978 John Wiley & Sons, Inc.
0021-8995/78/0022-0801$01.00

Yarn processing and treatment have considerable effect on adhesion. The lubricant finish applied on yarns for good processability (low friction) and fatigue (abrasion) resistance should be at a minimal level so it does not interfere with adhesion. Adhesion improvement by surface treatment of polyester yarns by gas plasma has been described in the literature.[5]

Adhesion of polymeric yarns is greatly influenced by the rubber compound. The presence of amines and water in rubber stocks was shown[6] to be detrimental to the adhesion of polyester cords. There are several references in the literature[7–11] on the effect of curing agents and adhesion promoters in rubber on the pull-out adhesion of steel cord and RFL-dipped textile cords.

The work described in this paper discusses the development of adhesion to Kevlar in terms of adhesive/substrate thermodynamic compatibility parameters and establishes the effects of elastomer compounding variables and adhesive modifications on the bonding of aramid cords to high-modulus rubber stocks of the types used in tires and hoses.

Mechanisms of Adhesion Development

Mechanisms of textile to rubber bonding have been reviewed recently.[12–14] Adhesion development can occur by primary bonds, specific physiochemical interactions such as H bonds, or diffusion between adhesion and substrate. Entropic (i.e., diffusion type) bonding becomes important for substrates that have limited capacity for H bonding. For such substrates (e.g., polyesters), thermodynamic compatibility of the substrate and adhesive was shown to be[4] a key requirement for promoting bonding. Such compatibility is attained when the solubility parameters (δ) of substrate and adhesive are matched. The solubility parameter concept for solutions, originally proposed by Hildebrand, was derived based on the "geometric mean rule" of molecular interactions and applies strictly for solvents free from strongly polar and hydrogen-bonding interactions. Application of this concept to explain compatibility/adhesion relationships for poly(ethylene terephthalate) (PET) was considered valid since the PET substrate does not have functional groups capable of such interactions. The thermodynamic compatibility concept can be extended to substrates, such as nylon and aramid, that have hydrogen-bonding functionality by the following considerations from the theoretical work of Gardon[15] on the influence of polarity on the solubility parameter concept.

For noninteracting systems, ΔH_m, the heat of mixing of two components is given by

$$\Delta H_m = V v_1 v_2 (\delta_1 - \delta_2)^2 \tag{1}$$

where V is the total volume of mixture, and v and δ are volume fraction and solubility parameter, respectively. Introducing an interaction parameter ϕ to correct deviations from the geometric mean rule, Walker[16] modified eq. (1) to become

$$\Delta H_m = V v_1 v_2 [(\delta_1 - \delta_2)^2 + 2(1 - \phi)\delta_1 \delta_2]. \tag{2}$$

The free energy ΔF for creating a new interface between two components is given by

$$\Delta F = \Delta H_m - T\,\Delta S \tag{3}$$

where T is temperature and ΔS is entropy change. For ΔF to be negative to favor bond formation [eq. (3)], $\Delta H_m \rightarrow 0$. The magnitude of ΔH_m will depend on δ_1, δ_2, and ϕ, as seen from eq. (2). Gardon's theoretical work showed that $\phi \leqslant 1$ for interaction due to dipole–dipole and induction forces. For noninteracting systems, $\phi = 1$ and hence $\Delta H_m = 0$ when $\delta_1 = \delta_2$ (matching solubility parameters), as shown before.[4]

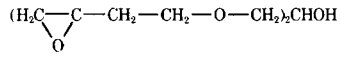
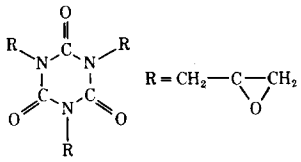
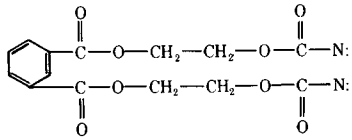
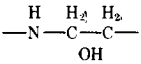
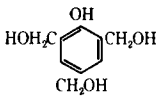
For specific interactions such as hydrogen bonding, no precise theoretical treatment is available. However, considerations based on Flory-Huggin's theory showed[15] that $\phi > 1$ for interactions due to H bonding. When $\phi > 1$ as in hydrogen-bonding systems, ΔH_m in eq. (2) can be zero *even when* $\delta_1 \neq \delta_2$. Consequently, bond formation is favored even when the δ values of the substrate and adhesive are not matched. The fact that a variety of adhesives (polymers) covering a wide range of δ can bond to nylon 66[4] supports this hypothesis and suggests a similar situation for aramid, although hydrogen bonding to the latter may be more difficult due to steric hindrance of aromatic groups.

Two-step adhesive systems (subcoat/topcoat), reported in the literature to give good adhesion to Kevlar, are based on subcoats containing bis(β-azidoformyloxyethyl) isophthalate[17] and polyethyleneimine.[18] In our work, we have attained good levels of adhesion with several epoxides (e.g., diglycidyl ether of glycerin and triglycidyl isocyanurate) as subcoats and an RFL dip containing HAF carbon black as topcoat. Patent literature[19] describes a single-step RFL adhesive containing trimethylolphenol.

The δ values of the active ingredients of the adhesives used on aramid should be useful in defining the mode of adhesion development. The active ingredient is believed to be involved in the initial bond development to the fiber substrate. Consequently, the δ of the active ingredient is considered rather than that of the final cured adhesive coating. Since heat of vaporization data are not available for a direct determination, δ was calculated from molecular structure by two recently published methods. The first method is due to Hoy[20] and is based on the additivity of molar attraction constants ($V\delta$) of atoms and groups proposed originally by Small.[21] Hoy analyzed the molar volume V and cohesive energy density ΔE of 640 organic compounds and derived a new set of molar attraction constants by regression analysis. Fedors' method[22] is based on the additivity of ΔE and V. Constants Δe and Δv for a large number of atoms and groups were derived by Fedors, whose method does not require a knowledge of the density of the compound.

Calculations show (Table I) that the aramid adhesives cover a fairly wide δ range of 22–34 (joules/m^3)$^{1/2}$, suggesting hydrogen-bonding mechanism for adhesion development. The two epoxides and polyethyleneimine have similar δ values. Since aramid does not swell in any common solvents, δ could not be obtained by the swelling technique for polymers. Structure calculations from the two methods gave a δ of 29, which is higher than that for epoxides but close to that for the nitrene and trimethylolphenol, where the reactive methylol is assumed to become CH_2. Hydrogen bonding is possible with the epoxides (OH, $\overset{\frown}{O} \rightarrow$ OH), polyethyleneimine (NH), and trimethylphenol (OH), whereas chemical interaction has been postulated with bisazidoformate by grafting of its thermal decomposition product nitrene with the aromatic nucleus.

TABLE I
Solubility Parameters of Adhesives

Adhesive	Solubility parameter δ, (joules/m^3)$^{1/2}$
DGEG 	23 (H)[a]
TGIC 	23 (H)
nitrene 	27 (F)
PEI 	22 (F)
TMP 	34 (F)
TMP[b] —CH_2OH ⟶ —CH_2	30 (F)

[a] Calculation method: H = Hoy, F = Fedors.
[b] Reactive methylol assumed to become —CH_2.

EXPERIMENTAL

Aramid 1670/1/3 cords were processed with two-step epoxy/RFL adhesives on the single-end Litzler or multiple-end Kidde machines. The epoxy subcoat, coded IPD-24, consisted of a, 2.2% aqueous solution of diglycidyl ether of glycerin (Dow XD-7160) and contained small amounts of NaOH (catalyst) and a surfactant, dioctyl sodium sulfosuccinate (Aerosol OT). The actual formulation used is: epoxide, 2.22; 10% NaOH, 0.28; 5% Aerosol OT, 0.56; water, 96.94.

The topcoat (coded D-5C) used in the work with rubber stocks was a modification of the standard RFL dip, D-5A,[23] containing 10% by weight of an HAF carbon black dispersion (25% solids). The subcoat and the topcoat were cured on the cord for 1 min at 232° and 246°C, respectively, unless otherwise specified. Aramid adhesion to rubber was determined by the 2-ply strip peel adhesion test (ASTM D-2630) on 2.5-cm-wide samples with a cord spacing of 11 ends/cm. Aramid and wire cord adhesion were also determined by the single-cord pull-out test (ASTM D-2229) with a cord embedment of 1.9 cm. The slot-type holding grip in the original ASTM test was modified by cutting a rectangular hole to eliminate stress concentrations near the slot. Peel force of strips in the 2-ply test are expressed in N/cm and the cord pull-out force in N. Appearance ratings of peeled 2-ply samples cover a range of 1 to 5, with 1 signifying clean cord/rubber separation and 5 indicating complete rubber tear.

The most widely used rubber stock for testing was a radial tire belt compound based on 100% natural rubber (Table II) having a high modulus and hot tear

TABLE II
Composition of Rubber Stock (A)

	Parts
Natural rubber	100
HAF black (N-330)	60
Stearic acid	2
ZnO	
Pine tar	5
Tackifier[a]	3
Antioxidant[b]	1
Accelerator[c]	0.7
20% Oiled, insoluble sulfur	3.13[d]
Scorch inhibitor[e]	0.3

[a] Blend of resin acids and amine resin soaps (Natac).
[b] 1,2-Dihydro-2,2,4-trimethylquinoline (Agerite Resin D).
[c] N-Cyclohexyl-2-benzothiazolesulfenamide (Santocure).
[d] 2.5 Sulfur + 0.63 oil (Crystex).
[e] N-(Cyclohexylthio)phthalimide (Santogard PVI).

strength. Two other stocks used in limited tests are high-modulus hose compounds based on 100% neoprene and 100% nitrile rubber. Typical properties of the three stocks are shown in Table III. A very high-modulus NR stock containing a high loading of carbon black and sulfur was also used for single-cord pull-out adhesion tests of aramid and wire cords.

RESULTS AND DISCUSSION

Effect of Rubber Curatives

Accelerators. Two-ply adhesion of aramid cord dipped with IPD-24/D-5C adhesive was tested in belt stocks containing different sulfenamides (morpholinyl, diisobutyl, tertiary butyl) at two levels (0.7 and 1.1 phr) in place of the 0.7-phr cyclohexylbenzothiazolesulfenamide in control stock A. The object was to determine if the different types of amines liberated from sulfenamides would diffuse into the subcoat and influence adhesion by interaction with the epoxide.

TABLE III
Properties of Rubber Stocks

Properties[a]	Stock A (NR)	Stock B (neoprene)	Stock C (nitrile)
Mooney scorch, 132°C, 5-point rise, min	14	20	30
Tensile strength, MPa	21.8	14.3	15
Elongation, %	420	210	200
100% Modulus, MPa	3.9	9.4	7.7
300% Modulus, MPa	15.9	—	—
ODR torque (N m)	7.7	9.2	7.3
Shore A hardness	73	87	80
Tear strength,[b] kN/m			
25°C	—	55	46
140°C	64	—	—

[a] Cure: 160°C/20 min.
[b] ASTM, D-624, Die B, nicked.

The stocks covered a range of tensile strengths (24.1–27.3 MPa), 300% moduli (16.1–19.2 MPa), and ODR torque values (7.6–9.3 N m). Since 2-ply adhesion is sensitive to stock modulus[6] or stiffness, adhesion versus modulus or torque plots should be useful in determining the influence of sulfenamides independent of the effects of stock properties. Adhesion showed a linear decrease (Fig. 1) with 300% modulus or ODR torque, suggesting that the different sulfenamide accelerators give similar adhesion levels after normalizing for stock modulus or stiffness.

Sulfur. Sulfur level in stock is known to strongly influence the adhesion of brass-plated steel cord. Relatively high proportions of sulfur (>3 phr) are needed to give adequate pull-out adhesion to steel wire.[7,8] However, the use of high proportions of sulfur is known to worsen reversion, heat-aged properties, and heat buildup of stocks. Consequently, it is desirable to attain good adhesion in stocks of relatively low sulfur content. Two-ply adhesion of aramid cords decreased (75–63 N/cm) with increasing sulfur level (2.5–4.5 phr) as anticipated from the increased stiffness of the rubber stock (9.1–12 MPa, 200% modulus). Consequently, lower levels of sulfur actually give better adhesion in this type of test.

Pull-out adhesion of aramid (IPD-24/D-5C dip) and wire cords of similar gauge was determined in the standard stock of low sulfur content (2.5 phr) and in a stock with high (7.5 phr) sulfur and carbon black (70 phr) levels. The latter also contained a small amount (0.5 phr) of cobalt naphthenate, reported[8] to improve adhesion to steel wire. Pull-out adhesion was tested initially and after heat aging in air and N_2 for 72 hr at 100°C. In the conventional stock with low sulfur content, aramid cords showed (Table IV) higher adhesion than steel in unaged and heat-aged samples. Adhesion retained after heat aging was 86% for aramid versus 66% for steel. In the stock with high sulfur content, both the cords showed good levels of adhesion in unaged samples but low adhesion in heat-aged (air) samples. The aramid cords from the heat-aged samples were completely rubber covered, suggesting rubber degradation as cause of low pull-out force. Oxidative degradation is indicated since pull-out values are high in N_2-aged samples. In summary, aramid cords show good levels of 2-ply and pull-out adhesion in conventional stocks of low sulfur content, so there is no need to formulate stocks of high sulfur content which have many deficiencies in properties.

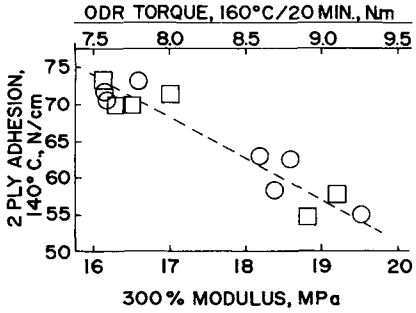


Fig. 1. Aramid adhesion as function of 300% modulus and ODR torque of rubber stocks containing four different sulfenamide accelerators (0.7 and 1.1 phr);)O) torque; (□) modulus.

TABLE IV
Adhesion of Aramid and Steel Cords in Stocks of High Sulfur Content

	Pull-out adhesion (1.9 cm) at 25°C, N			
	Stock A[a]		Stock D[a]	
	Aramid	Steel[b]	Aramid	Steel
Unaged	489	400	498	546
Heat aged, 100°C/72 hr[c]				
Air	422	262	320	338
N_2	484	369	573	556

[a] phr: Stock A = 2.5 S, 60 HAF; stock D = 7.5 S, 70 HAF, 0.5 cobalt naphthenate.
[b] 5 × 0.25 mm, 0.66 mm gauge.
[c] Aramid cords, complete rubber coverage; steel cords, brass showing to various degrees.

Adhesion Promotors In Stocks

Methylene donor/acceptor types of bonding agents were investigated as rubber stock additives to enhance the adhesion of adhesive-treated aramid cords. In preliminary tests, the well-known hexamethylenetetramine (HMT)/resorcinol system gave unacceptably low (<10 min, 5-point rise, 132°C) scorch time when added to the high-modulus belt compound (A). In subsequent work, methoxymethylmelamine/RF resin systems and a simpler single-component bonding agent, described as a "self-crosslinking hexafree RF resin," [24] gave acceptable scorch time and stress–strain properties similar to those of the control stock not containing any additives. Addition of the bonding agents had the desirable effect of increasing the hardness of the stock (+6–10 points, Shore A).

Aramid-dipped cords (IPD-24/D-5C) which had marginal adhesion in the control stock were deliberately selected for demonstrating the effectiveness of bonding agents in improving adhesion. The stocks containing bonding agents gave higher 2-ply peel force and appearance than the control stock with no additive (Table V). Adhesion failure was between the subcoat and topcoat in the control stock, whereas there was predominantly rubber tear in the adhesion-promoting stocks. Apparently, the bonding agents improve the subcoat/RFL topcoat bond, which is the weak link in the IPD-24/D-5C adhesive system.

In further tests, bonding agents in stocks also minimized the adhesion loss of dipped aramid cords exposed to ozone. This adhesion loss is a general phenomenon with all RFL-dipped cords[25] (e.g., nylon, polyester) and is due to impairment of RFL/rubber cocure because of ozone attack on double bonds of the butadiene component in RFL.[26] The stock containing a bonding agent (Table

TABLE V
Aramid Cord Adhesion in Stocks Containing Bonding Agents

Bonding 1agents,[a] phr	Hardness of stocks (Shore A)	2-Ply adhesion, 140°C, N/cm (appearance)
None	69	59 (2+)
3.5 MM + 2.8 RF	77	80 (4)
3.5 HMM + 2.8 RF	79	84 (4)
5 AR	75	82 (4)

[a] MM = Methoxymethylmelamine (Cohedur A); HMM = hexamethoxymethylmelamine (Cyrez 966); AR = self-crosslinking, hexa-free RF resin (Arofene 7209); RF = Schenectady SRF-1501, RF resin.

TABLE VI
Adhesion of Ozone-Exposed Aramid Cords in Adhesion-Promoting Stock

Bonding agent[a]	2-Ply adhesion, 140°C, N/cm (appearance)			% Retained adhesion	
	0 hr[b]	3 hr	8 hr	3 hr	8 hr
No	67 (2+)	44 (1)	18 (1)	66	26
Yes	86 (3+)	68 (3)	39 (1)	80	45

[a] 5 phr Arofene 7209.
[b] Exposure to 50 pphm ozone, 38°C.

VI) gave higher adhesion after ozone exposure (3–8 hr, 50 pphm) than the control stock without any additive. The per cent retained adhesion was also higher in the adhesion-promoting stock, so the improved adhesion after ozone exposure cannot be attributed to the higher initial adhesion. The active low molecular weight constituents of the bonding agent probably migrate into the RFL adhesive layer and minimize adhesion loss by bonding with sites not attacked by ozone.

In summary, bonding agents in rubber stock promote (a) subcoat/RFL bonding to give high initial adhesion and (b) RFL/rubber bonding to minimize adhesion loss due to ozone attack on dipped cords. The addition of bonding agents to rubber stocks offers a practical route to minimize the adhesion loss of commercially dipped fabrics due to environmental exposure. Another route involves[26] addition of migrating waxes to RFL dips.

Cord/Rubber Adhesive Systems

Improved Topcoat for Tire Cords. In early work, aramid tire cords showed marginal adhesion with an epoxy subcoat (IPD-24) and a conventional ammoniated RFL topcoat (D-5A) based on NaOH-catalyzed, *in situ* RF resin.[23] Subsequently, J. L. Brenner of our laboratory showed that addition of HAF carbon black (12% solids basis) to the D-5A dip significantly improved the adhesion. However, in continued use, adhesion with this dip (D-5C) containing carbon black has been borderline and variable. In these cases of deficient adhesion, the failure of peeled 2-ply adhesion samples was predominantly at the subcoat/RFL interface. Obviously, improved bonding of the epoxy subcoat to RFL topcoat was needed.

In recent tests, an RFL topcoat based on a preformed RF resin and containing carbon black has given consistently higher adhesion than D-5C. RFL dips for rayon and nylon based on preformed RF resins were first discussed by Dietrick[27] in 1957. Pamphlets containing dip formulations have been published by Koppers Co., Inc., Ashland Chemical Co., and Schenectady Chemicals, Inc., the manufacturers of preformed resins. The formulation used in our work consisted of Koppers' Penacolite R-2170 preformed resin, NH_4OH or NH_4OH + NaOH to bring pH to ~9.5, vinylpyridine latex (Gen-Tac), HAF carbon black, and formaldehyde to make the overall F/R mole ratio = 1.6 (vs 2.0 in D-5A). The total resin (i.e., preformed resin + HCHO) to latex ratio is 4.85 (vs 5.9 in D-5A). The optimum adhesion is attained with this dip at 7% dip pickup, normally achieved at 25–28% dip solids.

In tests with cords processed several different times on a multiend Kidde

machine, the preformed resin (PFR) dip gave higher peel force and appearance than the D-5C dip initially and after aging the dip (Table VII). A plot (Fig. 2) of adhesion versus dip pickup measured by chemical dissolution of aramid polymer shows the superiority of the PFR dip over D-5C over a wide range of dip pickup levels (4%–9%) and also illustrates the beneficial effect of carbon black in both the RFL dip systems.

Adhesive Characteristics. The curing characteristics and physical properties of the RFL adhesives were determined to see if they correlate with bond strength between cord and rubber. PFR and D-5C dips were dewatered, dried, and cold milled[25] with and without rubber curatives. The addition of curatives is to simulate migration of active ingredients from the rubber to the dip film during the curing of the cord/rubber composite. The proportion of curatives (ZnO, stearic acid, accelerator, scorch inhibitor, and sulfur) corresponded to the concentrations present in stock A. The curing of the adhesive was followed by the oscillating disk rheometer. Stress–strain properties of cured (160°C/20 min) slabs were measured.

The time to attain a specified ODR torque (4.5 N m) at a relatively low cure temperature (127°C) on samples without curatives was used to characterize initial cure. The longer time ($t_{4.5}$, Table VIII) for the PFR (vs D-5C) adhesive suggests a slower initial rate of cure that should be beneficial to adhesion, as found in early work[28] on effect of scorch time of rubber stocks on adhesion. The PFR adhesive showed a higher tensile strength, modulus, hardness, and ODR torque than the D-5C system. In summary, investigations on adhesive characteristics suggest that the slower initial cure rate and better cohesive properties (tensile strength, stiffness) of adhesives may be important in adhesion. Good mechanical prop-

TABLE VII
Aramid Adhesion with Different RFL Topcoats

Topcoat[a]	2-Ply adhesion, 140°C, N/cm (appearance)
(A) Unaged	
PFR	86 (3+ to 4+)
D-5C	68 (2)
(B) Aged 6 days at room temperature	
PFR	93 (4+)
D-5C	61 (2−)

[a] PFR = Preformed resin RFL; D-5C = in situ RF resin RFL.

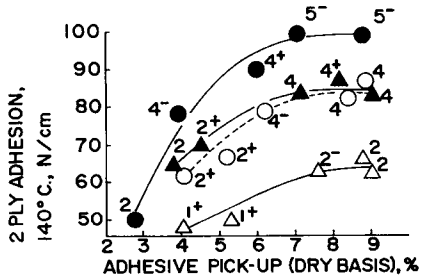


Fig. 2. Aramid adhesion as a function of adhesive pickup (dry basis). RFL topcoats based on: A = preformed resin and B = *in situ* RF resin. Numbers on points are appearance ratings of peeled samples (1 = clean cord, 5 = complete rubber tear). RFL A: (○) no HAF black; (●) with HAF black. RFL B: (△) no HAF black; (▲) with HAF black.

TABLE VIII
Properties of Adhesives

Adhesive	ODR,[a] $t_{4.5}$, min	Tensile strength,[b] MPa	50% Modulus,[b] MPa	Hardness,[b] Shore A	ODR torque,[b] N m
PFR	6	12	6.8	90	7.0
D-5C	2	8.5	4.9	85	5.9

[a] Time to attain 4.5 N m torque, 127°C; no curatives.
[b] Curatives present, 160°C/20 min cure.

erties of the adhesive may be necessary to accommodate the stresses in a composite of materials of very different mechanical properties (e.g., modulus), such as aramid cord and elastomer.

Adhesion to Nitrile and Neoprene Stocks. For consideration of aramid cords in high-pressure (hydraulic) hoses, it was necessary to first demonstrate acceptable adhesion (2-ply at 25°C: $\nless$26 N/cm) in the highly loaded, high-modulus nitrile and neoprene stocks typically used in these hoses. Properties of two such stocks (B and C) are shown in Table III. Simple adhesive systems are preferred for hose application.

Aramid cords gave acceptable adhesion (Table IX) when first heat treated (~220°C/min) with an aqueous epoxy dip on the Litzler. Then an air-drying, polyisocyanate-based cement was applied by a brush during building of 2-ply samples to simulate application of cements on braids or spiral wraps in hose manufacture. The aqueous epoxy dip was similar to that (IPD-24) described for tire cords except that an epoxy cresol novolak (Ciba-Geigy ECN-1299) is used in place of the diglycidyl ether of glycerin (DGEG). Both epoxides give equally good adhesion, but the less toxic epoxy cresol novolak is preferred, especially since subcoated yarns are likely to be handled during braiding operations.

In cases where solvent-based cements cannot be used, acceptable adhesion can be attained by using a two-step aqueous epoxy/RFL dip system. The subcoat used in tire cord, based on DGEG, and the standard D-5A topcoat (no carbon black), modified by substituting a chloroprene latex for part (>50%) or all of vinylpyridine latex, gave adequate adhesion in neoprene stock (Table X). In the nitrile stock, DGEG was ineffective, but good adhesion was obtained with a subcoat containing triglycidyl isocyanurate epoxide[29] and the D-5A topcoat, in which a medium acrylonitrile-content nitrile latex replaced the vinylpyridine latex. Good adhesion is not attained unless the latex is modified to make the topcoat compatible with the elastomer in the stock. That the problem is between the topcoat and rubber is confirmed by the poor adhesion of nylon cord to nitrile rubber when a standard RFL dip based on vinylpyridine latex was used.

TABLE IX
Aramid Adhesion To Hose Stocks With Epoxy/Cement Systems

	2-Ply adhesion, 25°C, N/cm (appearance)	
Cement[a]	Neoprene	Nitrile
No	18 (1)	12 (1)
Yes	32 (2–3)	30 (2–)

[a] Chemlok 402E cement (15% solids) on cords heat treated with aqueous epoxy subcoat.

TABLE X
Aqueous Adhesive System for Aramid Cords in Hose Stocks

Epoxy[a] in subcoat	RFL latex[b] modification	2-Ply adhesion, 25°C, N/cm (appearance)	
		Neoprene stock	Nitrile stock
DGEG	yes	33 (2+)	25 (1)
TGIC	no	—	12 (1)
TGIC	yes	—	39 (4−)
[Nylon	no	→	14 (1)]

[a] DGEG = diglycidyl ether of glycerin (Dow XD-7160); TGIC = triglycidyl isocyanurate (Araldite PT-810).

[b] 75% Neoprene 750/25% vinylpyridine (neoprene stock); 100% nitrile (Hycar 1562) (nitrile stock).

SUMMARY AND CONCLUSIONS

Adhesion development to Kevlar aramid tire yarn is discussed in relation to polymer characteristics and parameters of molecular structure that determine specific or entropic interaction with the adhesive. A thermodynamic concept of adhesive bond development based on solubility parameters that was previously derived for polymers lacking in opportunities for specific interaction was modified by theoretical treatment to include hydrogen-bonded substrates such as polyamides. Unlike the case for noninteracting substrates, matching of polymer and substrate was not a requirement for adhesion development for the interacting substrates. The δ values of adhesives used for aramid cords were calculated from molecular structure by recently published methods and covered a wide range of 22–34 (joules/cm^3)$^{1/2}$, suggesting hydrogen-bonding mechanism for adhesion development. The molecular structure of these adhesives suggests that the adhesives can hydrogen bond or chemically interact with the aramid substrate.

The effects of rubber compounding variables on adhesion of Kevlar tire cords treated with two-step (epoxy/RFL) adhesives were determined using the single-cord pull-out and 2-ply peel adhesion tests, which differ in sensitivity to physical properties (stiffness) of the rubber compound. Kevlar adhesion was unaffected by changes in the cure accelerator system. Good levels of adhesion were attained in stocks of low sulfur content (<3 phr), so there is no need to formulate stocks of high sulfur content that have many deficiencies in properties. Methylene donor/acceptor-type bonding agents in the compound improved the adhesion initially and after exposure of dipped cords to ozone (50 pphm, 3–8 hr). Bonding agents promote both the subcoat/RFL and RFL/rubber adhesion.

An RFL topcoat based on a preformed RF resin and containing carbon black has given consistently higher adhesion than the current RFL based on NaOH-catalyzed *in situ* RF resin. The curing behavior and physical properties of the RFL adhesives appear to be important in adhesion development. Work with dried and cold-milled dips showed that the preformed resin-based dip is initially slower curing and has higher cured strength and modulus than the *in situ* RF resin-based dip. Lastly, two types of adhesive systems were developed for bonding Kevlar to high-modulus nitrile and neoprene compounds used in hoses. The simpler system involves curing an aqueous epoxy dip and then applying an air-drying, solvent-based cement (polyisocyanate). The other consists of curing two aqueous dips (epoxy/RFL with latex modification).

The help and cooperation of the Elastomer Chemicals Department of the du Pont Company, Wilmington, Delaware, in compounding and characterizing rubber stock are gratefully acknowledged. The author wishes to thank J. Vieira for his assistance in this work. J. L. Brenner developed the IPD-24/D-5C adhesive system for aramid tire cords.

References

1. R. E. Wilfong and J. Zimmerman, *J. Appl. Polym. Sci.*, **17**, 2039 (1973).
2. Y. Iyengar, *J. Appl. Polym. Sci.*, **13**, 353 (1969).
3. J. E. Hansen (to E. I. du Pont de Nemours & Co., Inc.), U.S. Pat. 3,650,884 (March 21, 1972).
4. Y. Iyengar, *J. Appl. Polym. Sci.*, **11**, 2311 (1967).
5. E. L. Lawton, *J. Appl. Polym. Sci.*, **18**, 1557 (1974).
6. Y. Iyengar, *J. Appl. Polym. Sci.*, **15**, 267 (1971).
7. K. D. Albrecht, *Rubber Chem. Technol.*, **46**, 981 (1973).
8. M. P. Wagner, Technical Symposium, Akron Rubber Group, Akron, Ohio, 1972–73, p. 13.
9. M. J. Nichols and R. F. Ohm, paper presented at Meeting of the Rubber Division, American Chemical Society, New Orleans, Louisiana, October 7–10, 1975; *Rubber Chem. Technol.*, **49**, 408 (1976).
10. M. I. Dietrick, D. E. Emmert, and D. A. Lederer, paper presented at Meeting of the Rubber Division, American Chemical Society, New Orleans, Louisiana, October 7–10, 1975; *Rubber Chem. Technol.*, **49**, 409 (1976).
11. W. K. Cunningham and D. R. Hart, paper presented at Meeting of the Rubber Division, American Chemical Society, Philadelphia, Pennsylvania, October 15–18, 1974; *Rubber Chem. Technol.*, **48**, 346 (1975).
12. W. C. Wake, *J. Inst. Rubber Ind.*, **7**, 242 (1973).
13. A. G. Buswell and T. J. Meyrick, *Rubber Ind.*, **9**, 146 (1975).
14. F. H. Sexsmith and E. L. Polaski, paper presented at American Chemical Society National Meeting, Philadelphia, Pennsylvania, April 8, 1975; in *Adhesion, Science, and Technology*, Plenum, New York, 1975.
15. J. L. Gardon, *J. Paint Technol.*, **38**, 43 (1966).
16. E. E. Walker, *J. Appl. Chem.*, **2**, 470 (1952).
17. Hercules, Inc., Wilmington, Delaware, Bulletin OPD-21A, *Hercules Emulsion S2070*, 1975.
18. Goodyear Tire & Rubber Company, Akron, Ohio, Goodyear Chemicals Technical Book Facts, *Vinylpyridine VP-1*, 1973.
19. G. E. VanGils and E. F. Kalafus (to The General Tire & Rubber Company), U.S. Pat. 3,888,805 (June 10, 1975).
20. K. L. Hoy, *J. Paint Technol.*, **42**, 116 (1970).
21. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
22. R. F. Fedors, *Polym. Eng. Sci.*, **14**, 147 (1974).
23. The General Tire & Rubber Company, Chemical/Plastics Division, Akron, Ohio, "*Gen-Tac*" *Vinylpyridine Latex*, 1970.
24. Ashland Chemical Company, Columbus, Ohio, Product Bulletin 1159-3, *Ashland Rubber Industry Resins*, May, 1973.
25. H. M. Wenghoefer, *Rubber Chem. Technol.*, **47**, 1066 (1974).
26. Y. Iyengar, *J. Appl. Polym. Sci.*, **19**, 855 (1975).
27. M. I. Dietrick, *Rubber World*, **136**, 847 (1957).
28. Y. Iyengar, *Rubber World* **148**, 39 (1963).
29. K. Zushi, *Chem. Economy Eng. Rev.*, **5**, 36 (1973).

Received November 5, 1976
Revised December 15, 1976