

Tire Cord Adhesion—A TEM Study

GUNILLA GILLBERG and LINDA C. SAWYER, *Celanese Research Company, Summit, New Jersey 07901* and A. L. PROMISLOW, *Celanese Fibers Operations, Charlotte, North Carolina 28232*

Synopsis

Tire cords are commonly bonded to the rubber by means of resorcinol-formaldehyde-latex (RFL) adhesives. Modified systems involving compatible first dip resins or RFL additives are required for standard polyester (PET) cords. The tire composite contains several interfaces at which adhesive failure can be initiated. However, very little is known about the interfaces between the various materials. This paper describes a method which allows ultrathin sectioning and thereby TEM studies of cord sections embedded in rubber. The studies were performed on model samples produced in the laboratory as well as cord sections cut from commercial tires. The TEM micrographs clearly demonstrate the pronounced capillary flow of the RFL solution from outer fiber surfaces to fiber interstices. This flow leads to either no RFL or very thin RFL layers at the outer filament surfaces of the cord even in the case of high RFL levels (6%) and double dipping of the RFL. A qualitative relationship between adhesion and RFL surface coverage has been demonstrated. The RFL interface to rubber, to a second RFL dip, or to predips of other adhesives is generally very distinct and its texture similar to that of the bulk RFL. Also, no evidence for diffusion of either the predip or RFL components into the fiber surface could be found. This indicates that only limited interdiffusion of the polymeric materials of RFL and rubber phases takes place. Texture differences in the RFL and rubber phases between the various tires can be used to characterize the type of system used.

INTRODUCTION

Resorcinol-formaldehyde-latex (RFL) dip systems are the preferred adhesive since 1935 for reinforced rubber products. Rubber will be used in its popular meaning of the compounded elastomer. Typical additives are carbon black, oils, curative ingredients, pigments, etc. Each tire manufacturer has his proprietary rubber. These aqueous dips have the advantage of low viscosity and thus good wetting-out in the beginning of the curing process. When cured, they change to an insoluble system. The elastomer latex gives the adhesive necessary flexibility and reactivity to rubber, while the resorcinol-formaldehyde resins provide the desired heat and fatigue resistance by forming a 3-dimensional network. The presence of unreacted methylol groups in the resin offers reactivity to hydroxyl, amine, or amide groups on the surface of the reinforcing fibers. The mole ratio of resorcinol to formaldehyde, type of catalyst, and type of latex, as well as the ratio of resin to latex are varied in different RFL systems.

The RFL dips were originally introduced for rayon cords and the bonding can be ascribed to the reaction between rayon hydroxyl groups and RF methylol groups.¹ Similarly, the amide groups of nylon can undergo a reaction with these methylol groups,² although physical forces resulting from interpenetration and interlocking of the RF resin with the fiber have also been claimed to be a factor.³ The low level of reactive functional groups in poly(ethylene terephthalate) (PET) leads to unacceptable adhesion when standard RFL dips are used on PET.

TABLE I
 Dip Formulations

	Dry parts/100 RHC		
	Nylon ⁴	Rayon ⁴	PET ¹⁰
Resin master			
Resorcinol	11.0	11.0	16.6
Formaldehyde	6.0	6.0	5.4
Sodium hydroxide	0.3	0.3	1.3
	<u>17.3</u>	<u>17.3</u>	<u>23.3</u>
Total solids (%)	5.0	5.0	6.8
pH	7.0-7.5	7.0-7.5	
R:F Ratio	1:2	1:2	1:1.2
Final dip			
Vinylpyridine latex ^a (15% VP)	100.0	20.0	80.0
Styrene-butadiene latex	—	80.0	20.0
Resin master	17.3	17.3	23.3
Ammonium hydroxide (28%)	11.3	—	—
Total solids	20.0	12.0	20.0
pH	10.0-10.5	8.0-8.5	9.5-10.0

^a Vinylpyridine latex is a terpolymer of butadiene (70%), styrene (15%), and vinylpyridine (15%).

Three different methods are utilized for producing satisfactory adhesion between PET and rubber: double-dip systems, activated RFL systems, and adhesive-activated tire yarns. The double-dip systems involve a two-stage process in which the cord is first treated with an adhesive with good reactivity to PET and then treated with standard RFL. The most commonly used double-dip system is the D-417 adhesive^{4,5} followed by an RFL treatment. The D-417 adhesive consists of a blocked isocyanate and a glycerol-based polyepoxide.

Several activated RFL systems are described below. The Pexul or H-7 adhesive is the reaction product of *p*-chlorophenol with 2 mol of formaldehyde and 2 mol of resorcinol.⁶ It is effective either as a predip or as an RFL. N-3 is the reaction product of triallylcyanurate with resorcinol and subsequently with formaldehyde.⁷ Combined with an RFL, it yields a cost effective single-dip system with excellent adhesion to PET.⁸ Resorcinol-polysulfide can also be used to replace a portion of the RF resin in an RFL formulation.⁹ Materials which decompose to yield isocyanates on heat treatment are also used as RFL additives. Such systems include RF blocked isocyanates¹⁰ and aminimides.¹¹

The third adhesion improvement method utilizes surface-modified PET yarns and standard RFL dips. This surface modification, generally referred to as adhesive activation, is achieved during the yarn manufacturing process.¹² Adhesive-activated yarns continue to penetrate all areas of the rubber reinforcement market. They offer greater design flexibility in terms of oven zone requirements, useful treating temperature range, reduced fume emission concerns, and with the potential for improved end-use performance and reduced dip costs.

The RFL used varies in composition for different cord types. Some typical compositions are given in Table I. The crosslinking degree, and thereby the strength of the RFL, will depend on the F to R ratio. Low F to R ratios, of the

order of 1.2 to 1.4, are generally used for PET, and it is considered that the resultant linear, low molecular weight species are absorbed into the PET surface. To yield optimal adhesion, all outer fiber surfaces which will come in contact with rubber should be coated by an RFL layer. Proper dip penetration and encapsulation of the outer filaments are needed in single-dip systems, while the first dip in the double-dip systems blocks an extensive RFL penetration in these systems. The amount of RFL needed to give adequate adhesion is accordingly less for double-dip systems (2–3%) than for most single-dip systems (5–6%). Dip requirements can be reduced in both nylon and polyester single-dip treatments by cord precompaction achieved by a stretch treatment prior to dip application. This requires at least a two-zone treating unit. Dips with increased viscosity act in two ways to improve dip cost effectiveness.¹³ They reduce excessive dip penetration into the cord bundle and hold the dip more effectively on the convex filament surface where it is required.

Optical photomicrographs of cross sections of RFL-coated cords show the gross distribution of the RFL dip across the cord. The objective of the present work was to see if studies using the higher magnification available with a transmission electron microscope (TEM) could reveal further information about the cord-to-RFL interface and also about the RFL-to-rubber interface. The TEM analyses must be conducted on ultrathin cross sections of cord samples. However, large differences in hardness between the rubber, RFL, and fiber prevent successful thin sectioning. Experiments showed that crosslinking of the RFL with osmium tetroxide (OsO_4), typically used to harden and enhance contrast in rubbers, only partially hardened the RFL. A literature search indicated that the Ebonite treatment of Smith and Andreis¹⁴ could be a possible method.

EXPERIMENTAL

PET cords made from Celanese T-800 and T-811 tire yarns were treated with a standard PET RFL in a single-end Litzler apparatus. In addition, Celanese T-800 cord was also treated with the double-dip system of D-417 and RFL. The cords were embedded in rubber according to standard procedures for making H-test samples. Sections were also taken from the sidewalls of six commercial tires, selected to provide a range of yarn types (PET, nylon, rayon) and rubbers. These tire sections were also characterized for adhesion. The test consisted of peeling the carcass sections to expose the fabric and then measuring the force required to pull single cords from these sections at a 180° angle, both initially and after 2 h of steam (15 psig) exposure. The data presented in Table II has only qualitative significance since tire types, designs, and rubbers are different.

The reaction medium for the Ebonite treatment consists of molten sulfur/accelerator (*N,N*-dicyclohexyl-2-benzothiazolylsulfenamide)/zinc stearate in the weight ratio 90/5/5. Small pieces of coated cord were cut out from the RFL-coated cords, the H-samples, and the tire sections, respectively. Excess rubber was trimmed off in the case of the H-samples and tire sections. Cutting tire cords out of the tire sections is quite difficult and great care had to be taken to avoid tearing at the cord ends. The small cord sections are immersed in the molten sulfur mixture for 8 h at 120°C. Some of the excess sulfur was carefully scraped off from the outer surface before the section was embedded in an epoxy

TABLE II
Description and Qualitative Adhesion for Tires Examined by the TEM Method

Designation type	A 4-Ply bias	B 2-Ply bias	C 2-Ply bias	D Monoply radial	E 2-Ply bias	F Monoply radial
Fiber	PET	nylon	PET	rayon	PET	PET
Assumed adhesive system	D-417	RFL	Act. RFL	RFL	Act. RFL	Act. RFL
Initial adhesion						
Pounds	2.7	5.0	2.7	1.7	0.3	3.4
Rating ^a	5.0	5.0	2.0	5.0	1.2	4.6
Aged adhesion (2 h)						
Pounds	2.1	5.2	2.3	1.6	<0.2	2.6
Rating ^a	5.0	5.0	1.2	4.0	1.0	2.5

^a A 5 rating is equal to all cord surfaces covered by rubber, i.e., cohesive failure in the rubber face. A 1 rating is equal to no rubber on the cord surfaces, i.e., interfacial failure.

resin (Epon 812) according to standard procedures. The sample was then trimmed down, so that a small section containing 8–10 fibers, the RFL layer, and, when present, the rubber layer was obtained. This small section was preferably re-embedded in Epon 812 so that epoxy resin filled up the voids between the loose interior fibers and thereby aided in keeping the sample intact during the sectioning in the ultratome. It became more difficult to obtain good sections when several different materials with variation in hardness had to be sliced. Oils in the rubber, especially in the case of the tire sections, also caused problems. An LKB Ultratome III was used for diamond knife thin sectioning.

Electron microscopy was performed using the JEOL 100CX equipped with a Kevex 7000 energy dispersive X-ray spectrometer. This system permits EM imaging and elemental analysis down to sodium. The lateral resolution for elemental mapping of thin sections in this instrument is about 0.1 μm rather than the 1 μm area sampled in a scanning electron microscope. Line scans and similar techniques can also be used for identification, even though elemental mapping of fine structure at high magnification cannot be performed accurately. Alternate techniques, such as selected area electron diffraction, have lateral resolution limits of 1 μm , excluding identification of fine structures. Thus, TEM investigations generally rely on morphology studies, based on scattering variations, confirmed by X-ray analysis.

Accordingly, the structural TEM investigations rely on the fact that heavy elements cause greater electron scattering than light elements. Areas with high concentration of heavy elements will, therefore, appear darker on the TEM micrographs. High sulfur concentrations, darker areas, can be expected in regions which originally contained a high degree of unsaturation, e.g., the latex in the RFL. The presence of sulfur can also be confirmed by X-ray analysis. Since the diffusion of sulfur into PET is relatively slow, the PET areas can be expected to be light in the micrographs.

RESULTS

The simplest case, an RFL-coated cord, will be used as the first illustration of the TEM method. The cord is made from an adhesive activated tire yarn, T-811, with a 6% dpu of a standard RFL. The RFL treatment was made in a laboratory Litzler machine. The TEM micrographs in Figure 1 show the RFL distribution on one of the outer fibers of the cord. The RFL dip appears dark gray and the PET fiber white, suggesting an even diffusion of sulfur/zinc into the RFL but not into the PET fiber. Areas with high scattering power are seen at the RFL/Epon interface and also immediately below the skin [arrows, Fig. 1(A)]. These areas most probably represent a local high concentration of sulfur (or zinc). A concentration gradient showing higher concentrations of sulfur close to the RFL surface can arise if the RFL vulcanization during the Ebonite treatment takes place too fast. The presence of voids due to bubble formation in the RFL during the RFL curing would also yield areas for a high concentration. Spherical areas with very low scattering are seen in the interior of the RFL. The high contrast to the surrounding matrix indicates that the spheres are holes in the sample, the result of either gas bubbles in the RFL or removal of latex particles, not sufficiently crosslinked, during the sectioning. The gray and black bands on the PET surface are a result of folds formed during the sectioning.

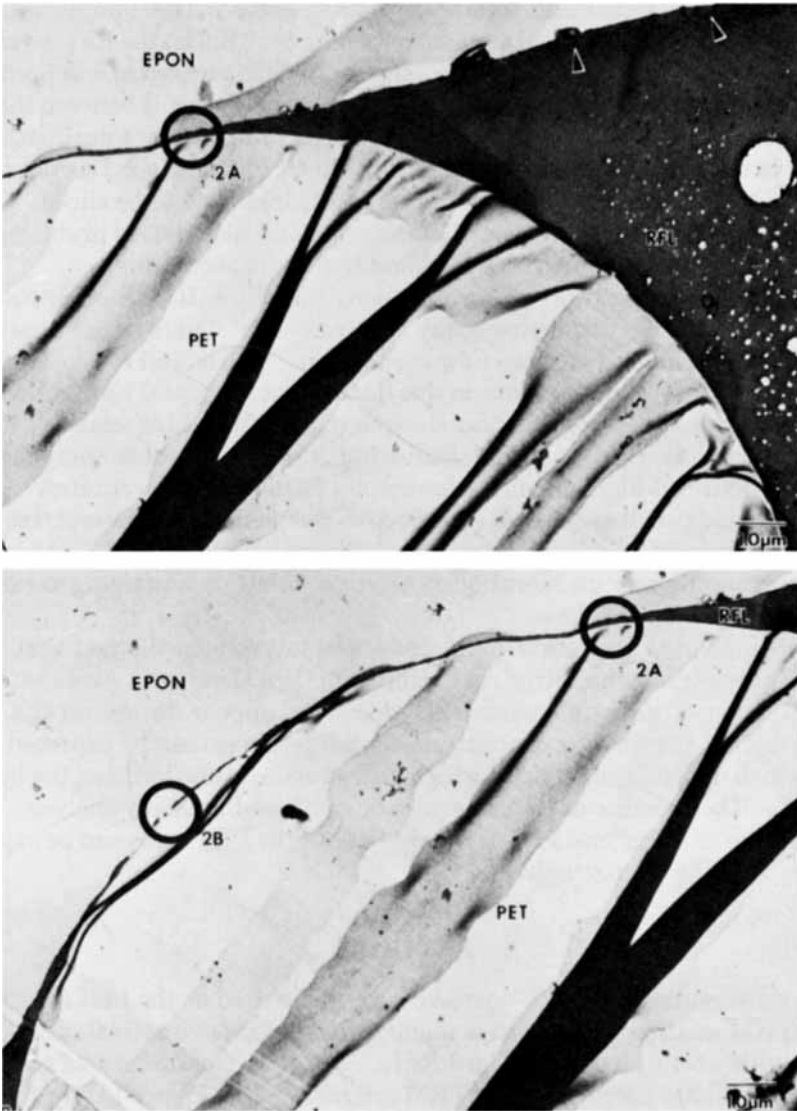


Fig. 1. TEM photomicrographs of an outer fiber of an adhesive-activated polyester cord (T-811) with 6% dpu of RFL. The gray RFL layer thins out significantly at the outer fiber edges (areas 2A and 2B). Dense circular areas at and near the RFL edge (arrows, A) are sulfur/zinc from Ebonite treatment. White areas in the RFL are holes (gas bubbles or removed latex particles).

Figure 1(B) shows the continuation of the outer periphery of the fiber in Figure 1(A). (The circle 2A encloses the same area in the two micrographs.) It is very evident from the pictures that most of the RFL is located in the interstices between the fibers [to the right in Fig. 1(A); to the lower left of Fig. 1(B)] and that the RFL layer thins out significantly on the outer convex fiber surface. Figure 2 shows a higher magnification view of areas 2A and 2B in Figure 1. The outer layer of dense sulfur/zinc particles at the RFL/Epon interface are clearly seen. The micrographs demonstrate that in some areas the thinning of the RFL is so extensive that the RFL layer becomes discontinuous [arrows in Fig. 2(B)]. The

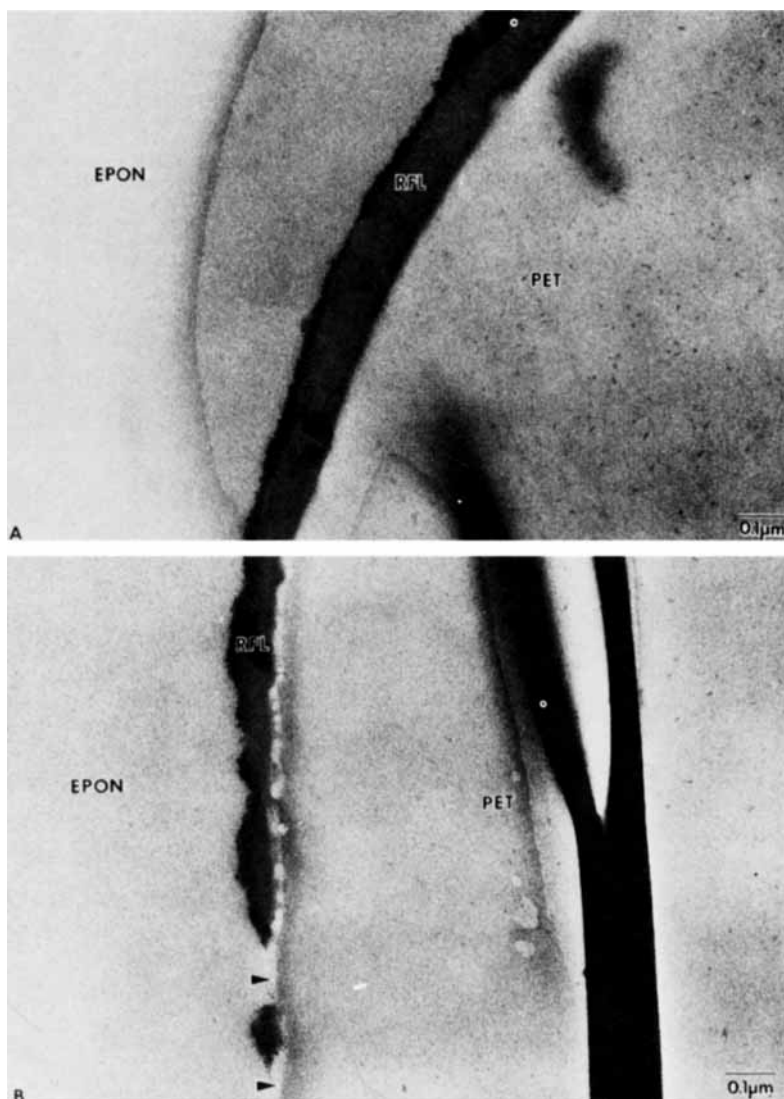


Fig. 2. TEM photomicrographs of higher magnification views of regions 2A and 2B in Figure 1. The RFL layer becomes discontinuous in some areas (arrows, B). Dense outer layer on the RFL is excess sulfur from the Ebonite treatment.

RFL layer adheres well to the PET, and no dense sulfur particles are observed at the PET/RFL interface.

The micrograph in Figure 3(A) shows a cross section of the previous cord embedded in rubber according to standard procedures for H-test samples. The capillary transport of most of the RFL from the outer convex fiber surface to interstitial regions is very clearly revealed in the picture. The RFL forms a very distinct interface to the rubber, and the obvious contrast between the rubber and RFL implies that no extensive interdiffusion of polymer has taken place. Figure 3(B) shows the rubber/RFL and RFL/PET interfaces at a higher magnification. Dense sulfur particles are seen in the RFL up to the PET interface

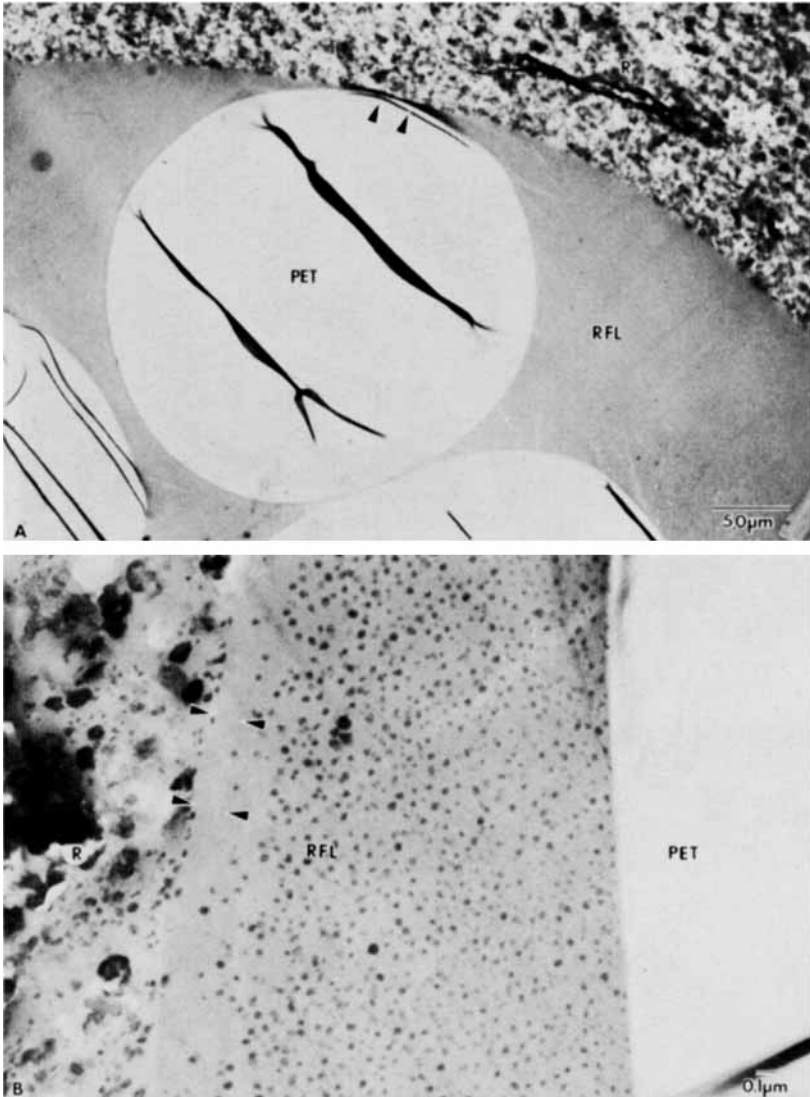


Fig. 3. TEM photomicrographs of an adhesive activated polyester cord (T-811) with 6% dpu of a standard RFL embedded in rubber (R). The tendency of the RFL to thin out at outer fiber surfaces (arrow, A) is clearly demonstrated. The RFL/rubber interface is very distinct. Fine dense particles of sulfur are seen in the RFL except for a zone next to the rubber interface (arrows, B).

(a fold of PET is seen at the interface). The sulfur specks are absent from the RFL surface layer next to the rubber.

The poor adhesion between non-adhesive-activated PET and standard RFL dips is illustrated in Figure 4. It was not possible to obtain any sections of this sample in which void spaces between the fiber and RFL [arrows, Fig. 4(A)] were absent. The easy tearing at the fiber and RFL interface during the sectioning is indicative of poor adhesion. A further confirmation of this observation is the presence of a high concentration of sulfur next to the fiber surface [Fig. 4(B)] confirmed by energy dispersive X-ray analysis (insert, Fig. 4). Evidently, sulfur very easily diffused in at the RFL/PET interface in this sample, while no sulfur layer existed in the case of the adhesive activated cord [Fig. 3(B)]. X-ray analysis

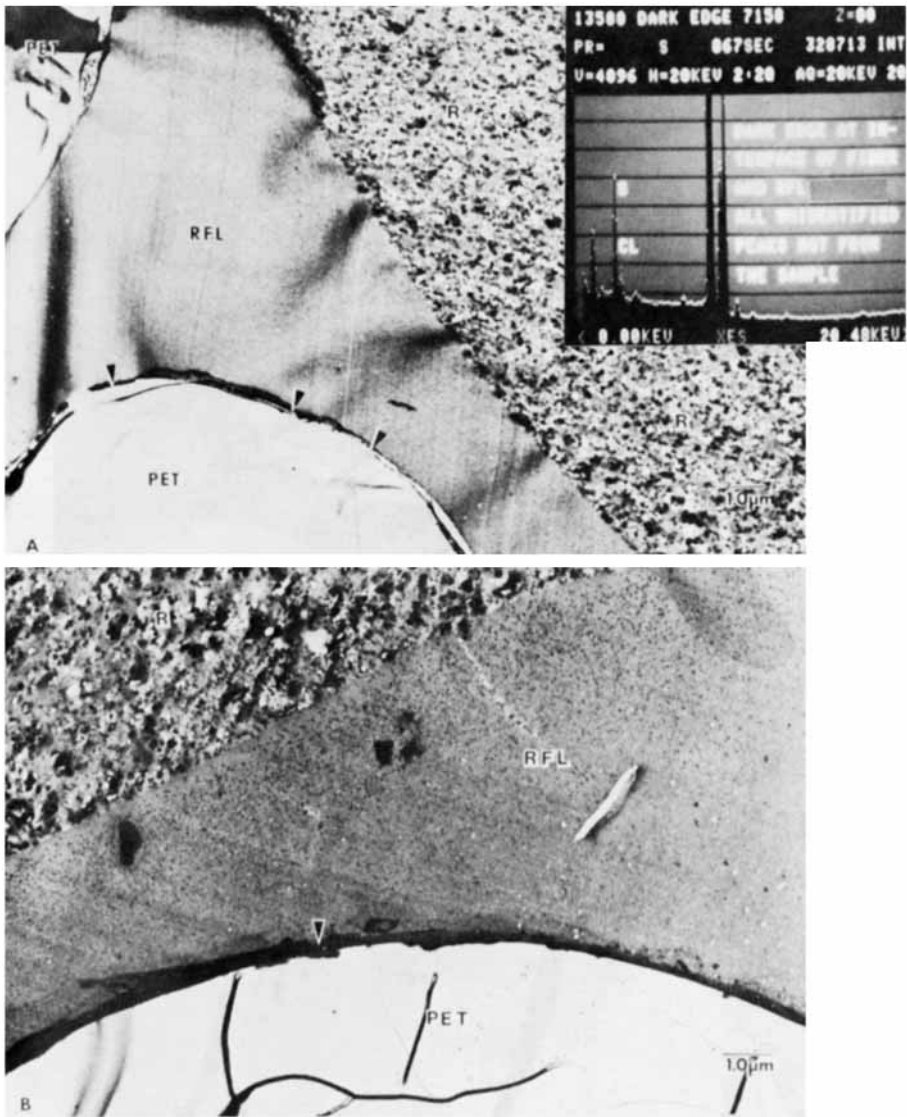


Fig. 4. TEM photomicrographs of a standard polyester cord (T-800) with 6% dpu of a standard RFL in rubber (R). Note the tears between the RFL and the fiber (arrows, A) and the presence of a dark band (arrow, B) at the PET/RFL interface in this sample. The presence of the dark sulfur band (X-ray analysis, insert, A) is indicative of poor adhesion.

also confirmed the absence of sulfur in the PET fiber and enrichment of sulfur and zinc in the rubber layer.

Predipping this non-adhesive-activated cord with 1% D-417 gives a cord surface which binds well to the standard RFL (Fig. 5). The interface of RFL to PET is generally free from voids, and no excess sulfur is seen at this interface. An excess of the predip is seen at fiber interstices and also intermittently along the fiber surface [arrows, Fig. 5(A)]. Although the layer of predip thins out and becomes discontinuous [Fig. 5(B)], the absence of a sulfur layer next to the fiber surface indicates an adhesion modification of the whole fiber surface. Diffusion of the predip into the PET surface cannot be seen.

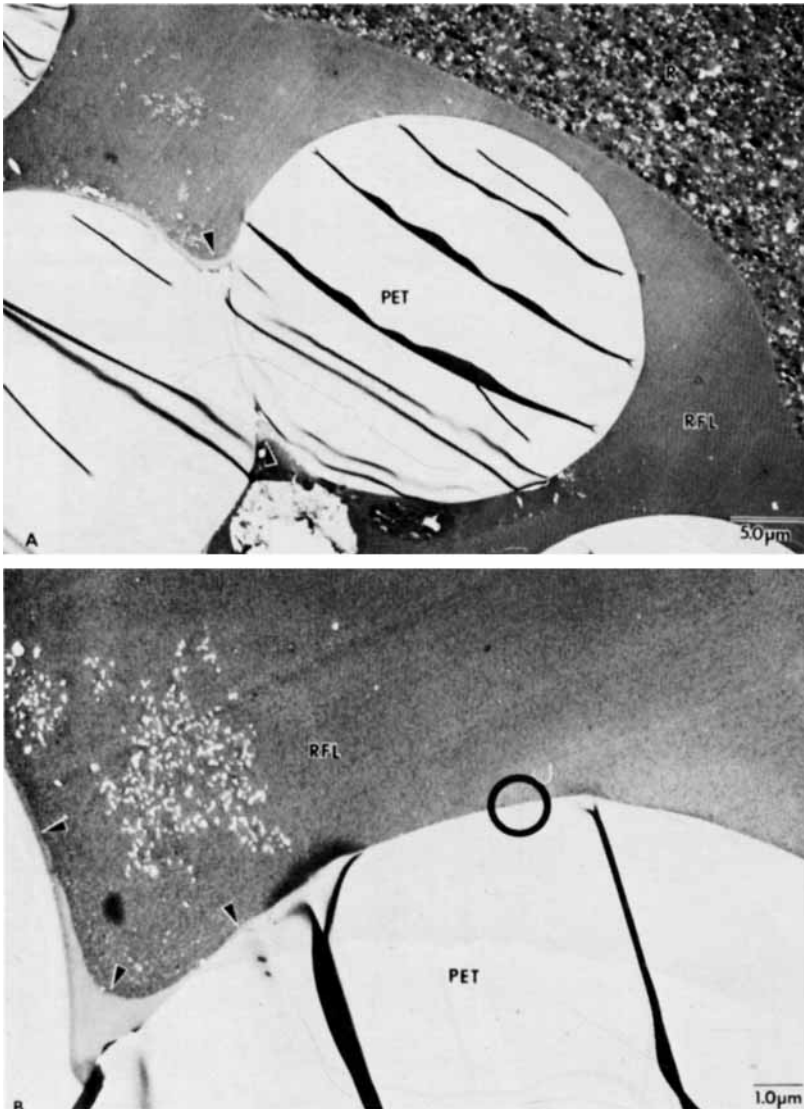


Fig. 5. TEM photomicrographs of a standard polyester-reinforced cord (T-800) treated with a double-dip system (1% D-417 + RFL). The excess predip is seen in the fiber interstices (arrows, A) and also along the fiber surface (arrows, B). Some areas, (circle, B) show no signs of the predip. However, the absence of a sulfur band suggests a surface modification by the predip.

We decided next to use the TEM method for investigation of some commercial tires (Table II). Tire A (Table II) has PET cords in a four-ply bias construction. The cords were treated with the D-417 double-dip system. The TEM micrographs in Figure 6 clearly show the presence of two dips, both of them concentrated at the fiber interstices. The RFL used for the tire was different from the dip used in the previous laboratory sample. Denser globules of varying size are seen in this RFL, which also yields a more diffuse interface to the rubber.

Figure 7 shows a two-ply, nylon bias tire (tire B). The general thinning out of the RFL at outer fiber surfaces is also seen for the nylon cord. High magnification views of the nylon fiber/RFL interface (not shown) are very similar to those of adhesive-activated PET. Accordingly, the TEM investigation does not

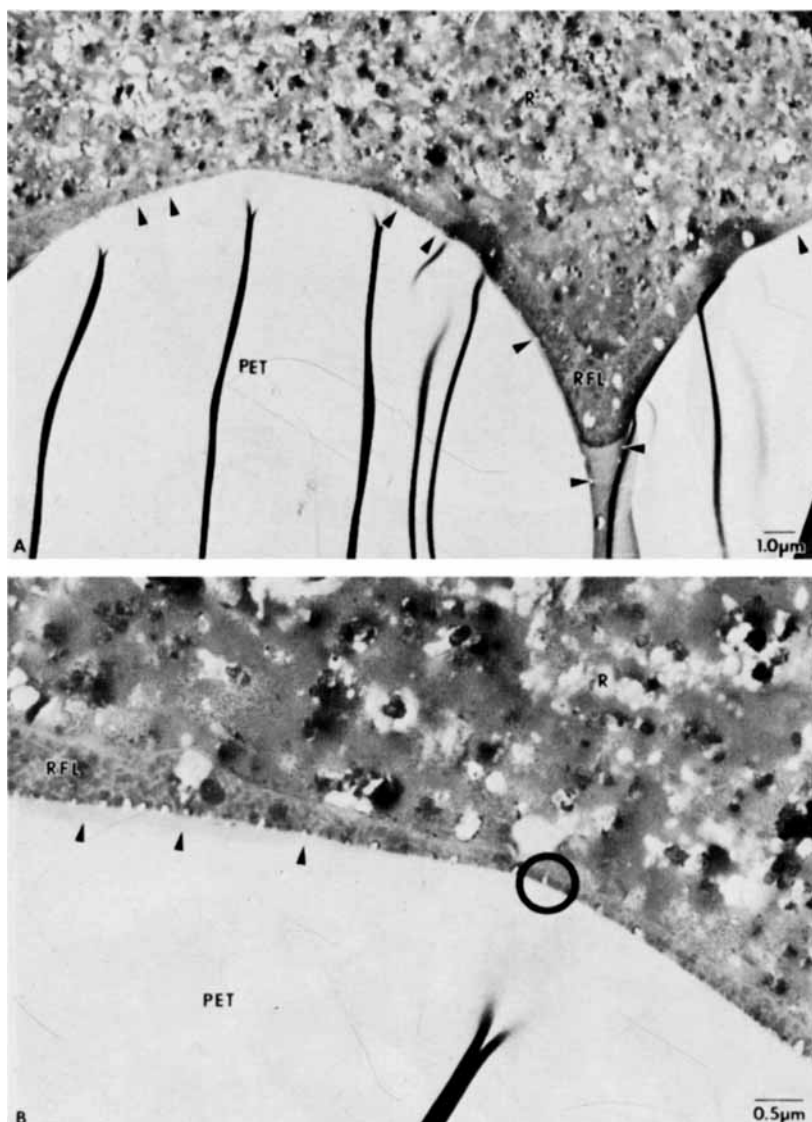


Fig. 6. TEM photomicrographs of a cord section cut from tire A, a four-ply-bias polyester-reinforced tire, presumably with a D-417 double-dip adhesive system. The predip (arrows, A and B) and the RFL are concentrated at the fiber interstices. Some outer fiber surfaces seem void of predip (circle, B). Dense globules of varying size are seen in the RFL. The RFL/rubber interface is more diffuse than in Figures 3–5.

show if any penetration of RF resin into the nylon has taken place. The dark band at part of the nylon/RFL interface in Figure 7(A) is a shadow caused by the sectioning. Higher magnification views show that a thin continuous RFL layer exists all along the fiber surface. However, the RFL dip in tire B is different from the RFL dip used for the PET-cord-reinforced tire, tire A. Thus, the micrographs in Figures 7(A) and 7(B) of tire B do not show the irregular globules in the RFL layer but rather the presence of sulfur specks and clusters of small carbon particles [single arrows, Fig. 7(B)]. The carbon black particles in the rubber have a larger size [double arrows, Fig. 7(B)] than those in the RFL. The interface of the nylon RFL to the rubber is very distinct.

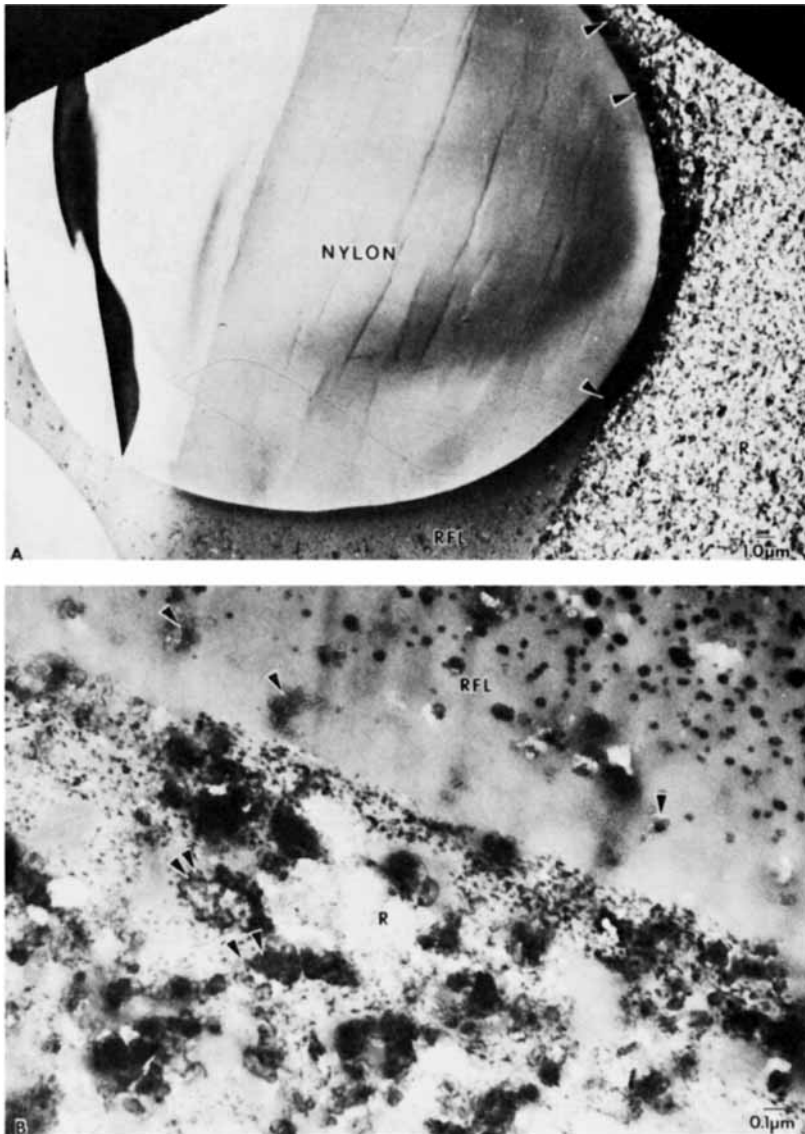


Fig. 7. TEM photomicrographs of a cord section cut from tire B, a two-ply-bias nylon-reinforced tire. The RFL is mainly located in the fiber interstices and only forms a thin layer on outer fiber surfaces (arrows, A). The RFL/rubber interface is very distinct (B). The RFL contains fine carbon black particles (single arrows, B) and sulfur specks while the carbon black in the rubber is larger (double arrows, B).

Figure 8 shows TEM micrographs of cord sections taken from tire C, a two-ply bias tire with PET cord and an activated RFL dip. The cord section in Figure 8(A) shows very little dip at the outer cord surface. However, a thin continuous layer seems to be present on all fiber surfaces [arrows, Fig. 8(A)]. (The very pronounced fold bands on the PET surface indicate high shear during the sectioning. The tears between the rubber/cord interface are rather a result of this high shear than of a poor adhesion.) Higher magnification views [Figs. 8(B)–(D)] confirm the presence of a separate phase next to the fiber surface (arrows) as well as in the form of globules [Fig. 8(B)] and layers next to the rubber phase [Fig.

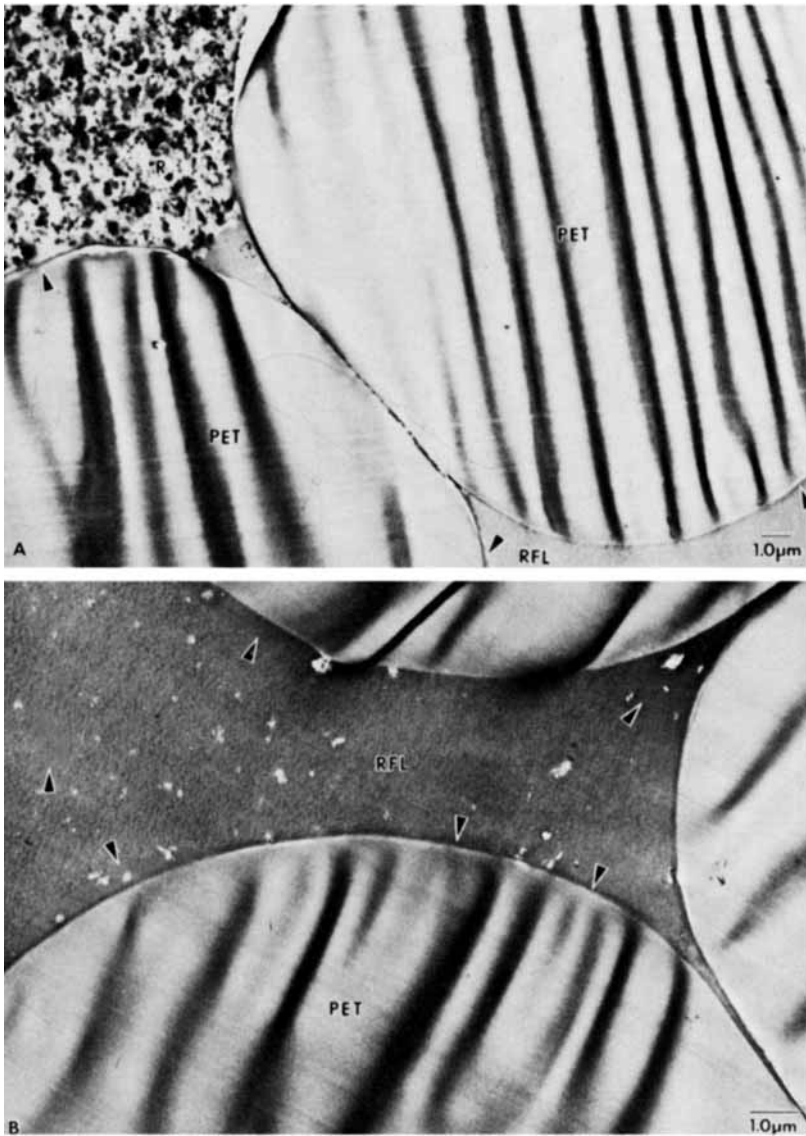


Fig. 8. TEM photomicrographs of a cord section taken from tire C, a two-ply-bias polyester-reinforced tire, presumably with an activated RFL dip. Figure 8(A) shows that most of the RFL is located in interior interstices but also shows the presence of a thin dense layer along all fiber surfaces (arrows). Larger amounts of this denser material are seen at fiber interstices, as thicker layers or as globules (arrows, B). The denser material is also found adjacent to the rubber (arrows, C). This dense phase seems to form an almost continuous layer along the PET surface (D) and most probably provides the adhesion to the polyester.

8(C)]. This separate phase, which appears denser on the micrographs, might be an excess of the adhesion activating chemicals, partially phase-separated out during the film formation of the RFL latex.

Tire D is a rayon-reinforced monopy radial tire. It is very difficult to obtain sections of this tire for the TEM investigations without extensive tear between the fibers and surrounding matrix. The overview given in Figure 9(A) clearly shows the irregular cross section typical of the rayon fibers. The RFL forms a

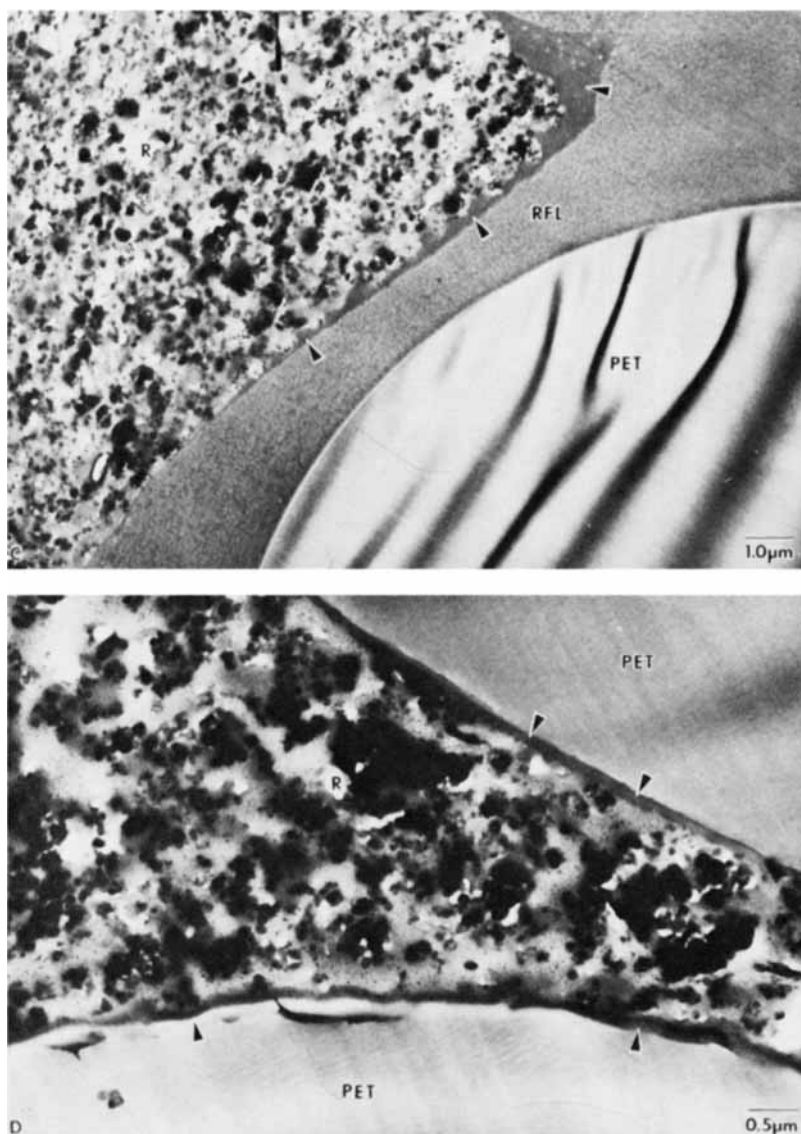


Fig. 8. (Continued from the previous page.)

diffuse interface to the rubber which is characterized by less dense material than the rubber in the preceding micrographs. Large globules with a lower density are seen within the RFL [Fig. 9(A) and arrow, Fig. 9(C)]. A layer of more dense material is generally seen at the fiber/RFL interface, and this layer, in some areas, borders directly to the rubber [arrows, Fig. 9(B)]. However, this denser layer is not always present, as illustrated in Figure 9(C).

Figure 10 shows TEM photomicrographs of a cord section taken from tire E. This tire has a two-ply PET fabric bias construction. Figure 10(A) shows the interstices between two outer PET fibers (the black bar is a part of the grid which is used to hold the sample). The photomicrograph shows that this cord had been dipped twice with RFL as shown by the interface between the RFL's (arrows). Higher magnification views of the two RFL's show that the RFL first applied contains carbon black particles [arrows, Fig. 10(B)] and has a well-resolved re-

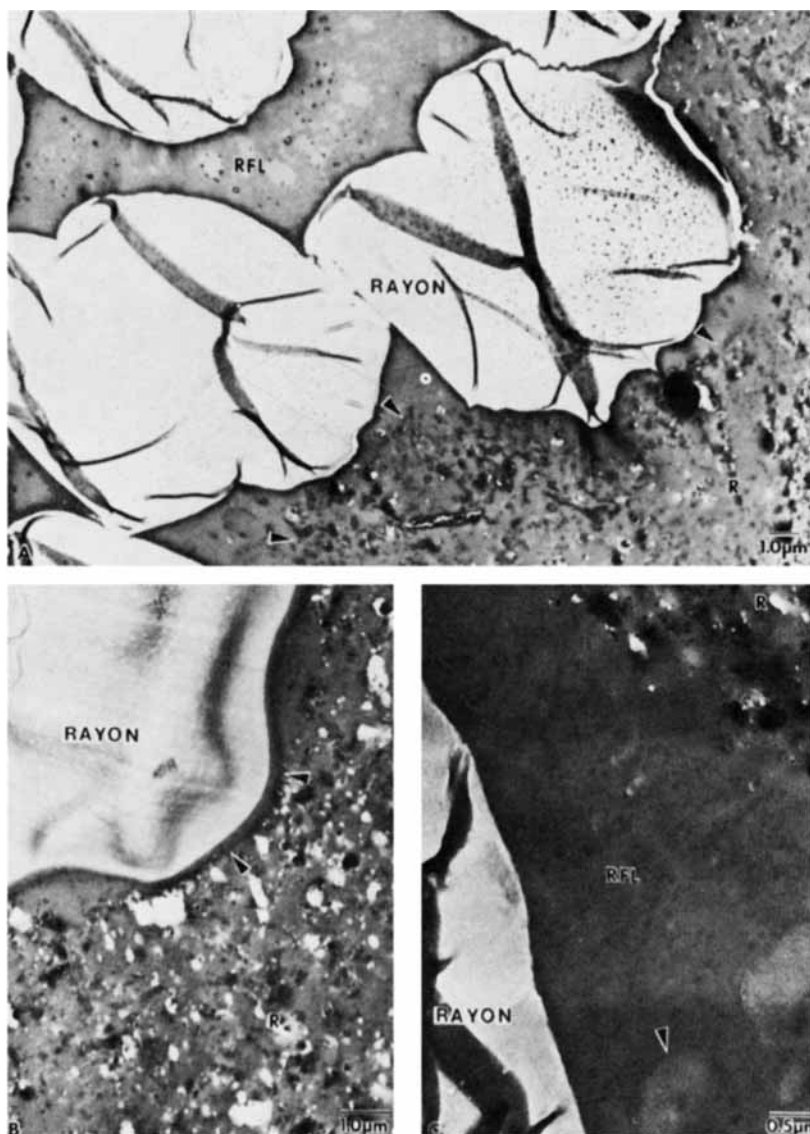


Fig. 9. TEM photomicrographs of a cord section taken from tire D, a monply radial rayon-reinforced tire. The rayon RFL shows a diffuse interface to the rubber (arrows, A), globules of low density (A and C), and generally a dense layer next to the fiber surface (A and B). The dense layer is sometimes adjacent to the rubber (B), but it is not always present (C). The rubber contains only small amounts of dense material.

ticular pattern. The second RFL contains the sulfur specks seen in other PET RFL's [Fig. 10(C)]. The interface to the rubber is very distinct, and the outer layer of the RFL shows the general low concentration of sulfur. Some cords have no RFL or only a very thin RFL layer in spite of the doubledipping [double arrows, Fig. 10(D); single arrows, Fig. 10(E)]. Observation of a second section suggested that a different construction was present. Optical reflected light study of the whole cord cross section [Fig. 11(A)] followed by higher magnification transmitted OM [Fig. 11(B)] and TEM [Fig. 11(C)] showed a three-ply construction with plies 1 and 3 probably PET tire yarn and ply 2 probably rayon.

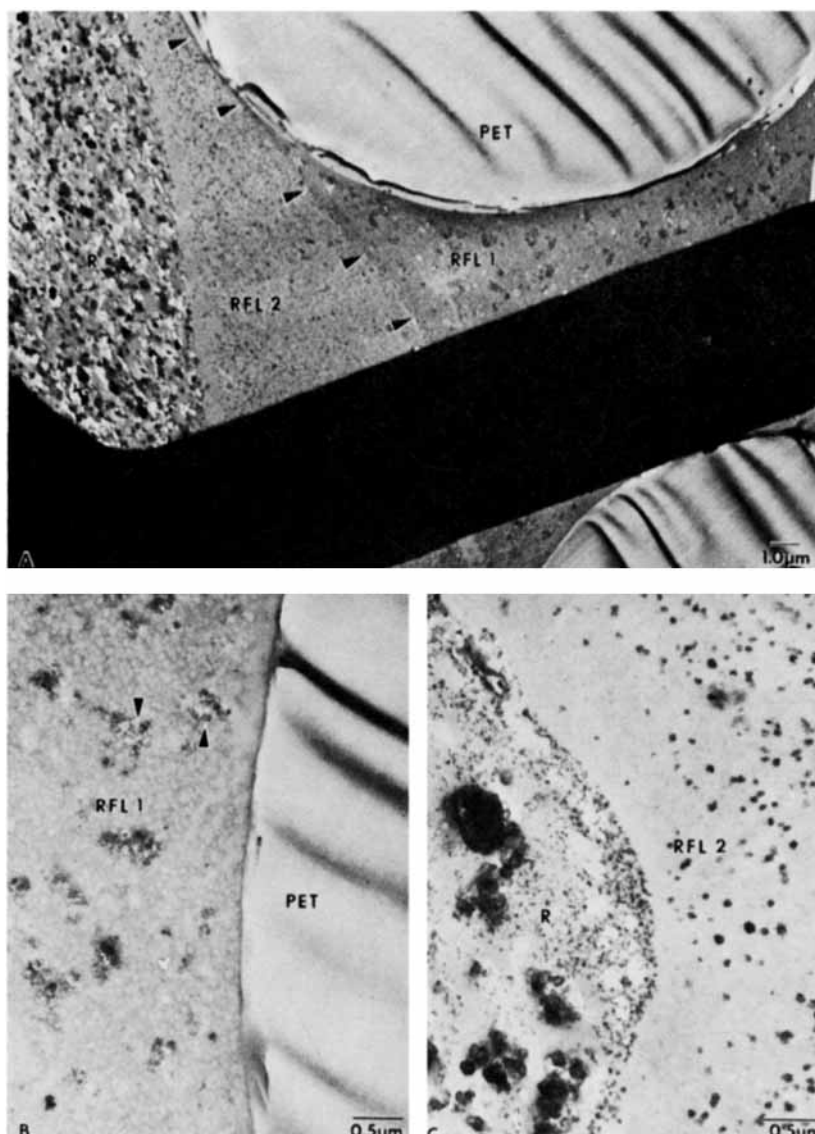


Fig. 10. TEM photomicrographs of a cord section taken from tire E, a two-ply-bias polyester-reinforced tire, with activated RFL. A clear interface (arrows, A) is seen within the RFL indicative of a double-dip system. Higher magnification views show that the first dip is a carbon-black-filled RFL (arrows, B) while the second RFL dip shows the presence of sulfur specks (C). Some cord areas show rubber adjacent to the fiber surface (double arrows, D). Higher magnification view indicates the presence of a thin layer separating the fiber from the rubber (arrows, E).

An optical overview of the entire section is necessary in all studies of tire yarns for this reason.

The cord section taken from the radial tire F shows a different rubber compared to the other tires (Fig. 12). The rubber contains large irregular white areas which are most probably holes since Epon resin seems to have filled them partially [arrows, Fig. 12(A)]. These holes might have formed during the Ebonite treatment by evaporation of a comparatively low boiling organic additive. The rubber also contains a small particulate filler with low electron density [Fig.

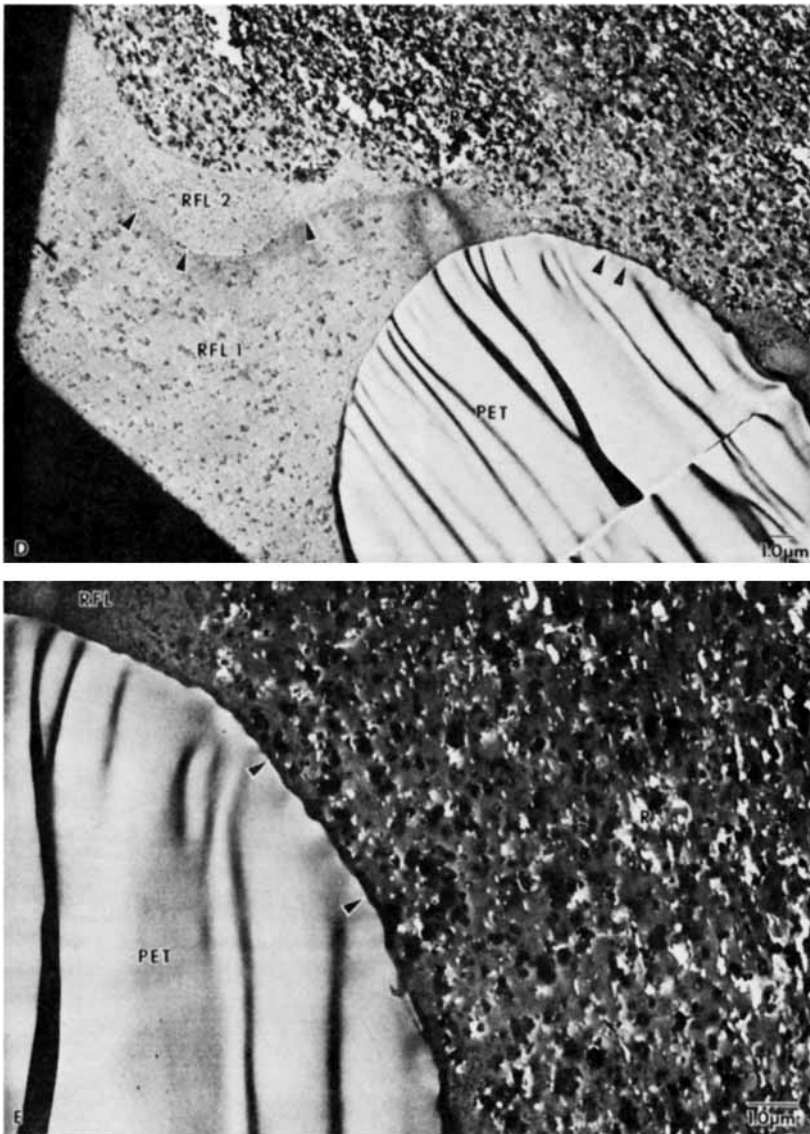


Fig. 10. (Continued from the previous page.)

12(B)] and a fine carbon black [arrows, Fig. 12(B)]. This carbon black is finer than in most other rubbers [see, e.g., Fig. 7(B)]. The RFL shows the presence of sulfur specks, but in this case they extend all the way to the rubber interface [Fig. 12(C)]. The diffuse layer seen at the PET interface is most probably a sectioning artifact. The RFL layer is very thin in some areas [Fig. 12(B)], but no discontinuities were observed in investigated samples.

DISCUSSION

The investigation performed shows that TEM studies offer valuable information about the location of predips and RFL and also allows, to a certain degree, a differentiation between dissimilar systems. The fact that comparatively high magnifications are needed to obtain this detailed information automatically

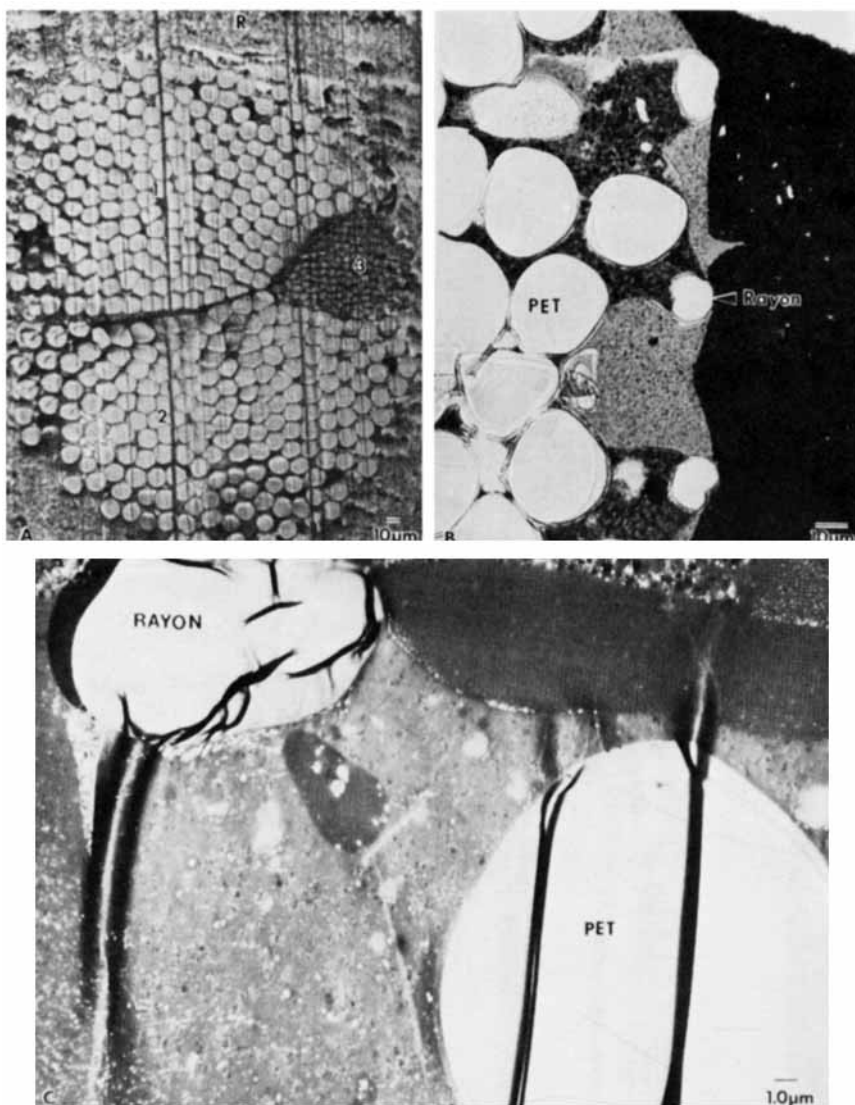


Fig. 11. Optical (A, B) and TEM (C) photomicrographs of a cord taken from tire E (Fig. 10). A view of the entire cord (A) in reflected light shows three plies, one of them of much lower denier. Optical inspection of a TEM section (B) suggests that the fine denier yarn is rayon, which is confirmed by a TEM study (C).

reduces the size of the sample which can be studied. There is also the risk that sample preparation techniques might introduce misleading structural changes. Thus, investigations of several different preparations should be performed to ascertain the generality of observations made. An optical inspection of the sections to be used in the TEM investigations, at an intermediate magnification (400 \times), allows a rapid screening for choice of relevant areas for the TEM study. The following general observations can be drawn from the present study.

The structure of the rubbers used for the bias constructed tires were very similar. They all contained large amounts of dense material in the form of black globules, smaller dense sulfur specks, and clusters of carbon black particles (Figs. 3–8 and 10). The rubbers of the two monopoly radial tires, tire D (Fig. 9) and tire

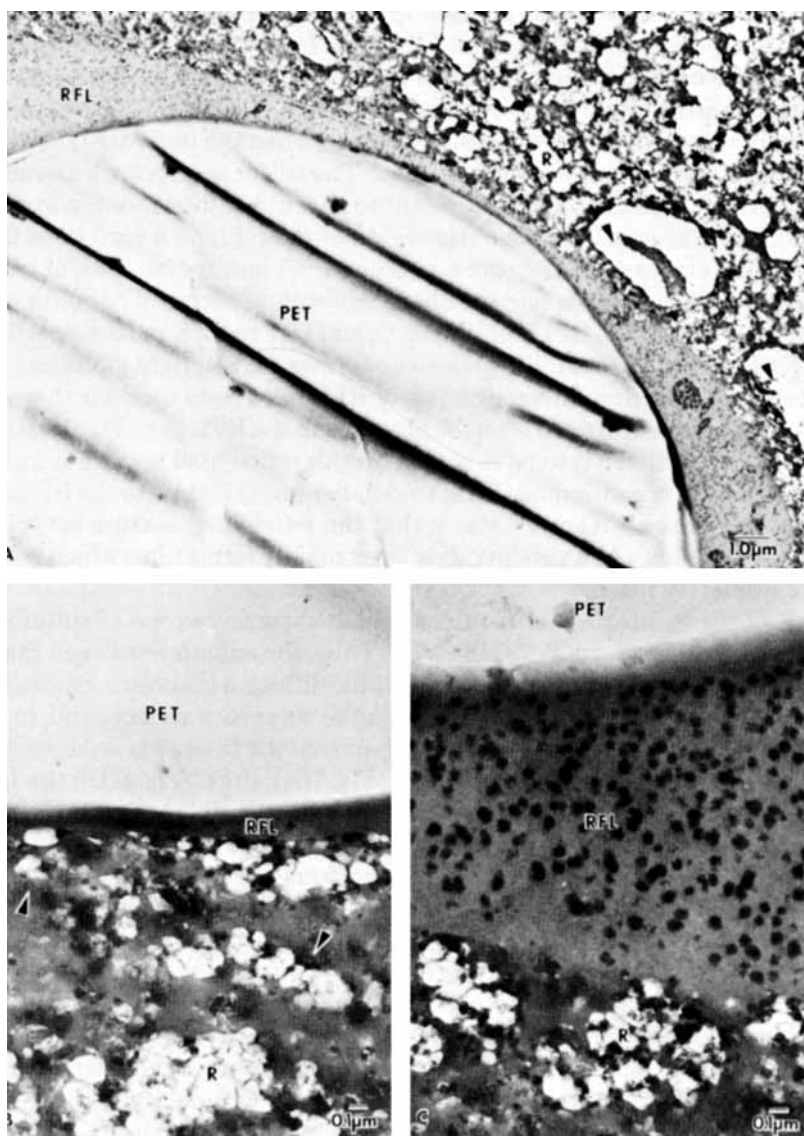


Fig. 12. TEM photomicrographs of a cord section taken from tire F, a monply radial polyester-reinforced tire. The rubber of this tire contains a filler with low electron density (white particles) but also large voids, which appear partly filled with the Epon resin (arrows, A). The rubber also contains fine carbon black particles (arrows, B). The RFL layer is seen as a very thin layer in some areas (B) and as a thicker layer with sulfur specks in other areas (C).

F (Fig. 12), contained less dense material than the two-ply-biased tires. The rubber of F showed large holes in the TEM sections, which indicates the presence of a liquid or low melting compound in this rubber.

The rubber to RFL interface was surprisingly distinct in most cases. Only tire D (Fig. 9) and tire A [Fig. 6(B)] show a diffuse and semidiffuse transition, respectively, between the RFL and the rubber. Fine dense particles of sulfur are seen in many of the RFL's [H-samples, Figs. 3(B) and 4(B); tire B, Fig. 7; tire E, Fig. 10; tire F, Fig. 12]. These sulfur specks were not observed in the RFL of the cords which were Ebonite-treated without a rubber layer (Figs. 1 and 2).

The same type of sulfur specks are seen in the rubber phase. This indicates that these sulfur specks have diffused into the RFL from the rubber during the vulcanization process and are not a result of the Ebonite treatment. This conclusion is further confirmed by the fact that only the outer of the two RFL layers of tire E generally shows the sulfur specks. However, when the inner RFL borders to the rubber, it too shows the sulfur specks. The sulfur specks are generally not seen in an outer zone of the RFL adjacent to the rubber interface (an exception is tire F). It is known that the outer region of the RFL on a cord loses its unsaturation by exposure to the ozone in the air,^{15,16} and the absence of reactive sites for the sulfur could explain the absence of sulfur specks. The sulfur specks were not observed in the RFL's of tires A, C, and D (Figs. 6, 8 and 9, respectively). These RFL's show, instead, the presence of either dark or light globules. Both observations imply that different types of RFL have been used for these tires. A fine reticulated texture can often be observed in the RFL [e.g., Fig. 10(B)]. (It seems that the section has to be very thin for this reticulated texture to be seen.) The volume ratio of continuous phase to globular phase is close to the RF to latex ratio generally used. Kanno¹⁷ states that the reticulated texture is typical of natural rubber latex while vinylpyridine latex rapidly forms films which are more or less completely fused.

The RFL/fiber interface of the tires did not show any excess of sulfur as did the RFL-treated tire yarn T-800 (Fig. 4). Thus, the adhesion between the fiber surfaces and RFL is good enough to prevent the diffusion of sulfur. Several cords showed an extensive thinning of the RFL on the outer cord surfaces and, in many cases, it appears that the rubber directly bonds to the fiber or is separated from the rubber only by a very thin layer [tire B, Fig. 7(A); tire C, Fig. 8(D); tire D, Fig. 9(B); tire E, Fig. 10(E); tire F, Fig. 12(B)]. It is not possible to assess the nature of these thin layers from the present investigations. Thus, they might be artifacts, i.e., folds or double layers originating from the sliding of the materials relative to each other during the sectioning. TEM investigations of sections of cords coated only with RFL would assist in the determination of the nature of these thin layers. However, it is interesting to note that even a double dipping with RFL, as in the case of tire E, will yield cord areas with very little or no RFL. The thinnest layers were observed for tires C, E, and F ($0.1\ \mu\text{m}$). These tires also show the poorest adhesion as seen in visual ratings in the qualitative peel test performed (Table II). (The measured force will partly depend on the strength of the rubber, as clearly illustrated by the data of tire D.) Adhesive failure will be initiated at sites where rubber borders to the fiber surfaces. Very thin adhesive layers between fiber and rubber ($<0.1\ \mu\text{m}$) will also be the focus of adhesive failure. Studies by Mather⁶ implied that the Pexul adhesive needs to be thicker than $0.2\ \mu\text{m}$ for optimal adhesion. Studies on elastomer-modified epoxy adhesives¹⁸ have also shown that the crack growth rate is highly dependent on the thickness of the adhesive and increases rapidly below a certain adhesive thickness. Thus, the location of the RFL seems to be the critical parameter for adhesion, as observed by these investigations. This fact implies that adequate cord/RFL adhesion has been achieved in all cases by the use of activated cords and/or activated RFL's.

It should be stressed that no attempt was made to relate adhesion level or the details of the fiber, RFL, rubber structure as observed by this TEM technique to tire performance. It is only expected that this procedure can be used as a tool to provide insight into the very complex relationship between composite structure and performance that exists in tires.

CONCLUSIONS

The investigation performed shows that TEM studies of ultrathin sections of cords embedded in rubber give valuable information about RFL and predip locations which cannot be obtained by standard optical methods. Fingerprinting of the RFL and rubber used should also be possible since clear differences in textures have been observed. The fact that very distinct interfaces between different RFL layers and between RFL and rubber were generally observed casts some doubt on the generally held assumption that extensive interdiffusion between the phases takes place. Clear differences at the RFL/fiber interface were not seen for the various samples, and the TEM study seems only to give minor information about the bonding mechanism of RFL to different types of fiber surfaces. The decisive parameter for the adhesion level in the investigated samples seems to be the degree of coverage of the cord surface by RFL.

Mr. R. Gursky's assistance in the TEM investigation is acknowledged. Drs. P. J. Harget and R. M. Mininni are deeply thanked for valuable comments to a preprint of this paper.

References

1. T. Takeyama and J. Matsui, *Rubber Chem. Technol.* **42**, 159 (1969).
2. R. H. Moul, in *Handbook of Adhesives*, I. Skeist, Ed., Reinhold, New York, 1962, p. 495.
3. P. Hope, R. Anderson, and A. S. Bloss, *Br. Polym. J.*, **5**, 67 (1973).
4. D. W. Anderson, *Rubber Age*, **52**, 69 (1971).
5. C. J. Shoaf, (to DuPont), U. S. Pat. 3,307,966 (1967).
6. J. Mather, *Br. Polym. J.*, **3**, 58 (1971).
7. W. D. Timmons, *Adhesive Age*, **10**, 27 (Oct. 1967).
8. L. B. Ingram, *Rubber Plast. News*, **12**, 56 (Oct. 1981).
9. H. Toshio, K. Eishi, F. Yokio, and Y. Kohayashi, U. S. Pat. 3,705,868 (1972).
10. G. W. Rye, A. H. Bridge, and F. J. Kovac, U. S. Pat. 3,226,276 (1965).
11. R. E. Field, S. F. Chappell III, and W. J. McKillip, *J. Elastomers Plast.*, **7**, 22 (1975).
12. E. B. McClary, (to Celanese Corp.), U. S. Pat. 3,775,150 (1973).
13. J. C. Wease, paper presented at meeting by International Soc. of Ind. Yarn Mfg., Charlotte, N.C., Nov. 15, 1978.
14. R. W. Smith and J. C. Andreis, *Rubber Chem. Technol.*, **47**, 64 (1974).
15. R. E. Hartz and H. T. Adams, *J. Appl. Polym. Sci.*, **21**, 525 (1977).
16. Y. Iyengar, *J. Appl. Polym. Sci.*, **17**, 855 (1975).
17. N. Kanno, *Nippon Gomukyokaiski*, **45**, 917 (1972).
18. J. L. Bitner, et al., *J. Adhesion*, **13**, 3 (1981).

Received January 19, 1983

Accepted June 1, 1983