Wool Butadiene Copolymers.
I. Preparation and Morphology

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Synopsis

Wool may be readily grafted with poly(butadiene) by gamma-ray mutual irradiation or solution-free radical techniques. Some factors important in the preparation are discussed. Through microscopic and chemical analyses, the radiation-grafted polymer has been shown to be largely associated with, and bound to, the high-sulfur matrix regions of the wool fiber, although there is some specific deposition in the outer exocuticle and in the normally inert regions of the cell membrane complex. The radiation grafted poly(butadiene) isolated by removal of the wool protein by acid hydrolysis has a crosslinked structure typical of other polybutadienes prepared by radiation-induced polymerization. As the grafting yield increased, the molecular weight between points of grafting to the wool increased.

INTRODUCTION

The internal grafting of synthetic polymers to wool has potential for modifying many fiber properties, and numerous studies on grafting processes have been made.[1,2] Relatively little work, however, has been conducted on the properties of the modified wool, and in no case has the wool polymer composite exhibited improved properties sufficient to warrant commercial exploitation. Most of the previous studies have concentrated on the grafting of stiff or brittle polymers such as polystyrene or polymethylmethacrylate, and the softer low-modulus polymers such as the polydienes have been largely ignored. This latter group of polymers are capable of further crosslinking, as, for example, in the vulcanization of polybutadienes. In principle, a new polymer network could be formed within a wool fiber in which the mechanical properties could be varied according to the degree of additional crosslinking imposed.

In this paper, we report the preparation and chemical and microscopic characterization of copolymers of wool with dienes. The majority of the copolymers were prepared using 1,3-butadiene by gamma-ray irradiation of wool in contact with monomer either in the vapor phase or dissolved in an appropriate solvent. An attraction of the vapor route was that the reactions were very clean; no homopolymer was observed on the fiber surface. Copolymers were also prepared using a two-phase (water/monomer) system using potassium persulfate as radical initiator. The only previous studies on the internal deposition of polybutadiene and copolymers into wool were conducted by McKinnon[3] in 1970 (using ferrous ion/peroxide initiation) and by Müller-Schulte[4] in 1980 (using gamma initiation). In both cases, there was little description of the physical properties of the copolymers.

Part I of this work describes a study of some of the factors affecting polymer deposition. A major aim was to characterize the wool-butadiene copolymers particularly with respect to the distribution of polymer throughout the fiber. Some of this information was obtained from transmission electron micrographs of the copolymers, and this work has been published elsewhere.[5] Further information was obtained by chemical and physical examination of the copolymers and of the rubbery residues obtained by preferential dissolution of the proteinaceous (wool) component of the copolymers with 6 M hydrochloric acid. In Part II,[6] we describe further characterization of the copolymers by measurement of their physical properties and report on attempts to modify the incorporated rubbery network by additional crosslinking reactions.

EXPERIMENTAL

Materials

A plain weave, light-weight worsted wool fabric (150 g/m^2) constructed from 45 tex yarns having 18 ends and 18 picks per centimeter was used as a substrate for most of the polymer grafting experiments.

Commercial 1,3-butadiene supplied by the Altona Petrochemical Company Ltd., Melbourne, was used without further purification. Isoprene and 2,3-dimethylbutadiene from Aldrich Chemical Co. were redistilled prior to use. All other reagents and solvents were of analytical grade.

Polymerization Procedure

Polymerizations initiated with gamma-radiation were conducted in cylindrical stainless-steel pressure vessels of 250 cm^3 or 700 cm^3 total capacity. Samples of wool, preconditioned to the required moisture content, were placed in the precooled pressure vessels containing solvent (if required), and liquid butadiene was added. Typically, 50 g of wool was treated with 100 cm^3 of liquid butadiene. The vessel was sealed, and a little butadiene gas was expelled from a vent to remove air remaining in the container. No attempt was made to degas the wool prior to its addition to the vessel.

The sealed vessels were irradiated with a ^{60}Co gamma-radiation facility at Ansell, Medical Aids, Melbourne. The dose rate was approximately 5 kGy/h, and the total dose was 25 kGy. The irradiated vessels were opened after 72 h, and the wool samples were sequentially washed in toluene, acetone, ethanol, and finally water. The polymer deposition was calculated as the percentage increase in the weight of the sample after exhaustive soxhlet extraction in toluene.

Polymerizations using potassium persulfate as initiator were performed as described for the internal deposition of vinyl polymers into wool[7] using stainless-steel pressure vessels of 250 cm^3 capacity.

Preparation of Rubber Residues

Wool-butadiene copolymers were hydrolyzed in sealed tubes in 6 M HCl at 105°C for 20 h. The acid was then decanted from the residues, and the hydrolysis

was continued in fresh 6 M HCl for an additional 20 h. The residues so obtained were thoroughly rinsed in distilled water and then dried in vacuum at 35°C.

Chemical Analysis of Rubber Residues

Total sulfur was determined using the standard method for sulfur in vulcanized synthetic rubber[8] except that the sulfate formed following the Schoniger oxidation was determined turbidimetrically.[9] Nitrogen was determined by Kjeldahl digestion followed by determination of the liberated ammonium ion by means of an ammonia-specific ion electrode.[9]

Amino groups in the residues were determined using a modification of the method developed by Gisin[10] for the determination of peptide amino groups within insoluble polystyrene supports. The rubber residue was allowed to swell in dichloromethane for 5 min and then neutralized with 5% (v/v) triethylamine in dichloromethane (2 × 3 min). After washing with dichloromethane (3 × 2 min), the residue was treated with 0.1 M picric acid in dichloromethane (3 × 2 min) and then thoroughly washed with dichloromethane (5 × 2 min). The picrate was then eluted with the above triethylamine solution (2 × 2 min) followed by dichloromethane (3 × 2 min), and the combined filtrate was diluted to 100 ml with 95% ethanol (final concentration of dichloromethane ≤ 20%). The absorbance was measured at 358 nm, and the concentration of picrate salt (equivalent to the total concentration of basic groups in the rubber) was determined from a calibration graph.

^{1}H and ^{13}C NMR spectra of the replicas were recorded at 250 and 63 MHz, respectively, for solid samples (finely divided) swollen in CDCl$_3$ on a Bruker WM250 spectrometer. Tetramethylsilane (TMS) was employed as an internal standard, and chemical shifts are reported in ppm downfield from TMS.

Amino Acid Analyses

Wool-butadiene copolymers (10 mg samples) were hydrolyzed in evacuated sealed ampoules for 22 h at 105°C in 6 M HCl containing 0.1% phenol. After evaporation to dryness, the residue was dissolved in 0.05 M citrate buffer (pH 2.2). The solution was filtered and then analyzed with a Beckman-Spinco 120C amino acid analyzer.

Contents of —SH and —SS— groups in the copolymers were determined using the method of Leach.[11]

Electron Microscopy

Scanning Electron Microscopy (SEM)

Samples of wool-butadiene copolymers and replicas were cut, mounted on brass stubs, and coated with a thin layer of gold with a Polaron cold sputter apparatus. The micrographs were obtained with a Joel JSM 35 scanning electron micrograph operating at 15 kV. Freeze-fractured samples of the replicas were prepared on a Joel Cryo-fracture unit attached to the stage of the electron microscope.

RESULTS AND DISCUSSION

Gamma-Radiation-Induced Polymerization

Since the major objective of the present work was to characterize the co-polymers with respect to the location of polymer within the fiber and to investigate the physical properties of the products, we have not made a detailed kinetic study of the factors affecting polymer deposition. Conditions were chosen to keep weight increases below 50%–100% and to work in a region where practical textile fiber products might be obtainable.

Preliminary experiments conducted with wool at ambient regain (approximately 12% moisture) showed that weight uptakes of polybutadiene of 40%–50% could be achieved when wool and butadiene were mutually irradiated with 25 kGy of gamma radiation at a dose rate of approximately 5 kGy/h. A few experiments were also conducted at the higher total dose level of 50 kGy, and the weight uptakes were approximately doubled. All subsequent experiments were conducted at a total dose level of 25 kGy. In the course of preparing the copolymers, the main factors affecting deposition were identified as the moisture content of the wool, the molecular size of the diene, and the presence of solvent.

The effect of moisture content (regain) of the wool on polymer deposition is shown in Figure 1. The weight increases attributed to graft polybutadiene in duplicate experiments were reproducible with the exception of those conducted with "dry" wool when weight uptakes varied from 10% to 20% (on mass fiber). Simpson[12] also observed that the drying history of wool influenced the polymer weight uptake when "anhydrous" wool and acrylonitrile monomer were mutually irradiated; he suggested that water in small amounts exerted a catalytic effect on both the rate and extent of graft polymerization. Significantly, it is only with low molecular weight monomers such as acrylonitrile ($M_r = 53$) and butadiene ($M_r = 54$) that polymer deposition into dry (nonswollen) wool has been observed. For larger monomers, for example, styrene, allyl methacrylate, and methyl acrylate,[13–15] a swelling agent such as water or methanol is essential
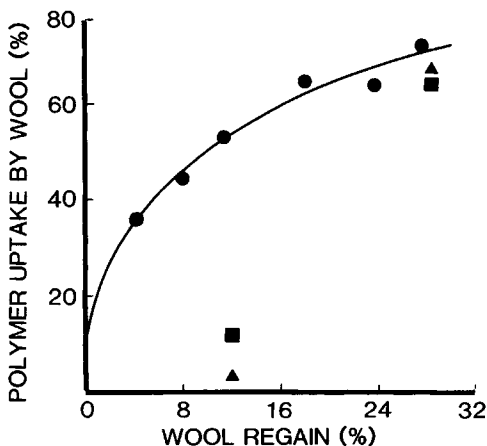

Fig. 1.   Effect of wool regain on the deposition of polydienes into wool. Polymerization initiated with 25 kGy of gamma-radiation: (●) butadiene; (■) isoprene; (▲) 2,3-dimethylbutadiene.

for polymerization to occur. In dry wool, the diffusion rate of all but the smallest monomers is presumably too slow to allow penetration to the radical centres formed by irradiation.[14] This conclusion is further supported by the results of grafting experiments with the larger diene monomers, isoprene ($M_r = 68$) and 2,3-dimethylbutadiene ($M_r = 82$) to wool at various regains (Fig. 1). Wool (thoroughly dried over P_2O_5 in vacuum) failed to show any weight uptake with either of these larger monomers, compared with a 10% weight increase observed for butadiene under otherwise identical conditions. At intermediate degrees of swelling (12% regain), the extent of reaction decreased with increasing relative molecular mass (size) of the monomers. However, at high degrees of swelling (28% regain), all diene monomers were grafted to approximately the same extent regardless of size.

The decisive effect of fiber swelling was also seen in grafting experiments conducted in various solvents. Table I gives the observed weight increases of wool samples at 12% regain irradiated with 25 kGy of gamma-radiation in the presence of butadiene dissolved in different solvents. There was an overall decrease in yield in this series because relatively less butadiene was used compared with results in Figure 1. These results show that grafting of polybutadiene was more effective from polar swelling solvents (ethanol, methanol) than from nonpolar solvents (heptane, toluene), again suggesting that a diffusion-controlled mechanism was predominant in the radiation-induced grafting of polybutadiene[14,17] to wool. Others[4,18] have suggested that some mechanism other than swelling by the solvent must be operative in the radiation-induced grafting of styrene and other vinyl monomers in solvents.

Potassium Persulfate Initiation

The polymerization of vinyl monomers into wool from aqueous media using potassium persulfate as initiator has been extensively studied,[1,2] and this strategy was investigated for preparing wool-butadiene copolymers. The procedure employed was similar to that described by Wolfram and Menkart[7] who polymerized acrylonitrile and other water-soluble vinyl monomers into wool using tetrakishydroxymethylphosphonium chloride (THPC) to act as an oxygen scavenger. In the present case, it was necessary to add isopropanol to the polymerization mixture to increase the solubility of butadiene in the aqueous

TABLE I
Effect of Solvent on the Radiation-induced Polymerization of Butadiene into Wool[a]

Solvent	Solvent swelling of wool fiber[b] (%)	Weight increase of wool (%)
Heptane	1	5
Toluene	2	6
Ether	—	16
Ethanol	7	23
Methanol	11	20

[a] 10 g wool + 10 cm³ of butadiene + 80 cm³ solvent, mutually irradiated with 25 kGy of gamma-radiation at approximately 5 kGy/h.
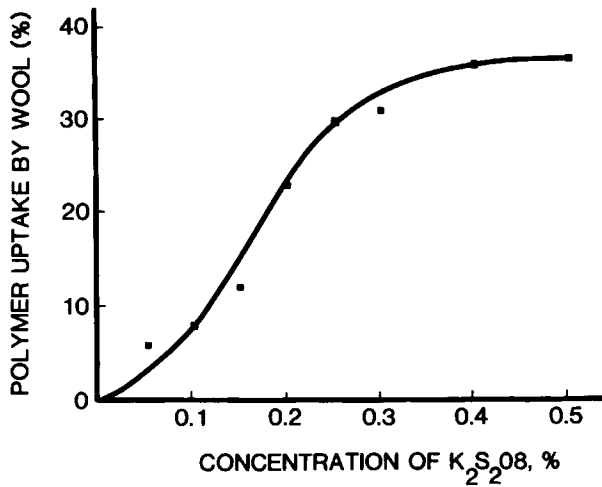[b] Ref. 16.

Fig. 2. Effect of persulfate concentration on the deposition of polybutadiene into wool. Experimental conditions: aqueous phase 50% isopropanol containing 0.3% THPC. Wool : liquor ratio 1 : 25; time of polymerization 90 min; temperature 50°C.

phase, and reaction weight increases up to 40% were readily obtained. Only traces of homopolymer were formed in the bulk of the mixture and on the wool surface.

The dependence of the polymerization on the persulfate concentration, the oxygen scavenger concentration, and the pH of the aqueous phase were in general similar to those observed for vinyl monomers[7,19] (Figs. 2–4).

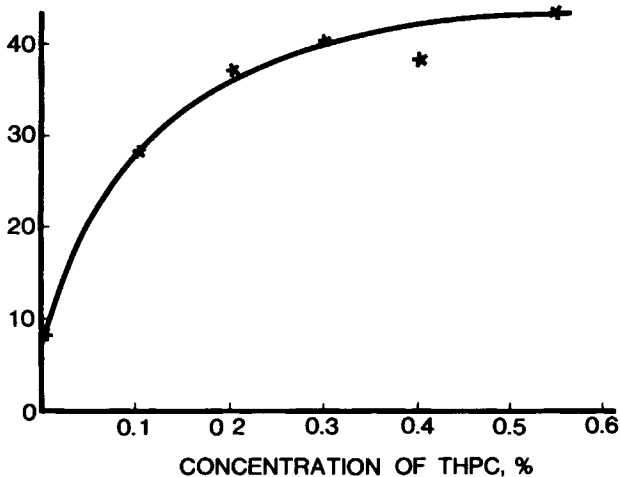The incorporation of isopropanol into the aqueous phase of the reaction

Fig. 3. Effect of THPC concentration on polybutadiene deposition into wool. Experimental conditions as indicated in Figure 2. Potassium persulfate concentration 0.3% in the aqueous phase.
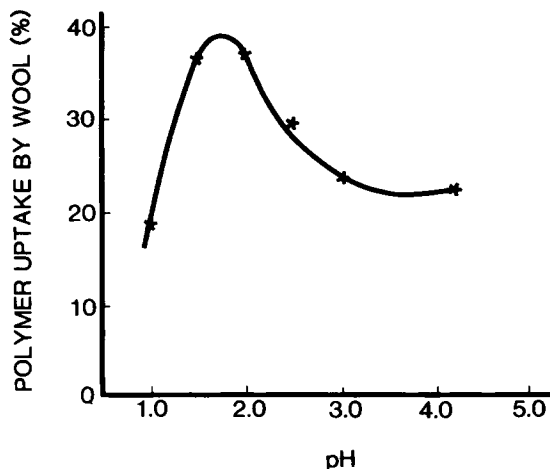
Fig. 4. Effect of pH on deposition of polybutadiene into wool. See Figure 2 for experimental conditions.

mixture increased polymer deposition (Fig. 5), but concentrations above 50% could not be used since persulfate was insoluble above this level. The beneficial effect of isopropanol may be due to the increased solubility of butadiene and/ or to a greater swelling of the wool, producing a faster penetration of monomer into the wool fiber.

It is apparent from the above results that gamma-radiation initiation gave copolymers with higher polymer adds-ons than did persulfate initiation. The characterization of the copolymers described below was, therefore, confined to the gamma-radiation-grafted copolymers.
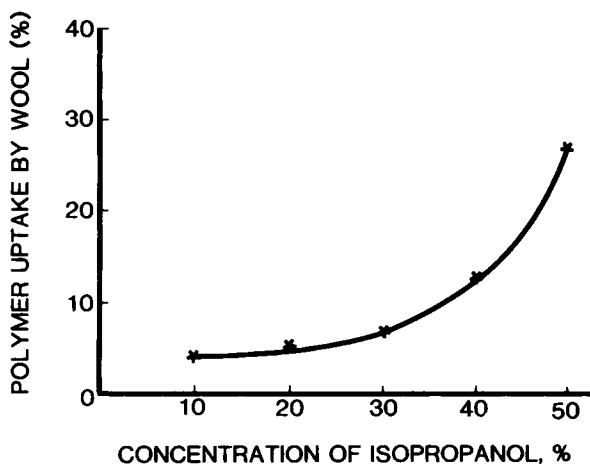

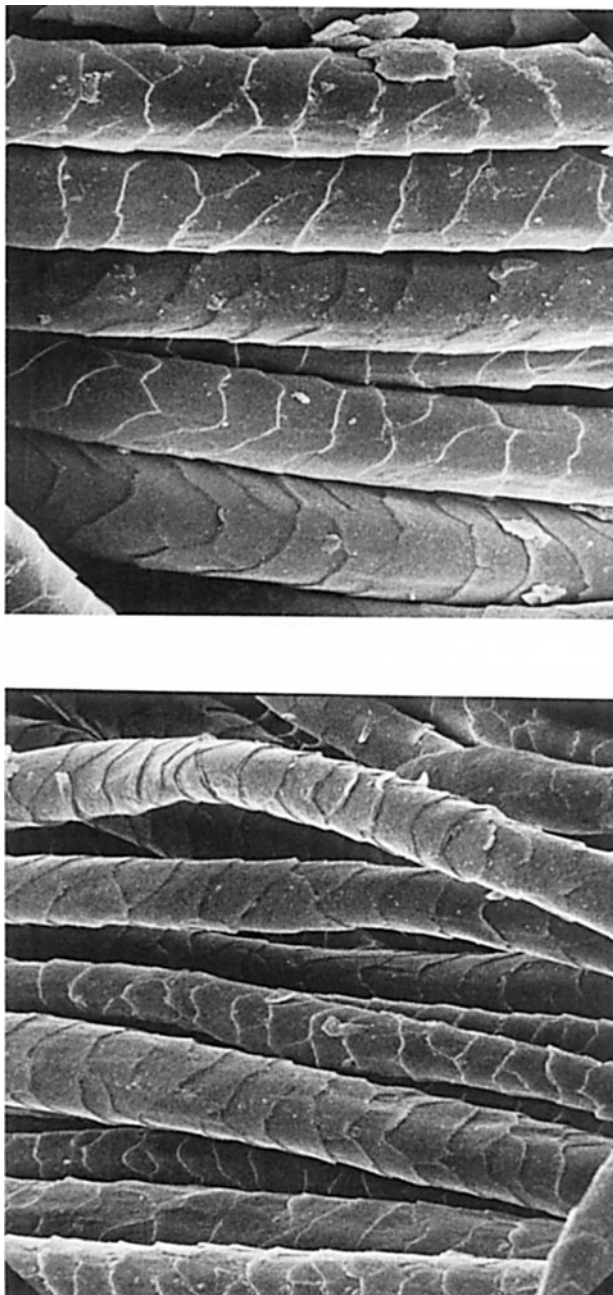Fig. 5. Effect of isopropanol concentration in the aqueous phase on the deposition of polybutadiene into wool.

Fig. 6.   SEM of (a) untreated wool fiber, and (b) gamma-radiation grafted wool-butadiene copolymer (44% add-on). ×500.

Examination of Wool Butadiene Copolymer

Scanning Electron Microscopy

Figure 6(b) shows a scanning electron micrograph (SEM) of a sample of a wool-polybutadiene composite fabric (44% polymer add-on) produced by gamma-radiation initiation. In comparison with untreated fabric [Fig. 6(a)], there was obvious swelling of the individual fibers and increased crowding of the fibers within the fabric. This latter effect has important consequences on the frictional properties of the fabric, and this will be discussed in the following paper.[6] It is apparent from Figure 6(b) that the surface-scale structure was free of homopolymer. Less than 1% of the weight of the wool-butadiene copolymer was lost on exhaustive (soxhlet) extraction with toluene, indicating that such polymer was either grafted to or highly entangled with the fiber.

Measurement of the cross-sectional areas of the gamma-grafted single fibers from the electron micrographs indicated that the swelling of the fibers increased approximately linearly with polymer add-on (Table II). Comparable lateral swellings were observed by Arai and Negishi[20] for wool grafted with various vinyl and allyl polymers.

Transmission Electron Microscopy

To gain further information on the location of the polymer within the wool fibers, transmission electron micrographs (TEMs) of gamma-grafted wool-butadiene copolymer were examined.[5] The micrographs of untreated wool and a wool-butadiene copolymer (44% weight uptake) were prepared after fixing with osmium tetroxide (OsO_4) but without the usual prereduction of the wool with thioglycollic acid.[21] Without such reduction, untreated wool reacts weakly with osmium tetroxide but predominantly with the matrix material,[21] giving electron micrographs with low contrast (Fig. 7). Our staining technique[5] relies on the well-known affinity of osmium tetroxide for polybutadiene and leads, without reduction, to a clear delineation of the microfibrils and matrix (Fig. 8). The

TABLE II
Average Cross-sectional Areas of Single Fibers for Wool-Butadiene Copolymers[a]

Polymer weight uptake % (oww)	Average cross-sectional area (micron^2)[b]
0	346
26	479
38	552
44	707
66	819

[a] Prepared using wool at various regains and butadiene gas by mutual irradiation with 25 kGy of ^{60}Co gamma-radiation.

[b] Measured from the scanning electron micrographs, mean of 50 fibers.
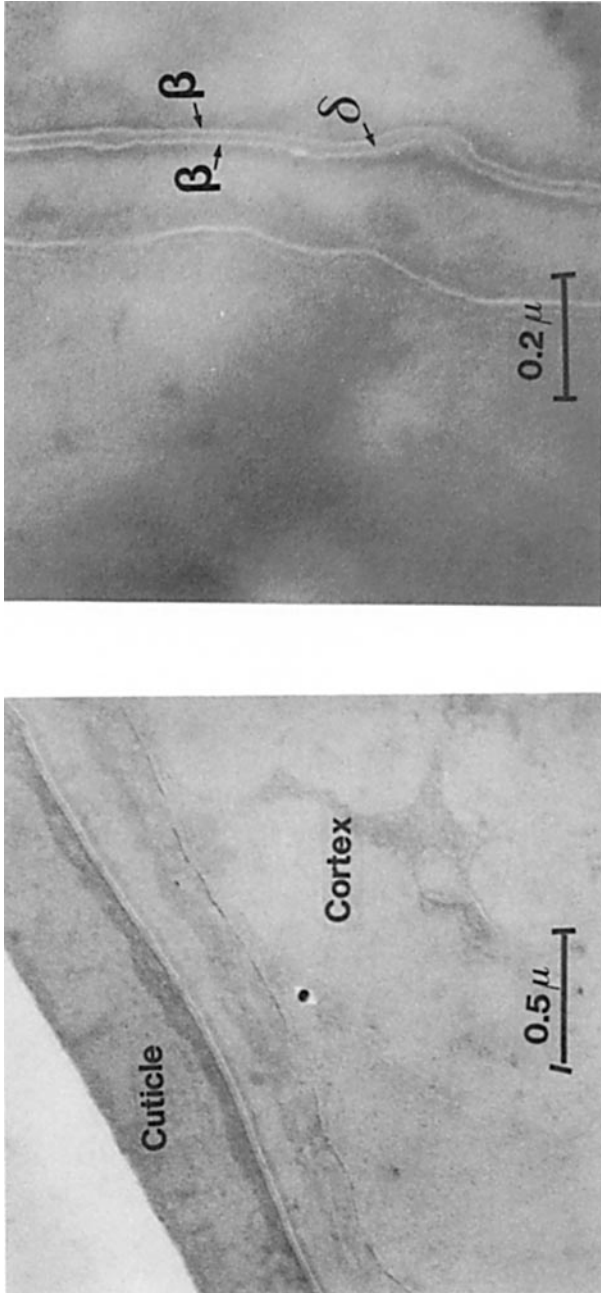
Fig. 7. Cross section of untreated wool fiber obtained after staining with OsO$_4$ but without prereduction. (a) The microfibril-matrix regions are difficult to discern and the cells of the cortex are only vaguely outlined. ×34,000. (b) The cell membrane complex region showing the stained intercellular component (gamma-layer) between the unstained beta-layers. ×79,000.

micrographs are thus "positive images" of the polymer deposition rather than the more usual "negative image" obtained previously for wool grafted with such polymers as polymethylmethacrylate or polystyrene.[1,22] No gross distortion of the fibers was apparent, and the grafted fibers appeared at the histological level to be similar to normal fibers. The polybutadiene had penetrated all morphological regions of the fiber with the possible exception of the microfibrils; the intermacrofibrillar material was quite dark, indicating that the high-sulfur matrix regions of the fiber were the main sites of butadiene deposition, especially in the orthocortex of the fiber [Fig. 8(c)].

Two regions of the fiber to show marked differences from a normal fiber were the cell membrane complex (CMC) and the cuticle shown in Figure 8(a) and (b). On grafting with polybutadiene, the usual staining pattern within the CMC was reversed; a relatively nonstained gamma-layer was enclosed by two heavily stained beta-layers. This observation is noteworthy since no heavy metal staining procedure to date has been found to stain the "inert" beta-layers[22,23] and, to our knowledge, polybutadiene is the first material to have a demonstrably high preference for this specific region of the fiber.

The intercellular cement (delta-layer) is currently believed to consist of nonkeratinous protein,[22,24-27] whereas the beta-layers are generally accepted as resulting from the membrane.[22,28-30] The deposition of polybutadiene into the beta-layers of the CMC may therefore be explained in terms of a strong mutual solubility of the two phases. Others have suggested that the beta-layer may be the resistant proteinaceous membrane that surrounds each cuticle and cortical cell[25,31]; in this case, the preferential reaction would need to be caused by the beta-layers being a strong site of radical formation.

The cuticle of the wool has also undergone noticeable changes following grafting with polybutadiene. The outermost part of the exocuticle, the so-called "a"-layer, appears to have taken up considerably more polymer than did the surrounding areas of this region. This observation is consistent with the relatively high sulfur content reported for the "a"-layer[31,32] since cystine radicals are known to be produced in wool by gamma-radiation.[33] However, there is not always a relationship with butadiene deposition and cystine content, and the endocuticle, the region just below the exocuticle [Fig. 8(a)] is more heavily stained than is the high-sulfur exocuticle immediately above it [Fig. 8(a) and (b)]. This differential uptake has been observed with other polymers[31] and may well be attributed to the soft and swellable nature of the endocuticle.[22]

Amino Acid Analysis

As expected, the low irradiation levels used in this work did not produce significant changes in the amino acid composition of wool irradiated in the absence of monomers[34,35] (Table III). However, the irradiation/grafting reaction caused the concentration of half-cystine of the wool base to be considerably reduced relative to the untreated control. The levels of all other amino acids including tyrosine and lysine that have been implicated in the gamma-radiation grafting of vinyl polymers to wool[4] were unchanged. Interpretation of this result is difficult since as indicated below hydrolysis of the composite was incomplete and some protein was retained by the polybutadiene residue.
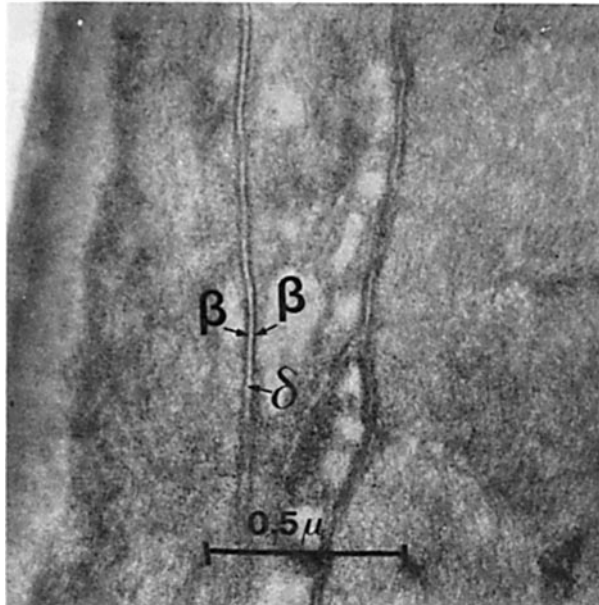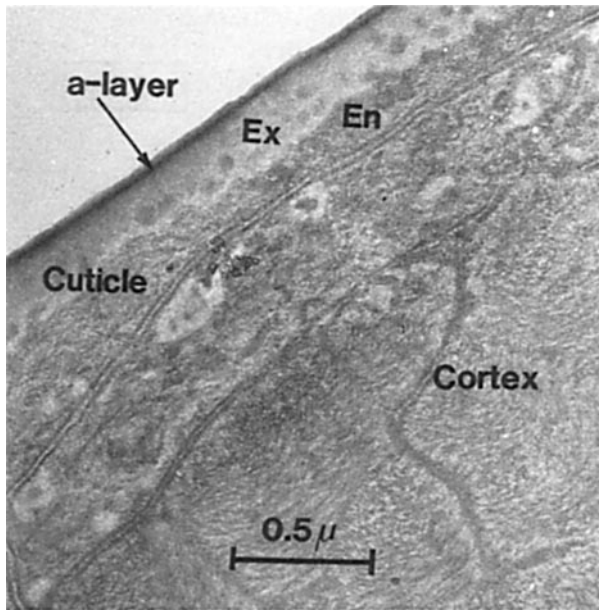
Fig. 8. Cross section of a 50% grafted polybutadiene wool fiber prepared by the mutual radiation procedure. (a) Cuticle and cortical regions of the fiber showing the darkly stained intermicrofibrillar material. Note the electron dense "a"-layer of the epicuticle, the lightly stained exocuticle (Ex), and the more heavily stained endocuticle (En). ×34,000. (b) The cell membrane complex of the cuticle and cortical regions showing the heavily stained beta layers and the relatively unstained delta layer. ×51,000. (c) Boundary of the orthocortex and paracortex showing the slightly heavier staining in the orthocortex. ×46,000.
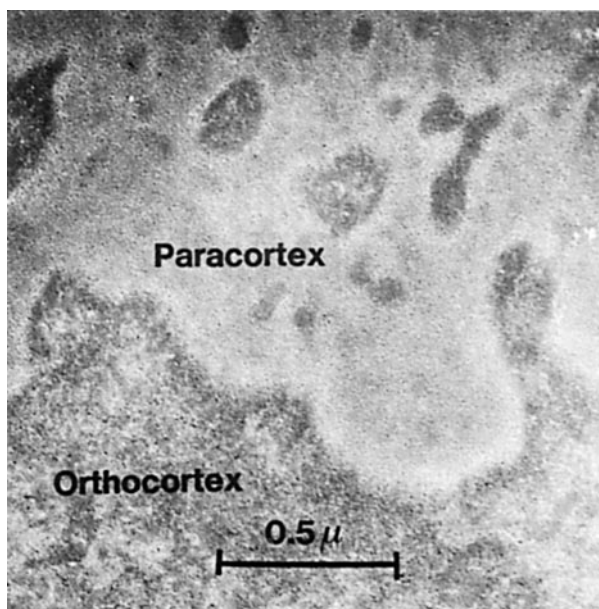
Fig. 8.　(*Continued*)

The most likely conclusion, however, is that the grafting of the polybutadiene chains to the wool proteins occurred predominantly through the sulfur-containing residues of cystine. This hypothesis is further supported by the loss of total disulfide and thiol groups within the wool base of the intact (i.e., unhy-

TABLE III
Amino Acid Composition (Moles/100 Moles of Amino Acids) of Wool-Butadiene Copolymers[a,b]

Amino acid	Whole wool	γ-Irradiated wool[c]	Wool-butadiene copolymers[d]		
			Sample A	Sample B	Sample C
Arginine	6.8	6.6	7.0	6.8	6.7
Aspartic Acid	6.1	6.2	6.4	6.2	6.1
Cysteic Acid	0.1	0.2	0.1	0.2	0.2
½-Cystine	10.2	10.1	8.1	8.4	8.9
Glutamic Acid	11.7	11.8	12.0	12.2	12.3
Lysine	2.7	2.7	2.8	2.8	2.7
Serine	10.5	10.6	10.8	10.8	10.9
Tyrosine	3.9	3.9	4.0	3.9	3.9

[a] Mean of duplicate determinations.
[b] All other amino acids were within 0.2% of values for whole wool.
[c] 25 kGy gamma-radiation.
[d] Sample A = 16% add-on; sample B = 52% add-on; sample C = 72% add-on. Copolymer prepared with wool at various regains in 1 : 1 heptane : butadiene.
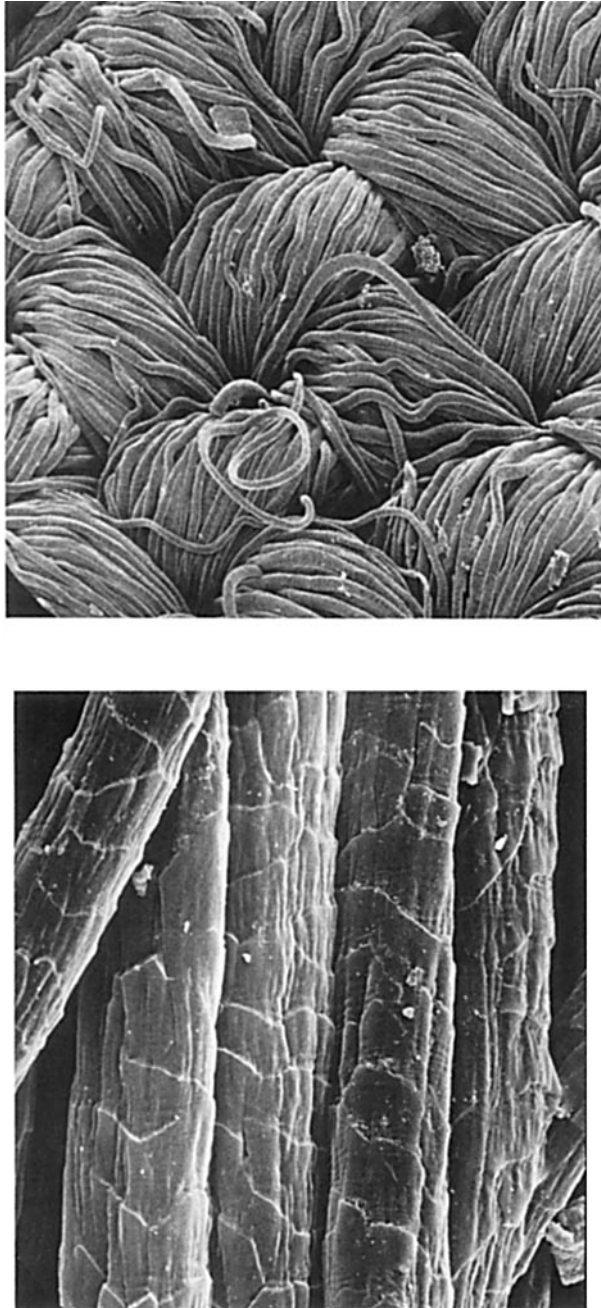
Fig. 9. Polybutadiene residues obtained from a copolymer (44% add-on) after removal of the wool by acid hydrolysis. (a) At low magnification, the woven fabric structure is clearly visible. ×50. (b) The "scale-like" structure on the surface of the individual rubber fibers can be observed. ×1000. (c) Freeze-fractured cross section of the residue showing the absence of voids. ×1000.
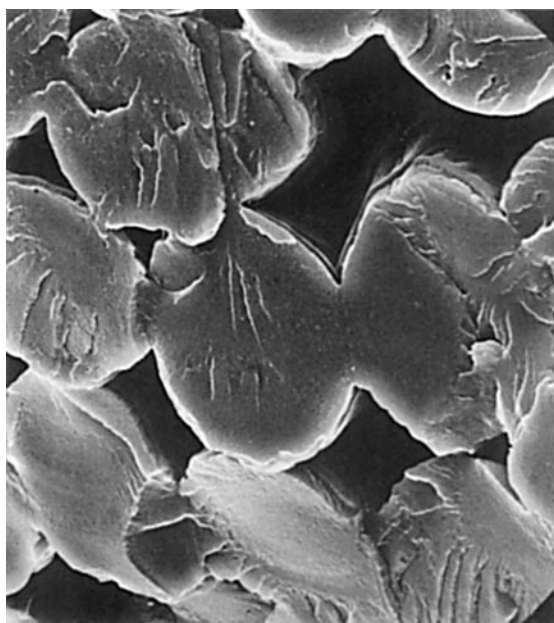
Fig. 9. (*Continued*)

drolyzed) copolymers (Table IV). Interestingly, both of these analyses showed that the concentration of cystine in the wool component increased slightly with polymer add-on, suggesting that the number of cystine graft sites decreased as the polymer weight uptake increased.

Examination of Butadiene Residues

Scanning Electron Microscopy

Tough, insoluble rubber residues were obtained from the copolymers on removal of the wool by extended acid hydrolysis. These residues retained the woven fiber/fabric structure of the original copolymer [Fig. 9(a)], complete with the characteristic "scale structure" of the original wool [Fig. 9(b)] though the surface appeared wrinkled and compressed, suggesting that some longitu-

TABLE IV
Contents of —SH and —SS— Groups in Poly(butadiene) Grafted Wool Fibers[a]

Sample	—SS— (μmole/g wool)	—SH (μmole/g wool)
Untreated wool	423	40
Grafted wool		
31% Graft	371	21
52% Graft	399	16

[a] Determined polarographically using MeHgI (Ref. 11).

dinal contraction may have taken place. Generally, there was little loss in fabric area, provided initial grafting levels were above 20%. In cross section, all residues appeared as "solid rods" free of voids or hollow cores [Fig. 9(c)], again suggesting uniform deposition of polymer through the fiber.

Chemical Analysis of Rubber Residues

Insoluble rubber residues were prepared by exhaustive acid hydrolysis of a graded series of copolymers prepared by mutual irradiation of wool at 12% regain with butadiene dissolved in heptane. The dried replicas were analyzed for total sulfur, total nitrogen, and primary amino groups. The results of these analyses are summarized in Table V.

All residues were at least 15% heavier than expected on the basis of the polymer weight uptake alone, indicating that they contained a significant amount of proteinaceous material even after extensive hydrolysis at 110°C. Significantly, the residues were relatively rich in sulfur and the sulfur content generally decreased with polymer add-on. When expressed as a percentage of the total sulfur in the wool base, the sulfur content of the residues represented between 9% and 17% of the total sulfur in the wool base, values in reasonable agreement with the loss of total cystine in the acid hydrolysates of the copolymers (Table III).

The residues also contained significant quantities of nitrogen. This decreased only slightly with polymer add-on so that the nitrogen to sulfur ratio effectively increased with polymer incorporation. These results suggest that at low additions deposition of polymer occurred preferentially into the sulfur-rich regions of the fiber, but as polymerization proceeded, the polymer was deposited into regions of lower sulfur content.

The concentration of free amino groups in the residues as determined by the picrate method (Table V) showed a steady decrease with polymer weight

TABLE V
Chemical Analyses of Rubber Residues Obtained on Protein Hydrolysis
of Wool-Butadiene Copolymers

Butadiene concentration in heptane (%)	Polymer weight uptake (%)[a]	Residue weight[b] (g)	Total sulfur		Total nitrogen		NH$_2$ end groups in residue (moles/g)	Nitrogen in residues as —NH$_2$ (%)
			In residue (%)	As % of total S in wool base[c]	In residue (%)	As % of total N in wool base[d]		
10	13	17	2.0	10	2.0	2	469	33
20	37	42	1.3	17	1.3	3	191	21
30	57	70	0.8	17	1.5	6	170	16
40	65	80	0.7	17	1.6	7	130	11
50	67	80	0.5	12	1.4	7	144	14
50	80	93	0.3	9	1.3	7	56	6

[a] On weight of wool.
[b] Grams residue for hydrolysis of (100 + add-on) g of dried composite.
[c] Wool base = 100 g; sulfur content of wool = 3.3%.
[d] Wool base = 100 g; nitrogen content of wool = 17.1%.

increase. The proportion of nitrogen in the residues present as amino groups was then calculated (column 9), and this suggested that the proteinaceous material within the residues contained an increasing amount of peptide (amide) nitrogen with increasing polymer add-on. This result may reflect the increasing length of polypeptide chains attached to or occluded within the residues that were increasingly inaccessible to acid as the proportion of polybutadiene to wool increases.

By making a number of assumptions, e.g., that the grafting of the polybutadiene to the wool was exclusively through cystine residues, and that there were no additional amino or thiol groups in any occluded protein in the rubber residues, then we can use the analytical results in Table V to calculate crudely the average number of butadiene units between adjacent graft sites (Table VI).

There was reasonable agreement between the values based on the sulfur and on the amino group analyses, especially as the assumptions made would probably tend to cause the sulfur-based values to be low and the amino-based values to be high. Although the absolute values should be viewed with caution, it appears that the main factor responsible for the higher weight uptakes was the increased chain length between graft sites, rather than in increased grafting to fresh wool sites.

Spectroscopic Examination of Residues

The rubber residues were quite insoluble in organic solvents (less than 1% weight loss on soxhlet extraction in toluene), indicating a high degree of cross-linking. Less than 10% of the residue dissolved in hexachlorobutadiene at 160°C (3 h); this treatment largely solubilizes sulfur-vulcanized polybutadienes, verifying that the radiation grafting had caused considerable self-crosslinking of the polybutadiene.[36]

Because the residues were insoluble, NMR spectra were conducted on solid residues swollen in $CDCl_3$. Figure 10 shows a 250 mHz ^1H spectrum of a typical

TABLE VI
Apparent Average Length of Polybutadiene Chains between Graft Sites
in Wool-Butadiene Copolymers

	Apparent average number (n) of butadiene units between graft sites[a]	
Polymer add-on (%)	Based on S analyses	Based on amino group analyses
13	48	63
37	83	177
57	125	184
65	143	240
67	206	224
80	366	610

[a] Calculated from $n = 2a/b$, where a = number of moles of butadiene units and b = concentration of sulfur (g atoms) or amino groups (g equivalents) in the residue. The factor of 2 was used because 2 sulfur atoms were involved in each cystine crosslink and each polypeptide chain was assumed to be linked to the polybutadiene through a half-cystine residue containing a terminal amino group.
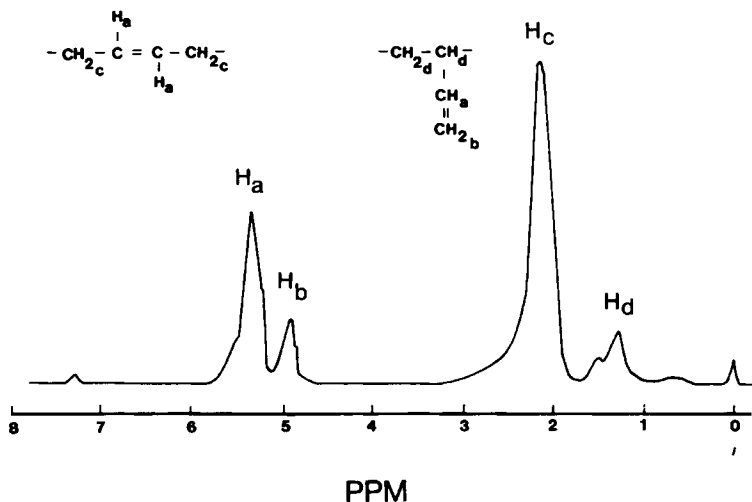
Fig. 10. ^{1}H NMR spectrum at 250 MHz of the insoluble butadiene residue (swollen in CDCl$_3$) obtained after exhaustive acid hydrolysis of a wool-butadiene copolymer.

residue. Comparison with previously published solution spectra of polybutadiene allowed the assignments shown in Figure 10 to be made. From the peak areas, the proportion of 1,2 polybutadiene was 18%.[37,38] The ratio of *trans*-1,4 to *cis*-1,4 polybutadiene was determined by examining the ^{13}C NMR spectrum. Again using literature values for soluble polybutadienes,[39,40] the approximate *cis* : *trans* ratio was given by the ratio of the aliphatic signals 2 : 4 in Figure 11, indicating that the residue represented a 69 : 31 *trans* : *cis* polybutadiene. The overall residue structure thus comprised 56% *trans* 1,4, 26% *cis* 1,4, and 18%
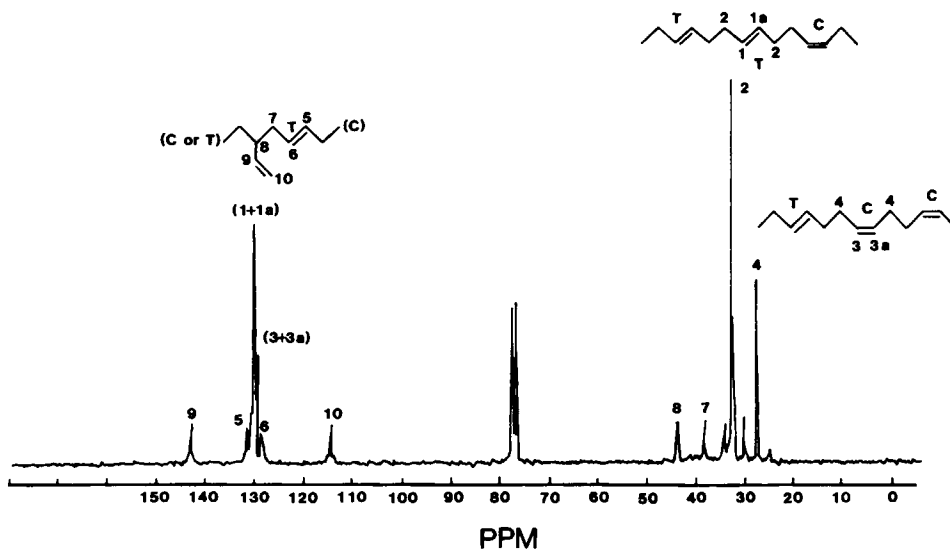

Fig. 11. ^{13}C NMR spectrum at 63 MHz of an insoluble butadiene residue obtained as in Figure 10. C = *cis*, T = *trans*.

vinyl 1,2 units, in good agreement with the microstructure of a free radical polymerized polybutadiene.[3,13]

CONCLUSIONS

Polybutadiene-grafted wool fibers are readily prepared with poly(dienes) by gamma-ray mutual irradiation or solution-free radical techniques. The reaction appears to be diffusion controlled, and molecular size of the monomer and degree of swelling of the wool fiber can limit the extent of grafting. Through microscopic and chemical analyses, the radiation-grafted polymer has been shown to be largely associated with, and bound to, the high-sulfur matrix regions of the wool fiber, although there is some specific deposition in the outer exocuticle and in the normally inert regions of the cell membrane complex. Cross sections of the tough, insoluble poly(butadiene) rubbers isolated by removal of the wool protein by acid hydrolysis were free of apparent voids. The grafted poly(butadiene) has a crosslinked structure typical of other radiation induced poly(butadienes). As the grafting yield increased, the molecular weight between points of grafting to the wool increased.

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