

The Formation in Wool of Copolymers of Butadiene with Acrylonitrile and Methyl Acrylate by Iron Salt-Hydrogen Peroxide Initiation

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Synopsis

The formation in wool of graft copolymers of butadiene with acrylonitrile and methyl acrylate has been studied, using the ferrous ion-hydrogen peroxide system as initiator and a heterogeneous liquid phase consisting of a dilute hydrogen peroxide solution and a monomer mixture. The effects of time and temperature, and the pH and concentrations of the ferrous ion and peroxide solutions, on the polymer add-on are discussed. The dependence of the composition of the graft copolymer on that of the monomer mixture has been determined. Certain features of the kinetics of the reaction are discussed.

INTRODUCTION

As part of a program of examining the properties of wool modified with a variety of graft copolymers, it was desired to determine the effects of forming crosslinked rubbery polymer networks within the wool structure. To this end, wools containing copolymers of butadiene with acrylonitrile or methyl acrylate have been prepared. The system ferrous ion-hydrogen peroxide has been used as initiator, as prior impregnation of wool with ferrous solutions provides a means of confining the polymerization to the wool. Such a system has been used by previous workers who have deposited polymers in wool.¹⁻³

Because the butadiene copolymers in the present study are crosslinked and because some chain transfer to wool (particularly via thiol) is inevitable, these polymers can justifiably be called graft polymers, even though no deliberate attempt has been made to effect covalent binding of the polymer to the wool substrate.

EXPERIMENTAL

Materials

A commercial undyed crossbred carpet yarn with an average fiber diameter of 41.5 μ was used as substrate for most of the polymer grafting experiments. In some experiments an undyed merino wool fabric with an average fiber diameter of 19.9 μ was used.

Acrylonitrile and methyl acrylate were of BDH laboratory reagent grade and were redistilled before use. Butadiene, from the Matheson Co., purity 99.5%, was used direct from the cylinder. Other chemicals used were of Analar or BDH reagent grade. The pH was adjusted with sulfuric acid.

Technique for Polymer Deposition

After experimenting with several grafting techniques, the following procedure was chosen as the most efficacious. Wool samples were impregnated in dilute solutions (usually 0.1%) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at a pH between 3.0 and 0.9 for selected times at given temperatures (usually 50°C) at a liquor:wool ratio of 50:1. The samples were degassed with a water pump to ensure thorough wetting of the wool and rinsed briefly in distilled water (liquor ratio 50:1), and excess moisture was removed by pressing between tissues.

The impregnated wool was dipped briefly in a dilute hydrogen peroxide solution at a given pH and the wool, wet with peroxide solution, was placed in a thin-necked glass ampoule. Acrylonitrile or methyl acrylate was added, and the ampoule was attached to a vacuum manifold where it was degassed by a freeze-thaw technique using liquid nitrogen and a vacuum of 10^{-4} mm Hg. Known amounts of butadiene, measured on a manometer calibrated in millimoles of butadiene, were then admitted to the evacuated system and frozen out in the ampoules, which were sealed. After thawing the ampoules were placed in a thermostatted bath for graft polymer formation.

Normally, 200-mg wool samples were treated with a total of 30 millimoles of added monomers, this quantity being sufficient to cover the wool samples completely. In most experiments, the monomer composition did not change much during the polymerization, but in experiments near the extremes of the monomer composition range, large alterations in monomer ratio during polymerization were precluded by increasing the total amount of monomer added. After polymerization, samples were rinsed in ethanol and extracted with good solvents for the polymers [chloroform for most copolymers, dimethyl formamide for polyacrylonitrile, and acetone for poly(methyl acrylate)]. The samples were then dried in an oven at 105°C for 1 hr, removed to a desiccator, and weighed when cool. The per cent weight increase was calculated, allowance being made for the measured moisture content of the original wool samples.

This technique resulted in much faster graft-polymer formation and, for a limited range of monomer ratios (near 1:1), very much more reproducible results than could be obtained using homogeneous liquid phases incorporating organic solvents such as propanol, acetonitrile, or dioxane. Very little polymer was formed in the liquid phase, and the fiber surfaces were quite free from contamination by particulate deposits of polymer. The amount of polymer which could be solvent extracted in the cold was very small (approx. 0.25–0.5% at 100% polymer add-on) and independent of the

polymer composition. Soxhlet extraction with trichloroethylene resulted in about 2% loss of weight, some of which was probably wool wax.

Determination of Iron in Samples

Iron-impregnated wool samples (200 mg) were digested by heating in Kjeldahl flasks in 3 ml of freshly prepared 3:1 nitric:perchloric acid mixture until all nitric fumes were expelled and only a clear residue of perchloric acid containing white crystals remained. After standing for four days, the residue was transferred to a 20-ml volumetric flask and 2 ml of 30% ammonium thiocyanate was added. The optical density of the solution at 480 m μ was measured promptly against an appropriate reference solution. The method was checked by digesting wool samples to which known amounts of iron had been added.

Copolymer Composition Measurements

Copolymer compositions were determined by elemental analysis of grafted samples (nitrogen in the case of acrylonitrile copolymers and carbon for methyl acrylate copolymers). Nitrogen analyses were performed on a Coleman Model 29 nitrogen analyzer, while carbon analyses were made by Dr. A. D. Campbell, Microanalytical Laboratory, University of Otago, Dunedin. Nitrogen and carbon analyses were accurate to about 0.1% and 0.3%, respectively, which allowed the content of acrylonitrile or methyl acrylate to be determined to about 1% and 2%, respectively, at 100% polymer add-on.

RESULTS AND DISCUSSION

A guide to the ranges of concentrations and pH values to be employed was obtained from earlier work, especially that of Lipson and Speakman.¹ The effect on the polymerization rate of varying each of the following factors separately was examined: (1) time, temperature, and pH of impregnation; (2) concentration of ferrous ion in impregnation solution; (3) pH and concentration of peroxide solution; and (4) time and temperature of polymerization.

As mentioned above, reproducible results were only obtained with monomer mixtures near a 1:1 ratio, and, unless otherwise stated, the following results apply to copolymers grafted from such monomer mixtures.

Impregnation with Iron

Effect of pH. Figure 1 shows the dependence of graft polymer add-on on the pH of the iron impregnation solution. The values of the parameters are shown in the caption. It is notable that as the pH is decreased from 2.5 to below 1, there is a rapid increase in add-on for AN-BU (acrylonitrile-butadiene copolymers) and a similar but less marked effect for MA-BU (methyl acrylate-butadiene) copolymers. This is in spite of the fact that absorption of iron by wool is favored by a higher pH. In most of the experiments

described below, an impregnation pH of 0.9 was therefore chosen as routine. Very variable results were obtained above a pH of 3.0, owing to the instability of iron solutions.

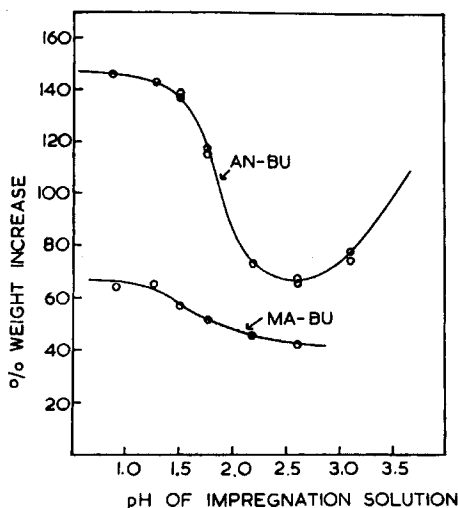


Fig. 1. Dependence on pH of impregnation solution of per cent weight increase after 90 min grafting at 50°C, 30 min impregnation at 50°C; 0.05*M* peroxide, pH 4.9 for AN-BU, 1.6 for MA-BU.

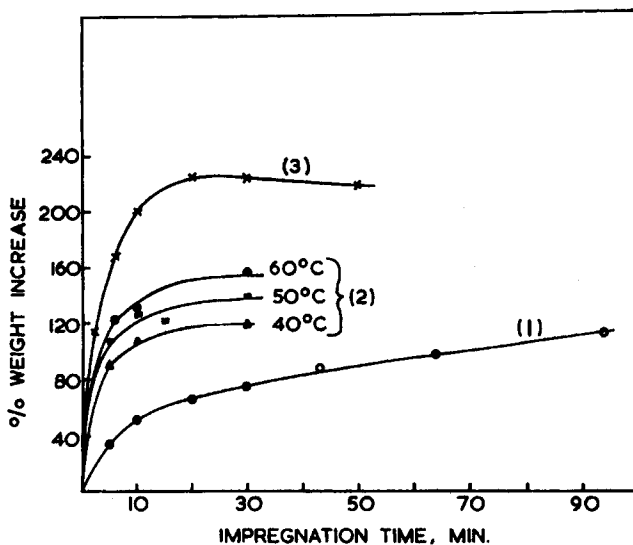


Fig. 2. Effect of time and temperature of impregnation on per cent weight increase of AN-BU polymer after 90 min grafting at 50°C: (1) impregnation at 50°C and pH 2.2 in 0.1% ferrous sulfate, 0.05*M* peroxide at pH 4.9; (2) impregnation pH 0.9, 0.1% ferrous sulfate, at the temperatures shown, 0.05*M* peroxide at pH 1.6; (3) as for (2) but 0.6% ferrous sulfate.

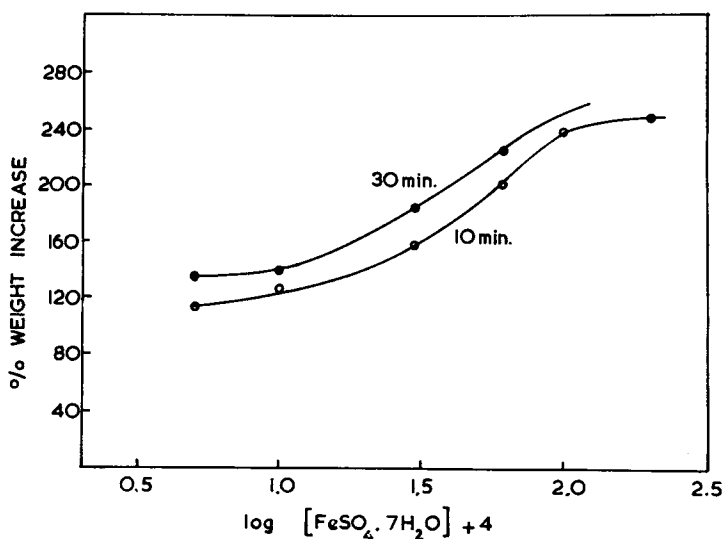


Fig. 3. Effect of iron concentration in impregnation solution on per cent weight increase of AN-BU polymer for 10 and 30 min impregnations at pH 0.9; 0.05M peroxide at pH 1.6.

The pH dependence of the rate of grafting may be explained by desorption of iron by acid from coordinating sites on the wool, and by the formation of sulfate complexes of iron at higher sulfuric acid concentrations leading to an increased rate of initiation.^{4,5} Thus, iron bound to wool at pH 2.2 may be comparatively ineffective in initiating reactions with peroxide, compared with "mobile" iron in the liquid swelling the fiber, particularly that in the form of a sulfate complex. Changes in volume swelling of wool with pH are small⁶ and cannot account for faster rates at lower pH through increased penetration of reagents.

Effect of Time and Temperature of Impregnation. Figure 2 illustrates the effect of time and temperature of impregnation on the yield of graft AN-BU polymer under conditions listed in the caption. It is clear that at pH 0.9 maximum grafting rates are achieved after a much shorter impregnation time than at pH 2.2. The effect of impregnation temperature on the polymer add-on is relatively small in the range of 40° to 60°C. For pH 0.9, curves versus time are shown for two different ferrous sulfate concentrations.

Effect of Iron Concentration. This is shown in Figure 3, for AN-BU polymers and ferrous sulfate concentrations between 0.05% and 2.0%. As expected, there is an increase in add-on with increased concentrations of ferrous sulfate. Above a concentration of 0.6%, however, there is a tendency for the wool to become discolored by the iron solution.

Amount of Iron in Wool. Table I gives the quantities of iron in wool ($\mu\text{g/g}$) for samples impregnated for various times in 0.1% ferrous sulfate solution at pH 0.9 and in a ferric nitrate solution at pH 0.9 of equivalent

TABLE I
Iron Content of Wool Impregnated with 0.1% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
or 0.145% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Impregnation time, min	pH	Fe in wool, $\mu\text{g/g}$	Ions in solution
0	0.9	58	Fe^{++}
5	0.9	98	Fe^{++}
10	0.9	105	Fe^{++}
15	0.9	91	Fe^{++}
20	0.9	96	Fe^{++}
30	0.9	100	Fe^{++}
20	2.2	179	Fe^{++}
30	2.2	173	Fe^{++}
20	0.9	137	Fe^{+++}
25	0.9	145	Fe^{+++}
30	0.9	149	Fe^{+++}

iron concentration. It is clear that there is no correlation between the rate of uptake of iron and the dependence of add-on on impregnation time (Fig. 2).

Ferric ions are more strongly absorbed than ferrous ions, and the amount of iron absorbed at pH 0.9 is much less than at higher pH, as expected.

Discussion of Initiation by Ferrous and Ferric Ion

Considerable graft polymer formation occurs in the absence of any iron impregnation step, owing to "native" iron in the wool. This is shown in

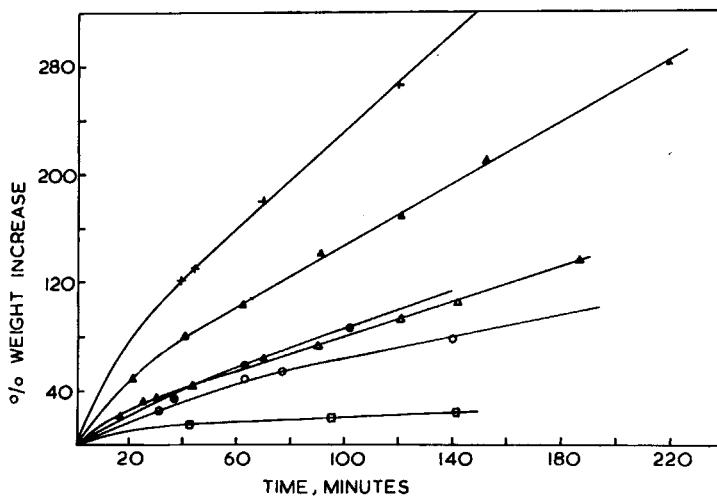


Fig. 4. Per cent weight increases of AN-BU polymer vs. time, with 0.05M peroxide at pH 1.6 for the following conditions of impregnation: (O) sulfuric acid, pH 2.2; (Δ) 0.1% ferrous sulfate, pH 2.2; (\bullet) sulfuric acid, pH 0.9; (Δ) 0.1% ferrous sulfate, pH 0.9; (+) 0.145% ferric nitrate, pH 0.9; (\square) 0.145% ferric nitrate, pH 0.9, with no peroxide in the grafting liquor.

Figure 4, in which is plotted the per cent polymer add-on versus time for samples impregnated beforehand for 30 min in sulfuric acid solutions of pH 0.9 and 2.2. For comparison, the curves for the reaction with added ferrous iron are included. In view of the high initial pH of the wool (9–10), it is to be expected that "native" iron will be in the ferric state. It is well known that ferric ions will catalyze the decomposition of hydrogen peroxide by a radical mechanism, though at a rate very much less than that of the ferrous ion reaction, and ferric ion–hydrogen peroxide systems have been used to initiate graft polymerizations.^{7,8} To check the effectiveness of ferric ions as initiators, wool samples were grafted after impregnation with a 0.145% solution of ferric nitrate nonahydrate at pH 0.9 (a ferric ion solution of the same iron concentration as 0.1% ferrous sulfate). The results are shown in Figure 4, and the quantity of iron absorbed by the wool is given in Table I. It is clear that ferric ions are very effective in initiation. Furthermore, at pH 0.9, the amount of polymer formed after any given time is closely proportional to the total iron content of the wool, as is shown in Table II. It is thus immaterial whether the iron is added as ferrous or ferric ions. This is to be expected from the rate constants of the reactions of hydrogen peroxide with ferrous⁹ and ferric¹⁰ ions, which when applied to the

TABLE II
Relative Polymer Add-ons at Three Polymerization Times^a of Wools
with Total Iron Contents in Ratio 0.59:1:1.47

Time, min	Ratio of polymer add-ons
50	0.52:1:1.52
90	0.57:1:1.53
130	0.56:1:1.55

^a From Figure 4.

present situation reveal that the ferrous ion in wool will be almost completely oxidized to ferric ion within a few seconds. Initiation thereafter ensues via a small steady-state concentration of ferrous ions proportional to, and of the order of 10^{-4} of, the ferric ion concentration. The rate of initiation of polymerization on the established mechanism⁹ is equal to the rate of production of hydroxyl radicals and proportional to the ferric ion concentration. The rate of polymerization should therefore be proportional to the square root of the iron content of the wool, assuming a classic vinyl polymerization, whereas it is observed to be first order in iron. This suggests that the termination step is first order in the growing radical concentration. This may not be unreasonable in the circumstances, as within the fiber the analog of a pronounced gel effect may prevail, so that the rate of second-order termination between polymer radicals may be greatly reduced and termination may occur predominantly by reaction with hydroperoxy radical or transfer to hydrogen peroxide leading to relatively inactive $\text{HO}_2\cdot$ radicals.

There are functional groups, notably thiol, in wool which can initiate polymerization through participation in redox reactions with peroxide.^{11,12} However, treatment of wool with a thiol-blocking reagent (iodoacetic acid) does not change the grafting behavior significantly, and it is concluded that, in normal unreduced wool, initiation by thiol is negligible. Figure 4 also shows the rate of grafting of ferric ion-impregnated wool in the absence of peroxide. The small weight increase is presumably due to chemical reactions of monomer with wool by cyanoethylation¹³ and possibly redox initiation between ferric ion and thiol.

Effect of pH and Concentration of Peroxide

Figure 5 illustrates the effect of peroxide pH on polymer add-on for both copolymers, for two different impregnation pH values. The decrease in add-on observed at low peroxide pH following impregnation at pH 0.9 is probably due to leaching of iron from the wool. The effect of peroxide pH following impregnation at pH 2.2 is consistent with the effects discussed in relation to impregnation, namely, activation of bound iron by desorption from coordinating sites and acceleration of the rate of initiation by formation of sulfate complexes.

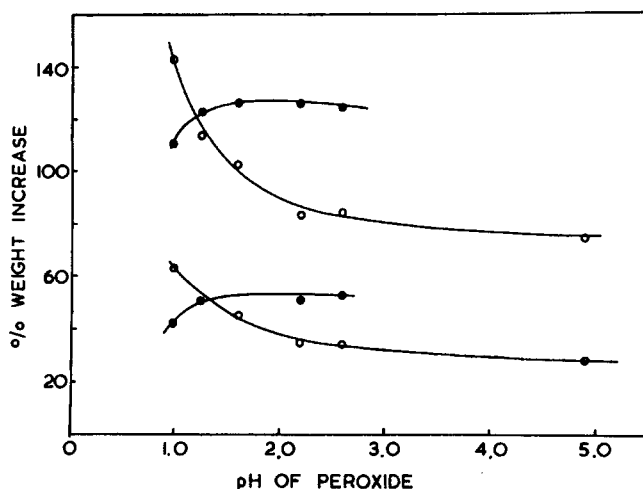


Fig. 5. Per cent weight increase vs. pH of 0.05M peroxide solution for AN-BU (upper curves) and MA-BU (lower curves), after 90 min at 50°C: (○) 30 min impregnation in 0.1% ferrous sulfate at pH 2.2; (●) 10 min impregnation at pH 0.9.

Maximum rates are observed after impregnation at pH 2.2 and a peroxide dip at pH 1, conditions which approximate to the optimum found by Lipson and Speakman¹ in their investigations with methacrylic acid. However, under these conditions, results are less reproducible than with impregnation at pH 0.9 and a peroxide pH of 1.6, and the latter conditions have been preferred in much of this work.

In the system under study, there is almost no dependence of grafting rate on peroxide concentration up to $0.25M$, whereas in solution redox polymerizations, the rate is reduced due to competition by peroxide for hydroxyl radicals. The suggestion of a termination step involving peroxide would explain why the rate is nearly independent of peroxide concentration.

Effect of Polymerization Temperature and Time

Curves of polymer add-on versus time are shown in Figure 6 for AN-BU polymers at temperatures 40, 50, and $60^{\circ}C$, and for MA-BU polymers at 50 and $60^{\circ}C$. In all cases the curves become linear after an initial nonlinear portion. The Arrhenius activation energy for the polymerization reaction calculated from the steady rate portion of the curves is 13.3 ± 1.0 kcal/mole for AN-BU polymers and 12.8 ± 1.0 for MA-BU polymers. The activation energies calculated from the initial rates are the same as these within experimental error, which suggests that the mechanism of the reaction is the same throughout its course and, in particular, that diffusion is not a limiting factor at any stage. At high polymer add-ons, such as seen in the $60^{\circ}C$ curve for AN-BU polymers, there is an acceleration in the rate. This is presumably due to gross changes in the grafting substrate.

If a sample is removed from the grafting medium, rinsed, dried, weighed, and then used as substrate in a new grafting experiment, the reaction continues on its normal kinetic curve as though it had never been interrupted. This indicates that the initial curvature in the kinetic plots

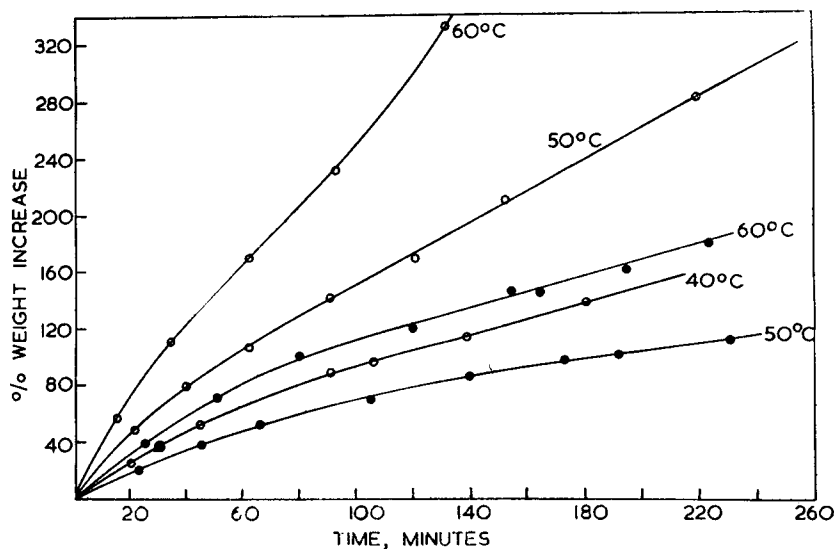


Fig. 6. Effect of time and temperature on per cent weight increases for: (O) AN-BU polymers; (●) MA-BU polymers. Impregnation 30 min at pH 0.9; $0.05M$ peroxide at pH 1.6.

is not associated with the attainment of a steady state by a chemical reaction or in the distribution of a reactant, but rather is due to an initially higher concentration of monomer in voids in the fiber and to a diminution in this overall concentration as the voids become filled with polymer.

Effect of Monomer Composition

As mentioned above, highly reproducible results can only be obtained by the present technique for monomer compositions near a 1:1 mole ratio. However, effective grafting occurs at all monomer compositions, as shown in Figure 7, in which the add-on of MA-BU polymer after 90 min at 60°C is plotted against the mole fraction of MA in the initial monomer mixture. The type of scatter in results which occurs is shown in this figure. In the case of AN-BU copolymers, reasonably reproducible results are obtained only after impregnation at low pH (0.9), and then the dependence of add-on on monomer composition is rather complex. Figures 8 and 9 show plots of the mole fraction of MA and AN in the monomer mixture versus composition for the graft copolymer formed. From these data, formal reactivity ratios may be calculated for the monomers by the Fineman-Ross procedure.¹⁴ These reactivity ratios are considerably different from those normally accepted.¹⁵ Because the relative concentration of monomers inside the fiber is probably quite different from that in the bulk monomer mixture, a more valid approach would be to accept the usual reactivity ratios and calculate the monomer ratio inside the fiber. In Figures 8 and 9, the calculated mole fraction of methyl acrylate and acrylonitrile in the wool fiber is plotted against the mole fraction in the monomer mixture. It is surprising, in view of the accepted hydrophilic nature of wool, that in both cases butadiene is preferentially absorbed. This suggests that there are regions of hydrophobic character in the fiber capable of being swollen with butadiene. These conclusions must be viewed with caution, because the polymerization may be initiated with varying degrees of effectiveness in different regions of the fiber. It is also possible that the monomer ratio within the fiber changes substantially during grafting, but it is difficult to detect this, as calculated polymer compositions are inaccurate at low add-ons.

Effect of Chemical Pretreatments on Grafting

Considerable variation between wools in the rate of their graft polymer uptake has been observed, possibly because of variations in grease content and degree of surface damage. These factors were investigated on a knitted merino fabric which grafted polymer slowly in the absence of any pretreatment. The effects of four pretreatments were examined: Soxhlet extraction with petroleum ether and alcohol, treatment with alcoholic alkali to disrupt the epicuticle,¹⁶ acid chlorination (2 g/l. NaOCl, pH 4, 1 min), and reduction of disulfide bonds. Figure 10 shows the results after these treatments. There is no significant difference between the effects of

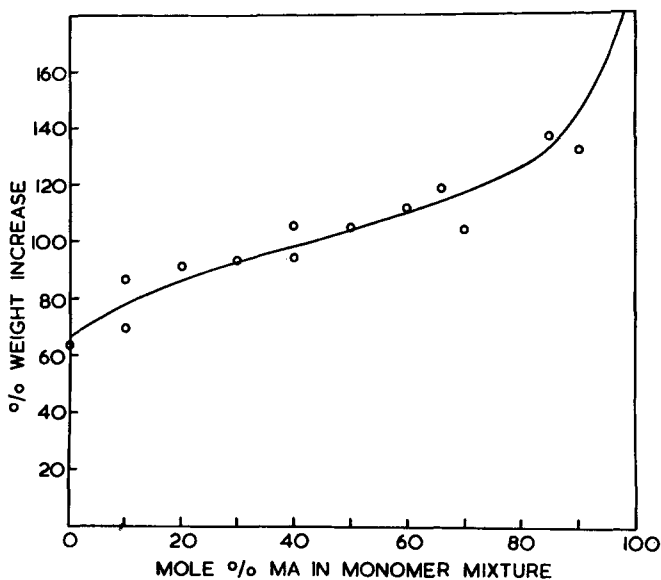


Fig. 7. Per cent weight increase of MA-BU polymers after 90 min at 60°C vs. mole-% MA in monomer. Impregnation for 30 min with 0.1% ferrous sulfate, pH 0.9; 0.05M peroxide, pH 1.6.

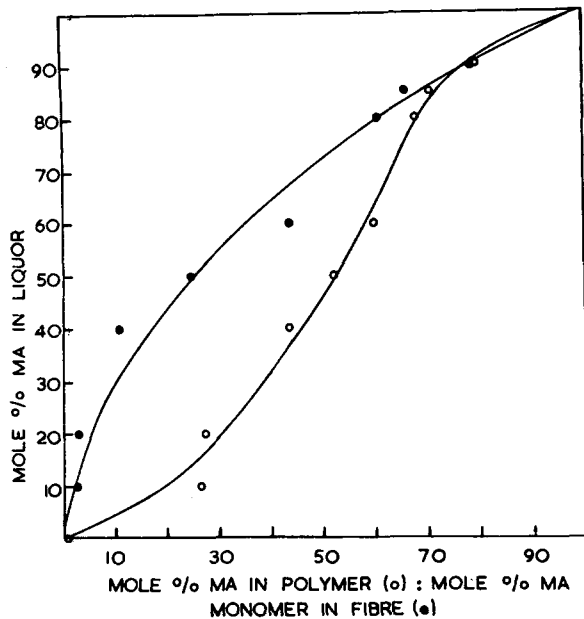


Fig. 8. Mole-% MA in monomer liquor vs. (O) mole-% MA in polymer, and (●) mole-% MA in monomer within fiber calculated from Fineman-Ross equation assuming normal reactivity ratios.

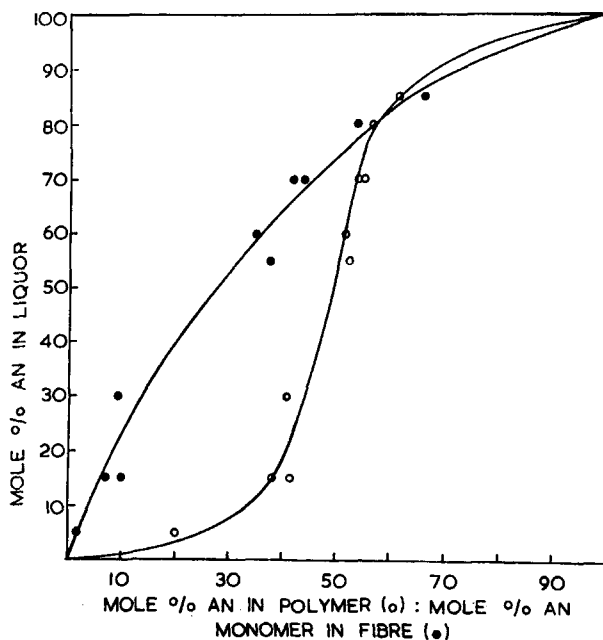


Fig. 9. Mole-% AN in monomer liquor vs. (O) mole-% AN in polymer, and (●) mole-% AN in monomer within fiber, as for Fig. 8.

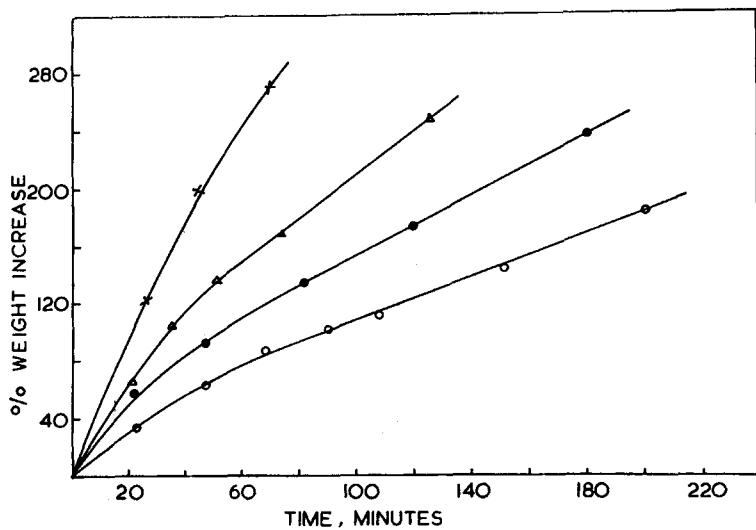


Fig. 10. Per cent weight increase vs. time of AN-BU polymer on merino cloth subjected to chemical pretreatments: (O) no pretreatment; (●) Soxhlet extraction and treatment with alcoholic alkali; (Δ) mild acid chlorination; (+) reduction with mercaptoethanol (25% disulfide reduced). Impregnation for 10 min in 0.1% ferrous sulfate, pH 0.9; 0.05M peroxide, pH 1.6.

Soxhlet extraction alone and in combination with alcoholic alkali. Reduction with mercaptoethanol for 145 min¹⁷ (approx. 25% reduction of disulfide to thiol) results in a greatly enhanced rate of grafting, no doubt through redox reactions between thiol and peroxide; thiol efficacy in initiating polymerization is very much less than ferric ion, however, as even native wool has approx. 2400 ppm cysteinyl residue or 20 μ mole/g. The similar effects of Soxhlet extraction and alcoholic alkali are probably due to both treatments acting predominantly by removal of wool wax, whereas acid chlorination causes chemical degradation of the fiber surface, mainly by oxidation of disulfide bonds.¹⁸

Observations on Polymer Residues after Protein Hydrolysis

The wool and graft butadiene copolymer may be separated by hydrolysis of the protein in 6*N* HCl overnight at 70°C. Considerable hydrolysis of the acrylate ester to acrylic acid residues occurs, and a minor amount of nitrile hydrolysis also takes place. No attempt has been made to characterize chemically the resulting materials. The polymer residues have considerable elasticity and strength and are insoluble in all solvents, indicating that the polymer is crosslinked.

In the case of deposits of homopolyacrylonitrile, the polymer was purified by dissolution in dimethylformamide, filtration, and precipitation in water. Nitrogen analysis indicated that 96% of the nitrile groups remained intact, and the infrared spectrum contained no absorptions attributable to peptide contamination. The viscosity-average molecular weight, determined from the relation of Cleland and Stockmayer for polyacrylonitrile,¹⁹ was 230,000. The presence of carboxyl groups raises the measured intrinsic viscosity, so that this molecular weight is probably too high.

The morphology of these polymer residues and their distribution within the fiber are at present being studied.

Application to Larger Wool Samples

The technique described, employing a liquor which is mostly monomer, is unsuitable on a large scale. However, qualitatively similar results are achieved on larger samples by employing a monomer emulsion. This has been established in experiments in which 2-lb lots of wool have been grafted with rubbery acrylate copolymers (e.g., ethyl acrylate-ethylene glycol dimethacrylate copolymers) in a Vald-Henriksen sample pressure dyeing machine, the liquor consisting of a monomer emulsified with sodium dodecyl sulfate in dilute acidified hydrogen peroxide solution.

Comparison with Previous Work

In comparing results described above with those obtained by other workers using the ferrous ion-hydrogen peroxide system, a number of differences are found. While the conditions for optimum polymer deposition may well vary from monomer to monomer, in our work the conditions which

promote the incorporation of copolymers also promote incorporation of any of the homopolymers—polyacrylonitrile, polybutadiene, and poly(methyl acrylate).

The most important parameters for polymer deposition are the pH's of the iron impregnation and the peroxide solutions. In this respect our observations accord well with those of Lipson and Speakman.¹ On the other hand, D'Arcy, Hall, and Watt,³ who investigated the effect of impregnation pH at two levels (approx. 1.3 and 3.3), claim that the effect of peroxide solution pH is negligible and that increase in the impregnation pH caused a small increase in the rate of polymer add-on. It is possible that the very high ferrous ammonium sulfate concentrations (1% and 4%) used by D'Arcy and co-workers result in such an excess of free iron in the fiber that the effect of pH is depressed. At such high iron concentrations, the wool becomes discolored by the absorbed iron.

Valentine² has suggested, on the basis of a weight increase linear in (time)^{1/2} and the observation of a saturated weight increase, that the deposition of polyacrylonitrile is diffusion controlled. There seems to be no reason why such a reaction should be linear in (time)^{1/2} or show a saturation weight increase when the diffusing species is undergoing a chemical reaction. D'Arcy and co-workers point out that the polymer appears to be uniformly distributed through the fiber and claim that diffusion does not affect the rate of polymerization.

In the present work, the rate of graft polymer formation depends primarily on the catalyst (iron) concentration (at sufficiently low pH), which demonstrates that there is always enough monomer within the fiber to scavenge all reactive primary radicals effectively. Treatments such as mild acid chlorination presumably facilitate polymerization by opening up regions of the fiber previously inaccessible to monomer, thereby increasing the overall initial monomer concentration. The facts that the initial rate is faster than the final rate and that the activation energies of the initial and final rates are comparable together mean that diffusion cannot be responsible for the initial nonlinear rate. It is concluded, therefore, that diffusion effects are negligible in this type of graft copolymerization.

The interest and advice of Dr. W. S. Simpson are gratefully acknowledged. Mr. D. D. Haden performed the analyses, and Miss M. A. Burrows assisted with some of the experimental work.

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