Polymer Deposition in Sisal Fibers: A Structural Investigation

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Synopsis

Sisal (Agave sisalana) fibers were graft copolymerized with certain vinyl monomers (methyl acrylate, ethyl acrylate and methyl methacrylate) using gamma irradiation and ceric ammonium nitrate as initiation techniques. Examinations of the surface topology and the internal structure of the grafted fibers were made by scanning electron microscopy. The results derived from the SEM observations on transverse sections of the grafted fibers were supplemented by information obtained by polarized light microscopy. Polymer was deposited not only on the surface of the fiber substrate, but also in the lumen, the middle lamellae, and throughout the cell wall network of the multicellular aggregates. The degree of polymer inclusion in the lumen (which is the most conspicuous of all the available internal sites) was found to depend on the percentage graft copolymer add-on, as well as on the previous history of the fiber (natural or chemically modified). The mechanical properties of the grafted fibers were investigated (by means of an Instron tensile tester).

INTRODUCTION

Since the development of synthetic polymers, there has been a growing area of research devoted to the modification of natural textile fibers and fabrics by incorporating specific polymers to bring about changes in their physicochemical properties, e.g., stiffening, softening, wrinkle resistance, abrasion resistance, tear resistance, and shrink-proofing.[1] Although graft copolymerization of monomers onto sisal fibers has not been studied to date, a vast amount of work has been reported on the grafting of wool, silk, cotton, rayon, and some other man-made fibres.

It has been shown[2,3] that graft copolymerization on textile fibers is a suitable means of adding new and desired properties without drastically affecting the basic properties of the substrate. Indeed, shrink-proofing by an interfacial polymerization process,[4,5] oil-repellent finish by grafting of fluoropolymer,[6] and grafting of some vinyl monomers onto wool to give the fiber a less hydrophilic character have found commercial applications. In cotton fibers, Goynes[7] has reported that radiation-induced grafting of methyl methacrylate and acrylonitrile increases their thermoplasticity, as well as their abrasion and rot resistance.

In this report, experimental results are presented of our investigation of graft copolymerization of some vinyl monomers on to sisal fibers with particular reference to their structural modifications.

EXPERIMENTAL

Materials and Methods

Sisal fibers were dewaxed by Soxhlet extraction for 24 hr using a mixture of benzene and alcohol (1:1). After a thorough washing in distilled water, the sample was allowed to dry in air and eventually conditioned at 65% R.H. and 22.2°C.

Methyl acrylate (MA), ethyl acrylate (EA), methyl methacrylate (MMA), and acrylonitrile (AN) monomers, all from Köch-Light Laboratories Ltd., were purified by distillation at their respective boiling points in order to free the monomers from stabilizers.

The irradiation was carried out using gamma rays from a ^{60}Co source, stationing the sample in the radiation chamber at a precalibrated position at which the approximate dose rate was 2×10^4 J/kg-hr (2 Mrad). MA and EA were used for the graft copolymerization reactions by the irradiation technique, and AR grade ceric ammonium nitrate (CAN), also obtained from the Köch-Light Laboratories Ltd., was used as the initiator for polymerization of MMA and AN.

The scanning electron microscopy (SEM) was accomplished with a Cambridge Stereoscan S4 operating in the reflection mode. The samples were coated with silver by evaporating *in vacuo* before the SEM examination so that detailed information of the surface characteristics could be obtained. The optical micrographs were obtained by using a Baker polarizing microscope, for which the fiber cross sections were prepared in a Hardy microtome.

RESULTS AND DISCUSSION

Radiation-Induced Graft Copolymerization

Two different methods were followed to bring about graft copolymerization of MA and EA onto untreated sisal fibers using the irradiation techniques of (1) preirradiation and (2) mutual irradiation. For (1) a known amount of fiber was subjected to a required dose of radiation from the ^{60}Co source and was subsequently immersed in a monomer–water mixture which was kept at a constant temperature in a water bath. For (2), a known amount of the fiber was immersed in a monomer–water mixture and then irradiated for a required length of time at room temperature. In both methods the fibers were first extracted with hot acetone and finally with hot benzene to remove nongrafted homopolymers. The treated fibers were then conditioned at 65% R.H. and 22.2°C until a constant weight was obtained. The increase in weight of the conditioned grafted fiber, expressed as a percentage of the original weight of the conditioned ungrafted fiber, has been taken as the percentage graft (add-on).[8] By varying the irradiation dosage, the monomer concentration, and the reaction time, varying degrees of add-ons were obtained. These are summarized in Tables I–IV.

In agreement with published work on other cellulosic fibers,[9,10] it was observed that the add-ons were greater using the mutual irradiation technique. However, the formation of homopolymers in this technique of polymerization is always higher, and hence the exact amount of the true graft may be subject to a considerable degree of error.

TABLE I
Preirradiation Grafting with MA[a]

Bath temperature, °C	Reaction time, hr	Add-on, %
20	4	0.7
20	18	0.7
20	138	1.3
20	284	5.0
25	116	7.0

[a] Conditions: Monomer:water, 10:100; sisal sample, 1 g; irradiation dose, 5×10^4 J/kg.

TABLE II
Mutual Irradiation Grafting with MA[a]

Irradiation dosage, J/kg	Monomer:water	Reaction time, hr	Add-on, %
6×10^4	10:100	3	13.5
2×10^4	20:100	1	20.0

[a] Conditions: Temperature 20°C; sisal sample, 1 g.

TABLE III
Preirradiation Grafting with EA[a]

Reaction time, hr	Add-on, %
18	2.3
72	2.6
138	3.3
165	3.6
222	2.7

[a] Conditions: monomer:water, 20:2; bath temperature, 30°C; irradiation dose, 2×10^4 J/kg; sisal sample, 1.5 g.

TABLE IV
Mutual Irradiation Grafting with EA[a]

Reaction time, hr	Add-on, %
0.5	25.8

[a] Conditions: monomer:water, 15:0.5; sisal sample, 0.5 g; irradiation dose, 1×10^4 J/kg; temperature, 20°C.

The importance of the study of radiation-induced graft copolymerization to cellulosic substrates has been clearly emphasized by Guthrie[11] in a recent review article. Although industrial interest in this technique of modifying fiber properties is minimum, there has already been enough experimental work to show that some physicochemical properties can be improved by controlled reactions with specific polymers. Several reviews[12-14] have been reported on the nature of the reactions and the properties of the grafted materials. In a cellulose graft

copolymer, the resultant properties have been shown to be a combination of the natural properties of the substrate and those of the grafted polymer.[14,15]   The reaction mechanism of the high-energy radiation grafting consists of

1. initiation by radical formation, 2. initiation of grafting at the free radical sites, 3. propagation of the grafting reactions, and 4. termination by radical recombination or by completion of copolymerization with possible homopolymer as the byproduct.

A complete list of preirradiation and mutual irradiation techniques of grafting to cellulosic materials has been presented by Guthrie,[11] with relevant remarks on the experimental data.

Chemical Initiation of Graft Copolymerization

Speakman and Barr[16] deposited vinyl monomers onto wool fibers by the method of "redox activation," using hydrogen peroxide and a catalyst solution. A vapor-phase technique of vinyl monomer deposition in delignified jute fibers was employed by Sengupta.[17]   Using thermal and free-radical initiation methods, Landells and Whewell[18,19] obtained a considerable degree of grafting of some monomers in cellulosic fibers and concluded that polymer deposition took place inside the fibrous structure.   In their further experiments[20] they studied the physicochemical properties of the grafted fibers and showed that the water of imbibition of cellulosic fibers could be reduced by the deposition of hydrophobic polymers.

The use of CAN as an initiator was first shown by Mino and Kaizerman[21] in the copolymerization of acrylamide in polyvinyl alcohol.   Since then the use of the cericcerous redox system to initiate graft copolymerization of vinyl monomers with cellulose has been reported by many investigators.[22-25]

The graft copolymerization of monomers onto cellulosic substrates by ceric ion initiation mechanism is also a free-radical process, similar to the case of gamma-irradiation initiation.   It has been shown by Arthur[26] that in acid solution, ceric ions chelate with the cellulose molecule, causing oxidative degradation and formation of transient free radicals, presumably at C_2 and/or C_3 atoms of the anhydroglucose unit:
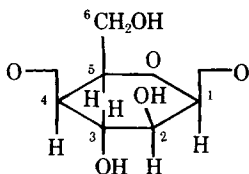
These free-radical sites are all accessible to vinyl monomers for the formation of graft copolymers with the substrate.[27]

In our method of polymerization, the initiator solution was prepared by dissolving 5.48 g CAN in 100 ml $0.5M$ HNO_3 solution.   The initiation of graft copolymerization of MMA and AN was carried out on sisal fibers pretreated with 8% and 16% NaOH solutions, respectively, for 1 hr at 20°C, washed, and dried. The required amount of pretreated sisal fiber (conditioned at 65% R.H. and

22.2°C) was soaked in the distilled monomer solution in a dyeing tube which was clamped on the rotating frame of a thermostatic bath. The initiator solution was also allowed to reach the bath temperature, before adding to the reaction tube, and allowed to react for a required period of time. The results of the grafting reactions are presented in Table V.

It can be seen from Table V that at a particular temperature of polymerization, the percentage copolymer add-on is dependent on the monomer initiator ratio and type of the monomer, as well as on the pretreatment of the sisal fiber. It was shown[28] that with increasing concentration of NaOH solution, an increasing degree of fibrillation can be achieved for sisal fibers. This "intracrystallite" process of fibrillation in the alkali-treated fiber provides a condition for higher degrees of polymer deposition, which has been revealed in the PMMA grafted fibers.

Surface Morphology of the Grafted Sisal Fibers

The surface characteristics of the untreated and the grafted sisal fibers as obtained by SEM are shown in Figs. 1–6. In order to elucidate the detailed topological changes under the grafting reactions, the micrographs of the grafted fibers are presented with two different instrument magnifications. Since the surface of the untreated sisal fiber (Fig. 1) contains extraneous cellulosic residues as a result of the decortication process, the topographical changes in the fiber at lower levels of grafting are found to be difficult to differentiate from the ungrafted surface. A similar conclusion was arrived at by Goynes[7] in his microscopic characterization of grafted cotton fibers. However, with higher add-ons of copolymer, the surface characteristics become significantly different from those of the untreated sample. A large amount of foreign matter can be seen (20% PMA grafted sisal) on the surface of the grafted fibers, which must therefore be deposited polymer. The anchoring sites for the deposited polymer in the fiber surface are the positions of the vestigial attachments of the paranchymatous cells

TABLE V
Grafting on Sisal by CAN Initiation[a]

Sample	Monomer/ volume ml	Remarks
1.5 g sisal (16% NaOH)	AN/50	The whole of the AN polymerized to a solid block from which the sisal fiber could not be extracted with dimethylformamide (almost all homopolymer).
1.5 g sisal (16% NaOH)	AN/15	Almost all the homopolymer was extracted with difficulty, leaving 250% add-on (copolymer). Too much homopolymer.
1 g sisal (8% NaOH)	MMA/10	Homopolymer was easily extracted with hot acetone and then with hot benzene, leaving 109% add-on (copolymer)
1 g sisal (16% NaOH)	MMA/10	Homopolymer was easily extracted with hot acetone and then with hot benzene, leaving 127% add-on (copolymer).

[a] Conditions: Bath temperature, 48°C; reaction time, 1 hr; initiator volume, 50 ml.
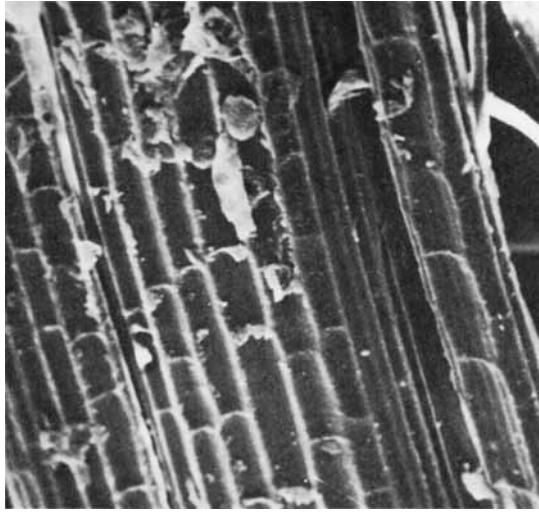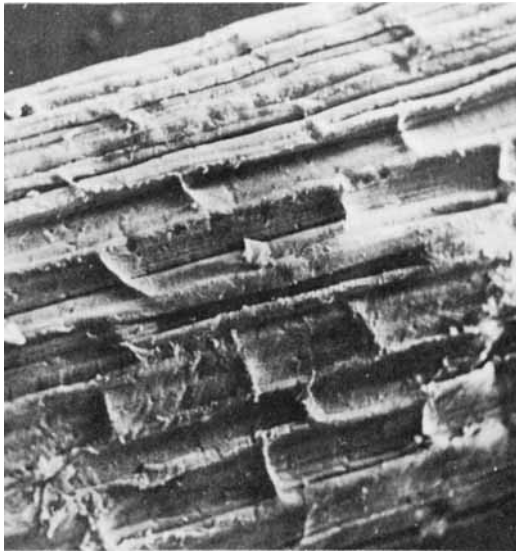
Fig. 1. Surface topology of untreated sisal fibers, ×300.

Fig. 2. Surface topology of 0.7% PMA grafted sisal fibers, ×300.

in which the fiber is embedded in the plant leaf. At a much higher level of polymer deposition, as obtained for PMMA with a chemical-initiation technique, the surface topology has undergone marked changes (Figs. 5 and 6). The fibers became "woolly," and occasional polymer bridges could be seen between the separated bundles of sisal ultimates. The appearance of "cracked" polymer deposits on the surface is evident at higher magnifications. During PMMA grafting, due to the mechanical action involved, the fibers were found to be disintegrated, and ultimates were occasionally removed from the fiber surface.
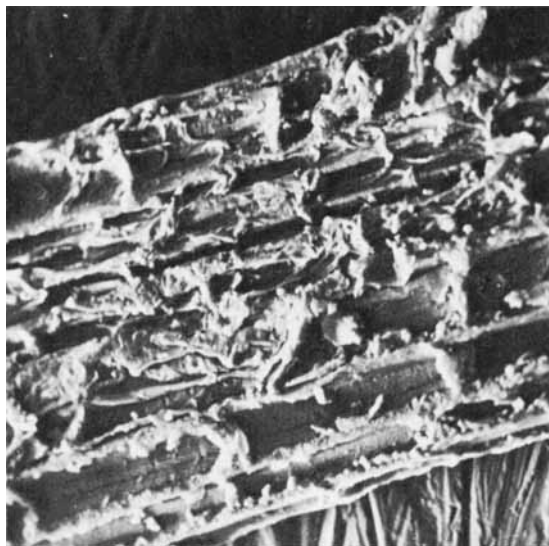
Fig. 3. Surface topology of 20% PMA grafted sisal fibers, ×300.

Fig. 4. Surface topology of 20% PMA grafted sisal fibers, ×1500.

Location of Grafted Copolymer Inside the Fiber

The effect of the distribution of the polymer in the fibrous structure determines the characteristic properties of the grafted fiber. Light and electron microscopy have been successfully used by various authors to identify the polymer location and its distribution inside the fiber.[7,29-32] No report to date has, however, been published on the grafting behavior of the sisal fibers. We have therefore studied the distribution of the deposited graft polymer in sisal fibers with SEM and polarized light microscopy.

The micrographs obtained by SEM from the transverse sections of ungrafted and PMMA grafted fibers are shown in Figures 7 and 8, respectively, and those

Fig. 5. Surface topology of 109% PMMA grafted sisal fibers, ×480.

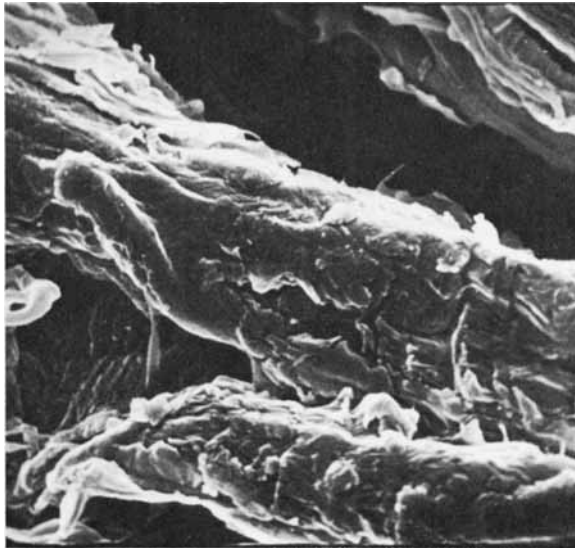

Fig. 6. Surface topology of 109% PMMA grafted sisal fibers, ×1200.

obtained by polarized light microscopy, using the analyzer and polarizer at crossed position, are presented in Figs. 9–11. The multicellular structure of the natural sisal fibers is characterized by a large number of prominent lumen, the middle lamellae (where the lignin content is shown to be concentrated), and the thickened cell walls (Figs. 7 and 9). In the SEM photograph the differentiation of the S_1, S_2, and S_3 layers in the cell wall cannot be obtained. They are, however, well resolved in the polarized light micrograph (Fig. 9). The transverse sections of the grafted fibers as obtained by SEM show very few open lumen (Fig. 8), and most of the fibers appear to possess a solid structure. The light micrographs
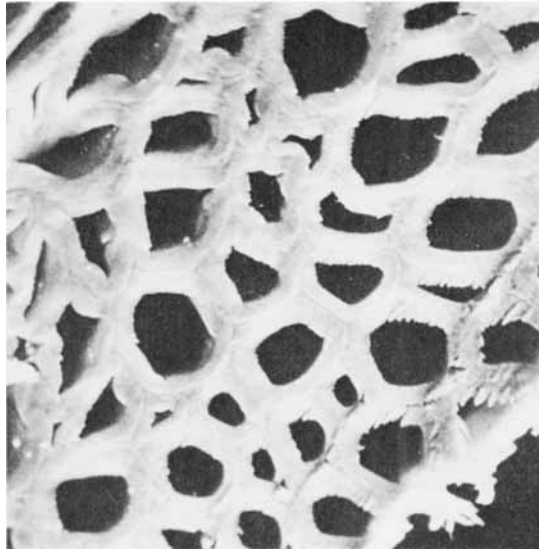
Fig. 7. SEM photograph of a transverse section of untreated sisal fibers, ×1300.
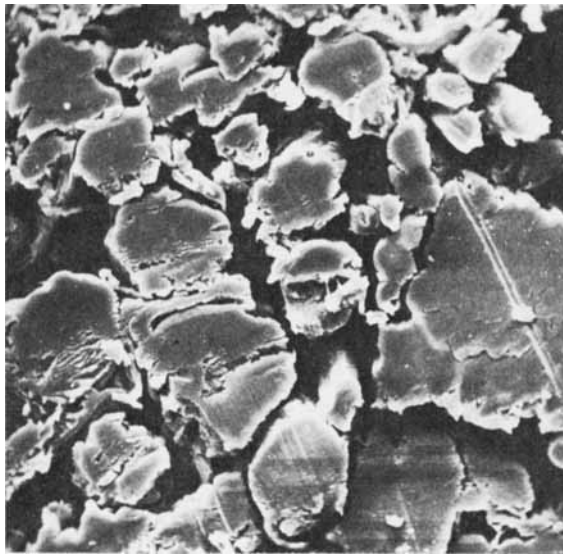

Fig. 8. SEM transverse section of 127% PMMA grafted sisal fibers, ×480.

of the grafted fibers (Fig. 11) clearly demonstrate that with a higher degree of grafting, the polymer is not only located on the surface as was stated earlier, but also in the lumen, the middle lamellae, and to a certain extent between the cell wall network of the fiber structure. But with 26% PEA grafted fiber very little deposition was obtained in the lumen (Fig. 10). Our results are in good agreement with those of Kaepper et al.,[31] who showed that the voids in Fortisan fibers were filled up when grafted with polystyrene. Uniform distribution of polymer
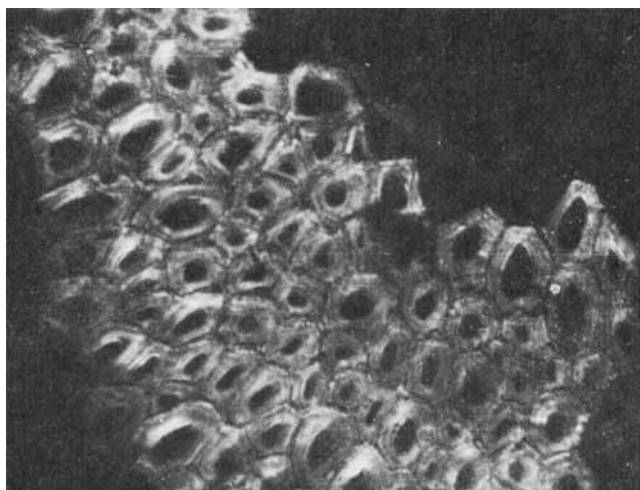
Fig. 9. Polarized light micrograph of a transverse section of untreated sisal fibers, ×400; photomag ×5.

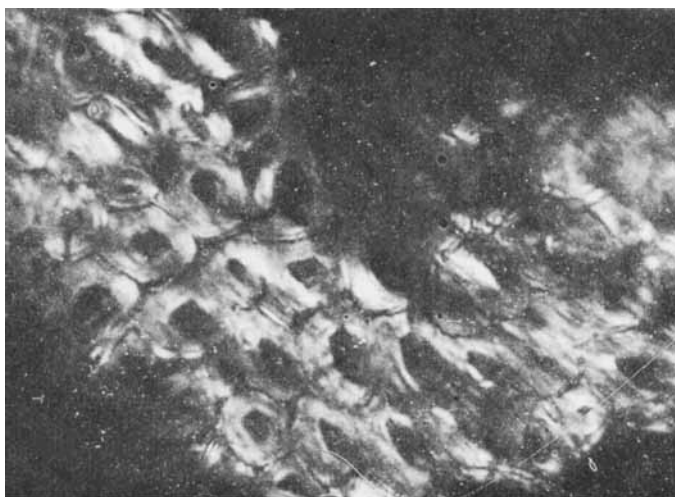Fig. 10. Polarized light micrograph of a transverse section of 26% PEA grafted sisal fibers, ×400; photomag ×5.

in cotton fibers was obtained by Arthur[22,33] and others in the chemical redox initiation technique with Ce^{4+} ion. Rollins and his associates[34] are of the opinion that the morphological characteristics of grafted cellulose fibers depend on (1) the method of initiation, (2) experimental conditions during the copolymerization, (3) chemical modification of the cellulose before polymerization, and (4) the type of monomer used. The roles that these factors play in determining the polymer location and its distributions in grafted cotton fibers have been illustrated by Arthur.[14] It is thus apparent that by the inclusion of specific and varied degrees of polymer in the sisal fibers, the modification in their fiber properties can be brought about.
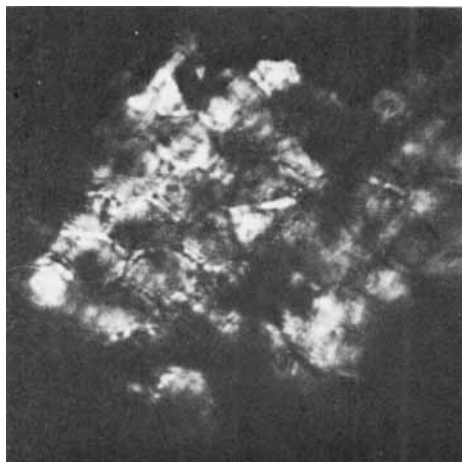
Fig. 11. Polarized light micrograph of a transverse section of 109% PMMA grafted sisal fibers, ×400; photomag ×5.

X-Ray Diffraction Data of the Grafted Sisal Fibers

The molecular structures of the natural and the grafted sisal fibers were studied by means of x-ray diffraction. The x-ray diffraction photographs of untreated, 13.5% PMA grafted (irradiation technique) and 127% PMMA grafted (chemical redox initiation technique) sisal fibers are shown in Figs. 12–14. No apparent changes could be observed in the natural crystalline lattice structure of sisal cellulose in the grafted samples. The diffraction photograph of the untreated fiber is marked by a diffused background, typical of the lignocellulosic fibers with unresolved reflections from the 101 and 10$\bar{1}$ planes. The background is brighter in the diffraction patterns of the grafted samples. While there is no change in the crystallinity or orientation of the 13.5% PMA grafted fiber, there is evidence of an increased resolution of the reflections from the 101 and 10$\bar{1}$ plane and the degree of crystallinity and orientation in the 127% PMMA grafted sample. In the case of wool fibers grafted with PMMA, Arai and Negishi[35] have shown that the α-diffraction pattern does not change on grafting with PMMA.
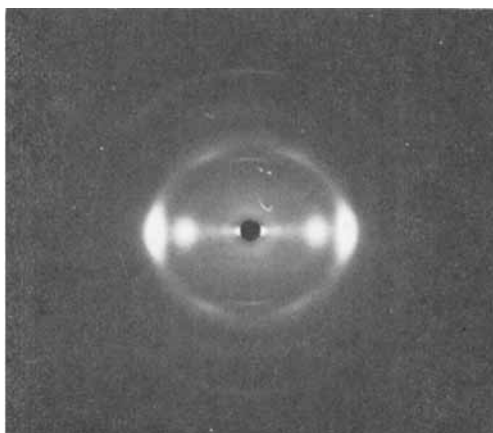

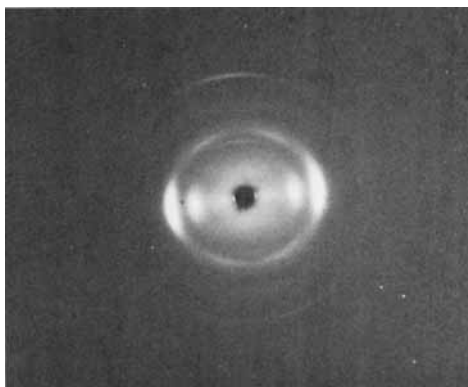Fig. 12. X-ray diffraction photograph of natural sisal fibers.

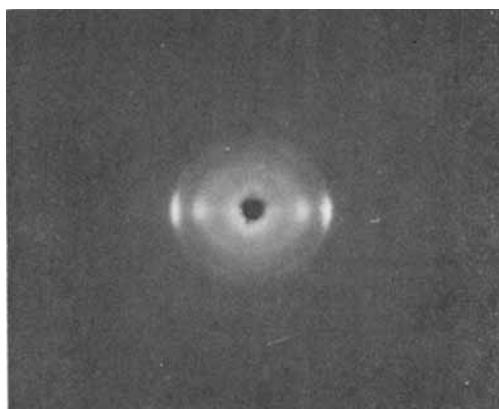Fig. 13. X-ray diffraction photograph of 13.5% PMA grafted sisal fibers.

Fig. 14. X-ray diffraction photograph of 127% PMMA grafted sisal fibers.

However, they have reported that the PMMA halo is found superimposed in the diffraction photograph. It is believed that in the present experiments on sisal, the amorphous halo due to the polymer is merely contributing to the background scattering. It can be suggested that the polymer deposition contributes only to the amorphous regions of the fiber, without any disturbance to the crystalline lattice. The penetration of the polymer molecules in between the cellulose layers brings about the increased crystallinity and orientation. In his work on microscopic observation of the grafted Fortisan, Kaepper[31] showed that polystyrene filled up the cellulose microfibrils and that an isometric expansion of the filaments due to the polymer impregnation took place. Although the present experiments cannot prove the penetration of polymers in the microfibrils, in light of the x-ray diffraction work it can be tentatively suggested to be unlikely.

Mechanical Properties of the Grafted Sisal Fibers

The load-extension characteristic curves of the natural and grafted fibers were obtained by means of an Instron tensile tester. It was observed that the load-extension curves of the sisal fibers were dependent on the rate of traverse of the crosshead. While a straight line graph was obtained for all the samples using a crosshead speed of 5 cm/min, the characteristic graphs employing a crosshead

speed of 2 cm/min are shown in Fig. 15 for raw, PEA, PMA, and PMMA grafted fibers. These graphs are all characterized by three distinct regions: the Hookean, yield, and the postyield. The yield region occurs at a load range of approximately 0.55–0.65 kg for all the samples except for the fibers with 127% PMMA graft, for which the yield region occurred at a load range of 1.2–1.25 kg, as can be seen from the figure. Thus the load-extension behavior of the grafted sisal fibers were not altered, although different slopes for the initial, yield, and the postyield regions were distinctly apparent. All the grafted samples have lower values for the breaking load, signifying that a loss in fiber strength resulted during the polymerization reactions, although there was grafted copolymer inside the fiber. Variation in the values of the breaking extensions was also observed for the grafted fibers. Lower values of about 3% for 109% PMMA, 3.6% PEA, and 5.0% PMA grafts, 4% for 0.7% PEA and 20.0% PMA grafts; and higher values of 8% for 127% PMMA and 7.5% for 13.5% PMA grafts were observed compared to a breaking extension of about 5.0% for the natural fiber. The apparent lack of correlation between the type of polymer and the breaking load and breaking extension can be attributed to the changes in the fiber dimensions inherent in, and brought about by, the polymerization reactions to the sample. Such variations in load-extension properties of wool fiber grafted with various polymers have been summarized by Arai.[36] Explanation of the alterations in the slope characteristics of the three regions for grafted wool fibers is possible in terms of polymer–polymer, polymer–microfibril, polymer–matrix, and microfibril–matrix interactions, as was shown by Arai. However, considerable disagreement still exists about the stress-strain behavior of graft-modified wool fibers. The
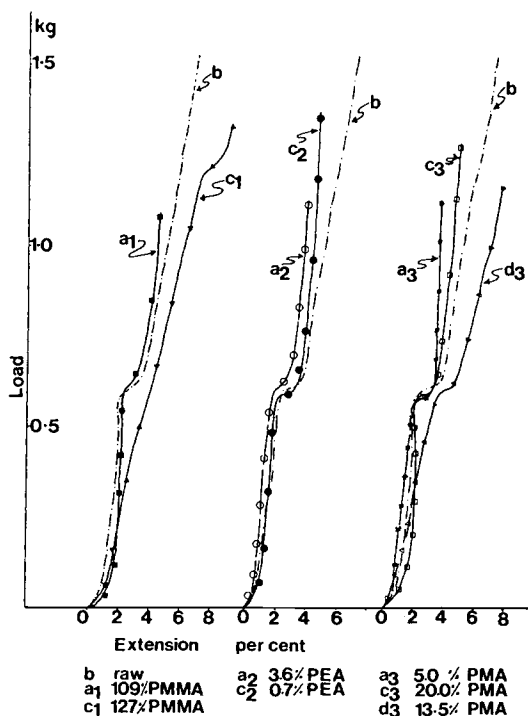

Fig. 15. Characteristic load-extension curves of untreated and grafted sisal fibers.

enormous variation in structural properties of the sisal fiber, both within an individual fiber along its entire length and between different fibers in the same leaf or from different leaves, makes the study of the mechanical properties rather complex. These first results obtained on grafted sisal show that by a suitable choice of polymer, the fiber's mechanical properties can be modified so that use can be made of the fiber in a desired commercial field. As was shown earlier in the morphology of the graft copolymer, the tensile behavior of grafted sisal also depends on (1) the method of initiation, (2) the type of the monomer, and (3) the percentage graft copolymer.

CONCLUSION

The present investigation has shown that a substantial graft on sisal fibers can be obtained in simple polymerization processes in aqueous medium, either by high-energy irradiation or by using chemical redox systems. By varying the reaction parameters, it is possible to obtain different degrees of copolymerization, which brings about changes in the physicochemical properties of the fiber. The fibers grafted with PEA and PMA by the irradiation technique were found to possess a soft hand, whereas those grafted with PMMA had some stiff properties. The hand of the fibers in the latter process of grafting depends on the degree of mercerization before polymer deposition.

It is believed that with an optimum amount of grafted stiff polymer, sisal fiber can be used as a brush-making material. Softened grafted sisal may be used in making underfelt and carpet backings. Moreover, if experience with similar grafts on other naturally occurring fibers is followed, the polymer-treated sisal is likely to resist microbial damage and have soil-resistant properties. These latter properties will have a great bearing in the manufacture of agricultural twines and baling twines for the shipping industry.

The structural studies of the grafted fibers with respect to the polymer location and distribution, together with the study of the load-extension characteristics of the grafted fibers, have formed a basis to understand the fiber properties resulting from their modification by polymer deposition.

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