Effect of Radiation Chemical Treatment on Sisal Fibers I. Radiation Induced Grafting of Ethyl Acrylate

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Synopsis

Radiation induced graft copolymerization of ethyl acrylate onto sisal fibers was investigated. It was found that the percent added-on of ethyl acrylate to sisal fibers was prohibitively low when using the direct grafting method due to excessive homopolymerization. The preirradiation method was found to be invalid for improving the grafting content. In the presence of small amounts of styrene (St) the copolymerization can be achieved with little homopolymer formation by the direct grafting technique. The presence of sulfuric acid in the grafting solution enhances the grafting of styrene–ethyl acrylate comonomer to sisal fibers. the effect of different solvents, monomer concentration, and irradiation doses were followed. Sisal fibers were treated with sodium hydroxide, sulfuric acid, and combined treatment of both of them. The effect of these treatments on the grafting content was investigated. The grafting yield decreased when sisal fibers were subjected to alkali treatment under tension. However, sisal fibers pretreated with 0.4N sulfuric acid showed a slight increase in the grafting yield over the untreated samples.

INTRODUCTION

Sisal is a hard vegetable fiber obtained from the leaves of plants growing mainly in tropical countries. They are used most extensively for cordage. Wilson[1] studied the possiblility of chemically modifying the fibers, but he rejected the idea due to the loss in strength accompanying the chemical treatments. Barkakaty[2] also investigated the chemical modification of sisal fibers by treatments with sodium hydroxide and sulfuric acid. In a recent report,[3] sisal fibers were graft copolymerized with acrylonitrile, ethyl acrylate, and methyl methacrylate using gamma radiation, and ceric ammonium nitrate, as source of initiation. The surface topology and the internal structure of the grafted fibers were investigated, but no systematic study was done on the grafting process.

In this report radiation induced graft copolymerization of ethyl acrylate onto sisal fibers was investigated. As radiation doses over 0.02 MGy may cause degradation to the fiber, and since ethyl acrylate is very sensitive to radiation, grafting conditions have to be found which minimize both irradiation dose and homopolymerization. The effect of adding styrene as a protecting agent to the grafting solution, and the effect of mineral acids on the enhancement of the grafting process were considered.

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EXPERIMENTAL

Materials and Methods

Materials

Sisal fibers were furnished by El-Canal Ropes Co., Port Said, Egypt. The fibers were dewaxed by extraction in benzene and methanol followed by washing with distilled water. The samples were dried under vacuum at room temperature and were stored under dry conditions before investigation. Ethyl acrylate (EA) obtained from Koch Light Laboratories Ltd., (UK) was purified by distillation. Styrene (St) supplied from Backer Chemical Co. was washed successively with solutions of 2% sodium hydroxide, 2% sulfuric acid, and with distilled water, dried over calcium chloride and then distilled prior to use. All other chemicals were reagent grade and were used as supplied.

Methods

In all the experiments reported 220 Canadian Type Gamma Cell of 6300 Curie Co[60] was used. It had a dose rate of 0.32 Gy/s. The percent graft was defined as 100 $\times$ increase in weight of the sample divided by the original weight. All samples were extracted with the appropriate solvent for the homopolymer in a Soxhlet to constant weight.

a. **Grafting via Preirradiation Method**. Sisal samples were first irradiated in air. The samples were then placed in contact with the monomer solution in the reaction tube. The contents of the tubes were degassed by three freeze and thaw cycles at 10^{-3}mm Hg. The samples were then kept in a temperature-controlled water bath for the required time and temperature.

b. **Grafting via Mutual Method**. The sisal samples and the monomer solution were assembled together in the grafting tube. Nitrogen gas was bubbled in the monomer solution for about 10 min and then the tubes were sealed under a nitrogen atmosphere. These samples were irradiated to the desired dose. The sisal fibers were then extracted with benzene and acetone, dried, and weighed.

c. **Sodium Hydroxide Treatment.** Sisal samples were treated with sodium hydroxide solution of different concentrations (8, 16, and 30%) at room temperature for 40 min, under a low tensile stress. The treated samples were washed several times with distilled water and dried.

d. **Acid Treatment.** Sisal samples were treated with 0.4N sulfuric acid solution for 40 mins at the boil. The samples were then washed several times with distilled water.

e. **Combined Treatment.** Sisal fibers were treated with sodium hydroxide followed by the acid treatment described previously.

RESULTS AND DISCUSSION

Exploratory experiments concerned with the radiation grafting of EA to sisal fibers using the direct method with a 20–80 mixture of monomer and aqueous methonal showed a grafting yield not more than 1%. When high

doses were employed, crosslinking of poly(ethyl acrylate) occurred, and sisal fibers could not be isolated by extraction (Table I). Similar behaviour was observed in the radiation induced grafting of acrylic acid and 2, 3 dibromopropylacrylate onto nylon-6[4] and polyester,[5] respectively. Under these conditions, the preirradiation method would be a suitable technique for suppressing homopolymerization and increasing the grafting yield. Unfortunately, this was not the case. Homopolymerization was reduced because ethyl acrylate was not directly subjected to gamma irradiation, but the grafting content was still too low ($\simeq$ 1%) (Table II).

Grafting to sisal can differ from grafting to purer forms of cellulose in respect to: (1) the accessibility or swelling characteristics, particularly with water; and (2) the presence of materials such as lignin which may act as an inhibitor of the grafting reactions. Phillips et al.[6] studied the effect of lignin on the radiation grafting of some vinyl monomers onto wood pulp. They pointed out that the presence of lignin retards polymerization. However, it was reported that the graftability of lignin containing pulps appeared to be highly dependent on the particular monomer used. Thus, in the grafting of styrene to wood pulps grafting yield was found to increase with lignin content of the pulp,[7] while the grafting of acrylamide is strongly inhibited by only a few percent lignin.[8] The reasons for these differences are not clear.

According to the preliminary data given above and since sisal contains 8% lignin,[1] the retardation in grafting of EA to sisal can be explained partially by the high susceptibility of EA to radiation and partially by the retarding effect of lignin. Similar behavior was reported.[9]

To overcome these difficulties, styrene was added to the grafting solution. The comonomer technique using sytrene as one of the monomers in the mixture was reported for the grafting of radiation sensitive monomers.[10] Moreover, the presence of styrene may overcome the barrier of lignin which retards ethyl acrylate grafting. It was reported[7] that the grafting of styrene to wood pulp increased with the lignin content of the pulp. Consequently, it was expected that carrying out mutual irradiation grafting of ethyl acrylate on sisal fibers in the presence of styrene would make the technique more efficient.

Effect of Styrene Content

Figure 1 shows the effect of adding different amounts of styrene to the monomer solution on the grafting of ethyl acrylate onto sisal fibers. The grafting solution contains 50% monomer and 50% solvent (vol %). The

TABLE I
Mutual Irradiation Grafting to Sisal Fibers with EA

Irradiation dosage (kGy)	Monomer solution			Grafting percentage
	EA	H_2O	Me OH	
1	20	10	70	1.0
2	20	10	70	Homopolymer
5	20	10	70	Homopolymer
10	20	10	70	Homopolymer

TABLE II
Preirradiation Grafting to Sisal Fibers with EA

Irradiation dosage (MGy)	Reaction time (h)	Bath temp (°C)	Grafting percentage
0.02	2	40	0.1
0.02	4	40	0.4
0.02	6	40	0.3
0.02	8	40	1.0

solvent contains 80 parts methanol and 20 parts distilled water. The percentage weight increase due to grafting increases sharply with styrene content then reaches a maximum at about 25% styrene. Thereafter, the grafting percentage decreases gradually as the styrene content increases. This is true for both the samples irradiated up to a total irradiation dose of 0.017 MGy and 0.0078 MGy.

The extent of grafting by the direct irradiation method depends on the relative G values for radical formation of the polymer and the monomer.
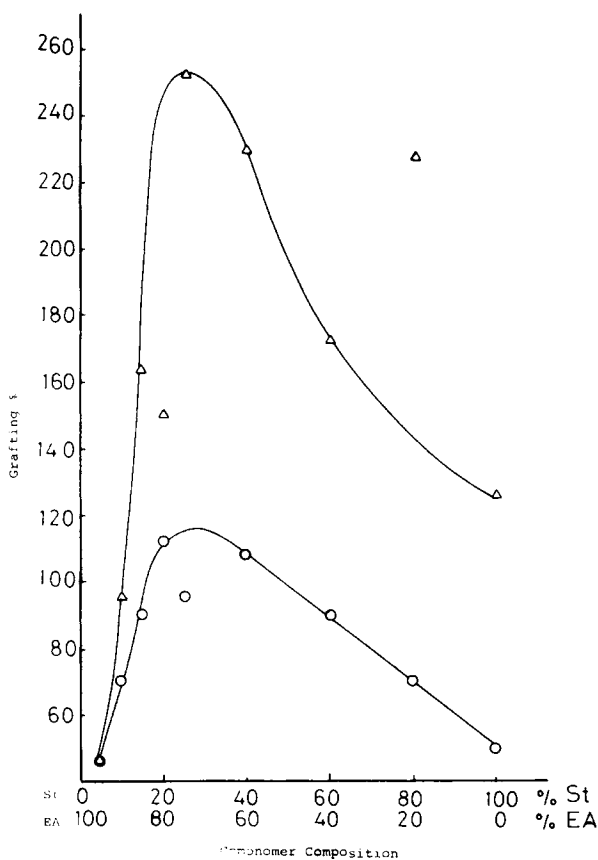

Fig. 1.   Effect of styrene content, 50% total monomer: ($\triangle$) irradiation dose 0.017 MGy; ($\bigcirc$) irradiation dose 0.0078 MGy

In the case of the ethyl acrylate–sisal system, where ethyl acrylate is very sensitive to radiation, most of the free radicals will be from the monomer and the system exhibits a marked tendency towards homopolymerization. By adding styrene to the grafting mixture, the grafting percentage increases as the styrene content increases and reaches a maximum. As styrene contains aromatic rings which have a resisting nature to radiation, the presence of styrene in the monomer solution protects ethyl acrylate. In this case the number of free radicals formed in the monomer solution should be decreased as the styrene content increases. This situation favor the grafting process.

When the styrene fraction exceeds 25% of the monomer content, the grafting percentage decreases and reaches a minimum value at 100% styrene. As the styrene content increases, the tendency towards homopolymerization decreases. Consequently, the viscosity of the monomer solution decreases. In a system of low viscosity the mobility of free radicals increases, and the probability of these free radicals combining with each other increases. In this medium the rate of termination increases by increasing styrene concentration. This accounts for the decrease in the grafting percentage as the styrene content increases over 25%.

Effect of Comonomer Concentration

The effect of comonomer concentration on the grafting yield was studied using four different comonomer compositions. The total dose was kept constant (0.0117 MGy). The comonomer–solvent ratio was changed without altering the solvent composition [80:20 (v/v) methanol:water]. These data are depicted in Figure 2.

Generally the percentage weight increase due to grafting increases as the comonomer concentration increases. However, at a low styrene content in the comonomer, the grafting percentage levels off at about 30% comonomer. While the system containing 10% styrene levels off at about 50% comonomer. On the other hand, in the systems containing higher styrene contents, the weight gained due to grafting, increases as the comonomer concentration increases up to about 80%.

As the concentration of the comonomer increases, the amount of aqueous methanol in the mother liquor decreases. Styrene–ethyl acrylate comonomer is of limited solubility in cellulose, and swelling of cellulose is caused mainly by sorption of aqueous methanol.[11] Thus, at low aqueous methanol concentrations the amorphous regions of cellulose, where grafting predominates,[12] would swell to a lesser extent and would be a medium of higher viscosity. In this medium, the rates of propagation and chain initiation increase with increasing concentration of comonomer available for grafting. The net result is an increase in the grafting yield due to the gel effect.

The tendency of the four different systems under investigation to reach plateau at certain monomer concentration can be explained by the relative susceptibility of the four different systems to radiation.

Effect of Acid

The solvents used in the grafting process play an important role. They participates in the overall reaction as an energy transfer agent and may increase the formation of free radicals in the polymer.
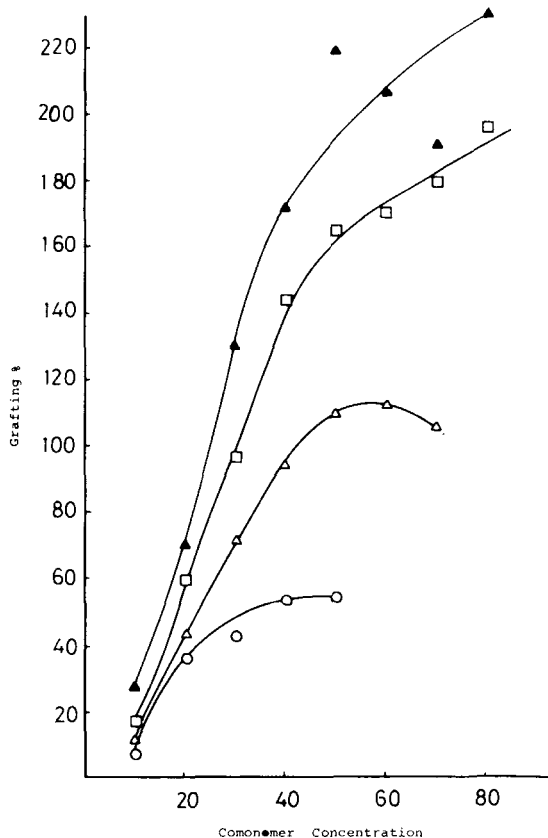
Fig. 2. Effect of comonomer concentration, dose 0.0117 MGy styrene percent in the comonomer: (▲) 20%; (□) 15%; (△) 10%; (○) 5%.

Figure 3 shows the results obtained in the grafting of ethyl acrylate–styrene comonomer on sisal fibers using sulfuric acid of different concentratios. The monomer concentration was kept constant (25% vol %) throughout all the experiments. All the samples were irradiated to 0.0078 MGy. From Figure 3 it is clear that the presence of sulfuric acid accelerates the grafting process. Moreover, the grafting yield increases as the concentration of sulfuric acid increases. The enhancement of grafting due to the presence of sulfuric acid has been reported elsewhere.[13,14] The presence of sulfuric acid affects the yields of radiolyses products from methanol. Thus, there is a considerably higher concentration of excited states, radicals, and ions, particularly hydrogen atoms, with increasing acid concentration in the methanol–monomer grafting solution. Styrene and ethyl acrylate being strong radical scavengers will readily react with the above species, particularly the hydrogen atoms, leading to both higher homopolymerization and grafting rates.

Dilli and Garnett[15,16] have discussed the formation of radical sites in the trunk polymer by hydrogen abstraction reactions

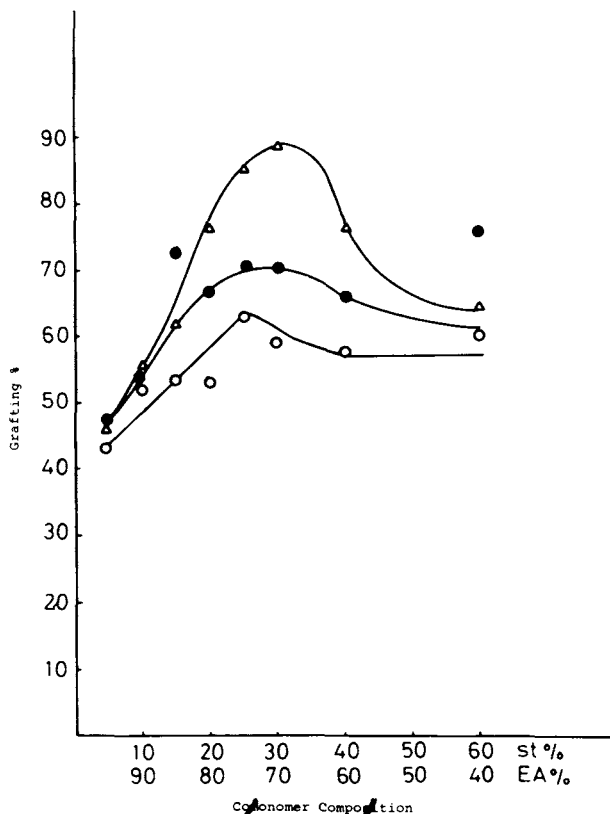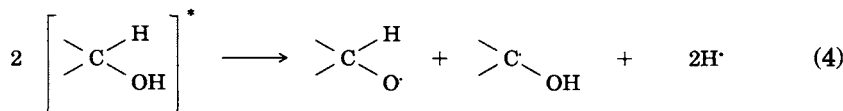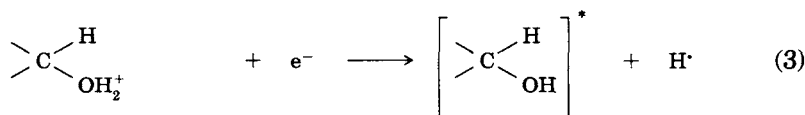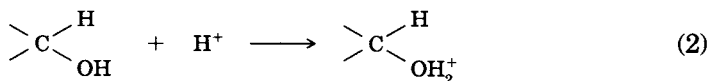$$(Ce) + H \rightarrow Ce^\bullet + H_2 \tag{1}$$

Fig. 3. Effect of acid, 25% total monomer, dose 0.0078 MGy solvent composition: (○) 80% MeOH + 20% H_2O; (●) 80% MeOH + 20% $0.2N$ H_2SO_4; (△) 80% MeOH + 20% $0.4N$ H_2SO_4.

Addition of mineral acids to the grafting solution leads to protonation reactions in cellulose of the type depicted in eq (2). the capture of secondary electrons by the charged species in eq. (3) leads to excited cellulose molecules. Decomposition of such excited cellulose molecules yields macroradicals capable of grafting [eq. (4)]. Thus it is apparent that the inclusion of acid in the grafting solution could increase the number of sites available in cellulose for radiation copolymerization, paticularly due to reactions involving hydrogen atoms.

$$>C{<}^H_{OH} \quad + \quad H^+ \quad \longrightarrow \quad >C{<}^H_{OH_2^+} \tag{2}$$

$$>C{<}^H_{OH_2^+} \quad + \quad e^- \quad \longrightarrow \quad \left[>C{<}^H_{OH} \right]^* \quad + \quad H{\cdot} \tag{3}$$

$$2\left[>C{<}^H_{OH} \right]^* \quad \longrightarrow \quad >C{<}^H_{O{\cdot}} \quad + \quad >C{<}_{OH} \quad + \quad 2H{\cdot} \tag{4}$$

Effect of Irradiation Dose

Figure 4 shows the results obtained in the direct irradiation grafting of styrene–ethyl acrylate comonomer on sisal fibers from 25% comonomer solution in aqueous methanol. Grafting was carried out at doses ranging from 0.003 to 0.027 MGy. It can be seen that, with the increase in dosage and, consequently, the increase in number of activated sites on sisal, the extent of graft copolymerization increased. This behavior was observed in the systems containing high contents of styrene. But, in the presence of a low styrene concentration, and with increasing dosage, the grafting yield increases at the initial stages of irradiation and reaches a limiting value at about 0.01 MGy. Under the latter conditions, considerable homopolymerization was observed.

Effect of Pretreatment

Figure 5 shows the results obtained in the radiation grafting of styrene–ethyl acrylate comonomer onto sisal fibers subjected to different pretreatments. The comonomer concentration was kept constant at 25% (10:90 St:EA) in aqueous methanol. The samples were subjected to different irradiation doses. It is clear from this figure that the grafting yield of the
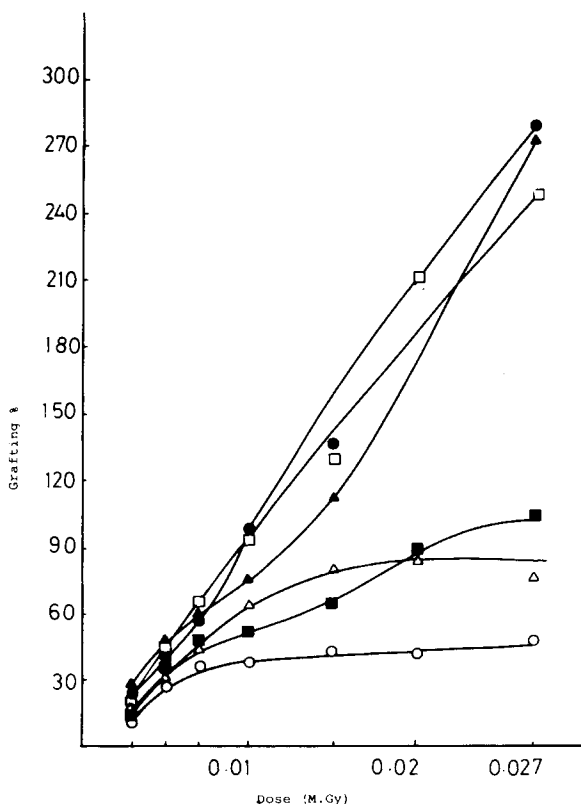

Fig. 4. Effect of irradiation dose, 25% total monomer styrene percent in the comonomer: (○) 5%; (▲) 20%; (□) 30%; (●) 50%; (■) 100%; (△) 10%.
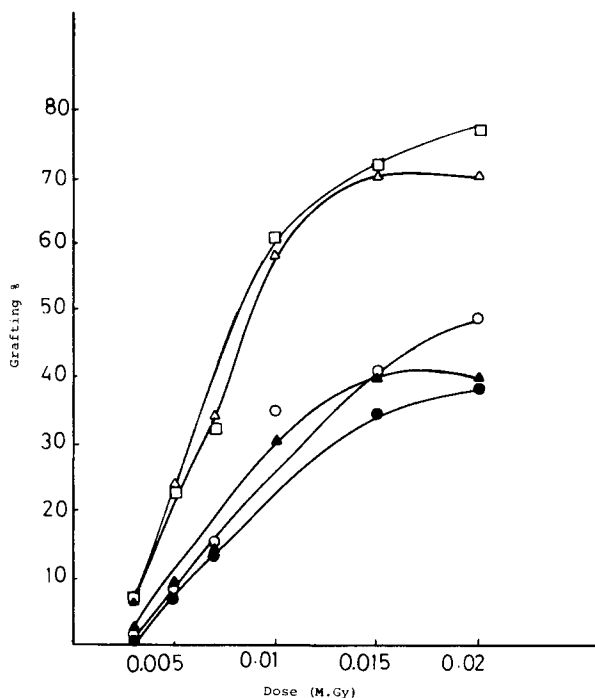
Fig. 5.   Effect of pretreatment, 25% total monomer (△) pure sisal; (□) pretreated by 0.4 N H₂SO₄; (○) pretreated by 8% NaOH; (▲) pretreated by 16% NaOH; (●) combined treatment.

pretreated sisal fibers with $0.4\,N$ sulfuric acid is higher than the untreated samples. The effect of mineral acids on cellulosic materials is, in general, to cause depolymerization, resulting in short chain fragments. The microscopic examination of the surface structure of the sulfuric pretreated fibers (Fig. 6) shows fibrillation due to intracrystallite swelling by the acid. This effect may facilitate the subsequent penetration of the monomer solution during the grafting process. Thus the monomer available for grafting increases. This accounts for the increased grafting yield of the sample pretreated with acid.

Figure 5 shows that the grafting yield decreases when sisal fibers were subjected to alkali treatment under tension. Moreover, the grafting yield decreases as the concentration of the alkali solution increases. The lowest grafting percentage was observed for samples subjected to the combined treatment.

The increase in the molecular interaction beside the increase in crystallinity due to the alkali treatment will result in a reduction in the sorbtion capacity of the fiber. As a result, the amount of monomer solution sorbed in the fiber during the grafting process will be reduced. This accounts for the decrease in the grafting percentage of sisal fibers subjected to alkali treatment. When the fibers were subjected to the combined treatment, the fibrillation which is due to the intracrystallite swelling by the acid, facilitates the subsequent penetration of the sodium hydroxide solution bringing about modification to cellulose.[17] Moreover, the combined treatment may
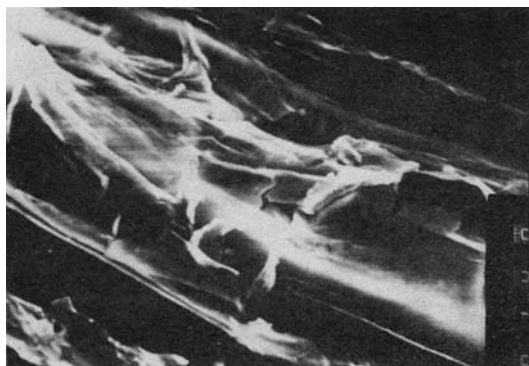
Fig. 6. Surface morphology of sisal fibers treated by 0.4N sulfuric acid, magnified 1000 times.

result in increase in ordering of the fibers beside the increase in the crystalline regions. These effects are reflected in the slight decrease in the grafting yield of the fibers subjected to the combined treatment compared that of the fibers subjected to the alkali treatment alone.

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