Uncatalyzed Photografting of Polyacrylamide from Functionalized Cellulosic and Lignocellulosic Materials

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ABSTRACT: Photoinitiated graft copolymerization of polyacrylamide (PAAm) occurred on one cellulosic (cotton fabric) and one lignocellulosic (sisal fiber) substrate using a novel photocatalytic system. The samples were photoexposed with oxalic acid solutions, differing in acid concentrations, which functionalized the backbone materials to different extents with carboxyl groups, and at the same time rendered them photoactive. Afterwards, the functionalized samples were again photoexposed with monomer (AAm) solution and photografting was found to take place without any initiator from outside. The effects of increased acid dose level and increased monomer concentration on different grafting parameters were measured. The graft copolymer formation was confirmed by FTIR and DSC studies; XRD and SEM techniques were applied for morphological studies. Textile-related properties, namely tensile properties, moisture regain, and dye uptake properties of both the ungrafted and grafted materials were also measured using proper instruments and techniques. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1623–1634, 1999

Key words: photografting; photofunctionalization; cellulose; lignocellulose; polyacrylamide; textile properties

INTRODUCTION

Graft copolymerization of vinyl and related monomers on preformed polymeric backbones of different origins[1–6] offers an effective way of modification of the physical and chemical properties of the polymers to different degrees. This technique was most widely studied in connection with the modification or tailoring of the properties of naturally occurring cellulosic and lignocellulosic materials.[7,8] A host of polymers, namely polyacrylamide (PAAm), poly(methyl methacrylate) (PMMA), etc., and some of their copolymers,[9,10] were successfully grafted on the cellulosic and lignocellulosic substrates (fiber, fabric, film, pulp, powder, etc.) by thermal and/or photochemical processes[9,11] by using water soluble/insoluble initiators.[8,11,12] Again, functionalization of existing polymeric backbones prior to graft copolymerization, aiming at successful modification of the former, is also a well-established technique.[13] In each case, some of the physical, chemical, and textile-related properties, like crystallinity,[7] tensile strength, dyeability,[10] ion exchange properties,[3,14] etc., are found to be significantly modified. However, the selection of catalyst is very important in this context in keeping the susceptibility of cellulose toward oxidative and hydrolytic degradation in view.

In this article, a novel method of graft copolymerization of acrylamide on a cellulosic (cotton fabric) and a lignocellulosic (sisal fiber) substrate

is described by using a novel photocatalytic system, in which the catalyst is already present in the backbone. In one of our previous communications, we reported the acid functionalization of some cellulosic and lignocellulosic fibers using the aqueous solution of some photoactive organic acids.[15] It was also reported there, that the fibers, after functionalization, are rendered photoactive and can initiate the graft copolymerization of acrylamide when photoexposed in N_2 atmosphere without using any initiator from the outside. In the present article, this method of uncatalyzed photografting is studied in detail by using one cellulosic and one lignocellulosic system.

Graft copolymerization cannot run equally well with cellulosic and lignocellulosic substrates; lignin present in the lignocellulosic materials is reported to inhibit the grafting reaction by destroying the free radicals generated.[16,17] To get a complete picture of this new photocatalytic system, we have therefore chosen one cellulosic and one lignocellulosic system as polymeric backbones for graft copolymerization. Sisal fiber is a lignocellulosic-fiber, chemical composition, and the uses of which were reported earlier.[18,19] However, its susceptibility toward graft copolymerization is not as well explored as jute fiber. In our present work, we selected this leaf fiber with the aim of modifying different properties of it. Conventional grafting parameters, along with the changes in some of the physical, chemical, and textile-related properties as a result of the graft copolymerization, were measured, and relevant results are reported with proper explanation.

EXPERIMENTAL

Materials

Fiber/Fabric

Raw sisal fiber and plane-weave cotton fabric (weighing about 108 g m^{-2}, having an average of 315 end and pick per decimeter and an average warp and weft count of 47.23 tex) were supplied by Institute of Jute Technology, Calcutta, India.

Chemicals

Both the oxalic acid (used for photofunctionalization) and acrylamide (AAm; used as monomer) were obtained from E. Marck, Calcutta, India. Acid-dye Sandolon Black and Sandolon-E. Bri

supplied by Atic Industries, Gujrat, India were used for dyeability studies of the grafted samples.

Methods

Pretreatment of Fabric/Fibers

Defatting of Fabric/Fiber. Portions (10 g) of each of the fabric and the raw fiber were subjected to defatting under reflux condition using a benzene–methanol (1 : 2 v/v) mixture for 6 h at 80°C. Afterwards, the solvent was taken out and the defatted samples were dried at room temperature in a flow of dust-free air.

Scouring of Fabric/Fiber. Defatted substrates were scoured by boiling with a dilute (1%) solution of NaOH for 10 min for removal of gummy matters. The samples were washed thoroughly with hot and cold water and dried at 50°C.

Photofunctionalization Prior to Grafting. A 1 g portion of each of the scoured and dewaxed cotton fabric and sisal fiber samples was treated with three different dose levels of oxalic acid as described elsewhere.[15] After the mentioned time of acid treatment, the functionalized samples were washed thoroughly with hot and cold water to remove the free acid and dried at 50°C.

Graft Copolymerization.

A known weight of each of the acid functionalized fiber/fabric samples were immersed in an aqueous solution of AAm (in Pyrex tubes) varying in concentration of the monomer. The material/liquor ratio was kept as 1 : 10 in each case. The test tubes were stoppered tightly after a flow of N_2 for 3 min and were then photoexposed to a pair of fluorescent lamps 40 W each inside a photochamber for 8 h at 30°C. A control experiment was done in each case where the unfunctionalized fibers (only scoured and defatted) were photoexposed under identical conditions. Afterwards, the graft copolymer, along with a considerable amount of formed homopolymer, was precipitated out by using distilled methanol and subsequently dried in vacuum at 50°C to obtain the gross polymer product. Polymerization was not observed with the control systems. The free polymer was separated from the gross product by extraction with distilled water under reflux condition in a soxhlet apparatus for the required time. The residue was dried again at 50°C to get the apparent graft copolymer. Total conversion, percent of grafting, and grafting efficiency were calculated in the usual manner.[1]

Characterizations Done

Infrared (IR) Spectroscopy. IR spectra of finely powdered, grafted and ungrafted fabric, and fiber samples were taken using a Perkin–Elmer (1600 series) FTIR spectrophotometer, employing KBr disk technique.

Differential Scanning Calorimetry (DSC). Thermal analyses of the test samples were done by DSC using a Mettler TA 3000 system under N_2 atmosphere maintaining a heating rate of $20 \pm 1°C \ min^{-1}$ and sample weight of about 6.2 mg.

Scanning Electron Microscopy (SEM). Surface morphology of ungrafted and grafted sisal fiber samples were examined using a Hitachi S-415A electron microscope at 25 kV, following a sputter-coating technique. The same study was not done on cotton fabric samples.

X-Ray Diffraction. X-ray diffraction patterns of ungrafted (acid functionalized) and grafted cotton fabric and sisal fiber samples were taken from pressed pellets using a Philips Difractometer (PW 1710).

Measurements of Textile Properties

Tensile Testing. The fiber tenacity, elongation at break or breaking extension, and initial modulus values of fabric and fiber samples were evaluated using a Zwick 1445 CRT universal tensile testing machine as per IS: 1969–1968.[20] Fiber samples of 2.0-cm length and fabric samples of 5.0×2.0 cm size, taken from warp direction, were used for tensile testing. Initial modulus values were calculated at 0.5% elongation.

Dyeability Studies. Both ungrafted and grafted fabric and fiber samples were subjected to dyeing by using an acid dye Sandolon-E Bri ($\lambda_{max} = 560$ nm, C.I. = 105) and Sandolon Black ($\lambda_{max} = 480$ nm, C.I., 155), respectively. The dye receptivity, K/S value of the dyed fibers, were examined in a Macbeth 2020+ reflectance spectrophotometer interfaced with a computer. The reflectance values (R) of the dyed samples at the wavelength of maximum absorption (λ_{max}) were converted to the corresponding K/S values using the Kubelka–Munk equation (i.e., $K/S = (1 - R)^2/2R$), where K is the absorption coefficient and S is the scattering coefficient.[21]

Measurement of Moisture Regain. Initial and grafted fabrics and fibers, dried at 100°C for 2 h, were allowed to stand in a closed chamber for 72 h over saturated $NaNO_3$ solution (65% relative humidity) at 30°C for assessment of their moisture regain values, calculated from the gain in weight.

RESULTS AND DISCUSSION

It was reported that the photoexposure of cellulosic and lignocellulosic fibers with an aqueous solution of oxalic acid not only functionalizes the cellulosic backbone with —COOH functional groups but also renders the fibers photoactive so that uncatalyzed photografting of acrylamide can take place on them. In one of our previous reports, different aspects of the photofunctionalization part of this work was thoroughly discussed.[15] However, detailed studies regarding the graft copolymerization reaction were awaited. A thorough and careful study, relating the effects of different experimental conditions on the grafting parameters and the effect of PAAm grafting on mechanical, thermal, morphological, and textile-related properties of the fibers, is the primary subject in this article. The work was performed with two different types (one cellulosic and one lignocellulosic) of substrates; the results of the experiments and analyses are discussed here.

Graft Copolymerization

Effect of Variation of Acid Values of the Fibers

It was reported that acid values of the fibers increase significantly on increasing the initial concentration of the acid used for functionalization. The effect of acid value of the substrates on different grafting parameters was studied using cotton fabric and sisal fiber (Tables I and II), both treated with three different dose levels of oxalic acid as substrate and AAm as monomer. In the case of grafting with PAAm on both the substrates, the percentage of grafting is found to increase remarkably with an increase in acid values of the substrates, when a high monomer concentration is maintained. But with lower monomer concentration, the change in substrate acid value hardly affects the percentage of grafting. With the cotton cellulose, the percentage of grafting increases almost regularly with an increase in the substrate acid value, whereas the same varies

Table I   Graft Copolymerization of Acrylamide on Acid-Functionalized Cotton Fabric

Oxalic Acid Used for Pretreatment (g)	Acrylamide Used (g)	Gross Polymer (g)	Apparent Graft Copolymer (g)	Total Conversion (%)	Grafting (%)	Grafting Efficiency (%)
	0.5	1.113	1.012	22.60	1.20	10.57
	1.0	1.242	1.036	24.20	3.60	14.90
1.0	1.5	1.363	1.055	36.50	5.50	10.10
	2.0	1.872	1.088	46.30	8.80	10.10
	2.5	2.235	1.122	49.40	12.2	9.90
	0.5	1.136	1.022	27.20	2.20	16.20
	1.0	1.290	1.048	29.20	4.80	16.44
1.5	1.5	1.910	1.086	60.80	8.60	10.11
	2.0	1.930	1.164	46.30	16.40	19.44
	2.5	2.890	1.150	75.44	15.50	8.20
	0.5	1.160	1.028	31.80	2.82	17.72
	1.0	1.530	1.055	53.50	5.50	10.38
2.0	1.5	1.690	1.114	45.74	11.40	16.60
	2.0	2.360	1.176	68.23	17.60	12.90
	2.5	3.100	1.189	84.00	18.90	9.53

Cotton fabric taken: 1.0 g; temperature: 30°C; time of photoexposure: 8 h; material/liquor: 1 : 10.

almost randomly where acid-functionalized sisal fibers are concerned.

The present photocatalytic system is characterized by lower grafting efficiency values lying in a range of 7–20% for cotton fabric and 1.5–6.5% for sisal fiber. These values are not found to vary regularly with variation in acid values of substrates. Odd effects observed with sisal fiber may be a consequence of the presence of lignin, which very often hinders grafting. For convenience of discussion, acid values of both cotton and sisal fiber, before and after treatment with oxalic acid,

Table II   Graft Copolymerization of Acrylamide on Acid-Functionalized Sisal Fiber

Oxalic Acid Used for Pretreatment (g)	Acrylamide Used (g)	Gross Polymer (g)	Apparent Graft Copolymer (g)	Total Conversion (%)	Grafting (%)	Grafting Efficiency (%)
	0.5	1.270	1.016	54.00	1.6	5.92
	1.0	1.762	1.022	76.20	2.2	2.90
1.0	1.5	1.513	1.033	34.10	3.4	6.44
	2.0	2.400	1.040	70.00	4.0	2.85
	2.5	3.450	1.055	77.70	5.6	2.83
	0.5	1.280	1.018	55.40	1.8	6.50
	1.0	1.450	1.024	45.10	2.4	5.32
1.5	1.5	1.730	1.036	48.50	3.6	4.94
	2.0	2.043	1.056	52.15	5.6	5.40
	2.5	2.420	1.092	56.76	9.2	6.50
	0.5	1.333	1.020	66.60	2.0	6.00
	1.0	1.923	1.027	92.30	2.7	2.90
2.0	1.5	1.790	1.057	52.50	5.7	7.20
	2.0	2.455	1.110	70.50	11.0	7.80
	2.5	2.495	1.160	59.90	15.9	10.70

Sisal fiber taken: 1.0 g; temperature: 30°C; time of photoexposure: 8 h; material/liquor: 1 : 10.

Table III   Acid Values[a] of Scoured and Defatted Fabric/Fiber Before and After Acid Functionalization

Name of the Substrate	Acid Value of Substrates Before Photofunctionalization	Dose Level of Oxalic Acid (g) per Gram of Substrate	Acid Value of Substrate After Photofunctionalization
Cotton Fabric	0.41	1.0	0.81
		1.5	1.01
		2.0	1.37
Sisal Fiber	0.78	1.0	1.26
		1.5	2.52
		2.0	3.58

[a] Acid values are expressed as grams of KOH consumed per 100 g of substrate.

are shown in Table III cited from our previous communication.[15]

Effect of Variation of Monomer Concentration

The effect of the increase in monomer concentration on different grafting parameters is discussed separately for the cotton fabric and the sisal fiber. With cotton fabric of a particular acid value, the percentage of PAAm grafting increases regularly with the rise in monomer concentration and ultimately saturates at the values of 12%, 16%, and 19%, respectively, for fabric samples of three different acid values (Table I, Fig. 1). With a few
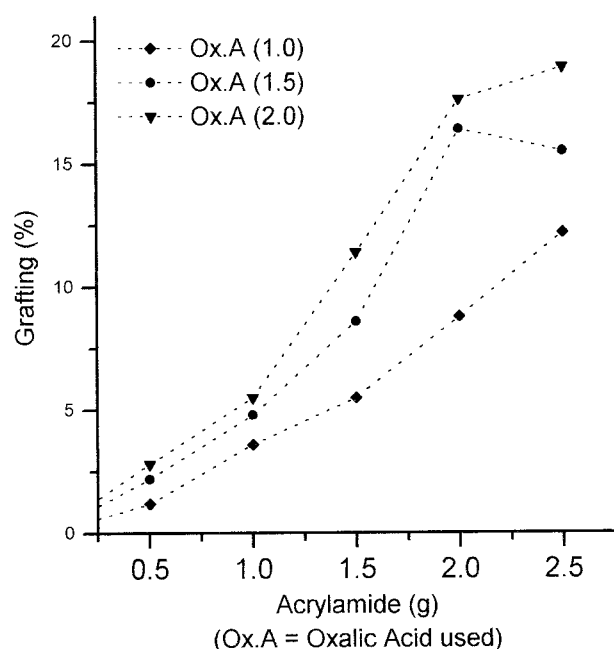
Figure 1   Effect of variation of monomer concentration on grafting (%) of PAAm on cotton fabric.

exceptions, the percentage of total conversion also follows an increasing trend with an increase in monomer concentration. However, an increase in the percent of total conversion, as well as the percent of grafting, is not always in combination with a parallel increase in grafting efficiency values.

A similar effect of increasing monomer concentration is observed for percentage of grafting values in the case of grafting on photoactive sisal fibers. But for presence of lignin, having a hindering effect on grafting, the values obtained are less than those with the cotton fabric even when the maximum acid dose level and the highest monomer concentration are taken. However, the percentage of total conversion, despite not having any particular trend of variation with monomer concentration, is, in general, satisfactory. The lower percentage of grafting, in combination with a higher percentage of total conversion, results in lower values of grafting efficiency (Table II, Fig. 2).

Characterizations Done

Infrared Spectroscopy

The IR spectra of grafted cotton (cellulose) samples are found to develop an additional strong absorption band at around 1653 cm^{-1}, as compared to the ungrafted samples [Fig. 3(a)]. This band is ascribed to the C=O stretching band of PAAm[10,22] and is indicative of the presence of polyacrylamide moieties in the samples. Lignocellulosic sisal fiber itself possesses a number of stretching bands in the region of 1650–1750 cm^{-1}, owing to the presence of aldehyde, keto, carboxyl, and ester groups contributed by the lignin and hemicellulosic constituents. On PAAm
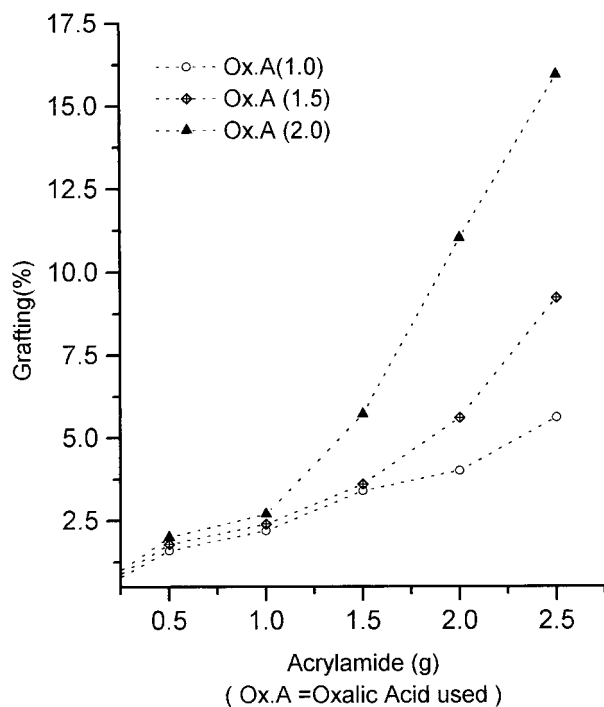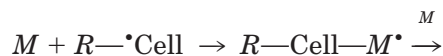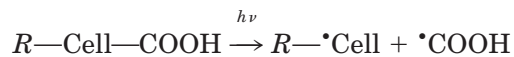
Figure 2 Effect of variation of monomer concentration on grafting (%) of PAAm on sisal fiber.

grafting, the carbonyl peak of sisal fiber at 1650 cm^{-1} sharpens, indicating the success of grafting.

Mechanism

In the presence of visible light, the photoactive acids, including oxalic acid, are found to produce carboxy-free radicals which can functionalize the cellulosic backbones and render them photoactive. The way they break up and combine with the cellulosic systems was discussed earlier.[15] The photoactivity (that is, the capability of initiating photopolymerization of vinyl monomers without further addition of initiator) that the cellulosic materials acquire, is found to be retained over years, which supports the effectiveness of this chemical combination. These acids, moreover, are found to initiate photopolymerization of vinyl monomers quite effectively, and therefore, carboxy-free radicals are obviously effective radical initiators of photopolymerization. In the present system, no initiator was added from the outside. Therefore, the carboxy-free radicals originating in the acid-functionalized backbones are the only possible initiators in the present photografting reaction. That is, at the first step, the —COOH or —RCOOH groups from the functionalized backbones decompose into radicals and generate a

radical site on the cellulose chain; afterwards, the cellulosic macroradical initiates the graft copolymerization described in the following manner.

$$R\text{—Cell—COOH} \xrightarrow{h\nu} R\text{—}{}^{\bullet}\text{Cell} + {}^{\bullet}\text{COOH}$$

$$M + R\text{—}{}^{\bullet}\text{Cell} \rightarrow R\text{—Cell—}M^{\bullet} \xrightarrow{M}$$

$$R\text{—Cell—}M\text{—}M^{\bullet}$$

M = monomer, acrylamide

(initiation and propagation

of graft copolymerization)

Therefore, the copolymerization is suggested to take place in the "grafting-from" mechanism.

DSC Analysis

DSC curves of ungrafted and grafted cotton fabric and sisal fiber are shown in Figure 4(a) and (b), respectively. Ungrafted cotton fabric shows a strong endothermic peak at around 100°C due to water evaporation and another endotherm beginning at 360°C and ending at 400°C owing to the decomposition of α-cellulosic materials.[23] The DSC curve of PAAm shows an endothermic peak at around 220–230°C due to melting and a sharp decomposition peak at around 275°C. In the DSC curve of PAAm-grafted cotton fabric, the characteristic peaks of both α-cellulose and PAAm are found to be present. Melting and decomposition peaks of PAAm at 230 and 275°C, respectively, appear in proper positions where cellulose itself has no important peak. However, the original cellulosic decomposition peak in the 360–400°C region remains unaffected by grafting.

Sisal fiber shows a similar strong endothermic peak at 100°C due to water evaporation. This is succeeded by a weak exotherm at around 275–280°C, an obvious exotherm at 360°C, and a sharp exotherm at 420°C. These peaks are attributed to the decomposition of hemicellulose, α-cellulose, and lignin part of the fibers, respectively. Another broad shoulder centering at 200°C and ending at 230°C is also observed in the same curve, which is attributed to the slow pyrolytic decompositions.[23] PAAm grafting brings about significant changes in the decomposition pattern of the sisal fiber. The water-evaporation endotherm is shifted to
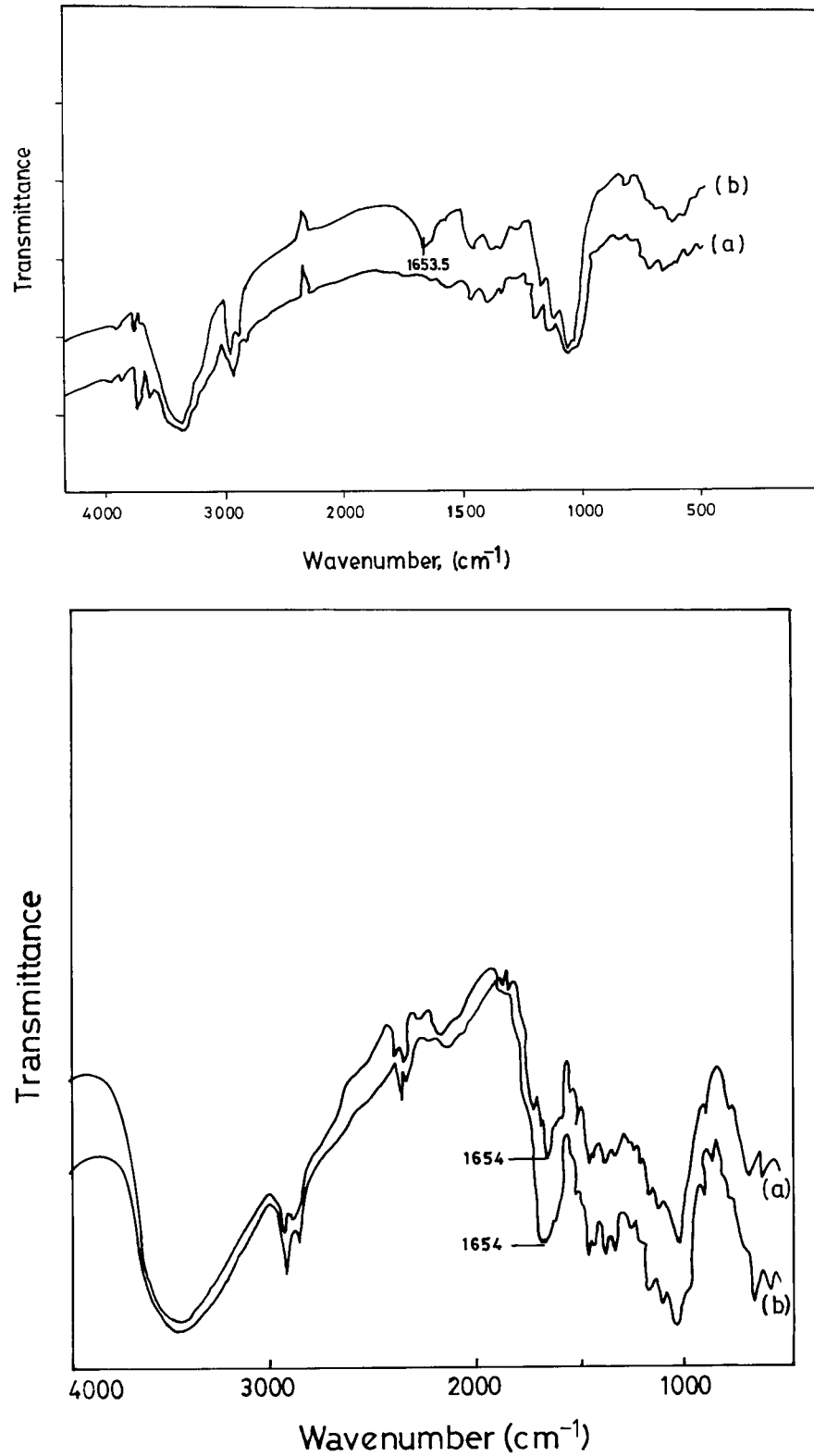
Figure 3 (a) FTIR spectra of (i) ungrafted (acid functionalized), and (ii) PAAm-grafted cotton fabric. (b) FTIR spectra of (i) ungrafted (acid functionalized), and (ii) PAAm-grafted sisal fiber.
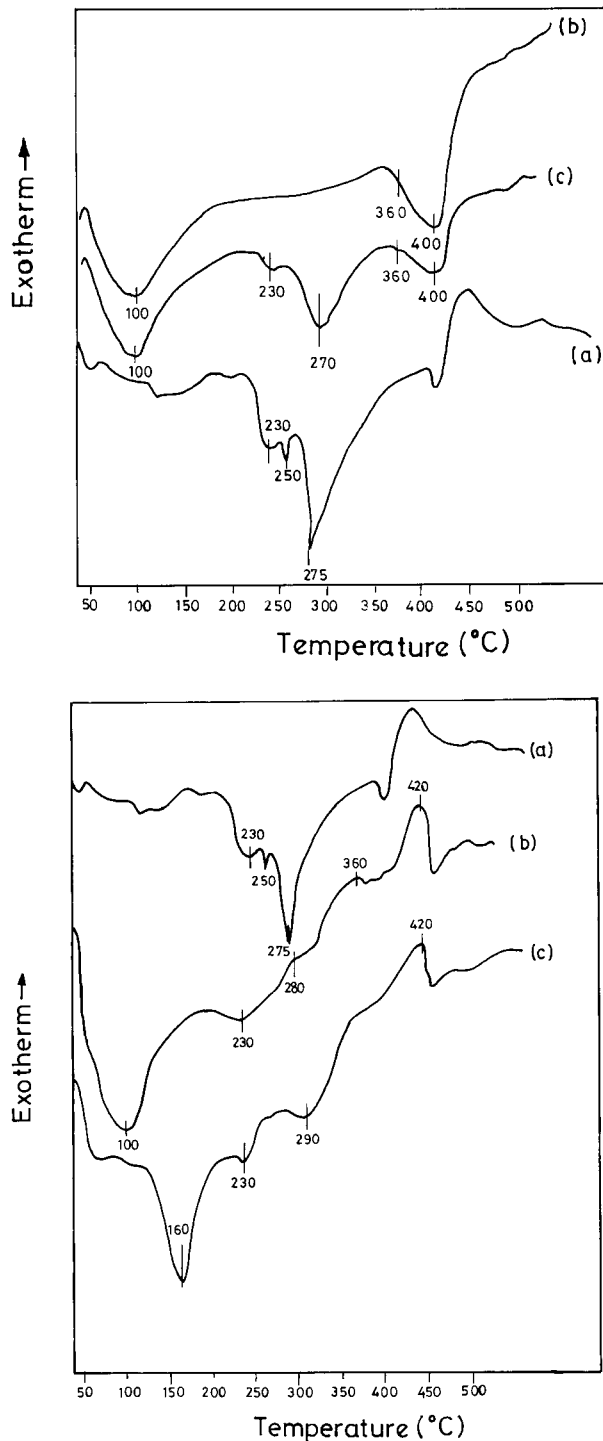
Figure 4 (a) DSC curves of (i) PAAm, (ii) scoured and defatted cotton, (iii) PAAm-grafted (17%) cotton. (b) DSC curves of (i) PAAm, (ii) scoured and defatted sisal fiber, (iii) PAAm-grafted (15%) sisal fiber.

160°C, indicating a sharp improvement in the moisture retention property of the sisal fiber. The melting endotherm of PAAm is observed in its

proper position (viz. at 230°C), which almost overlaps with the shoulder at the 200–230°C region. Again, the heat absorbed during the decomposition of PAAm outweighs the heat liberated in hemicellulose decomposition; therefore, these two different peaks are also in effect overlapped to give rise to an endotherm at about 290–300°C. The peak at 360°C, accounting for the depolymerization of α-cellulose, is blurred, whereas the lignin decomposition exotherm at 420°C remains unaffected. This observation is in accordance with the previous results reported[7]; this may indicate that grafting takes place mainly at the α-cellulose part of the fiber, whereas the lignin part does not participate in grafting. However, in the cases of both the cellulose and lignocellulose, mixtures of the grafted fabric/fiber and free polymer produce very complicated DSC curves (not shown in figure), which are completely different from those of the grafted samples.

SEM Studies

Surface morphology of sisal fiber, before and after functionalization and grafting, is shown in Figure 5(a)–(d). From the micrographs it is obvious that surface morphology of sisal fiber remains almost unchanged on acid functionalization [(a) and (b)], but suffers a remarkable change on PAAm grafting [(c) and (d)]. Grafted-on polymer is observed to be deposited on the fiber surface as well as in the intercellular regions of the grafted fiber. With a higher percent of grafting (d), deposited PAAm almost covers the fiber surface with an uneven covering. In that case, the difference in surface morphology of grafted fibers from ungrafted fibers may be observed visually and felt on touch.

X-Ray Diffraction

Cotton fabric and sisal fiber produce almost similar X-ray diffraction patterns for which cotton is shown in Figure 6. The pattern remains unchanged on PAAm grafting. This observation reveals that the structures of the crystalline part of these two materials are similar and graft copolymerization takes part mainly at the amorphous region, leaving the crystalline region unaffected.

Measurement of Textile Properties

Tensile Properties

Tenacity, elongation at break (EB), and initial modulus (IM) values of untreated (scoured and
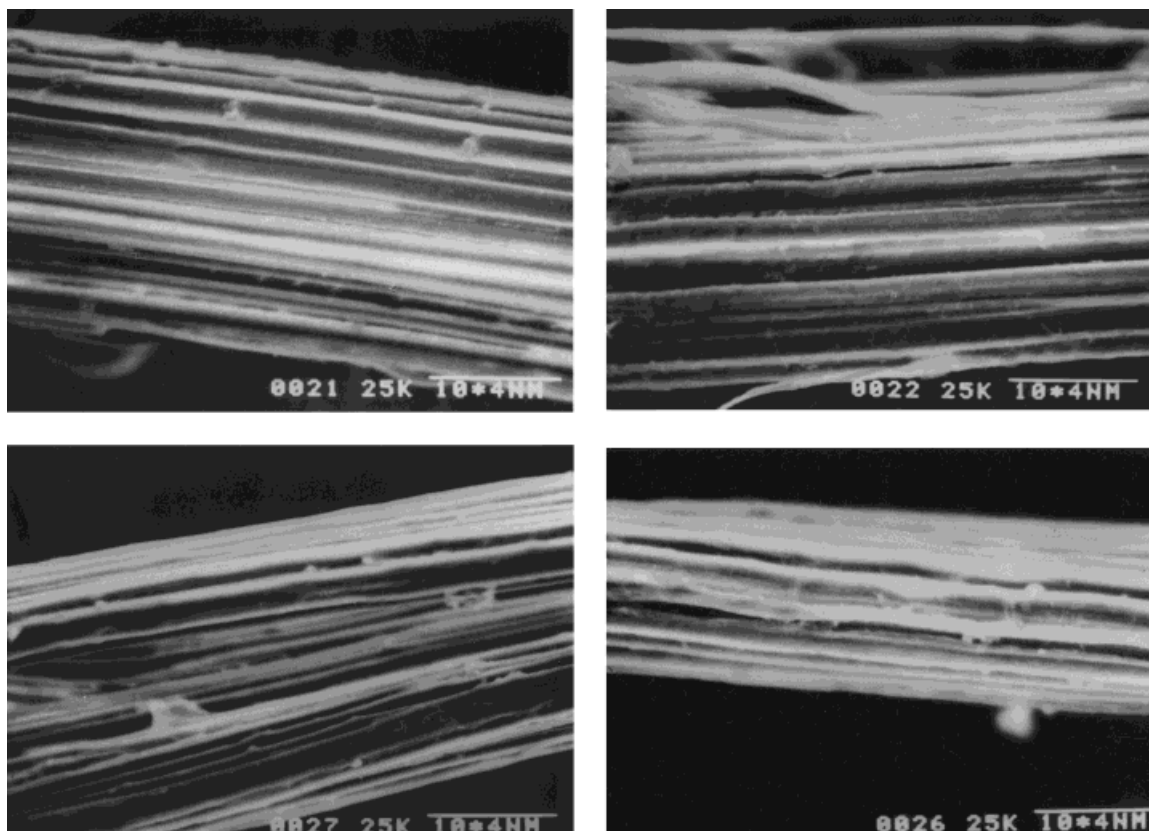
Figure 5   SEM micrographs of sisal fiber. (a) Scoured and defatted (×750), (b) oxalic-acid treated (×750), (c) 5% PAAm-grafted (×750), (d) 15% PAAm-grafted (×750).

dewaxed), and oxalic acid treated-cotton and sisal fiber are shown in Table IV. In cotton fabric, acid treatment results in the lowering of tenacity with an overall retention of the EB and IM values. This
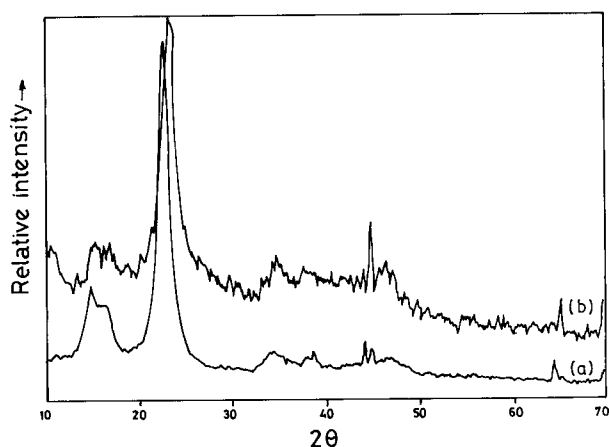
Figure 6   X-ray diffraction patterns obtained from (a) scoured and defatted cotton fabric, (b) PAAm grafted, (17%) cotton fabric.

is explained as a direct consequence of hydrolytic degradation of the α-cellulose part of the cotton during the acid treatment over the considerable time period of 8 h. An almost opposite trend is observed with sisal fiber where increasing dose levels of acid do not greatly affect the tenacity and the IM values, whereas the EB suffers a significant lowering. The lignin and hemicellulose components present in the sisal fiber may have a protective effect from hydrolytic degradation during prolonged acid treatment.

Influence of increased PAAm-grafting level on the abovementioned mechanical parameters of PAAm-grafted cotton fabric and sisal fiber are shown in Table V. In both cases, PAAm-grafted samples, with the highest dose level of acid and variation in grafting level, were chosen for tensile testing. With cotton fabric, a progressive increase in the percentage of grafting leads primarily (up to ~ 11% grafting) to some enhancement in fabric tenacity with a slight increase in its EB value and a simultaneous lowering of its IM values. Therefore, a lower degree of grafting results in the

Table IV   Effect of Increased Oxalic Acid Dose Level on Tensile Properties[a] of Cotton Fabric and Sisal Fiber

Sample (fiber/fabric)	Acid Dose Level (g)	Tenacity[b]	Elongation at Break (%)	Initial Modulus[b]
Cotton	0.0	0.150 (5.87)	19.10 (12.36)	0.420 (6.80)
	1.0	0.115 (11.36)	18.34 (08.10)	0.418 (7.90)
	1.5	0.102 (9.53)	18.00 (4.56)	0.425 (9.77)
	2.0	0.098 (10.24)	17.98 (4.36)	0.415 (8.25)
Sisal	0.0	0.255 (15.77)	17.30 (16.80)	18.8 (27.30)
	1.0	0.251 (23.36)	13.61 (27.10)	18.9 (24.51)
	1.5	0.248 (21.75)	13.02 (27.8)	17.6 (29.80)
	2.0	0.250 (16.91)	12.96 (20.40)	16.3 (23.75)

[a] Data in parentheses correspond to the coefficients of variation.
[b] The unit of tenacity and IM is N/mm^2 for cotton fabric and in N/tex for sisal fiber.

improvement of the desirable properties like strength and flexibility of the fabric. However, a higher grafting level (18%) results in a small degree of lowering of the tenacity and a sharp rise in the EB value with a pronounced decrease in the IM value. Such a higher grafting level causes some uneven distribution of the grafted-on polymer on the fabric surface and to some extent hampers or masks its original properties. For the PAAm-grafted sisal fibers, increased grafting level results in a gradual increase in the tenacity and the EB values, whereas the IM primarily drops remarkably and then levels off. Therefore, the strength and flexibility of the sisal fibers are improved by the grafted PAAm. Fibers possess voids in their structure (particularly in the inter-

cellular matrix regions of the multicellular fibers like sisal), which are filled up by the grafted material. Therefore, the effect of the grafting on the polymer is more obvious in the case of the fiber rather than the fabric.

Polyacrylamide is a brittle polymer when completely dried up. This hydrophilic polymer has good moisture absorption and moisture retention properties and in the presence of moisture shows good flexibility and elasticity. The present test materials were dried at 50°C. Moreover, these samples were conditioned at 65%, relative humidity for 72 h before the tensile measurements were done. In such conditions, the grafted-on PAAm absorbs moisture and shows flexibility, and the stiffness of the grafted samples are decreased as

Table V   Effect of PAAm Grafting on Tensile Properties[a] of Acid-Functionalized Cotton Fabric and Sisal Fiber

Sample (fiber/fabric)	Grafting Level (%)	Tenacity[b]	Elongation at Break (%)	Initial Modulus[b]
Cotton Fabric	0.00	0.098 (10.24)	17.98 (4.36)	0.415 (8.25)
	2.82	0.112 (12.40)	18.37 (8.55)	0.389 (11.46)
	5.50	0.127 (11.80)	18.82 (7.81)	0.378 (12.92)
	11.40	0.145 (15.60)	19.63 (12.55)	0.315 (13.53)
	17.60	0.156 (17.34)	23.06 (16.10)	0.306 (16.81)
	18.90	0.150 (19.81)	23.43 (14.79)	0.296 (18.63)
Sisal Fiber	0.00	0.250 (16.91)	12.96 (20.40)	16.30 (23.75)
	2.00	0.258 (17.87)	14.48 (23.87)	15.25 (19.81)
	2.70	0.265 (34.55)	16.20 (27.75)	11.50 (26.80)
	5.70	0.272 (28.78)	18.90 (20.50)	10.35 (27.80)
	11.00	0.289 (22.62)	17.29 (26.10)	11.44 (25.49)
	15.90	0.296 (23.70)	15.69 (28.65)	11.25 (22.90)

[a] Data in parentheses correspond to the coefficients of variation.
[b] The unit of tenacity and IM is N/mm^2 for cotton fabric and in N/tex for sisal fiber.

evident from enhanced EB and declined IM values.

Moisture Regain and Dyeability

Polyacrylamide itself being a hydrophilic polymer, PAAm grafting is expected to improve the moisture regain property of the base polymer. The effect of increased PAAm-grafting level on the moisture-regain property of cotton fabric and sisal fiber is shown by the data tabulated in Tables VI and VII, respectively. With both cotton fabric and sisal fiber, moisture regain values do not change primarily with very low PAAm grafting level; above 5–6% grafting this value increases, reaches a maxima at about 11% grafting, and then saturates. A similar trend is observed regarding the acid–dye uptake properties of both the grafted fabrics and fibers. Dyeability of both the samples increases with an increase in PAAm grafting, reaches a maxima at around 11% grafting, and then saturates. Therefore, regarding moisture regain and dye uptake properties, 10–11% PAAm grafting shows the most balanced and optimum results, beyond which the grafted-on polymer shows a masking effect on the properties of the base polymer and a leveling trend is observed.

CONCLUSION

The novel photocatalytic system applied here works well with grafting PAAm on the backbones of both the cellulosic and lignocellulosic materials. From the results obtained it is obvious that a controlled degree (10–11%) of grafting of PAAm improves the tensile strength as well as the stiffness, moisture regain, and dye uptake properties of the substrates so that the application prospects

Table VI   Dye Uptake and Moisture Regain Properties of PAAm-Grafted Cotton Fabric

Grafting (%)	K/S Values of Dyed Fabrics (at λ_{max} = 560 nm)	Moisture Regain (%)
0.00	10.95 (—)	6.4
2.82	11.55 (5.00%)	6.6
5.50	12.95 (18.2%)	7.5
11.40	15.34 (40.1%)	9.6
15.50	15.61 (42.5%)	10.4
17.60	15.86 (44.84%)	10.1

Table VII   Dye Uptake and Moisture Regain Properties of PAAm-Grafted Sisal Fibers

Grafting (%)	K/S Values of Dyed Fibers (at λ_{max} = 480 nm)	Moisture Regain (%)
0.0	16.7 (—)	9.2
2.1	16.8 (0.6%)	9.2
2.7	17.6 (5.4%)	9.8
5.67	18.5 (10.7%)	10.1
10.4	19.1 (14.4%)	12.8
15.9	18.8 (12.6%)	10.9

of both the fabric and fiber are enhanced, although a much higher degree of grafting is undesirable for both of them. However, the monomer/substrate ratio must always be kept very high, which is a serious drawback of the system. Moreover, since the initiator is chemically bound to the substrate in almost a trace amount, the molecular weight of the homopolymer formed becomes very high, which often causes gelling of the free polymer and poses some serious problems in homopolymer removal.

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