Grafting of Acrylic Acid onto Flax Fibers Using Mn(IV)-Citric Acid Redox System

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ABSTRACT: When the flax fibers (machine tow) were treated with $KMnO_4$ solution, MnO_2 was deposited over all the fiber surface. The amount of MnO_2 deposited relied on the $KMnO_4$ concentration. Subjecting the flax-containing MnO_2 to a solution consisting of monomer (acrylic acid, AA) and citric acid, CA (or any acid used in this work) resulted in formation of poly(AA)-flax graft copolymer. Dependence of the polymer criteria, namely, the total percentage conversion (%TC) and the carboxyl content of the grafted flax fibers on various grafting parameters, viz., concentrations of the redox pair as well as AA, material-to-liquor ratio (M/R), duration and temperature of polymerization, kind of the acid and kind of the flax fibers pretreatment was studied systematically. The results indicated that the polymerizability of AA molecules, expressed as %TC (i.e., counting both grafting and homopolymerization) and thence the carboxyl content (i.e., evaluating the extent of AA grafting along the flax backbone) was optimized with the following conditions: [AA], 100% (based on weight of flax fibers, owf); [CA], 0.4 meq/1 g flax; [MnO_2], 0.4 meq/1 g flax; polymerization temperature, $40°C$; polymerization time, 30 min; and the M/R, 1 : 50. A tentative mechanism for grafting of flax fibers with AA using MnO_2-acid redox system was elucidated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3028–3036, 2006

Key words: graft copolymers; initiators; monomers; modification; radical polymerization

INTRODUCTION

Chemical modification of substrate polymers and fibers, both natural and synthetic, either through functionality changes involving acetylation, etherification, esterification, amidation, cyanoethylation, xanthate ester formation, crosslinking, gelatin, and/or graft copolymerization has immensely contributed to improving the physical, mechanical, chemical, and biochemical properties of such materials and the resulting products find wide industrial and biomedical applications.[1–3] Among these, grafting seems to be most versatile and promising.

During the last few decades, graft copolymerization onto textile fibers showed great potential for tailoring the material properties to specific end-uses.[4]

The grafting can be expected to add new properties associated with the side chains without drastically changing the basic properties of the fiber matrix.[5]

Grafting of vinyl monomers onto cotton,[6–13] starch,[14–20] wool,[21–23] silk,[24–27] etc., was the subject of extensive investigations during the last several years. It was surprising that comparatively little attention was paid towards grafting vinyl monomers onto flax fibers.[28–30]

The present study was on graft copolymerization of acrylic acid (AA) on the flax machine tow fibers by a potassium permanganate/CA initiation system in aqueous media. The features of the reactions and of the characterized graft copolymers are reported and discussed in this article.

EXPERIMENTAL

Materials

Flax fibers (Machine tow) were kindly supplied by Tanta Flax and Oil Company, Mit-Hebaish El-Bahria, Tanta, Egypt.

Chemicals

The following reagent grade chemicals were used without further purification: potassium permanganate, potassium bromate, potassium bromide, potassium iodide, sodium hydroxide, sodium thiosulphate, hydrochloric acid, sulfuric acid, oxalic acid, tartaric acid, succinic acid, citric acid (CA), and acrylic acid (AA).

Procedures

Unless otherwise stated, treatment of flax fibers with $KMnO_4$ and grafting of the so-treated fibers with AA were carried out as described below.

Treatment with $KMnO_4$

The flax sample (2 g) was immersed in an aqueous $KMnO_4$ solution (0.01N–0.1N) in a bottle kept at $50°C$

for 15 min using a material-to-liquor ratio of 1 : 50 under continuous shaking to ensure the homogeneity of MnO_2 deposition overall the sample surface. After impregnation, the sample were washed repeatedly with distilled water and squeezed between two filter papers before introducing to the polymerization medium. Manganese dioxide (MnO_2) was determined quantitatively by impregnating the $KMnO_4$-treated flax fibers with known concentration of oxalic acid solution in a clean conical flask. Oxalic acid was added in excess amount (V_{total}) to assure the dissolution of MnO_2. The flask contents were heated to about 60–70°C with vigorous shacking till the brown color of MnO_2 was completely disappeared. The unconsumed amount of oxalic acid ($V_{unconsumed}$) was then back-titrated against standard $KMnO_4$ solution. The amount of MnO_2 ($V_{total} - V_{unconsumed}$) deposited over all the flax surface is expressed in meq/100 g flax.

Graft polymerization

The permanganate-treated sample was put into a reaction bottle containing a solution consisting of known concentrations of CA and AA at different temperatures and duration. More details about the grafting conditions are given in the text. At the end of the reaction, the sample was removed, thoroughly washed several times with cold and boiled water, and dried at 105°C for 3 h then weighed.

Analysis

It is worthy to mention that the machine tow flax fibers under investigation contain complex mixture of polysaccharides and cellulose represents 88.9% of its composition and the rest are natural impurities such as lignin, pectin, waxes, coloring material, ash, etc.[31] During the whole-course of its treatment, viz., the treatment with $KMnO_4$ followed by the grafting, the flax sample would undergo several structural changes. First, it is expected to loss, to certain extent, one or more of the aforesaid impurities owing to the strong oxidizing action of $KMnO_4$ as well as the hydrolytic action of citric acid (or any acid used in this work). Second, small fragments of the flax fibers may be washed-out upon the repeating washing with water. Accordingly, the flax fiber sample may suffer from loss in its weight.

   Based on the abovementioned facts, it is more convenient to determine the carboxyl content as a measure to the extent of polyacrylic acid grafts along with the backbone of the flax fiber chains. The carboxyl content was determined according to the general procedure described by Pascu and Hiller.[32] Efficiency of the $KMnO_4$/CA initiation system to polymerize AA to both grafts and homopolymer was monitored via determining percentage of the AA total conversion

(%TC). The latter was calculated via quantitative estimation of the free double bonds of the acrylic acid before, during, and after the polymerization process according to a method reported elsewhere.[33]

RESULTS AND DISCUSSION

To study the grafting of AA onto the machine tow flax fibers using the $KMnO_4$/CA initiation system, the graft polymerization reaction was carried out under different conditions. Variables studied include concentrations of the initiating components and AA as well as the material-to-liquor ratio, duration and temperature of polymerization, nature of acid, and kind of the pretreatment of the flax fibers. However, before going into detailed investigation of these parameters, it may be of importance as a start to shed some insight on the mechanism involved in grafting using the said initiation system.

Tentative mechanisms

When the flax sample (machine tow) was treated with $KMnO_4$ solution, it was turned to a dark brownish, or even black color, depending on the concentration of the $KMnO_4$ used, as described in the Experimental section. The color formed was due to the deposition of manganese dioxide (MnO_2) molecules over-all the sample surface. This outcome was expected as a consequence of the reducing properties of the flax fibers. The latter (reductant) reduce the heptavalent manganese ion (Mn^{7+}) in $KMnO_4$ (oxidant) to form the tetravalent ion (Mn^{4+}) in the form of MnO_2. Determination of the MnO_2 content of the treated sample revealed that the MnO_2 content increases substantially by increasing the concentration of $KMnO_4$ solution within the studied range (shown in Fig. 1).
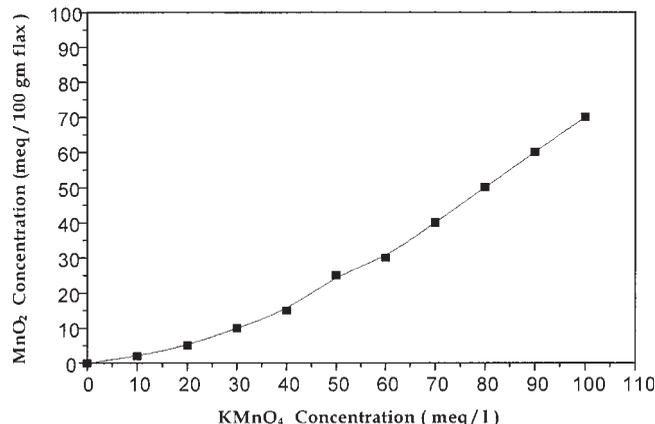
Figure 1 Relation between the amount of MnO_2 deposited on the flax fiber surface and $KMnO_4$ concentration: Time of sample impregnation, 15 min; impregnation temperature, 50°C; material-to-liquor ratio, 1 : 50.

It is logical to assume that MnO_2 particles are deposited uniformly over-all the sample surface and are located at certain sites, most probably at the hydroxyl groups of the flax cellulosic chains. In the presence of an acid, either carboxylic or mineral, primary radical species formation occurs as a result of the acid's action on the deposited MnO_2. Hence, different primary radical species are created, depending upon the type and the nature of the acid used.

In the case of citric acid, creation of primary free-radical species occurs, most probably, according to the following mechanism.[34]

$$Mn^{4+} + \begin{array}{l} CH_2 - COOH \\ | \\ C(OH)COOH \\ | \\ CH_2 - COOH \end{array} \longrightarrow \begin{array}{l} \dot{C}H - COOH \\ | \\ C(OH)COOH \\ | \\ .CH - COOH \end{array} + Mn^{2+} + 2H^+ \tag{1}$$
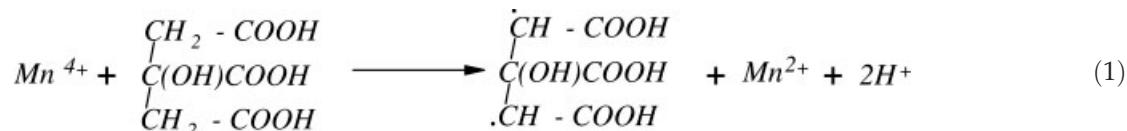
Similar mechanism is proposed for the formation of succinic acid diradicals:

$$Mn^{4+} + \begin{array}{l} CH_2 - COOH \\ | \\ CH_2 - COOH \end{array} \longrightarrow \begin{array}{l} \dot{C}H - COOH \\ | \\ \dot{C}H - COOH \end{array} + Mn^{2+} + 2H^+ \tag{2}$$
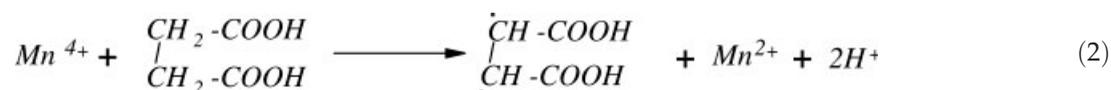
whereas, in the case of tartaric acid, generation of primary free radical species occurs, most likely, as given by the following mechanisms:[35]

$$Mn^{4+} + \begin{array}{l} CH(OH)-COOH \\ | \\ CH(OH)-COOH \end{array} \xrightarrow{Slow} \begin{array}{l} \dot{C}H(OH) \\ | \\ CH(OH)-COOH \end{array} + Mn^{3+} + CO_2 + H^+ \tag{3}$$

$$Mn^{4+} + \begin{array}{l} \dot{C}H(OH) \\ | \\ CH(OH)-COOH \end{array} \xrightarrow{Fast} \begin{array}{l} CHO \\ | \\ CH(OH)-COOH \end{array} + Mn^{3+} + H^+ \tag{4}$$
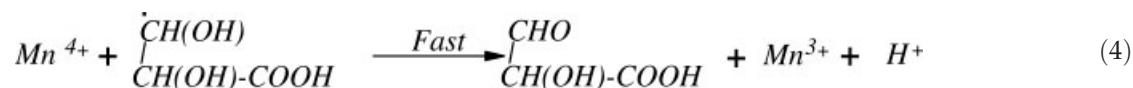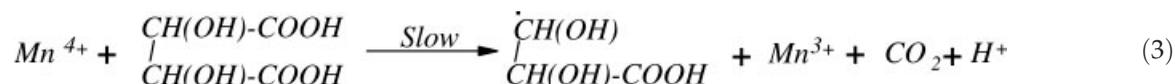
and in the case of oxalic acid, the carboxyl radical ions constitute the primary radical species and are possibly formed as given below[36,37]

$$Mn^{4+} + C_2O_4{}^{2-} \xrightarrow{Measurable} Mn^{3+} + CO_2 + COO^- \tag{5}$$

$$Mn^{4+} + COO^- \xrightarrow{Rapid} Mn^{3+} + CO_2 \tag{6}$$

$$Mn^{3+} + 2 C_2O_4{}^{2-} \underset{}{\overset{Rapid}{\rightleftharpoons}} \left[Mn(C_2O_4)_2 \right]^- \tag{7}$$

$$Mn^{3+} + C_2O_4{}^{2-} \xrightarrow{Measurable} Mn^{2+} + CO_2 + {}^{\cdot}COO^- \tag{8}$$

$$Mn^{3+} + {}^{\cdot}COO^- \xrightarrow{Rapid} Mn^{2+} + CO_2 \tag{9}$$
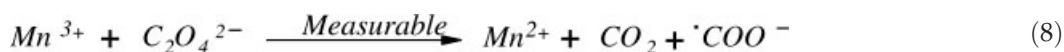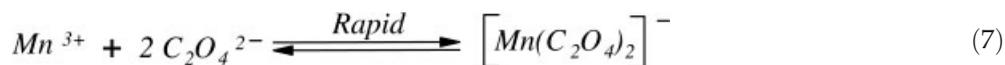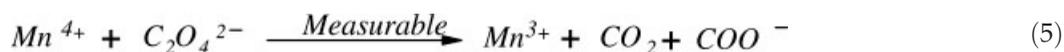
With respect to sulphuric acid, it appears that the sulfate ion is oxidized by fresh MnO_2, to produce the sulfate ion radical:[38]

$$Mn^{4+} + H_2SO_4 \longrightarrow Mn^{3+} + {}^{\cdot}SO_4^- + 2H^+ \tag{10}$$
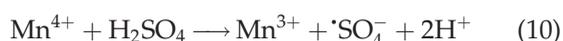
which acts as the primary radical species.

Other free radical species, namely the hydroxyl radical, may also be formed:

$$Mn^{4+} + H_2O \longrightarrow Mn^{3+} + {}^{\cdot}OH + H^+ \tag{11}$$

$$Mn^{3+} + H_2O \longrightarrow Mn^{2+} + {}^{\cdot}OH + H^+ \tag{12}$$
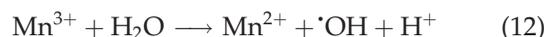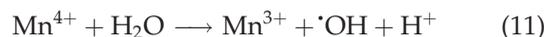
Once these free-radical species R˙ are created, they produce cellulose macroradicals via direct abstraction of hydrogen atom from the hydroxyl groups of the flax cellulose molecules; thus:

$$Cell - OH + R^• \longrightarrow Cell - O^• + RH \qquad (13)$$

Cellulose macroradicals may also be formed by direct attack of Mn^{4+} or Mn^{3+} ions on the cellulose molecule, via abstraction of hydrogen atom:

$$Cell - OH + Mn^{4+} \longrightarrow Cell - O^• + Mn^{3+} + H^+ \quad (14)$$

$$Cell - OH + Mn^{3+} \longrightarrow Cell - O^• + Mn^{2+} + H^+ \quad (15)$$

In the presence of a vinyl monomer (AA), the cellulose macroradical is added to the double bond of the vinyl monomer, resulting in a covalent bond between the monomer and the flax cellulose, with creation of a free radical on the monomer, i.e., a chain is initiated.

$$Cell \text{-} O^• \ + \ CH_2{=}C\!\begin{smallmatrix}/H\\\\\\COOH\end{smallmatrix} \longrightarrow Cell\text{-}O{-}CH_2{-}\overset{•}{C}\!\begin{smallmatrix}/H\\\\\\COOH\end{smallmatrix} \qquad (16)$$
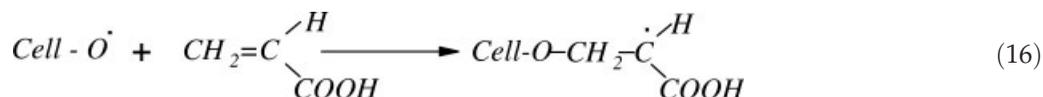
Subsequent addition of monomer molecules to the initiated chain propagates grafting onto the flax cellulose.

$$Cell\text{-}O{-}CH_2{-}\overset{•}{C}\!\begin{smallmatrix}/H\\\\\\COOH\end{smallmatrix} + n\ CH_2{=}C\!\begin{smallmatrix}/H\\\\\\COOH\end{smallmatrix} \longrightarrow Cell\text{-}O{-}\!\left[CH_2{-}\overset{H}{\underset{COOH}{C}}\right]_n\!CH_2{-}\overset{•}{C}\!\begin{smallmatrix}/H\\\\\\COOH\end{smallmatrix} \qquad (17)$$
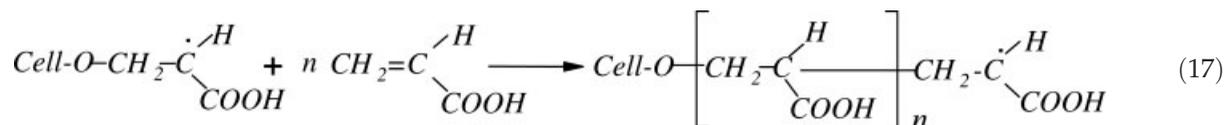
The propagation chain of cellulose may be terminated via two possible routes, namely disproportionation and/or recombination between two growing cellulose–polymer chain radicals.[39]

Effect of redox pair concentration

Figure 2 shows the dependence of the extent of polymerization of AA, expressed as percentage total conversion (%TC), on the concentration of the redox
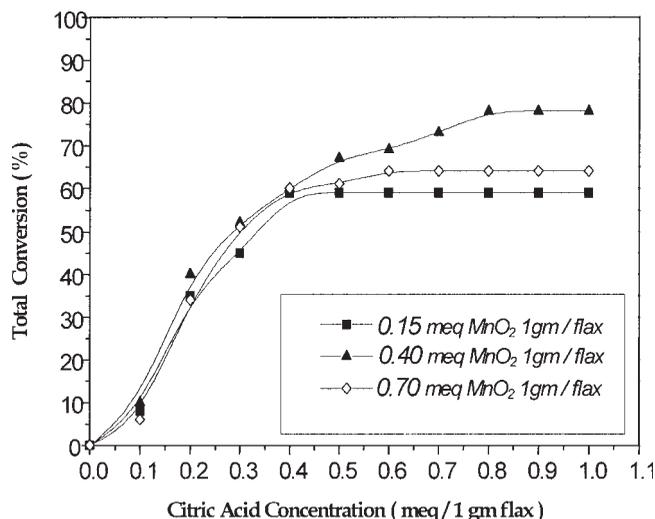
Figure 2 Effect of the redox pair concentration on the percentage total conversion of acrylic acid. Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); material-to-liquor ratio, 1 : 50.

components. The polymerization reaction was carried out using flax fibers having different amounts of deposited MnO_2 (0.15–0.7 meq MnO_2/1 g flax fiber), CA concentrations ranging from 0 to 1 meq/1 g flax fiber. The reaction conditions were completed by using AA {200% based on weight of flax (owf)}; the polymerization temperature, 70°C; the reaction time, 2 h; and the material to liquor ratio, 1 : 50.

It is seen from the data (Fig. 2) that the %TC of acrylic acid increases significantly by increasing the concentration of MnO_2 deposited on the flax fiber surface up to 0.4 meq/1 g flax then decreases. The enhancement in the total conversion percent (both grafts and homopolymer) by increasing MnO_2 concentration signifies the necessity of the presence of certain amounts of deposited MnO_2 on the flax fiber to act thereupon to produce ultimately cellulose macroradicals capable of initiation grafting. Besides, the primary free-radical species of CA generated by the action of MnO_2 are also responsible for the formation of the acrylic acid homopolymer. On the other hand, the decrement in the percentage of the total conversion of acrylic acid by using MnO_2 concentration higher than 0.4 meq/1 g flax may be associated with: (i) excess deposited MnO_2 colloidal particles impede diffusion of monomer from aqueous phase to the fiber phase; (ii) higher production of inhibiting oxygen at higher MnO_2 concentration due to the side reaction:

$$MnO_2 + 2H^+ \longrightarrow Mn^{2+} + H_2O + (O) \qquad (18)$$
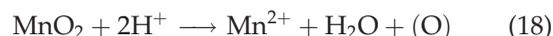
and (iii) abundance of primary radical species of CA accelerate the termination rate, via bimolecular collision between two chain radicals.

Figure 2 shows also that, regardless of the amount of MnO_2 deposited on the flax fiber surface, increasing the amount of CA incorporated in the polymerization medium up to 0.4 meg/1 g flax fiber is accompanied by significant increase in the %TC. Further increase in the CA concentration is accompanied by a marginal increase in the %TC and then levels off. Enhancement of acrylic acid conversion to both grafts and homopolymer is due to the generation of successive free-biradical species of CA capable of polymerizing acrylic acid. Beyond the said concentration of CA, the polymerization medium is repleted by these radical species, which tend to recombine with each others rather than to initiate polymerization of acrylic acid molecules, as mentioned earlier.

Figure 3 shows the effect of the redox components concentrations (MnO_2 and CA) on the carboxyl content of the grafted flax samples. The data of this figure reveal that (a) irrespective of the amount of MnO_2 deposited on the flax fiber surface, the carboxyl content increases by increasing the amount of CA incorporated in the polymerization medium up to certain limit then decreases; (b) the maximum value of the carboxyl content is reached when an equivalent amount of both MnO_2 and CA was used. This value corresponds to the equal ratio 0.4 meq MnO_2 : 0.4 meq CA/1 g flax fiber.

MnO_2/citric equiratio

The relationship between the concentration of the redox components, expressed in meq/1 g flax fibers, on the total conversion percentage of acrylic acid is

Figure 4 Dependence of AA total conversion (%TC) on the equal MnO_2; CA ratio: Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); material-to-liquor ratio, 1 : 50.

shown in Figure 4. The reaction was carried out using equal ratios of MnO_2 : CA ranging from 0.1 to 0.7 meq/1 g flax. Other conditions embrace: the reaction temperature, 70°C, the reaction time, 2 h, AA concentration, 200% (owf) and the material-to-liquor ratio, 1 : 50. Under these conditions, the extent of AA-conversion is greatly enhanced by increasing the equal MnO_2 : CA ratio from 0.1 to 0.4 meq/1 g flax. Further increase beyond this limit brings about not striking increments in the percentage of total conversion of AA. The ratio of the redox pair corresponds to 0.4 : 0.4 meq/1 g flax seems to be the optimum ratio for copolymerization of AA molecules onto flax fibers.

Figure 5 shows the dependence of the carboxyl content of the flax fibers on the equal ratios of the MnO_2 : CA redox components when these fibers were grafted under the reaction conditions cited in Figure 4. The data of Figure 5 reveal clearly that the

Figure 3 Effect of the redox pair concentration on the carboxyl content of the grafted flax fibers. Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); material-to-liquor ratio, 1 : 50.
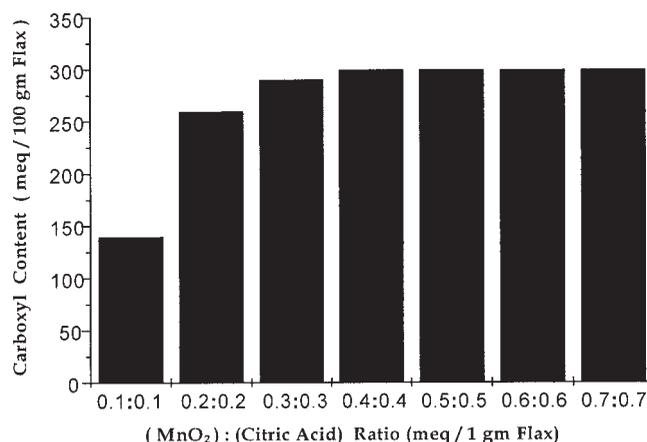
Figure 5 Influence of MnO_2: CA equiratio on the carboxyl content of the AA-grafted flax fibers. Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); material-to-liquor ratio, 1 : 50.

carboxyl content of AA-grafted flax fibers increases sharply by increasing the MnO_2 : CA equal ratio upto 0.4 meq/1 g flax then levels off. With this redox pair concentration, the carboxyl content reached about 300 meq/100 g flax. This proves that the said ratio is the optimum one to maximize the graft yield of AA onto the flax fibers. Leveling off of the carboxyl content beyond the 0.4 ratio is mainly due to complete depletion of AA molecules.

Material-to-liquor ratio

The reliance of the polymer criteria, namely, AA total conversion (%TC) and carboxyl content of the poly(AA)-grafted flax fibers (meq/100 g flax) on the material-to-liquor ratio (M/R) is shown in Figures 6 and 7, respectively. Obviously, the AA conversion and, thence, the carboxyl content increase as the M/R increases upto 1 : 50, and thereafter decrease.

Increasing the AA-conversion as well as the carboxyl content of the grafted fibers as the polymerization medium is diluted upto the ratio 1 : 50 may be interpreted in terms of:

1. increase the dissolution of AA and CA molecules and thence the diffusion of these molecules from the aqueous phase to the fiber phase ameliorates and,
2. enhancement of the opening up of the flax cellulose structure and thence the penetration of AA and CA molecules through the fiber pores and crevices enlarges.

However, further dilution of polymerization medium beyond the ratio 1 : 50 may decrease the number of both AA monomer molecules as well as CA

Figure 7 Effect of material-to-liquor ratio on the carboxyl content of the grafted fibers. Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); [CA], 0.4 meq/l g flax; [MnO$_2$]; 0.4 meq/l g flax.

molecules in the vicinity of the flax cellulose chains, from which the %TC and carboxyl content of the grafted fibers diminish.

Acrylic acid concentration

Figures 8 and 9 impart the influence of AA concentration on the total conversion percentage and the carboxyl content of the grafted flax fiber, respectively. It is seen that these polymer criteria increase by increasing the concentration of AA within the studied range. This would be associated with the higher availability of monomer molecules in the proximity of cellulose macroradicals as well as in the polymerization medium at higher monomer concentration. It is understandable that greater availability of the monomer in the poly-

Figure 6 Effect of material-to-liquor ratio on the %TC: Polymerization temperature, 70°C; polymerization time, 2 h; [AA], 200% (owf); [CA], 0.4 meq/l g flax; [MnO$_2$]; 0.4 meq/l g flax.
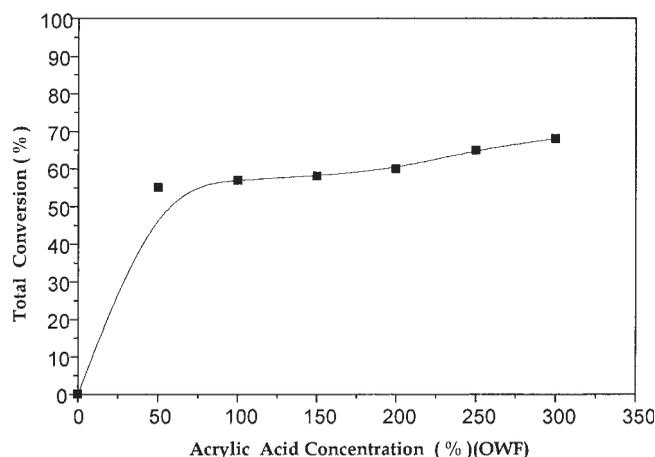
Figure 8 Effect of AA concentration on the percentage total conversion. Polymerization temperature, 70°C; polymerization time, 2 h; [CA], 0.4 meq/l g flax; material-to-liquor ratio, 1 : 50.
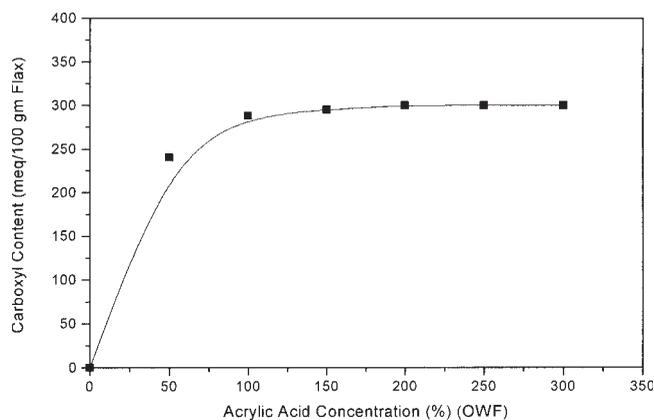
Figure 9 Effect of AA concentration on the carboxyl content. Polymerization temperature, 70°C; polymerization temperature, 2 h; [CA], 0.4 meq/l g flax; [MnO₂]; 0.4 meq/l g flax; material-to-liquor ratio, 1 : 50.

merization medium acts in favor of molecular collision, thereby enhancing polymerization. Furthermore, the increase in the AA concentration would greatly enhance the swellability of the flax fibers. Thereupon, the grafting reaction would be enhanced.

Duration and temperature of polymerization

To investigate the effect of temperature on the rate of polymerization (expressed as total conversion percent and carboxyl content), the flax fiber samples were subjected to graft polymerization with AA (100% owf) using a flax cellulose-MnO_2-CA redox system at different temperatures, viz., 30, 40, 50, 60, and 70°C for varying lengths of time (5–60 min). Other reaction conditions were adjusted as follows: [CA] and [MnO_2], 0.4 meq/1 g flax, and M/R, 1 : 50. Results are shown in Figures 10 and 11.
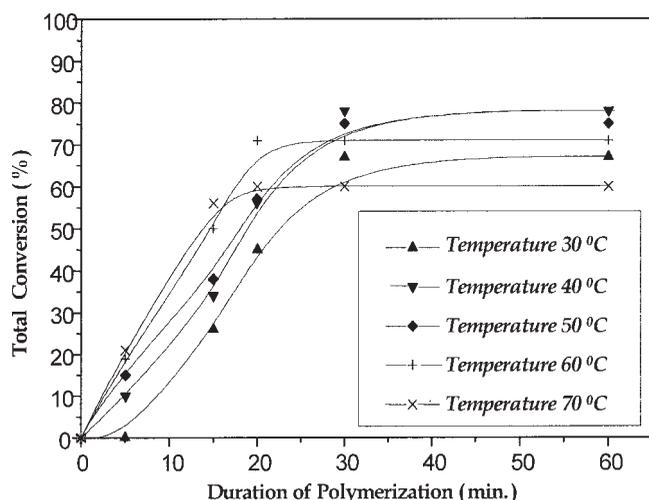
Figure 10 Effect of polymerization time and temperature on the total conversion. [AA] 100% (owf); [CA], 0.4 meq/1 g flax; [MnO_2]; 0.4 meq/1 g flax; material-to-liquor ratio, 1 : 50.
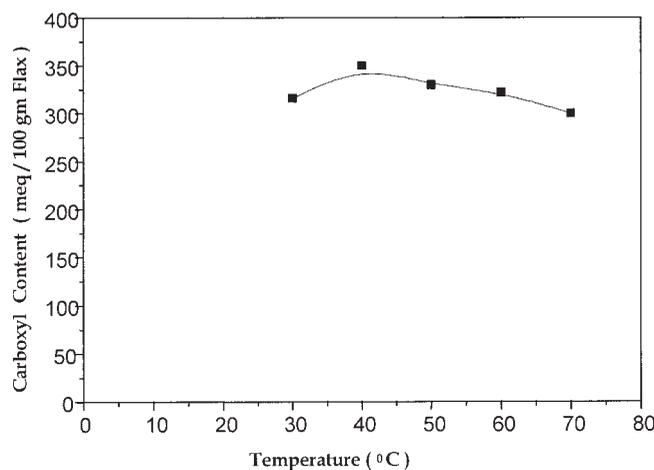
Figure 11 Variation of the carboxyl content with the polymerization temperature. Polymerization temperature, 60 min; [AA] 100% (owf); [CA], 0.4 meq/1 g flax; [MnO_2]; 0.4 meq/1 g flax; material-to-liquor ratio, 1 : 50.

Data of Figure 10 reveal that the extent of polymerization exhibits an initial fast rate which slows down with time, then levels off at the later stages of the reaction. This is observed regardless of the polymerization temperature applied. Depletion of both monomer and initiator concentrations as polymerization reaction proceeds accounts for this. The data of this figure show also that the polymerization reaction is temperature-dependent, that is, during the first 15 min of polymerization the total conversion is higher the higher the temperature of polymerization. Different situation is encountered after the said time. This suggests that the polymerization temperature performs the following functions: (a) increasing the concentration of active species, i.e., free radicals, in the polymerization system, (b) accentuating the swelling properties of flax fibers, (c) accelerating diffusion of AA from polymerization medium to the flax fiber surface, (d) enhancing the rate of initiation and propagation of the graft on the fiber, and (e) enhancing the rate of termination between two growing chains. While functions (a)–(d) lead to increased grafting the function (e) bring about lower grafting. The same arguments are awarded to the results of the carboxyl content of the grafted flax fibers (Fig. 11) The data of Figures 10 and 11 disclose that with the polymerization temperature corresponds to 40°C, both %TC and carboxyl content reached to maximum values. The temperature 40°C is therefore the optimum temperature for polymerizing AA onto flax fibers.

Kind of acid

Table I shows the effect of kind of acid on the %TC. and carboxyl content of the grafted flax fibers. Acids used were citric, tartaric, succinic, oxalic, and sulfuric. As is evident, the polymer criteria, %TC and car-

TABLE I
Effect of Kind of Acid on the Polymer Criteria[a]

Type of acid	TC (%)	Carboxyl content/100 g flax
Sulfuric	7	90
Succinic	13	150
Tartaric	14	150
Oxalic	51	236
Citric	87	350

[a] Polymerization conditions: [MnO_2], 0.4 meq/1 g flax; [acid], 0.4 meq/1 g flax; [AA], 100% (owf); time, 30 min; temperature, 40°C; material-to-liquor ratio, 1 : 50.

boxyl content, are acid nature-dependent, and follow the order:

Citric > oxalic > tartaric > succinic > sulfuric

The abovementioned order reflects differences among the acids used with respect to (a) nature of the primary free radical formed and their affinity to the flax cellulose, (b) the half-life time of these primary free radicals, and (c) ability of these free radicals to react with other reaction ingredient rather than the flax cellulose.

The higher total conversion and carboxyl content in case of CA could be ascribed to the generation of two stable radicals [eq. (1)]. These radicals cannot be further oxidized by Mn^{III} ions. In other words, the lowest total conversion and carboxyl content obtained with sulfuric acid suggests that Mn^{III} ions tend to attack and oxidize the formed radical [eq. (10)], thereby suppressing the rate of initiation.

Kind of the pretreatment

Figures 12 and 13 show the dependence of the %TC and carboxyl content on the pretreatment of the
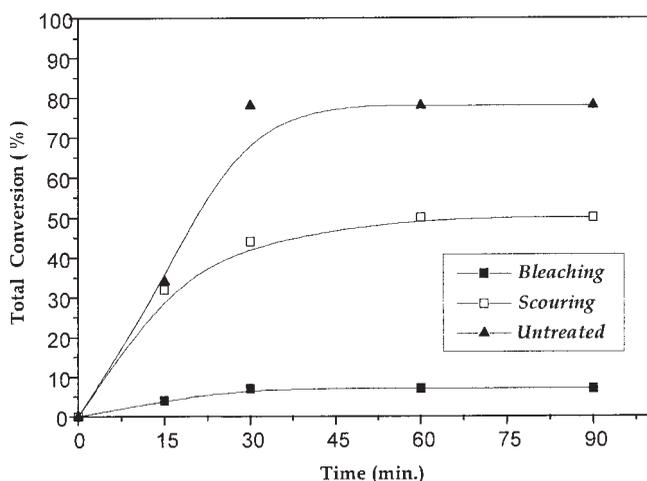
Figure 12 Dependence of %TC on the pretreatment of the flax fibers. [AA], 100% (owf); [CA], 0.4 meq/1 g flax; [MnO_2], 0.4 meq/1 g flax; polymerization temperature, 40°C; material-to-liquor ratio, 1 : 50.
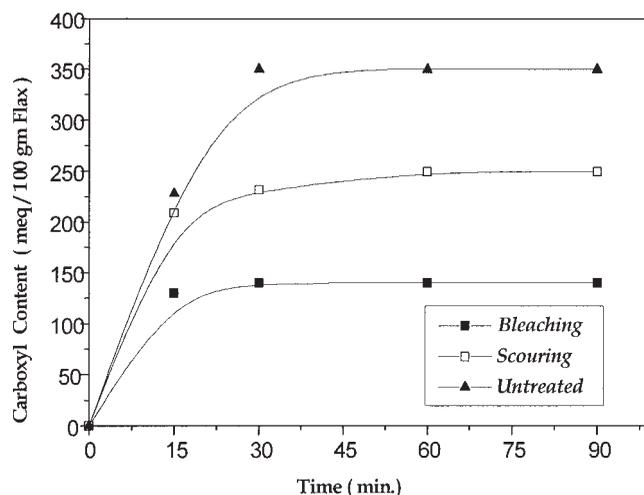
Figure 13 Dependence of the carboxyl content on the pretreatment of the flax fibers. [AA] 100% (owf); [CA], 0.4 meq/1 g flax; [MnO_2]; 0.4 meq/1 g flax; polymerization temperature, 40°C; material-to-liquor ratio, 1 : 50.

machine tow flax fibers. Concerning this, untreated (blank), scoured and bleached flax fibers were grafted with AA under the optimum conditions obtained throughout this work. Data of Figures 12 and 13 reveal that the %TC and carboxyl content of the grafted flax fibers are strongly depend on the nature of the flax fibers used, and follow the order:

untreated flax > scoured flax > bleached flax fibers

The abovementioned order could be explained in terms of percentage of fiber impurities. The machine tow flax fibers (blank) contain many natural impurities such as lignin, pectins, waxes, water-soluble matters and others[1a]. Most of these impurities are reducing in their nature and, therefore, may enlarge the reducing capacity of the initiation system, in question, as a whole. Consequently, the fibers having higher impurities would bring about higher AA-conversion and higher carboxyl content. This is the case of the untreated flax fibers. On the other hand, complete removal of these impurities will suppress the efficiency of the redox initiation system and thereof the magnitude of the polymer criteria decreases, as in the case of the bleached flax fibers.

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