Graft Copolymerization of Vinyl Monomers onto Modified Cottons. XII. Grafting of 1,1-Dihydroperfluoroheptyl Acrylate onto Cellulose Carbamate using Hydrogen Peroxide as Initiator

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Synopsis

Cellulose carbamate having 1.4% N was grafted with 1,1-dihydroperfluoroheptyl acrylate (DHPFHA) using H_2O_2 as initiator under a variety of conditions. The technique used involved padding the fabric in H_2O_2 solution at room temperature followed by impregnating it in an aqueous emulsion of DHPFHA. The graft yield, expressed as fluorine percent, was found to depend upon monomer and initiator concentration, temperature, and reaction time and pH of the polymerization medium as well as upon the carbamate content of the modified cotton. Increasing the monomer concentration up to 5% caused a considerable enhancement in grafting. The same holds true for initiator concentration up to a certain limit after which the grafting decreases. Raising the reaction temperature up to 100°C was accompanied by an increment in the magnitude of grafting reaction. The latter was characterized by an initial fast rate followed by a slower rate. Slightly acidic media (pH 5–6) proved to be the best for performing grafting. The graft yields were quite poor when grafting was carried out in acidic (pH 2–4) or alkaline (pH 8–12) media. The presence of a relatively smaller amount of carbamate groups in the cellulose molecules decreases its susceptibility to grafting. The opposite holds true for larger amounts. Incorporation of $FeSO_4$ at low concentration in the monomer emulsion had no effect on the graft yield. However, the latter decreases at higher $FeSO_4$ concentration. Grafted cellulose carbamate having ca. 15% fluorine showed very good oil and water repellency. The grafted product retained ca. 85% of the strength of cellulose carbamate.

INTRODUCTION

Graft polymerization of vinyl monomers onto chemically modified celluloses has evoked considerable interest in recent years. Previous studies have dealt with graft polymerization onto cellulose xanthate using H_2O_2 as initiator,[1] phosphorylated cellulose using the Fe^{2+}–H_2O_2 redox system,[2] and cyanoethylated cellulose using γ-irradiation[3] or the ceric ion method for initiation.[4,5] The ceric ion method has also been used for vinyl graft polymerization onto partially carboxymethylated cellulose,[6] acrylamidomethylated cellulose,[7] acetylated cellulose,[8] carbamoylethylated cellulose,[7] crosslinked cellulose,[5,9] oxidized cellulose,[10–14] and cellulose bearing sulfur-containing groups,[15] carboxyethyl together with cyanoethyl[7] or carboxymethyl along with cyanoethyl,[7] and allylated cellulose.[15] The use of dimethylaniline–benzyl chloride mixtures for initiation of graft polymerization of methyl methacrylate onto partially carboxymethylated cotton was reported.[16] Potassium permanganate[17] and azobisisobutyronitrile[18] have also been reported to initiate grafting of vinyl monomers onto modified celluloses. In addition, sodium periodate[19] and hydrogen peroxide–thiourea redox systems[20] have been used to initiate graft polymerization onto oxidized celluloses.

In a very recent work we have reported[21] that cellulose carbamate reacts with H_2O_2 to yield an adduct analogous to the corresponding adduct of H_2O_2 and urea $[CO(NH_2)_2 \cdot H_2O_2]$. Decomposition of cellulose carbamate hydrogen peroxide yields ·OH radicals in close proximity of cellulose. These free radicals are capable of inducing grafting of styrene to cellulose.

In this work cellulose carbamate was allowed to react with H_2O_2 in a separate step instead of its incorporation in the polymerization system with a view of minimizing homopolymer formation. In addition, 1,1-dihydroperfluoroheptyl acrylate (DHPFHA) was used as a monomer to impart oil and water repellency to the modified cotton fabrics.

EXPERIMENTAL

Mill-desized, kier-boiled, and bleached cotton fabric (140 g/m^2) was kindly supplied by Misr El Bieda Co., Kafr El-Dawar. The fabric was further purified by treating it with a 20 g/l. sodium carbonate solution, thoroughly washing and drying at ambient conditions.

Cellulose carbamate was prepared by impregnating the cotton fabric in an aqueous urea solution (60%) for 10 min at room temperature. The fabric was then squeezed to give a wet pickup of ca. 100%, followed by air drying and heat treatment at 180°C for 30 min. At this end, the fabric was thoroughly washed with deionized water and finally air dried. Modified celluloses having various amounts of carbamate groups were obtained by changing the urea concentration.[22] The amount of carbamate groups is expressed as percent nitrogen. The latter was determined by the Kjeldahl method.[23]

1,1-Dihydroperfluoroheptyl acrylate (DHPFHA) was distilled before use. Hydrogen peroxide and ferrous sulfate were of analytical grade.

Grafting was carried out by first impregnating the cellulose carbamate sample in an aqueous solution of H_2O_2 (15%) at room temperature for 15 min. The sample was then squeezed to ca. 100% wet pickup and dried in a stream of air at room temperature. A sample of H_2O_2–cellulose carbamate-treated fabric was placed in a dry Erlenmeyer flask. Freshly distilled DHPFHA finely dispersed in water by an emulsifier (Emulphor P) was added to this. The reaction was then allowed to proceed at the specific temperature for the desired duration (details of the conditions used are given in the text). The grafted fabric samples were then repeatedly extracted with a boiling solution of 3% soap and 2% Na_2CO_3 till no more extractable homopolymer was detected. The percentage of fluorine found, based on the initial dry weight of fabric, was designated as percent graft yield.

Fluorine analysis was carried out according to a method described by Vogel[24] with the following modification: A sample of a treated fabric (ca. 20–25 mg) is composted in an Erlenmayer flask containing 20 ml bidistilled H_2O and filled with O_2. The flask was then allowed to cool at room temperature under shaking. After washing the glass stopper and the platinum wire with the least amount of bidistilled H_2O, 0.6 ml of 0.1% aqueous alizarine solution was then added. A few drops of 0.1% NaOH were then added to this solution till a pink color appeared, followed by few drops of diluted HNO_3 (1:40, acid:H_2O) till the lemon-yellow color reappeared, and finally 2.6 ml of the buffer solution (pH 2.9–3) was added. Titration against $0.01N$ $Th(NO_3)_3$ till a pale pink appeared was then carried out. The percent fluorine was calculated as follows:

$$\%F = \frac{(V - V_1) \cdot N \cdot 0.019 \cdot 100}{G}$$

where V and V_1 = volume (in ml) of $0.01N$ $Th(NO_3)_3$ of solution and blank, respectively; N = normality of $Th(NO_3)_3$; and G = weight of sample (in g).

RESULTS AND DISCUSSION

In order to discover the optimal conditions for grafting DHPFHA onto cellulose carbamate and nonmodified cellulose using H_2O_2 as initiator, polymerization was carried out under various conditions as per the technique described in the experimental section.   Variables studied included H_2O_2 concentration, DHPFHA concentration, polymerization temperature, reaction time, pH of the polymerization medium, and amount of carbamate groups in the modified cellulose.   In addition the effect of incorporation of ferrous sulfate in the polymerization system was also studied.   Presented below are the results obtained with their appropriate discussion.

Concentration of H_2O_2

Figure 1 shows the effect of H_2O_2 concentration on the graft yield, expressed as %F, obtained with cellulose carbamate having 1.4% N and nonmodified cellulose when DHPFHA was used as a monomer.   It is seen that with both substrates, the graft yield increases as the H_2O_2 concentration increases, attains a maximum at certain concentration, and then falls upon further increase in the H_2O_2 concentration.   However, for a given H_2O_2 concentration the graft yield
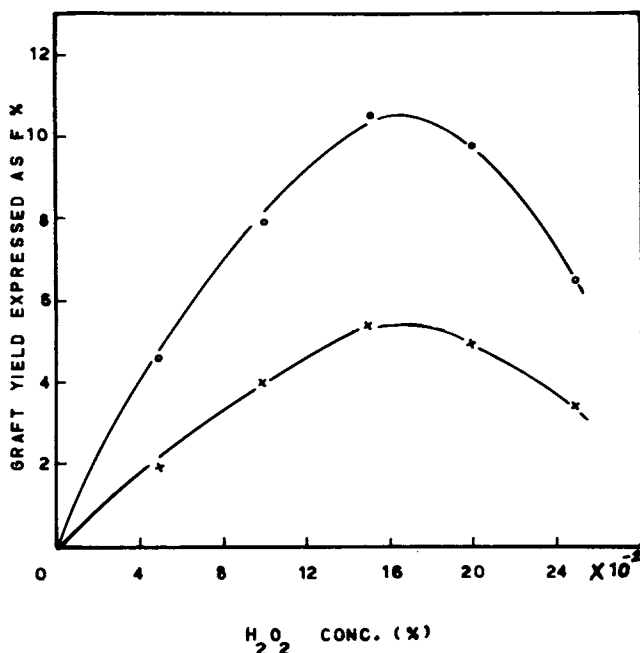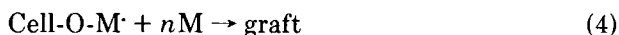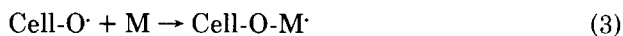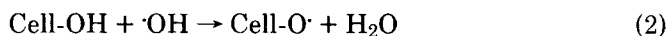

Fig. 1. Effect of concentration of H_2O_2 padding solution on the graft yield of DHPFHA expressed as %F on (x) unmodified cellulose; (o) cellulose carbamate having 1.4% nitrogen; DHPFHA concentration, 1.6%; pH, 6; temperature, 90°C; time, 120 min; material:liquor ratio, 1:60.

obtained with cellulose carbamate is significantly higher as compared with the nonmodified cellulose.

The higher graft yields obtained upon using relatively lower concentration of H_2O_2 suggest that cellulose–H_2O_2 forms a redox system where decomposition of H_2O_2 proceeds most probably as shown by the reaction suggested by eq. (1):

$$H_2O_2 \rightarrow \cdot OH + \cdot OH \qquad (1)$$

The $\cdot$OH radical abstracts hydrogen atom from the cellulose backbone to yield a cellulose macroradical capable of initiating grafting as shown by the mechanism suggested by eqs. (2)–(4):

$$Cell\text{-}OH + \cdot OH \rightarrow Cell\text{-}O\cdot + H_2O \qquad (2)$$

$$Cell\text{-}O\cdot + M \rightarrow Cell\text{-}O\text{-}M\cdot \qquad (3)$$

$$Cell\text{-}O\text{-}M\cdot + nM \rightarrow graft \qquad (4)$$

where M is the vinyl monomer. The reactions suggested by eqs. (1)–(4) seem to proceed favorably up to certain H_2O_2 concentration. Beyond this, the $\cdot$OH radicals may largely participate in termination process with the growing polymer chain. The $\cdot$OH radicals may also further decompose H_2O_2 as shown by eqs. (5) and (6):

$$\cdot OH + H_2O_2 \rightarrow H_2O + \cdot OOH \qquad (5)$$

$$\cdot OOH + H_2O_2 \rightarrow \cdot OH + H_2O + O_2 \qquad (6)$$
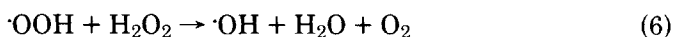
and result in oxygen which may inhibit the polymerization process. In addition, combination of the $\cdot$OH radicals gives rise to higher H_2O_2 concentration in the polymerization mixture and facilitate the reactions represented by eqs. (5) and (6). The ultimate effect of participation of $\cdot$OH radicals in termination, combination, and decomposition of H_2O_2 is certainly lower grafting.

The finding that cellulose carbamate showed significantly higher graft yields than the nonmodified cellulose is in full agreement with previous work.[21] Cellulose carbamate forms a complex with H_2O_2 (Cell-O-CO-$NH_2 \cdot H_2O_2$). Decomposition of this complex results in $\cdot$OH radicals in close proximity of cellulose, thereby favoring creation of cellulose macroradicals capable of initiating grafting.

Monomer Concentration

Figure 2 depicts the effect of DHPFHA concentration on grafting of the latter on cellulose carbamate having 1.4% N. As is evident, there is a significant increase in the graft yield by increasing DHPFHA concentration within the range studied. This could be associated with higher availability of monomer molecules in the proximity of cellulose macroradicals at higher monomer concentration. It is understandable that cellulose macroradicals are immobile, and for grafting to occur the monomer molecules should be in close vicinity of the cellulose. This seems to be justified at higher monomer concentration.
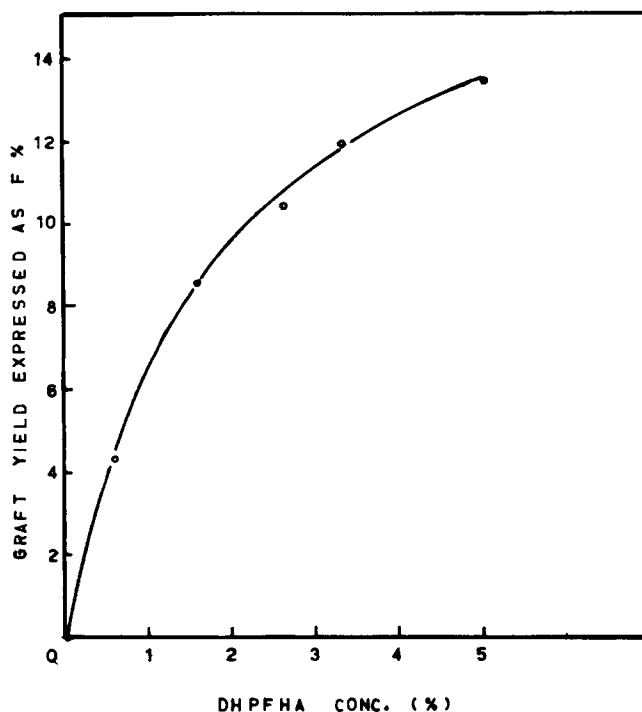
Fig. 2. Influence of DHPFHA concentration on grafting of cellulose carbamate having 1.4% nitrogen: H_2O_2 concentration on the fabric, 0.21%; pH, 6; time, 120 min; temperature, 90°C; material:liquor ratio, 1:60.

Polymerization Temperature

The effect of raising the polymerization temperature up to 100°C is to bring about a significant increment in grafting of DHPFHA onto cellulose carbamate having 1.4% N (Fig. 3). This could be associated with (a) a faster rate of decomposition of Cell-O-CO-NH_2·H_2O_2, giving more ·OH radicals in close proximity of cellulose, (b) enhancement in swellability of cellulose carbamate, (c) increased mobility of DHPFHA molecules, (d) higher rate of diffusion of monomer from the reaction medium to the cellulose carbamate, (e) possible reactions between the growing homopolymer chain with cellulose carbamate and/or the cellulose macroradicals, and (f) enhancement in the rate of initiation and propagation of the graft. The net effect of these factors would be expected to lead to higher grafting.

Reaction Time

Figure 4 shows the graft yield as a function of reaction time. It is clear that the grafting reaction shows an induction period of about 15 min. Thereafter, the reaction proceeds initially fast up to 80 min then slows down, further prolonging the duration of polymerization. In other words, the grafting reaction is characterized by an initial fast rate followed by a slower one. The slower rate of grafting could be ascribed to depletion in monomer and initiator concentration as well as shortage of available grafting sites (cellulose hydroxyls) as the reaction proceeds.
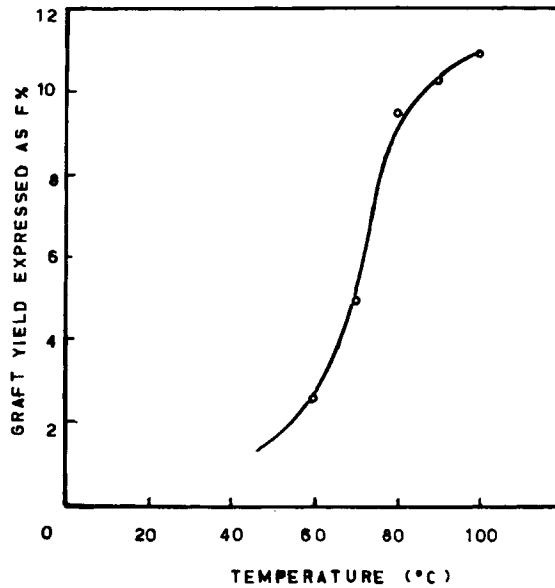
Fig. 3. Effect of temperature on grafting of cellulose carbamate having 1.4% nitrogen with DHPFHA: DHPFHA concentration, 1.6%; amount of H_2O_2 on the fabric, 0.21%; pH, 6; time, 120 min; material:liquor ratio, 1:60.

pH of Polymerization Medium

Figure 5 illustrates the effect of the pH of the polymerization medium on grafting of DHPFHA onto cellulose carbamate having 1.4% N. Obviously, poor graft yields are obtained when grafting is carried out in either relatively high acidic (pH 2–4) or alkaline (pH 8–12) media, whereas substantial grafting occurs
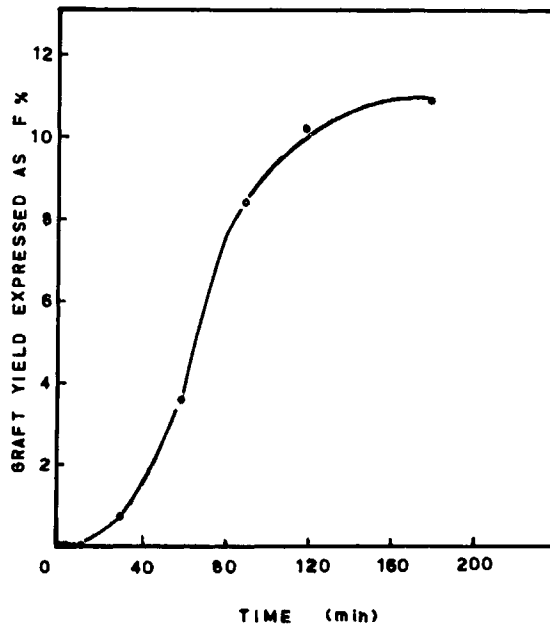

Fig. 4. Rate curve of graft polymerization of DHPFHA on cellulose carbamate having 1.4% nitrogen: DHPFHA concentration, 1.6%; amount of H_2O_2 on the fabric, 0.21%; pH, 6; temperature, 90°C; material:liquor ratio, 1:60.
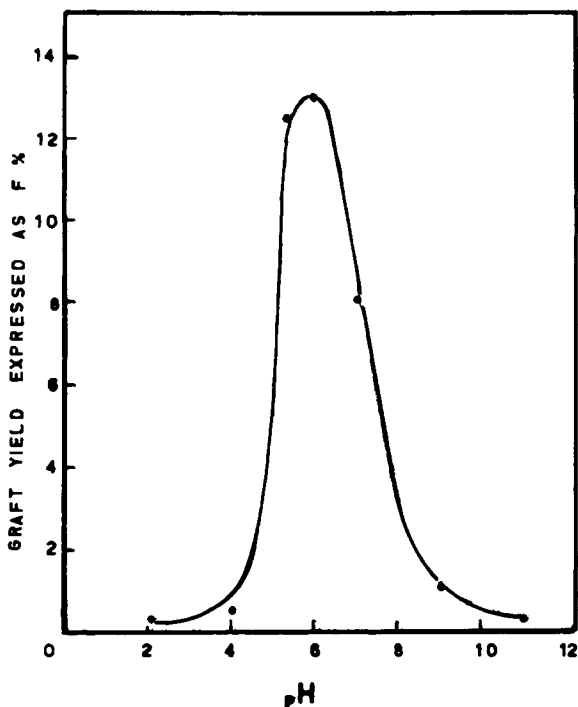
Fig. 5. Effect of pH of the grafting solution on the graft yield of DHPFHA on cellulose carbamate (1.4% N) expressed as %F: DHPFHA concentration, 1.6%; amount of H_2O_2 on the fabric, 0.21%; temperature, 90°C; time, 120 min; material:liquor ratio, 1:60.

in neutral medium (pH 7). Slightly acidic media (pH 5–6), on the other hand, favors grafting considerably.

The lower graft yields in strongly acidic media suggest that at higher hydrogen ion concentration the proton acts as free-radical scavenger; it terminates both the cellulose macroradical, growing polymer chains as well as ·OH radicals. In alkaline media, decomposition of H_2O_2 seems to proceed essentially via evolution of O_2 as suggested by the reaction represented by eq. (7):

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{7}$$

Thus, the action of hydrogen as free-radical scavenger and the mode of decomposition of H_2O_2 are responsible for the lower graft yields obtained when the grafting was carried out in acidic and alkaline media, respectively.

Degree of Cellulose Modification

Figure 6 shows the effect of the carbamate content (expressed as %N) on the magnitude of grafting of DHPFHA onto cellulose carbamate. It is obvious that the presence of relatively smaller amounts (to as low as 0.8% N) of carbamate groups in the cellulose structure lowers the susceptibility to grafting. The reverse is the case with higher amounts of carbamate groups. A similar finding was previously reported.[21] This phenomenon could be explained in terms of the magnitude of the complex formed between the carbamate groups and H_2O_2 (Cell-O-CO-NH_2·H_2O_2) and its further decomposition to yield ·OH radicals. It is to be expected that at a constant H_2O_2 concentration, the magnitude of this
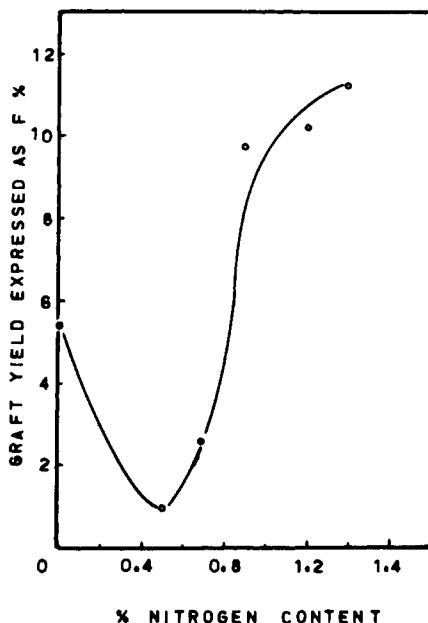
Fig. 6. Influence of carbamate content on percentages graft yield: DHPFHA concentration, 1.6%;
H_2O_2 concentration on the fabric, 0.21%; pH, 6; time, 120 min; temperature, 90°C; material:liquor
ratio, 1:60

complex would increase with the amount of available carbamate groups in the
cellulose molecules. Decomposition of the complex gives rise to ˙OH radicals
the concentration of which is higher at higher complex concentration. Ab-
straction of hydrogen atoms from cellulose by these ˙OH radicals leads to cellulose
macroradicals capable of initiating grafting. Besides, decomposition of H_2O_2
by ˙OH radicals in its vicinity may take place [eqs. (5) and (6)], thereby creating
other ˙OH radicals which may participate in initiation of grafting. This would
account for the enhanced susceptibility toward grafting of cellulose containing
larger amounts of carbamate groups.

   The lower graft yields obtained with modified cellulose having small amounts
of carbamate groups suggests (a) that the carbamate groups, in this case, are
widely distributed in a random manner along the cellulose chain molecules, (b)
that H_2O_2 is exclusively attached to the carbamate group perhaps via strong
hydrogen bonds, (c) that the complex of H_2O_2 with the carbamate group is not
easily decomposable, and (d) that the complexed H_2O_2 requires ˙OH radicals in
its vicinity for decomposition to occur. Though ˙OH radicals are formed through
partial decomposition of the complex, the scarcity of complexed H_2O_2 does not
allow for creation of other ˙OH radicals in the manner shown above. Grafting
in these cases would essentially be initiated by ˙OH radicals resulting from partial
decomposition of the complexed H_2O_2. This is very likely to be valid when
cellulose carbamate having ca 0.4% N is used. Introducing smaller amounts of
carbamate groups than this indicated value seems to play no significant role as
far as complexation and further decomposition of H_2O_2 are concerned. This
might be the reason for increasing grafts at very low nitrogen contents.

Addition of Ferrous Sulfate

Previous reports have disclosed that the presence of Fe^{2+} ion during free-radical polymerization of vinyl monomers onto cellulose enhances grafting significantly.[2] Therefore, it appears of interest to establish the influence of such ion on grafting of cellulose carbamate with DHPFHA using the technique in question.

Figure 7 shows the effect of incorporation of various concentration of ferrous sulfate in the monomer suspension on the graft yield. It is seen that presence of Fe^{2+} at a concentration of 0.001% leaves the graft yield practically unaltered. Further increase in the Fe^{2+} concentration up to 0.01% is accompanied by a significant decrease in the graft yield, in accordance with previous work.[21] The Fe^{2+} seems to act as free-radical scavenger rather than forming a $Fe^{2+}-H_2O_2$ redox system efficient for producing free-radical species.[2] Moreover, it is likely that Fe^{2+} contributes to the termination of the graft, leading to lower molecular weight and therefore lower grafting.

Properties

Some properties of cellulose carbamate before and after grafting with DHPFHA were examined. These include strength and oil and water repellency.

Strength. Tensile strength was monitored using the ASTM test method.[26] Table I shows that grafting of cellulose carbamate with DHPFHA using H_2O_2
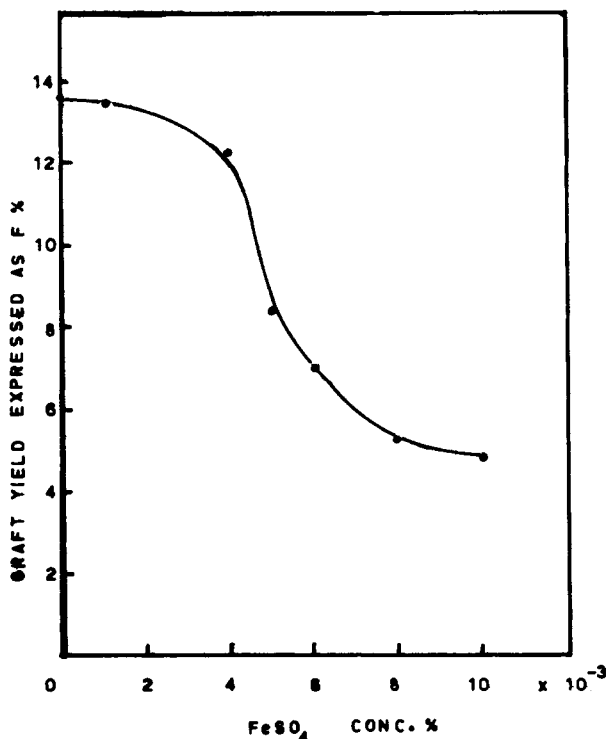

Fig. 7. Effect of ferrous sulfate concentration on grafting of DHPFHA on cellulose carbamate having 1.4% nitrogen: DHPFHA concentration, 1.6%; H_2O_2 concentration on the fabric, 0.21%; pH, 6; time, 120 min; temperature, 90°C; material:liquor ratio, 1:60.

	Substrate	
Property	Cellulose carbamate (1.4% N)	Cellulose carbamate (1.4% N) after grafting with DHPFHA (15.4% F)
Tensile strength, kg	56.16	47.5
Elongation at break, %	9.1	10.0
Strength retention, %	100	84.58
Kit numbers	1	10
Water column height, cm	0.00	11.2

as initiator under the conditions indicated above in this work causes a decrease in tensile strength and an increase in elongation. Indication of this is that grafting disrupts the molecular arrangements of the cellulose. That is, the presence of the grafted polymer in the cellulose structure seems to lessen the degree of packing of the cellulose molecules, thereby decreasing the strength and increasing the elongation at break. However, the contribution of cellulose degradation, if it occurs under the influence of H_2O_2, to the loss in strength cannot be ruled out.

Oil Repellency. The "Kit numbers" system[25] was applied to determine the oil repellency characteristics of cellulose carbamate grafted with DHPFHA. The Kit numbers are an expression of hydrocarbon repellency of a treated article measured by various mixtures of castor oil, toluene, and n-heptane. The Kit number assigned for any given sample is the number of the designated composition containing the least amount of castor oil that will stand on the surface of the treated article for 15 sec, in the form of drops, without penetrating the exposed area underneath. There are twelve Kit numbers that correspond to the parts-by-volume ratio of the mixture: Kit number 1 means that the article acquires very poor oil repellency, whereas Kit number 12 indicates excellent oil repellency.

Table I shows that with cellulose carbamate grafted with DHPFHA a Kit number of 10 could be achieved. This contrasts with a Kit number of 1 for cellulose carbamate before grafting. The implication of this is that grafting DHPFHA on cellulose carbamate imparts to the latter very good oil repellency. Durability of the latter properties was assessed by subjecting the grafted substrate to 15 washings at 90°C in a soap solution. No change in the value of the Kit number was assessed, indicating that the grafted substrate acquires permanent oil repellency properties. It is understandable that the oil repellency is due to the presence of grafted chains containing fluorine in the cellulose molecules.

Water Repellency. Water repellency characteristics of cellulose carbamate before and after grafting with DHPFHA were assessed by using the water pressure test (Schopper), DIN 53886. A column of water exerts uniformly increasing pressure (10 cm/min) on the underside of a specimen mounted in the testing apparatus. The test continues until the first three droplets of water appear on the face of the fabric sample. The weight of the column is measured and the resistance of the fabric sample to hydrostatic pressure is given in terms of centimeter water gauge.

Table I shows the values of the water column for cellulose carbamate before and after grafting. It is seen that a value of 11.2 cm could be obtained with the grafted substrate, in contrast to cellulose carbamate which failed completely to pass the test. This implies that grafting of DHPFHA to cellulose carbamate confers on the latter very good water repellency. Moreover, this latter property is durable since no substantial change in the water column value was observed when the grafted sample was subjected to 15 washings as described above.

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