Graft Copolymerization of Acrylic Acid onto Caesarweed Fibers by Cerric Ion–Toluene Redox Pair

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SYNOPSIS

The graft copolymerization of acrylic acid onto caesarweed fibers in aqueous media by cerric ion–toluene redox pair has been investigated. The percentage graft increased and then decreased with cerric ion concentration ranging from 8.3 to 100.0 $\times$ $10^{-3}M$ with a peak value of 17%. The effects of toluene, substituted toluenes, acids, and acrylic acid were examined. The percentage graft increased and then decreased with toluene concentration with an optimum value of 53% at 18.0 $\times$ $10^{-4}M$ toluene. Under identical reaction conditions, the percentage graft after 30 min for the graft polymerization initiated by substituted toluenes are in the order of p-toluene sulfonic acid > toluene > p-Xylene $\simeq$ o-toluidine. Low concentrations of acetic acid were favorable to the graft polymerization. The percentage graft increased linearly with acrylic acid concentration reaching a value of 53% at 1.39M acrylic acid. The presence of neutral salts had nominal effects on the percentage graft. The effect of temperature was investigated between 20 and 60°C. The percentage graft increased with temperature up to 40°C but showed a negative temperature dependence beyond 40°C. The calculated activation energy was 6.2 kcal mol^{-1}. Characterization of the physical properties of the grafted fibers was also conducted. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Chemical modification of cellulosic fibers by graft copolymerization of vinyl monomers has been extensively studied by several workers.[1-4] Such graft copolymers invariably acquire new properties, notably, improved elasticity, sorbency, ion-exchange capabilities, thermal resistance, etc. depending on the nature of the monomers. Specifically, acrylic acid having a carboxylic function coupled with its hydrophilicity is known to improve ion-exchange and water sorbency properties of cellulose–polyacrylic acid graft copolymer.[5]

Caesarweed plant, *Urena lobata* possesses bast fibers that are cellulosic, closely resembling jute, albeit shorter and coarser. The morphological features of the fibers have not been reported and commercial utilization of the fibers in the textile industries is limited. However, in some applications it is used as a substitute for jute fibers.

Studies on the graft copolymerization of meth-ylmethacrylate (MMA) onto caesarweed fibers by potassium permanganate in the presence of toluene have been reported.[6] Significant graft levels were obtained and toluene exhibited dual properties by enhancing and retarding the graft polymerization.

Previous report by Das et al.[4] indicates that cerric ion in combination with toluene is an effective redox pair for initiation of graft polymerization of MMA onto jute fibers.

Studies on the graft copolymerization of acrylic acid onto caesarweed fibers by cerric ion–toluene redox pair are presented in this communication. The effects of substituted toluenes on the polymerization reaction and the physical properties of the graft copolymer were investigated and are discussed in this article.

EXPERIMENTAL

Purification of acrylic acid (Aldrich Corp.) was by fractional distillation after it was washed with 5% aqueous sodium hydroxide and sodium chloride solutions and dried over anhydrous calcium chloride.

Other reagents, that is, cerric ammonium sulfate, glacial acetic acid, sulfuric acid ($\sim$ 18M), p-Xylene, o-toluidine, and p-toluene sulfonic acid were used as supplied.

The purification of toluene, pretreatment of the fibers, and the method of graft copolymerization reaction were as reported in a previous communication.[6]

The fiber–polyacrylic acid graft copolymer was purified by extraction of the homopolymer with hot water (60°C) and then by soxhlet extraction with water to constant weight.

The percentage graft was calculated from the relation: % grafting = $[(W_2 - W_1)/W_1]/100$ where W_1 and W_2 are the weights of fibers and grafted fibers, respectively.

The determination of water retention capacity and solubility in acid of the graft copolymer were carried out by standard methods.[7,8]

RESULTS AND DISCUSSION

Effect of Cerric Salt Concentration

The effect of cerric salt concentration on the graft copolymerization of acrylic acid onto caesarweed fibers at 30°C is shown in Figure 1. The graft yield increases and then decreases with the concentration of cerric salt. At the optimum concentration of 50.0 $\times$ 10^{-3} M of the latter, the corresponding graft yield is low, that is, not greater than 17%. Low grafting yield is, however, characteristic of acidic monomers because of their sensitivities resulting in the preponderance of homopolymerization.[5] The effect of cerric salt in Figure 1 has been reported for a number of graft copolymerization reaction albeit dependent on the monomer type. For example, the graft copolymerization of MMA onto jute fibers by cerric ion–toluene redox pair showed an initial increase in graft yield with the concentration of cerric ion and then leveled up at high concentrations of the ion.[4]

The decrease in the graft yield for acrylic acid at high cerric salt concentrations may be explained in classical terms[9] viz:

1. Termination of the fiber macroradicals by electron transfer to cerric ion is enhanced at high concentrations of the latter.
2. Increased homopolymer formation at high cerric salt concentrations may result in low amount of monomer available for graft polymerization.
3. Enhanced formation of a stable complex between the cerric ion and the hydroxyl group
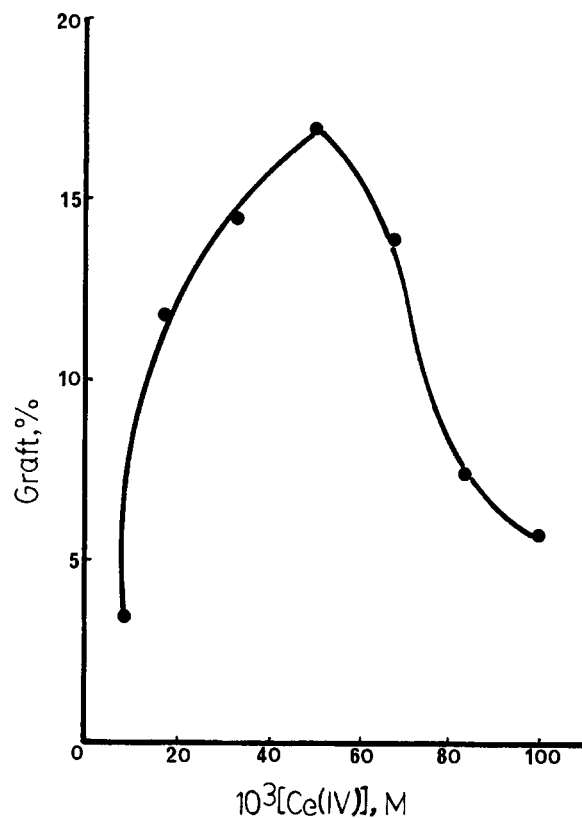
Figure 1 Effect of [Ce(1V)] on graft yield: [AA] = 0.46M, [TL] = 9.0 $\times$ 10^{-4}M, [H$^+$] = 0.6M, [AcOH] = 5.5M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

on the cellulosic fibers[10] may result in reduced number of grafting sites on the latter.

An enhanced homopolymer formation at high cerric salt concentration is consistent with the observed low grafting yield since both acrylic acid and its polymer are soluble in aqueous media. Moreover, solvents that solubilize homopolymers in the course of graft reactions are believed to influence low graft yield.[11]

Effect of Toluene Concentration

The inhibition of polymerization of vinyl monomers by toluene has been reported.[12] In addition, it has been reported that toluene can enhance and retard graft copolymerization of vinyl monomers onto cellulosic fibers.[4,6]
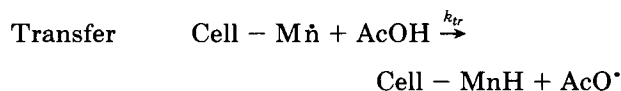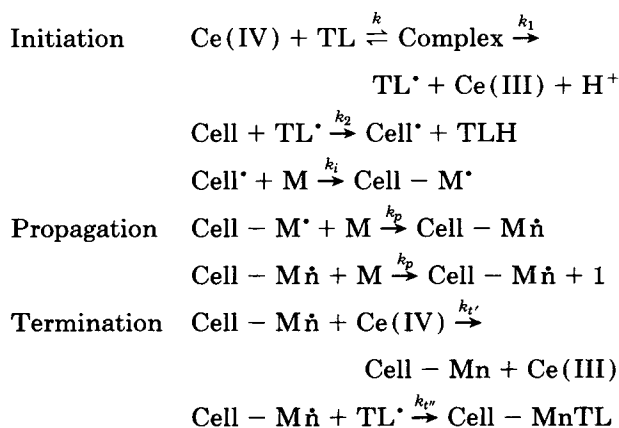
Figure 2 shows the effect of toluene concentration on graft yield. Over the concentration range of 3.6–27.0 $\times$ 10^{-4}M, the graft yield increases and then decreases with a peak value of 53% corresponding to toluene concentration of 18.0 $\times$ 10^{-4}M. The reproducibility of results is not better than 10% and
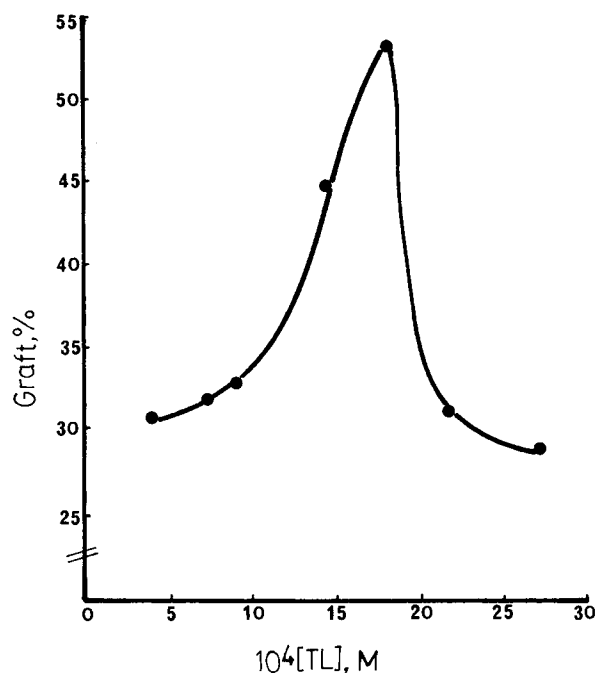
Figure 2 Effect of [TL] on graft yield: [AA] = 0.46M, [Ce(1V)] = 33.3 × $10^{-3}M$, [H$^+$] = 0.6M, [AcOH] = 1.1M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

may be attributed to (i) the heterogenous nature of the reaction and (ii) a possible nonuniformity in the morphological features of the fibers. For the latter, differences in the degree of swelling of the crystalline and amorphous regions of the fibers may lead to uneven accessibility of the monomer to the grafting sites on the fibers.[11]

An appropriate mechanism is proposed for the graft copolymerization of acrylic acid onto caesarweed fibers by cerric ion–toluene redox system. The form of the initiation process is analogous to the one earlier proposed by Das et al.,[4] that is, formation a benzyl radical via a precursor cerric ion–toluene complex.

Initiation   Ce(IV) + TL $\overset{k}{\rightleftharpoons}$ Complex $\overset{k_1}{\rightarrow}$

            TL$^{\bullet}$ + Ce(III) + H$^+$

            Cell + TL$^{\bullet}$ $\overset{k_2}{\rightarrow}$ Cell$^{\bullet}$ + TLH

            Cell$^{\bullet}$ + M $\overset{k_i}{\rightarrow}$ Cell – M$^{\bullet}$

Propagation   Cell – M$^{\bullet}$ + M $\overset{k_p}{\rightarrow}$ Cell – Mṅ

            Cell – Mṅ + M $\overset{k_p}{\rightarrow}$ Cell – Mṅ + 1

Termination   Cell – Mṅ + Ce(IV) $\overset{k_{t'}}{\rightarrow}$

            Cell – Mn + Ce(III)

            Cell – Mṅ + TL$^{\bullet}$ $\overset{k_{t''}}{\rightarrow}$ Cell – MnTL

Transfer   Cell – Mṅ + AcOH $\overset{k_{tr}}{\rightarrow}$

            Cell – MnH + AcO$^{\bullet}$

where TL, TL$^{\bullet}$, M, AcOH, AcO$^{\bullet}$, Mṅ, and Cell represent toluene, benzyl radical, monomer, acetic acid, acetyl radical, polyacrylic acid radical of n repeating unit, and caesarweed fibers, respectively.

The increase in graft yield with toluene concentration may be due to a kinetically favored redox reaction between the fiber cellulose and benzyl radical. At high concentrations of the latter, however, termination of cellulose macro radicals and those of the grafted copolymer by benzyl radicals may become predominant resulting in lowering of graft yield. Of course, it is expected *a priori* that the reactivity of the benzyl radical may depend on its stability. A test of this is shown by the effects of toluene derivatives on the graft copolymerization as represented in Figure 3. Judging by the graft yields after 30 min under identical reaction conditions, the reactivities of the toluenes in combination with cerric ion is *p*-toluene sulfonic acid > toluene > *p*-xylene $\simeq$ *o*-toluidine. For *p*-xylene and *o*-toluidine, the graft yield is zero after 30 min. Beyond 30 min, *p*-xylene yields higher level of graft copolymer than *o*-toluidine. However, the graft yields after 3 h for toluene and derivatives other than *o*-toluidine are comparable and are much higher by one-half times the value (17%) for the latter derivative. The rel-
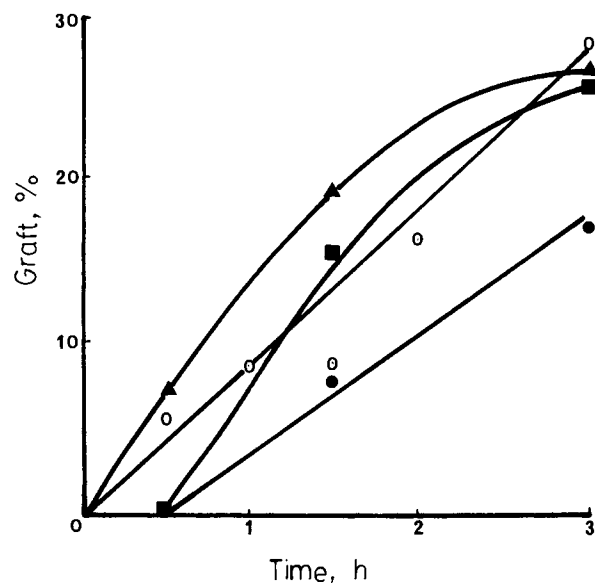
Figure 3 Effect of substituted toluenes on graft yield: [AA] = 0.46M, [Ce(1V)] = 33.3 × $10^{-3}M$, [H$^+$] = 0.6M, [AcOH] = 1.1M, [TL] = 9.0 × $10^{-4}M$, Cell = 0.1 g, temperature = 30°C, (O) toluene, (▲) *p*-toluene sulfonic acid, (■) *p*-xylene, (●) *o*-toluidine.
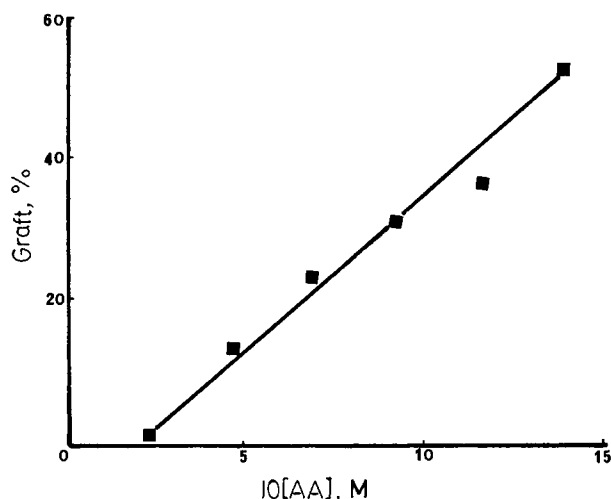
Figure 4 Effect of [AA] on graft yield: [Ce(1V)] = 33.3 × 10⁻³M, [TL] = 9.0 × 10⁻⁴M, [H⁺] = 0.6M, [AcOH] = 5.5M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

ative graft yields for the toluenes may be due to the nature of the substituents, that is, the electron-withdrawing sulfonyl group facilitates resonance stabilization of the benzyl radical in contrast to the electron-donating methyl substituent of p-xylene.

Effect of Monomer Concentration

The graft yield increases linearly with acrylic acid monomer (AA) concentration over the range of 0.23–1.39M as shown in Figure 4. At lower concentrations of the monomer, the yield is zero. The solubility of the monomer and its polymer in aqueous

Table I Effect of [H⁺] and [AcOH] on Graft Yield[a]

[H⁺] (M)	[AeOH] (M)	Graft (%)
0.18	5.5	10.9
0.30	5.5	17.7
0.60	5.5	12.2
0.90	5.5	16.7
1.20	5.5	15.9
0.60	1.1	33.5
0.60	2.2	17.4
0.60	3.3	16.7
0.60	4.4	14.9
0.60	5.5	12.2
0.60	6.7	9.3

[a] [AA] = 0.46M, [TL] = 9.0 × 10⁻⁴M, Cell = 0.1 g, [Ce(1V)] = 33.3 × 10⁻³M, T = 30°C, time = 3 h.

media results in nonpolymer deposits on the fibers. Consequently, at low conversion and in the absence of Trommsdorff effect, the graft yield as a function of the monomer concentration may depend on simple kinetic parameters, that is, the reactivity of the monomer and its rate of diffusion to the radical sites of the fibers. The latter parameter is expected to increase with increase in monomer concentration.

Effect of Acid Concentration

Table I shows the effect of sulfuric (H⁺) and glacial acetic (AcOH) acids on graft yield. For sulfuric acid, the graft yield increases and then decreases with concentration in the range between 0.18 and 1.20M. Graft yield is not greater than 17.7%. For glacial acetic acid, graft yield decreases with increasing concentration of the acid. An increase in the concentration of glacial acetic acid from 1.1 to 6.7M results in a fourfold decrease in graft yield.
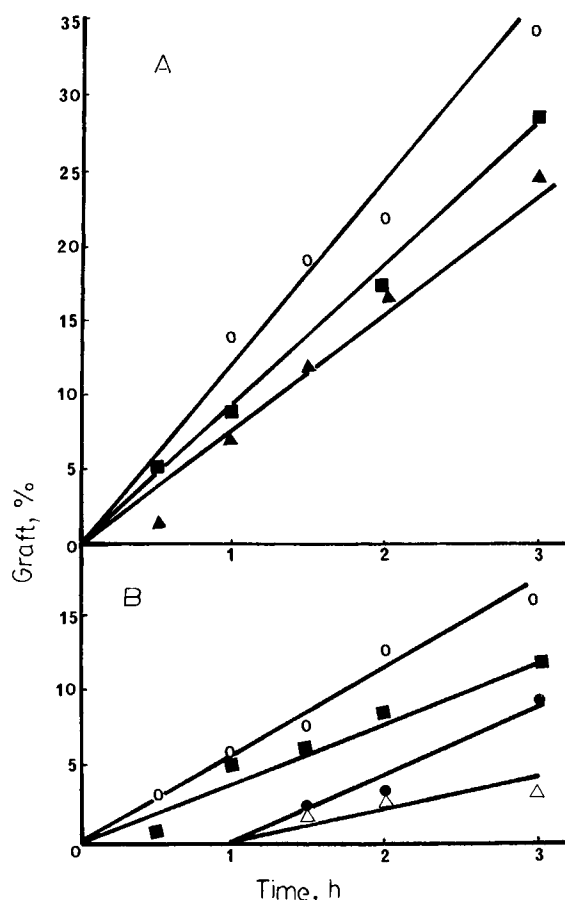
Figure 5 Effect of temperature on graft yield: [Ce(1V)] = 33.3 × 10⁻³M, [TL] = 9.0 × 10⁻⁴M, [AA] = 0.46M, [H⁺] = 0.6M, Cell = 0.1 g, (▲) 20°C, (■) 30°C, (O) 40°C, (●) 50°C, (△) 60°C, (A) [AcOH] = 1.1M, (B) [AcOH] = 5.5M.

Acetic acid was used for the graft reaction to facilitate the solubility of toluene and its derivatives in aqueous media. From Table I, it can be seen that graft yield is appreciable at low acetic acid concentration. The low graft yield, which is evident at high acetic acid concentration, may be due to chain transfer reactions[12] by the latter and a concomitant increase in homopolymerization reaction.

Effect of Temperature

The time–temperature conversion for the graft copolymerization was investigated over a temperature range of 20–60°C at $1.1 M$ and $5.5 M$ acetic acid concentrations. Investigation at the lower acetic acid concentration is ostensibly to improve the graft yield. The results are represented in Figure 5 [(a) and (b)], and it can be seen that the graft yield increases linearly with time and increases with temperature between 20 and 40°C. A further increase in temperature from 40 to 60°C is accompanied by a fourfold decrease in graft yield after 3 h [Fig. 5(b)].

Negative temperature dependence of graft yield for cerric-ion-initiated polymerization has been reported[9,13] and is attributed to (i) instability of cerric salt at high temperature and (ii) increased termination of grafted polymeric chains. However, for the graft copolymerization of MMA on jute fiber by cerric ion–toluene redox pair,[4] the graft yield showed positive temperature dependence up to 60°C. Thus, high-temperature instability of cerric salt is not a probable reason for the decrease in graft yield at high temperature in the case of acrylic acid. Rather, it seems more plausible to suggest that the

Table II Effect of Cations on Graft Yield[a]

[Salt] 0.02M	Graft (%)
Control	27.4
LiCl	25.8
CuCl$_2$	23.3
NiCl$_2$	28.5

[a] $[H^+] = 0.6M$, $[AcOH] = 1.1M$, $[Ce(IV)] = 33.3 \times 10^{-3}M$, $[AA] = 0.46M$, $[TL] = 9.0 \times 10^{-4}M$, Cell = 0.1 g, $T = 30°C$, time = 3 h.

negative temperature dependence of graft yield at high temperature is associated with increased termination of the grafted polymer chains arising from an enhanced chain transfer reactions by acetic acid.

An Arrhenius plot of the rate of graft (R_g) versus the reciprocal of temperature is represented in Figure 6. The activation energy for the graft copolymerization is 6.2 kcal mol^{-1}. The latter is low and inconsistent with the low graft yields. However, the low graft yields have been explained as arising in part from a competitive homopolymerization reaction.

Effect of Cations

Several workers have shown that the presence of some metallic ions in graft copolymerization of vinyl monomers onto cellulosic materials can influence the graft yield significantly.[2,14,15] Table II shows the effect of three inorganic salts on the graft yield. Graft yield is increased nominally by Ni^{2+} but reduced by Li$^+$ and Cu^{2+} ions. The effect of the latter cation is more potent, that is, a reduction in graft yield by
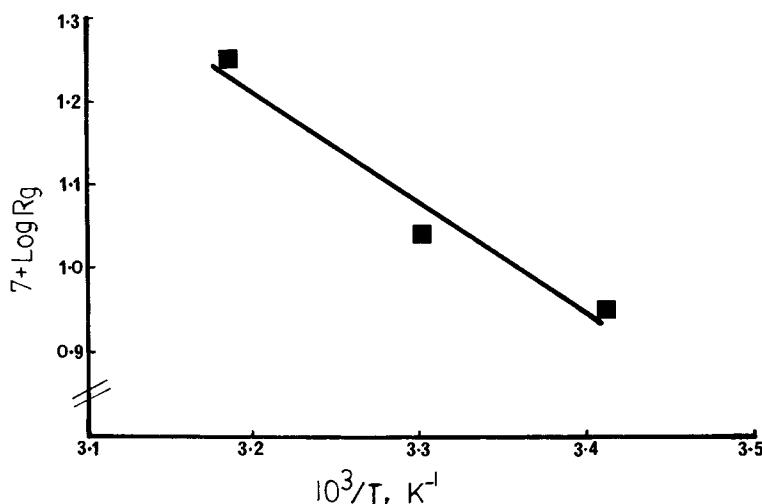
Figure 6   Arrhenius plot of rate of graft vs. the reciprocal of temperature.
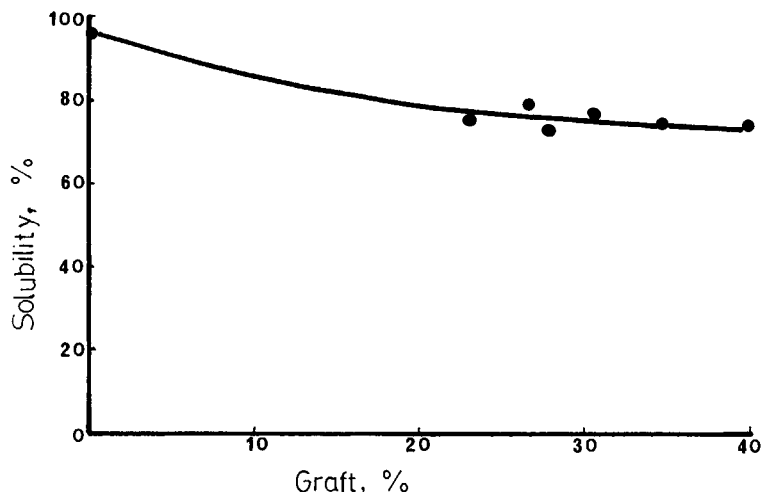
Figure 7   Solubility of caesarweed fiber–polyacrylic acid graft copolymer in 72% sulfuric acid.

15% over the control value of 27.4%. The reduction in graft yield may be associated with sorption of the metallic ions by the cellulosic materials, which may lead to a reduction in free hydroxyl groups. Sorption of metallic ions from aqueous solutions has been demonstrated for many cellulosics.[16-19] The graft yield may also be reduced by the cations acting as radical traps. This is, however, unlikely because it would lead to a more significant reduction in graft yield than found. In general, the effect of Cu^{2+} on the graft yield is consistent, albeit less marked, with a previous report.[4]

CHARACTERIZATION OF THE GRAFTED CAESARWEED FIBER

Water Retention Capacity

Water retention capacity (WRC) is an important property of textile fibers. Water may be retained to varying degrees by surface tension in the capillary spaces between the fibers, the form of which is dependent on the fiber packing.[20] In the case of the cellulosics, WRC may also be enhanced by hydrogen

Table III   Water Retention Capacity of Caesarweek Fiber–Polyacrylic Acid Graft Copolymer

Graft (%)	WRC (g/g)
23.3	4.29
31.0	5.28
53.0	5.39

bonding between the hydroxyl groups and water molecules. Grafting of hydrophilic monomers is expected to increase WRC as earlier demonstrated by some workers.[7] The results of WRC for caesarweed fiber–polyacrylic acid graft copolymer are presented in Table III. The WRC increases with graft yield by 26% in the range 23.3–53.0 percentage grafting.

Solubility of Caesarweed Fiber–Polyacrylic Acid Graft Copolymer in 72% Sulfuric Acid

Figure 7 shows the solubility of caesarweed fiber–polyacrylic acid graft in 72% sulfuric acid as a function of the percentage graft. The solubility decreases with increase in percentage graft. The solubility of the ungrafted fiber is 96% and decreases by 22% over a 39.7% increase in percentage graft. The reduction in solubility is comparable to that of cotton–polystyrene graft (23.9%) for a 39.01% increase in percentage graft.[8] The decrease in the solubility of the fiber–polyacrylic acid graft may be due to structural changes in the fiber matrix on grafting.

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