

Graft Copolymerization of Methacrylonitrile on Kenaf Fibers by Ceric Ion–Toluene Redox Pair

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SYNOPSIS

The graft copolymerization of methacrylonitrile onto kenaf fibers by a ceric ion–toluene redox pair was investigated in aqueous media. Graft yield of up to 212% was found, but the grafting efficiency was not greater than 17.6%. At varying concentrations of toluene, the conversion in graft yield passed through a maximum and thereafter decreased by as much as 46% for a two-half increase in the concentration of toluene. Similarly, acetic acid showed an initial increase in graft yield in the concentration range of 0.58–1.17M and a reduction to zero graft at a 11.67M concentration of the acid. Under identical reaction conditions, acetic acid and its derivatives decreased the graft yield in the order trichloroacetic acid > monochloroacetic acid > acetic acid > formic acid. The effect of the chlorinated acids was considered as a composite consisting of normal transfer reactions and a hydrolytic effect, as strong acids, on the grafted polymers. The percentage graft yield showed a normal temperature dependence over the range 30–60°C with a calculated activation energy of 6.52 kcal mol⁻¹. The amount of grafted polymer increased with monomer concentration, but the average molecular weight decreased with the latter, suggesting an enhanced utilization of more grafting sites on the fibers. The water-retention capacity of the graft copolymer showed an 85% reduction in its value over a threefold increase in the graft yield.

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INTRODUCTION

A number of cellulosic fibers such as caesarweed, kenaf, and roselle are presently of limited commercial interest even though they have physicochemical properties of close resemblance to those of the more popular fibers, namely, flax, hemp, and jute. Of particular interest is kenaf, *Hibiscus cannabinus*, which is fairly new on the world market. Its fiber strands are light and creamy in color and show the same luster and comparable strength as those of jute fibers. It grows well in the tropical and subtropical regions and may find applications in cordage, stuffing, carpet backing, sacks, etc.

Graft copolymerization of vinyl monomers onto cellulosic fibers is a subject of intense studies.^{1–10} In some cases, remarkable changes in the physicochemical properties of the grafted fibers have been

demonstrated. Specifically, grafting of a hydrophobic styrene monomer onto cotton fibers yielded a graft copolymer of improved resistance to wetting.¹¹ Similarly, poly(acrylic acid)–cellulose and poly(methacrylic acid)–cellulose graft copolymers, prepared, in some cases, by hydrolysis of polyacrylonitrile–cellulose and polymethacrylonitrile–cellulose graft copolymers, respectively, are known to be suitable as super water absorbents.^{12,13}

Grafting of methacrylonitrile onto cellulose initiated anionically has been reported.¹⁴ The present study was on the graft copolymerization of methacrylonitrile on kenaf fibers by a ceric ion–toluene redox pair in aqueous media. The features of the reactions and of the characterized graft copolymers are reported and discussed in this article.

EXPERIMENTAL

Methacrylonitrile (Aldrich Corp.) was washed with 5% aqueous sodium hydroxide and then with dis-

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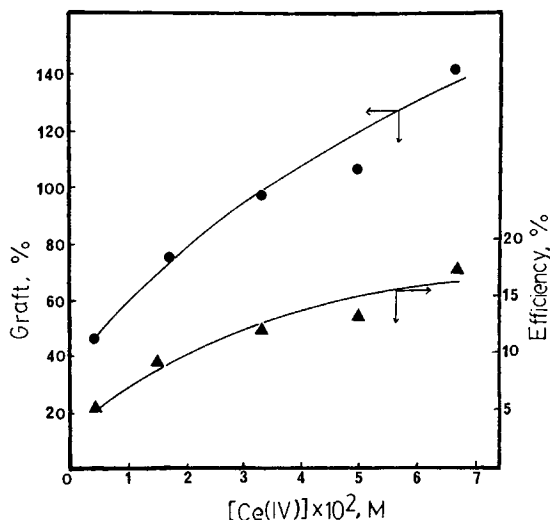


Figure 1 Effect of $[\text{Ce(IV)}]$ on graft yield: $[\text{MA}] = 0.40M$, $[\text{TL}] = 0.9 \times 10^{-3}M$, $[\text{AcOH}] = 2.92M$, $[\text{H}^+] = 0.62M$, Cell = 0.1 g, time = 3 h, temperature = 30°C .

tilled water to neutral pH. It was dried over anhydrous calcium chloride and fractionally distilled. Toluene (BDH) was treated with sulfuric acid, washed with distilled water to neutral pH, and fractionally distilled after drying with anhydrous calcium chloride. Other reagents, i.e., ceric ammonium sulfate, glacial acetic acid, sulfuric acid ($\sim 18M$), formic acid, and mono- and trichloroacetic acids, were used as supplied.

Kenaf plant was obtained from the University's botanical garden at Yola. The bast fibers were air-dried and beaten in a mortar. The methods of preparation of bleached holocellulose from the fibers and of the graft copolymerization were as reported in a previous article.⁸

The fiber-polymethacrylonitrile graft copolymer was purified by extraction of ungrafted homopolymer with acetone to constant weight. The percentage graft and percentage efficiency were calculated from the relation

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1] \times 100$$

$$\% \text{ Efficiency} = [(W_2 - W_1)/W_3] \times 100$$

where W_1 , W_2 , and W_3 are the weights of the fiber, the grafted fiber, and the monomer, respectively. The water-retention capacity and solubility in acid of the grafted copolymer were determined by standard methods.^{11,15}

The grafted polymer was removed from the fiber by hydrolysis in 100 mL of boiling 3% sodium hydroxide solution for 30 min.¹⁵ The resultant mixture

was filtered hot on a Buchner funnel and washed with distilled water to neutral pH.

The isolated polymer was dissolved in acetone and the average molecular weight determined from the viscosity of the acetone solution using the Mark-Houwink equation¹⁶: $(\eta) = 95.5 \times 10^{-3} \bar{M}_v^{0.56}$.

The molar number of graft polymer per 100 g of fiber, Ng , was determined from the weight of the grafted polymer, Wg (in g/100 g fiber), and the average molecular weight, \bar{M}_v , by the relationship¹⁷ $Ng = Wg/\bar{M}_v$.

RESULTS AND DISCUSSION

Effect of Ceric Salt Concentration

Figure 1 shows the effect of ceric salt concentration on the graft copolymerization of methacrylonitrile (MA) onto kenaf fibers at 30°C . The graft yield increased with ceric salt in the concentration range of $4.2\text{--}66.7 \times 10^{-3}M$, yielding a value of up to 141%. The percentage efficiency also increases correspondingly but with values that are low, i.e., not greater than 17.6% at the highest percentage graft. The form of the curve for percentage graft vs. ceric salt concentration indicates a slowing down of the graft reaction at high ceric salt concentration. This is to be expected if termination of the growing graft polymer by the ceric ion becomes significant at high concentrations of the salt. Further, the methacrylonitrile monomer is reactive and the low grafting efficiency may be associated with a kinetically favored homopolymerization reaction.

Effect of Toluene Concentration

The dual properties of toluene (TL) as an accelerator and a retarder of homopolymerization and graft copolymerization reactions have been demonstrated for a number of monomer-initiator systems.^{8,10,18} The effect of TL on the graft copolymerization is represented in Figure 2. The percentage graft increases and decreases after an optimum value of 126.7%, corresponding to toluene concentration of $1.44 \times 10^{-3}M$.

The mechanism of graft copolymerization proposed in a previous communication⁸ is applicable, i.e., the formation of an initiating benzyl radical via a precursor ceric ion-TL complex as represented below:

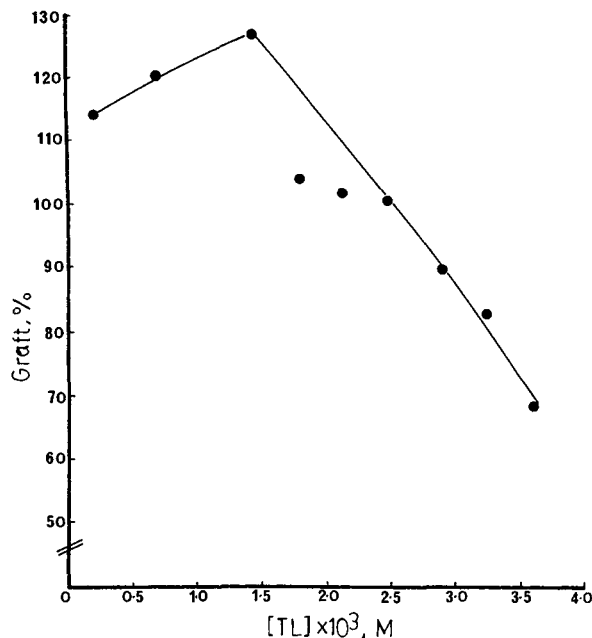
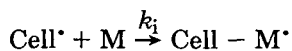
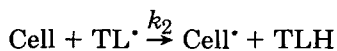
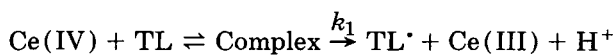
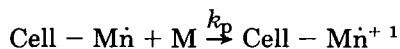
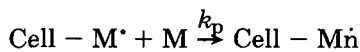


Figure 2 Effect of [TL] on graft yield: [MA] = 0.40M, [Ce(IV)] = $33.3 \times 10^{-3}M$, [AcOH] = 2.92M, [H⁺] = 0.62M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

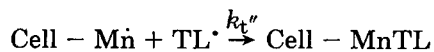
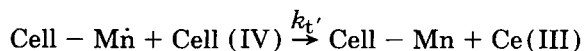
Initiation



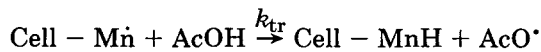
Propagation



Termination



Transfer



where TL, TL[•], M, AcOH, AcO[•], and Cell represent toluene, the benzyl radical, the monomer, acetic acid, the acetyl radical, and kenaf fibers, respectively.

The retardation of the graft polymerization by TL at high concentrations is associated with a dominant termination of cellulose macroradicals and those of the grafted polymer by benzyl radicals.

Effect of Monomer Concentration

The graft yield increases linearly with the concentration of methacrylonitrile (MA) over the range 0.08–0.60M as shown in Figure 3. In the graft-copolymerization of acrylonitrile¹⁹ and methyl methacrylate⁸ by redox initiators in aqueous media, the graft yield showed acceleration at high monomer concentrations and was attributed to gel effects. As can be seen in Figure 3, there is no acceleration in graft yield, indicating a simple monomer dependence of the grafting reactions over the concentration range investigated.

Effect of Acid Concentration

The effects of sulfuric (H⁺) and glacial acetic (AcOH) acids are shown in Table I. Graft yield generally decreases with increasing concentration of the acids.

For sulfuric acid, a 10-fold increase in concentration results in about 50% reduction in the graft yield. Reduction in graft yield through hydrolysis of the grafted chains is a feature of strong acids.

In the case of acetic acid, graft yield increases initially by 32% in the concentration range of 0.58–1.17M and thereafter decreases to a zero value for a 10-fold increase in concentration of the acid. In a previous communication,⁹ the reduction in graft yield by acetic acid was associated with a transfer reaction by acetyl radicals. A test of this is demonstrated in Figure 4, showing the effects of acetic acid and derivatives on the graft copolymerization reaction. Under identical reaction conditions and 1.79M concentrations of acetic acid and derivatives, the conversion in the graft copolymer is reduced in

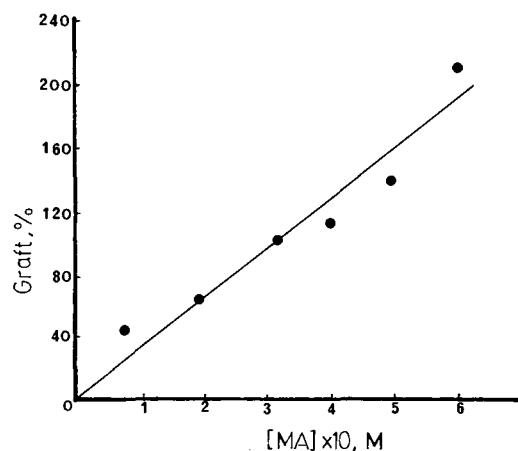


Figure 3 Effect of [MA] on graft yield: [Ce(IV)] = $33.3 \times 10^{-3}M$, [TL] = $0.9 \times 10^{-3}M$, [AcOH] = 2.92M, [H⁺] = 0.62M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

Table I Effect of Acetic (AcOH) and Sulfuric (H⁺) Acids on Graft Yield

[AcOH] (M)	[H ⁺] (M)	Graft (%)
0.58	0.62	48.8
1.17	0.62	64.2
2.92	0.62	34.3
5.83	0.62	30.5
8.75	0.62	5.0
11.67	0.62	0
1.17	0.06	58.8
1.17	0.31	39.9
1.17	0.62	31.7
1.17	0.94	32.5

[MA] = 0.20M, [Ce(IV)] = 33.3×10^{-3} M, [TL] = 0.9×10^{-3} M, Cell = 0.1 g, time = 3 h, temperature = 30°C.

the order trichloroacetic acid > monochloroacetic acid > acetic acid > formic acid. If transfer reactions were a dominant feature of these acids in the graft copolymerization reaction, the order above would suggest that trichloroacetic acid is more active as a transfer agent. This would, however, be inconsistent with expectation since the powerful electron-withdrawing chlorine atoms of the acid are expected to render the acetyl radical less active in transfer reactions. By the same argument, the order of reactivity for formic and acetic acids is consistent with a greater reactivity of the latter facilitated by the electron-donating methyl group.

The apparent contradiction in the order of reactivity of the chlorinated acids in relation to formic and acetic acids may be reconciled by the understanding that the former acids are strong and may thus partake in the hydrolysis of grafted polymers. The initial rates of graft, R_g , in the presence of the acids are presented in Table II. The value for formic acid is a factor of 3 greater than that of trichloroacetic acid.

Effect of Weight of Kenaf Fibers on Graft Yield

Intrinsically, the cellulosic fiber is a two-phase system consisting of a crystalline and an amorphous region which show varying reactivities toward oxidizing agents.²⁰ Thus, in graft reactions, the yield may depend on the morphological features of the fiber.

The effect of the amount of fiber on graft yield is represented in Figure 5. The graft yield passes through a maximum in the range 0.05–0.25 g of the fiber. An optimum value of 60.2% in graft yield cor-

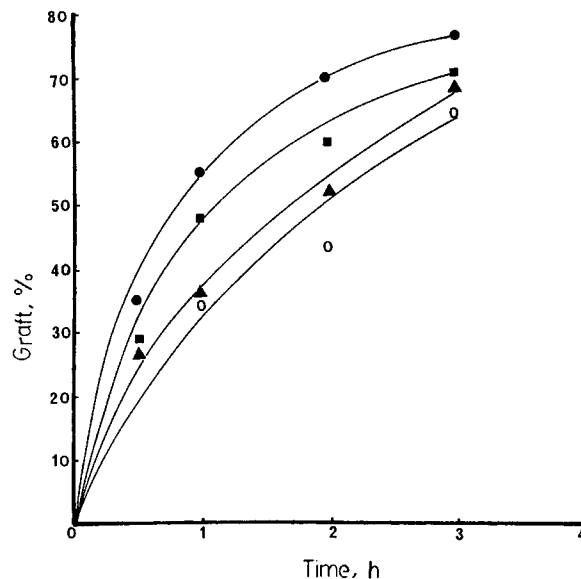


Figure 4 Effect of acetic acid derivatives on graft yield: [MA] = 0.22M, [Ce(IV)] = 37.0×10^{-3} M, [TL] = 1.0×10^{-3} M, [AcOH] = 1.29M, [H⁺] = 0.69M, Cell = 0.1 g, temperature = 30°C. (●) Formic acid; (■) acetic acid; (▲) chloroacetic acid; (○) trichloroacetic acid.

responds to a fiber weight of 0.15 g. The percentage efficiency increases with fiber weight but approaches a plateau at a high amount of fiber.

For the graft copolymerization of methyl methacrylate onto jute fibers,⁶ the graft yield approached a plateau at a high amount of the fiber. However, a fall in percentage graft yield is to be expected beyond a critical value of fiber weight since the number of grafting sites on the fiber is largely determined by the efficiency of the redox initiating system.

Effect of Temperature

The effect of temperature was investigated in the range of 30–60°C and at low acetic acid concentration of 1.29M. The results are represented in Figure

Table II Effect of Acetic Acid Derivatives on Initial Rate of Graft

Acid	$R_g \times 10^3$ mmol/Ls
Formic	18.4
Acetic	11.5
Monochloroacetic	9.2
Trichloroacetic	5.9

[MA] = 0.22M, [Ce(IV)] = 37.0×10^{-3} M, [TL] = 1.0×10^{-3} M, [AcOH] = 1.29M, [H⁺] = 0.69M, Cell = 0.1 g, temperature = 30°C.

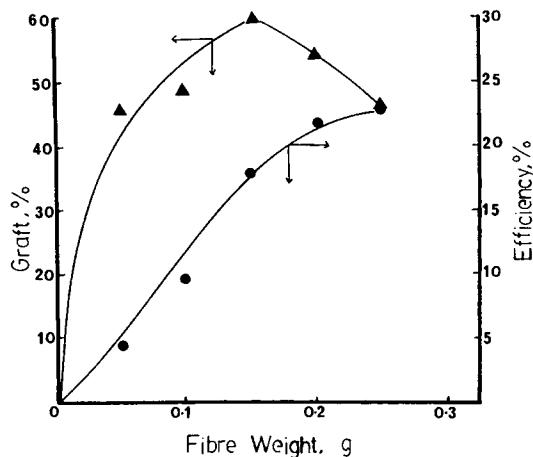


Figure 5 Effect of fiber weight on graft yield: $[MA] = 0.20M$, $[Ce(IV)] = 33.3 \times 10^{-3}M$, $[TL] = 0.9 \times 10^{-3}M$, $[AcOH] = 1.17M$, $[H^+] = 0.62M$, time = 3 h, temperature = $30^\circ C$.

6. The graft yield in time-temperature conversion shows a positive temperature dependence up to $60^\circ C$.

For the graft copolymerization of acrylic acid onto caesarweed fibers initiated by a ceric ion-TL redox pair,⁹ a negative temperature dependence in graft yield was observed beyond $40^\circ C$. This was attributed to an enhanced chain-transfer reaction by acetic acid at high temperatures. The positive temperature dependence exhibited by the MA-ceric ion-TL system over the same temperature range in the presence of the same level of acetic acid suggests that the effects of transfer reactions are masked by the reactivity of the monomer in graft reactions. This is corroborated by the high graft yields obtained with MA compared to acrylic acid.⁹

An Arrhenius plot of the rate of graft vs. the reciprocal of temperature is shown in Figure 7. The calculated activation energy for the graft reaction is $6.52 \text{ kcal mol}^{-1}$.

CHARACTERIZATION OF GRAFTED KENAF FIBERS

Molecular Weight of Graft Polymer

The average molecular weight of a grafted polymer is known to increase with decreasing ceric salt and increasing monomer concentrations.^{17,21} For grafting of MA onto kenaf fibers, the average molecular weight of the graft polymer decreases with increasing monomer concentration over the range $0.40\text{--}0.60M$

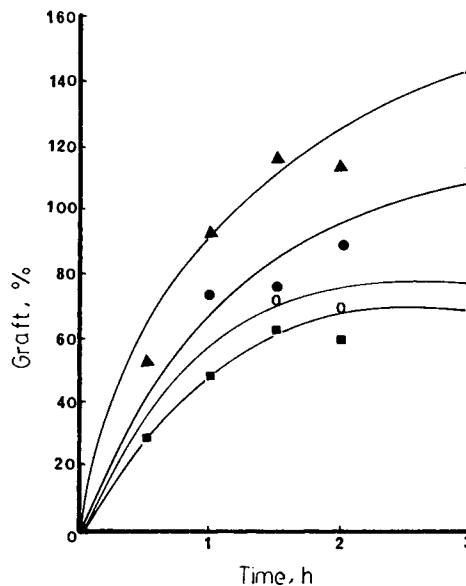


Figure 6 Effect of temperature on graft yield: $[MA] = 0.22M$, $[Ce(IV)] = 37.0 \times 10^{-3}M$, $[TL] = 1.0 \times 10^{-3}M$, $[AcOH] = 1.29M$, $[H^+] = 0.69M$, Cell = 0.1 g. (■) $30^\circ C$; (○) $40^\circ C$; (●) $50^\circ C$; (▲) $60^\circ C$.

as shown in Table III. The amount of graft polymer, however, increases with monomer concentration.

A decrease in the average molecular weight of the graft polymer as the monomer concentration increases may be caused by three factors, namely:

1. Increased homopolymer formation via transfer to the monomer.

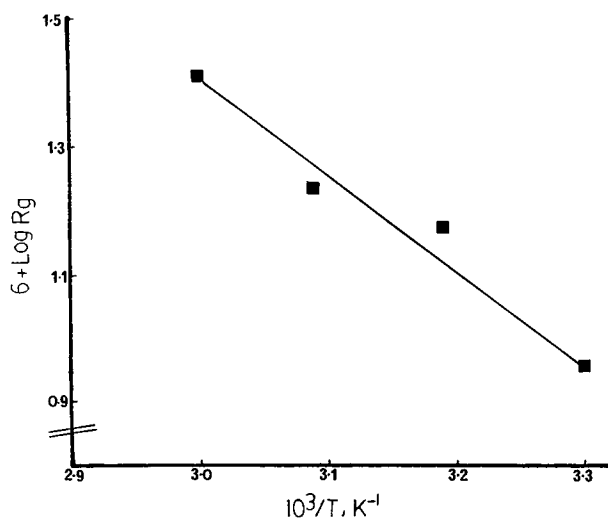


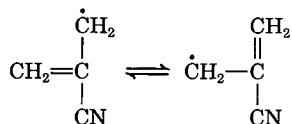
Figure 7 Arrhenius plot of rate of graft vs. the reciprocal of temperature.

Table III Effect of [MA] on Number and Molecular Weight of Grafted Polymer

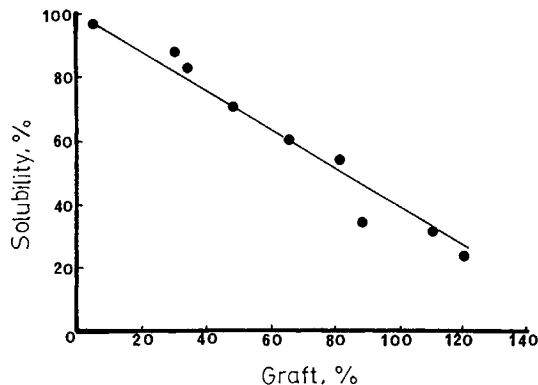
[MA] (M)	Graft (%)	$\bar{M}_v \times 10^{-3}$	Amount Grafted Polymer mmol/100 g
0.40	113.7	4.68	45.6
0.50	141.5	2.81	85.8
0.60	212.2	2.08	150.5

2. Termination of the graft reaction by monomer radicals.
3. Enhanced utilization of grafting sites on the fiber.

For a transfer reaction involving the monomer, a radical species of the form represented below may be formed, i.e.:



If transfer/termination reactions are predominant, increased monomer concentration may lead to higher concentrations of its radical species and an overall reduction in the average molecular weight of the graft polymer. This argument is tenuous *a posteriori* judging from the effect of the monomer on the graft yield in Figure 3 above. An enhanced utilization of more grafting sites on the fibers with increase in monomer concentration seems more plausible with the attendant effects of increased graft yield and a reduced average molecular weight of graft polymers.

**Figure 8** Solubility of kenaf fiber-polymethacrylonitrile graft copolymer in 72% sulfuric acid.

Solubility of Kenaf Fiber-Polymethacrylonitrile Graft Copolymer in 72% Sulfuric Acid

The solubility of the kenaf fiber-polymethacrylonitrile graft copolymer in 72% sulfuric acid is represented in Figure 8. As can be seen, the percentage solubility of the copolymer decreases linearly with increasing graft yield. This property has been demonstrated for a number of graft copolymers^{9,11,22} and indicates an improved resistance of the copolymer to the action of acids.

Water-retention Capacity

The water-retention capacity (WRC) for a cellulose-vinyl monomer graft has been reported for hydrophilic^{9,12,15} and for hydrophobic¹⁵ vinyl monomers. For hydrophobic monomers, the WRC of graft fibers is expected to decrease with increasing graft yield. Table IV shows the effect of graft yield on the WRC for a kenaf fiber-polymethacrylonitrile graft copolymer. A threefold increase in the graft yield results in an 85% reduction in the WRC of the graft copolymer.

The authors wish to thank Emeritus Professor D. C. Pepper of Trinity College, Dublin, Ireland, for his gift of methacrylonitrile. The services provided for this work by Messrs S. A. Osemeahon (senior technologist), Benson Aliyu (assistant technologist), and Ishaku Maizana (laboratory assistant), all of the Department of Chemistry, are gratefully acknowledged.

Table IV Water-retention Capacity of Kenaf Fiber-Polymethacrylonitrile Graft Copolymer

Graft (%)	WRC (g/g)
52.7	11.87
93.1	4.45
113.3	2.23
116.5	2.19
144.2	1.78

REFERENCES

1. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulose Copolymer*, Springer-Verlag, Berlin Heidelberg, New York, 1981.
2. P. K. Ray, *J. Appl. Polym. Sci.*, **12**, 1787 (1968).
3. M. M. Huque, M. D. Habibuddowla, A. J. Mahmood, and A. J. Main, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1447 (1980).
4. P. Ghosh and S. K. Paul, *J. Macromol. Sci. Chem. A*, **20**(2), 169 (1983).
5. P. Ghosh, A. R. Bandyopadhyay, and S. Das, *J. Macromol. Sci. Chem. A*, **19**(8,9), 1165 (1983).
6. M. Misra, *J. Appl. Polym. Sci.*, **33**, 2809 (1987).
7. B. B. Samal, S. Sahu, B. B. Chinara, S. Nanda, P. K. Otta, L. M. Mohapatro, T. R. Mohanty, A. R. Ray, and K. C. Singh, *J. Polym. Sci. Part A Polym. Chem.*, **26**, 3159 (1988).
8. I. C. Eromosele and T. J. Hamagadu, *J. Appl. Polym. Sci.*, **50**, 645 (1993).
9. I. C. Eromosele, *J. Appl. Polym. Sci.*, to appear.
10. H. K. Das, N. C. Nayak, and B. C. Singh, *J. Macromol. Sci. Chem. A*, **28**(3,4), 297 (1991).
11. N. Thejappa and S. N. Pandey, *J. Appl. Polym. Sci.*, **27**, 2307 (1982).
12. S. B. Vitta, E. P. Stahel, and V. T. Stannett, *J. Appl. Polym. Sci.*, **32**, 5799 (1986).
13. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 3143 (1973).
14. B.-A. Feit, A. Bar-Nun, M. Lahav, and A. Zilkha, *J. Appl. Polym. Sci.*, **8**, 1869 (1964).
15. E. F. Okieimen and J. E. Ebhoaye, *J. Appl. Polym. Sci.*, **31**, 1275 (1986).
16. N. Fuhrman and R. B. Mesrobian, *J. Am. Chem. Soc.*, **76**, 3281 (1954).
17. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. Part A-1*, **5**, 2791 (1967).
18. B. C. Singh, B. K. Misra, A. Rout, N. Mallick, and M. K. Rout, *Makromol. Chem.*, **185**, 953 (1979).
19. I. C. Eromosele, *J. Appl. Polym. Sci.*, **51**, 1817 (1994).
20. O. Y. Mansour and A. Nagaty, *Prog. Polym. Sci.*, **11**, 91 (1985).
21. A. Bazuaye, E. F. Okieimen, and O. B. Said, *Eur. Polym. J.*, **24**(8), 811 (1988).
22. S. Dasgupta, *J. Polym. Sci. Part C*, **37**, 333 (1972).

Received February 27, 1995

Accepted May 5, 1995