Behavior of Cellulose Graft Copolymer towards Persulphate Oxidation. III. Poly(acrylonitrile) Graft Copolymers

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Synopsis

Cotton cellulose was graft copolymerized with poly(acrylonitrile) to different levels. The copolymers so obtained together with the nongrafted cellulose were oxidized at different pH's (4–10) and temperatures (50–70°C) with potassium persulphate. The oxidation reaction was studied with respect to oxygen consumption, mass loss, and changes in copper number and carboxyl content of the cellulosic materials. It was found that the rates of oxidation at pH 4 for the copolymers are substantially higher than that of the nongrafted cellulose and the rate of oxidation is higher the higher the level of grafting. The reverse is the case at pH 10. The mass loss increases as the oxygen consumption increases irrespective of the substrate used and the pH employed. The magnitude of the mass loss is substantially lower in the case of grafted cellulose than in the case of nongrafted cellulose. The cellulosic copolymers with higher graft levels show lower mass loss than those having lower graft levels. However, the copper number and carboxyl content of the oxidized grafted cellulose are higher than those of the nongrafted cellulose at the same oxygen consumption. It is believed that the presence of poly(acrylonitrile) graft in the molecular structure of cellulose impedes cellulosic chain scission without necessarily preventing oxidation of cellulose hydroxyls.

INTRODUCTION

Chemical modification of cellulose via vinyl graft polymerization has been extensively studied and reviewed recently.[1] However, few studies[2,3] have dealt with the behavior of cellulosic graft copolymers towards oxidation. This work is undertaken with a view of studying the susceptibility of poly(acrylonitrile)-–cellulose graft copolymers towards oxidation with potassium persulphate under different conditions.

EXPERIMENTAL

Materials

Cellulose

Cotton slivers (Geza 45) were purified by alkaline scouring (2 g/L sodium hydroxide, 2 g/L sodium carbonate, and 0.1 g/L sodium bisulphite) at about 110°C and 6–10 lb/in.^{2} for 4 h. The boiled material was then washed with water and neutralized with dilute acetic acid, thoroughly washed with distilled water, and air dried.

Acrylonitrile (AN) (Merk), freshly distilled, and potassium permanganate, analytical grade (BDH) were used. Poatium persulphate, analytical grade (BDH) was used as oxidant. Persulphate solutions of varied concentration were

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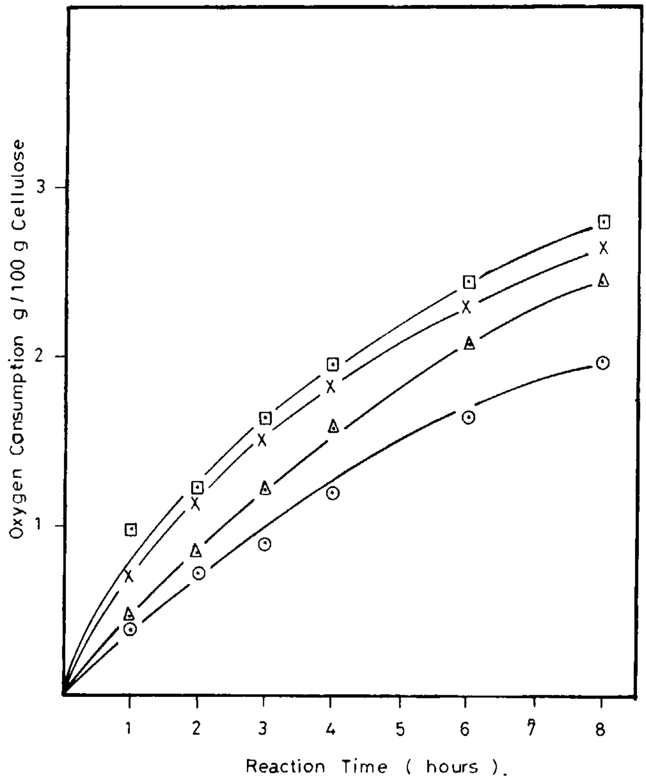

Fig. 1. Rates of oxidation of cellulose and cellulose copolymerized with poly(acrylonitrile) at pH 4. [Persulphate], 0.1 N; temp = 60°C: (O) nongrafted cellulose; (△) 6% graft; (X) 28% graft; (□) 43% graft.

prepared by dissolving potassium persulphate in a solution containing 0.25 mol/L of disodium hydrogen phosphate. The desired pH was attained by either addition of phosphoric acid for alkali, and the solution was then standardized by using the ferrous sulphate and potassium permanganate system.[4]

Polymerization Procedure

The cotton cellulose samples were grafted with acrylonitrile using Mn^{IV} as initiator according to a method described elsewhere.[5] The samples were introduced into a solution containing $KMnO_4$ (25 meq/L), H_2SO_4 (250 meq/L), and methanol (15%). A material-to-liquor ratio of 1:100 was used. The graft polymerization reaction was conducted at 50°C for 1 h. Different graft levels were obtained by varying the monomer concentration. The samples were then subjected to repeated soxhlet extraction with dimethyl formamide as a solvent until constant weight. The increase in weight is considered as a graft.[1]

Oxidation Procedure

Cellulose or grafted cellulose was treated with potassium persulphate solution (0.1 N or 0.18 N) for varying periods at a specific temperature. The oxidation was carried out at 50–70°C with the persulphate solution and pH values of 4–10 for periods up to 8 h.

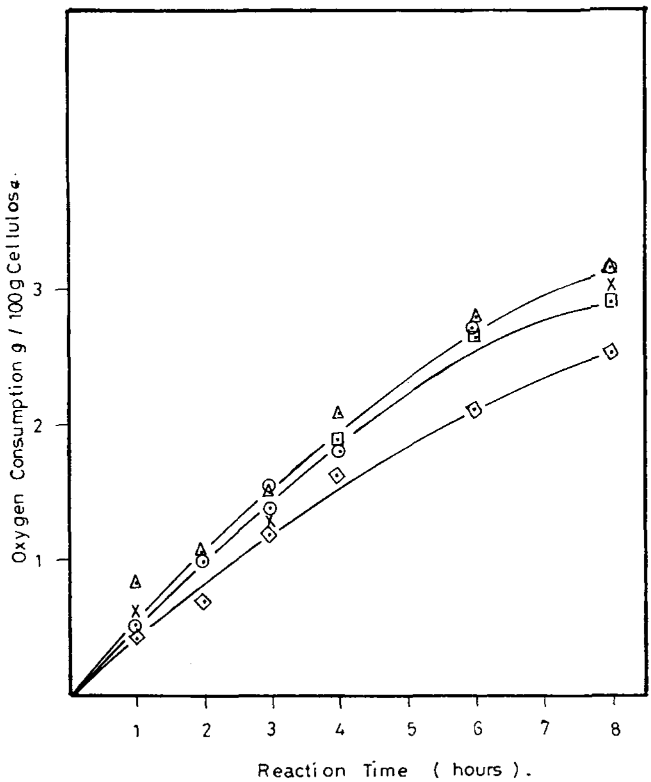

Fig. 2. Rates of oxidation of cellulose and cellulose copolymerized with poly(acrylonitrile) at pH 6. [Persulphate], 0.1 N; temp = 60°C: (O) nongrafted cellulose; (△), 6% graft; (X) 28% graft; (⊡), 34% graft; (◇) 43% graft.

Analysis

Oxygen Consumption (OC)

The oxygen consumption (oxygen/100 g cellulosic sample) was calculated from the difference in persulphate concentration[4] before and after oxidation.

Mass Loss

The mass loss (g/100 sample) was calculated from the dry weights of the cellulose sample before and after oxidation.

Copper Number

The copper number was estimated by the micro Braidy method as modified by Heyes[6].

Carboxyl Content

The carboxyl content was estimated by the alkalimetry method.[7]

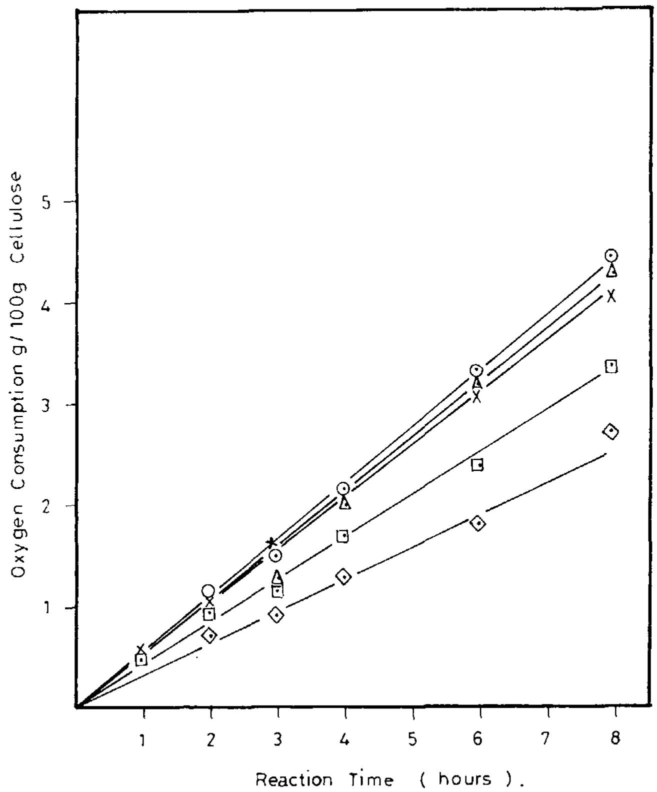

Fig. 3. Rates of oxidation of cellulose and cellulose copolymerized with poly(acrylonitrile) at pH 8. [Persulphate], 0.1 N; temp = 60°C: (O) nongrafted cellulose; (△) 6% graft; (×) 28% graft; (⊡) 34% graft; (◇) 43% graft.

RESULTS AND DISCUSSION

Cellulose and cellulose copolymerized with poly(acrylonitrile) to different levels were subjected to oxidation with potassium persulphate under different temperatures (50–70°C), pH's (4, 6, 8, and 10), and durations (1–8 h).

Figure 1 shows the degree of oxidation at pH 4, expressed as oxygen consumption (OC) per 100 g cellulose, vs. duration at 60°C. It is seen that the OC increases by increasing the duration of oxidation within the range studied. This is observed irrespective of the substrate used. Nevertheless, the rates of oxidation for the copolymers are substantially higher than that of the nongrafted cellulose. Furthermore, the rate of oxidation is higher the higher the level of grafting. Similar trends were observed when oxidation of these substrates were carried out at pH 4 and at 50°C and 70°C.

Figure 2 shows the rate of oxidation at pH 6 of cellulose and the cellulosic copolymers when the oxidation reaction was carried out at 60°C. Unlike oxidation at pH 4, cellulose copolymerized with poly(acrylonitrile) shows a rate of oxidation which is comparable with that of the ungrafted cellulose. However, the rate of oxidation of the grafted cellulose tends to be lower at higher levels of grafting. The same phenomenon was encountered at 50°C and 70°C when the oxidation reaction was carried out at this pH, i.e., pH 6.

Figure 3 shows that the poly(acrylonitrile)-grafted celluloses are less suscep-

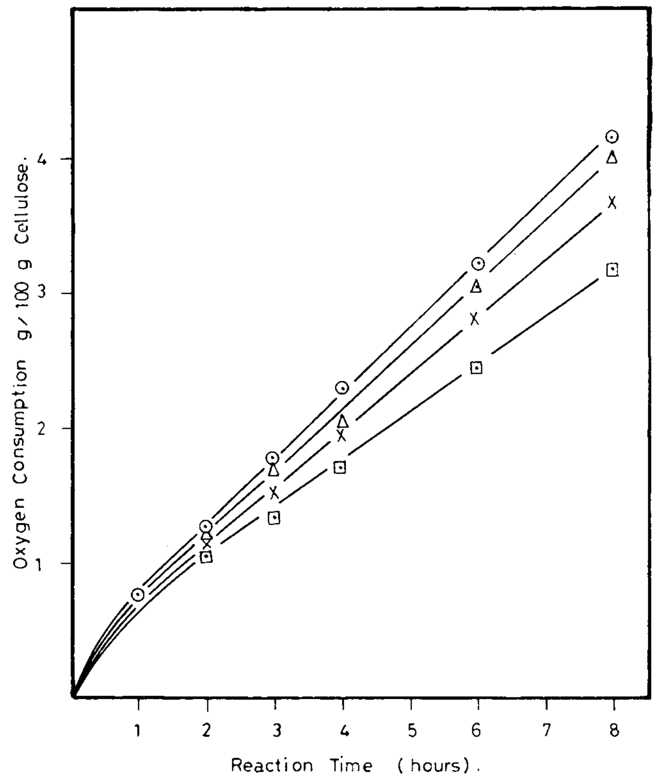

Fig. 4. Rates of oxidation of cellulose and cellulose copolymerized with poly(acrylonitrile) at pH 10. [Persulphate], 0.1 N; temp = 60°C: (O) nongrafted cellulose; (△) 6% graft; (X) 28% graft; (⊡) 43% graft.

tible to oxidation with potassium persulphate solutions of pH 8 at 60°C since their rates of oxidation are lower as compared with the ungrafted cellulose. It is also seen that the rate of oxidation of the poly(acrylonitrile)-grafted celluloses depends upon the level of grafting: the higher the level of grafting, the lower the rate of oxidation. This is the trend observed with oxidation at pH 6. Similar trends were observed on carrying out the oxidation at 50°C and 70°C, using a persulphate solution of pH 8.

Figure 4 depicts that the rates of oxidation of the cellulosic copolymers at pH 10 and 60°C are lower than the rate of the ungrafted cellulose. The figure also shows that the rates of oxidation of the highly grafted cellulose copolymers are higher than those of lower graft yields. This trend was found to persist even when the oxidation reaction was carried out at 50°C and 70°C, similar to oxidation at pH 6 and pH 8.

A comparison between Figures 1, 2, 3, and 4 would indicate that: (a) The rates of oxidation of the ungrafted cellulose are higher than the rates of the ungrafted cellulose at pH 4, and the reverse is the case at pH 10, in agreement with previous reports[2,3] dealing with oxidation of cellulose grafted with either poly(methyl methacrylate) or poly(methacrylic acid) under similar conditions. (b) Increasing the magnitude of the graft in poly(acrylonitrile)–cellulose-graft copolymers enhances the rate of oxidation at pH 4, also in agreement with previous reports.[2,3]

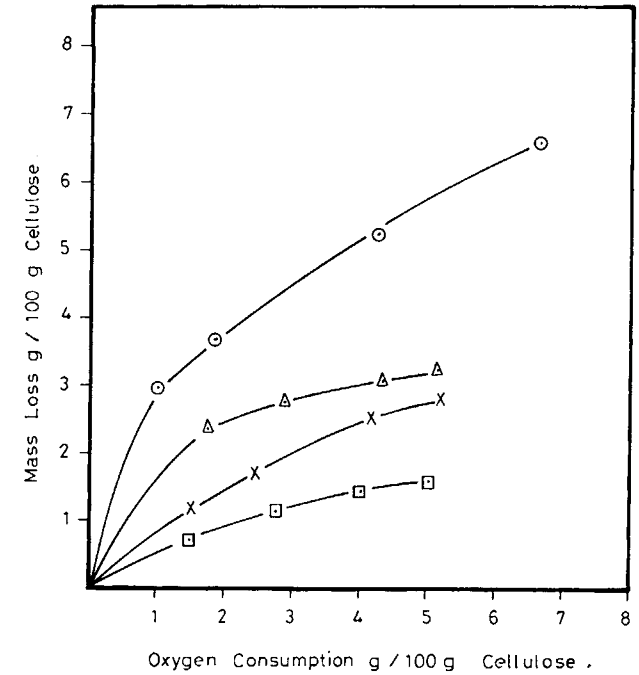

Fig. 5. Mass loss as a function of oxygen consumption. [Persulphate], 0.18 N; pH 4; temp = 70°C: (○) nongrafted cellulose; (△) 28% graft; (×) 34% graft; (□) 43% graft.

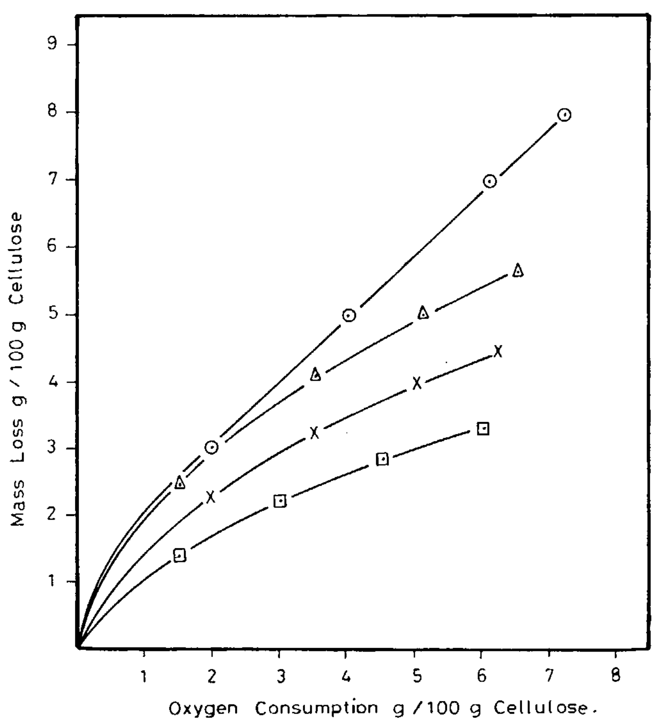

Fig. 6. Mass loss as a function of oxygen consumption. [Persulphate], 0.18 N; pH 10; temp = 70°C: (○) nongraft; (△) 6% graft; (×) 28% graft (□) 43% graft.

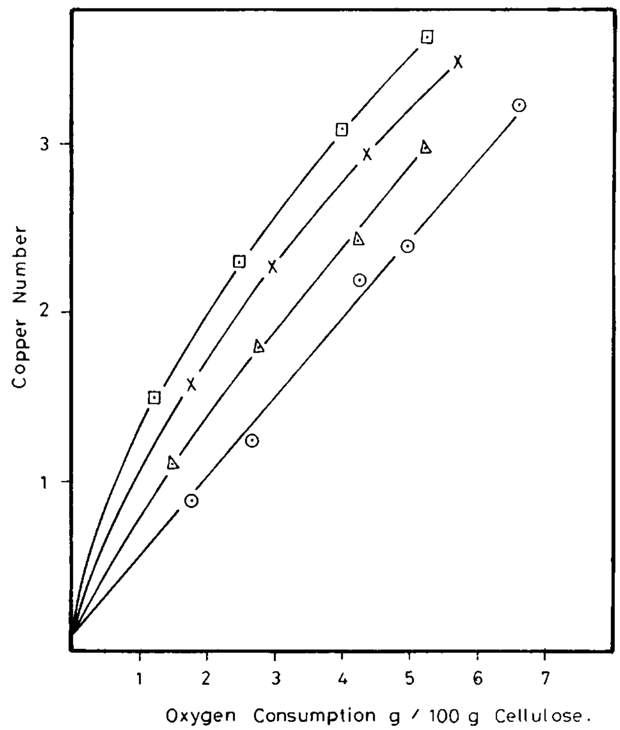

Fig. 7. Relationship between oxygen consumption and copper number. [Persulphate], 0.18 N; pH, 4; temp = 70°C: (O) nongrafted cellulose; (▲) 6% graft; (X) 28% graft; (⊡) 43% graft.

(c) The higher the graft yields of the poly(acrylonitrile)–cellulose-graft copolymer, the lower the rate of oxidation when the oxidation was carried out at pH 10. This is in contrast to the results previously reported for oxidation of poly-(methyl methacrylate) cellulose graft copolymers and poly(methacrylic acid)–cellulose-graft copolymers.[2,3]

With the above in mind, it is obvious that grafting of cellulose with vinyl monomers exerts a considerable effect on the susceptibility of cellulose towards oxidation with persulphate. For a given condition, the rate of oxidation depends upon the amount and nature of the graft. It is to be expected that nature of the graft would rely on the nature of the monomer, which, in turn, would affect molecular weight and molecular weight distribution of the graft as well as frequency of branching. This would account for differences in response of the different copolymers towards oxidation.

Mass Loss

Figures 5 and 6 show the mass loss as a function of the OC when the ungrafted cellulose and the poly(acrylonitrile)–cellulose-graft copolymers were oxidized with potassium persulphate at pH 4 and pH 10, respectively. The mass loss was expressed as g/100 g cellulose. Obviously, the mass loss increases as the OC increases irrespective of the substrate used and the pH of the oxidation employed. However, the magnitude of the mass loss is substantially lower in the case of the grafted cellulose than in that of the nongrafted cellulose. Moreover, the cellulosic

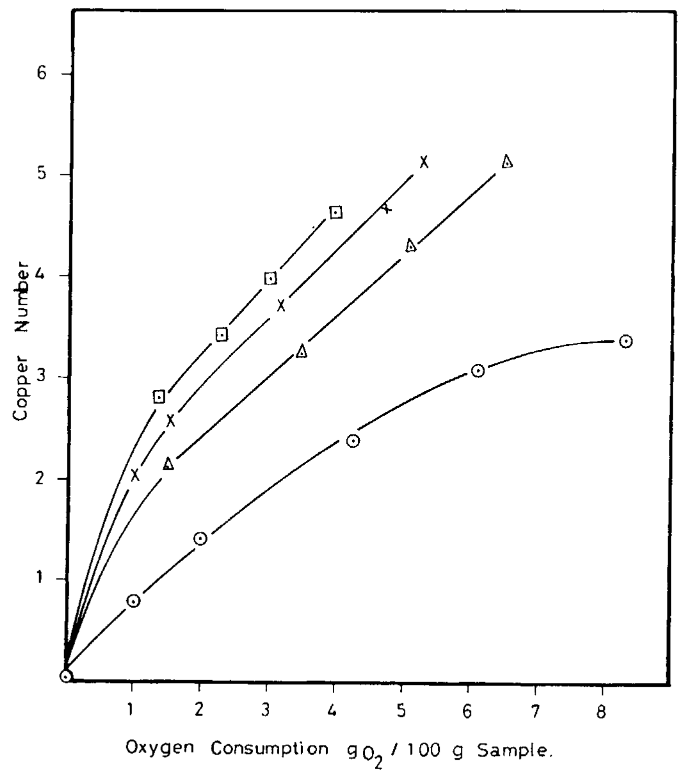

Fig. 8. Relationship between oxygen consumption and copper number. [Persulphate], 0.18 N; pH 10; temp = 70°C: (O) nongrafted cellulose; (△) 6% graft; (×) 28% graft; (□) 43% graft.

copolymers with higher graft yields show lower mass losses than those with lower graft yields. This is in accordance with a previous report dealing with oxidation of poly(methyl methacrylate)–cellulose-graft copolymers.[2] The presence of poly(acrylonitrile) graft in the molecular structure of cellulose seems to impede cellulosic chain scission, similar to the case for poly(methyl methacrylate) grafts. As a result, formation of short degraded cellulosic chains which are amenable to washing is minimized, and, as a consequence, the mass losses with the poly(acrylonitrile)–cellulose-graft copolymers are lower than the nongrafted cellulose.

Copper Number

Figures 7 and 8 show the relation between OC and the copper number of the oxidized grafted and nongrafted cellulose when oxidation was carried out at pH 4 and pH 10, respectively. The relation reveals (a) that the copper number increases with increasing OC, (b) that the lines representing this relation for grafted celluloses lie above those of the nongrafted cellulose, indicating that the grafted cellulose is more susceptible to oxidation than the nongrafted cellulose, and (c) that at the same OC cellulosic copolymers with higher graft yields show higher copper number than those having lower graft yields. These are in contrast with those found with oxidized poly(methyl methacrylate)–cellulose-graft copolymers and poly(methacrylic acid)–cellulose-graft copolymers.[2,3]

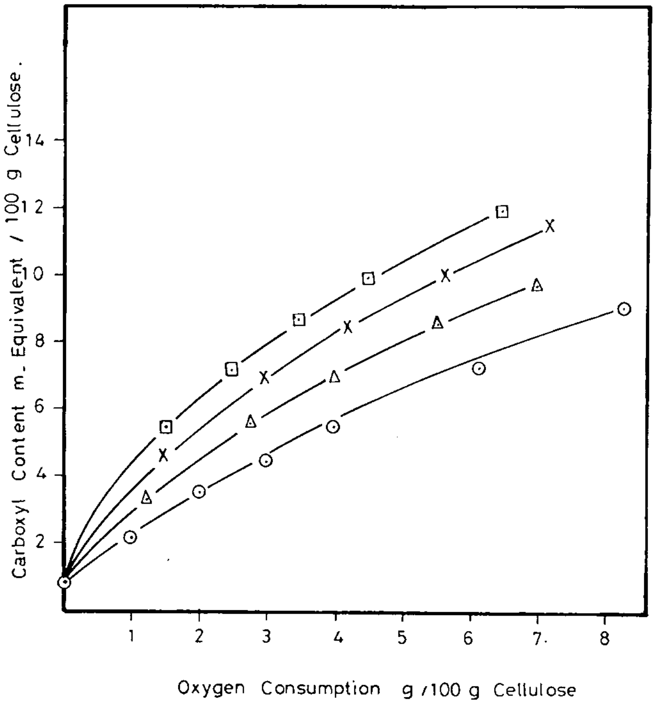

Fig. 9. Carboxyl content vs. oxygen consumption. [Persulphate], 0.18 N; pH 4; temp = 70°C: (O) nongrafted cellulose; (▲) 6% graft; (X) 28% graft; (⊡) 43% graft.

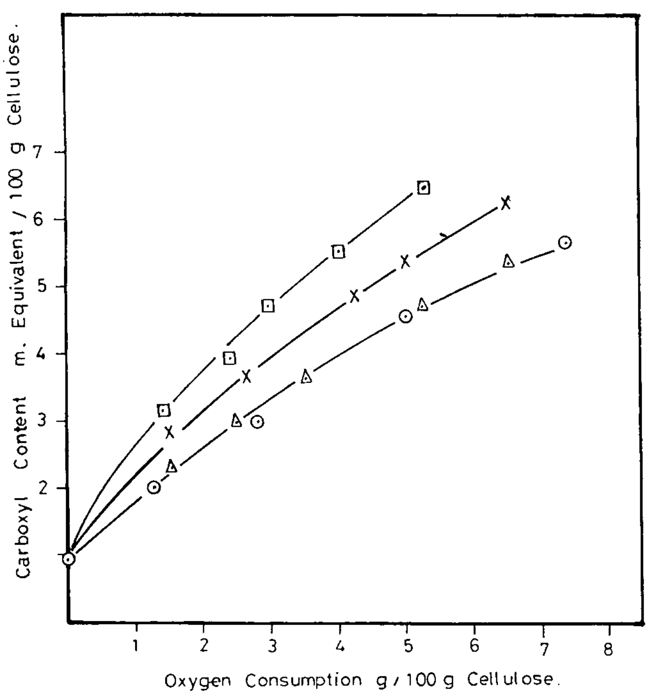

Fig. 10. Carboxyl content vs. oxygen consumption. [Persulphate], 0.18 N; pH, 10; temp = 70°C: (O) nongrafted cellulose; (▲) 6% graft; (X) 28% graft; (⊡) 43% graft.

The presence of the poly(AN) graft in the molecular structure of cellulose seems to protect the cellulosic against chain scission without necessarily preventing oxidation of cellulose hydroxyls. This is particularly seen at higher levels of grafting, where the copolymer acquires a more open structure.

Carboxyl Content

Figures 9 and 10 show the carboxyl content (meq/100 g cellulose) of the poly(AN)—cellulose-graft copolymers and nongrafted cellulose vs. OC. As is evident, the carboxyl content increases in proportion to OC regardless of the substrate used. However, the data imply that the grafted cellulose is more amenable to oxidation than the nongrafted cellulose. Moreover, at the same OC oxidized poly(AN)—cellulose-graft copolymers with higher graft yields show higher carboxyl content than those having lower graft yield. This is in agreement with the results of copper number discussed above.

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