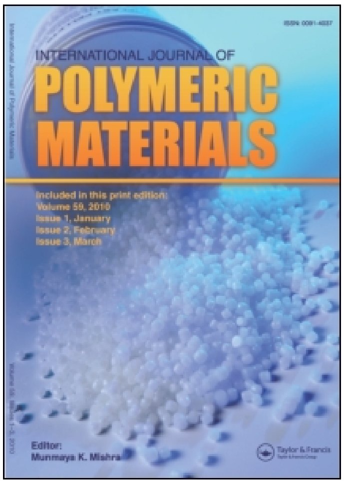

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CHEMICALLY INDUCED GRAFT COPOLYMERIZATION OF ACRYLIC ACID ONTO CELLOPHANE FILMS

Mahmoud M. El Awady, Nagwa I. El-Awady,
and M. S. Mohy El-Din
Polymers and Pigments Department
National Research Centre (NRC)
Dokki, Cairo, Egypt

Grafting of acrylic acid (AA) onto cellophane films was studied using ferrous ion-hydrogen peroxide a redox initiator system. Different variables affecting the grafting yield, graft efficiency and total weight conversion were studied. The swelling properties as well as I.R. spectroscopy analysis of the grafted films were also examined in the hope of developing improved membranes.

Keywords: Copolymerization; Acrylic acid; Grafting cellophane; Films; Redox system

INTRODUCTION

Two types of regenerated cellulose films Cuprophane, (produced by cuprammanium process) and Cellophane (prepared by xanthate process) have been widely used as hemodialysis membranes, owing to their good solute permeability and mechanical strength. However, it is also known that diffusive permeability of solutes of molecular weight ranging from hundreds to thousands is not so good. Various monomers [1–4] were grafted onto cellulosics and the permeabilities of the grafted copolymers toward salts and water were examined in the hope of developing improved membranes. In the present study, we chose a hydrophilic monomer, acrylic acid (AA) to graft onto cellophane films. It is expected that the affinity of membrane for water would increase. Graft copolymerization of (AA) onto cellophane films was studied using ferrous ammonium sulphate (FAS) and hydrogen peroxide (H_2O_2) a redox initiator system. Reaction time and temperature, concentrations of initiator (H_2O_2), ferrous cation and monomer were varied to find optimum conditions under which grafting onto cellophane films would occur most effectively. Swelling properties and analysis by infrared

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Address correspondence to Mahmoud M. El Awady, Polymers and Pigments Department, National Research Centre (NRC), Dokki, Cairo, Egypt.

spectroscopy of the grafted films were investigated. Possible grafting mechanisms are discussed to account for the experimental results obtained.

MATERIALS AND METHODS

A. Materials

Cellophane sheets: were kindly supplied by Misr Rayon Co. Kafr El-Dawar, Egypt, with the following specifications.

Type: uncoated sheets, dimensions 10 × 10 cm and thickness about 20 microns. Cellulose content: 80% regenerated cellulose, additives content: 20% glycerol and Na_2SiO_3.

The cellophane film was used after extraction with hot distilled water to remove the surface additives.

Monomer: Acrylic acid of 99% purity (BDH chemicals).

Initiators: Hydrogen peroxide was a product of prolabo. Ferrous ammonium sulphate was a product of BDH chemicals.

Solvents and other chemicals were analytical grades and were used without further purification.

B. Methods

Grafting Procedure

Graft copolymerization of acrylic acid onto cellophane is performed using hydrogen peroxide – ferrous ion redox initiator system.

The cellophane films were soaked for 20 min at room temperature in (0.01 – 0.1 N) solutions of ferrous ammonium sulphate dissolved in 0.1 N acetic acid, then removed and dried at 40°C. The treated films were graft copolymerized with acrylic acid by introducing about 2 gm. (≈ 7 films) into 100 ml capacity test tubes containing 60 ml of the reaction solution at a prescribed temperature. The reaction solution consisted of water, monomer and H_2O_2 initiator which had been saturated with purified N_2 gas. The tubes were covered, kept in a water thermostate and shaken occasionally during the reaction period which ranged from 1 to 4 hours at a reaction temperature of 30 – 60°C. At the end of reaction period, the films were washed thoroughly by distilled water, dried and weighed. The crude grafted cellophane films were extracted for about 24 hrs with hot distilled water to remove the acrylic acid homopolymer (PAA).

The graft products were characterized by the following parameters.

1. Weight conversion, (WC%)

$$= \frac{\text{Total wt. of vinyl polymer formed}}{\text{wt. of monomer used.}} \times 100$$

2. Grafting percentage (G%)

$$= \frac{\text{wt. of grafted film (after ext.)} - \text{wt. of original film}}{\text{wt. of original film}} \times 100$$

3. Grafting efficiency (GE%)

$$= \frac{\text{wt. of grafted film} - \text{wt. of original film}}{\text{Total wt. of vinyl polymer formed}} \times 100$$

4. Homopolymer percentage (H%).

The Swelling Properties of the Grafted Films

The oven dried grafted and ungrafted films of known weights were immersed in distilled water for 24 hrs at room temperature ($\approx 25-30°\text{C}$).

The films were removed, blotted by filter paper and quickly weighed. The water uptake percent was calculated as follows:

$$\text{Water uptake\%} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 represent the weights of dry and wet films, respectively.

Infrared Spectrophotometric Analysis

Analysis by I.R. spectroscopy of different grafted and ungrafted films was carried out using (JASCO–FT/IR–300E) Fourir Transform Infrared spectrophotometer.

RESULTS AND DISCUSSION

At the outset, it was observed that no grafting reaction occured when unextracted collaphane films were subjected to graft copolymerization using acrylic acid as a monomer and $H_2O_2-Fe^{+2}$ ions as initiator system regardless the conditions of the reaction. Meanwhile a termendous amount of homopolyacrylic acid formation tookplace. On the other hand, grafting was found to proceed successfully when the surface additives of the films were previously removed by soxhlet extraction with hot distilled water for ≈ 48 hours.

Effect of Reaction Atmosphere

The grafting reaction of acrylic acid was carried out under nitrogen atmosphere. The degree of grafting obtained after treatment by nitrogen was compared with that initiated in absence of N_2 *i.e.*, in air, as shown in Table 1. The results indicate that the presence of N_2 enhanced the grafting and there was a marked difference between the degree of grafting

TABLE 1 Effect of reaction atmosphere on the grafting of AA onto cellophane

Monomer	*Grafting* %	
conc. %	*In* N_2	*In air*
5	6	8.8
10	15.5	14.7
15	47.4	19.5
20	91.2	34.3
25	135.0	39.8

$[H_2O_2]$, 0.025%; Time, 4hr; Temp. 60°C; $[Fe^{+2}]$ 0.1 N in acetic acid 0.1N.

obtained after treatment under the two conditions. For example, a maximum graft yield of 135% could be attained in the presence of N_2 atmosphere, while a graft yield of only about 40% was obtained in absence of N_2. The presence of N_2 in such a system would be expected to reduce to a large extent the decay of free radicals and simultaneously enhances the grafting process.

Effect of Monomer Concentration

The effect of the monomer concentration on the grafting parameters is illustrated in Figure 1. The results show a continuous increase in the grafting yield (G%) as a function of monomer concentration. It reached a maximum value of $\simeq 135\%$ at monomer concentration of 25%. The same trend was found to be true for total weight conversion percentage (WC%). As it is also shown from the figure, the grafting efficiency percentage (GE%) increases with the increase in monomer concentration to reach a maximum value of about 86% at 10% monomer concentration. Thereafter, it decreases gradually at higher concentrations. These results could be attributed to: (1) increasing the monomer concentration facilitates the diffusibility of monomer towards the initiated radical sites on the cellulosic chains, which consequently increase the graft yield on the expense of the amount of homopolymer formed; (2) at later stages of the copolymerization reaction, and at higher monomer concentrations the viscosity of the medium increases due to large amount of homopolymer formation on the expense of the grafting as evidenced by the decrease in GE% at high monomer concentrations.

Effect of Reaction Temperature

Figure 2 shows the effect of polymerization temperature on the grafting of acrylic acid onto cellophane. Upon increasing the reaction temperature from

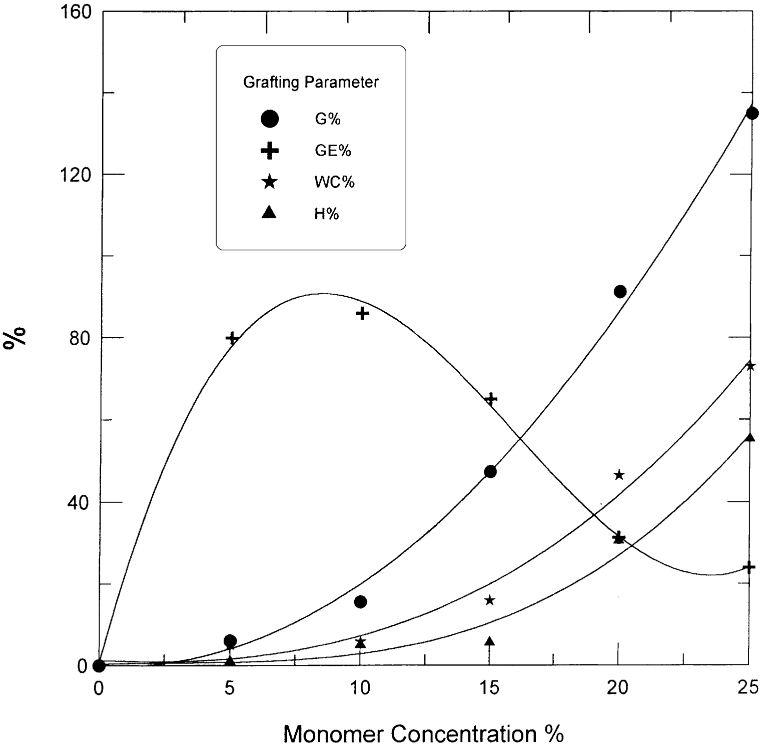


FIGURE 1 Effect of monomer concentration on grafting of acrylic acid onto cellophane films. [H_2O_2], 0.025%; Time, 4 hrs; Temp. 60°C; [Fe^{+2}] 1N.

40–60°C, a substantial increase in the graft yield was observed. The maximum value of 135% was observed at a polymerization temperature of 60°C. The enhancement in grafting of acrylic acid onto cellulosic derivatives upon raising the reaction temperature might be attributed to the favourable effect of temperature on:

(1) Diffusion of acrylic acid from the solution phase to the swellable cellulose phase.
(2) Adsorption of acrylic acid on cellophane films and possible reaction with basic groups of cellulose molecules.
(3) Initiation of free radical sites on the film backbone.
(4) Formation and propagation of grafted chains.

The net effect of all these factors leads to high grafting with the increase of reaction temperature.

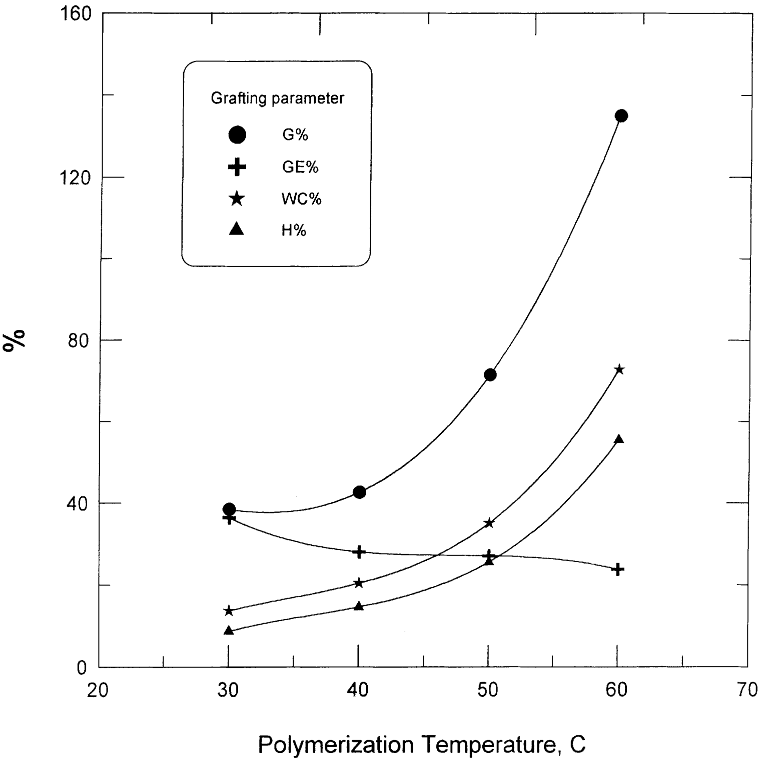


FIGURE 2 Effect of polymerization temperature on grafting of acrylic acid onto cellophane films. [H_2O_2], 0.025%; [AA], 25%; Time, 4 hrs; [Fe^{+2}] 0.1N.

Effect of Reaction Time

The effect of the copolymerization time on the grafting parameters (G%, WC%, GE%) is illustrated in Figure 3. The results reveal that a graft time of two hours was sufficient to raise the grafting yield to a value near 110%. However, increasing the reaction time from two hours to four hours affects to a lesser extent the graft yield ($\approx$110% after 2 hours as compared with 135% after 4 hours grafting). The same trend was found to be true for the weight conversion (WC%). On the other hand, the GE% was found to increase up to the first hour of polymerization and then levelled off after two hours. In comparison Mc Dowall *et al.* [5] showed that the grafting of polyacrylic acid increased initially and then levelled off after six hours, they ascribed the levelling off to the exhaustion of ceric ion catalyst.

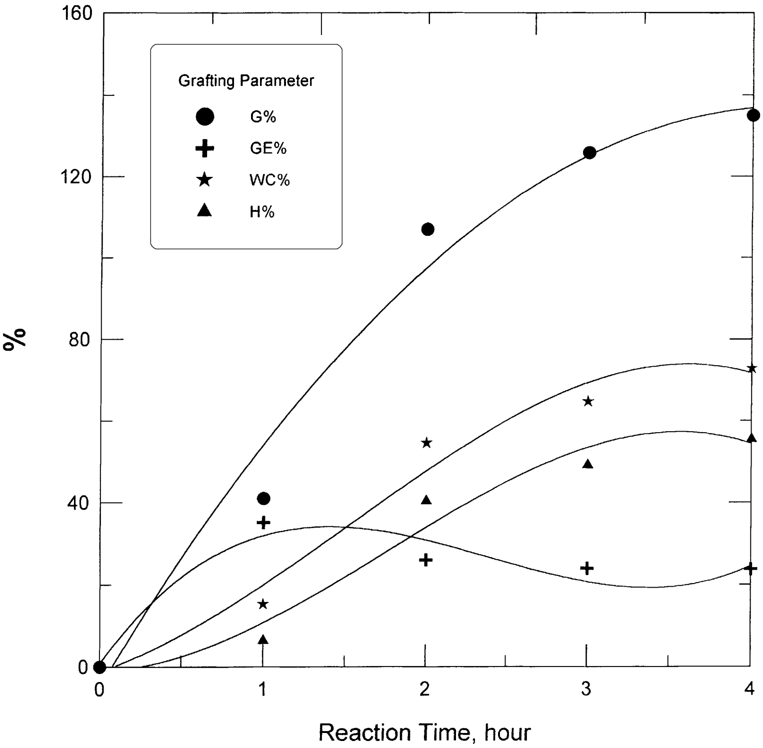


FIGURE 3 Effect of reaction time on grafting of acrylic acid onto cellophane films. [H_2O_2], 0.025%; [AA], 25%; Temp. 60°C; [Fe^{+2}] 0.1N.

Effect of Initiator System (H_2O_2 and Fe^{+2})

Dependence of Grafting on [H_2O_2]

Figure 4 illustrates how the grafting of (AA) onto cellophane film containing fixed amount of Fe^{+2} ion was affected by initiator (H_2O_2) concentration. The results reveal that as the initiator concentration is increased, the grafting percentage and weight conversion increase steadily reaching maximum values of 135% and 90%, respectively, at initiator concentration of 0.025%, then both values fall upon with further initiator increase up to 0.03%. On the other hand, the grafting efficiency (GE%) increases sharply at very low H_2O_2 concentration and attains a maximum value of 75% at a lowest initiator concentration used (0.003%), then gradually decreased with further increase of initiator concentration to reach a minimum value of 15% at 0.03% H_2O_2 concentration.

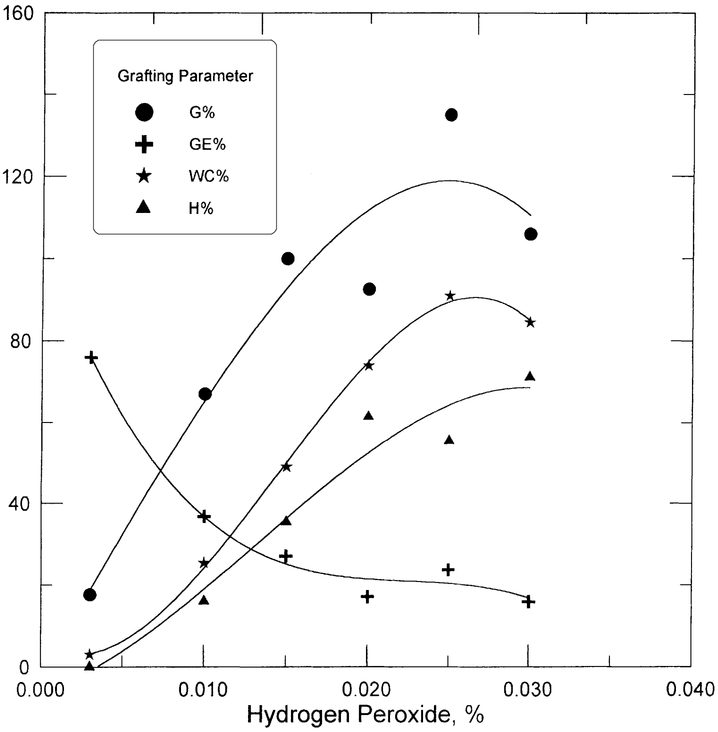


FIGURE 4 Effect of initiator [H_2O_2] on grafting of acrylic acid onto cellophane films. [AA], 25%; Time, 4 hrs; Temp. 60°C; [Fe^{+2}] 0.1N.

The decrease in grafting parameters (G% and GE%) at high initiator concentration may be due to termination with primary radicals of either cellulose macroradicals or growing grafted chains or both.

Dependence of Grafting on [Fe^{+2}] Cation

It was confirmed [6] that ferrous ion adsorbed firmly on cellulose and was hardly eluted into aqueous solution in contact with H_2O_2 aqueous solution.

Dependence of the grafting parameters (G%, GE%, WC%) on the amount of (Fe^{+2}) cation adsorbed on cellophane films were shown in Figure 5. The results indicated that the adsorption of Fe^{+2} ion on cellophane films played a significant role in initiating the grafting reaction. For example a graft yield of about 80% could be attained with the films of lowest ferrous ion concentration and as the cation concentration increases the graft yield increases. This is in agreement with the results obtained by Ogiwara *et al.* [7–8] who previously studied the initiation mechanism of

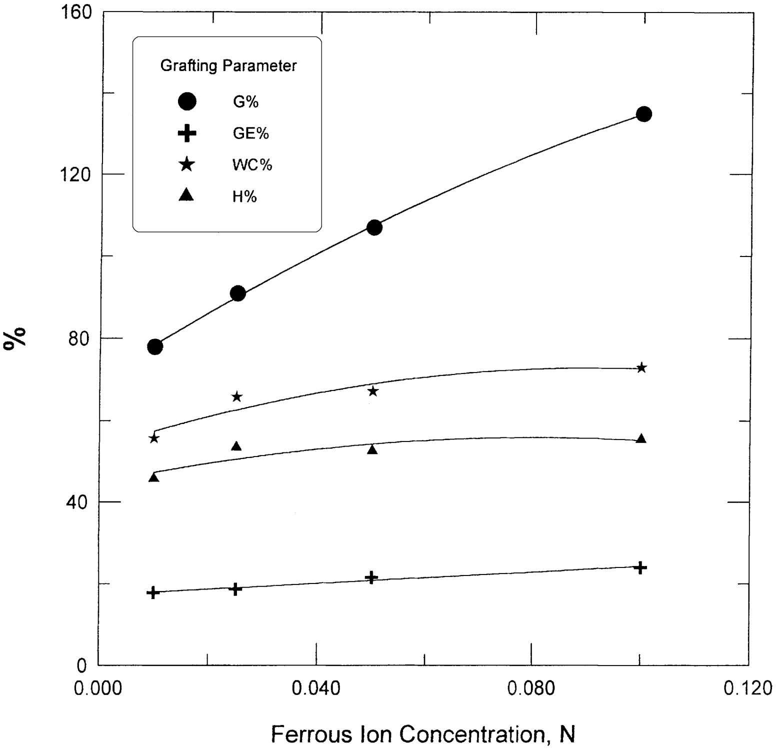


FIGURE 5 Effect of cation [Fe^{+2}] on grafting of acrylic acid onto cellophane films. [H_2O_2], 0.025%; [AA], 25%; Time, 4 hrs; Temp. 60°C.

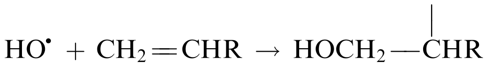
ferric and ferrous ions-hydrogen peroxide system in graft copolymerization of MMA onto cellulose. They observed a good linear relation between the amount of hydrogen peroxide decomposed in the initial stage of the reaction and the amount of ferrous ion adsorbed on cellulose. They also reported that although the ability of cellulose itself to decompose hydrogen peroxide was extremely small, cellulose samples on which ferric or ferrous ion was adsorbed obviously accelerated the decomposition of hydrogen peroxide, and it was observed that, the amount decomposed at the initial stage with higher rate, increased as the amount of ferrous ion adsorped became larger and the initial concentration of hydrogen peroxide became higher.

The Mechanism of Reaction

It is well known that the graft copolymerization of vinyl monomers on cellulosic materials is initiated by many kinds of oxidizing agents. When hydrogen peroxide is used as an oxidizing agent, ferrous ion is generally used with it, in order to form a redox system and to produce hydroxyl radicals easily [9] as follows:

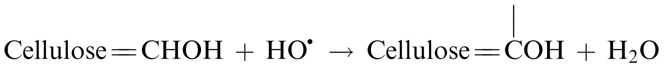
$$H_2O_2 + Fe^{+2} \rightarrow HO^{\bullet} + HO^{-} + Fe^{+3}$$
$$HO^{\bullet} + Fe^{+3} \rightarrow HO^{-} + Fe^{+2}$$

The predominant mode of initiation of homopolymerization of vinyl monomer has elucidated by Baxendale, Evan and Park [10] as follows:

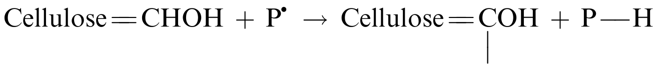


$$HO^{\bullet} + CH_2{=}CHR \rightarrow HOCH_2{-}\overset{|}{C}HR$$

The most probable mechanism of initiation of graft polymerization is the abstraction of hydrogen from cellulose [11] either by hydroxyl radical (OH$^{\bullet}$) or by a polyvinyl radical (P$^{\bullet}$)

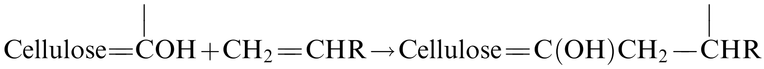


$$\text{Cellulose}{=}CHOH + HO^{\bullet} \rightarrow \text{Cellulose}{=}\overset{|}{C}OH + H_2O \quad \text{I}$$



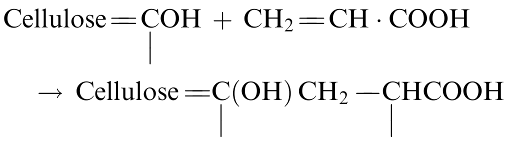
$$\text{Cellulose}{=}CHOH + P^{\bullet} \rightarrow \text{Cellulose}{=}\underset{|}{C}OH + P{-}H \quad \text{II}$$

Many investigators suggested that the reaction II does not play an important part in the grafting process. The most likely mechanism of graft polymerization is, therefore, reaction I followed by



$$\text{Cellulose}{=}\overset{|}{C}OH + CH_2{=}CHR \rightarrow \text{Cellulose}{=}C(OH)CH_2{-}\overset{|}{C}HR$$

Thus in the presence of acrylic acid the reaction may be as follows:



$$\text{Cellulose}{=}\underset{|}{C}OH + CH_2{=}CH \cdot COOH$$
$$\rightarrow \text{Cellulose}{=}\underset{|}{C}(OH)\,CH_2{-}\underset{|}{C}HCOOH$$

Properties of Cellophane-g-poly(acrylic acid) Copolymers

Swelling Properties

It is very important for the practical application of the cellophane grafted films as an ion exchange membrane or ultrafiltration one that the grafted films must exhibit a suitable hydrophilicity. By introducing hydrophilic groups into the cellophane films by grafting monomers such as acrylic acid, the graft copolymer will exhibit excellent hydrophilic properties and easily swell in water.

The effect of the grafting degree on swelling and surface dimensional change of cellophane film is shown in Figures 6 and 7, respectively.

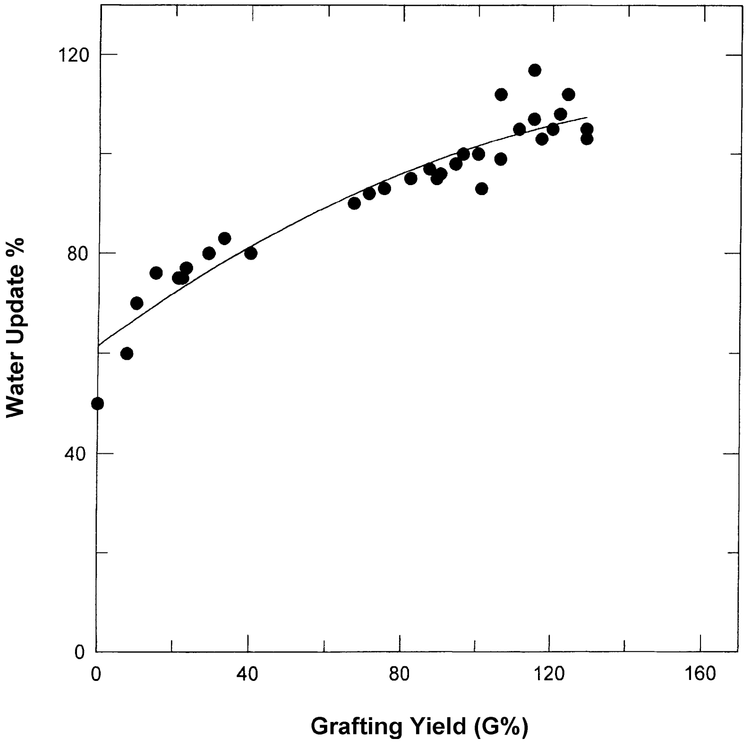


FIGURE 6 Water uptake in cellophane/PAA grafts.

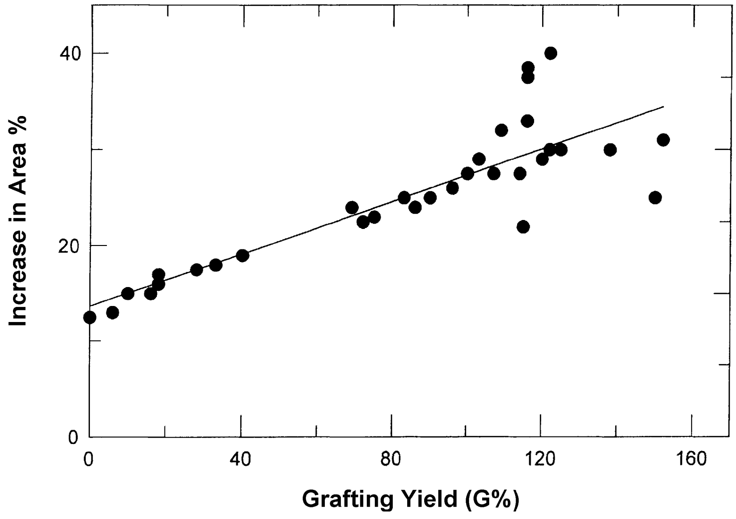


FIGURE 7 Surface area change of cellophane/PAA grafts on swelling.

The data clearly indicate that the percentages of water uptake and the change in surface area of the cellophane films are increased as the extent of grafting increases. It can be seen from Figure 6 that at zero graft level (control), the water uptake was about 50%, while below 20% grafting level, the water uptake reached 75%. However, above 20% graft level and up to 130% the percentage water uptake increases but gradually. At grafting levels greater than 130%, the water uptake percentages fall and the values become more scattered and they found to be independent on the grafting yields. This phenomenon is most likely to be the result of increasing the molecular weight of grafted polyacrylic acid, which reduces to a large extent the ability of water to diffuse to cellophane film surface and the graft. It has been reported [12] that polyacrylic acid of molecular weight of 5×10^6 is totally insoluble in water, and in powder form shows a hydrophobic behaviour. It is, therefore, possible that water will behave in a similar manner to more elevated levels of grafted polyacrylic acid produced in such experiments. An alternative explanation, is that tightly bounded grafted polyacrylic acid chains impervious to water are formed as a result of the increased hydrogen bonding between neighboring carboxyl groups, or the presence of anhydride linkages formed intermolecularly [13–18].

The results represented in Figure 7 seem to indicate that the behaviour of surface area change of the film on wetting is greatly influenced by the interaction between acrylic acid and the regenerated cellulosic film. An almost linear relationship is observed between the grafted yield percentage and the increase of surface area of the grafted film. As the amount of grafted polymer increases, an apparent increase of surface area of the grafted films is noted.

After drying the films in the oven, we noticed that the grafted films characterized by grafting yield lower than 100%, had relatively smoother surface with no deformation in their dimensions. This means that during the process of copolymerization there was enough space for the branched polymer to fill the free volume that exists in the cellophane film [19]. On the other hand, the films with 100% graft or more, the poly acrylic acid formed may fill more than the free volume which exists in cellophane film, this will, therefore, cause more expantion of the film [19]. This is observed experimentally as curling of the grafted film. As expansion occurs, stress produced in the surface of grafted film may cause fissures to appear. So, as the grafting level increases the fissures and brittleness of the film are found to appear easily especially after drying the wetted films. The scattered results observed in Figure 7 may substantiates the above explanation.

In conclusion, the results suggest that the degree of swelling (water uptake and dimensional change) depends mainly on the degree of grafting and the amount of hydrophilic groups in the film. These results coincide with those obtained for the grafted polyethylene with acrylic acid in previous studies [19].

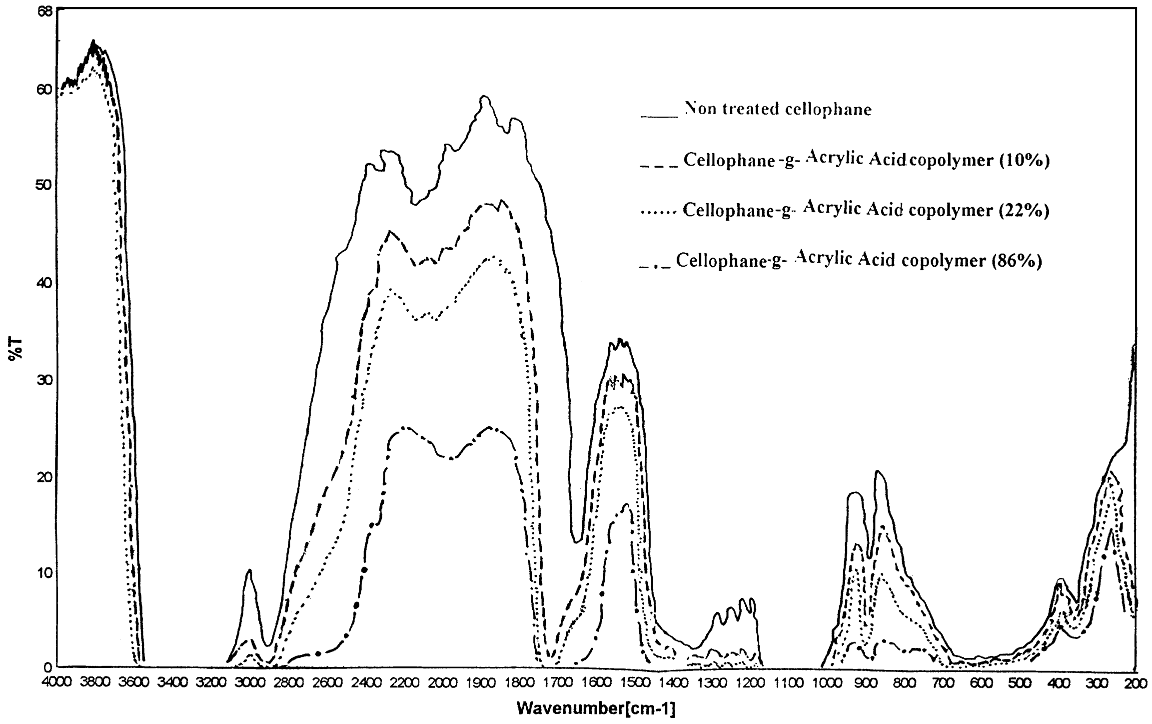


FIGURE 8 I.R. Spectra of cellophane and cellophane-g-acrylic acid copolymers.

Infrared Spectroscopy Analysis

I.R. spectroscopy analysis of grafted and ungrafted cellophane films was made to elucidate the formation of graft chains and the network structure in the grafted films. The spectra of original cellophane film and the cellophane-g-polyacrylic acid films are shown in Figure 8.

Curve A shows the infrared bands of ungrafted cellophane, while curves B, C and D represent the infrared spectra of grafted copolymer films having different degrees of grafting percentage 10%, 22% and 86% respectively. The characterestic bands of cellulose film and polyacrylic acid graft chains appear clearly in the graft copolymer. As can be seen from the figure the peak appeared around $1700\,\mathrm{cm}^{-1}$ confirms the existence of carbonyl groups and increases as the degree of grafting increases, indicating that the attachment of poly(acrylic acid) to cellulose backbone has been taken place.

The figure also shows that the treatment of cellophane film with acrylic acid produced a detectable change in the intensities of all bands of cellulosic film. This means that the treatment causes a great change in the original structure of the cellophane film. This also strongly indicates that grafting of polyacrylic acid onto cellophane film, has taken place not only at the surface but also in the interior of the film. This is highly reasonable because acrylic acid in water is more diffusable into the swellable cellulosic film without any difficulty.

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