

## Corona-Induced Graft Polymerization of Ethyl Acrylate onto Cellulose Film

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### Synopsis

Ethyl acrylate was readily grafted from an aqueous solution onto cellophane film previously treated in a corona discharge at atmospheric pressure. The effect was found when the corona treatment was carried out not only in air but also in pure nitrogen. The observed grafting was not promoted but depressed by the presence of ferrous ion, which indicated that peroxide radicals were not initiating the graft. A high grafting efficiency was obtained, and the grafted surface was covered with a smooth uniform layer of polymer.

### INTRODUCTION

The method of initiating graft copolymer synthesis by electrical discharges has not, so far, been applied widely, and no work has been reported on grafting initiated by a corona discharge at atmospheric pressure. Bamford and Ward<sup>1</sup> have shown that several polymers, when subjected to a high-frequency discharge through hydrogen at reduced pressure (0.1 mm Hg), produce radicals in a surface layer less than 1  $\mu$  thick. Such radicals were used to obtain grafts of vinyl polymers on the surfaces of polyethylene and polypropylene. This technique is of interest because of its simplicity. However, no grafting to cellulose could be achieved by the method in spite of the production of detectable radicals in the cellulose.

In view of the above, the present work was undertaken to investigate the application of the corona treatment to the initiation of graft polymerization of ethyl acrylate onto cellulose films. The corona treatment of cellulose films was carried out not only in air but also in pure nitrogen at atmospheric pressure to assess the effect of peroxide formation on the grafting. The subsequent grafting of ethyl acrylate onto the corona-treated films was performed in an aqueous solution of monomer under various conditions. The effects of corona treatment time and the addition of ferrous ion were examined, and surfaces of the grafted films were characterized by scanning electron microscopy.

### EXPERIMENTAL

#### Materials

A sample (PUT 300/20) of unplasticized and uncoated cellophane 0.023 mm in thickness was kindly donated by British Cellophane Limited. The

film was cut into pieces 9.5 cm × 12.5 cm and, before corona treatment, was equilibrated to constant moisture content by standing over a saturated salt solution in a desiccator. In all experiments a moisture content of 10% was employed.

Ethyl acrylate monomer was purified in the usual manner by successive shaking with saturated sodium bisulfite solution, 5% sodium hydroxide solution, and 20% sodium chloride. It was then distilled under reduced nitrogen pressure (bp 54°C, 157 mm Hg) and stored in a refrigerator before use. As the ferrous ion, pure-grade ferrous ammonium sulfate was used without further purification. Other chemicals were all reagent grade (Fisher ACS Certified).

### Corona Treatment

For corona treatment in air or nitrogen, a flat plate corona discharge cell with a 3-mm gap was used. The film was held midway between the electrodes, which were mounted in a gas reaction vessel with suitable inlets and outlets. The potential applied could be varied between 0 and 15,000 volts. Unless otherwise stated, a potential of 15,000 volts was used.

The nitrogen used was stated to be 99.998% pure. For complete removal of oxygen, the nitrogen was passed through a pyrogallol-alkaline solution, then dried by passing through a silica gel column and then through Dry Ice-acetone traps. The corona cell was evacuated to  $10^{-3}$  mm Hg in a vacuum system and then filled at atmospheric pressure with the purified nitrogen. This was repeated three times before the corona treatment was begun.

### Graft Copolymerization

A reaction vessel equipped with a condenser and gas inlet and outlet tubes was used for the graft copolymerization. After corona treatment, the films were immediately placed in the reaction vessel together with 80 ml deionized pure water and 8 ml ethyl acrylate monomer (EA). In some experiments, a measured amount of ferrous ion solution was added to the monomer solution. The vessel was put into a thermostat bath at 50°C for a given time with nitrogen gas bubbling through the monomer solution during the course of polymerization. After polymerization, the film was washed briefly with methanol to remove the residual monomer and traces of homopolymer on the surface of the film, dried, and weighed. The films were then extracted with acetone for 48 hr followed by methanol for 48 hr in a Soxhlet apparatus to remove completely the homopolymer. The grafted films were then dried under vacuum at 30°C and weighed to determine the extent of grafting.

The degree of grafting was calculated as follows:

degree of grafting (%)

$$= \frac{\text{wt. of grafted film (after extraction)} - \text{wt. of original film}}{\text{wt. of original film}} \times 100 \quad (1)$$

The grafting efficiency, a measure of the efficiency with which the monomer will graft polymerize, was defined by

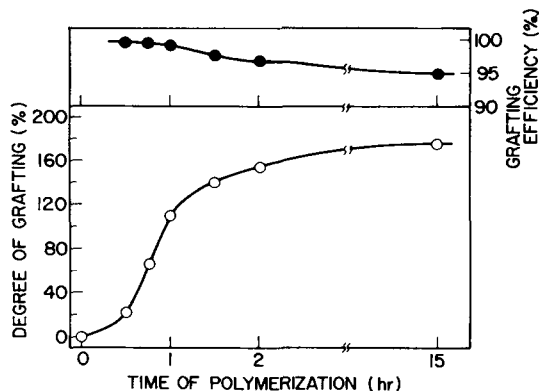


Fig. 1. Changes of degree of grafting and grafting efficiency with time of polymerization in the grafting onto corona-treated cellulose films. Corona treatment: 1 hr.

grafting efficiency (%)

$$\begin{aligned}
 &= \frac{\text{wt. of grafted polymer}}{\text{wt. of (grafted polymer + homopolymer)}} \times 100 \\
 &= \frac{\text{wt. of film after extraction} - \text{wt. of original film}}{\text{wt. of film before extraction} - \text{wt. of original film}} \times 100 \quad (2)
 \end{aligned}$$

After measurement of the dry weight, the grafted films were reswollen by overnight soaking in water, spread over glass plate, and dried at room temperature.

### Microscopy

Scanning electron micrographs of the surfaces of the grafted films were taken, using a Cambridge Steroscan electron microscope. A sample of commercial coated cellophane was also photographed and compared with the grafted films.

## RESULTS AND DISCUSSION

### Effect of Time of Polymerization

As shown in Figure 1, grafting of ethyl acrylate onto the film treated by corona discharge in air occurred readily. However, an induction period of about 20 min was observed which may have been due to the delay in a penetration of the monomer into the film.

### Effect of the Time of Corona Treatment

The degree of grafting depended on the time of the corona treatment in air. This is shown in Figure 2. For the untreated film, no grafting was obtained. The degree of grafting increased with increase in the time of treatment and then remained fairly constant after a treatment time of 20 min.

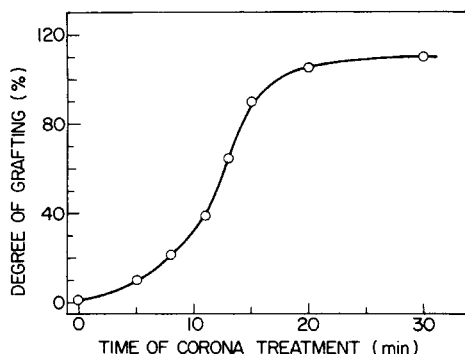


Fig. 2. Effect of time of corona treatment on degree of grafting. Polymerization: 1 hr.

### Formation of Homopolymer

The amounts of the homopolymer produced in the aqueous solution of the monomer were usually undetectable. Homopolymer formation within the cellophane film was also very small. The weight loss of the grafted films after extraction with solvents was always only a few percent of the weight increase of the films.

As evident from the data in the upper curve of Figure 1, a markedly high value in grafting efficiency was obtained. The grafting efficiency eq. (2), usually exceeded 95%. This compares favorably with other methods of grafting to cellulose when fairly extensive formation of the homopolymer usually occurs.<sup>2,3</sup>

### Addition of Ferrous Ion to the Polymerization System

It is well known that, when polymers are subjected to oxidation by an appropriate method such as high-energy radiation in air or treatment with ozone or other oxidizing agents, macromolecular peroxides, capable of an initiating grafting reaction, are sometimes formed.<sup>4,5</sup> Polymeric peroxy species are easily decomposed to radicals with ferrous ion, and this results in an ac-

TABLE I  
Effect of Addition of Ferrous Ion on Grafting of Ethyl Acrylate onto Corona-Treated Films

Experimental conditions	(Fe <sup>2+</sup> ), mole/l.	Degree of grafting, <sup>a</sup> %
Corona treatment in air: 15 kV, 20 min	0	105
	$1.0 \times 10^{-2}$	1.0
	$1.0 \times 10^{-3}$	2.7
	$1.0 \times 10^{-4}$	3.5
	$1.0 \times 10^{-5}$	5.5
Corona treatment in nitrogen: 15 kV, 20 min	0	98.0
	$1.0 \times 10^{-3}$	2.7
	$1.0 \times 10^{-4}$	3.0

<sup>a</sup> Grafting; 50°C, 1 hr.

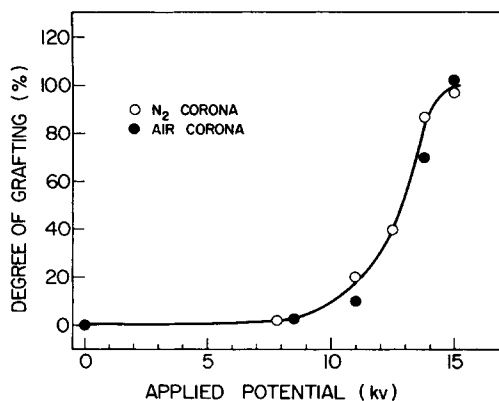


Fig. 3. Changes of degree of grafting with applied potential of corona treatment in air and in nitrogen. Corona treatment: 20 min; polymerization: 1 hr.

celeration of the subsequent grafting of monomer onto the polymeric radicals.<sup>6,7</sup> If the corona-induced grafting observed in the present investigation is due to the formation of such cellulose peroxides by the corona treatment in air, enhanced grafting might be expected when ferrous ion is added to the polymerization system.

Table I shows the influence of ferrous ion on the grafting. The results indicate that the addition of ferrous ion inhibited rather than enhanced the grafting. These results demonstrated that the observed corona-induced grafting is not caused by a radical mechanism initiated by decomposition of cellulose peroxide which may be produced in the corona treatment of films. Furthermore, the determination of peroxide groups in the corona treated films was attempted by iodometry.<sup>8</sup> However, no peroxide was detected for times of treatment of up to 30 minutes.

### Effect of the Corona Discharge in Nitrogen

The degrees of grafting obtained after treatment by a nitrogen corona was compared with that initiated by air corona treatment in Figure 3. For a range of applied potential, there was no marked difference between the degree of grafting obtained after treatment in the two gases. Since it is unlikely that peroxide groups were formed in the cellulose film treated in purified nitrogen, the data in Figure 4 are further evidence that formation of cellulose peroxides cannot be the cause of the grafting onto the cellulose films. In addition, it was observed that nitrogen corona-induced grafting, like air corona-induced grafting, was markedly inhibited by the presence of ferrous ion as shown in Table I (series B).

### Surface Morphology of Grafted Film

Grafted cellulose films were examined in the scanning electron microscope to detect any changes in the surface morphology. As shown in Figure 4, the surfaces of the grafted films were smoother than that of the original film at moderate degrees of grafting (21.6% and 52.5%). For the higher degree of

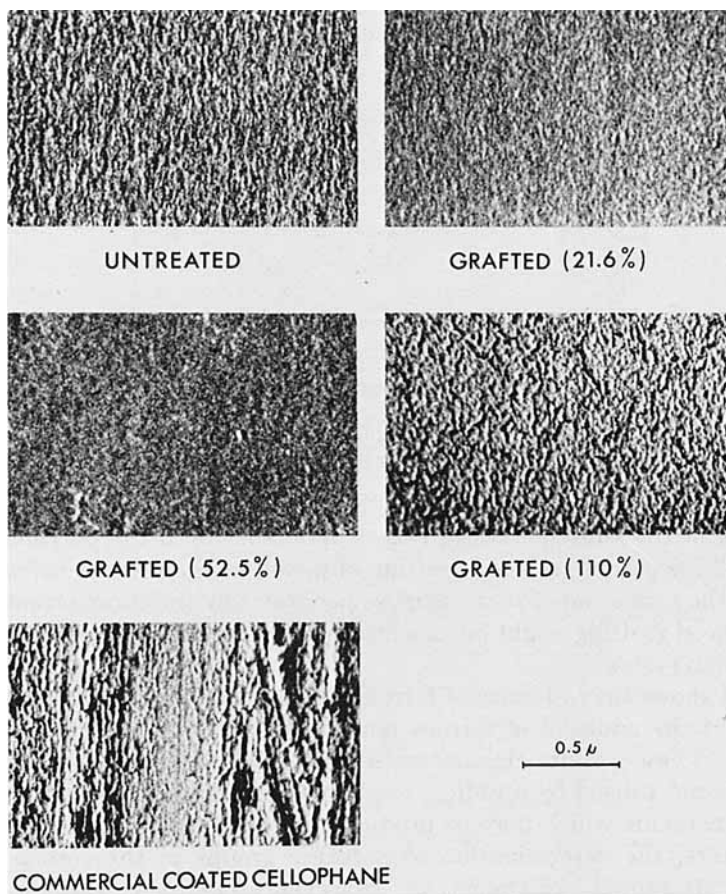


Fig. 4. Scanning electron micrographs of the surfaces of cellulose films before and after grafting and of commercial coated cellophane. (The figures in parentheses refer to the degree of grafting.)

grafting (110%), fine cracks were observed which were probably caused during drying of the film. However, all the grafted surfaces were much smoother than that of a commercial coated cellophane.

### CONCLUSIONS

The results show clearly that it is possible to initiate graft polymerization of ethyl acrylate on cellophane by pretreatment of the cellophane in a corona discharge. The grafting efficiency is rather high, and electron micrographs show that the surfaces are smoothly coated with polymer.

Not much can be said on the mechanism of the grafting. The increase in the adhesive properties of polyethylene films treated in the corona discharge has been associated with the possibility of electret formation in the polymer film.<sup>9</sup> However, in the present work it is difficult to see how electrets can survive in a polar matrix such as water-swollen cellophane. Perhaps the discharge produces some other type of active ionic site on the cellophane which then induces the monomer to polymerize. It is interesting to note that Wil-

liams, Verma, and Stannett<sup>10</sup> have observed "spontaneous" grafting of ethyl acrylate onto water-swollen rayon after a long induction period. The authors suggest that such grafting is initiated by radicals formed initially by bond breaking arising from the strong swelling forces with water. Grafting in the present system may be produced in an analogous manner by the corona-induced rupture of covalent links in the cellulose. Whatever the mechanism, it seems certain that the graft is not induced by the peroxy radical route. The inhibiting effect of ferrous ion, the absence of peroxide groups, and the similarity of the effects of the treatment in air and pure nitrogen all indicate that peroxide-induced polymerization is not the mechanism.

With respect to the possible commercial application of corona-induced grafting onto cellulose, both the time of treatment and the time of polymerization is far too long under the conditions studied in the present work. Treatment times might be speeded up by using more powerful discharges at higher frequencies.<sup>11</sup> The polymerization could be accelerated by working at a higher temperature. Further experiments along such lines could indicate the industrial potential of the method.

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