# Graft Copolymerization of Acrylonitrile onto Hemicellulose Using Ceric Ammonium Nitrate

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## Synopsis

The ability of ceric ammonium nitrate to induce graft copolymerization of acrylonitrile onto hemicellulose was investigated. The graft yield depends on monomer and initiator concentrations as well as reaction time and temperature. Chemical analysis of the reaction product of hemicellulose and acrylonitrile in the presence of ceric ammonium nitrate revealed that the ceric ammonium nitrate acted as initiator for polymerization of acrylonitrile and as oxidizing agent for hemicellulose. Proof for grafting of hemicellulose was provided through IR analysis.

## INTRODUCTION

The term hemicellulose refers to mixtures of low molecular weight polysaccharides which are closely associated in plant tissues with cellulose. Different methods have been developed for the isolation of hemicellulose from plant materials.[1,2] The hemicelluloses in their natural state are generally considered to be noncrystalline. This is due to the heterogenity of their chemical constituents, the presence of short side grouping, and in some cases branching. As the hemicelluloses are structurally related to cellulose, their reactions are very similar. The hemicelluloses form addition compounds at their hydroxyl groups, which also can be substituted to ester and ether groups.[3] Ohtani and co-workers[4] studied carboxymethylation of hydrolyzed hemicellulose and starch, which are useful as builders for detergents. Others[5] studied the crosslinking, cyanoethylation, and hydrolysis of cellulose, starch, and hemicellulose to give products with different ion exchange capacities. Various studies were done for using the hemicellulose and oxidized hemicellulose as a binder in paper making.[6,7]

No work, so far, has been yet published on the graft copolymerization of vinyl monomers onto hemicellulose; in spite of the intensive investigations that had been done for various cellulosic materials and starch.[8,9]

This work presents the results of studies of graft copolymerization of acrylonitrile onto hemicellulose isolated from bagasse using ceric ammonium nitrate as initiator for grafting.

## EXPERIMENTAL

### Materials

#### *Hemicellulose Preparation*

Egyptian bagasse (depithed) was finely ground to 40–60 mesh and extracted with ethanol–benzene 1:1 for 6 h. The holocellulose was prepared using the acetic acid–sodium chloride treatment.[1] The hemicellulose was

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then obtained from the holocellulose by extraction with 10% sodium hydroxide for 20 h at room temperature and liquor ratio 1:20. Then it was precepitated by acidification with 50% acetic acid to pH 4.5, followed by adding 3 volumes 95% ethanol. The hemicellulose was separated by decantation and solvent exchanged with 75% ethanol, 95% ethanol and ether, and dried under vacuum over calcium chloride.

*Hydrolysis of Hemicellulose and Analysis of the Resulted Sugars*

The hemicellulose was acid hydrolyzed according to Whistler and Gaillard.[10] It was neutralized with barium hydroxide, filtered and concentrated under reduced pressure, and chromotographed on paper with ethylacetate–pyridine–water (8:2:1 v/v). The sugars were eluted using cold water and quantitatively determined by the phenol–sulfuric acid method.[11]

## Grafting

Acrylonitrile (AN) monomer was freshly distilled before use. Ceric ammonium nitrate (CeAN) BDH reagent grade was used after standardization with ferrous sulfate.[12] The polymerization reaction was carried out as follows. To 30 mL acidified (1% nitric acid) CeAN, kept at the desired temperature, then 1 g of acrylonitrile was added followed by 1 g hemicellulose powder, and the flask was well shaken. At the end of the desired time, the samples were washed well, giving a slight souping, to remove the loosely adhering polymer, washed with distilled water, and dried. The grafting yield % was determined from the values of the nitrogen content[13] of the grafted samples. It was observed that the grafted samples were extracted with dimethylformamide; it shows that there is no homopolymer.

## Carboxyl Content

The carboxyl content (meq COOH/100 g hemicellulose) was determined iodimetrically.[14] Infrared spectra was determined on potassium bromide discs with a fully automatic UR-10 spectrophotometer.[15]

# RESULTS AND DISCUSSION

The hemicellulose isolated from bagasse was found to have the following analysis: 73.4% pentosan, 0.0% ash, and 3.3 meq carboxyl content. The sugar constituents of the hemicellulose were 58.5% xylose, 25.5% arabinose, 12% glucose, and 4.0% glactose.

The grafting of hemicellulose with AN using ceric ammonium nitrate (CeAN) as initiator were studied. Variables studied were monomer, initiator concentration, and reaction time as well as temperature.

## Initiator Concentration

The effect of CeAN concentration on grafting of AN onto hemicellulose is shown in Figure 1. The graft yield increases as the CeAN concentration increases. Further increase more than 0.1*M* CeAN brings about lower yields. This is in agreement with previous results,[16] where this phenomenon was

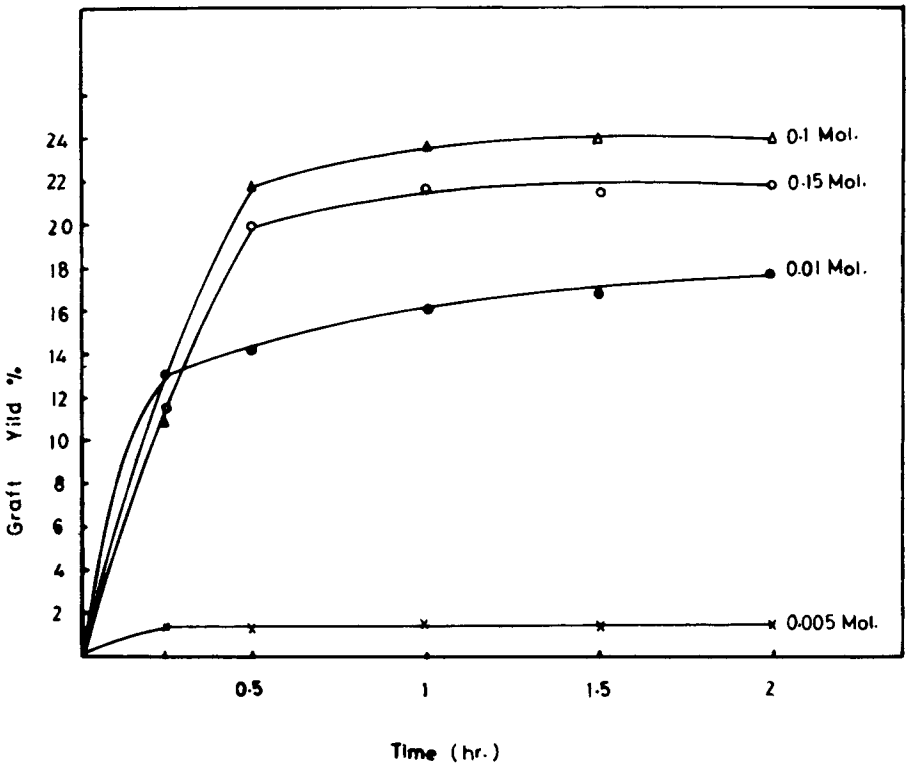


Fig. 1. Effect of CeAN concentration (AN = 1 g/g hemi-, at 40°C).

ascribed to fast termination of the growing polymer chains owing to the presence of excess ceric ion.

Figure 1 clears that the grafting is characterized by an initial fast rate followed by a slower rate, which levels off after a certain time; it depends on the nature of the substrate and the reactivity of the monomer. Leveling off of grafting with time could be attributed to the decrease in concentration for both initiator and monomer, as well as the decrease in the available sites for grafting on hemicellulose molecule. Figure 1 indicates that a re-

TABLE I
Effect of Ceric Ammonium Nitrate Concentration on Grafting

| | 0.005*M* CeAN | | 0.01*M* CeAN | |
|---|---|---|---|---|
| Reaction time (min) | $N_2$ content (%) | $CO_2H$ (meq/100 g hemicellulose) | $N_2$ content (%) | $CO_2H$ (meq/100 g hemicellulose) |
| 0 | 0.0 | 3.3 | 0 | 3.3 |
| 15 | 0.365 | 11.69 | 3.064 | 6.43 |
| 30 | 0.343 | 14.14 | 3.285 | 8.19 |
| 60 | 0.370 | 14.5 | 3.664 | 10.55 |
| 90 | 0.376 | 14.87 | 3.804 | 12.05 |
| 120 | 0.383 | 15.023 | 3.967 | 12.1 |

action time of 0.5 h constitutes the optimal duration for grafting of AN onto hemicellulose using CeAN as initiator under the conditions used. Current work reveals that CeAN acts as initiator for polymerization of AN and as oxidizing agent for hemicellulose under the conditions studied, but the rate of oxidation is higher at lower than that at higher Ce(IV) ion concentrations (Table I), suggesting that termination of hemicellulose free radicals occurs most probably via occluded oxygen. The reverse seems to be the case at higher $Ce^{IV}$ concentration where termination occurs via Ce(IV) ions by virtue of their availability at high concentration.

## Monomer Concentration

Figures 2 and 3 show the graft yield vs. acrylonitrile concentration. It can be seen that the graft yield increases by increasing the monomer concentration within the range studied. However, at lower monomer concentration, i.e., 0.5 g grafting continues to increase with increasing reaction

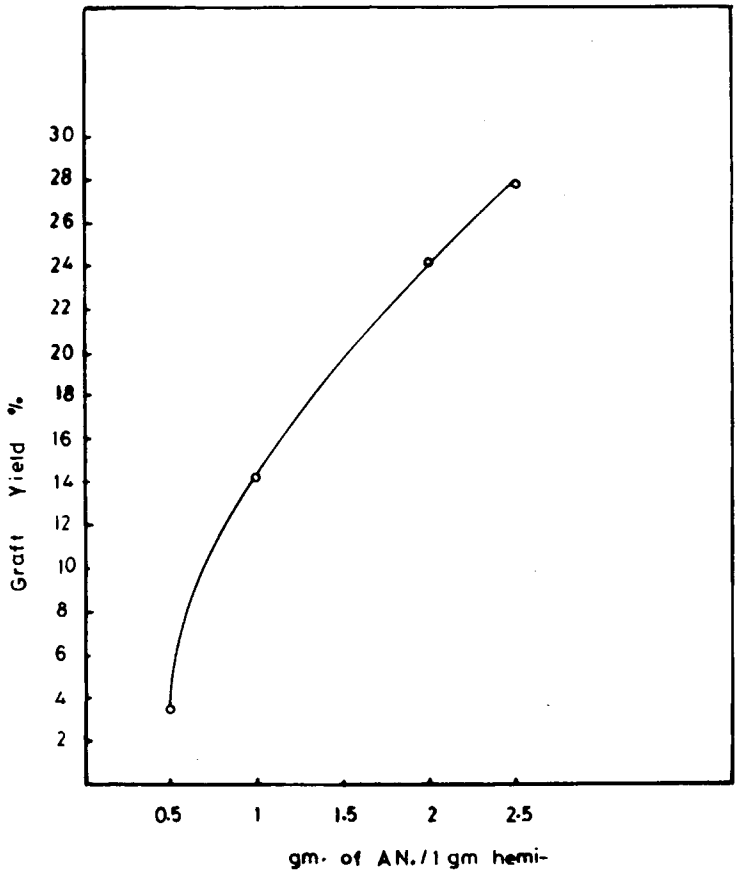


Fig. 2. Effect of AN concentration (CeAN = 0.01 mol, at 40°C, for 0.5 h).

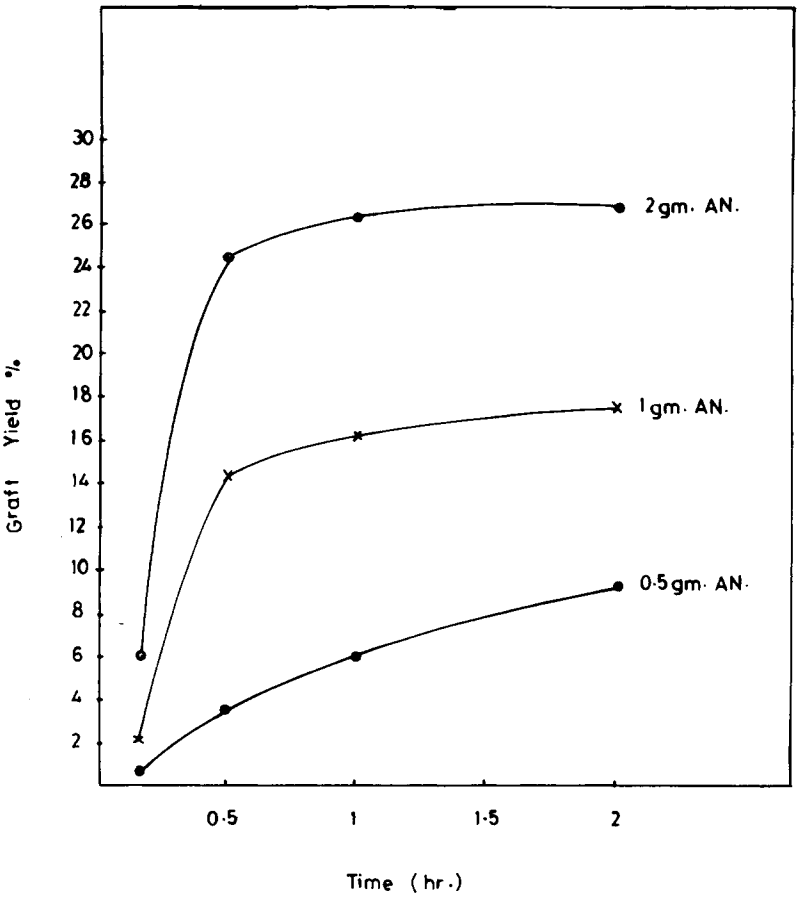


Fig. 3. Effect of AN concentration (CeAN = 0.01 mol, at 40°C).

time up to 2 h. On the other hand, with higher monomer concentration, 1 g AN, 2 g AN, though the grafting proceeds at a rate which is higher than those of lower monomer concentration, yet the rate of grafting does slow down and then levels off to give a maximum yield. Leveling off of grafting in this case could be attributed to the substantial amount of polymer grafted onto the hemicellulose which impedes diffusion of Ce(IV) as well as monomers into the hemicellulose for further grafting.[17]

## Reaction Temperature

Figure 4 depicts the effect of temperature on grafting of hemicellulose with acrylonitrile. As is evident, the graft yield decreases by raising the reaction temperature from 20°C to 60°C. At temperature 60°C, the hemicellulose is greatly soluble than at other temperatures. The decrease in the graft yield could be ascribed to the partial solubility of hemicellulose in acidic medium before grafting especially at high temperature.

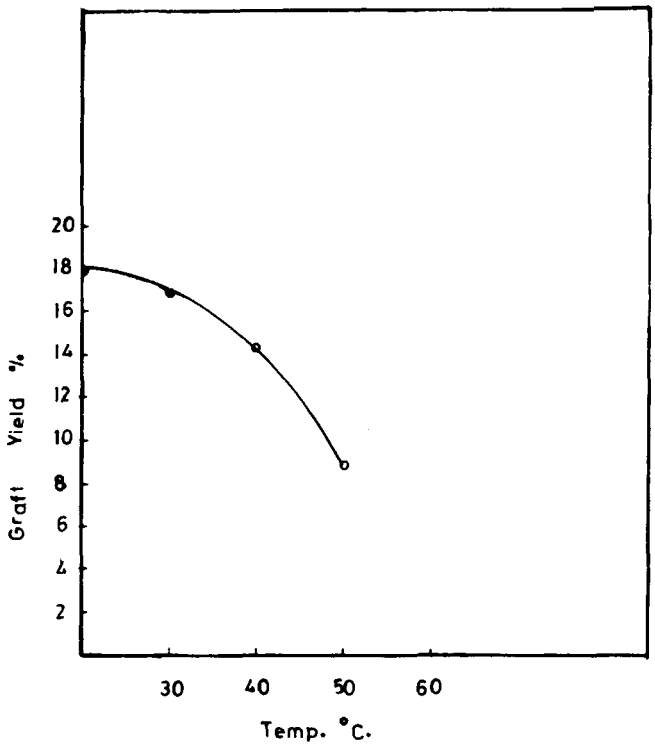


Fig. 4. Effect of temperature (AN = 1 g/g hemi-, CeAN = 0.01 mol, for 0.5 h).

## Infrared Spectra

Figure 5 illustrates the infrared spectra of ungrafted hemicellulose and hemicellulose-grafted copolymers. A comparison between the spectra of grafted hemicellulose and that of ungrafted hemicellulose reveals the following:

1. In the spectra of grafted hemicellulose (2,4,5,) a new band appeared at 2225 $cm^{-1}$ which corresponds to —C≡N groups of AN of grafted hemicellulose.
2. The disappearance of the band at 2225 $cm^{-1}$ (—C≡N group) in the grafted hemicellulose (sample 3) indicates that the grafting does not complete.
3. The decrease in the intensity of original bands of hemicellulose.
4. Disappearance of the band at 1400 $cm^{-1}$ which corresponds to $—COO^-$ groups in the plane vibration (1).
5. In sample 4 a new medium band appeared at 1455 $cm^{-1}$, which may be due to the conjugated stretching vibration as a result of increasing the cyano group in the sample.
6. The weak band at 1675 $cm^{-1}$, which corresponds to C=O stretching vibration of aldehyde groups in grafted hemicellulose suggests that this group is present but with only very low concentrations. This also constitutes a further proof of grafting.

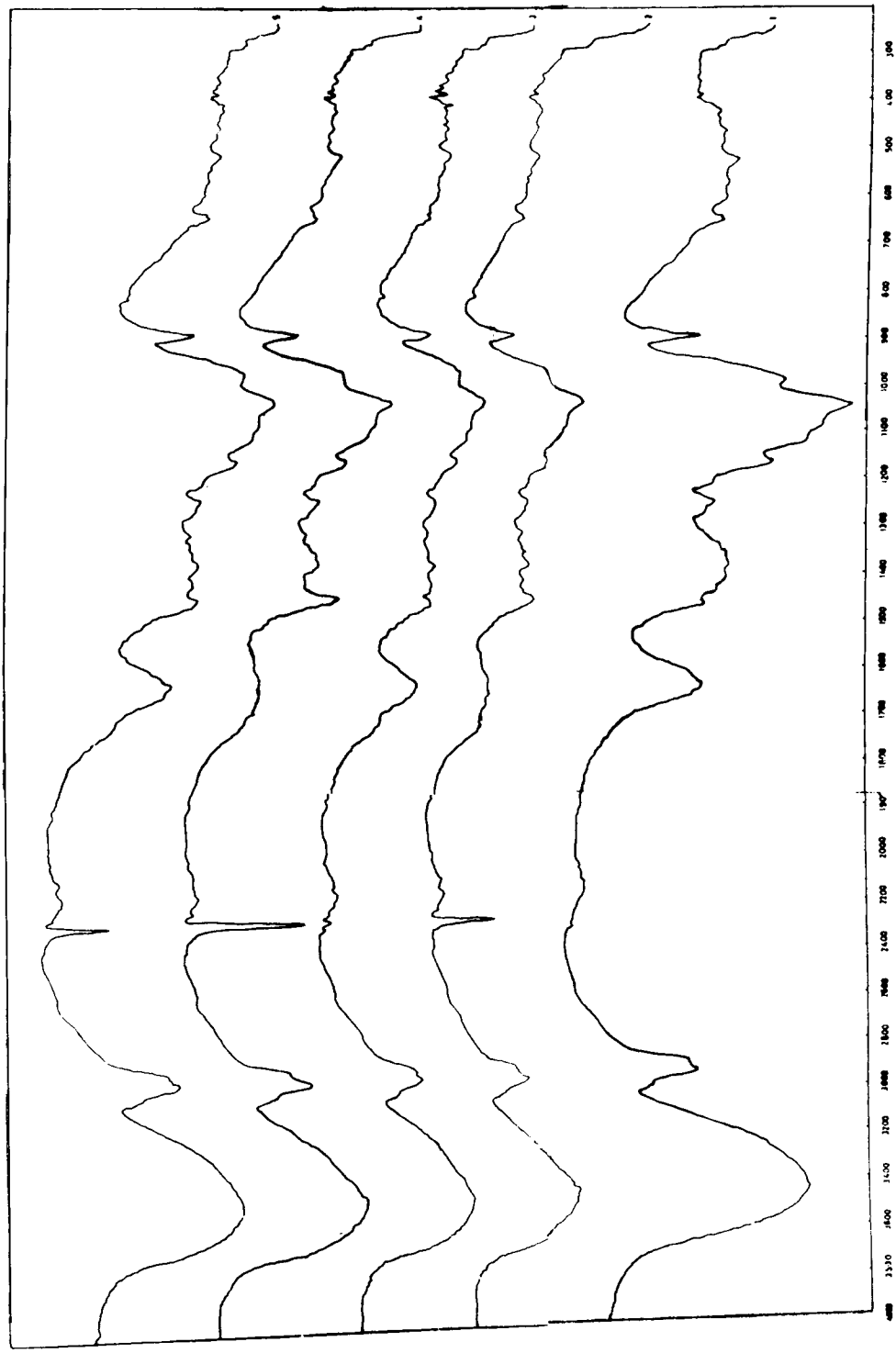

Fig. 5. Infrared spectra of hemicellulose before grafting and after grafting.

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