

Structural Changes on Plasma Irradiation of Ethyl–Cyanethyl Cellulose as Revealed by Infrared Spectroscopic Technique

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SYNOPSIS

Ethyl–cyanethyl cellulose was treated with oxygen plasma using the RF glow discharge technique. Three different plasma-treated samples, including gel fraction, soluble fraction, and newly polymerized product by small moleculars given off by ethyl–cyanethyl cellulose, were obtained. With the infrared spectroscopic technique, the structural differences caused by plasma were studied. The effect of different gas plasma N_2 , Ar, and O_2 on the structure of ethyl–cyanethyl cellulose was also studied.

INTRODUCTION

In the last two decades, plasma irradiation has been widely studied as an effective surface modification method for materials, but the studies relating to changes of chemical groups in polymer materials are rather scarce and are mainly about synthetic polymers.^{1–4} Cellulose and its derivatives are an important kind of nature material. Its property modification by plasma irradiation, including surface adhesiveness, roughness, and dyeability, has been reported in the literature, but there seem to be few published reports about its structural changes.^{5–9}

Recently our laboratory has done some research on ethyl–cyanethyl cellulose (ECC) membrane, and found that the plasma irradiation treatment on ECC membrane could modify its water flow rate and rejection remarkably. It is our interest to know the structural changes that are brought about by plasma irradiation on ECC. In the present investigation, ECC was irradiated with O_2 , N_2 , and Ar plasma. The irradiated products include gel fraction (GECC), soluble fraction (SECC), and newly formed fraction that deposited on the plasma irradiation chamber (DECC). DECC is the polymerized product of small moleculars given off by ECC in plasma. We attempted to study the structural

changes of these three plasma irradiated products with infrared spectroscopic technique, and obtain some information about the ECC reaction mechanism in plasma irradiation.

EXPERIMENTAL

The plasma irradiation chamber was made of glass and is fitted with a gas inlet, pressure gauge, vacuum system, and matching network for capacity coupling of a 13.56 MHz radio frequency source. It is schematically represented in Figure 1. After three evacuations of treatment gas, the irradiation system was kept at a pressure of 0.1 torr. The radio frequency power was turned on at 200 W, and the plasma irradiation was conducted at a definite time (10 min). At the end of irradiation period, the pressure was raised to atmospheric pressure using air. The irradiated ECC was then extracted in a Soxhlet extractor with chloroform for 2 h using a stainless wire basket, and GECC was obtained. The SECC sample was obtained from the above-received chloroform solution by precipitation in hot water (80°C). The deposited sample DECC was received directly from the plasma irradiation chamber. All samples were dried in a vacuum oven for 24 h at 80°C before IR measurement.

The ECC powder sample was obtained by reaction of ethyl cellulose with acrylonitrile in the presence of sodium hydroxide as a catalyst. The general cy-

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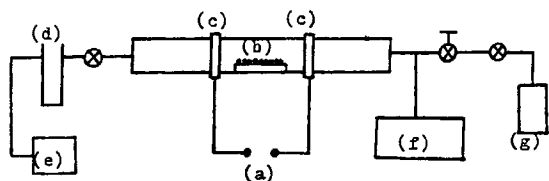


Figure 1 Plasma irradiation system: (a) radio frequency source; (b) ECC samples; (c) electrode; (d) cold trap; (e) vacuum pump; (f) pressure gauge; (g) oxygen chamber.

anethylation procedure and an example were as follows: Ethyl cellulose (substitution degree for ethyl group was 2.1) (30 g) was dissolved in 750 mL acrylonitrile after being stirred. The reaction temperature was adjusted as needed (such as 50°C), and then 90 mL aqueous solution of sodium hydroxide 5% (w/v) was added as the catalyst. The reaction lasted for 3 h, and was stopped at the predetermined reaction time by adding 225 mL aqueous solution of acetic acid 5% (w/v). The reaction mixture was then poured into 1000 mL boiling water. Under the temperature of about 80°C, the unreacted acrylonitrile was removed, and ECC was precipitated in the mixing solution. The obtained ECC was washed thoroughly with water and dried. The ECC samples of different cyanethylation, expressed as the degree of substitution group that was calculated from the nitrogen content measured by the element analysis method, were obtained with a different reaction time. In this study the degree of substitution for the cyanethyl group was about 0.2. The ECC molecular weight (\bar{M}_n) was about 61,000. The chloroform was a chemically pure reagent.

The IR spectra of ECC, SECC, GECC, and DECC were studied by an Analcett RFX-65 FT-IR spectrometer by means of KBr pellets. IR measurements were made three times for each sample in continued months to confirm spectral reproducibility. It was not easy to prepare a homogenous mixture of GECC and DECC with KBr powder, so that there was some difficulty in taking spectra of them.

RESULTS AND DISCUSSION

The infrared spectra of ECC and its plasma irradiated products were recorded over the spectral range 400–4000 cm^{-1} . Figure 2 presents the infrared spectra of ECC and its oxygen-plasma-irradiated products SECC, GECC, and DECC. The assignments of some bands for ECC and GECC IR spectra are listed in Table I. Examination of the spectra of the samples revealed that the most striking difference observed in the spectral curves of oxygen-

plasma-irradiated samples from the ECC spectrum was the appearance of the carbonyl group absorption band. The band intensity order among the oxygen-plasma-irradiated products was DECC > GECC > SECC. The wave number values were also different one another, and were 1716, 1736, and 1709 cm^{-1} for SECC, GECC, and DECC, respectively. Based on the wave number value, the carbonyl groups in GECC were supposed to be mainly in the form of ester, and in DECC mainly in the form of ketone. For the existence of a shoulder peak of 1745 cm^{-1} in the SECC carbonyl absorption band, the form of carbonyl groups in SECC may include ketone, ester, and some others.

It is well known that the cold plasma is generated by gaseous electric discharge, and provides new chemically active species of atoms, ions, and free radicals by collision of high energy electrons with neutral gas moleculars. The underlying process of oxygen plasma irradiation effect exerted on the ECC is likely to be photooxidation proceeding through a peroxide mechanism. The reaction of peroxide gives CO and other carbonyl groups, and the reaction of two radicals leads to crosslinking of ECC with the ester groups as linkage. A large number of small

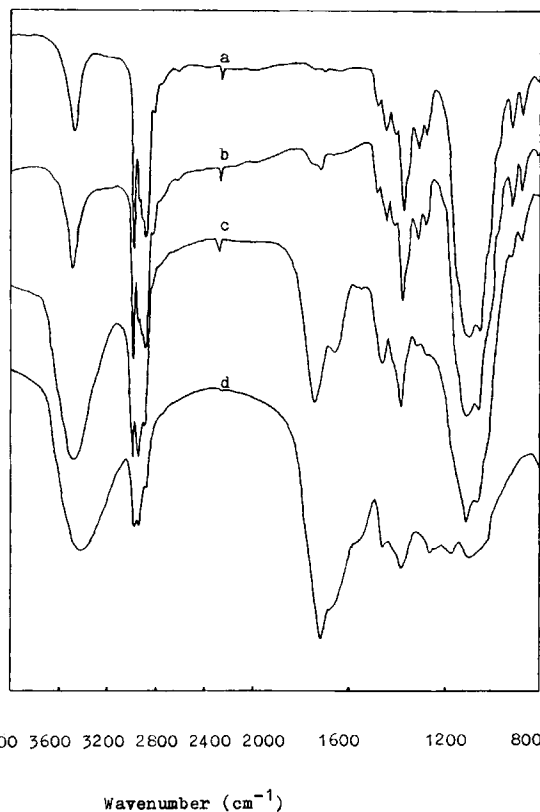


Figure 2 IR spectra of ECC and its oxygen plasma irradiated products: (a) ECC; (b) SECC; (c) GECC; (d) DECC.

Table I IR Spectra Assignments for ECC and GECC^a

ECC		GECC	
Wave Number (cm ⁻¹)	Assignment	Wave Number (cm ⁻¹)	Assignment
3479	ν OH	3464	ν OH + NH
2974	ν_{as} CH ₃	2974	ν_{as} CH ₃
2927	ν_{as} CH ₂	2925	ν_{as} CH ₂
2897	ν_s CH ₃		
2873	ν_s CH ₂	2874	δ_s CH ₂
2343	ν CN	2342	ν CN
1483	δ_{as} CH ₂ (OCH ₂)	1736	ν C=O(ester)
1445	δ_{as} CH ₃	1653	ν C=O(amide)
1406	δ_{as} CH ₂ (CH ₂ CN)	1456	δ_{as} CH ₂
1375	δ_s CH ₃	1381	δ_s CH ₃
1107	ν_{as} COC	1113	ν_{as} COC
1059	ν_{as} COH	1061	ν_{as} COH
920	δ CH ₃	918	δ CH ₃
881	δ CH ₃	879	δ CH ₃

^a ν = stretching mode, δ = deformation mode, s = symmetrical, as = asymmetrical.

molecular compounds, such as methanol, methane, ethane, hydrogen, carbon dioxide, and water, are formed, as the secondary destructive products of D-glucose and oligosaccharides, both of them developed in a primary process of chain scission.

Analysis of the shape and intensity of C-H vi-

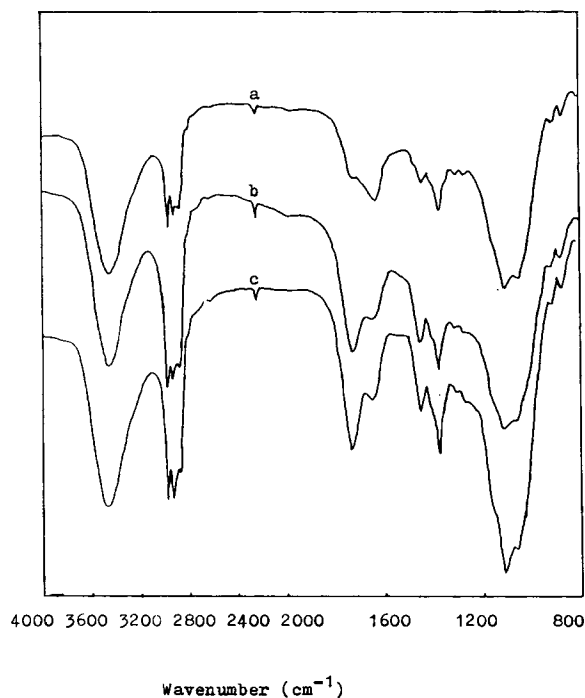


Figure 3 IR spectra of GECC samples that resulted from different gas plasma irradiation: (a) N₂; (b) Ar; (c) O₂.

bration absorption bands in IR spectra of ECC and its oxygen-plasma-treated products revealed the relative intensity of the ν_{as} CH₂ band at about 2930 cm⁻¹ becoming larger for GECC and DECC and the appearance of the δ_{as} CH₂ band at 1456 cm⁻¹ with the disappearance of δ_{as} CH₂ (-OCH₂-) at 1483 cm⁻¹ that indicated the cleavage of the -OCH₂CH₃ group from the ECC molecular chain. The ν_{as} CH₂/ ν_{as} CH₃ band intensity ratio became higher in GECC and DECC than in ECC. That was also reflected by the increase of relative intensity between δ_{as} CH₂ at 1456 and δ_s CH₃ at 1380 cm⁻¹. The further evidence is that the CH₃ deformation absorption bands in 920 and 881 cm⁻¹ become weak. The intensity decrease of CH₃ absorption bands in comparison with CH₂ absorption bands could be attributed to the fact that the -OCH₂CH₃ group is more susceptible to change by oxygen plasma than the -CH₂CH₂CN group. This was also proved by the fact that no distinct changes existed in the CN stretching band among ECC, SECC, and GECC spectra. The very small band of 2340 cm⁻¹ attributed to the CN group for DECC suggested that there were not many CN groups in the gaseous plasma products.

The absorption band in 1653 cm⁻¹ appeared in GECC and DECC. IR spectra were attributed to amide groups. The broadening and wave number decrease of the band at about 3450 cm⁻¹ also suggested it. The amide groups were supposed to result from the N₂ contamination in the vacuum system and treated gas.

Figure 3 is the IR spectra of the GECC samples that come from O₂, N₂, and Ar plasma irradiation.

All spectra of these three samples have a little similarity with one another, especially for the two GECC samples from O₂ and Ar plasma irradiation. In the IR spectrum of GECC (N₂), the carbonyl groups bands were attributed mainly to amide groups. This was very different from GECC (O₂) and GECC (Ar). Comparing the intensity ratio of the ν_{as} CH₂ band with that of the ν_{as} CH₃ band among three GECC samples, the ratio order was found to be GECC(O₂) > GECC(Ar) > GECC(N₂), which indicated that the cleavage of -OCH₂CH₃ groups most easily occurs in O₂ plasma and most difficulty occurs in N₂ plasma. The existence still of a shoulder peak at 1483 cm⁻¹ (-OCH₂-) for GECC (N₂) also suggested it.

From the above IR spectral analyses of ECC and its plasma irradiated products, it can be seen that plasma treatment is an effective method to bring new chemical groups into the structure of ECC. With different treated gas, this technique has a wide adaptability for surface modification. IR spectroscopic technique provides us a very useful means to elucidate the property changes on the chemical structure level.

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