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THE ASSESSMENT OF HOMOGENEOUS GRAFTING OF CELLULOSE NITRATE†

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ABSTRACT

The homogeneous grafting of polymethyl methacrylate onto cellulose nitrate has been assessed by the techniques of spectroscopy and microscopy combined with chemical procedures. FTIR spectroscopic and electron microscopic evidence confirmed the existence of a true graft copolymer. Homogeneous grafting took place in both the surface layer and the interior of the supermolecular structure of cellulose nitrate. X-ray diffraction provided further evidence that the grafting reaction also occurred in certain ordered domains of cellulose substrate. It is suggested that the free radical graft copolymerization for cellulose nitrate could be performed via a mechanism of denitration and enolization rather than dehydrogenation.

INTRODUCTION

The graft copolymerization of synthetic polymer onto cellulose and cellulose derivatives is a useful, interesting, and promising approach for the chemical modification of polymers. This topic has been the subject of sustained study since it was

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first reported in the 1950s, and it continues to arouse great scientific interest in academic and industrial circles [1–6].

In recent years, much more attention has been given to cellulose nitrate since there is ever-increasing use of this cellulose ester as a coating and adhesive material. However, in most of the past research, the interest generated was mainly relating to the characterization, properties and applications of graft copolymers using IR, NMR spectroscopies, and thermal analysis. The search for a deeper understanding of the nature of graft copolymerization is usually conducted by investigating the reaction kinetic parameters [7]. Additionally, a large number of the graft copolymerizations have been carried out on heterogeneous systems. It has been perceived by many scholars and technologists in the cellulose field that grafting occurs in the amorphous regions and not in the crystalline regions of cellulose.

In this paper an attempt is made to assess the homogeneous grafting of polymethyl methacrylate (PMMA) onto cellulose nitrate (CN) by such spectroscopic and microscopic techniques such as Fourier transform infrared spectroscopy (FT-IR), scanning and transmission electron microscopy (SEM, TEM), and x-ray diffraction.

EXPERIMENTAL

Synthesis of Grafted Specimens

The grafting reaction was performed by dissolving the RS ½ grade of cellulose nitrate in methyl isobutyl ketone, using methyl methacrylate (MMA) as the monomer and benzoyl peroxide as the initiator in a nitrogen atmosphere at 70°C for 2–6 hours. The grafted specimen (CN-*graft*-PMMA) was obtained by precipitation with petroleum ether and selective extraction of the homopolymer (free PMMA) with benzene. The true graft copolymer was obtained by the further extraction of ungrafted cellulose nitrate.

The definition of percent grafting is as follows:

$$\%\ \text{grafting} = \frac{\text{wt of (CN-}\textit{graft}\text{-PMMA)} - \text{wt of CN}}{\text{wt of CN}} \times 100$$

FT-IR Absorption Spectroscopic Analysis

The FT-IR spectra of specimens were recorded using KBr pellets in a Analect RFX-65 FT-IR spectrophotometer. The band absorption intensities were measured by the baseline method [8].

X-Ray Diffraction Measurement

The x-ray diffraction diagrams were obtained with a TUR-M62 x-ray diffractometer with K_α radiation.

Electron Microscopy Examination

The specimens for SEM were coated in a vacuum evaporator by a thin layer of gold and examined in a Hitachi S-430 Scanning Electron Microscope. The specimens for TEM were embedded with expoxide resin and cut into ultrathin sections with glass knives, finally observed in a JEM-100CXII.

RESULTS AND DISCUSSION

Proof for the True Graft Copolymer

The purpose of this paper is to demonstrate that PMMA can be grafted onto cellulose as opposed to generating a physical mixture. In earlier work, many techniques were used to compare grafted products and mixtures. Among them, intrinsic viscosity [9], solubility [10, 11], fractional precipitation [12], turbidimetric titration [13], and density-gradient ultracentrifugation [14] are the most commonly used methods. The difference in these parameters for the graft copolymer relative to a mixture of homopolymer having the same composition would be considered as an indication of true grafting.

As shown in Fig. 1, the grafted IR spectrum (CN-*graft*-PMMA) contains both main characteristic absorptions of CN and PMMA, such as:

From original CN: 2920 cm^{-1} (—OH stretching), 2980 cm^{-1} (—CH, —CH$_2$ stretching), 1656, 1282 cm^{-1} (—NO$_2$ stretching), 842 cm^{-1} (—O—NO$_2$ stretching), and 752 and 682 cm^{-1} (—O—NO$_2$ deformations) [15].

The additional absorption bands from PMMA: 1728 cm^{-1} (—C=O stretching), 2953 and 1482 cm^{-1} (α-CH$_3$ stretching and deformation) [16].

Obviously, the appearance of new bands in the spectrum of the grafted specimen can be recognized as a consequence of the introduction of new functional groups from PMMA polymer into cellulose nitrate. The above result, on the other hand, did not answer the question of whether the polymer branches were held in

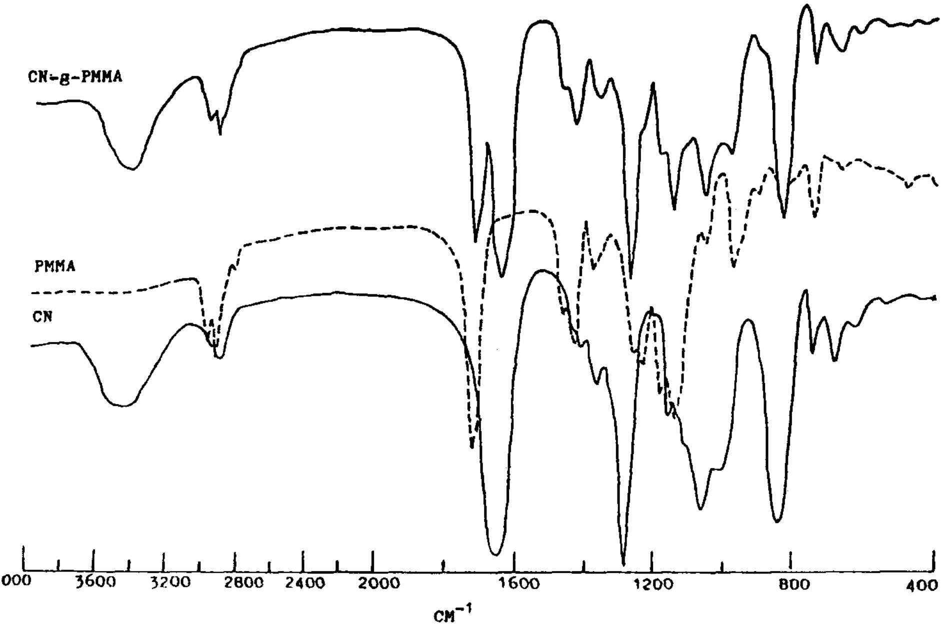


FIG. 1. FTIR spectra of grafted cellulose nitrate (CN-*graft*-PMMA), cellulose nitrate (CN), and monomer polymer (PMMA).

the system by chemical bonds or by a physical entanglement or blend since the IR spectra of the grafted and blended specimens are very much alike. Consequently, to verify actual grafting, FT-IR spectrometry combined with chemical extractions have been employed in this study.

First, by using 72% H_2SO_4 to remove the cellulose nitrate backbone from the polymer branches, FT-IR analysis of the residue showed that the absorptions are exactly the same as those of PMMA. This fact shows that monomer/polymer PMMA was present in the grafted specimen.

Second, both grafted and blended specimens with the same composition were reextracted exhaustively with benzene in order to remove PMMA. FT-IR results show that there are no differences for the grafted specimen before and after extraction, but only CN absorption bands for the blended specimen were observed after extraction.

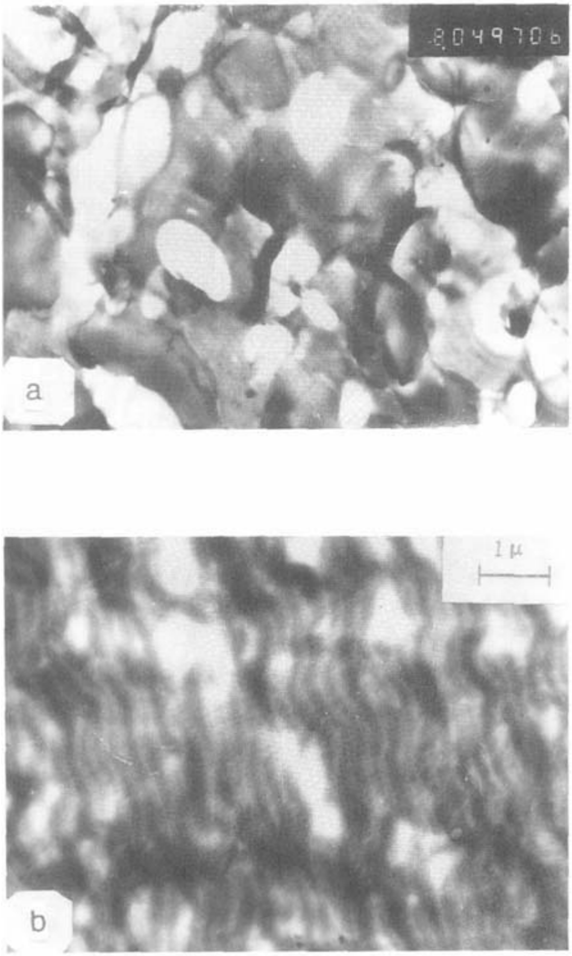


FIG. 2. TEM micrographs. (a) True graft copolymer without homopolymer and ungrafted CN. (b) CN. (c) PMMA. (d) Physical blend of CN and PMMA.

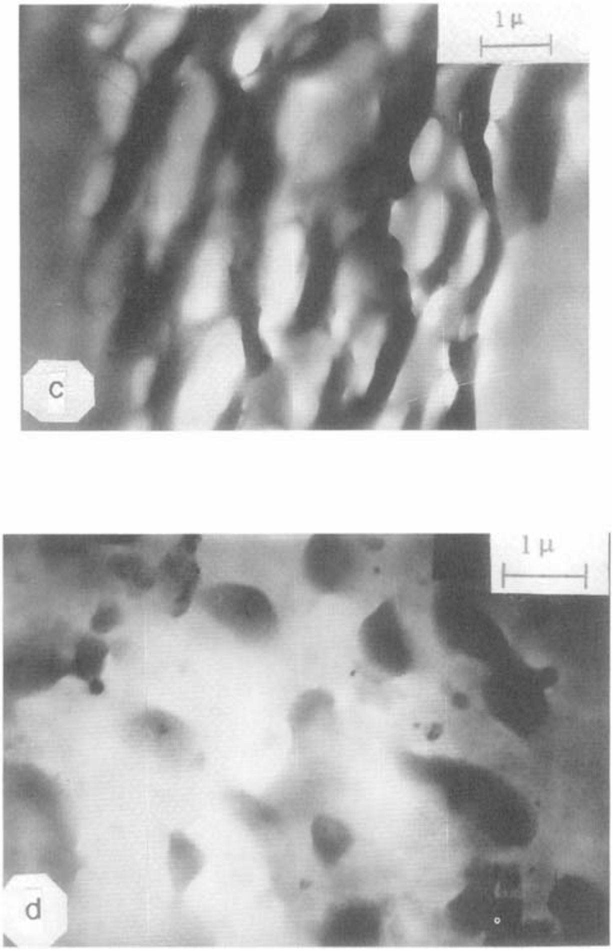


FIG. 2 (continued).

The above results of comparison studies confirmed that CN-*graft*-PMMA is a true graft copolymer, i.e., the polymer branches of PMMS are attached to the cellulose backbone by chemical bonds. Further evidence on true grafting comes from examinations of the morphological change by TEM in Fig. 2. The true graft copolymer (a) exhibits both the morphological character of CN (b), and of PMMA (c) obtained by evaporating extractives of PMMA homopolymer. It also distinguishes it from a physical blend with the identical composition (d).

Location of Grafting Reaction and Distribution of Grafted Polymer

It is well known that heterogeneous grafting occurred principally on the surface of the supermolecular structure of cellulosics and led to changes in its morphological structure [17]. The changes in surface morphology of the grafted CN became

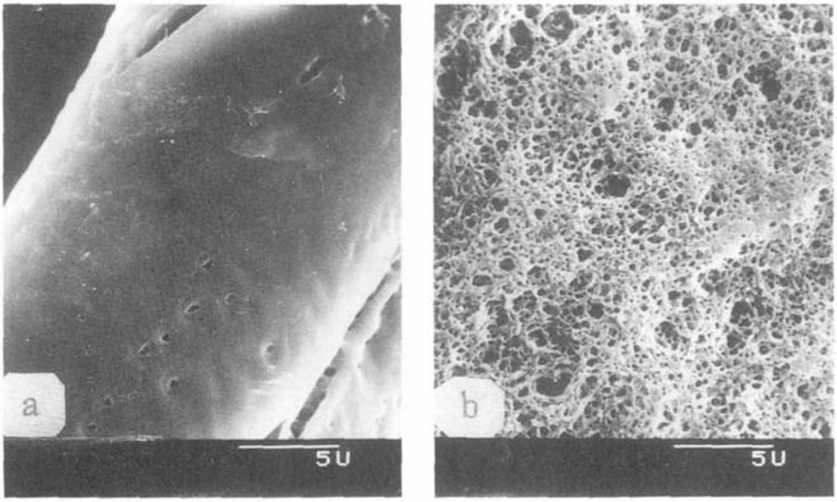


FIG. 3. SEM micrographs. (a) CN. (b) CN grafted with 77% PMMA.

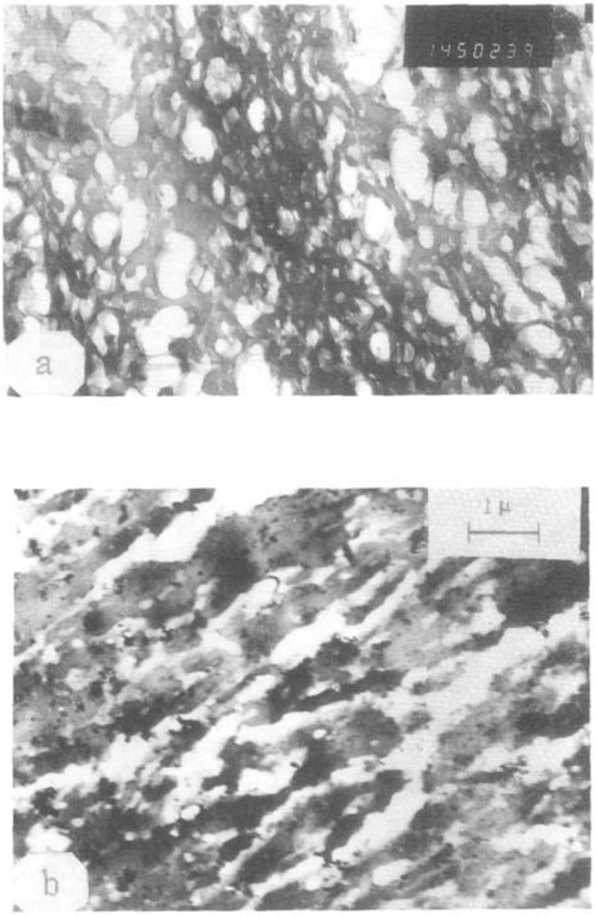
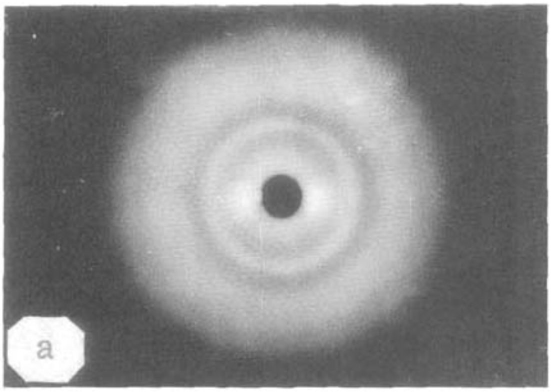


FIG. 4. TEM micrographs. (a) CN grafted with 16% PMMA. (b) CN grafted with 77% PMMA.



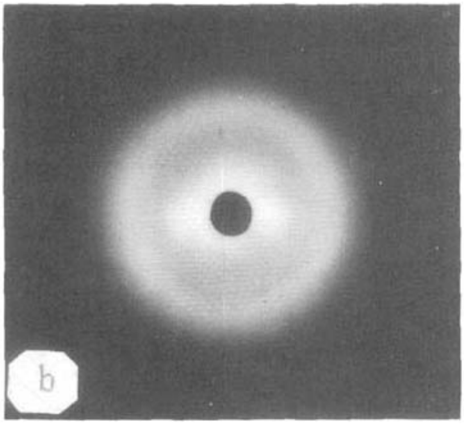


FIG. 5. X-ray diffractograms. (a) CN. (b) CN grafted with 62% PMMA.

evident with homogeneous grafting processes: a smooth surface (Fig. 3a) changed into a finely textured net (Fig. 3b) in the SEM photomicrographs.

The examinations of TEM even clarified that homogeneous grafting has penetrated into the interior of the cellulose microstructure, i.e., the internal morphology changed from a large globular texture (Fig. 4a) to a continuous smoothed ridge texture (Fig. 4b) as the grafting reaction advanced.

It is notable that homogeneous grafting of cellulose nitrate took place in both the surface layer and the interior of the supermolecular structure of cellulose. This is quite different from the result of earlier research in which grafting only occurred on the surface layer of the supermolecular structure of the fiber [18].

As indicated by the electron micrographs, homogeneous grafting is capable of uniformly distributing the grafted polymer over the whole mass of cellulose substrate. X-ray diffraction provided more convincing evidence that the grafting reaction also occurred in the crystalline domains, i.e., some well-defined rings of the cellulose nitrate structure (Fig. 5a) were diffused, shifted, and even disappeared in

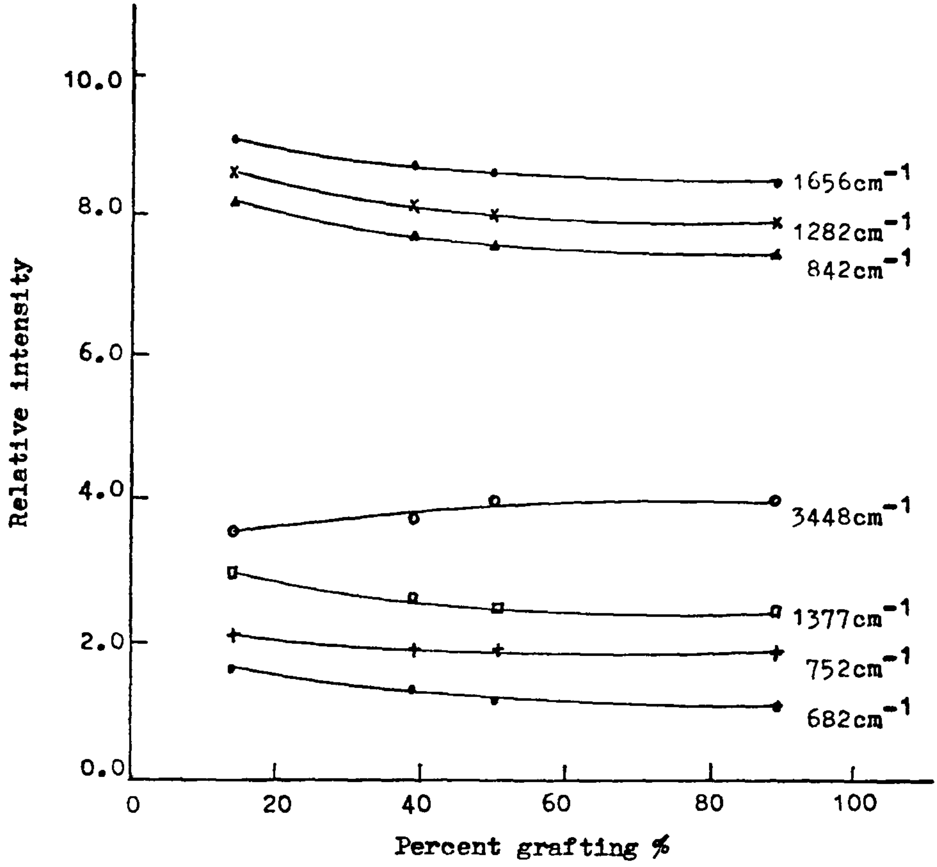


FIG. 6. The variations in intensities of the absorption bands associated with CN.

an x-ray photograph of the grafted specimen (Fig. 5b). These changes suggested an increase in the degree of disorder in cellulose molecules due mainly to the growth of the grafted polymer toward the ordered structure. In other words, homogeneous grafting appears in both the amorphous and the ordered domains of cellulose nitrate.

Possible Mechanism for the Homogeneous Grafting of Cellulose Nitrate

It is widely accepted that the free-radical graft copolymerization of a vinyl monomer onto cellulose possibly involves the cleavage processes: dehydrogenation, dehydroxylation, depolymerization or cleavage of the glucopyranoside ring.

FT-IR quantitative analysis in the present study provided substantial evidence for the possible mechanism of homogeneous grafting of cellulose nitrate via the processes of denitration and enolization. The evidence in favor of such a reaction mechanism is presented by the following facts:

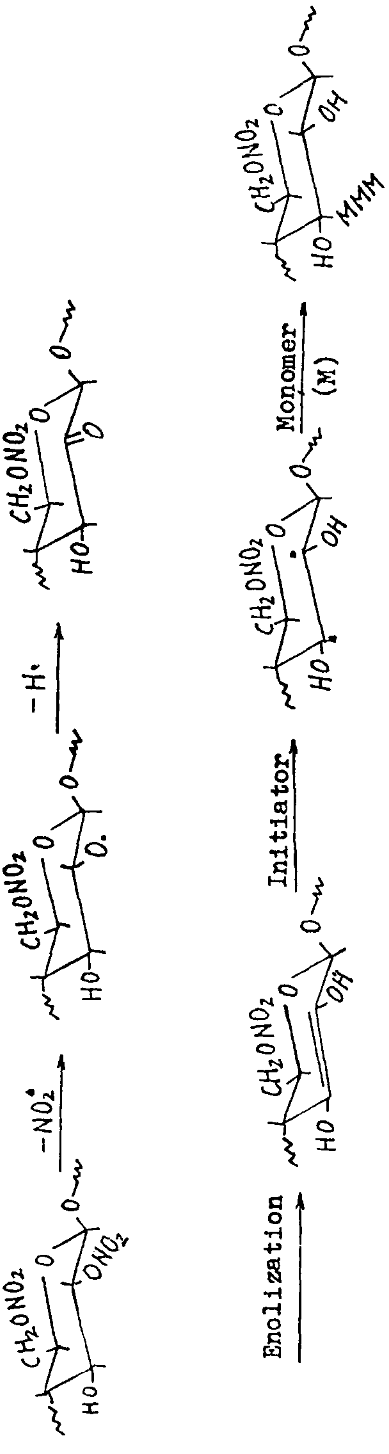


FIG. 7. Possible mechanism for the homogeneous grafting of cellulose nitrate.

1. The FT-IR characteristic band at 3448 cm^{-1}, attributed to the —OH group, increased rather than decreased in intensity as the graft increased (Fig. 6).
2. Conversely, the bands associated with —O—NO_2 (842, 752, and 682 cm^{-1}), —NO_2 (1656, 1282 cm^{-1}), and —CH (1377 cm^{-1}) from cellulose nitrate showed a tendency to decrease in intensity as the grafting level increased (Fig. 6).
3. The nitrogen content of CN was reduced from 11.6 to 6-8% after graft copolymerization in the present investigation.

These experimental results are compatible with the probable mechanism based on the bromination test by earlier researchers (Fig. 7) [19]. Naturally, the accuracy of FT-IR quantitative analysis in this study could reasonable establish this grafting mechanism since it would not be interferred with by the presence of the unsaturated compounds which might be encountered in the bromination test.

As can also be seen from Fig. 6, the changing trend of the curves representing —NO_2 and —O—NO_2 intensities, to decrease the intensity at an initial faster rate followed by an almost constant rate, implied that the denitration chiefly occurred in the early stages of homogeneous grafting, while in the later stages the grafting reaction was dominated mainly by the growth of grafted chains. Additional evidence in support of this view has emerged in TEM examinations, that is, the grafted branches appear in the morphology of separated microdomains at lower graft content (Fig. 4b), but appear in the pattern of the smoothed ridges (Fig. 4c) at higher graft content.

CONCLUSION

In this paper it has been demonstrated that homogeneous grafting can be assessed more precisely by the spectroscopic and microscopic techniques when used in conjunction with x-ray diffraction.

Qualitative FT-IR analysis revealed the changes in functional groups of cellulose nitrate during the homogeneous grafting process when compared to a true graft copolymer. The TEM observations strongly support this point, i.e., the electron micrograph for the pure graft copolymer contained both the morphological character of CN and PMMA but was completely distinct from the physical blend having the same composition.

SEM and TEM examinations showed that the location of the homogeneous grafting reaction was not only on the surface layer but also in the interior of the supermolecular structure of cellulose nitrate. X-ray diffraction determinations further disclosed the possibility that the homogeneous grafting reaction occurred in the ordered domains of cellulosics. This is one of the differences between the present work and conventional investigations in which grafting reactions only occurred on the surface layer and in morphous regions of the cellulose substrate.

FT-IR quantitative analysis also substantiated a possible mechanism via denitration and enolization for the homogeneous grafting of cellulose nitrate.

REFERENCES

[1] D. N.-S. Hon, *Graft Copolymerization of Lignocellulosic Fibers* (ACS Symp. Ser. 187), 1982.

[2] Y. X. Zhang, J.-C. Chen, D. Patil, G. B. Butler, and T. E. Hogen-Esch, *J. Macromol. Sci.—Chem.*, *A25*, 955, 971 (1988).

[3] Nippon Oils & Fats Co., *Jpn. Patent Abstr.*, *89*, 15 (1989).

[4] T. Graczyk, *J. Macromol. Sci.—Chem.*, *A27*, 23 (1990).

[5] V. N. Kislenko and A. A. Berlin, *Polym. Sci., USSR*, *33*, 466 (1991).

[6] M.-K. Lee and C. J. Biermann, *J. Wood Chem. Technol.*, *12*, 231 (1992).

[7] A. Takahashi and Y. Sugahara, *J. Polym. Sci., Polym. Chem. Ed.*, *26*, 19 (1988).

[8] Z. M. Wang, X. X. He, and D. Q. Sun, *Applied IR Spectroscopy*, Petrochemical Industry Press, Beijing, 1978, p. 361 (in Chinese).

[9] D. K. R. Chaudhuri and J. J. Hermans, *J. Polym. Sci.*, *51*, 373 (1961); *48*, 159 (1960).

[10] E. Schwab, V. T. Stannett, and J. J. Hermans, *Tappi*, *44*, 251 (1961).

[11] A. Y. Kulkarni, A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polym. Sci.*, *7*, 1581 (1963).

[12] H. Yasuda, J. A. Wray, and V. T. Stannett, *J. Polym. Sci.*, *C2*, 378 (1963).

[13] H. W. Melville and B. D. Stead, *J. Polym. Sci.*, *16*, 505 (1955).

[14] H. A. Ende and V. T. Stannett, *J. Polym. Sci.*, *A2*, 4047 (1964).

[15] Jean-Jacques, Y. Harrison, S. Premont, and R. E. Prud'homme, *J. Appl. Polym. Sci.*, *33*, 1359 (1987).

[16] H. Naqai, *Ibid.*, *7*, 1697 (1963).

[17] R. I. Abdel-Hay, P. Barker, and J. T. Guthrie, *Makromol. Chem.*, *181*, 2063 (1980).

[18] A. Muratov, K. Kh. Razikov, S. G. Yu'lchikbaeva, R. M. Yusupaliv, and Kh. U. Usmanov, *Chem. Abstr.*, *86*, 156870 5v (1975).

[19] K. S. V. Srinavasan and D. N.-S. Hon, in *Graft Copolymerization of Lignocellulosic Fibers* (ASC Symp. Ser. 187), 1982, p. 155.

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