An Investigation in Solution Acetylation of Cellulose by Microscopic Techniques

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ABSTRACT: The solution acetylation process of cellulose has been investigated by means of scanning electron and transmission microscopic techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the different morphologies of cellulose acetates, which were prepared at different temperatures. Simply, for the high-temperature acetylation (90°C), the reagents progressed in a linear manner, consisting of the formation of continuous micropores, from the surface into the interior of the supermolecular structure. In contrast, for the low-temperature acetylation (45°C), the reaction took place only through the segregated micropores on the surface of cellulose. As a result, the successive layers and, subsequently, fragmented platelets of the acetylated surface were solubilized in the reaction medium, and a viscous solution was eventually obtained. The experimental conformity between the SEM and TEM results provided valuable information in support of different solution acetylation mechanisms at low and high temperatures. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1953–1960, 1997

INTRODUCTION

Acetylation is one of the most significant reactions for the derivatization or modification of cellulose and its allied lignocellulosics.[1–3] Consequently, cellulose acetate is one of the most important cellulose derivatives because of its broad applications in textiles, plastic film, packaging, and cigarette filter tow. Although research on the acetylation of cellulose was launched in the 1950s, improvements in the quality and performance of the products have not abated.[4]

Traditionally, quality control of cellulose acetylation is achieved by evaluating changes in the specifications of end products, such as the combined acetic acid content, filter value, distribution of substitution groups, and molecular weight, as well as molecular weight distribution.[5–7] These analyses are necessary for the evaluation of properties of the acetylated products; however, they reflect neither the changes that have occurred in the microstructure of cellulose nor the relationship between the property changes and the reaction mechanisms.

In recent years, several works related to the microstructure of cellulose acetate were reported in the literature. For instance, Cheng et al.[8] had studied the morphology of cellulose acetate membrane and observed a porous structure in the scanning electron microscopy (SEM) photomicrographs. Similar work was done by Sada et al.[9] Usmanov et al.[10] indicated that the surface of the cellulose diacetate (CDA) possessed a relief structure with deep folds, whereas the internal fragments of the specimens were practically structureless masses. They attributed this morphology

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to the results of dry out, hydrolysis, and precipitation. However, in a homogeneous acetylation, Ryskina and Fedorova[11] found that different supermolecular structures existed in cellulose triacetate (CTA) solution at different temperatures; i.e., globular supermolecular structures were featured at the high temperature (90°C), and a crystalline structure was featured at lower temperatures (50 and 60°C). In the latter study, based on microscopic examinations, the authors[12] also pointed out that a rise in temperature was accompanied by an increase in thermodynamic flexibility of the CTA chain, which led to the changes in the fluctuating network structure and the shape and the size of supermolecular formation of CTA in solution. More recently, Fleury et al.[13] demonstrated that different morphologies of microgel, which were elongated narrow particles with pointed ends and small shapeless aggregates, respectively, occurred in CDA solution of cotton linter and wood pulp.

These research findings provided useful information about the changes in the microstructures of cellulose by acetylation, but there is not yet any explanation that may offer a plausible acetylation mechanism for the morphological disparity. Despite the vigorous development and intensive research in various acetylation processes,[14–17] not many researchers have delved into the mechanisms of morphological changes taking place in solution. Hence, it would be of interest to explore the acetylation mechanisms of cellulose by using microscopic techniques.

In our previous article,[18] we have demonstrated the polymorphic transformations of cellulose at an elevated temperature acetylation by differential scanning calorimetry (DSC) and X-ray techniques. In this study, both SEM and transmission electron microscopy (TEM) were used to assess the acetylation mechanisms. The development of morphological patterns from the surface to the interior of the supermolecular structure of cellulose during the acetylation reaction was investigated.

EXPERIMENTAL

The cotton linter used in this study for making cellulose acetates was supplied by Hui-An Chemical Plant, China, without further treatment. It contains about 98% α-cellulose. The specimens of CTA with a degree of polymerization (DS) of 2.8 were prepared by a solution process employing sulfuric acid as the catalyst with acetic anhydride in an acetic acid solvent. The reaction was performed separately at a high temperature, i.e., 90°C, and at a low temperature, i.e., 45°C for 60–100 min. Cellulose diacetates (CDA) with a DS of 2.4 were obtained by hydrolysis of the CTA for 30–60 min at 120 and 60°C corresponding, respectively, to the high- and low-temperature acetylation processes.

Methods

For the SEM study, specimens were sputter-coated with gold palladium and examined with a Hitachi S-430 scanning electron microscope.

For the TEM study, specimens were embedded in epoxy resin and oven-cured. Ultrathin sections ($<$100 nm) of the specimens were cut with a glass knife and examined directly with a JEOL (JEM-100 CXII) transmission electron microscope.

RESULTS AND DISCUSSION

In industry, almost all cellulose acetates (CAs), with the exception of fibrous CTA, are manufactured by a solution process employing sulfuric acid as the catalyst with acetic anhydride in an acetic acid solvent. For this study, the same chemical makeup was used to prepare the acetylated celluloses. The effect of acetylation on the supermolecular structure of cellulose is greatly dependent on the history of heat and stress, which were encountered in the acetylation process. Morphological characterization of CTA is able to shed light on the influence of processing conditions on the reaction mechanisms.

The Surface Morphological Characterization

The surface of cotton fiber is normally smooth [Fig. 1(a)]. When acetylation proceeded at a low temperature at 45°C for 30 minutes, the roughening of the surface texture together with the manifestation of supermolecular structure of cellulose can be observed by the SEM, as shown in Figure 1(b). Higher magnification of the specimen revealed the presence of multifarious pinhole-like structures on the surface [Fig. 1(c)]. As the acetylation proceeded further to 100 minutes, the pinhole-like structures gradually grew in size into pores [Fig. 1(d)]. The transformation of CTA to CDA by hydrolysis also increased the dimension of the pores. Essentially, the dimension of

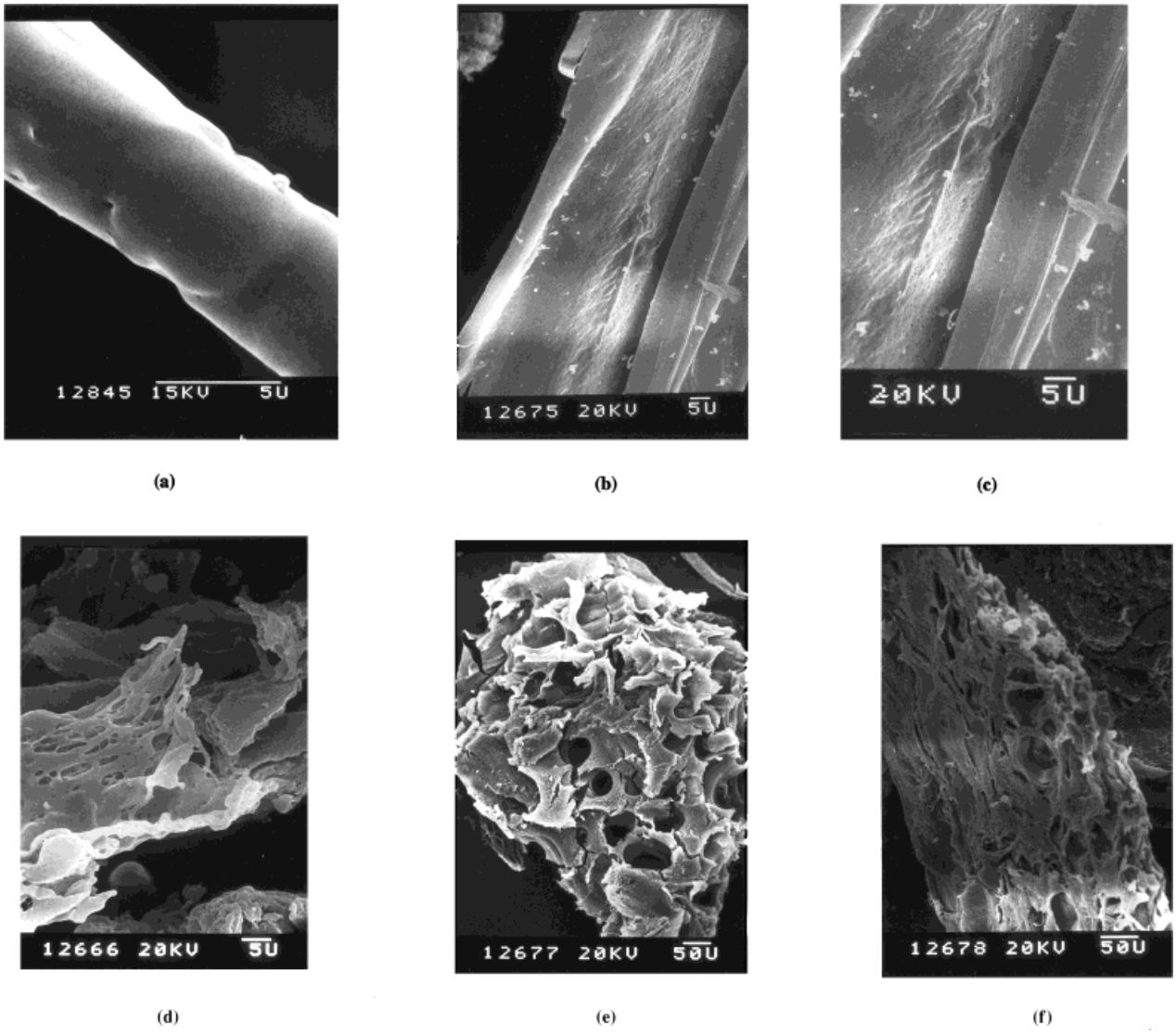

Figure 1 Progression of the acetylation reaction at 45°C, examined by SEM for cotton cellulose (a) CTA with a DS of 2.8 at (b) and (c) 30 and (d) 100 min and CDA with a DS of 2.4 at (e) 30 and (f) 60 min.

the pinholes enlarged from 0.1 [Fig. 1(b)] to 5–10 μm [Fig. 1(d)] for CTAs and to more than 50 μm for CDAs, which were obtained through 30 and 60 minutes hydrolysis, respectively [Fig. 1(e) and (f)]. These variations in the surface morphology suggested the erosion or degradation of the outer layer of cellulose tunicae during the acetylation reaction. Moreover, acetylation agents appeared to attack selective domains to create pinhole-like structures, which were further expanded into a larger dimension as acetylation proceeded. Apparently, the naturally occurring micropore structures on the cotton surface are the focal points where acetylation is preferentially initiated. When cellulose was swollen with acetic acid, it opens up its micropores to facilitate penetration of acetic anhydride for the acetylation reaction. Since acetylation proceeded rapidly in the amorphous region, the amorphous surface was greatly eroded, and the surface of crystallites was also affected. The subsequent hydrolysis of CTA to produce CDA assuredly facilitates the dissolution of the fragmental tunicae to enlarge the pore sizes.

When acetylation was carried out at a high temperature at 90°C, a different erosion mechanism was observed. It is perceived that the acetylation at 90°C proceeded much faster and uniform than that at a lower temperature, such as

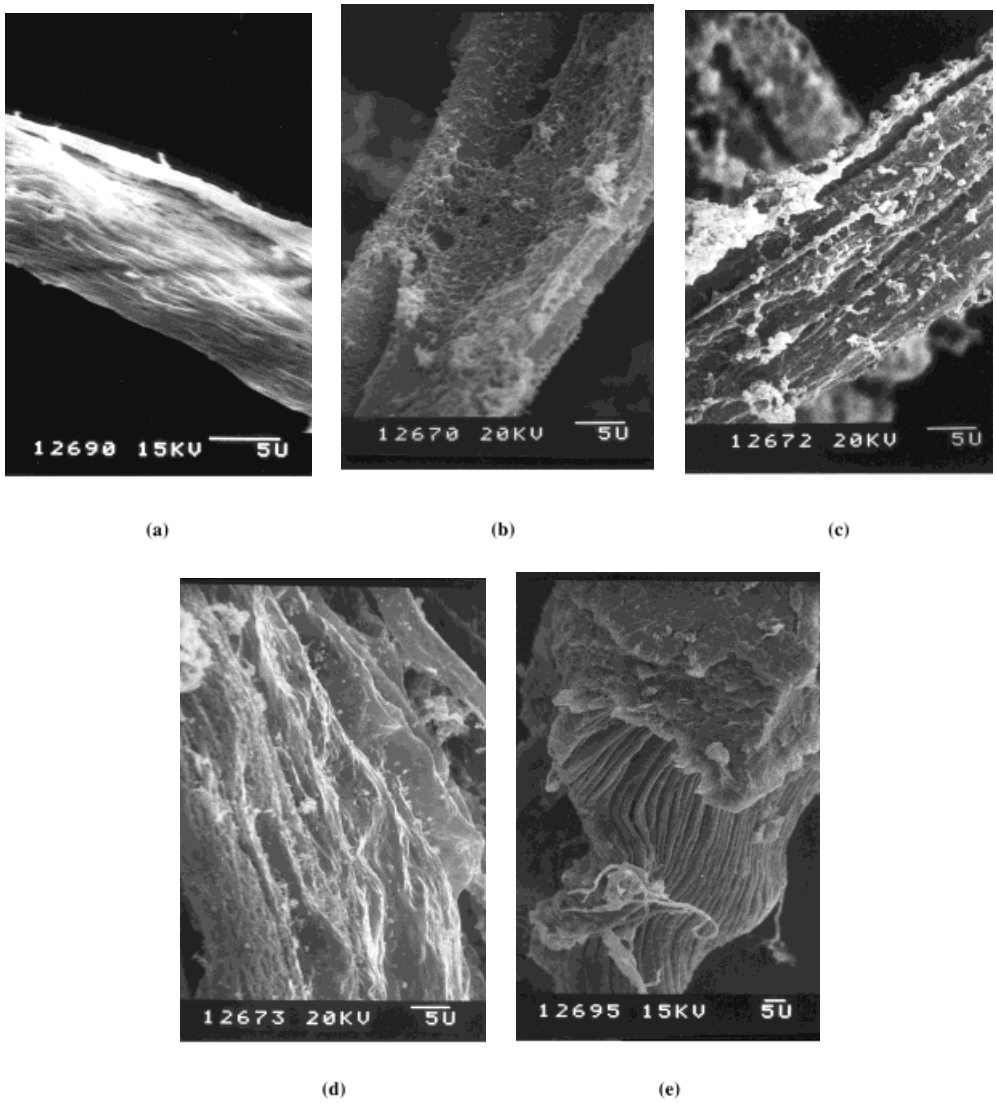

Figure 2 Progression of the acetylation reaction at 90°C, examined by SEM for CTA with a DS of 2.8 at (a) 30 and (b) 100 min and CDA with a DS of 2.4 at (c) 30 and (d) and (e) 60 min.

at 45°C. At the onset of acetylation for 30 minutes, roughening of the surface immediately took place, and the microfibrillar structure with many pores are observed as shown in Figure 2(a). As the reaction proceeded, the number and size of the pores on the surface increased rapidly, and certain tunicae layers were actually dissolved away from the surface. When acetylation carried out for 100 minutes, the void formation at the underneath surface of tunicae can be explicitly recognized [Fig. 2(b)]. It is interesting to note the presence of two rod-like structures at the right side of the microgram, indicating that certain parts of the cellulose were reacted and dissolved rapidly where the resistive rod-like structures emerged. When CTAs underwent the hydrolysis process for 30 and 60 minutes, the removal of the top layer, which led to the exposure of the underneath area, is more distinct as shown in those micrograms in Fig. 2(c) and (d). As the reaction proceeded, most vulnerable layers disappeared; only the lamellar structures were left behind for both CTA and CDA samples [Fig. 2(c)–(e). These lamellae were stacked on one another in a direction parallel to the axis of cellulose. The thickness of the lamellae changed from 5–10 μm in CTA specimens to about 1 μm in CDAs. The formation and change of the lamellar thickness apparently ascribed to the fact that the

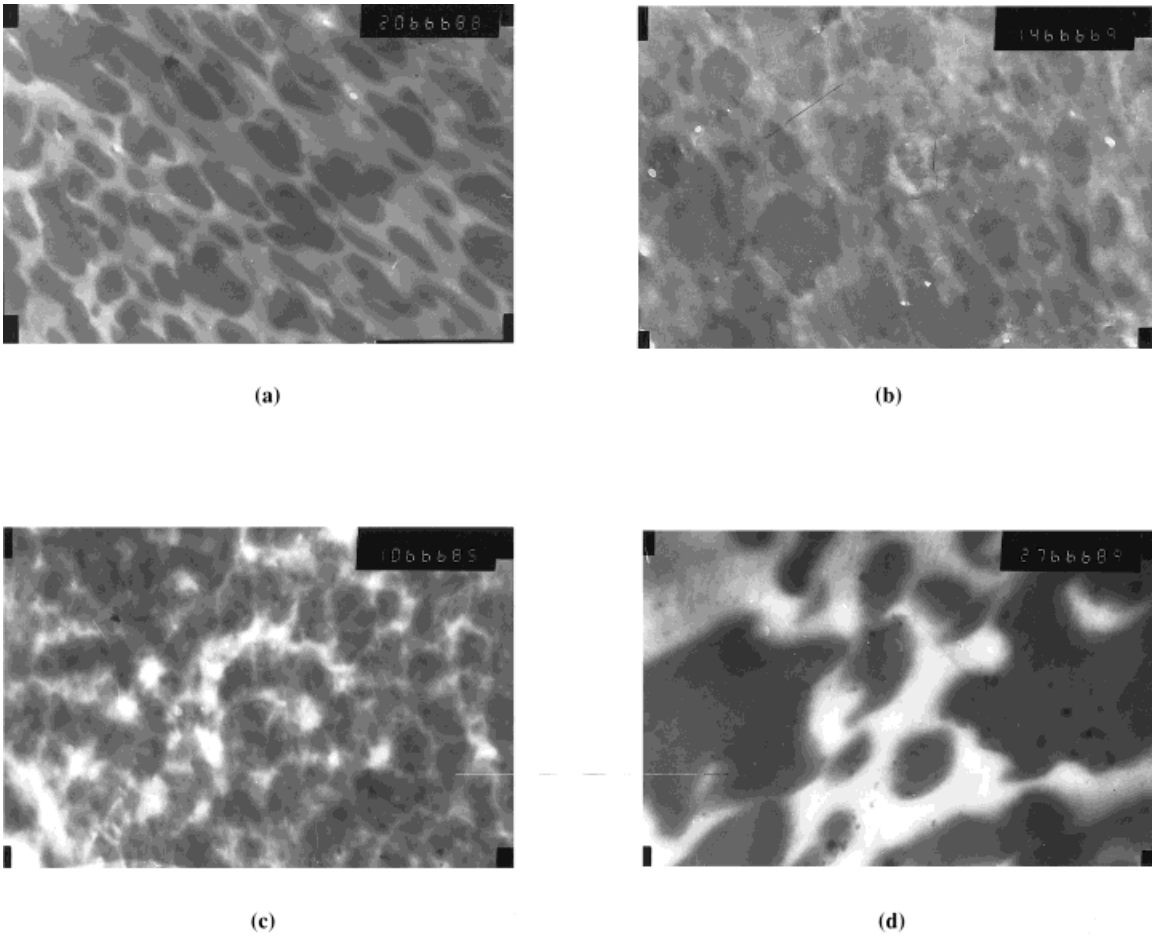

Figure 3 Progression of acetylation reaction at 45°C, examined by TEM for CTA with a DS of 2.8 at (a) 30 and (b) 100 min and CDA with a DS of 2.4 at (c) 30 and (d) 60 min.

acetylation took place at high temperature where the amorphous structure was dissolved readily, and the microstructure of crystallites of cellulose was subject to more degradation. This is quite different from the study of Ryskina and Fedorova,[11] who observed the formation of globular structure during acetylation at high temperature.

The different morphologies observed by the SEM are believed to be the result of different acetylation conditions. The acetylation by the solution process is a heterogeneous and topochemical reaction, and the cellulose is initially suspended in the reaction medium. After acetylation has taken place, the successive layers of the cellulose fibers were reacted and solubilized in the medium, thus exposing new surfaces for subsequent reactions. The reaction path is largely controlled by the rate of diffusion of the acetylating reagent into cellulose fibers. The reaction temperature is one of the important factors that dictates the acetylation path. At a higher temperature, such as at 90°C, almost all microholes on the surface of the porous structure of cellulose were opened up for the acetylating agents; the reaction progressed in a linear manner, consisting of the continuous microholes, from the surface into the interior of the supermolecular structure. The earlier work of Hiller[19] further substantiated that the increase in temperature helps to promote the rate of diffusion of reagents by overcoming the energy barrier due to hydrogen bonding. On the contrary, in the reaction conducted at the low temperature at 45°C, the diffusion of the reagents may only progress through the separated microholes that were in the opening-up condition on the surface of cellulose. This porous morphology is consistent with the SEM photomicrograph of cellulose acetate membranes observed by Cheng et al.[20]

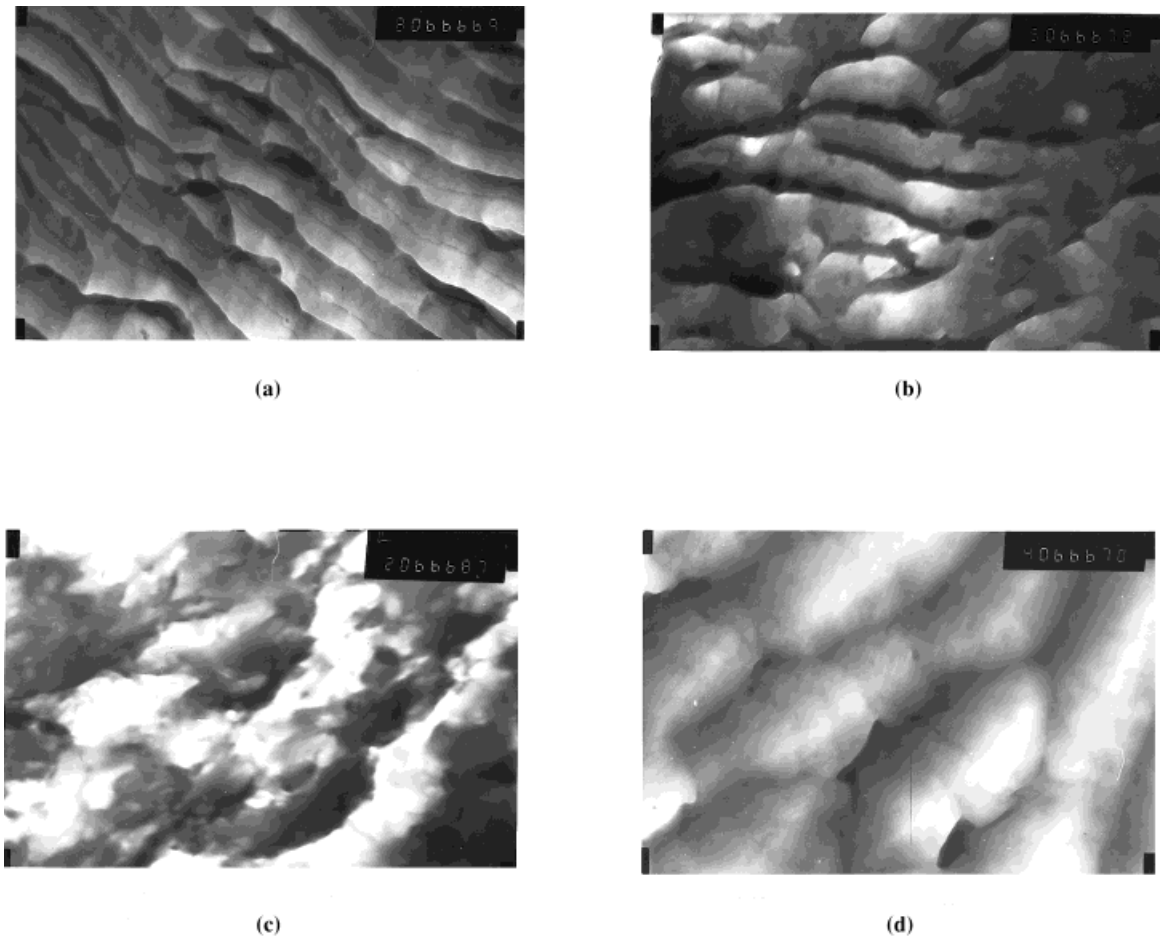

Figure 4 Progression of acetylation reaction at 90°C, examined by TEM for CTA with a DS of 2.8 at (a) 30 and (b) 100 min and CDA with a DS of 2.4 at (c) 30 and (d) 60 min.

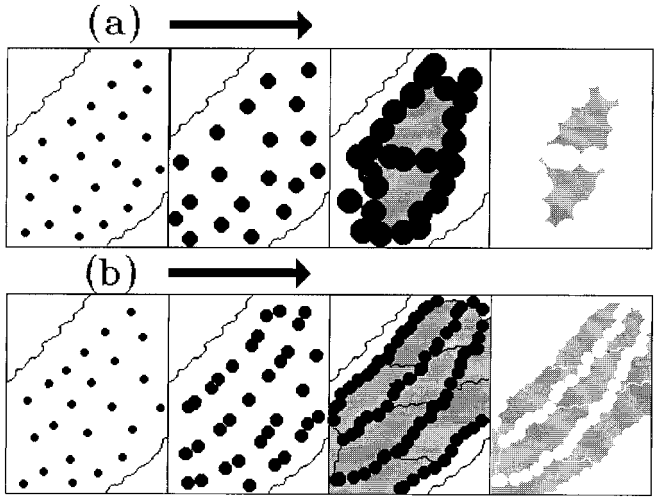

Figure 5 Schematic depiction of morphological development in cellulose during solution acetylation reaction at 45°C (a) and 90°C (b).

The Internal Morphological Characterization

SEM provides resolvable details in the changes of surface microstructure of polymers, but it has limited depth penetration in the field. Since the solution acetylation is a process transformed from an initially heterogeneous reaction into a homogeneous one finally, it is imperative to study the morphological transformation from bulk to solution during the acetylation. Accordingly, TEM was used to obtain additional information on the fine structures within the macrostructure and to clarify whether or not the presence of structural harmonization between SEM and TEM observations.

As opposed to SEM, which is useful for studying the surface, TEM micrograms present more details on the internal morphological structure. At the low temperature acetylation, micropores of CTAs were conspicuously displayed at the first 30 minutes of reaction [Fig. 3(a)]; they were transformed rapidly into irregular pores at another 30 minutes [Fig. 3(b)]. The fragmentary structures in CDAs [Fig. 3(c) and (d)] were the results of growth and connection of the micropores during the hydrolysis of CTAs. On the contrary, at the high-temperature acetylation, layered structures of microfibrils were observed. This implies that the top layer of microfibril where micropores were located reacted rapidly and dissolved; only those fibers without micropores stayed intact. Due to the loss of top, reactive layers, only the resistant layers emerging in the lamellae form were observed. As reaction proceeded, the stacked lamellar structure at the initial 30 minutes [Fig. 4(a)] transformed into loosely attached layers at 60 minutes of acetylation [Fig. 4(b)] in CTAs and into imperfect layers and segregated blocks after 30 and 60 minutes of hydrolysis into CDAs [Fig. 4(c) and (d)]. This result suggested further that some of the cellulose chains may be cleaved during acetylation at high temperature. Scission gives a description of solution acetylation in which the surface of the crystallite was attacked first and converted into the triester; subsequently, the reaction proceeds inward to produce a series of partly reacted areas between the unreacted interior and the completely reacted surface.

The TEM observations provided convincing evidence on the mechanisms of transformation of cellulose microfibril into layered and fragmented structures during the solution acetylation at low and high temperatures.

Based on these microscopic observations, the sequences of changes in cellulose structures during solution acetylation process at low and high temperatures can be clearly visualized. These changes are depicted schematically in Figure 5.

CONCLUSIONS

The typical morphological changes in cellulose acetates observed by the SEM and TEM revealed different mechanisms of acetylation. For the high-temperature acetylation at 90°C, SEM revealed that the acetylation progressed in a linear manner, involving the formation of continuous micropores, from the surface into the interior of the supermolecular structure. In contrast, for the low-temperature acetylation at 45°C, the reaction took place only through the segregated micropores on the surface of cellulose shown by SEM micrographs. Moreover, at high temperature, TEM demonstrated that the acetylation loosened the successive layers of the acetylated fibers, which were subsequently broken up and solubilized in the medium; whereas at low temperature, TEM revealed the formation and growth of the micropore structures, as well as fragmentation of the acetylated surface layer into platelets. The new surfaces of cellulose were thus exposed for the subsequent reactions. The experimental conformity between the SEM and TEM results provided substantial evidence for elucidating the acetylation mechanisms of the solution process. Obviously, these mechanisms of solution acetylation are much different from that of the fibrous acetylation process, in which an open and rupture of fibrillar structure were observed.[21]

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