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6. Prospects for Future Applications of Cellulose Acetate

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Summary: The prospects for future applications of cellulose acetate (CA) and cellulose esters (CE) were assessed via an analysis of literature data. An examination of more than 50,000 citations in the published literature with relevance to CA and CE has shown that, while the R&D effort continues without discernible slow-down, the emphasis has shifted in favor of D at the expense of R in recent years; more publications now originate in Southeast Asian countries; and most current journal articles deal with specialty products, such as membranes, controlled release agents, and biopolymers. The prospects for future applications are viewed as being related to the ability to add new performance features to CA, particularly thermal processability, water-dispersibility, and the ability to interact with other polymers on the molecular level. This can be achieved by such secondary modifications as the introduction of plasticizing (mixed) ester substituents, carboxyl groups, and the use of (monofunctional) oligomers in block copolymers, respectively. In addition, the adoption of acetylation technology to lower grade pulps and even wood and wood fibers may result in new business opportunities in thermoplastic and soluble wood esters, or in acetylated solid wood products with superior dimensional, biological and light-stability characteristics.

Keywords: Literature citation, solubility, thermal properties, plasticization, wood acetates, polymer segments.

Introduction

The prospects for future cellulose acetate (CA) and cellulose ester (CE) applications looks bright considering its abundant resource base in renewable biomass materials; the degree of refinement of its manufacturing process(es); its physical, chemical and biological characteristics; and its existing applications in both large and small-volume products. CA, and CE in general, are well known and well understood polymers with wide acceptance. In order to gauge the potential for future CA/CE applications, a historical perspective is applied to the existing body of knowledge. By analyzing the

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historical development of the CA technology through the published literature, a judgment may be derived for the prospects of future CA/CE-applications.

Analysis of the CA/CE Literature:

The SciFinder® program of the American Chemical Society is based on the collective 62-volumes of Chemical Abstracts. As of mid-2003, SciFinder® lists a total of 54,258 references to CA and CE. These references are categorized (by Chemical Abstracts) into 212 "sections." These sections provide a broad classification of chemical substances into general use categories. An analysis of publications by use area reveals that the leading nine (out of 212) sections cover approximately 40% of all references to CA/CE. This amounts to a body of literature that includes approximately 22,000 publications. The fields of usage that have attracted the greatest number of references to CA/CE are given in Table I. It is apparent that most of the publications were released in the section dealing with "Cellulose, Paper, and Wood Products," and thus can be expected to deal with source, provenance, and origin of CA/CE products rather than applications. Literature sections that follow dael. with pharmaceuticals, textile materials, plastics, coatings, and photographic products (Table I). Virtually all of the 200+ use areas have recorded references to CA/CE, but these are of a more sporadic and less focused nature. An analysis of the leading eight use areas (not including biochemical methods but also

Table I. Classification of published literature in the CA/CE field by use area – the leading nine use areas[1]

Use Area	**Publications (in % of 9 leading categories)**
Cellulose, Paper, and Wood Products	22.2
Pharmaceuticals	14.6
Dyes and Textile Chemistry	14.0
Plastics Fabrication and Uses	10.0
Biochemical Methods	9.2
Coatings and Inks	8.3
Textiles	7.9
Plastics Manufacture and Processing	7.1
Photochemistry, Photographics, and Reprographics	6.7
Total	100

[1] According to Chemical Abstracts from a total of 54,258 publications; the leading nine sections (out of a total of 212) represent 40% of all publications.

Table II. Corporations most frequently named on patents[1)]

Corporation	**Total Number**
Fuji Photo Film	415
Daicel Chemical Industries	228
Eastman Kodak	215
Konica Co.	200
Ricoh	138
Others	<100

[1)] Of a total of 9,445 patents with relevance to CA and CE listed in Chemical Abstracts.

including essential oils and cosmetics as well as food and feed chemicals) deals with approximately 16,000 references (29.4% of total). This analysis reveals that 59% of these publications were patents, 38.1% were journal articles, and the remaining 2.9% were all others, including reviews, conference proceedings, reports, dissertations, and books.

The very high proportion of patents is reflective of an R&D effort that largely favors “D” (development). This emphasis indicates that CA/CE is a mature product that experiences on-going technological (process) refinements. The 38.1% publications reported as “journal articles” can be expected to be more closely related to research (the “R”-component of R&D).

Most of the almost 10,000 patents listed in Chemical Abstracts have been issued to industrial organizations. Most prominent among those are five companies with close ties to the photographic industry (Table II). Among the companies being credited with more than 100 patents (Table II) are four Japanese and one U.S. American corporation.

Of the approximately 6,000 journal articles being listed as ‘publications’ in support of the R&D effort in eight leading use areas in Chemical Abstracts, the analysis provides a ranking of the journals that have participated in publishing R&D results relating to CA and CE products (Table III). It is apparent that most journal articles dealing with CA and CE products have been concerned with polymer issues. Leading application areas have dealt with plastics, separation science, and drug delivery (Table III). This focus is further accentuated if the R&D effort in the CA/CE field is

Table III. Journals most frequently publishing on CA and CE in 62 Volumes of Chemical Abstracts.[1)]

Journal Name	**Number of Publications**
J. Applied Polymer Science	256
Plast. Massy	131
J. Membrane Science	128
Zh. Prikl. Khim. (Leningrad)	111
Vysokomol. Soedin (2 series)	202
Cellulose Chemistry & Technology	90
Int. J. Pharmaceuticals	76
Drug Development Industrial Pharmaceuticals	66

[1)] Leading outlets for a total of 6,094 journal articles, according to Chemical Abstracts.

evaluated via the journal articles published in the last three years (2000-2002). The last three years, which have seen a greater publication rate than previous years (12% of all publications in the leading eight use sections have appeared in the last three years), provide a record of an average of 540 to 700 total publications, and 160 'journal articles', in each year. Whereas 80% of the total journal articles of the past three years were written in English, less than half (49.3%) of all publications used English as their primary language. This was followed by Japanese (37.5%), German (5.7%), and Chinese (2.8%). Of the approximately 1,000 publications of the past three years that were written in English, 55.2% were patents, again reflecting the prominent 'development'-emphasis of the R&D effort. The data suggest that, in the last three years, there were almost four patents published for each journal article.

The leading journals publishing articles that deal with CA and CE in the last three years are listed in Table IV. Compared to earlier years and the overall body of literature, the published research of the recent past (2000 to 2002) reflects an increasing concern with a general as well as specialized knowledge-generation process in the CA/CE field dealing with separation science, polymer science, and controlled release/pharmaceutical products.

When considering review articles in the CA/CE-field, it is revealed that less than half (48%) of all reviews were written in English, and the greatest number of reviews was published in 1967.

Table IV. Journals currently (last 3 years) publishing most frequently in English on CA and CE[1)]

Journal Name	Number of Publications (last 3 years)
J. Membrane Science	27
J. Applied Polymer Science	25
Drug Development Industrial Pharmaceuticals	12
Biomaterials	10
Polymer	10
Cellulose	9
J. Controlled Release	9
Interntl. J. Pharmaceuticals	8

[1)] From Chemical Abstracts.

In order to assess R&D directions in the CA/CE field, the titles (and references) of journal articles published in the last three years in English are summarized in Tables V to VII. These articles were published in the *Journal of Membrane Science* (Table V); in three periodicals dealing with drugs and controlled release, *Drug Development and Industrial Pharmaceuticals*, *Journal of Controlled Release*, and *International Journal of Pharmaceuticals* (Table VI), and in journals dealing with aspects of polymer science (*Journal of Applied Polymer Science, Biomaterials, Polymer, and Cellulose*) (Table VII). It is apparent that the titles of the articles communicate the research aspirations of scientists involved in the CA/CE field, and that these aspirations provide valuable information on potential and prospective future applications for CA and CE-products. This is the topic of the second part of this chapter.

Table V. List of Titles and References of Selected Journal Articles (in English) Dealing with CA/CE from the *J. Membrane Science* (Years 2000 – 2002).

Influence of acetylation degree of cellulose acetate on pervaporation properties for methanol/methyl tert-butyl ether mixture. *J. Membrane Sc.* 2000, 165(1), 89-97.
Methanol-selective membranes for the pervaporative separation of methanol-toluene mixtures. *J. Membrane Sci.*, 2000, 167(2), 187-201.
Comparison of microporous membrane morphologies using confocal scanning laser microscopy. *J. Membrane Sci.*, 2000, 168(1-2), 53-62.
Preparation and performance of cellulose acetate-polyurethane blend membranes and their applications. Part 2. *J. Membrane Sc.*, 2000, 169(2), 215-228.
Performances of glassy polymer membranes plasticized by interacting penetrants. *J. Membrane Sci.*, 2000, 172(1-2), 75-89.
Formation of polymeric membranes by immersion precipitation: an improved algorithm for mass transfer calculations. *J. Membrane Sci.*, 2001, 187(1-2), 287-296.

Separation of nutmeg essential oil and dense CO_2 with a cellulose acetate reverse osmosis membrane. *J. Membrane Sci.*, 2001, 188(2), 173-179.
Effect of separating layer in pervaporation composite membrane for MTBE/MeOH separation. *J. Membrane Sci.*, 2001, 194(2), 151-156.
Performance of ultrafiltration membranes in ethanol-water solutions: effect of membrane conditioning. *J. Membrane Sci.*, 2002, 198(1), 75-85.
Study of shear rate influence on the performance of cellulose acetate reverse osmosis hollow fiber membranes. *J. Membrane Sci.*, 2002, 202(1-2), 205-215.
Influence of viscosity slope coefficient of CA (cellulose acetate) and its blends in dilute solutions on permeation flux of their films for MeOH/MTBE mixture. *J. Membrane Sci.*, 2002, 203(1-2), 167-173.
Effect of organic solvents on membrane formation by phase separation with supercritical CO_2. *J. Membrane Sci.*, 2002, 204(1-2), 81-87.
Macrovoid pore formation in dry-cast cellulose acetate membranes: buoyancy studies. *J. Membrane Sci.*, 2002, 205(1-2), 11-21.
Optimization of cellulose acetate hollow fiber reverse osmosis membrane production using Taguchi method. *J. Membrane Sci.*, 2002, 205(1-2), 223-237.
Water and ions transport mechanism in hyperfiltration with symmetric cellulose acetate membranes. *J. Membrane Sci.*, 2002, 206(1-2), 319-332.
The wet phase separation: the effect of cast solution thickness on the appearance of macrovoids in the membrane forming ternary cellulose acetate/acetone/water system. *J. Membrane Sci.*, 2002, 207(1), 139-141.
Development of polyion complex membranes based on cellulose acetate modified by oxygen plasma treatment for prevarporation. *J. Membrane Sci.*, 2002, 208(1-2), 223-231.
Novel cellulose acetate membrane blended with phospholipid polymer for hemocompatible filtration system. *J. Membrane Sci.*, 2002, 210(2), 411-421.

Table VI. List of Titles and References of Selected Journal Articles (in English) Dealing with CA/CE from *Drug Dev. Ind. Pharm.*, *J. Controlled Release*, and *Int. J. Pharm.* (Years 2000 – 2003).

Captopril gastrointestinal therapeutic system coated with cellulose acetate pseudolatex: evaluation of main effects of several formulation variables. *Int. J. Pharm.*, 2000, 193(2), 147-156.
Studies of the drug permeability and mechanical properties of free films prepared by cellulose acetate pseudolatex coating system, *Drug Dev. Ind. Pharm.*, 2000, 26(1), 95-102.
Influence of three synthetic membranes on the release of caffeine from concentrated W/O emulsions. *J. Controlled Release*, 2000, 66(2-3), 243-254.
PH-independent release of a weakly basic drug of water-insoluble and –soluble matrix tablets. *J. Controlled Release*, 2000, 67(1), 101-110.
Physical structure characterization of theophylline in some acidic film-forming polymers. *Drug Dev. Ind. Pharm.*, 2000, 26(6), 687-691.
Monolithic osmotic tablet system for nifedipine delivery. *J. Controlled Release*, 2000, 67(2-3), 309-322.
Polymers with pH-dependent solubility: possibility of use in the formulation of gastroresistant and controlled-release matrix tablets. *Drug Dev. Ind. Pharm.*, 2000, 26(8), 837-845.
Emulsion/solvent evaporation as an alternative technique in pallet preparation. *Drug Dev. Ind. Pharm.*, 2000, 26(11), 1151-1158.
Bimodal drug release achieved with multi-layer matrix tablets: transport mechanisms and device design. *J. Controlled Release*, 2000, 69(3), 455-468.
Basic coating polymers for the colon-specific drug delivery in inflammatory bowel disease. *Drug Dev. Ind. Pharm.*, 2000, 26(12), 1239-1246.
An in vitro investigation of the suitability of press-coated tablets with hydroxypropyl methyl cellulose acetate succinate (HPMCAS) and hydrophobic additives in the outer shell for colon targeting. *J. Controlled Release*, 2001, 70(1-2), 97-107.
Effect of magnesium stearate or calcium stearate as additives on dissolution profiles of dilitiazem hydrochloride from press-coated tablets with hydroxypropyl methyl cellulose acetate succinate in the outer shell. *Int. J. Pharm.* (2001), 216(1-2), 137-146.

Drug release from and mechanical properties of press-coated tablets with hydroxypropylmethylcellulose acetate succinate and plasticizers in the outer shell. *Int. J. Pharm.*, 2001, 217(1-2), 33-43.
Evaluation of a floating dosage form of nicardipine hydrochloride and hydroxypropyl methyl cellulose acetate succinate prepared using a twin-screw extruder. *J. Pharm.*, 2001, 218(1-2), 103-112.
Controlled transport of timolol maleate through artificial membranes under passive and iontophoretic conditions. *J. Controlled Release*, 2002, 81(3), 335-345.
Plasticizer effect and comparative evaluation of cellulose acetate and ethylcellulose-HPMC combination coatings as semipermeable membranes for oral osmotic pumps of naproxen sodium. *Drug Dev. Industrial Pharm.*, 2002, 28(4), 403-412.
Investigation of cyclobenzaprine hydrochloride release from oral osmotic delivery systems containing a water-swellable polymer. *Drug Dev. Ind. Pharm.*, 2002, 28(6), 631-639.
Microencapsulation of semisolid ketoprofen/polymer microspheres. *.Int. J. Pharm.*, 2002, 242(1-2), 175-178.

Table VII. List of Titles and References of Selected Journal Articles (in English) Dealing with CA/CE from *J. Appl. Polym. Sci.*, *Biomaterials*, *Polymer*, and *Cellulose* (Years 2000-2002).

Miscible blends of cellulose acetate hydrogen phthalate and poly(vinylpyrrolidone) characterization by viscometry, ultrasound, and DSC. *J. Appl. Polym. Sci.*, 2000, 76(6), 859-867.
Phase diagram of water soluble semirigid polymers as a function of chain hydrophobicity. *Polymer*, 2000, 41(11), 4357-4360.
Activated carbon-filled cellulose acetate hollow-fiber membrane for cell immobilization and phenol degradation. *J. Appl. Polym. Sci.*, 2000, 76(5), 695-707.
Phase separation mechanism during membrane formation by dry-cast process. *J. Appl. Polym. Sci.*, 2000, 77(4), 776-783.
Structure and physical properties of poly(butylene succinate)/cellulose acetate blends. *Polymer*, 2000, 41(23), 8449-8454.
Polymer blend of cellulose acetate butyrate and aliphatic polyester-carbonate. *J. Appl. Polym. Sci.*, 2000, 77(13), 2908-2914.
Polymeric membrane formation by wet-phase separation; turbidity and shrinkage phenomena as evidence for the elementary processes. *Polymer*, 2000, 41(26), 9227-9237.
Fibrous long-chain organic acid cellulose esters and their characterization by diffuse reflectance FTIR spectroscopy, solid-state CP/MAS carbon-13 NMR, and x-ray diffraction. *J. Appl. Polym. Sci.*, 2000, 78(7), 1354-1365.
Cellulosic nanocomposites. I. Thermally deformable cellulose hexanoates from heterogeneous reaction. *J. Appl. Polym. Sci.*, 2000, 78(13), 2242-2253.
Electrorheological characteristics of phosphate cellulose-based suspensions. *Polymer*, 2001, 42(11), 5005-5012.
Simple and precise determination of sulfuric acid ester in unstabilized cellulose nitrate by acetone-hydrolysis-lead nitrate-dithizone titration method. *Cellulose*, 2000, 7(4), 337-345.
Physical aging of blends of cellulose acetate polymers with dyes and plasticizers, *Polymer*, 2001, 42(13), 5781-5792.
Calculation of alcohol-acetone-cellulose acetate ternary phase diagram and their relevance to membrane formation. *J. Appl. Polym. Sci.*, 2001, 80(10), 1650-1657.
Ring-banded spherulites in poly(ε-caprolactone) blended with hydroxyethyl cellulose acetate as an indication for partial miscibility. *J. Appl. Polym. Sci.*, 2001, 80(10), 1681-1686.
Study of the structure of asymmetric cellulose acetate membranes for reverse osmosis using electron spin resonance (ESR) method. *Polymer*, 2001, 42(15), 6479-6484.
Plasticization of cellulose diacetate by reaction with maleic anhydride, glycerol, and citrate esters during melt processing. *J. Appl. Polym. Sci.*, 2001, 81(1), 243-250.
Liquid crystalline solutions of cellulose acetate in phosphoric acid. *Polymer*, 2001, 42(17), 7363-7369.
Characterization of glow-discharge-treated cellulose acetate membrane surfaces for single-layer enzyme electrode studies. *J. Appl. Polym. Sci.*, 2001, 81(6), 1341-1352.
Effect of hydrolysis on porosity of cellulose acetate reverse-osmosis membranes. *J. Appl. Polym. Sci.*, 2001, 81(7), 1768-1775.

Use of enzymatic digestion and chemical methylation followed by matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry of sequence a 60 kDa commercial fraction of cellulose acetate. *Cellulose,* 2001, 8(1), 81-89.

Effects of polymer solvents on the performance of cellulose acetate membranes in methanol/methyl tertiary butyl ether separation. *J. Appl. Polym. Sci.*, 2001, 82(12), 2882-2895.

Modeling and simulation of the phase-inversion process during membrane preparation. *J. Appl. Polym. Sci.*, 2001, 82(12), 3036-3051.

Continuous cellulose fiber-reinforced cellulose ester composites. I. Manufacturing options. *Cellulose,* 2001, 8(2), 149-159.

Continuous cellulose fiber-reinforced cellulose ester composites. II. Fiber surface modification and consolidation conditions. *Cellulose*, 2001, 8(2), 161-169.

Continuous cellulose fiber-reinforced cellulose ester composites. III. Commercial matrix and fiber options. *Cellulose*, 2001, 8(2), 171-179.

Iodine-containing cellulose mixed esters as radiopaque polymers for direct embolization of cerebral aneurysms and arteriovenous malformations. *Biomaterials*, 2001, 23(1), 121-131.

Structure and physical properties of cellulose acetate/poly(butylenes succinate) blends containing a transition metal alkoxide. *J. Appl. Polym. Sci.*, 2002, 83(8), 1750-1758.

The biocompatibility of novel starch-based polymer and composites: in vitro studies. *Biomaterials*, 2002, 23(6), 1471-1478.

Effect of compatibility of cellulose acetate/poly(vinyl butyral) blends on pervaporation behavior of their membranes for methanol/methyl tert-butyl ether mixture. *J. Appl. Polym. Sci.*, 2002, 83(11), 2434-2439.

Effects of phase separation on stress development in polymeric coatings. *Polymer*, 2002, 43(8), 2267-2277.

Determination of the degree of substitution (DS) of mixed cellulose esters by elemental analysis. *Cellulose*, 2001, 8(3), 225-231.

New partially degradable and bioactive acrylic bone cements based on starch blends and ceramic fillers. *Biomaterials*, 2002, 23(8), 1883-1895.

Cellulose acetate and sulfonated polysulfone blend ultrafiltration membranes. II. Pore statistics, molecular weight cutoff, and morphological studies. *J. Appl. Polym. Sci.*, 2002, 84(2), 430-444.

Comparison of the antioxidant properties of HYAFF-11p75, AQUACEL and hyaluronan towards reactive oxygen species in vitro. *Biomaterials*, 2002, 23(10):, 2255-2264.

Kinetics of release of particulate solutes incorporated in cellulosic polymer matrices as a function of solute solubility and polymer swellability. III. Moderately soluble solute. *J. Appl. Polym. Sci.*, 2002, 84(11), 2028-2039.

Hybrids of cellulose acetate and sol-gel silica: morphology, thermomechanical properties, water permeability, and biodegradation evaluation. *J. Appl. Polym. Sci.*, 2002, 84(12), 2196-2205.

Evaluation of cell behavior related to physico-chemical properties of polymeric membranes to be used in bioartificial organs. *Biomaterials*, 2002, 23(12), 2485-2497.

Synthesis and characterization of ion conducting cellulose esters with PEO side chains. *Polymer*, 2002, 43(16), 4453-4460.

Structure and physical properties of cellulose acetate/poly(L-lactide) blends. *J. Appl. Polym. Sci.*, 2002, 85(6), 1219-1226.

Processing and properties of extruded starch/polymer foams. *Polymer*, 2002, 43(22), 5935-5947.

Studies on dielectric relaxation and a.c. conductivity of cellulose acetate hydrogen phthalate-poly(vinylpyrrolidone) blends. *J. Appl. Polym. Sci.*, 2002, 86(7), 1702-1708.

Cellulose acetate and sulfonated polysulfone blend ultrafiltration membranes. I. Preparation and characterization. *J. Appl. Polym. Sci.*, 2002, 86(7), 1749-1761.

Spectral and electrochemical studies on blends of polyanilline and cellulose esters. *J. Appl. Polym. Sci.*, 2002, 86(9), 2182-2188.

Synthesis of novel adamantoyl cellulose using differently activated carboxylic acid derivatives. *Cellulose*, 2002, 9(2), 193-201.

Cellulose derivatives from cellulosic material isolated from Agave lecheguilla and fourcroydes. *Cellulose,* 2002, 9(2), 203-212.

Development of chiral stationary phases consisting of low-molecular weight cellulose derivatives covalently bonded by silica gel. *Cellulose*, 2002, 9(3/4), 263-269.

This analysis of historic publication activity dealing with CA/CE allows the following conclusions to be drawn:

1. The R&D effort in the CA/CE-field is not diminishing: There are more publications being produced today than before.
2. "D" is greater than "R" with 55% of current (last three years) publications being patents, and four times as many patents being written than journal articles (i.e., 650 versus 160 per year).
3. There is a growing R&D effort in Southeast Asia (especially Japan) that is manifested by choice of language and patents issued.
4. Most current journal articles involving CA and CE deal with separation science (membrane development), pharmaceuticals and controlled release, and general (bio)polymer aspects.

Analysis of the CA/CE Prospects Based on Technical Developments:

The development of new CA/CE-applications in the future is subject to many factors, some of which may relate to the nature of the resource and others to product characteristics. Additional factors may involve societal preferences, legislative actions, market forces, price structures, and many others. However, the prospects for future applications can be estimated on the basis of technical development efforts that examine new performance features; that expand the understanding of product characteristics; and that test the use of so-far-uncommon resource materials. In addition, CA may become the raw material for products resulting from secondary modifications; or CA technology may be adopted for new classes of products. It is therefore of interest to review the reports of scientists that have recently aimed at (a) developing new CA/CE performance characteristics, and (b) that are adopting acetylation technology to new resources or for the purpose of generating new products. Each of these areas has the potential of significantly influencing future CA/CE prospects. The *thermal characteristics* relate to the potential of processing CA/CE from the melt-state in a manner similar to conventional thermoplastics. The *solubility characteristics* dictate important processing parameters as well as phase behavior in polymer blends. *Molecular weight characteristics* may open novel avenues for incorporating cellulose and cellulose derivatives into copolymers in which biological activity is important. *Cellulose ethers* *with uniform and controlled substituent distributions* require production from homogeneous phase solution, and this may most conveniently and cost-effectively be achieved by the involvement of CA. *CA and CE- products with lower purity* may originate from resources that are less pure than the typical high α-cellulose dissolving pulp-grades. In fact, acetylation is not confined to pulps at all: even (solid) wood and wood particles/fibers have been subject to reaction with acetic anhydride (i.e., *acetylated wood products)* in efforts to modify wood properties and expand markets in applications that are currently at risk of replacement by non-wood materials.

The following sections will provide a description of selected R&D efforts in each of those areas.

A. Thermal Characteristics

Cellulose esters are solvent-soluble but not necessarily melt-processable polymers that have attracted much attention in a variety of end use applications (1, 2). It has long been recognized that reduction in melting point (T_m)[1], and melt processability, can be achieved by incorporating bulky ester substituents into the cellulose backbone (3-7). The T_m of cellulose triesters decreases rapidly as the ester substituent grows in size (Figure 1).

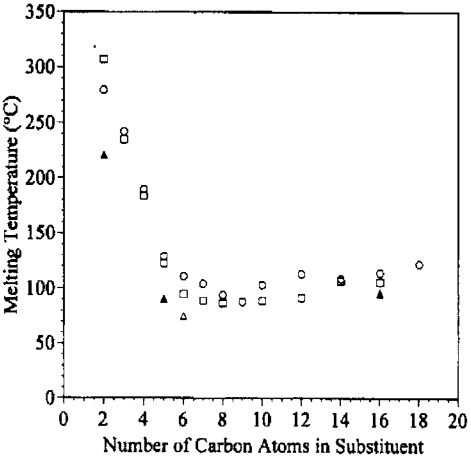

Fig. 1. The melting point of cellulose triesters in relation to the number of carbon atoms in the ester substituents. (From ref. 6 with data from ref. 4,5).

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[1] Virtually all cellulose esters have the ability to develop highly ordered ("crystalline") structures and display endothermic melt processes and exothermic crystallization events; however, since most cellulose esters have glass transition temperatures (T_g) that are within 5-40°C of their T_m (3), T_m and T_g are often combined in a "softening" process.

This lowering of T_m is dramatic between acetate (C2) and hexanoate (C6), and it remains more or less constant (or even rises slightly) for substituents having longer chains. This drop in T_m has been modeled as an internal plasticization process of CA with methylene-groups that follow the Fox relationship (7). Failure of waxy triesters (with acyl groups >C8) to follow this rule was explained with the formation of a liquid crystalline phase (8). Whereas the synthesis of mixed cellulose acetate propionates and butyrates, CAP and CAB, respectively, is practiced commercially, esters with longer chain (fatty) acids have so far remained laboratory curiosities. However, the synthesis of long chain cellulose esters with ester substituents larger than C4 is progressing towards practicality with the introduction of new catalysts (9, 10) and new modification techniques (11-17) (Figure 2). This creates the potential for the synthesis of mixed cellulose esters in which acetic acid groups are supplemented by longer chain fatty acids. By incorporating minor amounts of longer chain ester substituents into cellulose as mixed cellulose acetate esters, a rapid decline of T_g and T_m can be achieved (3, 18). In the case of cellulose acetate hexanoate (CAH), T_m can be lowered from greater than 300°C to circa 140°C as the hexanoate-content rises uniformly from a DS of 0 to 1. Higher amounts of hexanoate substituents produce a more gradual decline of T_m and T_g (3).

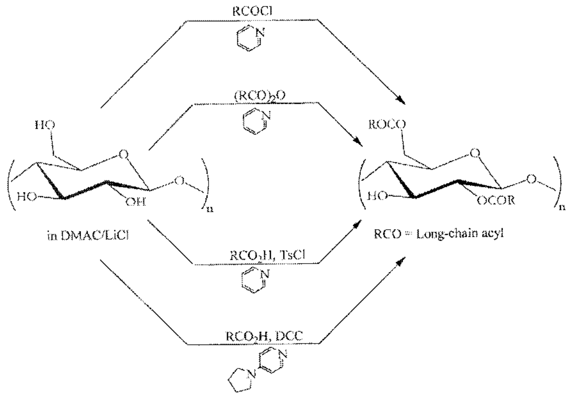

Fig. 2. Schematic reaction methods recently employed in mainly homogeneous derivatizations for the synthesis of long-chain cellulose esters (LCCE)
(According to Edgar et al., 2).

Melt viscosity is likewise sensitive to the presence of bulky ester substituents (9). A comparison of melt viscosities normalized to a molecular weight of 100,000 for different mixed esters is illustrated in Figure 3. Whereas the commercially available cellulose esters, CA, CAP and CAB, are virtually unprocessable by thermal means without the addition of large amounts of (external) plasticizers, cellulose acetate hexanoate (CAH) and cellulose acetate nonaoate (CAN) become melt processable without the addition of plasticizers (9). This is illustrated by comparing the melt viscosity (at 100 rad/s and 220°C) of a mixed CA ester having a DS of 0.7 of two different long chain ester substituents (normalized to a molecular weight of 100,000): In the case of propionate, this product has an estimated (by extrapolation) melt viscosity of 8,500 Pa.s, whereas the equivalent mixed ester with a nonaoate substituent has a melt viscosity of less than 1,000 Pa.s. Mixed CAP with a DS_P of 0.7 therefore requires 20% plasticizer before it can be melt processed (Figure 3) (9).

The implications of this finding are that minor amounts of long chain ester substituents improve the melt processability of CA dramatically. Such a substitution amounts to internal plasticization, and this adds a new dimension to CA products. The effective conversion of cellulose to melt processable cellulose ester products by substitution with long chain acids has been employed for preparing thermoplastic cellulose nanocomposites (19, 20).

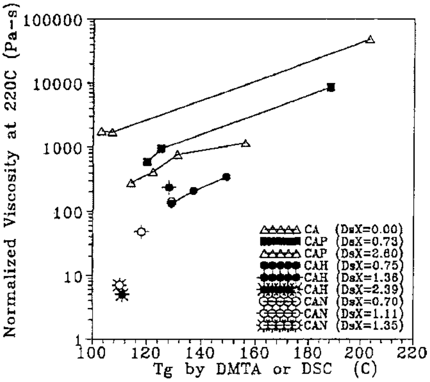

Fig. 3. Relationship between normalized (to a uniform molecular weight of 100,000 g^{-1}) melt viscosity at 220°C and the T_g (measured by DMTA or DSC) of cellulose esters. T_g varies in relation to substitution pattern and/or degree of (external) plasticization. Only the CA, CAP and CAH (DS = 0.70)-esters were plasticized. (From ref. 9).

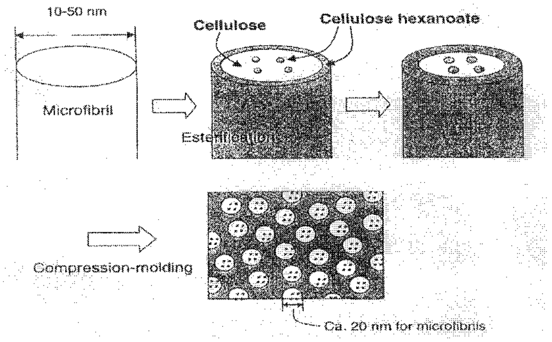

Fig. 4. Schematic illustration of the formation of cellulosic nanocomposites by the partial, heterogeneous esterification of microfibrils of pulp fibers with hexanoic anhydride. By conducting the reaction in a non-solvent for cellulose (cyclohexane), only the outsides of the microfibrils (and the lesser ordered fractions of the pulp fibers) are converted to melt-flowable cellulose ester while the core remains unchanged in cellulose I-crystalline state. (From ref. 19, 20).

This conversion is based on the partial derivatization of pulp fibers in heterogeneous state so as to leave crystalline cellulose intact (as cellulose I nano-crystals) (Fig. 4) and converting only the accessible cellulose fractions, those of low order and the surface layers of microfibrils, into melt flowable cellulose hexanoate esters. Pulp fibers modified in this way have been found to undergo melt flow when heated in a hot press, and they were shown to retain their original cellulose I crystalline order. Cellulose nano-crystals have cross sectional dimensions in the order of 10 to 50 nm, and they effectively reinforce a continuous cellulose hexanoate matrix.

B. Solubility Characteristics

The solubility of macromolecules is generally a function of their functionality, molecular size and molecular architecture. Polar groups, low molecular weight, branching and generally impeded crystallinity all contribute to improved solubility in polar solvents, especially water. While most cellulose esters are used in applications where water-solubility is undesirable, many processes that convert cellulose esters into end products employ solvents in some manner. Control over CA/CE solubility is therefore important for its future prospects. Unless cellulose esters become processable from the melt by adjusting thermal characteristics, they need to be processable from low-VOC solutions or suspensions.

Although cellulose esters can be dispersed in water, they are usually so nonpolar as to require unacceptably large amounts of organic solvents for the formation of stable dispersions. Their dispersibility needs to be raised by increasing CA/CE polarity. This strategy follows the widely accepted industrial practice of increasing cellulose triacetate (CTA)-solubility in such organic solvents as acetone and MEK by partial deacetylation. Although cellulose acetates can indeed be converted into fully water-soluble macromolecules by deacetylation to a DS of 0.5 to 1.0, this level of solubility would eliminate CA from many of its current markets. However, the preparation of high solids-dispersions in aqueous medium with the assistance of low-VOC organic solvents can be achieved via enhanced solubility characteristics in polar solvents.

The environmentally motivated demand for replacing organic solvents with water, especially in the coatings formulations that employ mixed CE products, has recently brought about a flurry of studies on CEs with improved dispersibility in aqueous formulations. The following principle strategies have been adopted to achieve this goal: (a) CEs with high hydroxy content and variable molecular weight; and (b) CEs with carboxyl groups. The latter strategy involves carboxylation by reaction with ozone; carboxylation by radical polymerization; carboxylation by reaction with dicarboxyclic anhydrides; or carboxylation by carboxymethylation.

These strategies have recently been reviewed by Edgar et al. (2), and they will be highlighted in the following.

CEs with high hydroxyl content: The relationship between dispersion stability and hydroxy content of cellulose esters has been well established (21). Several commercial products are available that contain between 0.3 and 1.27 hydroxy groups per anhydroglucose unit (Eastman's CAB-55-0.01 to 0.04). In addition, experimental cellulose esters with DS_{OH} 1.9 have been described (2). It is obvious that high-hydroxy CEs become increasingly interactive (swellable) with water unless they are formulated alongside other polymers, such as acrylic resin, melamine formaldehyde, or similar.

Carboxylated cellulose esters: The simplest method of introducing carboxy groups into cellulose involves the conversion of the primary methylol groups into carboxyl groups by reaction with ozone. With acid numbers in excess of 5, ozone-treated cellulose esters are commercially available (XAB® by Eastman). XABs with variable acid number and variable degree of depolymerization are described as highly dispersible coating agents that also function as rheology modifiers (22).

An alternative route to CE carboxylation involves functionalization with a carboxy group-containing substituent.

The introduction of acrylic acid, methacrylic acid, or both, by free radical grafting reaction which achieved in 1984 by Tobias (23). At a level of carboxylation corresponding to 8% acrylic acid by weight, the cellulose ester forms stable dispersions in water if formulated as anionic polymer with amines or ammonia.

The most obvious method of carboxylation, however, involves CE reaction with cyclic dicarboxylic anhydrides (Figure 5). Succinic, maleic, and phthalic anhydrides are the most common reagents. While phthalates are most common in pharmaceutical products, succinates are more common in coatings. A commercial product (CAB-SU 160 by Eastman) has an acid number of 60 corresponding to a DS_{SU} of 0.38 in addition to a DS_{OH} 0.58 (24). Succinated cellulose esters play a prominent role in automotive basecoats (25). They are purported to have attractive rheological properties in addition to dispersibility. While easy to make and highly dispersible, Edgar recently drew attention to the hydrolytic instability of these copolymers (26). A detailed kinetic analysis revealed that the succinyl groups are hydrolyzed at a considerably faster rate than other alkanoate groups under neutral or slightly alkaline conditions. In formulations with dimethylaminoethanol (DMEA), succinate hydrolysis was found to be first order in amine (i.e., the reaction was driven by amine concentration) (26). Succinate hydrolysis

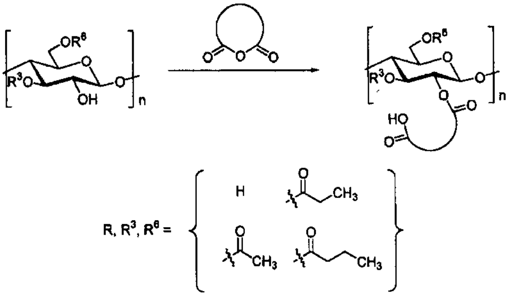

Fig. 5. Schematic carboxylation of cellulose esters by reaction with cyclic anhydrides. (According to Edgar et al., 2).

obviously results in rapid changes in dispersibility (i.e., dispersion stability) as well as viscosity.

By replacing succinic anhydride with maleic anhydride, mixed cellulose esters with maleate groups are formed that are somewhat more hydrolytically stable in addition to offering an attractive ethylenic functional group (27). The presence of the double bond results in radiation-curability when formulated with vinyl crosslinkers and a photoinitiator (27). Exposure of photocurable cellulose ester formulations to UV irradiation results in solvent and scratch resistant coatings.

Hydrolytic instability of cellulose esters carboxylated with dicarboxyclic anhydrides results in uncertainities especially if long storage times are encountered. This can be overcome if the carboxy-containing substituent is attached via an ether bridge. Carboxymethyl cellulose esters have recently been introduced in which the carboxyl groups is attached via such a hydrolytically stable bond (28, 29). CM-CAB is produced by esterifying carboxymethyl cellulose (CMC) with acidic and butyric anhydrides (or alternatively, with propionic anhydride) (2). A carboxymethylated cellulose ester is commercially available with a DS_{CM} 0.3, DS_{BU} 1.4 to 1.5 and DS_{AC} 0.3 to 0.55 (CMCAB-641-05 by Eastman Chemical Company). The commercial CMCCAB is recognized for its beneficial effects on the drying behavior of automotive basecoats, and the orientation of metal flakes in metallic paints (30, 31). The commercial CM cellulose ester product is said to hold promise in wood coatings, leather coatings and pigment dispersions (32).

A less obvious method of cellulose ester carboxylation has been introduced by Edgar et al. (33, 34) that is based on the acetoacetylation of cellulose esters with diketene.

In summary, the highly appealing film forming properties of cellulose esters that commenced with the use of cellulose nitrates for lacquers and motion picture films, and that has continued to be the basis of many cellulose ester businesses, can survive the switch from organic solvent- to water-based processing options. A modest adaptation to water based coating systems, and dispersibility in low-VOC, high-solids formulations, is generally achieved by the addition of hydroxy or carboxy functionality via either backbone modification or functionalization/derivatization.

C. Specialty Cellulose Ethers

The synthesis of cellulose ethers normally involves the reaction of wood pulp (or cotton linters) with strong alkali in heterogeneous phase (35). This reaction produces materials (in solid state) that have a non-uniform distribution of substituents reflective of the differential reactivity of hydroxy groups in the ordered *vs.* the disordered state. In cases where uniformity of substituent distribution is required, modification in homogeneous phase becomes necessary (36-38). While several solvent systems for homogeneous phase reactions of cellulose in alkaline medium have recently been described (16, 17), CA may offer a more convenient and cost-effective alternative for the uniform introduction of ether groups. Kondo and Gray have demonstrated that CA supports homogeneous phase conditions during alkaline etherification in DMSO while simultaneously leading to a product free of acetyl groups with virtually no loss of molecular weight (39). The universal problem of cellulose insolubility (at least in most industrially-acceptable solvents), which results in a non-uniform substituent distribution during cellulose modification, can thereby be prevented Since variations in substituent distribution have recently been revealed to play an important role on properties (37, 38, 40), CA may have a future as resource for (low-molecular weight) cellulose ethers with special property features.

D. Molecular Weight Characteristics and Oligomer Generation

Cellulose acetate is usually employed for the production of films or fibers. These applications require CA of high purity and high molecular weight. In the last two or three decades it has, however, been demonstrated that polymers with mixed molecular constituents, random copolymers and block copolymers, can have properties with widely different ("tailorable" or "engineerable") characteristics (41). As part of a copolymer, cellulose may potentially contribute properties with unique characteristics, such as biodegradability, biocompatibility, solubility and swellability (gel forming ability), crystallinity, etc. Several of these characteristics are so unique that man-made materials cannot achieve them. CA and cellulose esters in general are best qualified for the synthesis of CA or even cellulose (following saponification)-containing block copolymers (42). “Glycosylation” is a common attribute of enzymes and biocompatible molecules that can as well be employed for the modification of many small and large

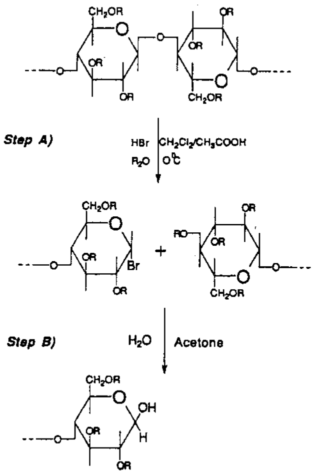

Fig. 6. Schematic depolymerization reaction of cellulose esters under esterification conditions according to Mezger and Cantow. The reaction produces OH-terminated, mono-functional oligomers with DP between 5 and 50. (From ref. 43)

molecular weight substances. Cellulose esters are amenable to depolymerization into mono-functional oligomeric segments in good yield and with targeted size. Using oligomeric cellulose ester segments for the synthesis of cellulose-containing block copolymers has previously been advocated by Mezger and Cantow (42) and Glasser et al. (43, 44).

In brief, the synthesis of mono-functional oligomeric cellulose ester segments of predetermined size is based on the depolymerization of CA/CE with hydrogen halides (most commonly bromide) to fully substituted cellulose esters under esterification conditions (42-44). The general reaction scheme is given in Fig. 6. It had been pointed out that this hydrolysis works best with cellulose triproprionate and cellulose tributyrate (CTB), or with mixed cellulose triesters (42, 43). Cellulose acetate or commercial cellulose propionate (with residual OH groups) proved less amenable to oligomer production (42, 44). Recently, however, Arndt et al. have modified this procedure to also succeed with cellulose acetates by employing pivaloic acid for depolymerization (i.e., pivaloylysis) (45). The consequence of this development is that the production of oligomeric cellulose ester segments with predetermined structure and molecular weight becomes practical.

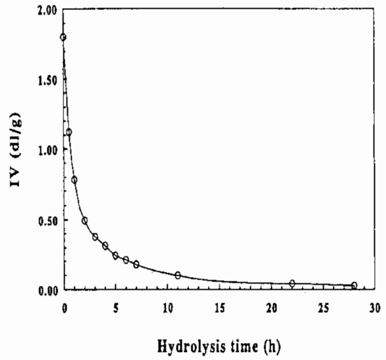

Fig. 7. Relationship between intrinsic viscosity (IV) and hydrolysis time for the depolymerization reaction of cellulose esters of Fig. 5. (From ref. 43).

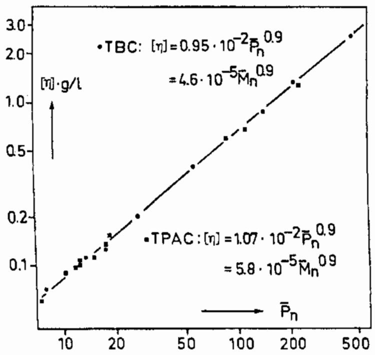

Fig. 8. Relationship between intrinsic viscosity ([η]) and degree of poly-merization (P_n) of cellulose tributyrates (TBC) and cellulose tripropionate acetates (TPAC) of different P_n. The oligomers were purified by fractionation. (From ref. 42).

The depolymerization reaction proceeds in a matter of hours, and it can conveniently be followed via intrinsic viscosity measurement (Fig.7, 8)(42, 43). The products of this reaction are mixtures of cellulose ester oligomers with polydispersities (M_w/M_n) ranging between 1.3 and 1.9. Fractionation into individual segments is said to be possible by preparative or analytical liquid chromatography for oligomers with low or high molecular weight, respectively (45). Arndt et al. have isolated a series of oligomeric CA segments in yields ranging between 3.7 (for the octanomer) and 44% (for the dimer) (45).

In summary, acetolysis or pivaloylysis are useful methods for the synthesis of oligomeric cellulose ester segments with DP-values ranging between two and fifty. These segments can be generated with mono- and possibly difunctional character, and they can be usefully employed in the synthesis of block copolymers (46-48) and glycosylated substances. It is anticipated that many polymeric substances for use especially in biomaterials stand to benefit from the presence of cellulose ester or cellulose (after saponification)-components. This approach opens new opportunities for the involvement of CA products in novel applications.

E. Acetylation of Lower Grade Pulps and Wood

The conversion of chemical and mechanical pulps of grades lower than are customarily employed for the manufacture of CA/CE products, of pulps with lower α-cellulose contents, of unbleached pulps, and even of wood, has been the subject of numerous studies (49-54). The conversion of wood and (unbleached) pulps into mixtures of soluble cellulose and lignin acetates is normally achieved by the involvement of catalysts or catalytic pretreatment protocols qualified to disrupt the lignin-carbohydrate complex. The hydrolysis of the lignin-carbohydrate copolymer bonds renders the individual wood components reactive, soluble and eventually separable. Pretreatment regimes have included mechanical pulping and steam explosion. The simultaneous acetylation of all three polymer components of wood produces a mixture that can conveniently be separated into individual polymers by solvent precipitation.

F. Acetylated Wood and Wood Fibers

The acetylation of solid wood, wood particles ("strands", etc.), and wood fibers has experienced significant interest in recent years (55-59). Acetylating wood or unbleached pulp does not necessarily and automatically result in the formation of thermoplastic or solvent-soluble polymers. The reaction may conveniently be limited to the most highly accessible regions of the biocomposite that represents wood. By limiting the acetylation reaction of wood (or pulps) to the readily accessible portions, products with weight gains in the order of 18-24% can be formed that have dramatically different material

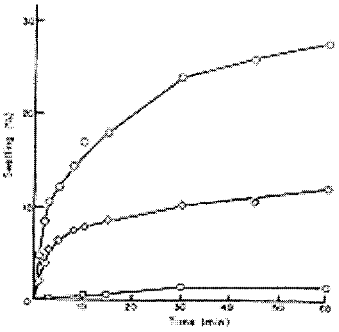

Fig. 9. The consequence of wood modification on swelling of flakeboards in water. Modification by reaction with butylenes oxide (middle) and acetic anhydride (bottom) as compared to unmodified wood (top). Weight gain of wood by acetylation was 24.4% (According to ref. 55).

characteristics than their unmodified counterparts (Fig. 9). Optical, biological and dimensional stability is achieved that creates new opportunities for the production of novel wood-based materials involving the adoption of acetylation technologies to wood fibers, wood particles (flake, strand, etc.) and solid wood. Extensive studies have demonstrated the virtues of these materials, and the technology has been pursued to pilot and production scale.

Conclusions

Cellulose acetates are becoming a group of mature cellulose derivatives with commodity character. Interest in their manufacture is rising in Southeast Asia, whereas the European, North American, and Japanese R&D efforts are progressively focusing on second-generation derivatives. CA is becoming a resource for the generation of products with high-tech character by being modified to serve a major role in the separation, pharmaceutical/controlled release, and (bio)polymer fields. Preparation for this service involves modification of the thermal, solubility and molecular size parameters. Additional opportunities are perceived in the application of acetylation technology to lower grade pulps for the generation of mixed (cellulose/lignin), soluble and thermoplastic esters; and to solid wood products with superior dimensional stability.

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