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Modification of Cellulose Acetate by Reactive Processing – Chemistry, Structure and Properties

Ph.D. Thesis

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1. Introduction

The interest in polymers from natural resources has been increasing continuously in recent years. Wood flour and natural fibers are used extensively for the reinforcement of commodity polymers and all wood composites are also prepared with the plasticization of cellulose. Cellulose, its derivatives, and starch are applied for various purposes from tissue engineering to matrices of composites. Natural polymers have numerous advantages. They are available in large quantities, cheap, come from renewable resources, and usually they are also biologically degradable, which is advantageous in some applications. On the other hand, these polymers have some disadvantages as well. Properties vary with the source of origin and the time of the harvest, the polymers may adsorb considerable quantities of water, what changes their properties, and they are sensitive to heat. However, one of the major drawbacks of natural polymers is the rigidity of their chains. The D-glucose rings of the main chain of both cellulose and starch, as well as the strong hydrogen bonds among their hydroxyl groups make the processing of these polymers difficult. The traditional technologies of thermoplastic polymers cannot be used for their processing without the modification of the process or the material.

The properties and processability of natural polymers can be improved by derivatization and plasticization. Cellulose acetate (CA) is a derivative often used in various applications, but its high viscosity and elevated glass transition temperature does not allow its processing as a thermoplastic material. In order to modify properties and facilitate processing, cellulose acetate is often plasticized by various aliphatic and aromatic esters. External plasticizers easily migrate from the polymer leading to environmental and health hazard, thus CA is plasticized internally, i.e. long chain molecules are grafted to cellulose acetate more and more often to achieve the required properties.

Recently several attempts have been made to graft aliphatic esters to cellulose acetate with various degree of success. Usually cellulose acetate with a degree of substitution of 2.5 is used in these attempts, since this polymer is available in the market. However, both chemical modification and biodegradability depend very much on the degree of substitution, they become more difficult with increasing acetylation of cellulose. Modification was carried out both in solution and melt under a wide variety of conditions. Often external plasticizers were used to assist processing and homogenization, and to improve the efficiency of grafting. The relative extent of

external and internal plasticization depended on the composition of the reaction mixture and on reaction conditions. Usually a catalyst was also used to help grafting.

The goal of my work was to modify cellulose acetate having different degree of substitution (DS = 1.7, 2.1) with caprolactone by reactive processing and to characterize the product. Grafting efficiency increased with increasing temperature and time when we used cellulose acetate with a degree of 2.1. The extent of grafting could be estimated from the amount of material extracted from the samples by toluene and by FTIR analysis, from the relative intensity of $-\text{CH}_2-$ and $-\text{CH}_3$ vibrations. The amount of polycaprolactone homopolymer was relative low at the end of the reaction; the efficiency of grafting was good. Although high temperature and long reaction time favored grafting, considerable degradation of the product occurred under these conditions. Quantitative analysis showed that the average length of grafted oligomeric caprolactone chains was around 3 monomer units. The chains attached to the CA backbone internally plasticized the polymer leading to a considerable decrease of its glass transition temperature.

The studies on cellulose acetate with different degrees of substitution showed that grafting proceeds slower than homopolymerization under most conditions used by us and contrary to our expectations, a larger number of free hydroxyls, i.e. the use of CA with a degree of substitution of 1.7, did not promote grafting at all. Quite the opposite happened, homopolymerization became even more pronounced than in the case of cellulose acetate with DS = 2.1, and high degree of grafting was achieved only at very high temperatures and long times. The length of grafted chains increased with increasing reaction time and temperature, but it was always much shorter than chain lengths obtained in solution polymerization. Changes in the degree of substitution during grafting were small, which, together with other evidence, indicated again that homopolymerization proceeds easier than grafting. Taking into account these observations, in the next step we decided to modify cellulose acetate with prepolymerized, oligomeric polycaprolactone in order to facilitate grafting and to accelerate the reaction. Caprolactone was polymerized for various times in the presence of alkyl tin catalyst to produce the oligomers and two products with slightly different molecular weights were used for the modification of CA by reactive processing. Results indicated the limited miscibility of PCL homopolymer with cellulose acetate.

In the early stages of our study, we focused our attention mainly on the efficiency of grafting and on the chemical structure of the copolymer ob-

tained. We observed that grafting of caprolactone to cellulose acetate changes the properties of the polymer as expected, but we did not analyze structure-property correlations in detail. As a consequence, later the experiments were directed towards the more detailed study of relaxation transitions, mechanical properties, plasticization, and generally towards structure-property correlations. As mentioned before, cellulose acetate consists of rigid chains with a relatively high glass transition temperature. The mobility of the chains is further decreased by hydrogen bonding, the number of which depends on the degree of substitution. A wide range is given for the glass transition temperature of cellulose acetate from 150 to about 250 °C. Obviously, the actual value obtained for a given polymer depends on several factors including the degree of substitution, water content, the conditions of the measurement, etc. The number of transitions and their assignment to structural units of cellulose acetate are rather confusing in the literature. Usually three to five peaks or transitions are detected on the dynamic mechanical spectra of these materials, and they are assigned to glass transition, to the movement of a part of the main chain, to that of glucose rings, to groups associated with water and to adsorbed water. Some of these transitions were assigned to grafted chains in CA modified with caprolactone. During our investigations, we detected several transitions on the dynamic mechanical spectra of the modified polymer, but a detailed study of the assignment of transitions published in papers revealed some contradictions and they were not always consistent with our observations. As a consequence, our main goals in this stage were the more detailed analysis of the relaxation transitions of modified cellulose acetate, and those of natural polymers generally, the identification of relaxation transitions, the investigation of the effect of external and internal plasticization on these processes, and the determination of structure-property correlations.

One of the most frequently used approaches to characterize modified cellulose acetate is thermal analysis. DSC and DMTA are widely applied to characterize its molecular and supermolecular structure, to identify transitions and to assign them to various elements of the structure. We recorded DMTA spectra of our modified cellulose acetate samples and analyzed those spectra. During the analysis we focused our attention mainly onto relaxation transitions of the main chain, tried to identify the number and location of the transitions on the temperature scale and to assign them to structural units. We compared the results obtained on grafted cellulose acetate to other cellulose polymers and tried to draw conclusions of general validity about molecular motions in these materials. Several groups used DSC analysis for the same purpose and they succeeded in identifying even

the transitions of grafted side chains. Not only the glass transition temperature, but also the melting of grafted aliphatic polyester chains could be detected and identified in some cases. In the last stage of the research we carried out both DMTA and DSC measurements of cellulose acetate grafted with caprolactone by reactive processing. In the study we tried to assign the detected transitions to the structure of the modified polymer both in the recorded DMTA and DSC traces. We compared our results to those published previously and tried to resolve some of the contradictions which we encountered during analysis.

The large number of experimental results obtained in the research supplied useful information and led to several conclusions, which can be used during further research and development on the modification of cellulose acetate, but also for the preparation of biologically degradable polymers in a wider scope. Nevertheless, quite a few questions remained open in the various parts of the study, their explanation needs further experiments. Research continues in this field at the Laboratory and we hope to proceed successfully further along the way indicated by this thesis.

2. Experimental

The cellulose acetate used in my experiments was supplied by Daicel Chemical Industries Ltd. and it had a degree of substitution of 1.7 and 2.1. ϵ -caprolactone was purchased from Sigma Aldrich. The reactions were carried out in a Brabender W 50 EH internal mixer at 50 ml charge volume. The caprolactone content was 45 wt% in each reaction, and 0.1 wt% catalyst was added to the reaction mixture. Reaction temperature changed between 120 and 220 °C, while reaction time varied between 5 and 45 min.

The composition and molecular weight of the product was determined by size exclusion chromatography (SEC), NMR and MALDI spectroscopy. SEC measurements were done in tetrahydrofurane using a Waters 201 chromatograph with 5 UltraStyragel columns. Polystyrene samples of narrow molecular weight were used for calibration. ^1H NMR spectroscopy was carried out using a Varian Unity Inova 400 MHz apparatus in deuterated DMSO at 40 °C. The concentration of the samples was 10 mg/ml. The MALDI MS measurements were performed with a Bruker BIFLEX III mass spectrometer (Bremen, Germany) equipped with a TOF analyzer. In all cases 19 kV total acceleration voltage was used with a 3 kV

pulse (extraction) voltage and with a delay time of 300 ns. An LSI type nitrogen laser (337 nm, 3 ns pulse width) operating at 2 Hz was used to produce laser desorption and 500 shots were summed. The matrix was dissolved in methanol at a concentration range of 20 mg/mL. The materials were dissolved in methanol at concentrations of 5 mg/mL. The ions were detected with a multi-channel plate (MCP) detector at the voltage of 1.65 kV. The spectra were externally calibrated with poly(ethylene glycol) (PEG) (Mn = 1450 g/mol, Mw/Mn = 1.02). A volume of 0.5 μl of these solutions was deposited onto the sample plate (stainless steel), and allowed to air-dry. 10 μm thick films were cast from the samples for FTIR analysis to describe grafting efficiency. Spectra were recorded using a Mattson Galaxy 3020 apparatus in the wavelength range of 4000 and 400 cm^{-1} by 2 cm^{-1} resolution in 16 scans. The color of the samples which could describe their degradation was determined with a Hunterlab Colorquest 45/0 apparatus on 1 mm thick compression molded plates. Standard yellowness index (YI) was calculated from color coordinates. Mechanical properties were characterized by tensile measurements. Dog-bone type specimens (115x10x1 mm) were cut from 1 mm thick plates compression molded at 160 $^{\circ}\text{C}$ using a Fontijne SRA 100 machine. Young's modulus was determined at 0.5 mm/min cross-head speed, while tensile strength and elongation-at-break values were derived from stress vs. strain curves recorded at 5 mm/min cross-head speed at a gauge length of 60 mm. To determine the relaxation transitions the samples were subjected also to dynamic mechanical analysis carried out using a Polymer Labs MkII DMTA apparatus at 1 Hz frequency and 2 $^{\circ}\text{C}$ heating rate in the temperature range of -100 and +200 $^{\circ}\text{C}$. DSC measurements were done using a Perkin Elmer Diamond DSC apparatus equipped with a cryofil cooling system. Two heating and a cooling run were carried out on 5 mg samples with 10 $^{\circ}\text{Cmin}^{-1}$ heating and cooling rates, respectively. The presence of polycaprolactone homopolymer was verified by XRD using a Phillips PW 1830/PW 1050 equipment with $\text{CuK}\alpha$ radiation at 40 kV and 35 mA anode excitation, between 4 and 35 2θ angles.

3. New scientific results

1. We successfully grafted polycaprolactone chains to cellulose acetate by reactive processing. We found that homopolymerization proceeds faster than grafting under mild conditions. Efficient grafting requires high temperature and long time, but considerable degradation of cellulose acetate takes place under such conditions.

2. We established for the first time, that contrary to expectations, grafting of caprolactone to cellulose acetate with larger degree of substitution is easier than to a polymer with larger number of free -OH groups. The possible reason of this behavior is that a larger number of free hydroxyls may form more hydrogen bridges, which can hinder grafting reactions.
3. We prepared oligomers and grafted them to cellulose acetate with a degree of substitution of 1.7. We found that a few long chains modified polymer properties in a large extent, but the relative ratio of chemical reactions (homopolymerization vs. grafting) and the kinetics of the reactions were not modified substantially.
4. We characterized the structure of cellulose acetate modified chemically with caprolactone by NMR spectroscopy. In accordance with other results we established that changes in the degree of substitution are relatively small, only a few caprolactone chains are attached to cellulose acetate. Chain length increases with reaction temperature and time, but remains much shorter than the average length of chains attached to CA in solution polymerization. PLC chains are coupled mostly to positions 2 and 6 of the glucose ring.
5. We developed a new technique for the characterization of cellulose acetate modified with long aliphatic chains. The relative ratio of the absorbance of the -CH₂- and -CH₃ groups appearing at 2943 and 1270 cm⁻¹, respectively, in the FTIR spectra recorded on cast films is in very close correlation with the amount of grafted polymer chains. The validity of the approach and the correlation was verified with several methods (NMR, extraction).
6. By the analysis of the dynamic mechanical spectrum of cellulose acetate and also that of other natural polymers with similar structure we determined three main relaxation transitions and assigned them to segments (α), to smaller structural units in the main chain, probably individual glucose rings (β), and to hydroxyl or hydroxymethylene groups (γ). Unlike others, we could not identify the transitions of grafted caprolactone either by DMTA or DSC.
7. Similarly to others we found that plasticization leads to a considerable decrease in the stiffness and strength of cellulose acetate. How-

ever, we called attention for the first time to the fact that external plasticization creates a larger number of small structural units, but the external plasticizer is less efficient in the decrease of stiffness than grafted polycaprolactone chains. Internal plasticization is more advantageous because it leads to higher flexibility at larger strength than external plasticization.

8. We established that oligomeric PCL homopolymer is not miscible with cellulose acetate and migrates to the surface of the polymer. Exuded PCL oligomers crystallize on the surface of samples and can be removed very easily, which is very disadvantageous and must be avoided in practical applications.

4. Publications

4.1. The thesis is based on following papers

1. Klébert Sz., Pukánszky B.: Műanyag hulladékok újrahaznosítási lehetőségei és a biológiailag lebomló műanyagok, *Műanyag- és gumipari Évkönyv* **2**, 35-39, (2004)
2. Vidéki, B., Klébert, Sz., Pukánszky, B., Grafting of caprolacton to cellulose acetate by reactive processing, *Eur. Polym. J.* **41**, 1699-1707 (2005)
3. Vidéki, B., Klébert, Sz., Pukánszky, B., External and Internal Plasticization of Cellulose Acetate with Caprolactone: Structure and Properties, *J. Polym. Sci. Polym. Phys. B.* **45**, 873-883 (2007)
4. Klébert Sz., Pukánszky B.: Cellulóz-acetát külső és belső lágyítása ϵ -kaprolaktonnal – szerkezet és tulajdonság összefüggések, *Műanyag és Gumi*, **44**, 52-56, (2007)
5. Számel, Gy., Klébert, Sz., Sajó, I., Pukánszky B., Thermal Analysis of Cellulose Acetate Modified with Caprolactone, accepted in *J. Therm. Anal. Calorim.*
6. Számel, Gy., Klébert, Sz., Domján, A., Pukánszky, B., Molecular Structure and Properties of Cellulose Acetate Chemically Modified with Caprolactone, accepted in *Eur. Polym. J.*

7. Klébert, Sz., Nagy L., Domján, A., Pukánszky, B., Modification of Cellulose Acetate with Oligomeric Polycaprolactone by Reactive Processing: Efficiency, Compatibility, Properties, before submission

4.2. Other publications

1. Urbánszki, K., Csiszár, E., Szakács, Gy., Klébert, Sz., Enzimes pamutelőkészítés: Celluláz, pektináz és xilanáz enzimek hatása írtelenített pamutszövet tulajdonságaira, *Magyar Textiltechnika*, **LIII**, 43-46, (2001)
2. Klébert, Sz., Juhász, P., Szulmanné Binet, M., Belina, K.: PET hulladék módosítási lehetőségeinek tanulmányozása, *Műanyag és Gumi*, **38**, 182-185, (2001)

4.3. Conference Presentations

1. Klébert, Sz., Belina, K.: PET hulladék módosítási lehetőségeinek tanulmányozása, *Műanyag kollokvium'99*, Lillafüred, 1999 október 7-8.
2. Klébert, Sz., Csiszár, E.: A cellulóz, mint lehetséges nyersanyagforrás a biológiailag lebontható polimerek előállításában, *MTA Műanyag Munkabizottság és a Debreceni Akadémiai Bizottság Polimer Munka-bizottsága együttes ülése*, Debrecen, 2000. november 9.
3. Klébert, Sz., Vidéki, B., Pukánszky, B.: Internal plastification of cellulose acetate for improved processability, *11th Rolduc Polymer Meeting*, May 5-8 2002, Kerkrade, The Netherlands (poster)
4. Klébert, Sz., Vidéki, B., Pukánszky, B.: Internal plastification of cellulose acetate to produce biodegradable polymer, *MODEST 2002 Conference*, 30 June – 4 July 2002 Budapest, Hungary (poster)
5. Klébert, Sz., Vidéki, B., Pukánszky, B.: Módosított cellulóz-acetát, mint potenciális biológiailag lebomló műanyag, *Kutatóközponti Tudományos Napok*, 2003. május 28-29.

6. Klébert, Sz., Vidéki, B., Pukánszky, B.: Módosított cellulóz-acetát, mint potenciális biológiailag lebomló műanyag, *BME Vegyészmérnöki kar Doktoráns konferencia*, 2003. november 26.
7. Bagdi, K., Müller, P., Klébert, Sz., Pukánszky, B.: Lágyított keményítő és kompozitjainak szerkezete és tulajdonságai, *MTA Anyagtudományi és Technológiai Komplex Bizottsága, MTA Műanyag, valamint Természetes Polimerek Munkabizottságai, DAB Polimer Munkabizottsága, együttes tudományos ülése*, Debrecen, 2004. április 6.
8. Bagdi, K., Müller, P., Klébert, Sz., Pukánszky, B.: Termoplasztikus keményítő és kompozitjainak tulajdonságai és szerkezetük vizsgálata, *MTA KK AKI, Kutatóközponti Tudományos Napok*, 2004. június 2-3.
9. Klébert, Sz., Pukánszky, B.: Plasticization of cellulose and its derivatives to produce biodegradable plastic, *5th International Symposium on "Materials made from Renewable Resources"*, *naro.tech 2005*, Messe Erfurt, Germany, 1st – 2nd September 2005. (poster)
10. Müller, P., Bagdi, K., Klébert, Sz., Pukánszky, B.: Properties and structure of thermoplastic starch and its composites, *5th International Symposium on "Materials made from Renewable Resources"*, *naro.tech 2005*, Messe Erfurt, Germany, 1st – 2nd September 2005. (poster)
11. Klébert, Sz., Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: Interfacial interactions in polypropylene/wood flour composites, *5th International Symposium on "Materials made from Renewable Resources"*, *naro.tech 2005*, Messe Erfurt, Germany, 1st – 2nd September 2005.
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13. Klébert, Sz., Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: *Wood flour reinforced PP composites*, *International Scientific Advisory Board, MTA KK AKI*, Budapest, 2006. június 7-8.
14. Klébert, Sz., Pukánszky, B.: Structure and properties of internally plasticized cellulose acetate, *1st European Chemistry Congress*, 27-31 August 2006. Budapest, Hungary

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