Properties and Applications of Cellulose Acetate

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Summary: Cellulose acetate is one of the most important esters of cellulose. Depending on the way it has been processed cellulose acetate can be used for great varies of applications (e.g. for films, membranes or fibers). The properties of the applied cellulose acetates are very important for these applications. A special field for using cellulose acetate is the synthesis of porous, spherical particles, so called cellulose beads. Different types of technical cellulose acetates were used and their ability to form such cellulose beads was characterized. First the different types of cellulose acetates were characterized by means of solubility; turbidity and degree of substitution. In addition the molar mass and the distribution of substituents along the polymeric chain were analyzed. Next, the cellulose beads were synthesized within an emulsion process using these different cellulose acetates. Then the properties (particle size, porosity, morphology) of the cellulose beads were determined. Finally, the relationship between the characteristic of cellulose acetates and properties of cellulose beads was investigated.

Keywords: cellulose acetate; cellulose beads; molar mass distribution; particle size distribution; structure-property relations

Introduction

Cellulose acetates (CA) are important esters of cellulose, which are obtained by reaction of cellulose with acetic anhydride and acetic acid in the presence of sulfuric acid.

The most common form of cellulose acetate fiber has an acetate group on approximately 2–2.5 of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as "acetate".

The solubility of cellulose acetate depends among other things on the degree of substitution (DS), CA with DS of 2 – 2.5 is soluble e. g. in acetone, dioxane and methyl acetate; higher acetylated types are soluble in dichloromethane. Acetic acid is in generally a good solvent for cellulose acetates with DS greater than 0.8.

Depending on its processing, cellulose acetate can be used for different applications. Films were made from cellulose triacetate, membranes and fibers from cellulose 2–2.5-acetate.

Cellulose-2.5-acetate is also a raw material for making so called cellulose beads. Cellulose beads are regenerated cellulose of the modification cellulose II. They are porous, spherical molds and they have a higher specific surface as the fibrous cellulose.

For the synthesis of cellulose beads seven technical cellulose acetates from different manufacturer were used and compared. All these acetates have a DS of about 2.5. In the following text the samples are referred to CA 1 to CA 7.

At first, the solubility and turbidity, the degree of substitution and the partial degrees of substitution determined by NMR and the molar mass of the available acetates were evaluated. Next the substituent distribution

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was measured using a new way to characterize the cellulose acetates.

The goal of this paper is to show the coherence between the properties of the cellulose acetates as cellulose derivate and the wide range of application. The focus of these investigations was to find a cellulose acetate which is especially suited to produce cellulose beads. Bead cellulose is cellulose with spherical shaped particles. The beads have particle diameters in a range of 1–1000 μm; they are hydrophilic, porous and have a high specific surface and good swelling properties. Bead cellulose offers good possibilities for functionalisation, for instance it is used as a special adsorbent or for controlled releasing of active agents.

To produce cellulose beads cellulose or a cellulose derivative is dissolved. The creation of spherical particles occurs by dispersion. Afterwards the particles are reinforced and cleaned. Then the cellulose is regenerated as beads.

The synthesis of cellulose beads using the samples CA 1 to CA 7 was carried out under the same conditions; all products were characterized by measurement of particle size and Scanning electron microscopy (SEM).

Properties of Cellulose Acetate

Solubility and Turbidity

At first the solubility of cellulose acetates was investigated. For that purpose solutions with 1% of the respective cellulose acetate were used. All tested cellulose acetates were soluble in acetone and in a dichloromethane-methanol-mixture (ratio = 80:20). The CA-solutions gave different turbidity in acetone. Only the CA 3 was soluble in ethyl acetate.

After the optical evaluation of solubility the turbidity was measured. Turbidity is the decrease in the transparency of a liquid caused by the presence of unsolved substances. The turbidity of the dissolved cellulose acetates was determined by nephelometric measurement, i.e. by determination of the scattered radiation at an angle of 90°. The solution turbidity was measured with a nephelometer 2100AN (Hach, Loveland, Colorado, USA).

All values are given in Nephelometric turbidity unit (NTU). As already noticed during the investigations of solubility there are broad differences between the turbidity of the samples. Samples CA 1 and CA 4 had the highest turbidity in acetone and in an ethyl acetate–methanol-mixture (ratio = 100:17.5). The results of these measurements are summarized in Table 1 and are exemplary shown in Figure 1.

It is in evidence that the different cellulose acetates samples differs in solubility as well as in turbidity. Five of the investigated cellulose acetates have low turbidity in ethyl acetate–methanol; they are clear soluble in this solvent. In contrast two samples are characterized by high turbidity of the solutions.

Molar Mass of the Cellulose Acetates

The distribution of molar mass was determined using the size exclusion chromatography (SEC). This method was described

Table 1.
Turbidity of cellulose acetates in different solvents given in NTU.

Sample	Solvents			
	Acetone	Dichloromethane- methanol (80:20)	Ethyl acetate	Ethyl acetate - methanol (100:17.5)
CA 1	67.7	3.7		370
CA 2	10.7	1.4		48
CA 3	24.8	4.1	84.5	87
CA 4	43.9	6.3		294
CA 5	5.4	0.9		39
CA 6	5.8	1.2		38
CA 7	2.8	1.1		33

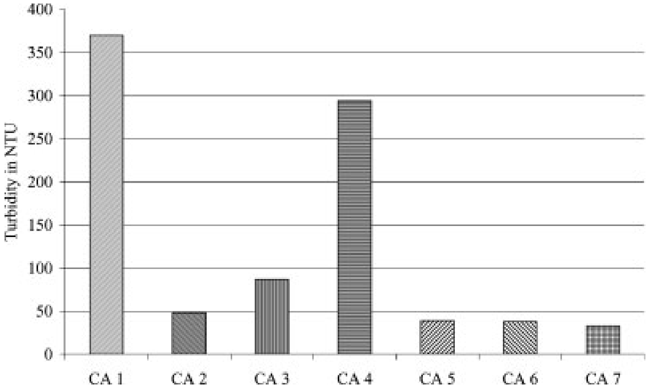

Figure 1.
Turbidity of cellulose acetates measured in an ethyl acetate-methanol mixture (ratio = 100:17.5) in NTU.

by Fischer et al.[1,2] All samples show similar graphs; the accurate parameters for the molecular mass (Mw) and the average numerical molar mass (Mn) are given in Table 2.

There are two groups of samples, CA 1 to CA 3 have a molar mass over 100,000, Mw of the other samples is lower than 100,000.

In Figure 2 the distribution of molecular weight is shown for three different samples. The distribution is similar for all samples.

Distribution of Substituents

The distribution of substituents along the polymer chain is an important issue for partial substituted cellulose derivatives as cellulose-2.5-acetate. It was measured by SEC including a multi angle laser light scattering and mass detection for measurement UV-active groups. The free OH-groups of cellulose-2.5-acetates have to be changed into UV-active groups under polymer analogous reaction conditions as shown in Figure 3.[3]

Table 2.
Molar mass parameters of different cellulose-2.5-acetates.

Sample	Mw	Mn	Mw:Mn
CA 1	136,100	88,300	1.54
CA 2	107,300	73,165	1.47
CA 3	111,100	65,800	1.69
CA 4	79,630	39,730	2.00
CA 5	86,400	51,140	1.69
CA 6	96,560	59,800	1.61
CA 7	83,580	50,280	1.66

By size exclusion chromatography using a multi-detection system it is possible to determine the introduced groups situated along the cellulose chain, whereas the light scattering detector and R1-detector are used for calculation of the molecular mass per slight, and an UV-detector for determining the introduced UV active substituents in relation on the molecular mass. From these measurements the DS of the acetates were calculated using a special developed program.[4]

In Figure 4 the molecular weight distribution and the degree of substitution for some selected samples are shown. The substituents of the samples CA 2 and CA 5 are evenly distributed; the distribution of substituents along the polymer chain of sample CA 6 is unbalanced. As already shown in Table 2 the sample CA 2 has a high molecular weight, sample CA 5 has a low one; the DS *SEC* is similar (Figure 4.1), in contrast the samples CA 5 and CA 6 have a similar molecular weight and different DS *SEC* (Figure 4.2).

Degree of Substitution by ^{13}C-NMR and SEC

The degree of substitution and the partial degrees of substitution were at first identified by ^{13}C-NMR.[5] The ^{13}C-NMR spectra were recorded by means of a Varian Unity 400 NMR spectrophotometer at a fre-

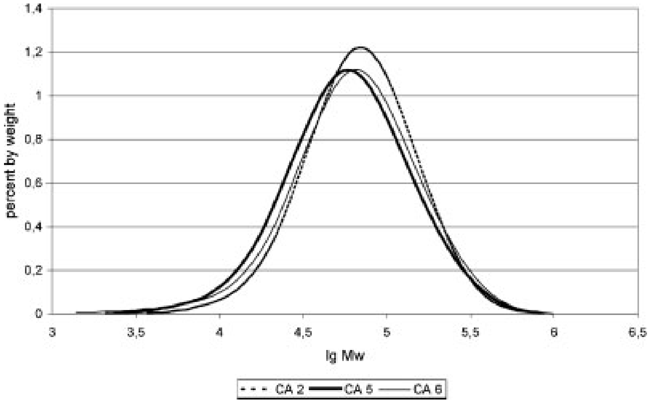

Figure 2.
Distribution of molecular weight for the samples CA 2, CA 5 and CA 6.

quency of 100.58 MHz. The differences between the samples using ^{13}C-NMR as measurement method are marginal and all the values are about 2.5. The values of the partial degrees of substitution are nearly similar too. All results of DS-measurements by ^{13}C-NMR are given in Table 3.

Next the DS-values were calculated by SEC as described by Fischer et al.[1] The values for DS *SEC* are about 2.3 and so they are generally about 0.2 lower than DS *NMR*.

As shown in Table 3 the results for the total DS determined by these different methods have a good correlation.

Bead Cellulose made from Cellulose Acetate

Technology

According to Stamberg[6] and Oliveira[7] cellulose beads can be produced by a variety of processes. Common are the solution of cellulose or its derivatives, the formation of a spherical droplet from the solution, the stabilization of the droplet, the phase inversion of the droplet and at least washing. The first beads were produced by extrusion method; later the dispersion method became more important. The raw materials are usually cellulose, cellulose xanthate (i.e. viscose) or cellulose acetate.

In patent EP0265924[8] a method is specified for preparing uniform polymer particles which have a volume average particle size of 10 to 1000 μm amongst others made from cellulose acetate with different degrees of acetylation.

The processes of making cellulose beads from cellulose acetate characterized in that a solution of cellulose acetate, which is free of halogenated hydrocarbons, is described in detail by Wagenknecht et al in patent EP 0750007.[8] The average particle size of the

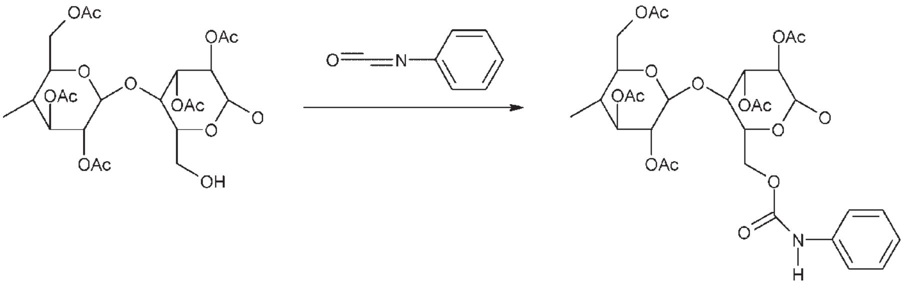

Figure 3.
Transformation of cellulose-2.5-acetates into perphenylcarbamoylated cellulose-2.5-acetate.

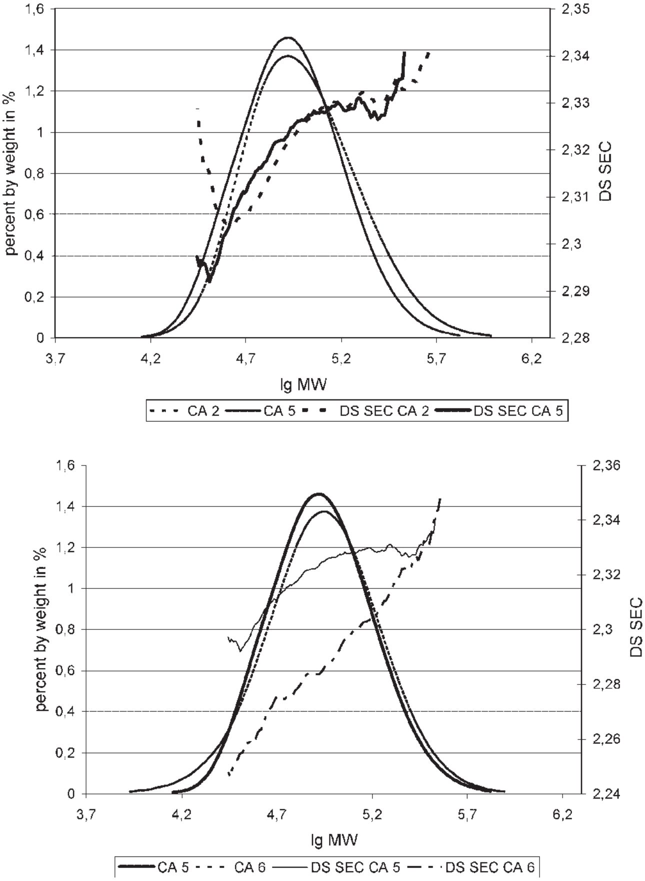

Figure 4.

top Distribution of molar mass and of substituents along the polymer chain for samples CA 2 and CA 5. below Distribution of molar mass and of substituents along the polymer chain for samples CA 5 and CA 6.

cellulose beads produced according to this technology ranges between 1 and 20 μm.

The experiments in the frame of this work were carried out according to this method. The general steps of this synthesis are shown in Figure 5.

Table 3.

Determination of partial and total degrees of substitution by ^{13}C NMR and SEC.

Sample	DS2 *NMR*	DS3 *NMR*	DS6 *NMR*	DS *NMR*	DS *SEC*
CA 1	0.84	0.92	0.79	2.55	2.36
CA 2	0.82	0.96	0.75	2.53	2.33
CA 3	0.87	0.96	0.71	2.54	2.36
CA 4	0.83	0.96	0.74	2.53	2.36
CA 5	0.85	0.96	0.74	2.55	2.32
CA 6	0.81	0.95	0.76	2.52	2.30
CA 7	0.82	0.96	0.79	2.57	2.33

Particle Size

The cellulose beads were characterized by measuring their particle size. The particle size distribution was determined with a LS 200 of Beckman Coulter.

The samples CA 1 to CA 3 have smaller particles and a narrow distribution; the samples CA 4 to CA 7 have larger particles and a broader distribution of particle size. The values for 10, 50 and 90 percent of all particles are given in Table 4. Results for 90% are very unsteady; suggesting the formation of agglomerates during the measurement. For that reason only the

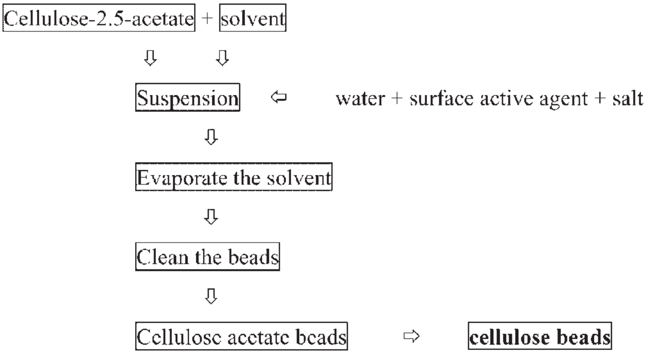

Figure 5.
Technology of synthesis cellulose beads according the cellulose-2.5-acetate technology developed by Wagenknecht et al.[9]

Table 4.
Values for particle sizes of bead cellulose made from different cellulose acetates.

Sample	10% < μm	50% < μm	90% < μm
CA 1	1.595	3.269	94.95
CA 2	1.389	2.949	10.62
CA 3	1.406	3.216	70.56
CA 4	1.737	3.556	7.177
CA 5	1.977	4.069	47.82
CA 6	1.629	4.519	21.44
CA 7	2.177	4.925	29.26

values for 10 and 50% were regarded as significant.

In Figure 6 the particle size distribution of two typical samples is exemplary shown for the samples CA 2 and CA 6. CA 2 has the smallest particle size of all samples; CA 6 has larger particles and a broader size distribution.

Scanning Electron Microscopy (SEM)

All samples were also investigated using Scanning electron microscopy (SEM). As examples three pictures are pointed in Figure 7. Figure 7.1 shows small particles with closed surface, synthesized by a cellulose acetate with molar mass over 100,000 and an evenly distribution of substituents along the polymer chain.

In Figure 7.2 cellulose beads with different particle size and structured surface are shown.

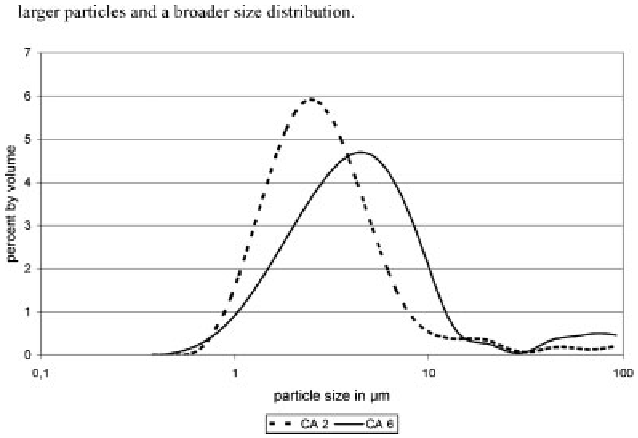

Figure 6.
Particle size distribution of sample CA 2 and CA 6.

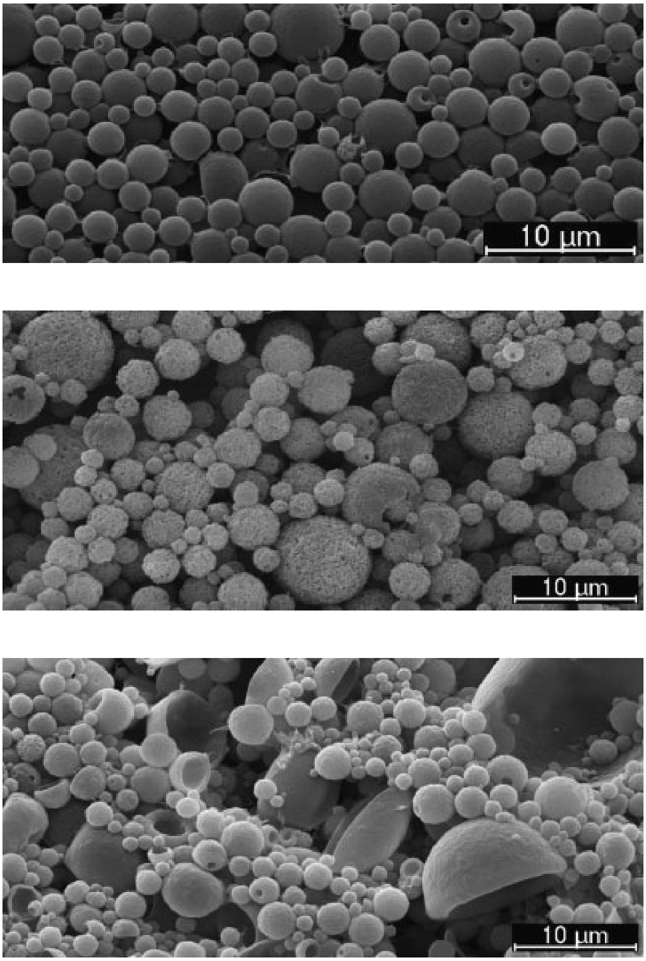

Figure 7.
Figure 7.1. Small particles of bead cellulose with closed surface (sample CA 2)
Figure 7.2. Particles with structured surface (sample CA 4).
Figure 7.3. Large particles of bead cellulose (sample CA 6).

Figure 7.3 shows particles with different size, the larger particles are partially deformed and hollow. The sample was synthesized from a cellulose acetate with a molar mass lower than 100,000 and unbalanced distribution of substituents along the polymer chain.

Relations Between Structure and Properties

In general the cellulose acetate with a higher molecular weight forms smaller particles with closed surface structure; the cellulose acetate with a lower molecular weight forms larger particles with structured surface. The cellulose acetate with the unsteady distribution of substituents along the chain (sample CA 6) forms large, partly hollow particles. These indications suggest that there is a correlation of the distribution of substituents along the chain with the synthesis of cellulose beads.

Application of Cellulose Beads

Cellulose beads were used e. g. for immobilization of enzymes, as specific adsorbents, for controlled releasing of active pharmaceutical ingredient and as medium for separation.

To use cellulose beads often an activation of the beads is necessary. This activation can be carried out with epichlorohydrin or sodium periodate.[10]

The development of specific adsorbents based on cellulose microspheres is described amongst others by Weber et al.[11] Wolf et al introduced bead cellulose as carrier for controlled delivery of drugs.[12]

Conclusion

In generally it is possible to form cellulose beads from all the invest\igated cellulose acetates. Under the same conditions for synthesizing there can be formed cellulose beads with different properties. The used cellulose acetates have an influence on the size and the surface of the formed particles. There are no correlations between the solubility of the cellulose acetate in the solvent, which is used as reaction medium for coagulation (ethyl acetate-methanol in ratio 100:17.5) and the properties of the formed beads.

The molecular mass has an influence on the particle size of the beads and the distribution along the chain has an effect on the uniformity of the formed beads. The presented new method for characterising the distribution of acetates substituents along the polymer chain should give new possibilities for investigations of molecular properties of cellulose acetates and products made of these materials. This method will further developed for other cellulose esters and also for cellulose ethers.

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