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Influence of Cryogenic Attrition Ball Milling on the Particle Size of Microcrystalline Cellulose at Different Moisture Contents

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Abstract. In this study the effect of attrition ball milling on cellulose particle size distribution was studied. The effect of moisture content of cellulose and grinding time were examined and grinding was carried out at room temperature and under cryogenic conditions, as well. The grinds obtained were studied with electron microscope, and the characteristic dimensions of ground particles were determined using image processing software. Results revealed that effective size decrease of cellulose particles was achieved at low moisture content at room temperature, while under cryogenic conditions high moisture content was necessary, i.e. frozen moisture enhances grinding efficiency in the latter case.

1. Introduction

Nowadays the so called nanomaterials gain more and more attention, as they can have outstanding physical, chemical or electric properties after adequate modification processes. Application of materials with smaller and smaller characteristic size is a global trend. Development of technology allowed us to design and produce devices at nano scale, and this way products with higher specific performance can be manufactured now, such as microprocessors or nanocomposites [1,2].

A promising material, nanocrystalline cellulose invented recently gains relatively a lot of attention. Its low density, high specific strength and elasticity modulus make it adequate for several engineering applications, such as nanocomposite production. Besides that it is also present as filling material in food and medicines, hence it is used in quite a large scope and in several different ways. It is important to note that cellulose is a renewable natural material, and the most often occurring organic material on Earth. It also reveals its excellent properties in nature, since a significant part of the base material of plants is cellulose that provides good mechanical strength for those, withstands slightly acidic or basic effects and is biologically degradable [3-5].

There are two main directions to decrease the size of cellulose particles, a chemical and a mechanical way. If the structure of cellulose obtained from any source is examined it can be observed that it is made up of crystalline and amorphous parts. The density of amorphous parts is smaller compared to that of crystalline parts; therefore bonds can be destroyed at these points using acids or kinetic energy. The chemical size decrease of cellulose is a time consuming process involving several steps and its automation is difficult, and a relatively small amount of products can be created this way. The proportion of different chemicals (acids, bases) have to be monitored precisely, because

contamination, salts may remain in the end product after the chemical reactions, and those are not allowed, as they may prevent further application. In case of the mechanical method size decrease can be realized in one single step. Different types of grinding devices can be used for this purpose and they can be automated in an excellent way. Huge amount of products can be manufactured, even enough for industrial demands, and grinding can be repeated more times. Milling machines use the kinetic energy of grinding bodies, the shearing and compression forces, or sometimes the evolving turbulence in order to achieve size decrease. Although the mechanical method is much simpler than the chemical one, its significant disadvantage is that much smaller cellulose particles can be produced using the chemical method [4-7].

In order to reach the required size decrease, different types of mills are available, different regarding their capacities, grinding efficiency and arrangement in order to provide adequate heat conduction and removability. Nowadays ball mills are gaining ground among mills, and especially a newer, more efficient type, the so called attrition mill. While in case of conventional ball mills rotation movement is carried out by the drum, in case of attrition mills balls are moved by rotational movement of the agitator. Its higher efficiency compared to conventional mills lies in the fact that the collision of balls with each other and with the wall as well as with the agitator all enhance particle size decrease [8]. Grinding efficiency can be increased further if grinding is realized under cryogenic conditions and this way particle size or agglomeration can also be decreased [9].

The aim of research is to determine how grinding parameters affect particle size of microcrystalline cellulose in case attrition milling.

2. Materials and methods

Materials

Base material is powdered microcrystalline cellulose type ARBOCEL UFC 100 (MCC) produced by J. RETTENMAIER & SÖHNE. Average particle size is 8 micrometer.

Sample preparation

In order to study the effect of moisture content the samples were placed in a conditioning equipment with 50% and 100% relative humidity at room temperature for one week, and dried samples were also prepared. The sample with 0% relative humidity was dried in a drying chamber at 105°C for 2 hours. The type of ball mill used for grinding was Union Process Szegvari Attritor Grinding System 01HD/01HDDM. The amount of filler during grinding was the same in case of all experiments. 1750 g stainless steel balls with the diameter of 3 mm as well as 35 g MCC were filled into the stainless steel grinding vessel. The rotational speed was 50 rpm. Grinding was carried out at room temperature and under cryogenic conditions (in liquid nitrogen medium) as well, grinding lasted for 20 minutes but samples were also taken from the grinds after 10 minutes in each case. The notation of samples consisted of three parts; the first one refers to the conditions of grinding: Cr-cryogenic and R-room temperature; then relative humidity, and finally grinding time follows. Hence Cr-100-20 means that cellulose held previously at 100% relative humidity was ground under cryogenic conditions for 20 minutes.

Characterization methods

The size of cellulose particles decreased during grinding but particles stuck to one another and formed aggregates. In order to be able to examine the single cellulose particles, these aggregates were dissolved in distilled water, and one drop was put onto the sample pin and then we let the water evaporate. The samples prepared this way were examined with a Jeol 6380 LA type scanning electron microscope (SEM) after sputtering them with a thin gold layer.

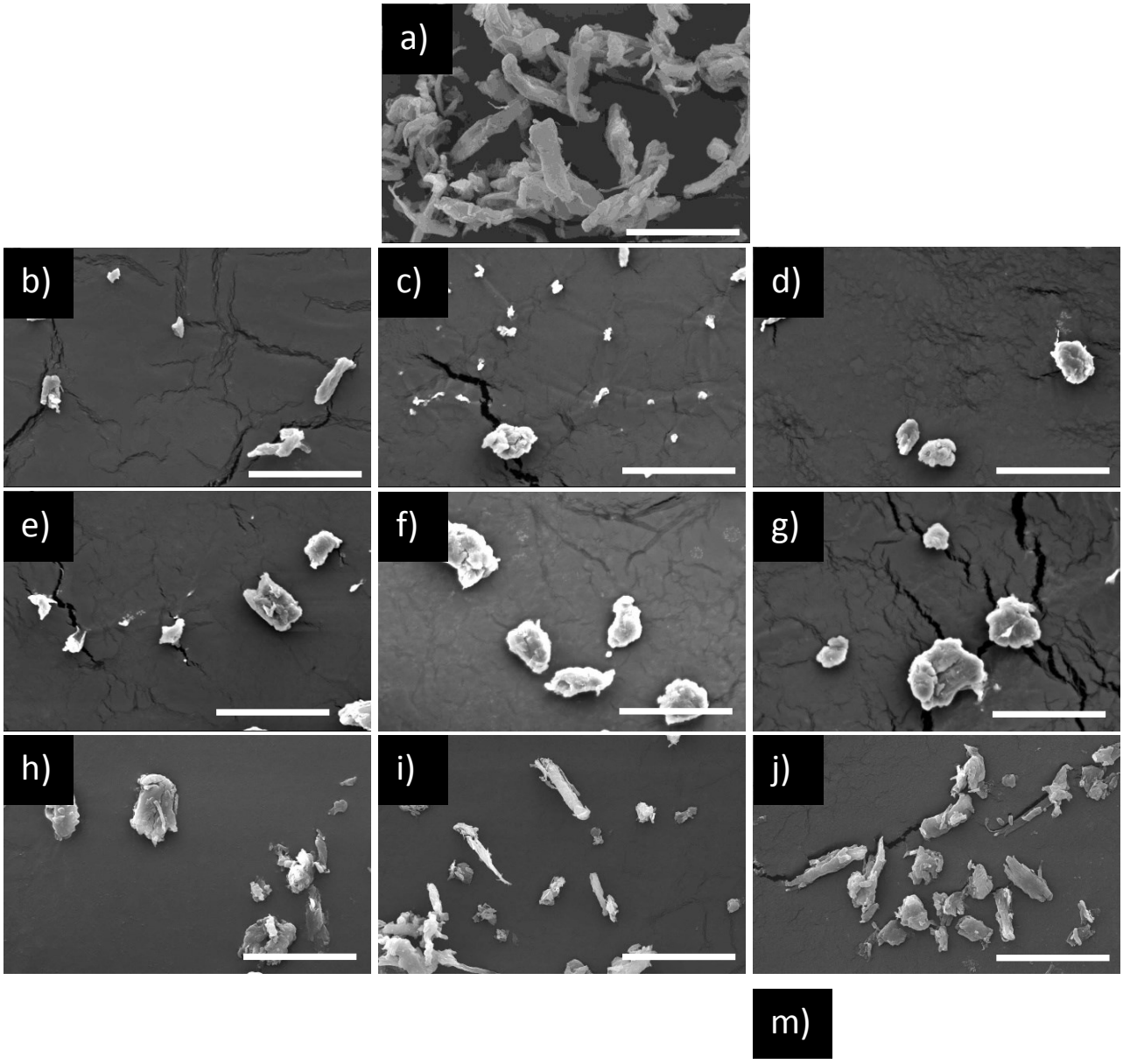
In order to be able to carry out statistical calculations and evaluate results adequate amount of particle sizes had to be recorded. We used image processing software analySIS Steel Factory 5.0 for this purpose. During the investigation the length (L [μm]) of particles (that is exactly the same as maximal Feret diameter), and the horizontal projection area (A [μm^2]) of particles were determined for each particle. At least 300 particles were examined in each sample. During evaluation the expected

value of particle length and the deviation of the expected value were determined assuming that the longitudinal dimension of particles follows lognormal distribution. Fitting test was done using χ^2 probe that verified the rightness of our assumption at minimum 95% probability level in each case.

3. Results and discussion

Scanning electron microscopy

Typical scanning electron micrographs of grinds produced in different ways are shown in Fig. 1. Differences are well visible even for the first sight. For example during room temperature grinding the particles are typically stuck together and formed a spherical shape (Fig. 1 b-g), while in cryogenic case the particles split longitudinally (Fig. 1 h-m) and the agglomeration of particles was less characteristic. In general it can be stated that in case of longer grinding time smaller particles also appeared besides the large ones, and at room temperature higher humidity resulted in larger particles, while in cryogenic case this effect was not experienced.



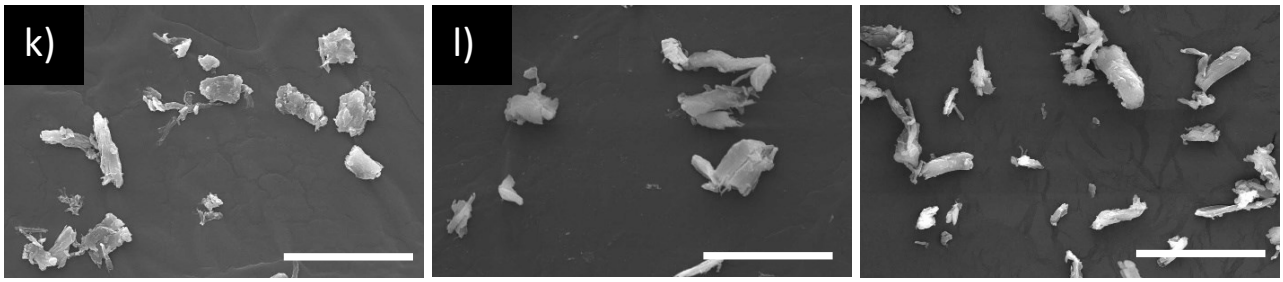


Figure 1. Electron micrographs of cellulose particles produced with different grinding parameters a) without milling; b) R-0-10; c) R-0-20; d) R-50-10; e) R-50-20; f) R-100-10; g) R-100-20; h) Cr-0-10; i) Cr-0-20; j) Cr-50-10; k) Cr-50-20; l) Cr-100-10; m) Cr-100-20;
(the white scale bars represent 20 μm)

Regarding the expected value of the length of particles it can be stated that higher grinding time resulted in smaller particles (Fig. 2). In case of cryogenic grinding the expected values decreased in smaller proportions than in case of grinding at room temperature. This is also true for the average area of the samples, too (Fig. 3).

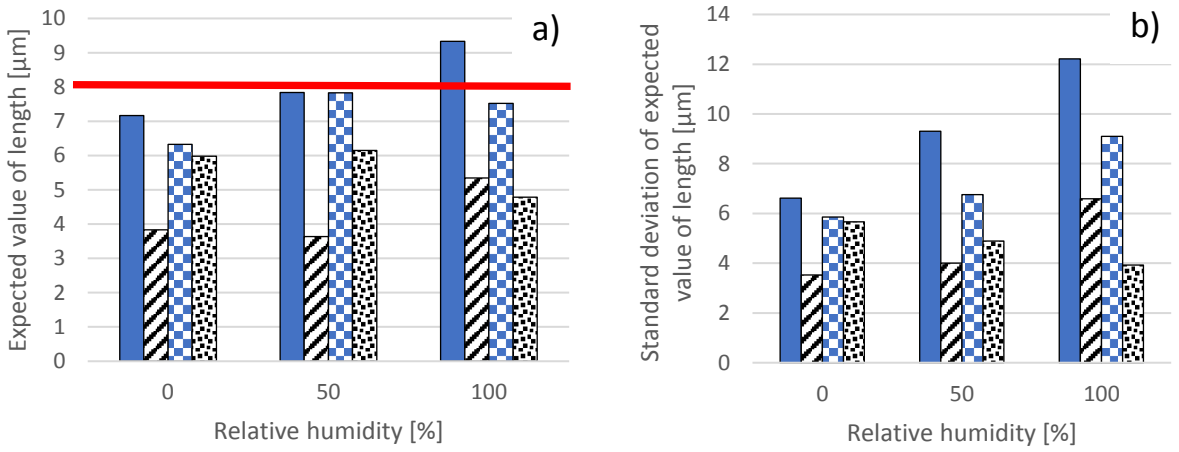


Figure 2. The expected value of length (a) and its standard deviation (b) as a function of the relative humidity of pre-treatment at different processing parameters (time and temperature). The red line shows the results for the raw material without milling
(room temperature milling for 10 min.; room temperature milling for 20 min.; cryogenic milling for 10 min.; cryogenic milling for 20 min.)

If the effect of moisture content is examined at room temperature the same can be found as it was already visible in electron micrographs, i.e. the average length of particles increases as a function of humidity, and that phenomenon can also be observed in case of average area values. The uncertainty of the process is revealed by the significant increase of deviations besides mean values. The process can be explained by the phenomenon that the rigidity of cellulose decreases, while its elasticity increases due to the adhered moisture but these are unfavorable properties regarding size decrease.

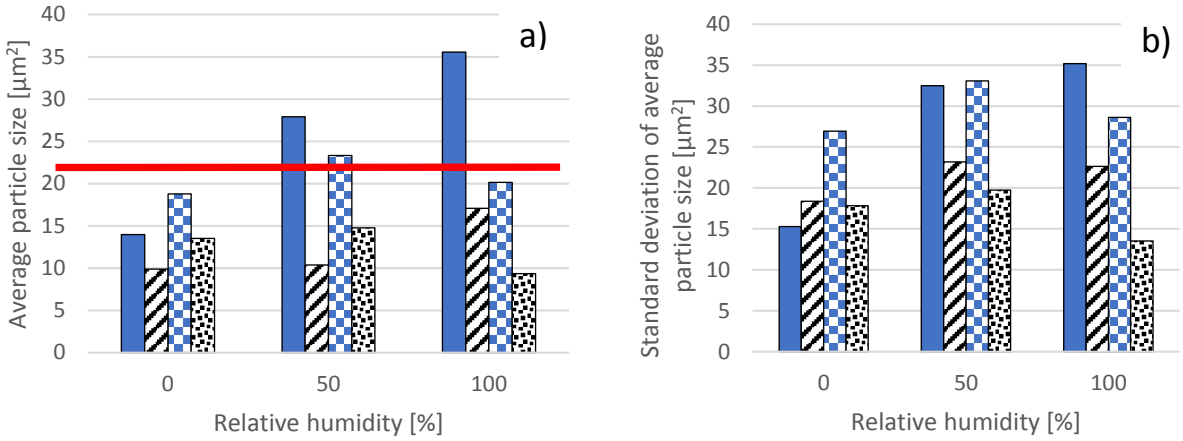


Figure 3. The average value of particle size (a) and its standard deviation (b) as a function of the relative humidity of pre-treatment at different processing parameters (time and temperature). The red line shows the results for the raw material without milling
(room temperature milling for 10 min.; room temperature milling for 20 min.; cryogenic milling for 10 min.; cryogenic milling for 20 min.)

As opposed to milling experiments at room temperature, if cryogenic media is applied the efficiency of milling increases if relative humidity increases. This is partly due to the fact that cellulose becomes more rigid at lower temperatures; on the other hand frozen moisture is present in the system as a hard, rigid material that enhances grinding. This way not only the grinding bodies carry out grinding but also cellulose particles that rub against one another increase the extent of size decrease. The expected value decreases if relative humidity increases, in case of longer time of grinding deviation gradually decreases; this way grinding can be planned better. This is also true for the measured areas.

Fig 2-3 reveal that if the relative humidity of cellulose can be kept below 50% dry grinding at room temperature should be chosen, as the results are significantly better than in the cryogenic case. Above 50% this advantage slowly disappears and in case of longer time cryogenic grinding provides better efficiency. If the areas are considered similar conclusions can be drawn: at low moisture content dry grinding has better results and particles with smaller surface can be achieved this way.

4. Summary

The aim of the study was to introduce the effect of high energy ball milling on the characteristic sizes of microcrystalline cellulose. During experiments the examined parameters were the moisture content of preliminary storage of cellulose, grinding time, and grinding temperature. Electron micrographs revealed that these parameters have significant effect on the particle size in the grinds formed and verified also by the numerical value of dimensions, i.e. the expected value of the length of particles and the average projection area. The increase of grinding time resulted in size decrease in each case, while the effect of grinding temperature depended significantly on the moisture content of the cellulose samples. The efficiency of dry milling decreased continuously due to the softening effect of water that makes cellulose more and more elastic. Oppositely, if the relative humidity increases, the efficiency of cryogenic grinding increases, the expected value and its deviation decreased. It was proven that relative humidity can be a decisive parameter when the technology has to be selected; grinding either at room temperature or under cryogenic conditions can be adequate in order to produce cellulose of a given particle size distribution. The former produces the smallest particle size at low and the latter at high moisture content if adequate energy is provided.

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