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Bionanocomposites of thermoplastic starch and cellulose nanofibers

Vật liệu nanocomposite sinh học cấu thành từ tinh bột nhiệt dẻo và các sợi

manufactured using twin-screw extrusion.

Abstract:

The aim of this study was to investigate if cellulose nanofiber (CNF) gels with high water contents can be processed to nanocomposites with starch powder using continuous twin-screw extrusion and to improve the mechanical properties and moisture sensitivity of thermoplastic starch. Nanocomposites with 0, 5, 10, 15 and 20 wt.% cellulose nanofiber content were prepared. The characterization methods were conventional tensile testing, UV/Vis spectroscopy, scanning electron microscopy and moisture absorption. The cellulose nanofiber gel with high water content was mixed with starch powder, fed to the extruder as powder, performing the gelatinization of starch as well as the mixing of CNF in one step. The microscopy study showed that the CNF aggregated during the process and that the screw configuration needs to be more distributive and dispersive to get homogeneous material. The results showed that the addition of CNF improved the mechanical properties and had a positive effect on moisture uptake of the thermoplastic starch. Also, the translucency of the TPS/CNF composite films remained, even with high CNF content (20 wt.%)

1. Introduction:

Interest in utilizing the unique properties of nanocellulose in various applications has been growing continuously since the first publications on fibrillation of wood pulp into

nano cellulose được sản xuất bằng phương pháp trộn nano hai trục vít.

Tóm tắt:

Mục đích của nghiên cứu này là khảo sát xem gel sợi nano cellulose (CNF) hàm lượng nước cao qua xử lý có thể tạo thành nanocomposites với tinh bột bằng phương pháp trộn nano hai trục vít liên tục và có thể cải thiện các tính chất cơ học và nhạy ẩm của tinh bột nhiệt dẻo. Chúng tôi tiến hành điều chế Nanocomposites với tỷ lệ phần trăm trọng lượng cellulose lần lượt là 0, 5, 10, 15 và 20 %. Các phương pháp kiểm tra bao gồm kiểm tra độ bền kéo thông thường, quang phổ UV/Vis, kính hiển vi điện tử quét và xác định độ hút ẩm. Gel sợi nano cellulose có hàm lượng nước cao được trộn với tinh bột, được cho vào máy ép đùn ở dạng bột, thực hiện quá trình hồ hóa cũng như trộn CNF trong một bước. Kiểm tra bằng kính hiển vi cho thấy rằng CNF đã kết hợp lại trong quá trình này và cấu hình trục trộn cần phải phân tán hơn và đồng đều hơn để thu được vật liệu đồng nhất. Kết quả nghiên cứu cho thấy việc thêm vào CNF cải thiện các tính chất cơ học và có ảnh hưởng đáng kể đến độ hút ẩm của tinh bột nhiệt dẻo. Ngoài ra, độ mờ của các màng composite TPS/CNF giữ nguyên, ngay cả khi hàm lượng CNF cao (20% trọng lượng)



cellulose nanofibers in the 1980s [1,2]. In addition to its mechanical properties, the main benefit of nanosized cellulose is that it can be considered a sustainable material due to its renewability, biodegradability and abundance in nature [3,4].

Cellulose nanofibers are typically separated from lignocellulosic plants, such as wood and agricultural crops, using mechanical treatment [5]. Usually, lignin is also removed from the plant cell wall prior to fibrillation using chemical treatment [5–7]. Depending on the source and separation method used, cellulose nanofibers are typically 20–40 nm in diameter and several micrometers long [3,8]. Unlike the cellulose nanowhiskers/crystals prepared by acid hydrolysis, cellulose nanofibers contain both the amorphous and crystalline regions of cellulose and can therefore create entangled networks [5,9].

Because of the specific characteristics of cellulose nanofibers, such as the high surface area and aspect ratio, it is of great interest to use them to enhance the properties of polymers. However, the suitable methods and matrices for composite manufacturing are somewhat limited due to the fact that nanocellulose is hydrophilic and forms irreversible aggregates when dried [3,10]. For this reason, the most successful methods used in the preparation of cellulose nanocomposites have been solution casting of dilute slurry of matrix and nanofibers [5,11–14] and

resin impregnation of a dried nanofiber network [15–18]. For larger scale production these methods are, however, slow and expensive. Extrusion compounding is one of the most promising methods for industrial processing due to easy scale-up and the possibility of further molding of the materials [9,19,20]. Yet there are only few published studies on extrusion processing of cellulose nanocomposites reinforced with cellulose nanofibers [20–22], which is why more research is needed.

Thus, the aim of this work was to study the extrusion processing of bio-nanocomposites of thermoplastic starch and cellulose nanofibers. The processing as well as the nanofibers' dispersion and effect on the mechanical, optical and moisture absorption properties of the composites were studied. Starch was chosen as the matrix polymer, as it can be processed into thermoplastic starch in the presence of water [23], and therefore the cellulose nanofibers can be used without drying in the compounding step. Basically, native starch can be converted into thermoplastic starch under heat and shear in the presence of plasticizer (typically water and a polyol, such as glycerol or sorbitol) [24]. Under these conditions the starch granules are deconstructed, plasticized and melted, forming a material which has a similar behavior to that of thermoplastics [24,25]. Earlier studies, in which the solution casting method

has been mainly used, have also shown that addition of cellulose nanofibers improves the mechanical properties and moisture sensitivity of starch matrix [8,11,14,25–27].

2. Materials and methods:

2.1. Materials:

Softwood wood flour (Scandinavian Wood Fiber AB, Orsa, Sweden) with a particle size range of 200–400 μm was used as a starting material for cellulose nanofibers. Sodium chlorite (Sigma–Aldrich, Germany) and glacial acetic acid (Merck, Darmstadt, Germany) were used in the delignification of wood flour. A potato starch, ELIANE™ 100 (AVEBE, Veendam, Netherlands) with high amylopectin content (>99%) was used as matrix, D-Sorbitol (Merck, Darmstadt, Germany) was used as plasticizer for starch, and stearic acid (VWR, Leuven, Belgium) was used as a lubricant.

2.2. Preparation of nanofibers:

Following the previous works of Abe et al. 2007, Iwamoto et al. 2008 and Gong et al. 2011 [28–30], the wood flour was delignified using acidified sodium chlorite solution using the Jayme-Wise method [31,32]. 250 g of wood flour (dry mass) was treated in a flask containing 3500 mL deionized water with 5 mL acetic acid and 33.5 g of sodium chlorite at 70–75 °C. Additions of acetic acid and sodium chlorite were continued at 2 h intervals until the wood became white, which in this case required 11 additions of acetic acid and sodium chlorite. The wood was washed twice during the treatment and at the

endwith minimum of 60 L of deionized water. Before washing,the wood was left in the acidified chlorite solution for 12 hat 70–75 C. The total treatment time of the wood flour inacidified chlorite solution was 58 h.

The cellulose nanofibers (CNF) were obtained fromdelignified wood flour through mechanical fibrillation. A3 wt.% suspension was prepared from the delignified woodflour and deionized water, dispersed homogenously usinga laboratory shear mixer (Silverson L4RT, SilversonMachine Ltd., England), and passed twice through anultrafine grinder, a super masscolloider MKCA6-3 (MasukoSangyo Co, Ltd., Japan), using rotational speed of 1440 rpm.The total grinding time was 16 min. After grinding the drymatter content of the CNF suspension was increased bycentrifuging to 12 wt.%.

Fig. 1 shows the visual appearance of wood flour in different stages of the preparation of cellulose nanofibersfrom macro- to nanoscale. As Fig. 1a and b show, the original wood flour consisted of small wood particles, and afterremoval of lignin by the sodium chlorite treatment, individual wood fibers were obtained. The ultrafine grindingtreatment of the bleached fibers resulted in a thick, viscousgel, and transmission electron microscopy (Fig. 1c) confirmed that nanoscale fibers were obtained.

2.3. Processing of the materials:

The TPS/CNF composites and neat TPS

samples were melt-compounded using a co-rotating twin-screw extruder (ZSK-18 MEGALab, Coperion W&P, Stuttgart, Germany) with an L/D ratio of 40. The extruder barrel was equipped with two atmospheric vents and vacuum ventilation in purpose to remove the vaporized water from the material. Feeding of the materials was done manually due to the small amounts of the prepared premixes (200 g). The extrusion set-up together with the screw configuration and the temperature profile is shown in Fig. 2. The materials were extruded using a die with a rectangular cross-section of 5 × 20 mm. The extrusion set-up used was similar to an earlier study made in our laboratory on thermoplastic starch reinforced with cellulose nanocrystals [33].

Fig. 1. Photographs and electron microscopy (SEM and TEM) images of cellulosic materials in preparation of cellulose nanofibers: (a) wood flour, (b) delignified wood flour, and (c) cellulose nanofibers after ultrafine grinding.

Fig. 2. Extrusion set-up used in the compounding of TPS/CNF composites.

Before extrusion, premixes of starch, sorbitol, stearic acid and cellulose nanofibers (12 wt.% concentration in water) were made with a Waring laboratory blender using short blending pulses of 3 × 3–5 s. All the premixes were in a powdery state, despite the fact that the cellulose nanofiber suspension had high water content in order to



avoid the formation of CNF aggregates in the composites. The CNF contents in the composites were 5, 10, 15 and 20 wt.% based on the dry weight. The amount of sorbitol was 30 wt.% and the amount of stearic acid was 1 wt.% based on dry starch. Stearic acid was added to prevent material sticking to the screws and clogging the die.

A speed of 200 rpm was used in the experiments, as it was found to be high enough to transport the material and to be able to have the vacuum venting on in the extruder in order to remove moisture from the material. Higher rotational speeds, on the other hand, reduce the residence time in the extruder, affecting the gelatinization of starch and the evaporation of water. In general, there were no problems during the compounding process of the materials. The cellulose nanofiber content mainly affected the extrudates' moisture content, as the materials with higher CNF content were stickier after extrusion due to higher water content. Because of this, the extruded materials were left to dry in room temperature and humidity (21°C, 22% RH) for one week before compression molding.

2.4. Specimen preparation:

After the extrusion, 10 g pieces of the extruded materials were compression molded into thin films with a thickness of 0.3 mm using a LPC-300 Fontijne Grottes hotpress (Vlaardingen, Netherlands). The material was placed between polyethylene terephthalate films and metal plates,

preheated in the press without pressure at 115°C for 3 min, pressed with 10.5 MPa for 3 min at 115°C, and then cooled to 25°C for 10 min under the same pressure.

2.5. Characterization:

2.5.1. Mechanical testing:

For tensile testing rectangular strips with the size of 80 x 5 x 0.3 mm were cut from the compression molded films. All test specimens were conditioned for at least two weeks in a desiccator of 53% relative humidity (RH) in room temperature before testing. The specimens were kept in the desiccator until the moment they were going to be tested, so as to minimize the variations in the moisture content. The tensile properties of the materials were tested using an Instron 4411 tensile testing machine with a 500 N load cell, gauge length of 40 mm and testing speed of 4 mm/min. At least six replicates of each material were tested.

2.5.2. Optical properties:

Transparency of the TPS and the TPS-CNF films was studied using UV/Visible light spectroscopy. A PerkinElmer UV/Vis Spectrometer Lambda 2S (Überlingen, Germany) was used to measure the light transmittance of the films in a light wavelength area from 300 to 1000 nm. The scan speed used in the analysis was 240 nm/min, and three replicates of each material were measured.

2.5.3. Microscopy:

Scanning electron microscopy (JSM-6460, Jeol Ltd, Japan; Zeiss ULTRA Plus, Carl Zeiss SMT AG,



Germany) and transmission electron microscopy (HT-7700, Hitachi, Japan) were used to study the microstructure of cellulosic materials as well as the fracture surfaces of the thermoplastic starch and the composite films. To create the fracture surfaces, specimens were first frozen under liquid nitrogen and then fractured. Specimens for SEM were sputter-coated with a thin layer of gold or platinum before observation.

2.5.4. Moisture absorption:

The effect of cellulose nanofibers on the kinetics of water absorption of the specimens was studied according to the ASTM D 5229 standard by exposing the samples to 98% relative humidity and determining the water uptake as a function of time until the moisture equilibrium content was reached. Specimens were cut from the compression molded films, and the specimen size was 15 x 15 x 0.3 mm. The film thickness 2 L was therefore considered thin enough for the molecular diffusion to be one-dimensional. Before absorption experiments, specimens were dried overnight in an oven at 100°C and then weighed. The average weight of the dried specimen was 72 mg (instead of the recommended 5.0 g in the standard due to lack of space). The oven-dry samples were placed in a desiccator with a 98% RH. At specific time intervals the samples were removed from the desiccator and weighed until an equilibrium moisture value was reached. Five replicates of each material were used in the analysis.

The moisture absorption values were calculated by taking the average of five values, and the moisture diffusion coefficient was determined using the slope of the initial linear part of the moisture absorption curve, which was plotted using the averaged moisture absorption values.

2.6. Statistical analysis:

One-way analysis of variance (ANOVA) followed by Tukey–Kramer multiple comparison tests with a 0.05 significance level was used to analyze the results from mechanical testing.

3. Results and discussion:

3.1. Mechanical properties of the materials:

Typical stress–strain curves for the TPS/CNF films are shown in Fig. 3, and the results obtained from the tensile testing are summarized in Table 1. From Table 1 it can be seen that the strength of the thermoplastic starch films increased with the addition of cellulose nanofibers. The strength increased with the cellulose nanofiber content up to 10 wt.% of CNF, but the higher nanofiber concentrations did not increase the strength significantly. The reason for this can be nanofiber agglomerates with higher CNF contents, as dispersion of nanosized reinforcement in the matrix polymer is the main problem in melt compounding of nanocomposites [9,19]. Nevertheless, with the addition of 10 wt.% of CNF, the strength of neat thermoplastic starch nearly doubled (8.8 and 16.4 MPa). The Young's modulus increased linearly with the increasing

cellulose nanofiber content, and the material containing 20 wt.% of CNF had the highest modulus of elasticity. When compared to the neat thermoplastic starch, the modulus increased from 455 to 1317 MPa (190%) with the addition of 20 wt.% cellulose nanofibers. As expected, the elongation at break reduced with the addition of cellulose nanofibers (Table 1, Fig. 3).

3.2. Optical properties:

Transparency can be used as an indirect measure of the size and dispersion of cellulose nanofibers in the matrix. If the cellulose reinforcement is not in nanoscale (nonfibrillated or aggregated), the transparency is lower due to the increased light scattering [16,34]. Fig. 4 shows the results from the UV/Vis spectroscopy for the TPS and TPS/CNF films. The addition of cellulose nanofibers reduced the light transmittance of the prepared films, indicating that the dispersion of CNF was not homogeneous in the composite films. At 550 nm light wavelength, which is approximately in the center of the visible light spectrum, the transmittance was reduced by 27%, 28%, 41% and 54% with 5, 10, 15 and 20 wt.% addition of CNF, respectively, when compared to the neat TPS matrix.

The transparency of the films was also examined visually against a background image (Fig. 5). From Fig. 5 it can be seen that all the films can be considered translucent, and up to 15 wt.% of CNF, there is no great reduction in the clarity of the films. In addition, no visible

aggregates of cellulose nanofibers can be seen by the eye in any of the films.

Fig. 3. Typical stress–strain curves of the TPS and TPS/CNF films.

Table 1: Mechanical properties of the films of thermoplastic starch (TPS) and thermoplastic starch reinforced with cellulose nanofibers (CNF) together with standard deviations.

*Means marked with the same superscript letter within the same column are not significantly different at 5% significance level based on the ANOVA and Tukey–Kramer pairwise comparison test.

