

Production and properties of micro-cellulose reinforced thermoplastic starch

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Abstract. Thermoplastic starch (TPS)/micro-fibrillated cellulose (MFC) composites were prepared from maize starch with different amount of distilled water, glycerol and cellulose reinforcement. The components were homogenized by kneader and twin roll technique. The produced TPS and TPS-based polymer composites were qualified by static and dynamic mechanical tests and their morphology was analysed by microscopic techniques. The results showed that the amount of water and the order of the production steps control the properties of both the TPS and its MFC reinforced version. With increasing content of MFC the stiffness and strength of the TPS matrix increased, as expected. Microscopic inspection revealed that the TPS has a homogenous structure and the MFC is well dispersed therein when suitable preparation conditions were selected.

1. Introduction

Nowadays considerable efforts are undertaken to modify biodegradable polymers (*e.g.* thermoplastic starch, polylactide acid) by cellulose micro- and nanoparticles to produce fully biodegradable composite materials with promising mechanical and barrier properties [1-4]. Cellulose is the most abundant natural biopolymer on earth. It is renewable, biodegradable and non-toxic. When extracted from natural fibers, the hierarchical organization of cellulose allows us to obtain micro-fibrillated (MFC). MFC is milled and submitted to bleaching to remove lignin and hemicellulose. The bleached fiber is then hydrolyzed or disintegrated mechanically or both. The resulting MFC is already available commercially by several providers. The diameter of MFC is in the range of 20-60 nm and has a length of several micrometers. Thermoplastic starch (TPS) can be produced from various starches (*e.g.* maize, potato) by the combination of temperature, shear and a plasticizer, which is usually water and/or glycerol. Disadvantages of the TPS are their poor mechanical properties and high sensitivity to humidity which limit their industrial applications.

The goal of this work was to study the effects of plasticizers added in different amount and introduced in different ways. A further aim was to assess the potential reinforcing effect of MFC on TPS (incorporated in various amounts) and clarify the related structure-property relationships. Accordingly, TPS was prepared using water and glycerol by melt kneading in an inner mixer. MFC



was introduced in both dry and wet forms. The latter means the introduction of MFC in aqueous suspension. The order of addition of plasticizer and MFC was also tested.

2. Materials and methods

2.1. Materials

As matrix material conventional maize starch (Hungramid F Meritena 100, Brenntag Ltd., Hungary) and as plasticizers different amount of distilled water and glycerol 99.5% (Csepp Bt., Hungary) were selected and used. Two kind of micro-fibrillated cellulose (Arbocell[®] UF100 (fiber length: 8 μ m) and B600 (fiber length: 60 μ m) from JRS GmbH, Germany) were applied as reinforcements. The moisture contents of the maize starch, UF 100 and B600 MFC, when stored at 24°C, 50% relative humidity, were 9%, 4% and 7%, respectively. These data were received in thermo gravimetric analysis performed at 10°C heating rate in the temperature range: 20-200°C. TPS and TPS/MFC systems were produced under different processing conditions. Table 1. shows the recipes of the materials.

Sample	Thermoplastic starch			MFC reinforcement		
	Starch [wt%]	Glycerol [wt%]	Distilled water [wt%]	Glycerol [wt%]	Distilled water [wt%]	Type of cellulose
Ref	60	20	20	-	-	-
2B	60	20	20	-	-	UFC100
2C	60	20	20	-	-	B600
3B	60	10	10	10	10	UFC100
3C	60	10	10	10	10	B600
5C-5	60	0	0	20	20	B600
5C-10	60	0	0	20	20	B600
5C-15	60	0	0	20	20	B600
6B-5	50	0	0	20	30	UFC100
6B-10	50	0	0	20	30	UFC100
6B-15	50	0	0	20	30	UFC100

Table 1. Recipes and production of the materials.

Coding: Ref: Thermoplastic starch (TPS) reference; 2: TPS produced by introducing dry cellulose; 3: TPS produced by halving the plasticizers for starch destructure and “wet” introduction of MFC; 5: TPS production when the whole plasticizer amount served to disperse the MFC and introduce it “wet”; 6: TPS produced as sample 5, however, with increased amount of plasticizer

2.2. Preparation of thermoplastic starch based composites

2.2.1. Kneading process. Maize starch was dried at 85°C for 10 hour by KDCL type dry air dryer prior the processing. The components were mixed together with a Brabender type of mixing paddles in different ways. First, the reference TPS was prepared (Ref). The maize starch, glycerol and the

water were mixed and fed to the kneading chamber (full amount was 200 g). To produce samples 2B and 2C the dry cellulose was mixed with the plasticized starch. In case of sample 3 series the plasticizer amount was halved: one half was used for TPS, whereas the other to predisperse MFC that was thus introduced in form of MFC suspension. In cases of the series 5 and 6 the whole amount of the plasticizers was used to make an MFC dispersion that was dosed to the dry starch in the kneader. The applied reinforcement content was 5 wt% uniformly, however, samples 5 and 6 were produced also with 10 and 15 wt% MFC contents to shed light on the reinforcement effect. Kneading occurred in two steps: first at 90°C for 2 min at 20 revolutions/min (rpm), and second at 120°C for 8 min mixing time at 20 rpm.

2.2.2. Sheetting process. The homogenized mixture of the components was fed to twin-roll mill (Labtech Scientific Ltd, Thailand) for sheetting. The related conditions were: back roll temperature: 40, 38, 40°C, front roll temperature: 60, 58, 60°C; gap: 0.7-2 mm; friction: 17:15 rpm; tolling time: 8 min. The final thickness of the sheets was 1.6 mm.

2.3. Specimens and their testing

The produced reference TPS and cellulose reinforced TPS sheets were air-conditioned in a Memmert HCP153 humidification chamber at 27°C and 50% relative humidity for 10 h prior to their testing.

2.3.1. Static tensile tests. Static tensile tests were performed on the sheets. From the sheets dumbbell specimens (EN ISO 8256 type 3) were cut off by punching. Tensile tests were carried out on a universal Zwick Z020 tensile machine according to the standard EN ISO 527. The cross-head speed was 5 mm/min and each test was performed at room temperature (24°C). At least five specimens were tested for each material.

2.3.2. Dynamic mechanical analysis (DMA). The DMA tests were performed on a DMA Q800 (TA Instruments, New Castle, USA) machine using three point bending and dual cantilever type loading conditions with the following parameters: frequency: 1 Hz, temperature range: -50 to 120°C, heating rate: 3°C/min. For the tests 60x15x1.6 mm specimens were cut from the sample 5 sheet. Before the DMA tests the surface of the specimens were coated with silicon based grease to avoid/hampers drying during the test [5].

2.3.3. Scanning electron microscope (SEM). Scanning electron microscopic pictures were taken from fracture surface (which was produced by cryogen cracking method) in a JSM-6380LA (Jeol, Tokyo, Japan) microscope. The sample's surface was sputter coated with gold alloy to avoid electrostatic charging.

3. Results and discussion

The primary goal of this work was to find a reproducible production method for TPS based composites which results in optimum properties (maximal strength while maximal modulus). Therefore, first the effects of the plasticizers were investigated. Without distilled water a homogenous, powder-like product was received whereby the kneading torque significantly increased. Omitting the glycerol from the recipe yielded a dry material. It can be thus claimed that the common use of distilled water and glycerol was necessary to produce TPS successfully. The common use of these two plasticizers along with the shearing and heating in the two-step kneading resulted in a dough-like material. Its appearance indicated the good destructurezation of the starch. The second mixing step at increased temperature (120°C) caused steaming that was most helpful to the homogenization.

3.1. Static tensile tests

Table 2. shows the mechanical properties of the TPS and TPS based composites. Sample 2 TPS systems exhibited very poor mechanical properties, nevertheless, with increasing amount of the

plasticizers the MFC reinforcing effect was enhanced. Comparing the effect achieved by the two different MFCs, it can be seen that the longer MFC (Arbocell B600, 60 μm) ensured better properties. In addition, the production of the corresponding TPS/MFC composite was easier and the cellulose dispersion became better (cf. Fig.3) than with the other MFC type (UFC 100). For the samples 5 incorporation of MFC in 15 wt% improved the yield stress by 120% and the Young's modulus by 66% compared to the TPS reference.

Sample	Yield stress [MPa]	Young's modulus [GPa]	Strain at F_{\max} [%]
Ref	4.2 \pm 0.3	0.3 \pm 0.02	28.9 \pm 2.6
2B	3.4 \pm 0.2	0.8 \pm 0.03	78.0 \pm 2.3
2C	5.2 \pm 0.4	0.3 \pm 0.01	22.6 \pm 2.0
3B	3.9 \pm 0.6	0.2 \pm 0.06	17.5 \pm 5.6
3C	6.3 \pm 0.9	0.2 \pm 0.03	13.3 \pm 3.0
5C-5	5.7 \pm 0.5	0.2 \pm 0.02	33.6 \pm 3.4
5C-10	4.8 \pm 0.7	0.2 \pm 0.04	27.8 \pm 3.6
5C-15	9.4 \pm 1.4	0.5 \pm 0.06	14.2 \pm 2.1
6B-5	2.4 \pm 0.3	0.05 \pm 0.01	69.3 \pm 2.3
6B-10	7.6 \pm 0.2	0.3 \pm 0.03	31.2 \pm 2.2
6B-15	7.9 \pm 1.0	0.4 \pm 0.05	15.6 \pm 3.3

Table 2. Mechanical properties of TPS and TPS/MFC composites

3.2. Dynamic mechanical analysis (DMA)

Figure 1 shows the DMA curves of the TPS based 5C composites which proved to be most promising in this test series (stable production technology, high mechanical properties).

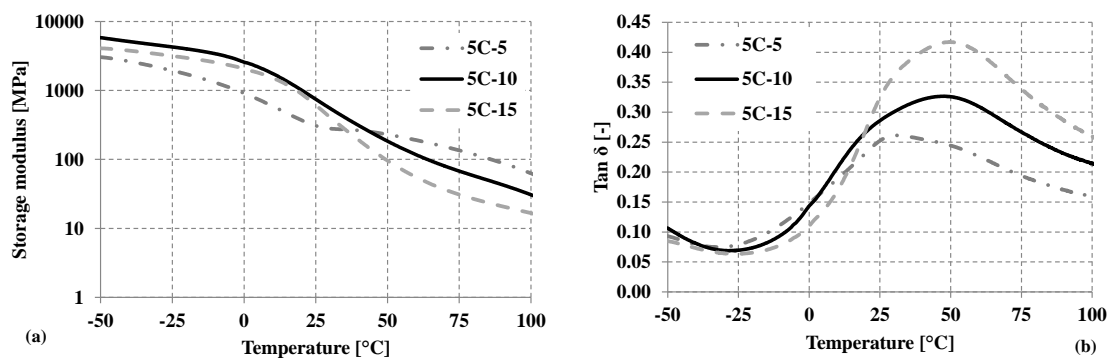


Figure 1. Storage modulus (a) and $\tan \delta$ curves (b) of the TPS composites (sample 5C), reinforced with different amounts of MFC

As expected from the thermoplastic nature of TPS, with increasing temperature the storage modulus decreased. The glass transition temperature values (read at the maximum of $\tan \delta$) of the composites were between 30 and 50°C. This is in accordance with the literature [6].

3.3. Scanning electron microscopy (SEM)

The SEM pictures from the fracture surfaces of TPS and TPS produced with dry MFC dosage can be seen in Figure 2.

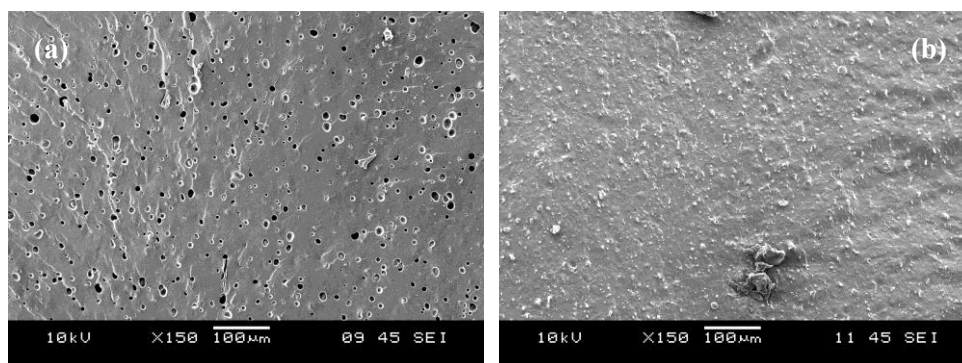


Figure 2. SEM pictures of the reference thermoplastic starch (a) and sample 2B (b).

The TPS was homogeneous but unfortunately contained many bubbles which is certainly decreased the mechanical properties. Their onset can be attributed to the steam development during kneading. When dry cellulose was added to the plasticized starch, no bubble formation could be resolved. Probably the excess water was “picked up” by the dry cellulose. In Figure 3. the fracture surfaces of sample 5 with 5 and 15 wt% MFC contents are collated.

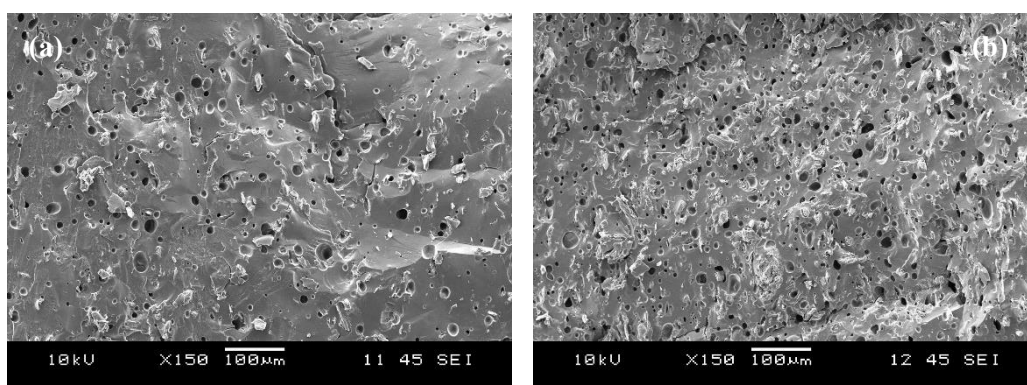


Figure 3. SEM pictures of the 5 (a) and 15 wt% (b) MFC-containing TPS composites (samples 5C-5 and 5C-15, respectively)

The dispersion of the cellulose particles seem to be fine, moreover, MFC is likely fairly adhered to the TPS matrix. Unfortunately, massive void formation due to steam bubbling is still there - its elimination is our major task in the future.

4. Conclusions

In this work TPS and TPS-based micro-fibrillated cellulose (MFC) reinforced composites were produced and tested. It was found that the preparation method and the plasticizers (amount and ratio) strongly affect the resulting properties. Incorporation of MFC increased the mechanical properties

(yield stress, Young's modulus, and even ductility). To avoid the agglomeration of MFC it has to be introduced in "wet" form, i.e. predispersed in the plasticizers. The results received will serve as base to produce TPS composites continuously using extrusion melt compounding.

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