EXPERIMENTAL INVESTIGATION ON THE MECHANICAL PROPERTIES OF MICROCRYSTALLINE CELLULOSE REINFORCED EVOH AND NYLON COMPOSITES

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Abstract
Microcrystalline cellulose (MCC) combines the advantages of cellulose (low density, high performance, biosustainability) with low cost and a thermal stability of up to 300 °C. This enables the use of MCC as a filler for engineering thermoplastics in automotive and food packaging industries. Ethylene-vinyl alcohol (EVOH) and polyamide 6 (Nylon) were compounded with MCC in a twin-screw extruder. Weight content of MCC, screw speed and screw configurations were varied as process parameters to apply low and high shear forces to the material during processing. As a result, flexural properties increased overall in comparison with the pristine material with increasing filler content and increasing shear force.

1. Introduction

Cellulose is the most abundant bio-polymer on earth possessing low density, high specific strength and stiffness and is recyclable. It has sparked interest as a substitute for traditional fillers like glass fibers, clays and kaolin [1, 2, 3]. Microcrystalline cellulose (MCC) is a crystalline form of cellulose produced from acid hydrolysis [1]. MCC has a lower price than other fillers and is commercially available [4]. Ethylene-vinyl alcohol (EVOH) is a semicrystalline copolymer of ethylene and vinyl alcohol with excellent barrier properties as well as tensile strength and stiffness used in food packaging [5]. Polyamide 6 (Nylon 6) is an aliphatic polyamide with the advantages of good resistance against abrasion and chemicals as well as good thermal and mechanical properties [2, 4]. Combining these materials could fulfill the need of the automotive and food packaging market for low density, high performance, economically viable and bio-sustainable composites [2, 3, 6]. Thermogravimetric analysis (TGA) indicates thermal stability of MCC up to 300 °C [3, 4]. This allows for the processing of MCC together with engineering polymers (melting point EVOH: 183 °C, Nylon 6: 223 °C). Xu combined cellulose fibers with Nylon 6 and Nylon 66 using low temperature extrusion and injection moulding to achieve improved fiber dispersion and mechanical properties [6]. Kiziltas et al. were able to enhance mechanical properties of Nylon 6-MCC composites compounding via a Brabender Prep-mixer® [2]. The novel approach presented in this study is varying processing parameters (weight content, screw speed, screw configuration) in compounding using a twin-screw extruder to investigate the effect on the morphological characteristics (dispersion) and flexural properties of EVOH-MCC and Nylon-MCC composites.

2. Experimental method

2.1. Materials

Ethylene vinyl alcohol (EVOH) (F 101B, EVAL Europe N. V., density: 1,180 kg/m^3) and polyamide 6 (Nylon) (Akulon® F223-D, DSM Engineering Plastics, density: 1,130 kg/m^3) were used as matrices. Microcrystalline cellulose (MCC) (Sigma-Aldrich, bulk density: 600 kg/m^3) was used as filler.

2.2. Preparation of EVOH/MCC and Nylon/MCC composites

EVOH and Nylon were ground using a cryogenic grinder (6850 Freezer/Mill, Rondol). Dry-mixing of the matrix powders and MCC was performed using a blender (Rondol). Blends with three different weight contents of MCC (5 wt.%, 10 wt.%, 15 wt.%) were prepared. Prior to melt-blending the powders were put in an oven at 80 °C for 8 hours to dry. A co-rotating 16 mm twin-screw extruder (L/D = 25) (HAAKE Rheomex OS PTW16, ThermoSCIENTIFIC) was used for melt-blending. The barrel temperature for EVOH was 210 °C, for Nylon 270 °C. The two processing parameters, screw speed and screw design, were varied to introduce different shear forces into the material. The screw speed was changed between 100 rpm, 125 rpm and 150 rpm while feed screw elements and kneading blocks were used to create two different screw configurations called 'Screw Designs' (SD1 and SD2), see Figure 1 (designed in Onshape, Onshape Inc.). SD1 introduces little shear into the material and mainly serves to convey the material towards the die. Hence, SD1 is a low shear configuration. Concerning SD2, kneading blocks are arranged to achieve the highest mixing effect (distributive and dispersive) while having little to no conveying effect. SD2 is a high shear configuration.

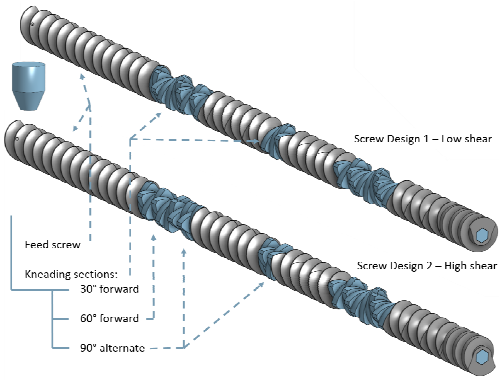

Figure 1. Different screw configurations providing different shear options for processing of EVOH/Nylon – MCC composites.

After melt-blending, the composites were further processed using a platen press (P 200 P, COLLIN). The composites were dried at 80 °C for 8 hours. Compression moulding (EVOH-MCC: 210 °C, Nylon-MCC: 240 °C) was performed according to ISO 293 with adjustments being made to avoid thermal degradation, voids and entrapped air. Test specimen were directly moulded from flash moulds.

2.3. Material characterization

A scanning electron microscope (FlexSEM 1000, HITACHI) was used to inspect the surface of cryo-fractured samples. The flexural properties were investigated as per ISO 178 using a 3-point bending fixture (Z100, Zwick/Roell, 23 °C, 50 % RH). The specimens were dried at 80 °C for 8 hours prior to testing. The crosshead displacement was used as deflection to calculate the flexural strain.

3. Results and discussion

3.1. Morphology characteristics

SEM images of the fracture surface of cryo-fractured EVOH-MCC (a, b) and Nylon-MCC (c, d) samples are shown in Figure 2. The composites in (a, c) were fabricated with SD1, in (b, d) with SD2.

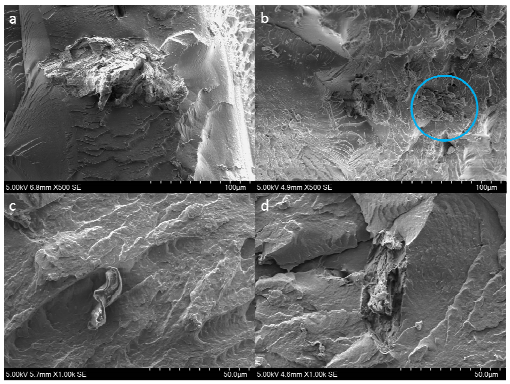

Figure 2. SEM pictures of EVOH and Nylon samples, a) EVOH, 5 wt.%, 100 rpm, SD1, b) EVOH, 15 wt.%, 100 rpm, SD2, c) Nylon, 5 wt.%, 100 rpm, SD1, d) Nylon, 5 wt.%, 150 rpm, SD2.

What can be seen in all the images is exfoliation of MCC. Exfoliation increases with increasing shear force introduced into the material for both EVOH and Nylon composites (b-blue circle, d). It is also found that MCC particles have been further reduced to smaller micro and nano sized particles through processing. A good fiber-matrix bonding is observed in all cases.

3.3. Flexural properties

The flexural stress-vs.-flexural strain graphs for EVOH-MCC and Nylon-MCC composites are shown in Figure 3. The corresponding results of the flexural properties are summarized in Table 1. For both polymers, with increasing weight content of MCC and with changing to SD2 an increasing flexural modulus, compared to the pristine polymers, is observed. This is also evident in Figure 3. With increasing weight content of MCC, the flexural strength and the flexural strain increase when using SD1. For SD2, the flexural strength and the flexural strain decrease with increasing weight content.

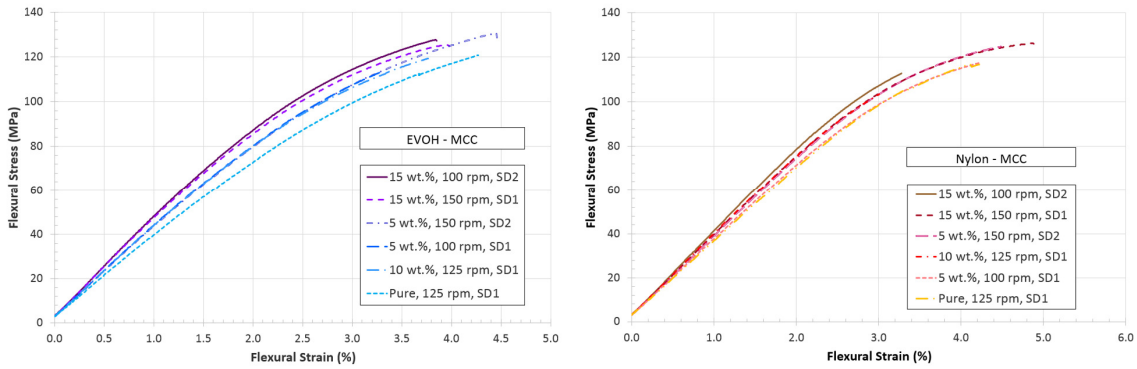

Figure 3. Flexural stress-vs.-strain graphs of EVOH-MCC (left) and Nylon-MCC (right) composites as a result of different process parameter settings.

Table 1. Flexural properties of EVOH-MCC (left set) and Nylon-MCC (right set) composites as a result of different process parameter settings.

	EVOH			Nylon		
Composite Type	E_f (MPa)	σ_{fM} (MPa)	ε_{fM} (%)	E_f (MPa)	σ_{fM} (MPa)	ε_{fM} (%)
15 wt.%, 150 rpm, SD1	4419	125.3	3.94	3561	126.6	4.93
5 wt.%, 100 rpm, SD1	4066	116.6	3.48	3361	120.8	4.73
15 wt.%, 100 rpm, SD2	4442	129.9	4.08	3689	118.7	3.73
5 wt.%, 150 rpm, SD2	4017	132.9	4.71	3494	124.8	4.48
10 wt.%, 125 rpm, SD1	4060	119.6	3.91	3638	109.8	3.44
Pristine, 125 rpm, SD1	3624	120.8	4.35	3270	117.1	4.20

It can be argued that at low shear, the formation of network-like structures caused by MCC interactions is dominant. These interactions increase with higher amounts of MCC [2, 3]. When processing the materials with SD2 these structures are broken down, but smaller MCC particles are created. This leads to an increase of surface area and nucleating sites increasing the crystallinity of the composite thus increasing the flexural strength. With higher MCC content the amount of particles restrict the mobility of the matrix polymer chains and negatively affect the crystal growth [3, 4]. In general, results show that an increase of flexural properties in comparison to the pristine material is possible through the inclusion of MCC in EVOH and Nylon. A maximum increase in the flexural modulus, flexural strength and flexural strain of 22.6 %, 10 % and 8.3 % (EVOH-MCC) and of 12.8 %, 8.1 % and 17.3 % (Nylon-MCC), respectively, were measured.

4. Conclusions

The processing of MCC in EVOH and Nylon led to exfoliation of MCC and an enhanced filler-matrix interaction. Flexural properties were increased in comparison to the pristine materials. Consequently, MCC can be effectively used to create low cost, low density, biosustainable thermoplastic composites with increased mechanical properties for such application as automotive components and food packaging.

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