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The effect of surface modification of microfibrillated cellulose (MFC) by acid chlorides on the structural and thermomechanical properties of biopolyamide 4.10 nanocomposites

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ABSTRACT

Microfibrillated cellulose (MFC) has recently been identified as an innovative product of wood and agriculture industry with potential applications as reinforcement and carrier for functional properties of polymer composite materials, such as improved barrier and optical properties. The widespread commercial application of MFC in polymer technology still requires the development of new methods of MFC surface modifications in order to provide stong interfacial adhesion and good dispersibility of additive in polymer matrix. In this work microfibrillated cellulose was modified by acid chlorides arranged in a homologous series that showed high efficiency in changing the surface properties of the material. The modified MFC displayed hydrophobic character combined with preserved fibrillar morphology and high crystallinity. Chemical modification of MFC was assessed by Fourier transformed infrared spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) analyses. Despite the fact that the reactivity of acid chloride slightly decreased with increasing chain length the total effect on MFC wetting with water was most pronounced for the modifier with the longest alkyl chain. Completely bio-based engineering nanocomposites of biopolyamide 4.10 (PA4.10) and surface modified MFC were prepared by melt blending. Structural, morphological and thermomechanical analysis by scanning electron microscopy (SEM), atomic force microscopy (AFM) and dynamic mechanical analysis (DMA) methods evidenced clear dependence of composite performance on the length of alkyl chain attached to the MFC surface. The modification of MFC by hexanoyl chloride produced nanofiller with good dispersibility in PA4.10 matrix and was favorable in terms of dynamic mechanical properties of composites. While PA4.10 composites containing MFC functionalized by longer alkyl chains (more than 10 carbon atoms) showed a decrease of storage modulus due to insufficient interfacial interactions or plasticization effect.

1. Introduction

Recently different types of cellulose micro and nanomaterials have been developed with fibrillar and whisker-like morphologies. Nanocellulose can be produced in a wide range of diameters, aspect ratios and entanglement of the fibers owing to multileveled architecture of raw materials and advantages in manufacturing technology (Nechyporchuk et al., 2017; Mariano et al., 2014; Moon et al., 2011; Jonoobi et al., 2015). Wide applications are foreseen for cellulose nanocrystals and nanofibers, for example structural and barrier materials and a variety of functional materials such as drug delivery systems, tissue and vascular engineering or water purification and filtration membranes (Azeredo et al., 2017; Ummartyotin and Manuspiya, 2015; Abdul Khalil et al., 2015; Abeer et al., 2014; Charreau et al., 2013; Rodionova et al., 2013; Lavoine et al., 2012). Polymeric composites containing micro- and nanofibrillated cellulose (MFC and NFC) as a mechanical reinforcement phase offered improved mechanical, optical and barrier properties (Miao and Hamad, 2013). New polymeric materials containing natural fillers are also potentially lighter and less abrasive during processing in comparison to common glass fiber reinforced plastic. Controlling the interfacial properties is one of the most important issues in composite technology since compatibility at the

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fiber-matrix interface is critical for good dispersion of the filler and mechanical enhancement of the material (Iwatake et al., 2008; Mathew et al., 2005). A variety of surface modifications of cellulose nanoparticles was carried out in order to change its hydrophilic character or attach new functionalities to the material (Missoum et al., 2013). Among them, esterification reactions play an important role. Recently Peng et al. (2016) have reported on the comparative study of cellulose nanocrystals (CNC) esterification using acid anhydrides, acid chlorides, acid catalyzed carboxylic acids, and 1′1-carbonyldiimidazole (CDI) activated carboxylic acids with different functional groups. It was evidenced that acid anhydrides with short aliphatic chains had better grafting efficiency than those with long chain moieties. Effective modification of cellulose and cellulosic nanomaterials with fatty acids was also reported by Junior De Menezes et al. (2009) and Uschanov et al. (2011). Vuoti et al. (2013) carried out an extensive study on esterification of nanofibrillated cellulose with a series of acid chlorides showing the influence of the solvent on the susceptibility of NFC to esterification and agglomeration. Heterogeneous esterification of cellulose nanomaterials by acid chlorides was reported as an effective approach for hydrophobization leading to a decrease in the permeability towards water vapor (Tomé et al., 2010). Bendahou et al. (2015) succeeded in a complete esterification of all accessible hydroxyl groups on the surface of CNC by acid chloride derivatives. Modification of NFC and CNC by lauroyl chloride enabled the preparation of surfactant free water-in-oil (w/o) double emulsions stabilized by nanocellulose at both interfaces (Cunha et al., 2014). Elsewhere, the surface modification of cellulose nanocrystals by acryloyl chloride improved the dispersion of CNC derivatives in aqueous acrylic coatings (Poaty et al., 2014). Berlioz et al. (2009) investigated the gas-phase modification of CNC with palmitoyl chloride and found that the grafting density depended not only on the reaction conditions, but also on the nature and conditioning of the cellulose fibers. In the work by Mukherjee et al. (2013), the introduction of short alkyl chains by surface acetylation of MFC with acetyl chloride resulted in improved dispersibility of the filler in poly (lactic acid) and higher storage modulus (*G′*) determined for composites in shear rheological tests.

Application of biopolymers as a composite matrix is most advantageous in terms of development of new environmentally friendly materials; however they usually offer moderate mechanical performance. In a wide variety of commercially available biopolymers, a new group of engineering biopolyamides has recently focused particular attention. To synthesize those polymers dicarboxylic acids and/or diamines, obtained from renewable raw materials, are used in polycondensation process; for instance sebacic acid synthesized from natural resourced castor oil that is further used in the production of biopolyamide 4.10.

Preparation of polyamide-based nanocomposites with cellulose is a challenging task due to high temperatures involved during melt blending, limited thermooxidative stability of carbohydrate polymers and problems related to the nanoscale dispersion. However, polyamides with long spacers and thus lower melting temperatures were successfully modified with nanocellulose. In the work of Panaitescu et al. (2013) nanocomposites of polyamide 11 and cellulose nanofibers showed improved mechanical properties in micro-mechanical test due to complex morphology comprising oriented bundles of lamellar stacks. In another study thermoplastic composites of polyamide-12 reinforced by cellulose nanofibers were superior to the PA12/organically modified montmorillonite (OMMT) nanocomposites in terms of Izod impact strength, bending modulus and strength as well as heat distortion temperature. Cationic pre-treatment of the cellulose nanofibers with polymeric modifier bearing ammonium cations was found to increase the dispersion of the fibers and played an important role in improvement of the mechanical performance of composite material (Semba et al., 2014). Recently we have reported on the influence of processing conditions on the structure and properties of biopolyamide 4.10/acetylated MFC nanocomposites (Leszczyńska et al., 2015). However, the engineering of interfaces and optimization of processing conditions of biopolyamides reinforced with cellulose micro- and nanofillers is still under-explored research area.

In this work microfibrillated cellulose was heterogeneously modified with homologous series of acid chlorides and then applied as a mechanical reinforcement phase for biopolyamide 4.10. Modified MFC and prepared biocomposites were examined in terms of structural, morphological and thermomechanical properties.

2. Materials and methods

2.1. Raw materials

Microfibrillated cellulose Arbocel MF 40-7 was obtained from J. Rettenmeier & Söhne GmbH + CO KG as aqueous dispersion containing 7 wt.% of dry cellulose. The raw MFC was characterized by means of SEM and WAXD methods. MFC after solvent exchange procedure and freeze drying consisted of whisker-like particles with the diameters in the range of 10 nm–2 μm and a degree of crystallinity of 69% as determined by WAXD. Hexanoyl, decanoyl and dodecanoyl chlorides (reagent grade) as well as acetone and toluene used in solvent exchange process were purchased from Sigma-Aldrich and used as received. Polyamide 4.10 is an engineering biopolyamide (with 70% of its building blocks originating from castor beans) produced by Koninklijke DSM N.V., Netherlands, under commercial name EcoPaXX Q-170MS. It shows a melt flow index (MFI) of 24 g/10 min, viscosity number of 170 cm^3/g and melting temperature of 250 °C at a heating rate of 10 deg/min.

2.2. Chemical modification of MFC by acid chlorides

Solvent exchange process of the aqueous dispersion of raw MFC to acetone and then to toluene was applied; it was done by consecutive (three-times) centrifuging and dispersing of the obtained sediment in the next portion of pure solvent. Pulsating sonication was utilized in each operation step to minimize the overheating effects and evaporation of solvent. Esterification of MFC by acid chloride was performed at 70 °C in inert gas atmosphere under continuous stirring. First, MFC dispersed in toluene was mixed and thermally-stabilized for approx. 20 min, then acid chloride was drop-wise added to the reaction system to set a 1:10 molar ratio of total cellulose hydroxyl groups to acid chloride (OH:AC). The reaction time varied from 30 to 360 min for different acid chlorides due to differences in their reactivity. The reaction was stopped by immersing the flask with 100 ml of reactive mixture in an ice bath (2000 ml). Immediately after the cooling, the cellulose suspension was solvent exchanged back to water. In a series of subsequent washing steps unreacted acid chloride and side-products, such as hydrochloric acid, were removed.

As a reference, a portion of MFC (denoted as MFC SolEx) was solvent exchanged using water, acetone and toluene, but not reacted with an acid chloride. The MFC suspensions were frozen by the liquid nitrogen in thermally isolated square bottom containers. The thickness of MFC suspension was not exceeding 5 mm to ensure rapid freezing. Then the materials were freeze dried using FreeZone 2,5 l Plus freeze dryer produced by Labconco Corporation (USA) equipped with shelf chamber. In the coding of modified samples H, D and DD stand for hexanoyl chloride, decanoyl chloride and dodecanoyl chloride, respectively, and the number describes the reaction time in minutes.

2.3. Preparation of polyamide 4.10/MFC composites

The freeze-dried MFC materials were blended with PA4.10 using a conical type laboratory co-rotating twin screw extruder with a barrel volume of 7 cm^3 (Mini CTV, Thermo Electron Corporation). The temperature of the barrel during processing was 270 °C. The cellulose reinforcing filler was added into the already melted polymer which