Industrial Crops & Products 119 (2018) 73–82

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Modified and thermoplastic rapeseed straw xylan: A renewable additive in PCL biocomposites

Antonia Svärd[a], Elisabet Brännvall[b], Ulrica Edlund[a],*

[a] Fiber and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, SE-100 44 Stockholm, Sweden
[b] RISE Bioeconomy, Research Institutes of Sweden, Box 5604, SE-114 86 Stockholm, Sweden

ARTICLE INFO

Keywords:
Rapeseed/canola straw
Xylan
Grafting
Hemicellulose
Biocomposite
Thermoplastic

ABSTRACT

Xylan extracted from rapeseed straw was chemically modified to gain hydrophobic and thermoplastic properties via macroinitiator formation followed by a free radical grafting-from polymerization with octadecyl acrylate. Biocomposites were then prepared by incorporation of 5 or 20% (w/w) rapeseed straw xylan into a poly(ε-caprolactone) (PCL) matrix by melt extrusion. The grafted xylan was homogeneously distributed within the biocomposite and reinforced the PCL matrix while at the same time preserving the ability to elongate to tensile strains > 500%. Analogous biocomposites made from unmodified xylan in a PCL matrix resulted in heterogeneous mixtures and brittle tensile properties.

1. Introduction

Rapeseed straw is an agro-industrial residue from the cultivation of rapeseed. The straw has few applications except burning or re-fertilizing the soil, while the seeds are high in demand for the production of cooking oil and biofuel.

Like all other high land-based plants, the straw consists primarily of the biopolymers cellulose, hemicellulose and lignin. If the rapeseed straw biopolymers were recovered, they could be converted to valuable products, such as gels, coatings and additives in plastics (Gabrielii and Gatenholm, 1998; Edlund et al., 2010; Laine et al., 2013; Farhat et al., 2017). This would mean increased revenues, useful renewable materials available to the market, and still the possibility of downgrading them to solid fuel or composting for recovery of nutrients after their service life. Biopolymers of interest are the hemicelluloses, a group of structurally diverse polysaccharides such as xylan and glucomannan. Together with sound methods for conversion, hemicelluloses offer renewable material alternatives to oil-based products.

We have shown that polymeric hemicelluloses can be extracted from rapeseed straw by hydrothermal extraction. The extraction conditions: temperature, time and pH, control the exact composition of the extracted hemicelluloses. An extract rich in xylan (a representative structure is depicted in Scheme 1) with high molecular weight (M_w ca. 30 000 g/mol) and a low content of lignin (3–5%) was obtained from extraction at 1.5 M NaOH(aq) at a temperature of 80–140 °C for 1 h (Svärd et al., 2017).

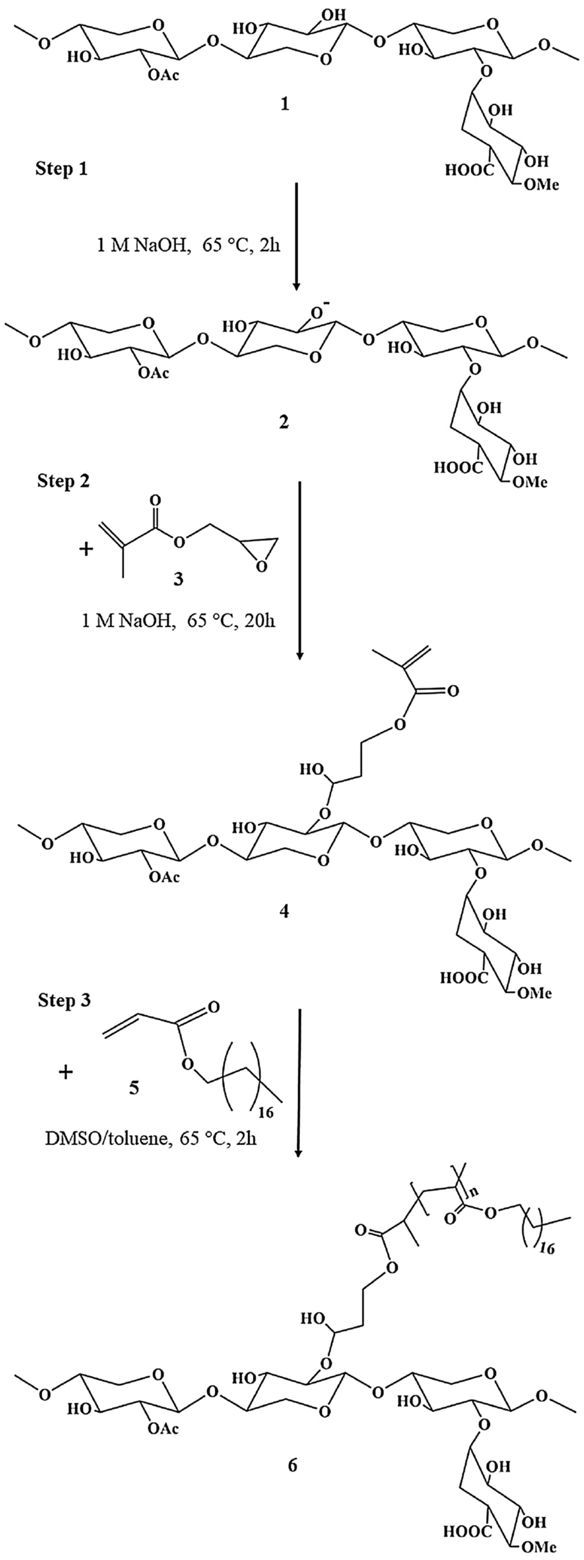
Hemicellulose-rich fractions are however not easily converted into valuable materials. Hemicelluloses are complex, displaying a variety of sugar compositions, molecular weights and degree of branching (Ebringerová et al., 2005). Hemicelluloses are not thermoplastic, instead, they are typically very brittle and in themselves poorly processable by conventional melt processing. In addition, the inherent hydrophilicity of hemicelluloses due to the presence of hydrophilic functional groups such as hydroxyl and carboxyl groups makes them typically poorly miscible with conventional bulk plastics and attempts to mix them usually result in heterogeneous blends or composites with agglomeration due to incompatibility (Faruk et al., 2012; Habibi, 2014). Chemical modification of hemicelluloses through esterification of the abundant hydroxyl pendant groups offers a straightforward pathway to derive hybrid hemicellulose materials and tune the properties. Esterification is a useful tool to immobilize reactive moieties, such as vinyl groups, onto the hemicellulose backbone, producing a polysaccharide macroinitiator for subsequent chain-growth grafting polymerization (Voepel et al., 2011; Voepel et al., 2010; Ibn Yaich et al., 2017). Grafting, in turn, would allow for the introduction of new polymer motifs to the hemicellulose, providing viable and new property profiles such as an enhanced compatibility with bulk plastics.

Common thermoplastic polymer matrixes in commercial composites are polyethylene and polypropylene (Faruk et al., 2012). The biodegradability of poly(ε-caprolactone), PCL, is a strong reason why this polymer is gaining increasing attention, although it is produced from crude oil. PCL finds its use in for example filaments for 3D printing and in polyurethane foams. By mixing PCL with biobased materials, such as xylan, the carbon footprint of the composite can be decreased. PCL is

---

* Corresponding author.
E-mail address: edlund@kth.se (U. Edlund).

https://doi.org/10.1016/j.indcrop.2018.03.067
Received 22 November 2017; Received in revised form 12 February 2018; Accepted 30 March 2018



Scheme 1. Chemical pathway for the grafting of rapeseed straw xylan: (Step 1) Pre-activation of xylan (1 → 2), (Step 2) Synthesis of a Xyl-GMA macroinitiator (4) with GMA (3), and (Step 3) Graft polymerization from the macroinitiator (4) with ODA (5) yielding Xyl-GMA-g-ODA (6).

hydrophobic, semi-crystalline, and has low viscosity. PCL has a melting temperature around 60 °C and a Tg around − 60 °C, which allows for melt-processing by conventional methods in a temperature range of 100–130 °C (Gross and Kalra, 2002; Mohamed and Yusoh, 2015), which is favorable when combined with polysaccharides where the thermal degradation starts at around 200 °C (Shen et al., 2010; Werner et al., 2014). Blending polysaccharides with a hydrophobic PCL matrix is not straightforward and usually leads to insolubility and phase-separation resulting in heterogeneous mixtures (Faruk et al., 2012). PCL was for example blended with starch (Kim et al., 2007), brewery spent grain (Hejna et al., 2015) and grafted cellulose nanoparticles (Siqueira et al., 2008; Herzele et al., 2016). The general trend was that the PCL-biocomposite became stiffer with increasing amount of filler and the materials ability to elongated decreased (Herzele et al., 2016; Hejna et al., 2015). Chemical modification of the polysaccharide pendant groups may help overcome the incompatibility with hydrophobic bulk plastics like PCL

Our aim was to convert xylan extracted from rapeseed straw to a graft-modified polysaccharide to improve the thermoplasticity of the xylan and its compatibility with hydrophobic matrix plastics. Our next aim was to use the modified xylan as a renewable plastic additive in a matrix of a biodegradable polymer: PCL, with the aim of producing a thermoplastic biocomposite demonstrating waste straw as a functional feedstock for biobased materials.

2. Experimental

2.1. Chemicals

Glycidyl methacrylate (GMA) (Aldrich Chemistry, > 97.0%, CAS: 106-91-2), octadecyl acrylate (ODA) (Aldrich Chemistry, 97%, CAS: 4813-57-4), ammonium persulfate (ACS reagent > 98%, CAS: 7727-54-0), DMSO (Merck, CAS: 67-68-5), toluene (Fisher Scientific, CAS: 108-88-3) and 2-propanol (VWR Chemicals, CAS: 67-63-0) were used in the chemical modification of xylan. Aqueous solutions of NaOH (1 M and 1 mM) were prepared from NaOH(s) pellets (Sigma Aldrich, CAS: 1310-73-2). Deuterium oxide (Cambridge Isotope laboratories, Inc., USA, 99.9%, CAS: 7789-20-0), DMSO-d_6 (Cambridge Isotope laboratories, Inc., USA, D, 99.9%, CAS: 2206-27-1) and toluene-d_8 (Cambridge Isotope laboratories, Inc., USA, 99.6%, CAS: 2037-26-5) were used as solvents for NMR analysis. In the reference polymerization of an ODA homopolymer, 2,2′-azobis(2-methyl-propionitrile) (AIBN) (Acros Organics, CAS: 78-67-1, 98%) was used as the initiator. Poly(ε-caprolactone) (PCL), (Aldrich Chemistry, average M_n 80,000 g/mol, pellets with a diameter of ~3 mm, CAS nr: 2480-41-4) was used as the polymer matrix in the prepared biocomposites.

2.2. Rapeseed straw xylan

Two different fractions of rapeseed straw xylan were obtained by extraction with 1 M NaOH at 80 °C and 110 °C, respectively, for 1 h. Both fractions, herein denoted XylA and XylB, had high molecular weight (determined using alkaline water SEC) and consisted mainly of xylan as determined by high performance liquid chromatography with a pulsed amperiometric detector (HPLC-PAD) (Table 1) (Svärd et al., 2017).

2.3. Chemical modification of the rapeseed straw xylan

The crude xylan extracts were chemically modified in a three-step process (Scheme 1).

2.3.1. Step 1: pre-activation of xylan

Freeze dried xylan (1 g) was dissolved in 8 mL of 1 M NaOH(aq) and stirred for 2 h at 65 °C.

2.3.2. Step 2: synthesis of the xylan macroinitiator

GMA (2 mL) was added to the reaction mixture to start the synthesis of the macroinitator and the reaction was left for 20 h at 65 °C. In individual experiments, the reaction time was varied from 2 to 26 h to analyze the conversion as a function of reaction time. The reaction