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Influence of lignin source and esterification on properties of lignin-polyethylene blends

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ABSTRACT

Lignins from pulp mills and biorefineries will gain increasing commercial importance in the next years. Their utilisation in polyolefin blends is of growing research interest as it offers a value-added usage of lignin as well as substitution of non-renewable resources. However, the low compatibility of lignin and polyolefins restrains a satisfying blend production and leads to poor mechanical properties. This can be overcome by modifying lignin prior to its incorporation into polymers in order to reduce its polarity. In this study, five lignins from different raw material sources and production processes were esterified with acetic, propionic and butyric anhydride and subsequently mixed with polyethylene with a weight ratio of 1:1. The paper provides a comprehensive and systematic evaluation of the influence of esterification as well as chemical composition of lignins on mechanical properties and, for the first time, water absorption of lignin-polyethylene blends. Properties of blends were found to improve upon lignin esterification. Compared to blends with unmodified lignin, a progressive increase of tensile (+45%) and flexural (+30%) strength could be observed with increasing length of the ester carbon chain. Lignin source and chemical composition affect water absorption of blends, but show no significant effect on mechanical properties as similar values were observed for blends produced with the respective lignin esters.

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1. Introduction

Lignin is an amorphous, aromatic, natural organic macromolecule built up from phenyl propane units. It is one of the most abundant biopolymers on earth, next to cellulose, and is obtained as a by-product from pulp and paper industries. Kraft, sulphite and soda are the established processes from which lignin can be obtained (Strassberger et al., 2014). Furthermore, Organosolv lignins are intensively investigated, although the process is not established on a commercial scale (Pan and Saddler, 2013). Currently, most of the available lignin is incinerated for energy production in the chemical recovery system of pulp mills. In the future, biorefineries, e.g. for cellulosic ethanol production, open up novel sources for lignin production. Here, great potential for lignin utilisation can be postulated (Podschun et al., 2015) as technology for lignin recovery in this sector is advancing (Larsen et al., 2012). Lignin structure and its chemical composition are known to differ according to plant material and are furthermore influenced by the conditions of the extraction process and subsequent treatment (Pouteau et al., 2003). Lignins deriving from pulp mills have extensively been characterised. For many biorefinery lignins, on the other hand, the knowledge regarding their structure, chemical composition, and properties is still limited. A detailed characterisation, however, is essential to assess lignin utilisation and to evaluate eligible applications. Besides the purity, molar mass distribution and OH group content decide on lignin usability in polymeric systems (Chiemniecki and Glasser, 1988; Pouteau et al., 2003; Pouteau et al., 2004).

A lot of research has been conducted on the use of lignin in polymeric systems and numerous comprehensive reports have been published on recent advances (Chung and Washburn, 2013; Doherty et al., 2011; Duval and Lawoko, 2014; Lora and Glasser, 2002; Ten and Vermerris, 2015). Focus was thereby put on lignin application in resins, adhesives and foams as well as polymer blends. In the field of polymer blends, lignin is a promising alternative to substitute inorganic fillers, since it is not abrasive and

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has a low density (Sánchez and Alvarez, 1999). Early investigations were dedicated to the incorporation of unmodified lignin into thermoplastics (Deanin et al., 1978; Pucciariello et al., 2004; Sánchez and Alvarez, 1999). This attempt resulted in an expected increase in stiffness, yet also displayed a significant reduction of tensile strength and elongation. Pucciariello et al. (2004) ascribed these observations to a poor adhesion between the polar lignin and non-polar polymer (in their case PP), which caused a poor stress transfer and yielding at lower tensile stress compared to neat polymer. Moreover, lignin particles were assumed to cause defects in the polymer matrix, acting as stress concentration points. The use of unmodified lignin is therefore limited (Duval and Lawoko, 2014). In their review on biobased polymers, Laurichesse and Avérous (2014) only recently stated that products based on the simple addition or incorporation of lignin were too brittle. Chiemniecki and Glasser (1988) furthermore related the deterioration of mechanical properties to a poor miscibility of lignin and polymer. Due to differences in the polarity, the solubility of lignin in the polymer matrix is low (Thielemans and Wool, 2005), indicating a low compatibility of lignin and polymer.

According to Feldmann (2002), the elucidation of the impact of material interactions on their miscibility in blends is one of the most noticeable advances in this research area over the last decades. Different strategies were developed to enhance lignin compatibility with polymers. One strategy is the addition of coupling agents such as ethylene-vinyl acetate (Alexy et al., 2004; Glasser et al., 1988), maleic anhydride grafted PP and PE (Sailaja and Deepthi, 2010; Toriz et al., 2002) or a mixture of both (Luo et al., 2009). The addition of coupling agents enhanced the compatibility of blends, yielding in higher tensile strengths compared to blends without coupling agent. A further strategy is the chemical modification of lignin, i.e. a derivatisation of its hydroxyl groups, as they are highly reactive and additionally responsible for lignin's polar character. Hence, their modification can introduce new reactive sites and at the same time reduce lignin polarity. Several approaches can be found in the literature, comprising the grafting of lignin with non-polar polymers (Casanave et al., 1996; Sailaja, 2005), alkylation (Chen et al., 2011; Li and Sarkanen, 2002, 2005; Maldhure et al., 2012), as well as esterification (Maldhure et al., 2011, 2012; Teramoto et al., 2009; Thielemans and Wool, 2005). The two last procedures are the more common ones (Duval and Lawoko, 2014), whereby in a direct comparison, esterified lignin was found to lead to less deterioration of mechanical properties than alkylated one (Maldhure et al., 2011). Regarding the esterification of lignin, Lewis and Brauns (1947) reported on the modification of lignin hydroxyl groups with carboxylic acid anhydrides, varying the chain length from C_2 to C_{18}. A reduction of the melting point and polarity of the lignin was observed with increasing length of the ester carbon chain. A similar approach was followed by Thielemans and Wool (2005), who esterified lignin with carboxylic acid anhydrides and *N*-methylimidazole as catalyst, showing that the solubility of lignin in non-polar solvent increases with increasing length of the ester carbon chain. Recently, Teramoto et al. (2009) reported a successful increase in the miscibility of Organosolv lignin and poly (ϵ-caprolatone) after esterification of lignin with C_2–C_5 anhydrides.

In the present paper, further investigations on the esterification of lignin with carboxylic acid anhydrides are performed. Therefore, five different technical lignins from conventional and biorefinery processing routes were derivatised and subsequently blended with polyethylene (PE-HD) at a weight ratio of 1:1. Detailed chemical analyses of the unmodified and derivatised lignins as well as mechanical and water absorption tests of lignin-polyethylene (L-PE) blends were performed. Based on the results, the influence of lignin source/production process and lignin modification on blend properties was evaluated.

2. Material and methods

2.1. Materials

2.1.1. Lignins

Industrial hardwood (*Eucalyptus* spp.) and softwood (*Pinus* spp./*Picea* spp.) Kraft lignins (**HW-KL, SW-KL**) were provided by Suzano Pulp and Paper, Brazil, and Stora Enso, Sweden, respectively. Organosolv (*Picea* spp.) lignin (**OSL**) from sodium hydroxide assisted methanol-water pulping derived from the former Organocell GmbH, Germany. Commercially available Soda (*Triticum* spp.) lignin (**SGL**) was purchased from Green Value SA, Switzerland. Hydrolysis (*Triticum* spp.) lignin (**HL**) derived from a bioethanol plant and was obtained after steaming followed by hydrolysis and alkaline purification.

2.1.2. Polymer

High density polyethylene (PE-HD) named Hostalen GC 7260 (LyondellBasell, Germany) served as matrix polymer for the lignin-polyethylene blends. Density: 0.96 g/cm^3, MFR: 8 g/10 min (190 °C, 2.16 kg).

2.2. Methods

2.2.1. Esterification of lignin

Esterification of lignin samples was performed according to a revised procedure by Thielemans and Wool (2005). Lignin was dissolved in acetic (100%; Roth, Germany), propionic (100%; Roth, Germany), and butyric anhydride (100%, Merck, Germany), respectively, with a 2:1 weight ratio of solvent to lignin, adding 0.01 ml *N*-methylimidazole (99%; Roth, Germany) as catalyst per gram of lignin. The reaction was performed at 50 °C for 3 h in a stirred glass reactor. Afterwards, the solution was poured into cold deionised water to quench the reaction and precipitate the lignin derivative. The solid was filtered and washed until the pH of the filtrate reached five. Lignin derivatives were dried in an oven at 50 °C. Modification yield was calculated based on the molecular weight, which was calculated from the C_9-formula, assuming a complete esterification of the lignin. Yields between 88 and 99% were achieved, whereby the yield increased with increasing length of the ester carbon chain. Derivatives of HW-KL showed distinctly lower values (65–70%).

2.2.2. Chemical characterisation

Lignins were subjected to quantitative 2-step hydrolysis with sulfuric acid (Lorenz et al., 2015). The solid residue after hydrolysis was recovered by filtration and considered as acid-insoluble lignin. Acid-soluble lignin was spectrophotometrically determined at 560 nm as described by Tappi UM250 um-83 (1991). Polysaccharide content of the hydrolysates was determined by borate anion-exchange chromatography with post-column derivatisation and detection at 560 nm as described by Lorenz et al. (2015). Ash content was determined gravimetrically as prescribed by TAPPI T 211 om-93 (1993) after incineration at elevated temperature of 800 °C. Higher temperature was chosen since lignin samples were not completely incinerated at 525 °C. Elemental analysis was performed using CE Instruments CHNS Flash 1112 analyser system, calculating the oxygen as difference from total sum (ash corrected). Standard protocol by Vieböck and Schwappach (1930) was followed to quantify methoxy group content. Size exclusion chromatography (SEC) of lignin samples was performed in dimethyl sulfoxide with 0.1% LiBr as eluent according to a protocol published by Schütt et al. (2013). Hydroxyl group content was determined by ^{31}P NMR spectroscopy, following the methodology described by Argyropoulos et al. (1993). Changes in the chemical structure of the lignins upon esterification were further analysed by Fourier Transform Infrared Spectroscopy (FTIR) using Bruker Vector 33 in

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