



Development of bioplastic materials: From rapeseed oil industry by products to added-value biodegradable biocomposite materials

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ABSTRACT

Rapeseed crops are mainly harvested due to its high oil content. Production of oil from rapeseed generates a significant amount of by-products like presscake or meal. The high protein content (~35%) of these rapeseed by-products makes them an interesting plant-derived alternative for the development of bioplastic materials. The generation of bioplastics from a rapeseed meal by injection moulding was studied herein at different mould temperatures (80, 100, 120 °C). Further processing of the meal (pelletizing, milling, sieving) on the bioplastics produced was also analysed using dynamic mechanical thermal analysis (DMTA), tensile tests and water uptake capacity. In all cases, strengthening of the samples occurred when moulding at high temperatures (120 °C), which might be related to thermally promoted protein cross-linking. This effect was reflected by an increase of 50% in the viscoelastic properties of the bioplastics when increasing the mould temperature from 80 to 120 °C. Biocomposites of rapeseed meal and polycaprolactone (PCL) at different PCL contents (0–20 wt. %) were also produced. The viscoelasticity of the biocomposites depended on PCL concentration. When PCL content was 20 wt.%, viscoelastic moduli (E' and E'') increased around 200%, which may be associated either to its role as a filler or to its integration into the protein matrix. These results indicate that rapeseed meal is a suitable alternative for the generation of bioplastic materials adding value to a by-product of the rapeseed oil industry.

1. Introduction

Rapeseed (*Brassica napus*) is the second-largest oilseed crop grown around the world, just after soybean, reaching around 450 mt/year, which represents 20% of the total world grain production (Carré and Pouzet, 2014). Due to their high oil content (approx. 40–48%), rapeseed is mainly processed to generate food grade oil or biodiesel (Hu et al., 2017; Saka and Kusdiana, 2001; Svärd et al., 2017). Rapeseed production has suffered a 42% increase, from 48.6 mt in 2006 to 68.8 mt in 2016 (FAO, 2018) resulting in a proportional production increase of its by-products (e.g. rapeseed cake and meal). These by-products generated following oil extraction have relatively high protein contents of approx. 35%, which represent around 55–60% of the initial weight of the seed (Wanasundara, 2011). However, rapeseed by-products contain also antinutritional compounds, such as glucosinolates, phytates or erucic acid, which make them unsuitable for human consumption (Pohl et al., 2018). Consequently, tons of rapeseed by-products are used in lowvalue applications such as animal feed, organic fertilizers or soil cover for erosion control (Pustjens et al., 2014; Troise et al., 2018). The inexpensive cost of rapeseed by-products (150–300 €/ton), up to 10 times less than rapeseed oil (300–1400 €/ton) (Carré and Pouzet, 2014), as well as their known techno-functional

properties (e.g. emulsifying, foaming and gelation properties) make these byproducts suitable as ingredients for pharmaceutical, cosmetic and bioplastic industries (Pohl et al., 2018; Sosada, 1996; Vuorela et al., 2004; Wanasundara, 2011). As for bioplastic market, the use of polylactic acid (PLA) and polyhydroxyalkanoates (PHA) as biofilms have led to an expansion of bioplastic industry, and predictions indicate to increase by 20% within the next five years (European Bioplastics, 2017). However, the potential use of plant-derived proteins in the field of biodegradable plastic has been demonstrated. Bioplastics obtained from maize and wheat (Reddy and Yang, 2013), soy (Fernández-Espada et al., 2016a) and sunflower proteins (Rouilly et al., 2006) have been generated and characterised. Rapeseed proteins could be also considered as ingredient in the development of bioplastics. Rapeseed is rich in cruciferin (60%) and napin (20%) proteins which would allow protein cross-linking (Monsalve et al., 1991; Sjö Dahl et al., 1991). Previous studies have used genetically improved rapeseed cultivars, termed canola, to obtain bioplastics (Chang and Nickerson, 2015; Shi and Dumont, 2014; Zhang et al., 2018). Canola should contain less than 5% erucic acid in the oil and 3 mg per gram of aliphatic glucosinolates in the meal (Eskin and Przybylski, 2003). However, there is limited scientific literature related to the generation of bioplastics with nonmodified rapeseed proteins from rapeseed oil industry.

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Patel et al. (2016), Panchal et al. (2015) studied bioplastic sheets generated from rapeseed meal through compression moulding. However, in that study the authors included polyvinyl alcohol (PVA) as well as calcium carbonate. They employed drastic processing temperature (140 °C) for long periods of time (2 h), which would not allow continuous processing. These biocomposite materials may be taken into account when the mechanical properties of one component are not adequate and a combination of two different materials may benefit if they act synergistically (Callister, 2007; Félix et al., 2015). Biocomposite materials can be developed from the combination of agricultural by-products and synthetic polymers (i.e. polycaprolactone, PCL) (Hejna et al., 2015). PCL is a biodegradable polyester obtained from oil, which exhibits suitable mechanical properties (Herzele et al., 2016; Wu, 2003). Svärd et al. (2018) combined a modified rapeseed protein meal obtained from rapeseed straw and PCL to obtain composite materials after a multi-step process. This processing may increase the cost of the materials when produced in a greater scale. However, costs may be reduced through the production of biocomposites using directly natural by-products from the rapeseed-oil industry and PCL.

The aim of this work was the evaluation of bioplastics generated with a by-product from the rapeseed-oil industry (rapeseed meal) using an easily scalable injection moulding technique. The effect of mould temperature (80, 100 and 120 °C), along with basic steps such as pelletizing, milling and sieving processing of the rapeseed meal on the bioplastic properties was studied. Additionally, biocomposite materials were generated with rapeseed meal and different PCL contents (5, 10, 15 and 20 wt.%). These materials were further characterised along the initial mixing stage of the ingredients, as well as the viscoelastic behaviour, tensile properties and the water uptake capacity of the final bioplastics.

2. Material and methods

2.1. Materials

In order to elucidate the effect of processing on rapeseed-based bioplastics, three different byproducts from the rapeseed oil industry were used within the framework of this study: a rapeseed meal (RM), a milled pelletized rapeseed meal (M-RM) and a milled and sieved pelletized rapeseed meal (MS-RM). RM was supplied by Distribuciones agropecuarias de Aragón, S.L (Spain), and M-RM and MS-RM were supplied by Zaipol S.L. (Spain). Samples were milled using a A10 Basic mill (IKA Labortechnik, Staufen, Germany) for 4 min, and sieved using a 0.42 mm mesh. The protein content of all protein systems was determined in quadruplicate as % N \times 6.25 using a LECO CHNS-932 nitrogen micro analyser (Leco Corporation, St. Joseph, MI, USA), being around 41 ± 1 wt.%. Moreover, the effect of the addition of a synthetic polyester, polycaprolactone (PCL), was evaluated. The PCL used (Capa™ FB100, 100 kDa) was supplied by Perstorp (Sweden). Glycerol (GL) was purchased from Panreac Química (Spain) and used as plasticizer.

2.2. Sample preparation

Bioplastic materials were obtained following a two-stage method. Firstly, polymer (RM, M-RM, or MSRM) and plasticizer (GL) were blended into a mixer in an appropriate protein/plasticizer ratio (60/40). The mixer used was a two-blade counter-rotating rheometer (Haake PolyLab QC, ThermoHaake), which permits the control of both temperature and torque values. After 15 min mixing at 25 °C and 50 rpm, dough-like blends were obtained.

Polymer/plasticizer blends were then submitted to an injection moulding process to obtain the bioplastics probes. A lab scale injection moulding machine MiniJet II (ThermoHaake, Germany) was used. Rectangular specimens (60 \times 10 \times 1 mm) were obtained using an injection pressure of 500 bar for 20 s, and a holding pressure of 200 bar for 300 s. The temperature of the injection chamber was 60 °C in all cases, whereas three different mould temperatures were tested (80, 100 and 120 °C).

Biocomposite materials were obtained following the same two-step

method, although only the RM protein system was selected. Then, the protein:plasticizer ratio was maintained constant (60:40), and the synthetic polymer PCL was introduced in order to yield blends with 5, 10, 15 and 20 wt.% PCL content in the resulting blend. As for the injection moulding stage, the same previous conditions were used, except for the mould temperature which was kept constant at 100 °C.

2.3. Characterization of bioplastics

2.3.1. Dynamic mechanical analysis (DMA)

Rheological characterisation of the final probes was carried out by means of DMA tests, which were performed using a RSA3 (TA Instruments, USA). A dual cantilever geometry was selected for these oscillatory bending tests. Frequency sweep tests were carried out for both bioplastics and biocomposites from 0.02 to 20 Hz at constant temperature (30 °C). Moreover, temperature ramp tests from 25 to 140 °C at 3 °C/min and at 1 Hz were performed on biocomposite materials. Both tests were carried out within the linear viscoelastic region.

2.3.2. Tensile tests

Uniaxial tensile tests were performed until reaching the breakdown of the probes using a RSA3 with a rectangular geometry (TA Instruments, USA). Initially, stress-strain curves were obtained and subsequently three parameters from these curves were obtained: i) Young's modulus (E), maximum stress (σ_{\max}) and strain at break (ϵ_{\max}). The strain rate selected was 10 mm·min⁻¹ and all tests were carried out at room temperature.

2.3.3. Water uptake capacity (WUC)

The WUC of bioplastics and biocomposites were determined according to a method described by Cuadri et al (2018). Probes were dried overnight in an oven at 50 °C (initial dry weight). Subsequently, they were introduced into distilled water for 24 h (wet weight). Finally, the probes were submitted again to a drying process (final dry weight). WUC and loss of soluble material (LSM) were determined using the following equations:

$$WUC (\%) = \frac{\text{wet weight} - \text{final dry weight}}{\text{final dry weight}} \times 100 \quad (1)$$

$$LSM (\%) = \frac{\text{initial dry weight} - \text{final dry weight}}{\text{initial dry weight}} \times 100 \quad (2)$$

2.4. Statistical analysis

Measurements were carried out in triplicate. Uncertainty was expressed as standard deviations whose values were plotted in all the parameters calculated.

3. Results and discussion

3.1. Development of bioplastic materials

3.1.1. Protein/plasticizer mixing

Fig. 1 shows temperature and torque profiles along with mixing time for the three different protein systems studied: RM, M-RM and MS-RM. All these profiles were characterised by initial low values which continuously increased over mixing time. This behaviour has been previously found for other protein/plasticizer blends, and it was related to shearinduced crosslinking among different protein chains (Félix et al., 2015; Jerez et al., 2007). On the other hand, RM and M-RM systems exhibited quite similar profiles, where MS-RM system showed the highest values. This may indicate that the thermomechanical history of the M-RM system (by means of pelleting and milling) had no effect on the protein-protein interactions developed during the first mixing stage.

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