Rheological and mechanical behaviour of PCL-Crayfish composites processed by injection moulding

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Abstract
This work is focused on the development of bio-composites materials based on crayfish flour (CF), by-products from food industry, processed by injection moulding. This material (bio-composites) could be a biodegradable alternative to conventional polymer-based plastics, particularly interesting for relevant industrial applications such as packaging, agriculture, etc. The effect of mixing for systems with different CF/ glycerol (GL)/polycaprolactone (PCL) ratios is evaluated obtaining a dough-like material. Rheological measurements of dough-like material are carried out in order to select suitable injection moulding parameters. Bio-composites characterization is performed by dynamic mechanical temperature, water uptake and tensile strength measurements. Good thermo-mechanical properties and better biodegradability, in comparison with derivate plastic, are exhibited by these bio-composites.

1. Introduction

A big amount of surpluses and by-products are produced every year by food industry that may involve environmental risks. In Andalusia there is particularly one example: The freshwater red-swamp crayfish (*Procambarus Clarkii*). This crustacean was introduced in the middle of the twentieth century and has undergone a fast widespread growth due to the weather conditions, abundant food and the lack of predators causing environmental issues [1]. This fact gives rise to the development of a strong local crayfish industry at the marshes of the Guadalquivir River [1]. Nevertheless, this industry generates too many surpluses that are commercialized by low added value by-product. Some authors have demonstrated the ability of these crayfish proteins in order to stabilized emulsions [2] or preparation of gels [3].

An attractive way to valorise these by-products is the manufacture of “green materials” from renewable resources such as cellulose, starch, polysaccharides and protein. Theses bio-materials may be used as substitutes for petrochemicals. This fact is due to petroleum has been an increase in production costs, which has led to higher prices for their products. An alternative that may minimize the petrol dependence could be the development of new plastic materials from flours with high protein content [4]. In this respect, proteins are exceptionally versatile materials, not only in the sources from which they can be obtained but also in the wide variety of possible modifications, which can be helpful in tailoring their properties to the particular requirements of a specific application. They present significant advantages because proteins are derived from a sustainable resource and can be processed in the same way as conventional synthetic polymers [5]. Proteins are generally mixed with a plasticizer in order to reduce intermolecular forces among polymer chains, increasing mobility and reducing the glass transition (such as glycerol, GL) [6].

Traditionally, protein films are processed by casting method [7], nevertheless classical polymer processing techniques are compression moulding or extrusion, for this reason these techniques are being increasing in this field [8]. Among them, injection moulding is a fairly attractive operation that has not received high attention yet. Typically in this process, polymeric materials are subjected to suitable thermal conditions, being injected at high pressure into the mould cavity [9]. Optimization of processing conditions is essential to achieve the desired properties of the final product. This is particularly relevant in protein-based materials that require thermoplastic mixing with a proper plasticizer but show a predominant thermoset character upon injection moulding.

There is not much information on the use of polycaprolactone (PCL) with protein concentrates. In this way, some authors studied mixtures of a synthetic commercial biodegradable polymer such as PCL with corn gluten meal [10], soy protein isolate [11] and starch [12]. However, authors do not found any information about crayfish CF-based bioplastics containing PCL.

The overall objective of this work is to develop bio-composites materials based on crayfish flour (CF), by-products from food industry, processed by injection moulding as alternative to conventional polymer-based plastics. A small-scale plunger-type injection moulding machine is used in this study to obtain CF/GL/PCL bio-composites, previously mixed by means of a mixing-rheometer that allows recording torque and temperature over mixing. Rheological measurements of these blends are also carried out in order to obtain information that may be used in the selection of suitable processing parameters for injection moulding operations (temperature and residence time in the pre-injection cylinder as well as the temperature of the mould). Final bio-composites characterization is performed by Dynamic Mechanical Thermal Analysis (DMTA), water uptake and tensile tests measurements.

2. Description of the analysis

2.1. Materials.

CF was obtained from ALFOCAN S.A. (Isla Mayor, Seville, Spain). The protein content was determined in quadruplicate as % N x 6.25 using a LECO CHNS-932 nitrogen micro analyzer (Leco Corporation, St. Joseph, MI, USA) [13] being 65 wt.%. GL was purchased from Panreac Química, S.A. (Spain) and PCL (Capa^{TM}FB100) was supplied by Perstorp (Sweden).

2.2. Sample preparation.

Systems with different CF/GL/PCL ratios (Table 1) were performed by mixing in a two-blade counter-rotating batch mixer Haake Polylab QC (ThermoHaake, Germany) at 25ºC and 50 r.p.m. for 60 min, monitoring the torque and temperature.

	Systems (wt.%)				
	(70/30/10)	(68/27/5)	(65/25/10)	(63/2215)	(60/30/10)
CF	70	67	65	62	60
GL	30	28	25	23	30

PCL	0	5	10	15	10

Table 1. Percentages (wt %) of different CF/GL/PCL systems. Note: the reference system correspond to 70 wt.% CF/30 wt.% GL/10 wt.% PCL

The dough-like materials obtained after mixing process were subsequently processed by injection moulding using a MiniJet Piston Injection Moulding System II (ThermoHaake, Germany) to obtain probes. Two types of moulds were used to prepare the probes: a 60×10×1 mm rectangular shape mould for both DMTA experiments and water uptake measurements and a Dumpbell type probe defined by ISO 527-2:1993 for Tensile Properties of Plastics.

2.2. Characterization of blends.

Blends containing 65 wt.% CF, 25 wt.% GL and 10 wt.% PCL and the reference blend (containing 70 wt.% CF and 30 wt.% GL) were characterized by Small Amplitude Oscillatory Shear (SAOS) measurements, using a controlled-strain rheometer (ARES), in order to select the optimum conditions for injection moulding. The geometry used has been a plate and plate geometry (dia: 25 mm) with a rough surface and a gap between plates of 2 mm. Low viscosity Dow Corning 200 fluid has been used as sealant to avoid sample drying. Strain sweep SAOS tests were also performed in order to establish the linear viscoelasticity range. Temperature ramp tests were carried out at 5 ºC/min from 20 to 100 ºC monitoring storage (G’) and loss (G’’) modulus at a constant frequency of 1 Hz. All the systems studied had the same thermorheological history performing any rheological test.

2.2. Characterization of probes.

2.2.1. Dynamic Mechanical Thermal Analysis (DMTA).

DMTA tests were carried out with a RSA3 (TA Instruments, New Castle, DE, USA), on rectangular probes using dual cantilever bending. All the experiments were carried out at constant frequency (1Hz) and strain (between 0.01 and 0.3%, within the linear viscoelastic region). The selected heating rate was 3ºC min^{-1}. All the samples were coated with Dow Corning high vacuum grease to avoid water loss.

2.2.2. Tensile strength measurements

Tensile tests were performed by using the Insight 10 kN Electromechanical Testing System (MTS, Eden Prairie, MN, USA), according to by ISO 527-2:1993 for Tensile Properties of Plastics. Tensile stress and elongation at break were evaluated from at least three duplicates for each product using type IV probes and an extensional rate of 10 mm min^{-1} at room temperature.

2.2.3. Water uptake capacity

Water uptake of bioplastics was determined following the ASTM D570 norm (ASTM D570-98, Standard test Method for Water Absorption of Plastics) using at least three 60×10×1 mm specimens immersed in distillate water for 2 h or 24 h at room temperature.

3. Results

3.1. Preparation of blends by thermoplastic mixing

Fig. 1 shows both torque (Fig. 1A) and temperature (Fig. 1B) profiles as a function of mixing time for blends obtained at different CF/GL/PCL ratios. These results put forward the remarkable dependence of these parameters on the CF/GL/PCL ratio. Thus, a rapid increase in torque up to a maximum value takes place, followed by an asymptotic decrease towards a plateau value. The maximum value is reached in first place for the system without PCL. However, in bio-composites containing, an increase of the CF/GL ratio lead to a shift of the maximum towards longer mixing time.

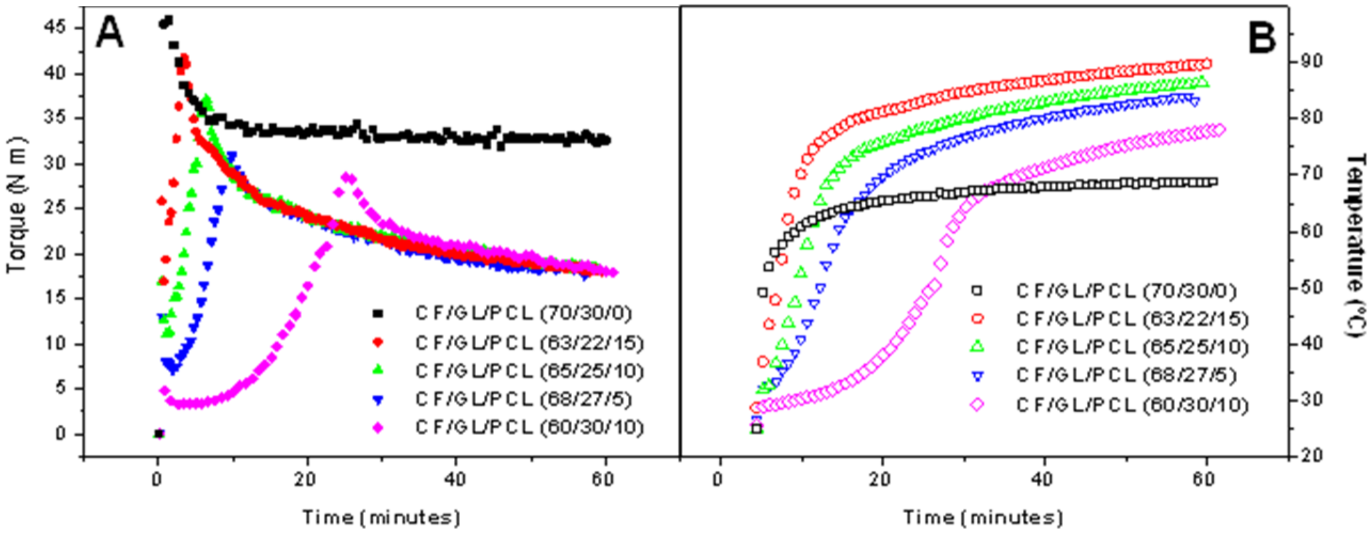

Figure 1. Evolution of torque and temperature as a function of mixing time for different CF/GL/PCL systems (70/30/0, 60/30/10, 67/28/5, 65/25/10 and 63/22/15)

From these results it can be concluded that the presence of PCL lead to a constant torque value after 40 min (Fig. 1A), probably, as a consequence of the melting point of PCL that takes place at c.a. 55ºC. This fact is verified in Fig. 1B where, in all cases, the melting temperate corresponding to PCL is exceeded. On the other hand, it can be also observed that while the highest torque values are reached by the system without PCL, the highest temperature observed correspond to the system with lower CF/GL ratio containing PCL. A suitable mixing time was selected for each system, as the 90 of plateau zone (10, 15, 17, 20 and 35 min for 70/30/0, 63/22/15, 65/25/10, 67/28/5 and 60/30/10 systems, respectively).

3.2. Characterization of blends

Fig. 2 shows the complex viscosity (η^*) (Fig. 2A) and loss tangent (tan δ) (Fig. 2B) obtained from Small Amplitude Oscillatory Shear measurements for CFP/GL (70/30) and for CFP/GL/PCL (65/25/10) blends as a function of temperature.
The viscosity profile is quite similar under the experimental temperature window with a well pronounced decrease of viscosity as temperature increase (Fig. 2A). It also can be noticed that η* correspond to PCL-containing blends is significantly higher and, consequently, these PCL-containing blends show less processability, however, its use can be justified by the potential enhancement in the final bio-composite materials. On the other hand, as for tan δ profile (Fig. 2B), both systems show elastic-dominant behaviour (tan δ < 1). In addition, tan δ results

reveal the occurrence of a glass-like transition at ca. 75ºC for the system without PCL. However, glass transition for the system (65/25/10) could be probably shifted to higher temperatures.

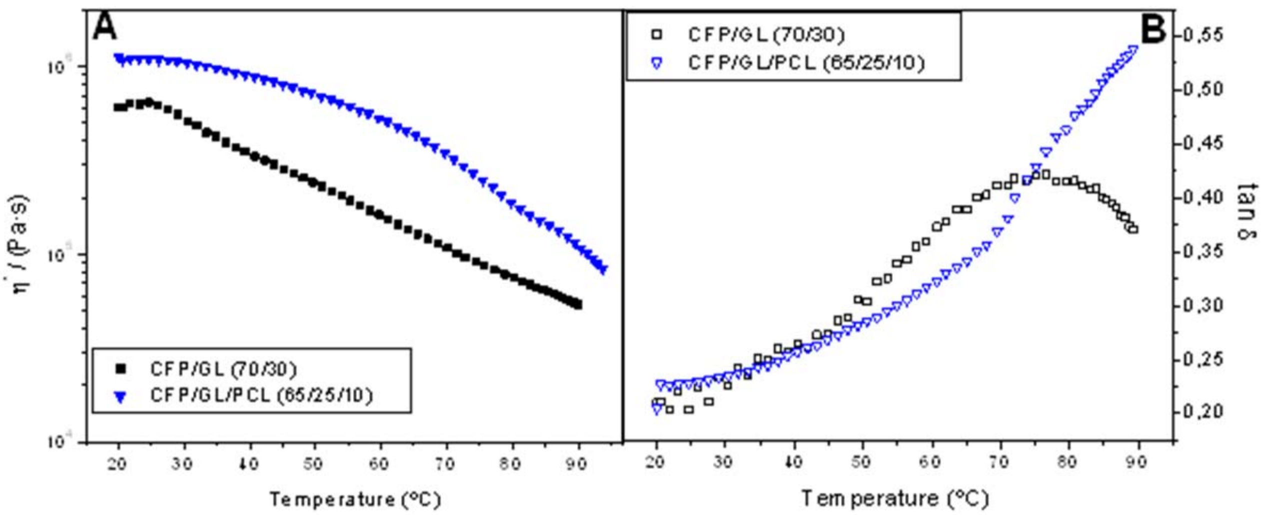

Figure 2. Complex viscosity (η*) (A) and loss tangent (B), at 1 Hz and 5 °C•min^{-1}, as a function of temperature, for CF/GL (70/30) and CF/GL/PCL (65/25/10) blends, subjected to thermoplastic mixing at 25ºC and 50 rpm for 10 and 20 min, respectively.

Finally, after mixing and rheological measurements, the temperatures selected to the injection-stage were 60ºC in the cylinder and 100ºC in the mould

3.3. Characterization of probes

3.3.1. Dynamic Mechanical Temperature Analysis (DMTA).

From DMTA scans, two parameters (E' and tan δ) have been selected at two different temperatures in order to compare the behaviour of bio-composites both under service conditions (20ºC) and at high temperatures (130ºC) that are shown in Table 2.

SYSTEM	**CF/GL/PCL (70/30/0)**	**CF/GL/PCL (63/22/15)**	**CF/GL/PCL (65/25/10)**	**CF/GL/PCL (68/27/5)**	**CF/GL/PCL (60/30/10)**
E' (MPa) 20ºC	139.0±8.5	285.0±6.4	275.0±0.1	231.0±4.2	154.0±9.9
E' (MPa) 130ºC	0.7<0.1	1.7±0.2	2.2±0.1	1.7±0.5	1.2±0.1
tan 20ºC	0.36±0.03	0.35±0.01	0.29±0.01	0.29±0.01	0.35±0.01
tan 130ºC	0.90±0.02	0.51±0.04	0.40±0.01	0.49±0.08	0.49±0.06

Table 2. Elastic modulus (E') and loss tangent (tan δ) at 20 and 130ºC obtained from DMTA for different CF/GL/PCL probes (70/30/0; 63/22/15; 65/25/10; 68/27/5 and 60/30/10)

Results from Table 2 evidence that those bio-composites containing PCL leads to higher values in the storage modulus (E') in the entire temperature range as compared with the reference system. Similar results were reported by Aithani and Mohanty (2006) [10], which found an increase in storage modulus for bioplastics containing PCL and corn gluten meal as the proportion of PCL increase. In addition, according to the results containing the same percentage of PCL (see systems CFP/GL/PCL (65/25/10) and (60/30/10)), regarding mechanical behaviour, not only is important the proportion of PCL, but also the proportion of protein and plasticizer.

3.3.2. Tensile strength measurements

Results obtained from uniaxial strength measurements are shown in Fig. 4. Fig. 4A displays the results of stress-strain curves obtained for systems (70/30/0) and (65/25/10). Both curves exhibit an initial linear elastic behaviour of high constant stress-strain slope yielding high values for the Young's Modulus (E), followed by a plastic deformation stage with a continuous decrease in the stress-strain slope after the elastic limit, reaching a maximum value for the stress (σ_{max}) and immediately followed by the maximum strain (ε_{max}).

Regarding the tensile properties, Fig. 4B shows the values of two parameters (maximum tensile strength and Young's Modulus) obtained from tensile tests applied to CF/GL/PCL bio-composites probes. PCL-containing bio-composite show higher values for σ_{max}, and E, with the notable exception of system 60/30/10 which show a clearly decrease in mechanical properties. This latter exception is attributed to the excess of glycerol that leads to brittle bio-composite with loss of plasticizer during storage.

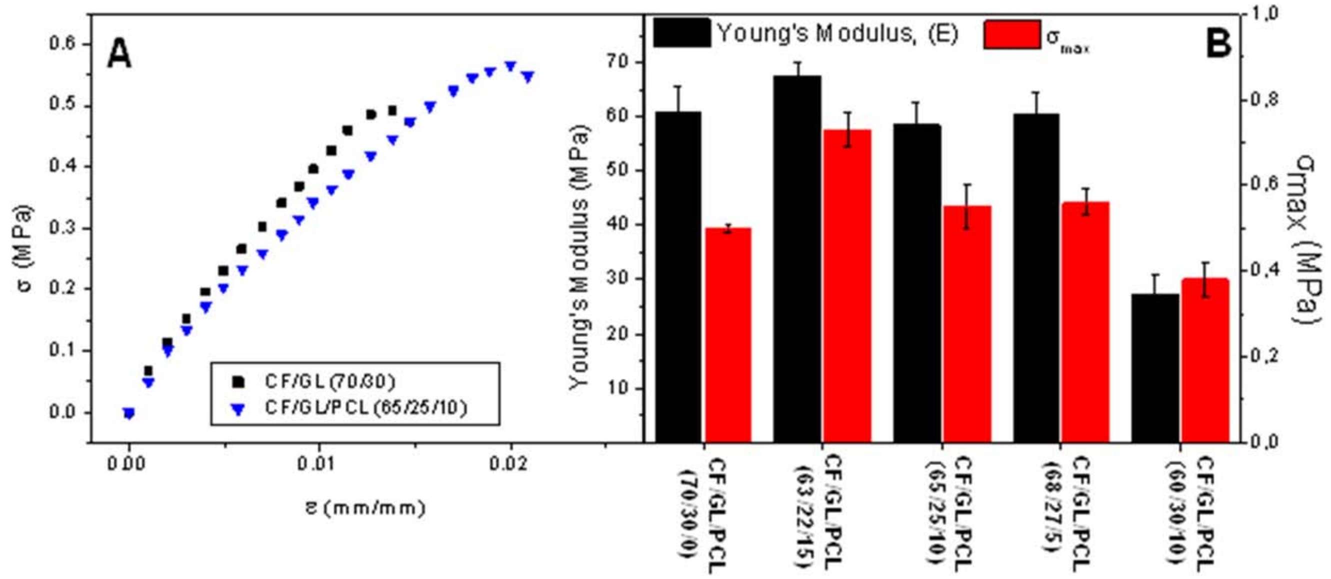

Figure 3. Results from tensile strength for different CF/GL/PCL: (A) Stress versus strain curves; and (B) parameters from tensile strength measurements: Maximum stress (σ_{max}), and Young's Modulus (E)

3.3.3. Water uptake capacity

Fig. 3 shows the results from water uptake measurements obtained after immersion of bio-composite samples for 2 and 24 h, as well as the water-soluble matter loss, as a function of PCL content. No significant differences between water uptake percentages after 2 and 24 h are found, regardless of the CF/GL/PCL ratio used in the bio-composite preparation by injection moulding. This fact indicates occurrence of relatively faster water absorption kinetics. In addition, an increase in PCL content reduces a progressive decrease in water absorption. It also may be attributed to a higher structure degree of the composite matrix. This is consistent with above-mentioned higher values from DMA and tensile tests. It can be observed that absorption at 24h is higher when GL/CF ratio also is higher. This behaviour support the results found by Guillard et al. (2013) [14], who reported that the swelling ratio of polymer matrices increase with protein mobility. In this case this protein mobility could be due to an increase in the plasticizer content.

The CF/GL/PCL (60/30/10) bio-composites shows negative absorption at 2 and 24h, this fact could be related with the glycerol exudation, which indicates an excess of plasticizer agent (glycerol) that is that is quickly dissolved in water, causing a net weight loss. As it can be observed from the water-soluble loss matter all systems shows a value around 40%. These results suggest that the loss of soluble matter mainly corresponds to the highly hydrophilic glycerol. The extra-loss matter observed should correspond to moisture content as well as to some protein that is not strongly associated to the network structure.

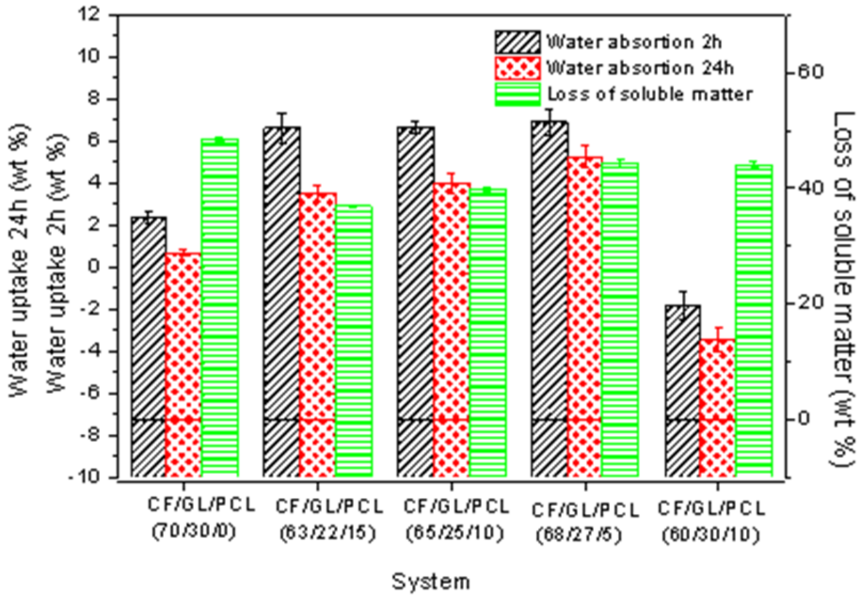

Figure 4. Evolution of water absorption capacity (wt.%) after immersion for 2 h and 24 h and loss of soluble matter (wt.%) for different CF/GL/PCL probes (70/30/0; 63/22/15; 65/25/10; 68/27/5 and 60/30/10)

4. Concluding remarks

The present work demonstrates the possibility to develop green bio-composites containing important amount of crayfish flour (a protein concentrate) and, therefore, finding value-added application for this crayfish protein by-products.

From the experimental results, it may be concluded that mixing of CF/GL/PCL systems, can be controlled by monitoring the torque and temperature in order to select the more suitable mixing time and formulation. Rheological measurements in the linear viscoelastic region (temperature ramps, particularly) of the obtained blends are also carried out in order to obtain information that may be used in the selection of suitable processing parameters for injection moulding operations (temperature and residence time in the pre-injection cylinder as well as the temperature of the mould).

The addition of PCL during mixing yields materials with different rheological properties (higher viscoelastic moduli) that can partially make injection process more difficult. However, PCL-containing bio-composites exhibit better results in DMTA parameters (higher E' and lower tan δ values) and no very important differences in tensile parameters. In addition, regarding bio-composite formulation, not only the PCL ratio is important but also the plasticizer ratio. In fact, the percentage of glycerol (plasticizer) is critical in order to obtain homogeneous, flat and featureless bio-composite plastic materials.

In general, bio-composite plastic materials with adequate mechanical properties can be made by injection moulding adjusting the formulation (protein concentrate/glycerol/PCL ratios) and selecting thermomechanical processing conditions.

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