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“Green composites based on wheat gluten matrix and *Posidonia Oceanica* waste fibers as reinforcements”

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“Green composites based on wheat gluten matrix and *Posidonia Oceanica* waste fibers as reinforcements”

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Abstract

In this work, green composites from renewable resources were manufactured and characterized. A fibrous material derived from *Posidonia Oceanica* wastes with high cellulose content (close to 90 wt. % of the total organic component) was used as reinforcing material. The polymeric matrix to bind the fibers was a protein (wheat gluten) type material. Composites were made by hot-press molding with varying the gluten content on composites in the 10-40 wt. % range. Mechanical properties were evaluated by standardized flexural tests. Thermo-mechanical behavior of composites was evaluated with dynamic mechanical analysis (torsion DMA) and determination of heat deflection temperature (HDT). Morphology of samples was studied by scanning electronic microscopy and the water uptake in terms of the water submerged time was evaluated to determine the maximum water uptake of the fibres in the composites. Composites with 10-40 wt. % gluten show interesting mechanical performance, similar or even higher to many commodity and technical plastics, such as polypropylene. Water resistance of these composites increases with the amount of gluten. Therefore, the sensitiveness to the water of the composites can be tailored with the amount of gluten in their formulation.

Keywords:

Posidonia Oceanica; green composites; gluten; mechanical properties

1. Introduction.

The development of materials from renewable resources is a growing research field. The use of these biobased materials can not only contribute to stop or prevent petroleum depletion, but also offers lower environmental impact than petroleum-based materials. The composite materials industry is highly sensitive to environmental concerns so that, important efforts are being made to provide new eco-friendly materials for uses at industrial scale. Many of these new green composite materials are based on natural fiber reinforcements and/or biobased polymer matrices. A wide variety of natural fibres such as kenaf, flax, hemp, jute, ramie, kapok, sisal, etc. have been extensively used in composite systems with thermosets and thermoplastic polymers.[1-7] Nowadays, attractive thermoset matrices are being developed: i.e. phenolic resins from cashew nut shell liquid (CNSL), unsaturated polyester (UP) with biobased polyols, epoxy resins (EP) from vegetable oils, etc.[8-14] These bio-based thermoset polymers can potentially compete with petroleum-based phenolics, unsaturated polyesters, epoxies, etc.[15] In addition to these high consumption resins, new ones based on the use of biobased monomers are also being developed; i.e. furfuryl palmitate with maleic anhydride and jute fiber as reinforcement has been successfully manufactured by impregnation and subsequent hot-compression;[16] methacrylated epoxidized soybean oil (MMSO) has been used in combination with jute fiber for the production of green composites without styrene addition.[17] With regard to thermoplastic matrices it is important to remark the increasing use of biodegradable polymers such as poly(lactic acid), poly(hydroxy-butyrates), thermoplastic starches, poly(caprolactone), etc.[3, 18, 19]

Natural polymers such as those derived from protein structures (gluten, soy protein, casein, ovalbumin, etc.) are quite interesting as matrix materials for composites. They are relatively cheap materials and, in many cases, they are obtained as wastes from the food industry. It is well known the intrinsic good adhesive properties of many proteins (soy protein, gluten, etc.) and, in fact, proteins are highly used in adhesive formulation.[20-22] This is a key factor in order to use proteins as matrices in composite materials as good fiber-matrix interactions can be expected. For this reason, different proteins have been used as matrix

materials for a wide variety of composite structures. In the case of soy protein composites the mechanical and thermal behavior has been analyzed, along with water resistance. In this way some experiments have been performed focused on increasing the water resistance of these composites. Casein is another protein used for manufacturing composite materials; casein is generally used in film form, and can be mixed with different crosslinkers to increase its chemical resistance.[23] In addition to these proteins, gluten is an attracting protein for composite manufacturing as it possesses non-water soluble components and this fact can contribute to high durability on composites. So that, it is possible to find different works related to the use of gluten matrices for composite materials with coconut, sisal, jute, hemp and basalt fibers.[24-27] It is quite usual the use of plasticizers such as sorbitol and glycerol because of the fragile nature of gluten thus leading to flexible materials which can be processed in a simple way.

The use of fibers from renewable resources as reinforcement in composite materials is an area that has been approached by a large number of research groups. Natural fibers coming from industrial crops such as flax, kenaf, jute, etc. have been extensively reported as in some cases they can give comparable properties to traditional fibers such as glass fiber. The use of these fibers is attractive from both technical and environmental points of view. But it is also important to consider fibrous wastes as potential candidates for green composites. On the one hand, it is possible to find fibrous materials as wastes derived from different industrial processes: i.e. husk rice, almond husk, olive pits, sawdust, sugar cane bagasse, etc.[28-32] On the other hand, great amounts of biomass (pine needles, algae wastes, leaves from deciduous forests, corn stalk, wood waste, etc.) are continuously generated and some final uses include compost, fuel manufacturing, conversion to thermal energy, etc.[33-35] In some cases it is possible to find new attracting uses for these biomass wastes as it is the case of fibrous wastes derived from algae such as *Posidonia Oceanica*. This is a Mediterranean endemic alga which appears in big amounts in the form of balls along many coastal beaches as a consequence of storms that tear off leaves, stems and, in some cases, the whole plant. These wastes reach the seacoast and the continuous movement over the sand causes formation of rounded balls. These

balls are removed from tourist beaches in order to obtain quality awards. Some studies have focused on the potential use of this fibrous waste as filler in potato starch-based films with varying amounts of *Posidonia Oceanica* in the 10-30 wt. % range with interesting results.[36] Other uses include filtration, liquid absorption, dye removing, base material for cellulose obtaining, etc.[37-41]

The main aim of this work is the upgrading of fibrous wastes from *Posidonia Oceanica* by using hot-press molding processes with wheat gluten protein as binder-matrix material to obtain a new set of polymer composites fully based on renewable resources with balanced mechanical and thermal properties.

2. Experimental.

2.1. Materials.

Posidonia Oceanica balls were collected from different beaches located in the Spanish Valencian Mediterranean coast. Wheat gluten was supplied in a powder form by Indespan (Indespan, Valencia, Spain). The moisture content (determined by drying at 100 °C for 24 h) of the gluten powder was 6.5 wt. %. Composition of the wheat gluten, on a dry basis, is characterized by a high protein content (80 wt. %), 15 wt. % starch, 4 wt. % lipids and less than 1 wt. % of fiber and other impurities.

2.2. Preparation of *Posidonia Oceanica* fibers.

Posidonia Oceanica balls were subjected to a milling process to convert them into a short fiber form using an industrial mill. The final length of the fibers was in the 2-8 mm range. Fig. 1 shows a photograph of the initial *Posidonia Oceanica* balls and short fibers obtained by the milling process. After the milling process, fibers were subjected to a washing stage with distilled water in order to remove sand, soil and other wastes. This stage is repeated until clean waste water is observed. After this, washed fibers are subjected to a NaOH (10 wt. % in water) treatment for 24 h in order to remove excessive impurities from the surface of the fibers and

made fiber swollen. After this, soaked fibers were subjected to a drying process at 60 °C for 24 h.

Figure 1

2.3. Chemical characterization of *Posidonia Oceanica* balls.

The *Posidonia Oceanica* fibres were hydrolyzed according to Theander et al.[42] The samples were subjected to further acid hydrolysis with H₂SO₄ in an autoclave for 60 min at 120 °C. Two different products were obtained: an insoluble product of lignin and inorganic residue and a soluble product of carbohydrates. The carbohydrate solution was then examined by Ionic Chromatography. Peaks were quantified by area, and a mixture of standards (glucose, mannose, xylose, arabinose and galactose) was used to elaborate calibration curves. The data from two replicates were averaged; in all cases, the standard deviations from replicates were below 1% of the mean values.

The insoluble product from the hydrolysis was washed repeatedly and dried at 110 °C during 24 h. This dry residue was finally weighed and recorded as *P*. The inorganic content was obtained by pyrolysis in a furnace during 24 hours at a temperature of 575 °C, and the remaining ashes were weighed (*P'*). Finally, the lignin content was calculated according to equation (1).

$$\text{Klason Lignins} = \frac{P - P'}{M} (\%) \quad (1)$$

where *M* is the initial dry mass, *P* is the weight of the dry residue after acid hydrolysis and *P'* is the remaining ashes after to be pyrolysed.

2.4. Processing of composite sheets by hot-press molding.

Firstly, the appropriate amounts of gluten powder and *Posidonia Oceanica* fibers were weighed to obtain different composite formulations in the 10 – 40 wt. % gluten. After this, the two components were mixed manually in a zip bag to provide good homogeneity. Subsequently, the homogeneous mixture was dropped into a cavity (4.5x7.0 cm²) of an aluminum mold and

placed between the plates of a hot-plate press. Then the mixture was subjected to a temperature of 120 °C and a pressure of 22 MPa during 10 min; after this, temperature was removed and a pressure of 22 MPa was maintained for additional 15 min. After this processing cycle, composite sheets with an average thickness of 3 mm were released from the mold and samples for different characterization techniques were prepared.

2.5. Mechanical characterization of composite sheets.

Three point bending tests were carried to composite materials following the guidelines of the ISO 178 in a universal test machine Ibertest Elib 30 (S.A.E. Ibertest, Madrid, Spain). A load cell of 5 kN was used and the crosshead speed was set to 5 mm min⁻¹. The impact energy of un-notched samples was determined using a 6 J Charpy pendulum by following the ISO179:1993 standard.

2.6. Surface characterization of composite materials by SEM.

Fractured samples from impact tests were observed by scanning electron microscopy (SEM) in order to evaluate interactions among fiber-matrix. A JEOL JSM-6300 (Jeol USA, Peabody) scanning electron microscope working at an acceleration voltage of 15 kV was used. Prior to sample observation, surface was covered with a gold layer in vacuum conditions with a Sputter Coater EMITECH mod. SC7620 supplied by Quorum Technologies (Quorum Technologies, East Sussex, United Kingdom).

3. Results and discussion

3.1. Chemical characterization of *Posidonia Oceanica* wastes.

Table 1 shows the chemical composition of *Posidonia Oceanica* in terms of acid soluble (glucose, arabinose, galactose, mannose and xylose) and insoluble (kraft lignin and ash) components. Glucose is the main building block of cellulose through dehydration of D-glucose, leading to long-chain linear polymers that can provide high mechanical performance on

cellulose-based composites. On the other hand, arabinose, galactose, mannose and xylose are typical building blocks of hemicellulose in plants. They have been reported as hemicellulose by other authors.[43] These monosaccharides also appear in *Posidonia Oceanica* and this fraction is characterized by short and branched polymer chains. *Posidonia Oceanica* is characterized by a relatively low amount of kraft lignin and inorganic components (ash content) around 9.2 and 12.6 wt. %, respectively. With regard to the organic fraction, it is important to remark the high cellulose content, which represents 70.16 wt. % of the total weight and 89.8 wt. % of the carbohydrate fraction. This value is similar to that of other natural fibers such as hemp (up to 75 wt. %) or flax (in the 65 – 85 wt % range) and clearly higher to typical values of wood (40 – 50 wt. %) thus indicating the potential of these waste fibers as reinforcements for polymer composites as the linearity and length of the cellulose chains can provide attracting mechanical performance.[44, 45] With regard to hemicellulose, the main monomer is xylose as observed in Table 1.

Table 1

3.2. Mechanical and thermal properties of Posidonia Oceanica composites.

Table 2 summarizes flexural properties of *Posidonia Oceanica* composites with different amounts of gluten protein as binder. Presence of a binder (in this case, gluten) is necessary to provide cohesion to *Posidonia Oceanica* waste fibers. Composites with less than 10 wt. % gluten present partial embedment of *Posidonia Oceanica* fibers, leading to a heterogeneous material that is impossible to test. However, composites with a 10 wt. % of gluten show high homogeneity and they can be properly characterized.

Flexural strength of composites with 10 wt. % gluten is 22.2 MPa and this value increases up to 40.8 MPa for composites containing 40 wt. % gluten. The standard deviation is relatively low (less than 10%) in all the formulations, proving the high homogeneity of the developed composites.

Flexural modulus is higher than 3 GPa for gluten compositions in the 20-40 wt. % range. Composites with 10 wt. % gluten show a lower modulus value of about 2.35 GPa. However even in this case the overall performance of these composites is interesting due to the high content on *Posidonia Oceanica*. These properties are similar to some commodity plastics such as polypropylene. Once again, the relatively low values of the standard deviation for flexural modulus indicate good homogeneity on composites.

The impact energy for all composites is close to 0.10 kJ m^{-2} with no significant change with the gluten content.

Table 2

The fractured surfaces from impact tests were also analyzed by SEM giving some evidences about the morphology of *Posidonia Oceanica* composites (Fig. 2) and the influence of the binder amount on final properties. Morphology of the fractured sample with 10 wt. % gluten (Fig. 2a) is characterized by a generalized fibrous structure. The binder amount is enough to provide cohesion but it is not possible to observe a continuous matrix. The microstructure is composed of pressed *Posidonia Oceanica* fibers linked all together with small interlock points of gluten protein. This microstructure is responsible for the lowest mechanical performance; the small amounts of gluten only provide cohesion to keep fibers together but there is not enough binder material to appropriately transfer stresses. An increase in the binder material (gluten protein) leads to a morphology characterized by a crosslinked gluten matrix in which *Posidonia Oceanica* fibers are embedded. This situation is clearly evident from observation of Fig. 2d which corresponds to composites with 40 wt. % gluten; a continuous gluten matrix and individual embedded *Posidonia Oceanica* fibers are differentiated. Poor interactions between a matrix and the reinforcement can be detected by the presence of a gap between them. In the case of low gluten amounts it is difficult to detect interface interactions due to the relatively small amounts of binder material which do not reach to form a continuous phase (Fig. 2a). Nevertheless, as we can see in Fig. 2d (40 wt. % gluten) a small gap between the fiber and the gluten matrix can be detected; so that, maximum interaction among fiber-matrix interface

cannot be expected but, the relatively small gap gives evidences of some interaction among fiber-matrix and this has a positive effect on maximum flexural stress. Poor interaction would lead to low flexural stress values due to the stress concentration effect of fibers. Nevertheless, as we have observed previously, the maximum flexural stress increases with the gluten content and this could be directly related to interface phenomena among fiber-matrix. Typical aminoacid functionalities of gluten can react with hydroxyl groups in *Posidonia Oceanica* to provide strong interactions between the fiber and the matrix.

Figure 2

In addition to mechanical properties it is important to know the effect of temperature on mechanical performance of these composites. For this reason, a DMA (torsion mode) characterization has been carried out. Fig. 3 shows a plot comparison of the temperature ramp curves for *Posidonia Oceanica*-gluten composites with different gluten contents. The storage modulus (G') at 40 °C is 0.7, 1.0, 1.2 and 1.8 GPa for composites containing 10, 20, 30 and 40 wt. % gluten respectively. Compositions comprising low gluten content (10 wt. %) show an initial storage modulus relatively low. Although this gluten content is enough to obtain homogeneous composite materials with good fiber embedment, mechanical properties are relatively poor since gluten acts only as a binder material to provide cohesion to composite. In addition, as gluten softening occurs at about 70-90 °C, the low amount of gluten on these compositions lead to short dependency on temperature as it can be observed in Fig. 3. *Posidonia Oceanica* composites with 40 wt. % gluten are in accordance with those obtained in flexural tests. Presence of higher amounts of gluten leads to better stress transfer and this has a positive effect on mechanical performance. Nevertheless, as gluten softening is located in the 70-80 °C range, we observe high dependency of mechanical properties as temperature increases.

Figure 3

As we have observed in the previous DMA analysis, gluten is highly sensitive to temperatures in the 70-90 °C range: a clear decrease in storage modulus (G') is detected in this temperature range. This sensitiveness of gluten to temperature leads to decreasing the thermal stability as the gluten content increases. This situation can be evidenced from observation of HDT values of composites (Table 3). Cellulose is characterized by high thermal stability while gluten suffers a softening in the 70-90 °C range. For this reason, high cellulose content composites show higher HDT value if compared to composites with high gluten content.

Table 3

3.3. Water uptake of Posidonia Oceanica-gluten composites.

Despite the numerous advantages (from both technical and environmental points of view) that natural fibers possess as reinforcement in comparison with synthetic fibers, it is important to note their main drawback: natural fibers are highly hydrophilic so that, composites with natural fibers are highly sensitive to moisture and water uptake.[46, 47] Typical hydroxyl groups of cellulosic structures attract water molecules thus leading to partial swelling of composites. For this reason it is important to study the rate at which the water uptake occurs as in some final applications, these composite materials can be exposed to water (i.e. water from rain) and this can lead to partial swollen thus promoting a change in dimensions which can compromise dimensional stability of the molded parts. Fig. 4 shows the water uptake behavior of *Posidonia Oceanica*-gluten composites when submerged in water.

Figure 4

As *Posidonia Oceanica* fiber is mainly composed of cellulose and hemicellulose, its sensitiveness to water is higher than gluten so that, as the total amount of gluten increases, the water uptake is reduced. Fig. 5 shows two SEM images corresponding to composites with 10 wt. % gluten (Fig. 5a) and 40 wt. % gluten (Fig. 5b). It is clearly evident from the observation

of these images the fibrous nature (high surface area) of *Posidonia Oceanica* component; this fact, together with the hydrophilic nature of cellulose (due to hydroxyl groups) and the typical tubular hollow structure that promotes water uptake by capillarity, is responsible for the high water uptake as observed in Fig. 4. For example, composites with 10 wt. % gluten tend to stabilize the water uptake at values close to 80% while composites with higher gluten amounts (40 wt. %) stabilize the water uptake at lower values (around 64% for 40 wt. % gluten). The initial water uptake rate is typical of lignocellulosic materials. So that, the water uptake is increased up to 70%, 64%, 59% and 53% in a relatively short period (24 hours) for *Posidonia Oceanica*-gluten composites with 10, 20, 30 and 40 wt. % gluten respectively. These results indicate that approximately an 80% of the total water uptake takes place in the first 24 hours; after this initial fast stage, the water uptake occurs but in a less extent.

Figure 5

4. Conclusions.

Manufacture of composites based on *Posidonia Oceanica* wastes and wheat gluten protein is an interesting solution to the management problem associated to the algae accumulation. Therefore, this solution is attracting from both technical and environmental points of view. These composites are fully based on renewable resources and could find interesting applications at industrial level as environmentally friendly materials that can substitute some commodity plastics or, even, some technical plastics.

The minimum gluten amount to obtain a homogeneous material is 10 wt. % and attractive properties can be obtained by varying the gluten content in the 10-40 wt. % range. SEM analysis has revealed good fiber-matrix interaction which is a key factor to avoid stress concentration phenomena. The water uptake sensitiveness is highly dependent on the cellulose content so that, increasing the gluten content is useful to lower the intrinsic water uptake.

We can conclude that the use of hot-press molding is an efficient method to obtain new set of environmentally friendly composite materials derived from algae wastes, giving a new

application to these wastes instead of leaving them in a landfill. In addition, the use of wheat gluten protein as binder (matrix) material for the algae wastes allow developing fully renewable materials characterized by very low environmental impact And potential use at industrial level.

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Table 1.- Chemical composition (wt. %) of carbohydrates and ash content in *Posidonia Oceanica*.

Carbohydrate Analysis	Arabinose	0.44±0.1
	Galactose	1.16±0.1
	Glucose	70.16±2.9
	Xylose	6.40±2.7
Lignin Analysis	Hidrosoluble	9.20±1.8
	Inorganic	12.64±0.1

Table 2.- Mechanical properties (flexural) of *Posidonia Oceanica*-gluten composites in terms of the gluten wt. %.

wt. % gluten protein	Flexural strength (MPa)	Flexural modulus (GPa)	Impact energy (kJ m⁻²)
10	22.2 ± 3.4	2.35 ± 0.22	0.10 ± 0.02
20	31.0 ± 2.6	3.99 ± 0.33	0.11 ± 0.04
30	35.4 ± 3.1	3.83 ± 0.37	0.10 ± 0.03
40	40.8 ± 0.8	3.36 ± 0.24	0.10 ± 0.01

Table 3.- Heat deflection temperature (HDT) values for *Posidonia Oceanica*-gluten composites with different gluten content.

wt. % gluten protein	HDT (°C)
10	94.4 ± 3.82
20	85.5 ± 0.07
30	83.6 ± 0.07
40	82.9 ± 4.03

Figure legends

Figure 1.- a) *Posidonia Oceanica* balls collected from seashore and b) short fibers from *Posidonia Oceanica* obtained by milling.

Figure 2.- SEM images of fractured surfaces from flexural tests, 750x for *Posidonia Oceanica*-gluten composites with different gluten content, a) 10 wt. %, b) 20 wt. %, c) 30 wt. % and d) 40 wt. %.

Figure 3.- Temperature ramp DMA curves of *Posidonia Oceanica*-gluten composites for different gluten content compositions.

Figure 4.- Plot representation of the evolution of the water uptake of *Posidonia Oceanica*-gluten composites in terms of the water submerged time.

Figure 5.- SEM images of fractured surfaces from impact tests, 2500x for *Posidonia Oceanica*-gluten composites with different gluten content, a) 10 wt. % and b) 40 wt. %.

Figure 1



Figure 2

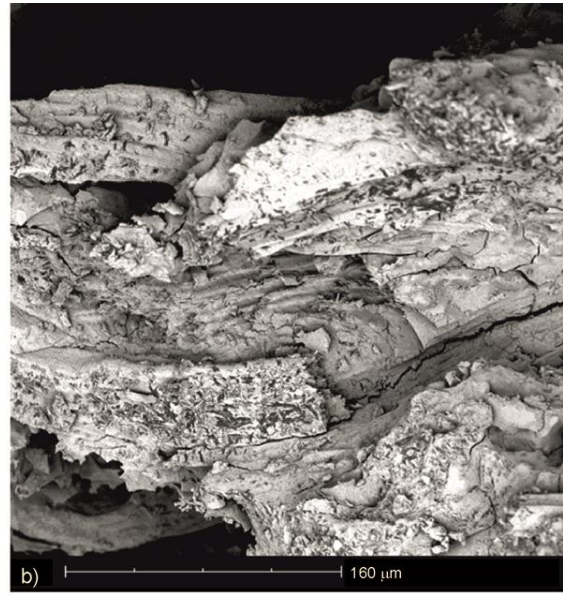


Figure 3

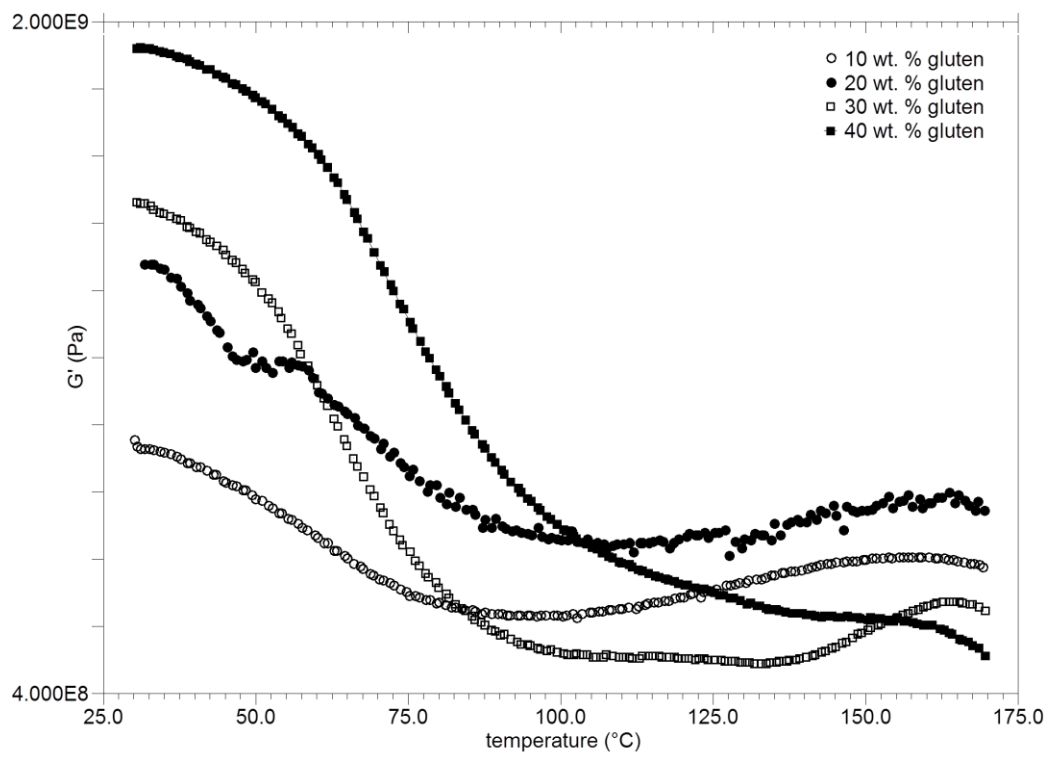


Figure 4

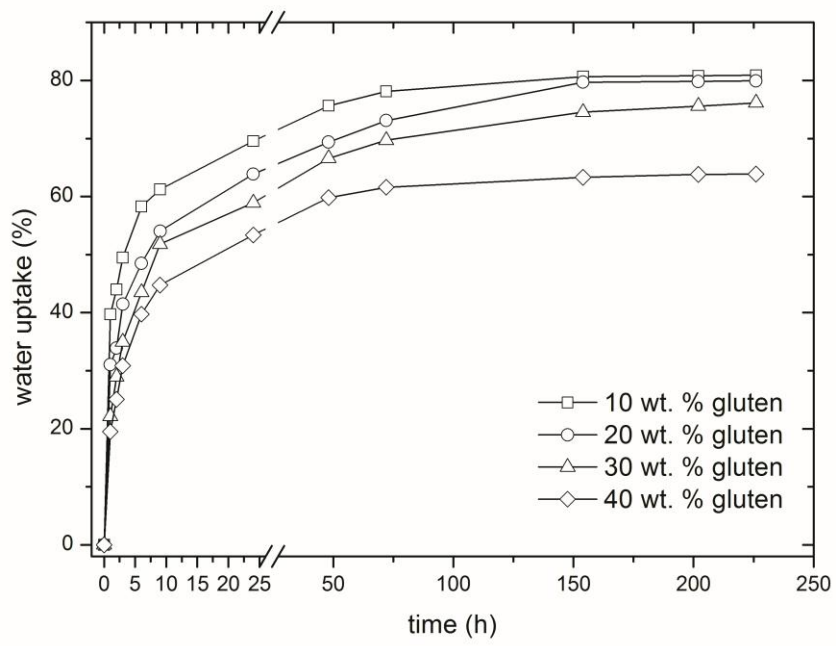


Figure 5

