# *Modelling of pyrolysis and combustion of gluten-glycerol-based bioplastics*

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## Abstract

Non-isothermal thermogravimetric analysis, under nitrogen and air atmospheres, has been applied to study the thermal degradation of wheat gluten and gluten-glycerol-based bioplastics. In order to explain experimental data, thermal degradation has been simulated using the so-called pseudo-components, which are related to protein fraction (mainly gliadin and glutenin), residual starch and plasticiser. Thus, the proposed models have been used to shed some light on the thermal decomposition of these materials, which has been found affected by their compositions and microstructures. Modelling confirms the experimental bioplastic and gluten isolate compositions, e.g. bioplastic moisture content, starch concentration and the expected gliadin/glutenin ratio. According to the simulation, the glycerol volatilisation is affected by bioplastic moisture content and hindered by the protein matrix. A fact pointing out that glycerol/water blend plays relevant plasticizing roles in the protein matrix through diverse physicochemical interactions.

Keywords: Bioplastic, gluten, pyrolysis, modelling, microstructure.

## 1. Introduction

In addition to their relevance in the human nutrition, proteins may play an important role in the substitution of crude oil-based non-biodegradable polymers by the development of novel films and plastics based on renewable agricultural resources. Among them, wheat gluten, a mixture of polymeric glutenin and gliadin monomers, can be considered as a suitable raw material for their manufacture. In this sense, world wheat production reached 602.4 million of tonnes in 2008. Moreover, with moderate prices, the projections for the next ten years anticipate an increase in the production to reach about 689.4 million of tonnes (OECD-FAO, 2008).

A protein-based material could be defined as a stable three-dimensional macromolecular network stabilized and strengthened by hydrogen bonds, hydrophobic interactions and disulfide bonds (Pommet et al., 2003). Specifically, the elastic properties of gluten mainly depend on the presence of high molecular weight glutenin and the ratio glutenin/gliadin, i.e. the existence of disulphide bonds between glutenin chains and non-covalent bonds between glutenin and gliadin chains (Beasley et al., 2002; Gupta et al., 1993 and 1995; Payne et al., 1981 and 1987; Belton et al., 1995; Wieser, 2007). However, proteins themselves do not have plasticity enough to be handled and a plasticiser is required. Plasticisers are molecules with low molecular weight and low volatility, which modify the three-dimensional structure of proteins, reducing their intermolecular forces and increasing the polymeric chain mobility. Plasticisers, such as water, glycerol, sorbitol, etc., have been used to reduce the glass transition temperature of wheat gluten proteins (Pouplin et al., 1999; Irissin-Mangata et al., 2001; Matveev et al., 2000; Gennadios, 2002; Jerez et al., 2007; Gómez-Martínez et al., 2009; González-Gutiérrez et al., 2010). Small plasticisers molecules have high mobility and would dissociate some of linkages within

protein chains promoting hydrogen bonds between the plasticiser and the protein (Zhang et al., 2005).

Thermogravimetric analysis, TG, is a powerful tool to monitor the thermal degradation of biopolymers under inert (pyrolysis) or oxidative (combustion) atmospheres (Barneto et al., 2009). TG analysis has been applied to study the thermal degradation of soy-based bioplastics (Swain et al., 2005; Das et al., 2008; Nanda et al., 2007). Swain et al., (2005) distinguished five stages in the TG combustion curve obtained from soy protein. According to these authors, the first stage (up to around 237 ºC) was attributed to elimination of water and the dissociation of the quaternary structure of proteins. The following two stages (from 243 to 382 ºC and between 388 and 583 ºC) are related to the cleavage of different bond types such as covalent bonds between peptides and S-S, O-N, and O-O linkages of protein molecules, respectively. The fourth stage (between 589 and 710 ºC) is associated to protein decomposition with volatiles formation and finally, beyond 710 ºC only char remains. Using different kinetic models, for each stage, these authors determine the kinetic parameters (pre-exponential factor and activation energy) that better fit the experimental data. As for biodegradable plastics based on glycerol-plasticized wheat gluten, Sun et al., (2007) qualitatively described their combustion and distinguish four stages: A) the first two stages are is related to the elimination of water (below 200 ºC) and glycerol (from 200 to 290 ºC); the third one (between 290 and 340 ºC) and the fourth (above 340 ºC) are related with the cleavage of different bonds; covalent peptide bonds in the amino acids residues, or S-S, O-N, and O-O linkages from protein molecules.

Previous TG studies have not provided quantitative discussions about the effect of the gluten-glycerol-based bioplastic formulation or a simulation of the thermal degradation of this type of materials. With the aim of achieving a further insight into the

thermal degradation of gluten-based bioplastics, a novel kinetic model has been proposed in this work which draws the different release/degradation patterns shown by the material compounds. In the present study, experimental thermo-gravimetric curves, obtained under nitrogen and air atmospheres, were modelled through nucleation kinetic equations (based on Prout-Tompkins model) and the so-called pseudo-components. A pseudo-component is a fraction of the sample that shows a characteristic degradation path but, nevertheless, it is not necessarily a pure substance. In addition, material composition and the role of the plasticiser have been analysed by comparing the degradation profiles of gluten protein, plasticiser and different gluten-based bioplastics.

Thermogravimetric analysis is a promising tool for monitoring bioplastic formulation and processing owing to the fact that thermal degradation of bioplastic is sensitive to changes in the interactions between plasticizer and protein matrix. TGA can quantitatively resolve complex mixtures using the characteristic thermal decomposition temperature of each component (Barneto et al., 2009). Furthermore, thermogravimetric data can be used to study the thermal stability of bioplastics.

## 2. Materials and Methods

Thermo-gravimetric studies were performed on wheat gluten isolate (WG), glycerol (G) and on two glycerol-gluten bioplastic materials (BWG), containing 33.3 and 40.0 wt. % glycerol in their formulations (referred to as BWG05 and BWG06, respectively). Glycerol, used as protein plasticiser, was supplied by Prolabo S.A. (Spain). Wheat gluten was provided by Riba S.A. (Spain), containing 83 wt.% protein, 10 wt.% residual starch, 1.5–2 wt.% lipid and 0.7–0.8 wt.% ash. Its moisture content was below 8 wt.% on dry basis. Crude gliadin from wheat gluten was provided by Sigma-Aldrich S.A. (Spain).

The bioplastic material was obtained by mixing glycerol and gluten in a kneading device, torque-rheometer Polylab-Rheomix 600p (Thermo Haake, Germany), which consists

of two counter-rotating rollers turning with different angular velocities (ratio 3:2). The mixing chamber was not cooled or heated, so it can be considered as adiabatic. The volume of the chamber (69 $cm^3$) was filled with approximately 56 g of sample, corresponding to 85% filling ratio. The mixing process was always carried out at 50 rpm (Jerez et al., 2005a). In order to get a bioplastic with suitable mechanical properties, the mixed product was subsequently moulded in a hot-plate hydraulic press, at 100 bar gauge pressure and 140ºC (Jerez et al., 2005b). Bioplastic moisture concentration was gravimetrically determined by heating samples of bioplastics in a ventilated oven at 110ºC for 24h. For both bioplastics, BWG05 and BWG06, the calculated moisture content was 10 wt. %. Once moisture presence was confirmed, for sake of comparison, a new material (dry-BWG05) was obtained by dehydrating bioplastic BWG05 in desiccator at room temperature.

Thermo-gravimetric curves, weight loss vs. temperature (TG) and time derivative of the TG (DTG) curves, were obtained in a TA Q50 analyser (TA Instruments, USA). Pyrolysis and combustion tests, between 40 ºC and 600 ºC, were carried out on 5-10 mg samples under nitrogen and air atmosphere. Three heating temperature ramps (5, 10 and 20 ºC/min) were selected.

## 3. Results and discussion

### 3.1. Thermo-gravimetric analysis

Figure 1 compares the thermal degradation of gluten and two bioplastics with different glycerol contents under inert and oxidative atmospheres. As we can see, from room temperature to 450 ºC (volatilization zone) the degradations profiles of gluten and bioplastics are slightly affected by air presence. However, at higher temperatures (oxidation zone) apparent differences are observed between them, related to the combustion of carbonaceous residues (char).

Regarding bioplastic materials, the experimental weight loss rate curves (DTG), obtained under nitrogen atmosphere, show at least four thermal events, labelled as peaks P1 to P4 (Figure 1A). Among them, peaks P3 and P4 (located at 230 and 309 ºC) are the most relevant ones and strongly affected by bioplastic composition. Instead, gluten volatilization is characterised by three main weight loss peaks (labelled as P1, P2 and P4 in Figure 1A). Additionally for all samples, a peak P5, associated to char oxidation, only appears under air atmosphere.

Table 1, which gathers some characteristic parameters calculated from TG and DTG curves under nitrogen atmosphere, has been used to compare the effect of the material composition on the degradation profiles of bioplastics BWG05 and BWG06. Initially, Table 1 shows that both bioplastics undergo similar weight losses up to 600 ºC for pyrolysis, $ML_{max} \approx 85$ wt. %. However, the height of peaks P3 and P4 seems to be strongly affected by the bioplastic formulation (see parameter $v_{max}$ in Table 1). Thus, bioplastic BWG05 exhibits a peak P3 lower than P4, whereas both peaks have similar height in bioplastic BWG06 (Figure 1 and Table 1). It is worth mentioning that sample BWG06 contains more glycerol (40.0 wt. %) than bioplastic BWG05 (33.3 wt. % glycerol). As a result, a higher glycerol/gluten ratio concentration leads to an increase in peak 3, whereas peak 4 becomes smaller. This fact points out the different nature of those bioplastic compounds responsible for the degradation of peaks P3 and P4.

According to Sun et al., 2007, the first (P1) and second (P2) peaks (located close to 80 ºC and 160 ºC, respectively) of the thermal degradation of gluten may be associated to the loss of free and bonded water respectively, whereas the fourth (P4) peak (close 320 ºC) would be related to the proteins volatilization. Likewise, according to experimental data shown in Figure 2A, glycerol volatilization start close 100 ºC and progressively

increase up to the highest weight loss rate close to 237 ºC. This result suggests occurrence of peak P3 is mainly related to the glycerol used as bioplastic plasticiser.

These assumptions are supported by a subsequently bioplastic drying. Figure 2B compares the pyrolysis of two bioplastics: BWG05 and dry-BWG05, moist and dry, respectively. As may be seen, the height of peak P4 increases due to the higher protein concentration of the dehydrated bioplastic (dry-BWG05), whereas peaks P1 to P3 decrease after the water loss. Accordingly, it is apparent that P1 arises for the loss of free water and P3 from the glycerol volatilization at high temperature. However, in moist bioplastics, the peak P2 (close 160 ºC) results from both the loss of bonded water and the loss of volatilized glycerol at low temperature (at 160 ºC the glycerol volatilization is close 6 wt%, see Figure 2A). These results are in good agreement with those obtained by Chen et al. (2005) for soy-protein-based materials, who suggested the weight loss below 150 ºC may be attributed to evaporation of absorbed water, weight loss between 150 and 290 ºC is due to glycerol evaporation and, finally, protein degradation would take place above 290 ºC.

Furthermore, the volatilization environment affects the protein degradation (peak P4). As seen in Figure 1, for gluten and bioplastics degradations, the oxygen presence makes sharper peak P4 and shifts it to lower temperature. This effect is more evident for gluten isolate (the peak P4 is shifted from 304 ºC to 282 ºC) than for bioplastics (e.g. for BWG05 the peak P4 is shifted from 308 ºC to 300 ºC). Gluten isolate is a complex blend that mainly contains residual starch and the gluten proteins: glutenin and gliadin. As commented above, both proteins present different molecular conformation and polymerisation degree so that different degradation paths should be expected during their pyrolysis or combustion. According to Figure 2A, under nitrogen atmosphere, pure gliadin reaches the highest weight loss rate at 315 ºC (using 10 ºC/min as heating rate),

yielding 25 % char. Regarding the other 75% volatiles, about 90 % of them are lost below 400 ºC. It is expected that monomeric gliadin degrades at lower temperature than polymeric glutenin, so that the long tail found at high temperature seems to be related polymeric glutenin. In addition, Peak 4 should also arise from the residual starch degradation that typically gives a sharp peak close to 300 ºC (Aggarwal, 1999), which is shifted to low temperature by oxygen presence (Barneto et al, 2010). Likewise, the more apparent tail, observed at high temperature during the bioplastic combustion (Figure 1B). As a result, the observed shifting of P4 in presence of air would be mainly related to residual starch and gliadin degradations.

### 3.2 Thermo-gravimetric model

As previously seen, wheat gluten thermal degradation occurs through different stages, which are related to the main gluten isolate compounds (mainly gliadin and glutenin proteins and residual starch) and material natural moisture. Similarly, DTG curves of the glycerol-gluten-based bioplastic pyrolysis have shown several peaks related to bioplastic formulation: water (P1); water/glycerol blends (P2 and P3); and gluten proteins and starch (P4).

In order to simulate experimental TGA data, the gluten and bioplastics degradations have been modelled on the basis of the simplified processes shown in Figure 3 (Table 2 gathers and identifies all parameter abbreviations used in the model). Under inert atmosphere, protein related pseudo-components ($S_i$) undergo volatilization that yield light volatiles ($V_{i1}$) and char ($R_i$), which remains in thermobalance. Under air environment, char previously obtained oxidises, yielding new volatiles ($V_{i2}$) and ash ($A$). On this regard, some assumptions have been made for sake of simplicity: i) although starch pyrolysis typically yields char, considering its residual concentration this will be considered

negligible, and therefore, only protein pseudo-components (*Glu* and *Glia*) yield char; and ii) the weight loss detected by thermobalance is the sum of independent pseudo-component degradations and, therefore, samples are considered as the sum of all pseudo-components.

As for gluten isolate, five pseudo-components were proposed: $S_{Wf}$ (free water), $S_{Wb}$ (bonded water), $S_{Sta}$ (residual starch), $S_{Glu}$ (glutenin) and $S_{Glia}$ (gliadin). For bioplastics, six pseudo-components were proposed: $S_{Wf}$ (free water), $S_{GWb}$ (bonded water and glycerol that volatilizes at low temperature), $S_{Glyc}$ (glycerol that volatilizes at high temperature), $S_{Sta}$ (residual starch), $S_{Glu}$ (glutenin) and $S_{Glia}$ (gliadin).

The thermal degradation of pseudo-components has been simulated by means of a nucleation model based on the Prout-Tompkims equation (Prout and Tompkins, 1944 and 1946). According to this, the reaction rate depends on both non-reacted and reacted fractions. In this work, a modified Prout-Tompkims differential equation, used by Burnham et al. (1996), has been used to describe the evolution of the reaction conversion ($\alpha_i$):

$$\frac{d\alpha_i}{dt} = k_i(1-\alpha_i)^n(s+\alpha_i{}^m) \qquad [1]$$

where the reaction order ($n$) and the nucleation order ($m$) affect non-reacted and reacted fractions, respectively. The factor $s$, usually assumed as 0.01 (Burnham et al, 1996), is a constant that assures coherent values for reaction rate when conversion is close to extreme values of 0 or 1. The kinetic constant ($k_i$) is expressed by the Arrhenius law [$k_i=k_{0i}\exp(E_i/RT)$], where $k_{0i}$ is the pre-exponential factor and $E_i$ the activation energy. Equation 1 turns into classical nth-order kinetic equation if the nucleation order is zero. When the importance of the autocatalysis increases (high heating rate and oxidative atmosphere), the nucleation order also increases (Barneto et al., 2009). This fact affects

the DTG curve, turning broad peaks into sharp peaks which are inconsistent with the nth-order model.

Using the volatile weight ($V_i$) obtained from each pseudo-component, Equation 1 can be expressed as follows:

$$\frac{dV_i}{dt} = k_i V_{\infty i}(1-\frac{V_i}{V_{\infty i}})^{n_i}[s+(\frac{V_i}{V_{\infty i}})^m] \qquad [2]$$

where $\alpha_i$ is replaced by $V_i/V_{\infty i}$ and $V_{\infty i}$ is the volatile weight at infinite time. As a consequence, it is necessary to determine five parameters for each component: pre-exponential factor, activation energy, reaction order, nucleation order, and mass of volatiles at infinite time.

Integration and optimization of the kinetic equations were carried out using the Runge-Kutta and Gauss-Newton methods, respectively. The objective function to be minimized is:

$$OF = \sum_{i=1}^{n}\left(\frac{dm_{\exp}}{dt} - \frac{dm_{cal}}{dt}\right)^2 \qquad [3]$$

where $\frac{dm_{\exp}}{dt}$ and $\frac{dm_{cal}}{dt}$ are, in that order, the experimental and calculated weight loss rates for the n points of each experiment. The model validity was tested by calculating the variation coefficient (*VC*):

$$VC(\%) = \frac{\sqrt{OF/(N-P)}}{\frac{d\overline{m}_{\exp}}{dt}}100 \qquad [4]$$

where $N$ and $P$ are the number of data points and parameters fitted, respectively; and $\frac{d\overline{m}_{\exp}}{dt}$ is the average of the experimental mass loss rates. Tables 3 and 4 show calculated kinetic parameters that characterise pyrolysis and combustion of gluten isolate and bioplastics at three heating rates.

### 3.3 Thermal degradation of gluten isolate

Therefore, this model proposes the thermal degradation of wheat gluten through its main compounds (starch, gliadin, glutenin and material natural moisture) by means of five pseudo-components labelled as $W_f$, $W_b$, *Sta*, *Glia* and *Glu*, which respectively represent free water, bonded water, residual starch, gliadin and glutenin proteins. It should be noticed that pseudo-component are not pure substances, but fractions that thermally degrades in a characteristic way (i.e. temperature range). As may be deduced from scheme *a)* in Figure 3, during pyrolysis the pseudo-components $W_f$ and $W_b$ completely volatise, as a result of a simple process of dehydration. The pseudo-component *Sta*, it is assumed, that completely volatilises. And, finally, pseudo-components *Gli* and *Glu* produce volatiles and carbonaceous residues (char), which remains in the thermobalance. Additionally, Scheme *c)* in Figure 3 depicts the combustion model for gluten, which, besides previous volatilization, also includes char oxidation for *Glia* and *Glu* pseudo-components.

Table 3 shows calculated kinetic parameters that characterise the thermal degradation of gluten at three heating rates (average values). As a whole, we can observe that kinetic parameters which characterise the volatilization of the pseudo-components in air atmosphere (first step of the combustion) are similar to those obtained from pyrolysis. Figure 4 shows the good agreement between experimental and calculated DTG curves, and the degradation profile simulated for each pseudo-component. According to the model, in both atmospheres, the highest weight loss rates of free and bonded water are reached close to 70 ºC and 168 ºC, estimating the gluten moist content as 3.5 wt. %, where about 2.1 wt. % appears as free water ($W_f$) and 1.4 wt. % as bonded water ($W_b$). Furthermore, the development of bonds between water and the protein matrix shifts the

activation energy values for the water release from 36 kJ/mol to 60 kJ/mol (see Table 3). Volatilization of residual starch takes place according to a first order kinetic with activation energy 131-136 kJ/mol. As occurs for cellulose (Barneto et al., 2010), under air, starch peak is shifted to low temperature (i.e. from 293 ºC to 273 ºC, using 5 ºC/min as heating rate) and nucleation order increases from 0.02 to 0.49. Oxygen presence also produces significant changes in protein fraction. Gliadin drastically reduces its volatilization from 29 % to 10 %, promoting the char formation under air. The broad glutenin peak (reaction order close 3) is shifted to lower temperature, about 48 ºC (from 355 ºC to 307 ºC, using 5ºC/min as heating rate) and gliadin peak becomes smaller (reaction order close 1) and is shifted from 320 ºC to 277 ºC, i.e. 33 ºC in the same direction. Moreover, activation energy values for both proteins decrease about 5 kJ/mol.

On the other hand, gluten composition can be estimated from kinetic data obtained under oxidative environment. Adding the weight of volatiles obtained from each pseudo-component in both volatilization and char oxidation, gluten composition calculated as: 2.1 wt. % free water, 1.4 wt. % bonded water, 10.9 wt. % residual starch, 43.2 wt. % gliadin and 39.0 wt. % glutenin (see table 3). According to Sun et al. (2007) the protein content in the wheat gluten is close to 75 wt. %, where 40-50 wt. % is gliadin and 35-45 wt. % is glutenin. Likewise, Pallos et al. (2006) affirm the amounts of gliadin and glutenin in vital wheat gluten are approximately equal. Furthermore, calculated residual starch is in good agreement with that indicated in the experimental section, about 10 wt. % residual starch.

### 3.4 Thermal degradation of gluten-glycerol based bioplastics

As shown in Figure 3, the thermal degradation of bioplastics has been modelled by means of six pseudo-components: free water ($W_f$), bonded water and glycerol that

volatilizes at low temperature ($GW_b$), glycerol (*Glyc*), residual starch (*Sta*), gliadin (*Glia*), and glutenin (*Glu*). As for the plasticiser, the main difference with gluten isolate is related to the bonded water, because a part of glycerol volatilizes in the same temperature interval. The interaction with the protein matrix causes that glycerol volatilization is more complex, being necessary two pseudo-components to represent its degradation. As seen for gluten, pyrolysis model of bioplastics (scheme *b)* in Figure 3) assumes that pseudo-components based on water, glycerol and starch fully volatilises, and only gliadin and glutenin proteins yield char. Finally, char obtained from gluten proteins oxidises under air environment (scheme *d)* in Figure 3). Table 4 shows kinetic parameters calculated for all studied bioplastics.

As may be observed in Figure 5, the model describes fairly well the bioplastic thermal decomposition, under air atmosphere, irrespective of its formulation (e.g. BWG05 y BWG06, respectively containing 33.3 wt. % and 40.0 wt. % glycerol). As expected, an increase in glycerol/gluten ratio leads to a higher amount of the pseudo-components $GW_b$ (from 6.6 to 8.9 wt%) and *Gly* (from 28.5 to 32.3 wt%). In addition, the increase glycerol/gluten ratio is also accompanied by a shifting of the $GW_b$ peak to a higher temperature, from 151 to 161 ºC, and by a higher the activation energy from 57 to 61 kJ/mol. These facts agree with a $GW_b$ pseudo-component relatively enriched in glycerol.

### 3.4.1. The role of plasticiser in gluten-glycerol based bioplastics

Aiming to a further insight in the plasticiser (water and glycerol) behaviour during bioplastic thermal decomposition, Figure 6 compares the DTG profiles under nitrogen for two bioplastics with different moisture contents. In addition, this figure includes calculated degradation profiles of pseudo-components.

According to the simulations of *BWG05-dry* and *BWG05* bioplastics (Table 4), water absorption increases the height of peaks P1, P2 and P3, changing pseudo-components: a) $W_f$ from 1.1 to 4.3 wt%; b) $GW_b$ from 4.5 to 6.8 wt %; and c) *Glyc* from 23.8 to 27.4 %. As a result, free water increases 3.2 wt%, bonded water increases 2.3 wt% and the water in P3 also increases 3.6 wt%. Adding these quantities and considering the residual moisture in dry bioplastic (1.1 wt%), the estimated water content in the bioplastic is 10.2 wt%, a value that agrees with the experimental moisture obtained for *BWG05* (see Experimental Section). In addition, these results confirm that peak P3 mainly arises from glycerol volatilisation (and some water). Similarly, Peak P2 refers to a water/glycerol blend, where some glycerol evaporates at low temperature and water release would be affected by certain interaction with the protein matrix (Sun et al. 2007). As calculated from gluten DTG curves, water release undergoes a significant delay in its temperature range, taking place between 60 and 200 ºC (e.g. see pseudo-components $W_f$ and $W_b$ in Figure 4).

Likewise, glycerol volatilisation profile is strongly altered by both the water content and interaction with the protein matrix, as may be deduced from simulation shown in inset of Figure 6. These simulated curves were obtained using the kinetic parameters calculated for pseudo-components $GW_b$ and *Glyc*. As may be seen, close to 150 ºC, the volatilization of glycerol and bonded-water take place simultaneously, leading to a shoulder in DTG curves, more apparent in the moist bioplastic (BWG05). On the other hand, instead of the sudden drop observed in the pure glycerol DTG curve above 240 ºC (Figure 2A), the protein matrix seems to hinder the glycerol release, which is delayed about 50 ºC and shows an apparent volatilisation tail up to 300 ºC (see bioplastic dry-BWG05, inset of Figure 6). A fact pointing out that glycerol plays relevant plasticizing roles in the protein matrix through diverse physicochemical interactions (hydrogen bonds,

hydrophobic, etc.). However, such interactions seem to be influenced by bioplastic moisture. Thus, it should be noticed that the presence of water promotes glycerol weight loss, shifting its peak from 240ºC for the dry bioplastic to 230ºC for the moist bioplastic BWG05 (Figure 6).

### 3.4.2. Estimation of bioplastic composition from thermogravimetry analysis

As previously seen for gluten isolate, bioplastic composition can be estimated using the weight loss calculated for each pseudo-component during its volatilization and char oxidation (Table 4). Accordingly, data shown in Table 5 have been obtained in dry and ash free basis and assuming, for dry bioplastics, that pseudo-component $WG_b$ is pure glycerol (and, therefore, without water). As may be seen, there is a good agreement between calculated and the actual bioplastic composition (see experimental section), e.g. estimated plasticiser concentration was for *BWG05-dry* about 32.2 wt% glycerol and for *BWG06-dry* bioplastic 39.6 wt% glycerol.

## 4. Conclusions

Thermal degradations of gluten and glycerol-gluten-based bioplastics have been simulated by models based on pseudo-components which refer to the main gluten isolate and bioplastic compounds, i.e. water, glycerol, starch, glutenin and gliadin. As a result, modelling confirms the experimental bioplastic and gluten isolate compositions, e.g. bioplastic moist content, starch concentration and the expected gliadin/glutenin ratio. According to the simulation, the glycerol volatilisation is affected by bioplastic moist content and hindered by the protein matrix. A fact that points out that glycerol/water blend plays relevant plasticizing roles in the protein matrix through diverse physicochemical interactions.

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# FIGURE CAPTIONS

Figure 1. Thermal degradation of gluten and two bioplastics (BWG5 and BWG06): a) under inert atmosphere, b) under air atmosphere

Figure 2. Glycerol and gliadin volatilization (a) and pyrolysis of two bioplastics with different moisture (b).

Figure 3. Simplified schemes for gluten pyrolysis (a), bioplastic pyrolysis (b), gluten combustion (c), and bioplastic combustion (d)

Figure 4. Simulation of the thermal degradation of gluten: a) under inert atmosphere, b) under air atmosphere

Figure 5. Combustion simulation of two bioplastics with different glycerol content: a) BWG05 with 33.3 wt%, b) BWG06 with 40.0 wt%

Figure 6. Simulation of the thermal degradation of a gluten-glycerol based bioplastic under inert atmosphere (pyrolysis): a) dry bioplastic (BWG05-dry), b) moist bioplastic (BWG05). Inset: Simulation of the plasticiser release from the protein matrix.

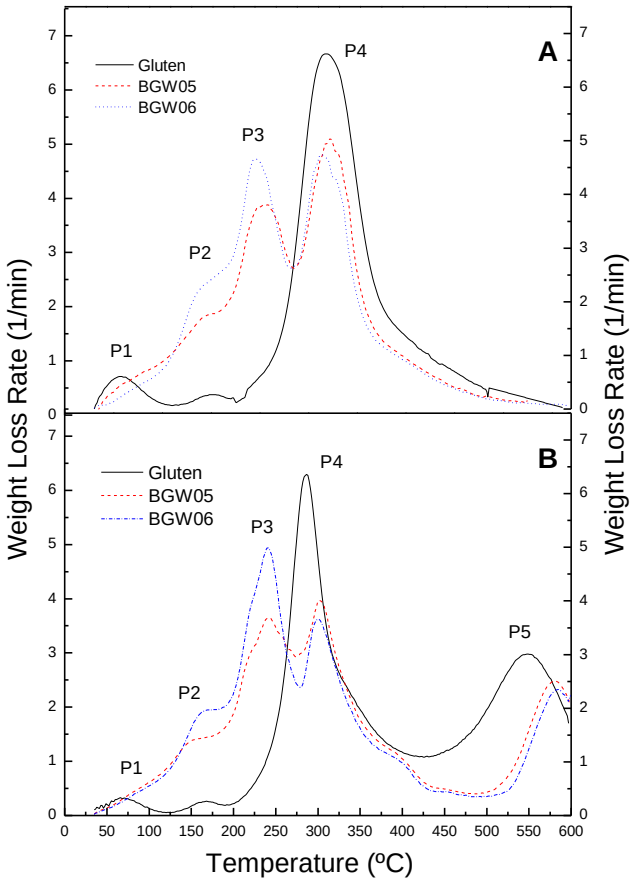


Figure 1. Gómez- Martínez et al.

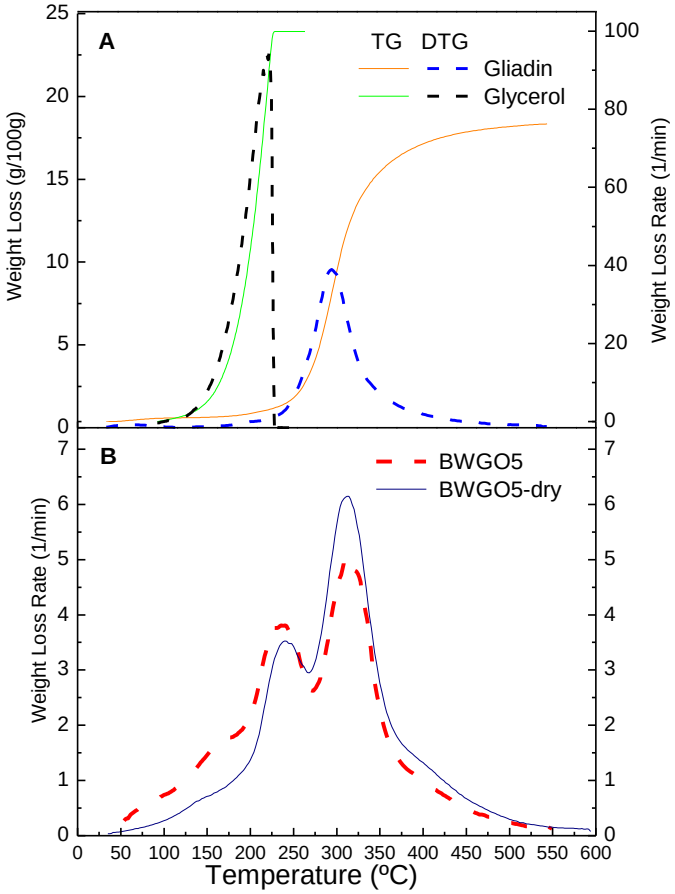


Figure 2. Gómez- Martínez et al.

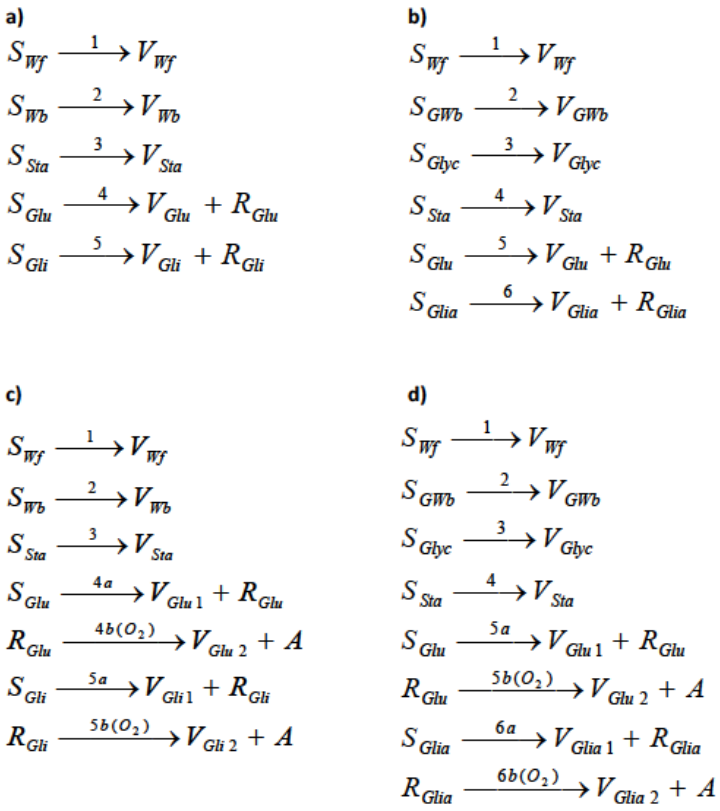


Figure 3. Gómez- Martínez et al.

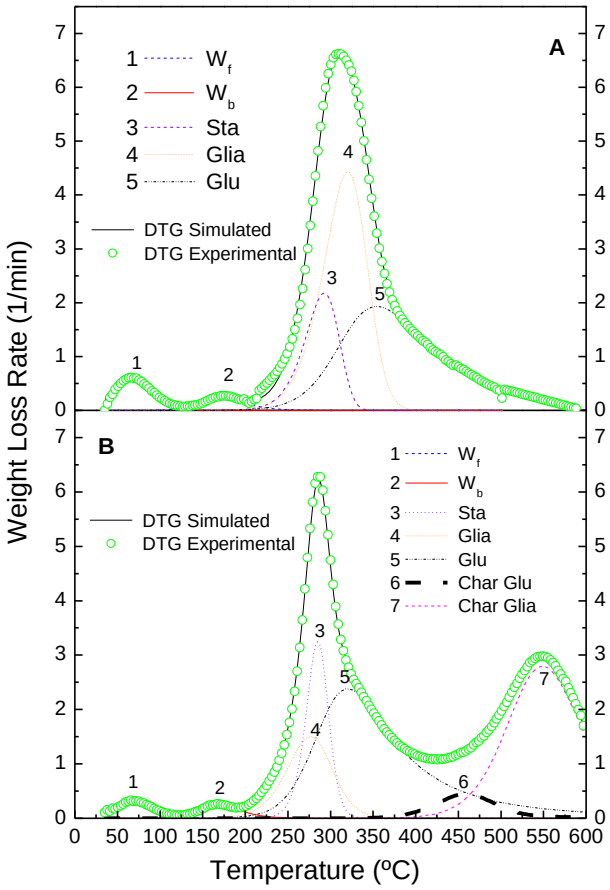


Figure 4. Gómez- Martínez et al.

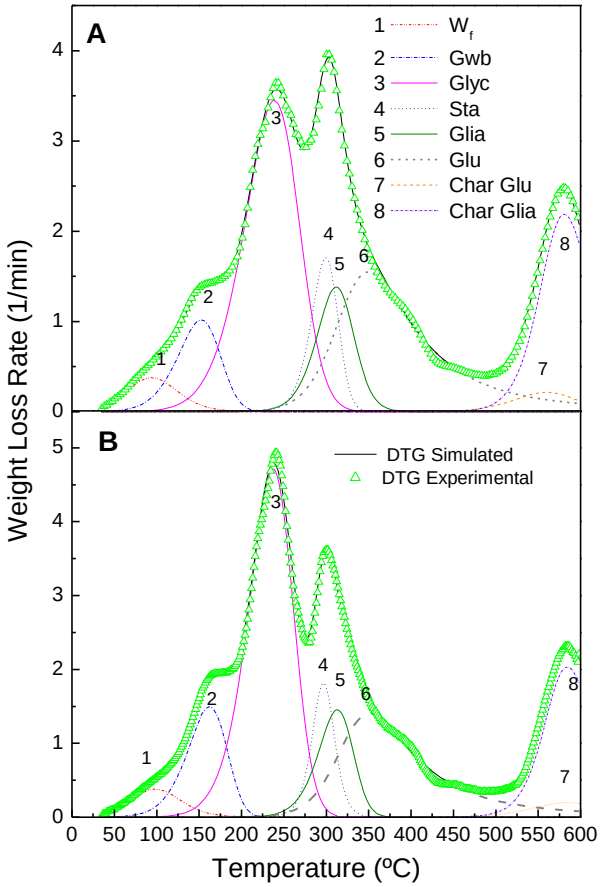


Figure 5. Gómez- Martínez et al.

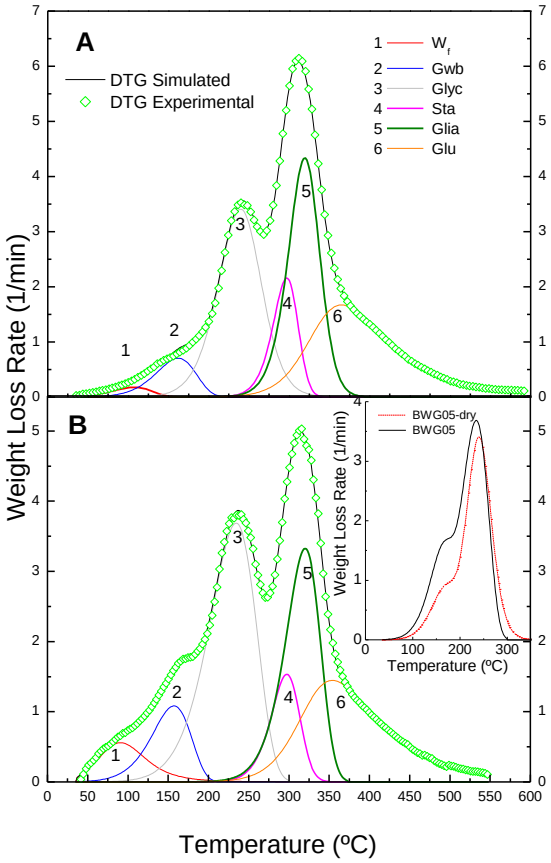


Figure 6. Gómez- Martínez et al.

Table 1. Thermal degradation parameters for two bioplastics with different gluten/glycerol ratio (subscripts 3 and 4 refer to P3 and P4 peaks in figure 2, respectively)

| Bioplastic | | $ML_{max}$ (g/100g) | $T_{max3}$ (ºC) | $v_{max3}$ ($min^{-1}$) | $T_{max4}$ (ºC) | $v_{max4}$ ($min^{-1}$) |
|---|---|---|---|---|---|---|
| *BWG05* | pyrolysis | 84.3 | 233 | 3.8 | 309 | 5.1 |
| | combustion | 99.0 | 243 | 3.6 | 304 | 3.9 |
| *BWG06* | pyrolysis | 85.9 | 230 | 4.6 | 308 | 4.7 |
| | combustion | 98.9 | 243 | 4.9 | 303 | 3.6 |

Table 2. Abbreviations used for parameters of the kinetic model.

| **Gluten Pseudo-components** | **Gluten-Glycerol based bioplastics pseudo-components** | **Kinetics parameters** |
|---|---|---|
| $W_f$ - free water | $W_f$ – free water | $k$ – kinetic constant |
| $W_b$ – bonded water | $GW_b$ - bonded water and glycerol that volatilizes at low temperature | $k_0$ - preexponential factor |
| *Sta* – residual starch | *Sta* – residual starch | $E$ – activation energy |
| *Glia* - gliadin | *Glia* - gliadin | $n$ – reaction order |
| *Glu* - glutenin | *Glu* - glutenin | $m$ – nucleation order |
| | *Glyc* - glycerol | $V_i$ – volatile weight |
| | | $V_{\infty i}$ – volatile weight at infinite time |
| | | $\alpha$- reaction conversion |

Table 3. Kinetic parameters for the thermal degradation of the gluten pseudo-components (average value and standard deviation)

| Pyrolisis | $W_f$ | $W_b$ | *Sta* | *Glia* | *Glu* | | |
|---|---|---|---|---|---|---|---|
| Ln $k_o$ ($s^{-1}$) | 8.2±0.4 | 11±1 | 26±3 | 18.7±0.4 | 7.5±0.1 | | |
| $E_{act}$ ($kJmol^{-1}$) | 36±2 | 61±6 | 135±2 | 116±1 | 66±2 | | |
| *n* | 1.7±0.5 | 1.6±0.1 | 1.1±0.1 | 1.1±0.1 | 2.9±0.1 | | |
| *m* | 0.3±0.2 | 0.3±0.2 | 0.02±0.02 | 0.02±0.02 | 0.4±0.1 | | |
| $V_\infty$ (%) | 2.1±0.5 | 1.4±0.2 | 10.9±0.5 | 29.1±0.5 | 32.2±0.3 | | |
| Combust | $W_f$ | $W_b$ | *Sta* | *Glia* | *Glu* | *Char Glia* | *Char Glu* |
| Ln $k_o$ ($s^{-1}$) | 7.9±0.1 | 11.7±0.1 | 24±1 | 19.4±0.1 | 7.3±0.1 | 19.55 | 19.55 |
| $E_{act}$ ($kJmol^{-1}$) | 36±1 | 60±1 | 131±1 | 111±1 | 61±3 | 169±1 | 148±1 |
| *n* | 1.2±0.2 | 1.7±0.1 | 1.2±0.1 | 1.4±0.1 | 3.0±0.1 | 2.0±0.1 | 1.5±0.1 |
| *m* | 0.2±0.1 | 0.5±0.1 | 0.49±0.05 | 0.01±0.01 | 0.5±0.1 | 0.1±0.1 | 0.1±0.1 |
| $V_\infty$ (%) | 2.1±0.5 | 1.4±0.1 | 10.9±0.4 | 10.2±0.3 | 34.7±0.1 | 33.0±0.5 | 4.3±0.1 |

Table 4. Kinetic parameters that describes the thermal degradation of three bioplastics (BWG05-dry, BWG05 and BWG06) under inert and oxidative environments

| ***BWG05 nitrogen*** | $W_f$ | $GW_b$ | ***Glyc*** | ***Sta*** | ***Glia*** | ***Glu*** | | |
|---|---|---|---|---|---|---|---|---|
| Ln $k_o$ ($s^{-1}$) | 8.1 | 11.3 | 11.2 | 24.2 | 18.5 | 7.9 | | |
| $E_{act}$ ($kJmol^{-1}$) | 39 | 58 | 69 | 135 | 114 | 68 | | |
| $n$ | 1.8 | 1.0 | 1.0 | 1.1 | 1.0 | 2.6 | | |
| $m$ | 0.2 | 0.01 | 0.01 | 0.2 | 0.2 | 0.4 | | |
| $V_\infty$ (wt. %) | 4.3 | 6.8 | 27.4 | 7.1 | 18.6 | 21.0 | | |
| ***BWG05 dry nitrogen*** | $W_f$ | $GW_b$ | ***Glyc*** | ***Sta*** | ***Glia*** | ***Glu*** | | |
| Ln $k_o$ ($s^{-1}$) | 8.4 | 12.0 | 11.0 | 23.6 | 18.4 | 7.9 | | |
| $E_{act}$ ($kJmol^{-1}$) | 43 | 62 | 68 | 133 | 113 | 69 | | |
| $n$ | 1.0 | 1.0 | 1.3 | 1.1 | 1.2 | 2.6 | | |
| $m$ | 0.1 | 0.01 | 0.3 | 0.3 | 0.4 | 0.4 | | |
| $V_\infty$ (wt. %) | 1.1 | 4.5 | 23.8 | 8.8 | 22.2 | 24.2 | | |
| ***BWG05 air*** | $W_f$ | $GW_b$ | ***Glyc*** | ***Sta*** | ***Glia*** | ***Glu*** | ***Char Glia*** | ***Char Glu*** |
| Ln $k_o$ ($s^{-1}$) | 7.8 | 11.3 | 11.1 | 24.1 | 19.0 | 7.1 | 19.6 | 19.6 |
| $E_{act}$ ($kJmol^{-1}$) | 39 | 57 | 69 | 135 | 115 | 63 | 172 | 171 |
| $n$ | 1.5 | 1.1 | 1.2 | 1.2 | 1.3 | 2.8 | 2.0 | 1.4 |
| $m$ | 0.1 | 0.05 | 0.01 | 0.3 | 0.3 | 0.5 | 0.4 | 0.04 |
| $V_\infty$ (wt. %) | 3.9 | 6.6 | 28.5 | 6.9 | 7.9 | 22.4 | 19.3 | 2.2 |
| ***BWG06 air*** | $W_f$ | $GW_b$ | ***Glyc*** | ***Sta*** | ***Glia*** | ***Glu*** | ***Char Glia*** | ***Char Glu*** |
| Ln $k_o$ ($s^{-1}$) | 7.8 | 12.0 | 11.3 | 23.8 | 19.7 | 7.2 | 19.6 | 19.6 |
| $E_{act}$ ($kJmol^{-1}$) | 40 | 61 | 69 | 131 | 118 | 63 | 173 | 176 |
| $n$ | 1.5 | 1.1 | 1.1 | 1.3 | 1.1 | 2.9 | 2.0 | 1.6 |
| $m$ | 0.1 | 0.1 | 0.2 | 0.5 | 0.2 | 0.5 | 0.5 | 0.01 |
| $V_\infty$ (wt. %) | 3.3 | 8.9 | 32.3 | 6.4 | 7.7 | 19.7 | 17.2 | 2.3 |

Table 5. Bioplastics composition based on pseudo-components (dry and ash free basis)

(average values and standard deviations for three runs)

| Bioplastic | *GW$_b$* (wt%) | *Glyc* (wt%) | *Sta* (wt%) | *Glia* (wt%) | *Glu* (wt%) |
|---|---|---|---|---|---|
| *BWG05-dry* | 6.5±0.3 | 25.7±0.6 | 8.0±0.3 | 31.2±0.5 | 28.5±0.1 |
| *BWG06-dry* | 8.8±0.7 | 30.8±0.5 | 7.5±0.9 | 27.6±0.2 | 25.3±0.4 |