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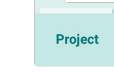
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Addition of Different Polysaccharides to Gluten-Based Biodegradable Polymeric Materials Plasticised with Glycerol/Water Mixtures

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Abstract

The influence of adding different polysaccharides (Locust Bean Gum, Methyl Cellulose and Carboxymethyl Cellulose) to gluten-based biodegradable polymeric materials was evaluated in this work. Glycerol/water mixtures were used as plasticiser. Gluten/plasticiser and gluten/polysaccharide/plasticiser blends were prepared at different pH values by mixing at 25°C under adiabatic conditions and subjected to thermomoulding at 9 MPa and 130°C. Bioplastic probes were evaluated using Dynamic Mechanical Thermal Analysis, Tensile strength measurements and water absorption capacity. Results indicate that a moderate enhancement of the network structure may be achieved by adding polysaccharide, which also confers a further thermosetting capacity to the system. However, the presence of charges seems to favour phase separation between gum and protein domains, although higher compatibility was found at acidic pH. Tensile properties and water uptake capacity also exhibited a strong dependence on pH. The former were favoured by increasing pH or adding gum at the isoelectric point. The later was largely favoured when bioplastic processing was carried out at pH 3, undergoing a moderate drop when polysaccharide was added.

Keywords: Gluten; Bioplastics; Thermomoulding; DMTA; Tensile strength test

1. Introduction

In recent years, there exists a great interest in the utilization of renewable biomass for the production of goods manufactured as an alternative to synthetic polymers, in order to reduce consumption of petrochemical feedstock and diminish environmental pollution. Thus, the global consumption of plastics in 2008 was higher than 245 million tonnes with an annual grow of approximately 5% [1]. One of the main applications of bioplastics is in the production of packaging films and containers made of by-products (e.g. plant proteins, polysaccharides, glycerine, etc.) [2]. Current European research

directives try to valorise agricultural surpluses for non-food uses, for example, by applying closed circle technology [3]. However, the development of bioplastic is only at an early stage and hardly represents 5-10% of the EU current plastic market [1]. On the other hand, edible protein-based films obtained by thermoplastic processes provide the opportunity to fulfil consumer demand and expectation of new food packaging systems that are convenient and environmentally friendly [4].

Proteins, lipids and polysaccharides have been proposed as biopolymers sources for many years. Most studies based on proteins have used vegetable proteins from corn, wheat gluten or soy to manufacture bioplastics [5]. Wheat gluten is a vegetable protein obtained as an agricultural by-product which shows fast degradation rates and can be processed by thermoplastic methods with the aid of plasticisers [6, 7]. The most common plasticisers, among a wide variety, are water and glycerol. The addition of polysaccharides to protein/plasticizer blends also may play a role, due to the relevance of non-covalent protein-polysaccharide interactions that can be used to design and fabricate materials with novel or improved properties. In the present study, wheat gluten (WG) was used as the protein component, a mixture of glycerol/water (GL) as the plasticizer and Locust Bean Gum (LBG), Methyl Cellulose (MC) and Carboxymethyl Cellulose (CMC) were selected as the polysaccharides. These novel bioplastics were obtained by a thermo-mechanical process that consisted of a mixing stage to produce the appropriate blends followed by a thermomoulding stage at controlled pressure.

The aim of this work is to evaluate the influence of the addition of different polysaccharides (gums) on Dynamic Mechanical Analysis (DMA), as a function of temperature, Tensile strength properties and water absorption capacity, of WG/Gum/GL blends subjected to thermoplastic compression moulding, comparing the results with those obtained using a WG/GL system without any polysaccharide. The influence of polysaccharide concentration and pH was also analysed.

2. Experimental Section

2.1 Materials. Wheat gluten (83 wt% protein, 3 wt% lipids, 1 wt% ash, 8 wt% moisture and 10 wt% starch) was provided by Productos Riba S. A. (Granollers, Spain). Glycerol, from Panreac Química S.A.U. (Castellar del Vallés, Barcelona, Spain) and distilled water were used as protein plasticisers. LBG, MC and CMC were provided by Sigma-Aldrich, (St. Louis, MO, USA).

2.2 Sample preparation. A gluten/glycerol/water system, denoted 50/18 (50 wt% gluten, 18 wt% glycerol and water up to 100 wt%), was mixed in a two-blade counter-rotating batch mixed turning at a 3:2 differential speed (Rheomix 3000p; ThermoHaake, Karlsruhe, Germany). Mixing was performed at 25°C and 50 rpm under adiabatic conditions. Different pH values were used by adding NaOH or HCl 2M solutions to the 50/18 blend. Bioplastic probes were prepared from the dough-like materials obtained after the mixing process by thermomoulding at 9 MPa and 130°C for 10 min. Two types of moulds were used to prepare the probes, a 50 x 10 x 3 mm rectangular shape mould and a type IV probe defined by the Standard Test for Tensile Properties of Plastic (ASTM D638). Rectangular and type IV probes were transferred into recipients at 53% relative humidity (RH) and allowed to reach moisture equilibrium at room temperature

for at least 2 weeks before testing. The desired RH value was achieved by means of a desiccator, using a saturated solution of $\text{Mg}(\text{NO}_3)_2$.

2.3 Dynamic Mechanical Thermal Analysis. DMTA tests were carried out using a RSA3 (TA Instruments, New Castle, DE, USA) by subjecting rectangular probes to dual cantilever bending. All the experiments were carried out at constant frequency (1 Hz) and strain (between 0.01 and 0.3%, within the linear viscoelastic region). The heating rate was $3\text{ }^\circ\text{C min}^{-1}$. Samples were coated with silicone oil to avoid water loss.

2.4 Tensile Strength Measurements. Tensile test were performed by using the Insight 10 kN Electromechanical Testing System (MTS, Eden Prairie, MN, USA), according to the ASTM D638 norm. Tensile stress and elongation at break were evaluated from at least three replicates for each product using type IV probes and an extensional rate of 20 mm min^{-1} at room temperature.

2.5 Water absorption capacity. Water uptake of bioplastics was determined following the ASTM D570 norm, using at least three rectangular specimens immersed in distillate water for 24 h at room temperature.

3. Results and Discussion

3.1 Dynamic Mechanical Temperature Analysis of bioplastic probes. Fig. 1 shows the values of the storage (E') and loss (E'') bending moduli (Fig. 1a) and the loss tangent ($\tan \delta$, Fig. 1b) from DMA temperature ramp measurements performed on 50/18 WG/MC/GL/water bioplastics. All the probes display similar behaviour to that one shown by the reference system (50/18 without gum). Thus, a remarkable decrease in E' and E'' generally took place as the temperature was raised until a plateau value was reached above $100\text{ }^\circ\text{C}$. This plateau is followed by an increase in both moduli for those systems containing MC or other gums. No apparent change in behaviour was brought about by the presence of gum. Thus, no significant differences were found at the experimental range of MC content. However, an apparent enhancement of E' and E'' values may be noted for those systems containing MC, excepting at low temperature at which the differences seem to vanish. As may be observed in Fig. 1B, $\tan \delta$ profiles at 1 Hz display two well-defined peaks at temperatures close to $0\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$. These two peaks were identified in a previous work for systems containing gluten as the biopolymer and glycerol/water as the plasticiser [7]. The first peak, $T_{\alpha 1}$, located at about $0\text{ }^\circ\text{C}$, would be mainly related to the characteristic glass transition of the plasticiser blend affected by some fractions of gluten isolate [7], whereas the second, $T_{\alpha 2}$, was attributed to a glass transition of the plasticised gluten [5, 8, 9]. A certain tendency to a separation of both peaks may be appreciated in Fig. 1B when MC was incorporated to the system. Thus, the specimen containing 0.5 wt% MC shows a displacement of the location of $T_{\alpha 1}$ towards a lower value in relation to the 50/18 system, whereas the second peak, $T_{\alpha 2}$, seems to maintain the same location. This effect suggests that the gum enables a certain tendency to produce segregation from the protein-rich phase, as is the case for many combinations of incompatible biopolymers [10]. However, in the case of MC containing probes, an inversion of the above effect with increasing MC content seems to take place. In fact, a tendency of both peaks to overlap may be appreciated, being indicative of an increase in the degree of compatibility between both biopolymers.

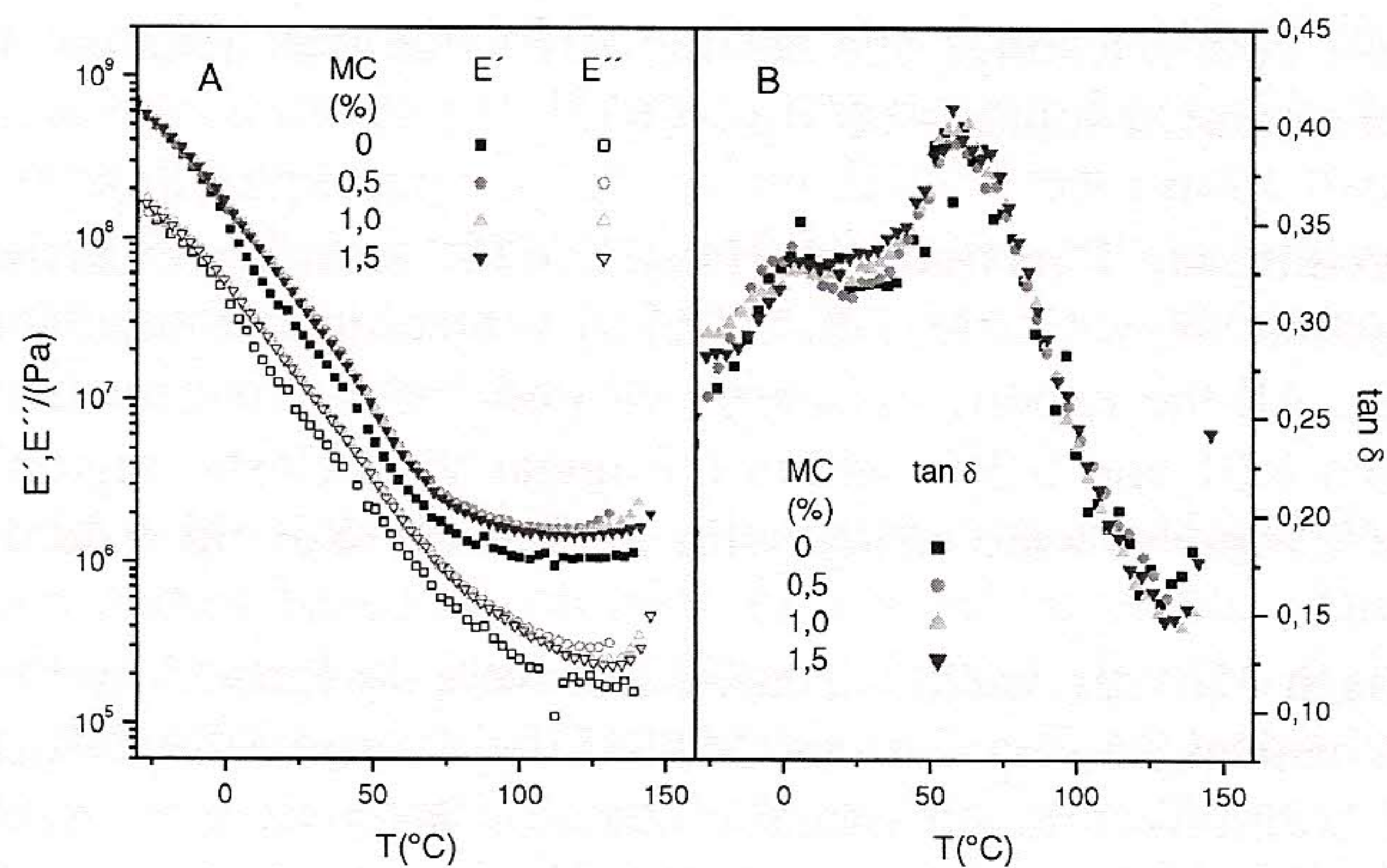


Figure 1. DMA temperature ramp measurements performed at constant frequency (1 Hz) and heating rate (5 °C min⁻¹) for 50/18 WG/MC/GL/water bioplastics, as a function of gum content

Fig. 2 shows the values of E', E'' and tan δ as a function of temperature for the different type of gums used. As may be seen, the behaviour found for all the polysaccharides studied is very similar to that one described previously for the reference system. All of the polysaccharide-containing specimens exhibit a certain degree of thermosetting potential. Moreover, the sequence of values for E' and E'', which may be significant or not depending on the temperature range, is as follows: Reference < CMC < LBG < MC. In addition, as may be deduced from the tan δ profiles shown in figure 2B, only MC-containing probes exhibited a clear tendency of both peaks to overlap and, as a consequence, an apparent enhancement of the compatibility degree with protein.

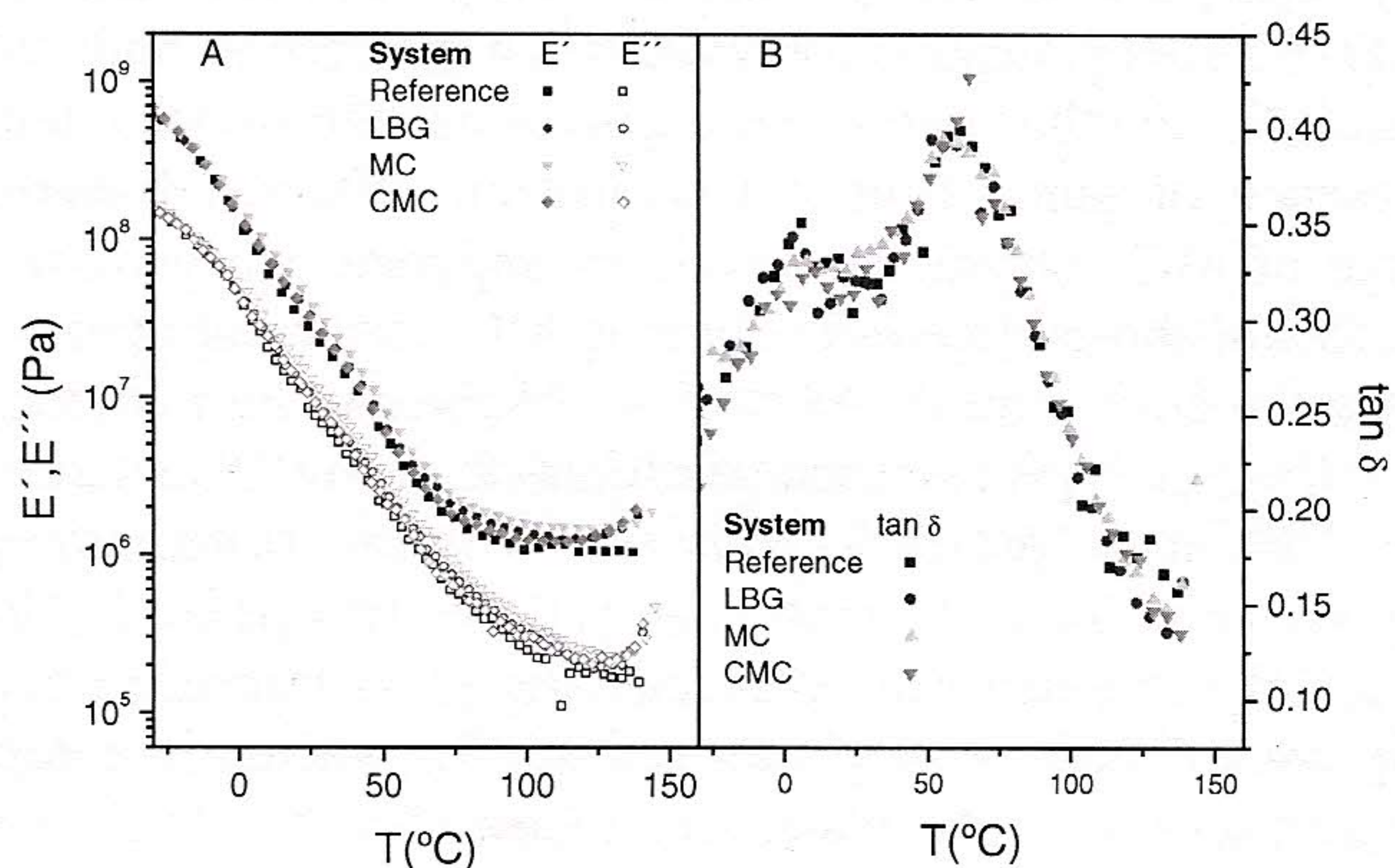


Figure 2. DMA temperature ramp measurements performed at constant frequency (1 Hz) and heating rate (5 °C min⁻¹) for bioplastics containing different polysaccharides

Fig. 3 shows the effect of pH on the values of E' and tan δ obtained as a function of temperature for 50/18 probes prepared either in absence or presence of LBG polysaccharide. Bioplastic probes prepared at pH 3 exhibited much lower E' values, as well as much higher tan δ values, than those probes prepared at native pH (ca. pH 6). This behaviour reveals that under acidic conditions the presence of positive charges on the protein surfaces interfere the development of the bioplastic microstructures during the

moulding process leading to a softer material with a high thermosetting potential (since the protein matrix would require higher moulding temperature). Conversely, alkaline conditions, at which negative charges are predominant at protein surfaces, led to a further enhancement of viscoelastic properties in absence of polysaccharide. The effect of adding LBG also depends on the pH conditions. Thus, a reduction in viscoelastic properties was generally produced if the pH is far from the isoelectric point (IEP), particularly at pH 9 and low temperature at which LBG brought about 50% reduction in E' . On the other hand, LBG conferred a moderate increase in viscoelastic properties to the bioplastic probes, being more evident at high temperature.

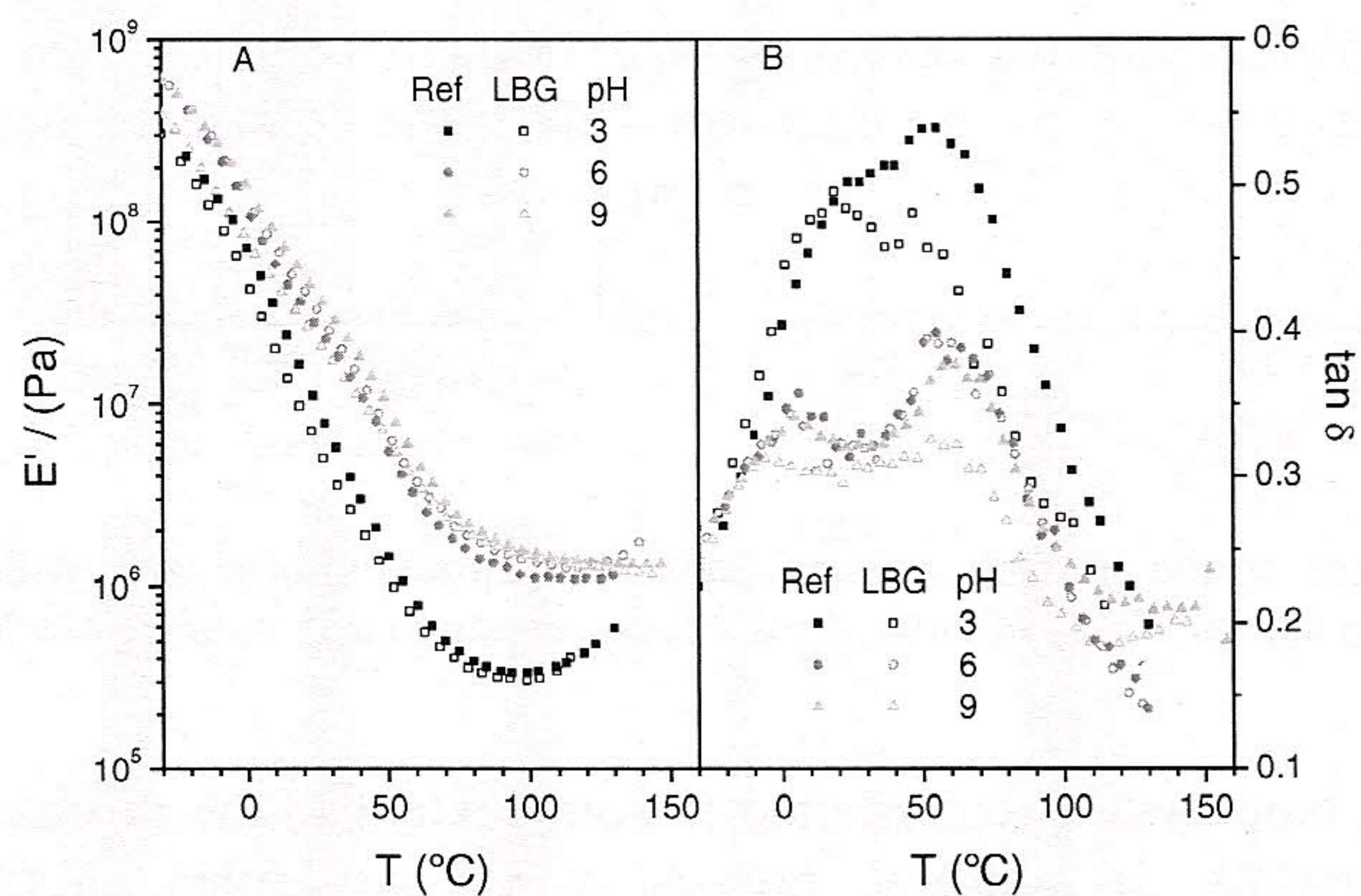


Figure 3. DMA temperature ramp measurements performed at constant frequency (1 Hz) and heating rate ($5\text{ }^{\circ}\text{C min}^{-1}$) for reference and LBG-containing bioplastics, as a function of pH

Fig. 3B shows how in absence of polysaccharide $T_{\alpha 1}$ undergoes a displacement towards lower values with increasing pH, whereas $T_{\alpha 2}$ remains essentially constant. Moreover, addition of LBG also led to a decrease in $T_{\alpha 1}$, excepting at pH close to the IEP at which the $\tan \delta$ profile remain unaltered by the presence of LBG.

3.2 Tensile strength measurements. Fig. 4A shows some typical stress-strain curves obtained after subjecting type IV probes to uniaxial extension tests at constant extensional rate. All the materials exhibit a linear elastic region with a marked increase in strength at low strain values, characterized by high values of the Young's Modulus (E), followed by an extensive plastic region showing a steady decrease up to a constant stress-strain slope, eventually leading to the rupture of samples once maximum stress (σ_{\max}) and maximum strain (ϵ_{\max}) are reached.

A comparison of those tensile parameters (E , σ_{\max} , and ϵ_{\max}) obtained for the specimens in absence or presence of different polysaccharides is shown in Fig. 4B. As may be observed, the presence of polysaccharide generally yields an apparent enhancement of tensile properties, particularly for MC and CMC-containing probes. All the three parameters follow the same general sequence: Reference < LBG < MC < CMC. However, the differences found for σ_{\max} , and ϵ_{\max} between the reference and LBG-containing probes turned out to be non significant. These results are in agreement with those reported by Zhou et al. [11] for soya-based bioplastic containing MC. According to these authors, the miscibility between protein components and polysaccharide (at low

content of the former) were responsible for the improvement of the strength and even resulted in the simultaneous enhancement of strength and elongation.

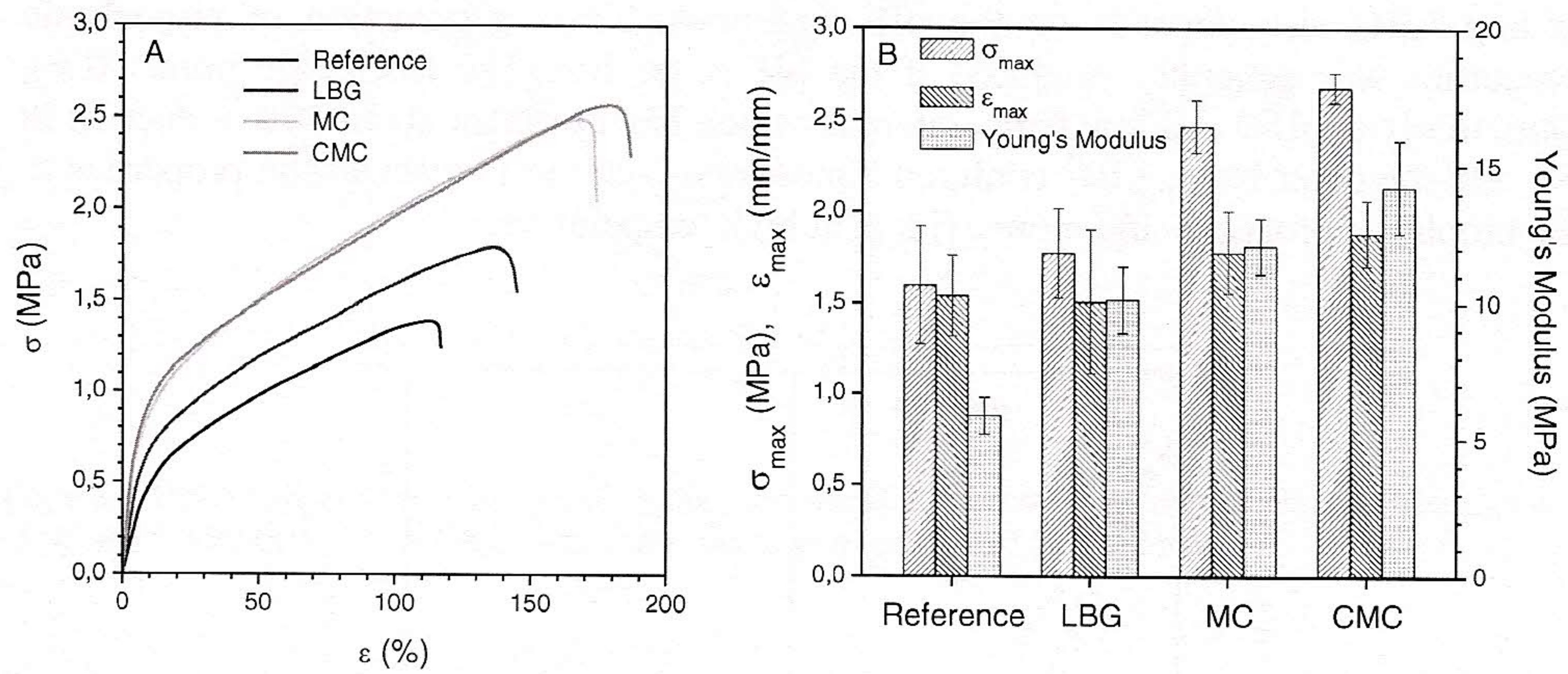


Figure 4. Results from tensile strength measurements for bioplastics formulated with different type of gum: (A) Stress-strain curves; (B) Maximum stress, Maximum strain and Young's Modulus

In any case, both biopolymers contributed to some extent to the mechanical properties of bioplastic materials. In addition, polysaccharide molecules might interact with protein chains altering the rigid structure of gluten and causing a reduction of hydrogen bonds. Then, the gum might play a plasticiser role which could explain the increase in ϵ_{max} , being more evident for the anionic gum (CMC).

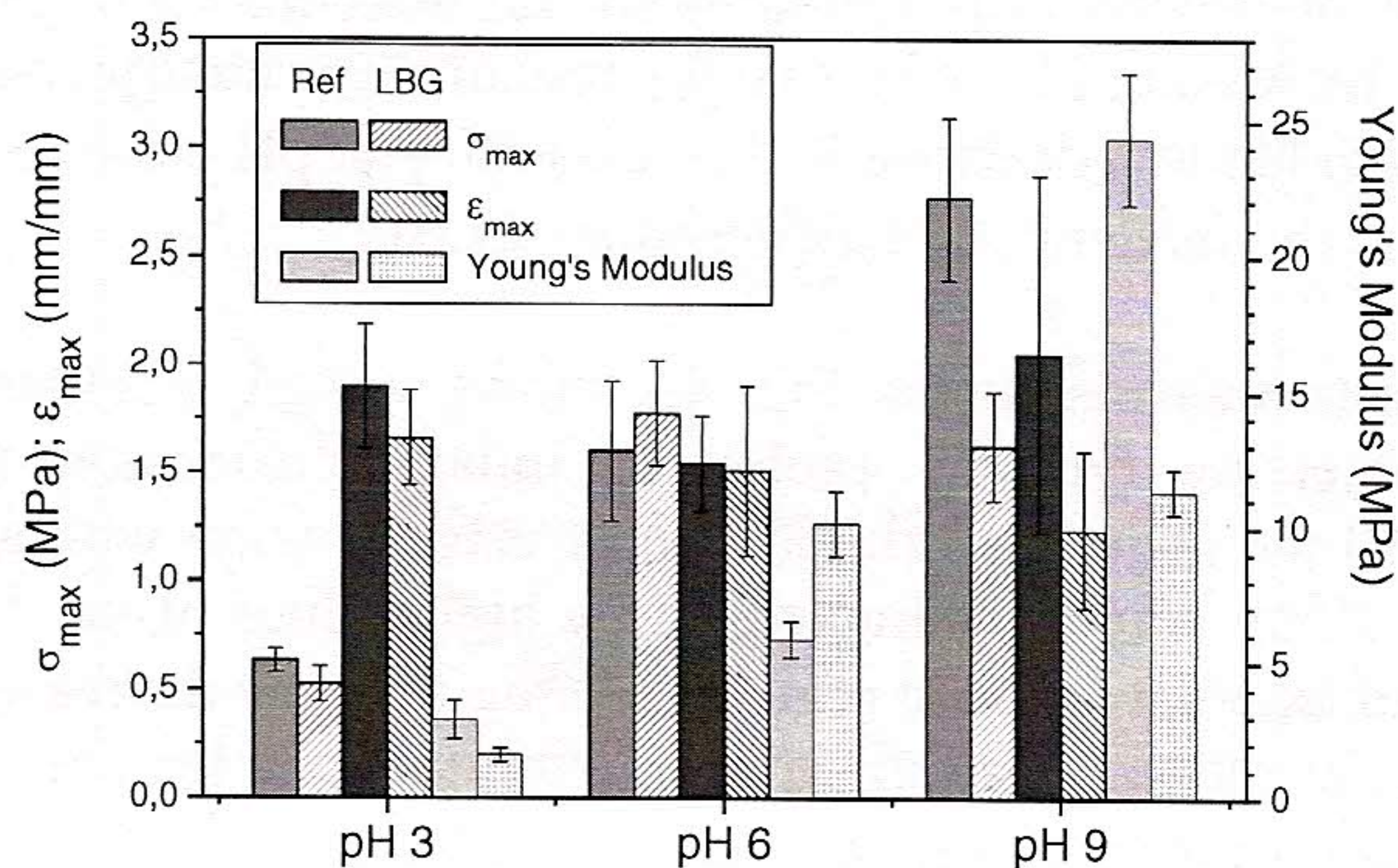


Figure 5. Tensile strength parameters (Maximum stress, Maximum strain and Young's Modulus) for the reference and LBG-containing bioplastic probes as a function of pH

Fig. 5 shows the evolution of tensile strength parameters for reference and LBG-containing probes processed at different pH values. As may be seen, the presence of charges may impart strong modifications to the tensile properties of the system. Thus, a remarkable increase in both σ_{max} , and E with increasing pH took place in absence of gum, whereas no significant evolution of ϵ_{max} may be noticed. The effect of adding gum on tensile properties is also strongly dependent on pH. Thus, the behaviour found at pH

6 does not apply far from the IEP. Conversely, addition of LBG when protein was charged always impairs the tensile properties of bioplastic probes, particularly at pH 9.

3.3 Water absorption capacity. Fig. 6 shows the values of water uptake capacity obtained for samples immerse after 2 and 24 h. The percentage of water-soluble matter loss is also plotted (Fig. 6A), being approximately the same for all the samples (ca. 23 wt%). A slight tendency to reduce water uptake capacity of bioplastic probes seems to be produced by adding gum (MC or CMC), although this effect losses significance after 24 h immersion. However, water uptake capacity exhibited a strong dependence on pH (Fig. 6B). Thus, when the pH at which the probes were processed was far from the IEP water uptake was favoured, particularly at pH 3, overcoming 300 wt% after 24h. Addition of gum resulted in a reduction of water uptake capacity which was significant at pH 3 and 9, being intensified after 24h, but remaining always lower than 10 %.

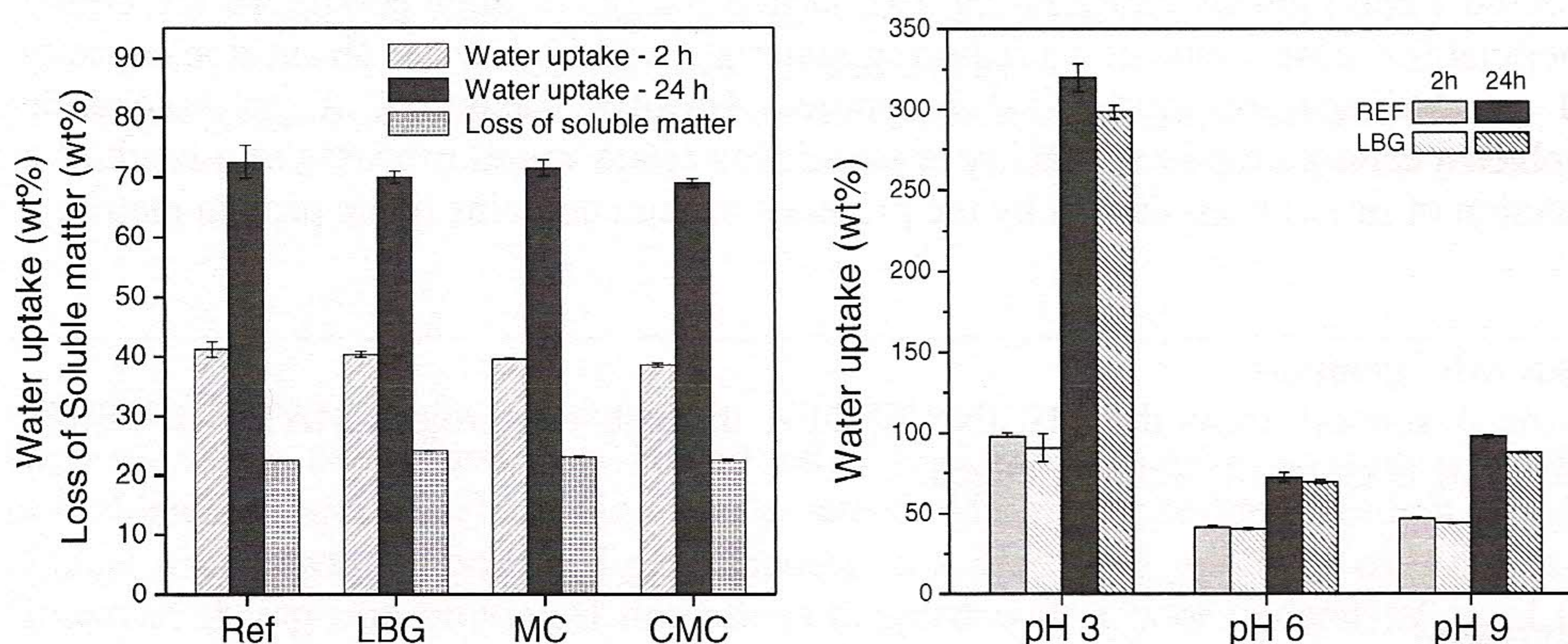


Figure 6. Tensile strength parameters (A) for bioplastics containing different type of gum; (B) for the reference and LBG-containing bioplastics as a function of pH

Regardless of the pH, the behaviour of gluten based bioplastics after addition of polysaccharide involved a certain drop in the ability of proteins to retain water that may be related to a reduction in interactions (i.e hydrogen bonds) as a result of the presence of gum domains in the protein matrix. In addition, gum molecules also exhibited a low capacity to link water after being trapped in the bioplastic microstructure and as a consequence of its low solubility at low temperature.

4. Concluding remarks

DMA results indicate that a moderate enhancement of the network structure may be achieved by adding polysaccharide, which also confers a further thermosetting capacity to the system. Thus, a further enhancement would be produced by increasing moulding temperature during bioplastic manufacture. The polysaccharide conferring the largest enhancement to the microstructure of 50/18 bioplastics was MC. This effect may be related to the thermogelation ability exhibited by this polysaccharide [12]. In contrast, LBG and CMC seem to play the typical role of a filling material (particularly moderate for CMC), indicating a low degree of interaction with gluten proteins. In addition, the

presence of charges at the gluten protein surfaces seems to favour phase separation between gum and protein domains, probably due to the so-called segregative separation effect [13]. However, $\tan \delta$ profile suggests a higher compatibility between both biopolymers at acidic pH, probably related to a higher water holding capacity under such conditions.

The presence of charges may also impart strong modifications to the tensile properties of the system. Thus, a remarkable increase in both σ_{\max} , and E with increasing pH took place in absence of gum. Moreover, the effect of adding gum to tensile properties is also strongly dependent on pH. Thus, the presence of gum generally yielded an apparent enhancement of tensile properties at the IEP (particularly for MC and CMC), but played a detrimental effect when electrostatic interactions were involved, particularly at pH 9.

Water uptake capacity also exhibited a strong dependence on pH, being largely favoured when bioplastic processing was carried out pH 3. Such conditions are highly beneficial for those applications requiring materials with high water absorption capacity and suitable end-use mechanical properties. However, addition of polysaccharide involved a certain drop in the ability of proteins to retain water, probably as a result of a reduction of interactions caused by the presence of gum domains in the protein matrix.

Acknowledgements

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