Plasticization of corn gluten meal and characterization of the blends

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SUMMARY: Corn gluten meal has thermoplastic properties enhanced by it's high zein content. The addition of an efficient plasticizer is necessary to lower the glass transition temperature. Homogeneous blends of plasticizer and corn gluten meal can be obtained either by a wet mixing technique or by compounding the two substances in an heated batch mixer. The resulting raw material is suitable for "thermoplastic forming" of low cost biomaterials.

Keywords : Plasticization, DMTA, corn gluten meal, biomaterial.

Introduction

Large efforts have been done recently to develop technical applications of biopolymers[1)]. For instance, some processes of producing renewable and biodegradable plastics, from agricultural raw materials, are based on thermoplastic properties of proteins under low water content conditions[2)]. During such thermoplastic processing of polymers, the temperature is increased above the glass transition temperature (Tg) of the polymer, and a rubbery moldable state is reached. Thermoplastic properties have been described for many plant proteins[2-3)], and in particular for zein[4-5)]. Corn gluten meal (CGM) is a coproduct of corn wet-milling industry, rich in zein (45% dry weight basis)[6)]. It has a cost as low as starch, because of a poor nutritional value. In previous studies[7-8)] thermoplastic properties of CGM were observed by dynamic mechanical thermal analysis (DMTA). The Tg was measured at 188°C, near the thermal degradation of the CGM. The addition of plasticizers to lower Tg is then necessary for good processing conditions. In this study, the plasticization of CGM is studied in relation with the mixing technique.

Experimental

Tested plasticizers were hydrophilic substances containing hydroxyl, ether or amino functions (glycerol, polyethylene glycol 300, urea and diethanolamine). In order to get an homogeneous

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blend of CGM and plasticizer (at 10 or 30 g plasticizer / 100 g dry CGM), three mixing techniques were developed: (1) Dry mixing = kneading CGM and the plasticizer in a mortar ; (2) Wet mixing = kneading CGM, plasticizer and water in a mortar and freeze-drying in order to eliminate the water; (3) Compounding = mixing CGM and the plasticizer in a two blade conter-rotating batch mixer (Brabender, Germany), thermostated with a temperature regulation liquid[9]. CGM and plasticizer blends were formed into tablets of cylindrical shape (5 mm diameter and 10 mm height) with a pharmaceutical tableting machine (Frogerais, Vitry-sur-Seine, France), by applying a pressure between 10 and 30 kN/cm^2. DMTA analysis of CGM-based tablets was conducted with a Dynamic Mechanical Thermal Analyser MK III (Rheometric Scientific, Piscataway, USA) as previously described[8]. A variable-amplitude, sinusoidal mechanical stress was applied to the sample (frequency = 1Hz) to produce a sinusoidal strain of preselected amplitude (16 μm peak-to-peak). Temperature scans (from -100°C to 260°C) were performed at a heating rate of 3°C/min.

Results and discussion

The tan δ curves from DMTA (Fig. 1) showed a single well defined peak at 167°C in case of wet mixing. This peak is typical of the α-relaxation phenomenon in proteins[10], and is associated with the glass transition of plasticized CGM.

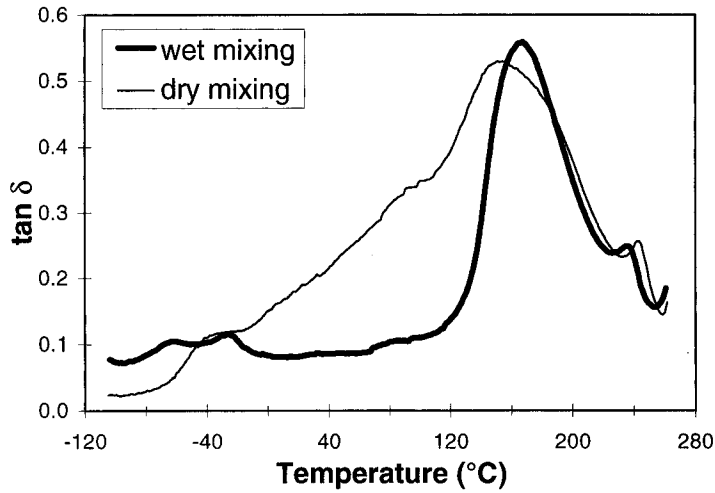

Fig. 1: DMTA tan δ cuves of corn gluten meal (10g glycerol / 100 g dry CGM)

In the case of a blend prepared by the dry mixing technique, a large shoulder below the peak (from -20 to +120°C) was observed (Fig. 1). This shoulder was related to an extended inhomogeneity of the blend because a single α-realxation of CGM was not observed. The α-relaxation occurred at varying temperatures, depending on the local amount of the plasticizer, that was not homogeneously distributed in the CGM.

In case of compounding CGM and the plasticizer in the batch mixer, when the temperature of the mixing chamber was higher than the Tg of the blend, a torque was quickly developed (Fig. 2). This torque development was related to the plasticization of CGM and the forming of a structured material that can be described as a CGM-based thermoplastic resin.

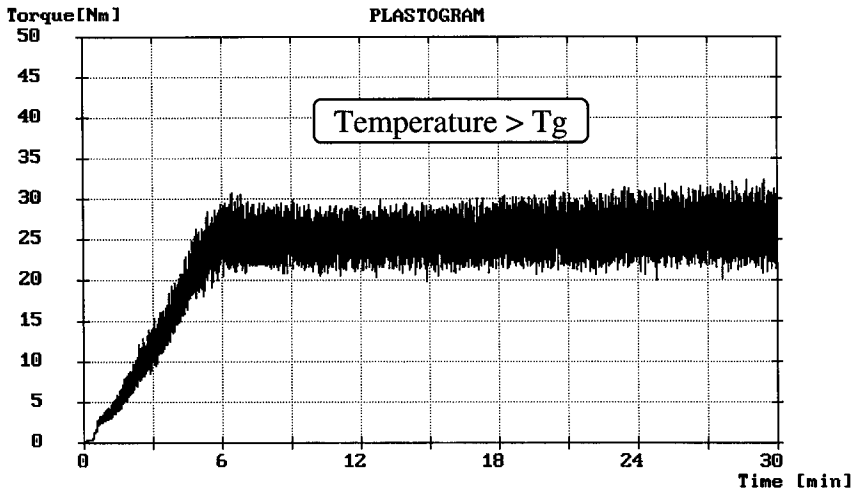

Fig. 2: Plastogram of corn gluten meal and glycerol (30g / 100 g dry CGM) with the evolution of the torque, for a mixing temperature > Tg

This resin was characterized by DMTA. As for the blend prepared by wet mixing, a single and well-defined peak was observed at the α-relaxation temperature (Fig. 3). This peak was perfectly superimposed to the peak obtained for the blend prepared by the wet mixing process. This was an indication that compounding corn gluten meal and a plasticizer was a suitable technique to get an homogeneous blend of these two components.

The dry CGM α-relaxation measured at 188-207°C[6], was lowered by more than 100°C at 30 g plasticizer / 100 g dry CGM content (Fig. 4). On a molar basis, it was observed that the

plasticizing efficiency (*i.e.* Tg decrease at a given plasticizer content) increased with the plasticizer molecular weight.

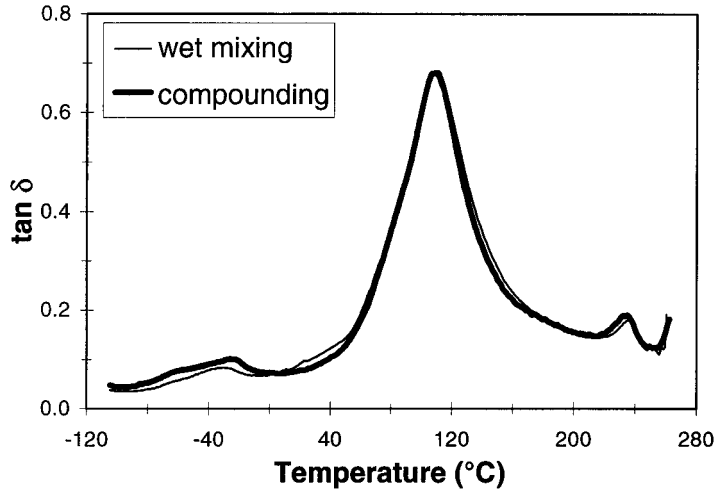

Fig. 3: DMTA tan δ cuves of corn gluten meal (30 g glycerol / 100 g dry CGM)

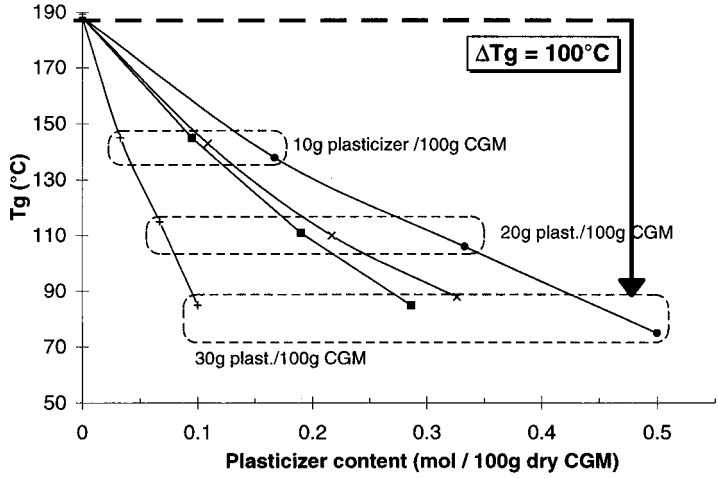

Fig. 4: Tg values of corn gluten meal as a function of plasticizer molar fraction; • = Urea (M_W = 60 g / mol), × = Glycerol (M_W = 92 g / mol), ■ = Diethanolamine (M_W = 105 g / mol), + = Polyethylene glycol 300 (M_W = 300 g / mol)

In case of glycerol and diethanolamine, the lowering of Tg due to the increase in plasticizer content was similar despite large differences in the molecular structure of these two

plasticizers (hydroxyl or amino functions). It is interesting to note that glycerol and diethanolamine have similar molecular weights. This result suggests that the plasticizer size is a very important factor related to the plasticizing efficiency.

Conclusion

Production of low cost bioplastics can be achieved with plant proteins. Corn gluten meal and an hydrophilic plasticizer were blended by different techniques, and in case of compounding by admixing above Tg in an heated batch mixer, an homogeneous blend was obtained. This compounding technique is very similar to the plasticization process used for synthetic polymers. It is a promising low cost technique to get a thermoplastic resin made of CGM and a plasticizer, for bioplastics preparation.

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