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Thermoplastic Foams from Zein and Gelatin

The aim of this study was to characterize the foaming of natural proteins as thermoplastic polymers. In particular, two proteins, one of vegetal origin, zein, and one of animal origin, gelatin, were processed to achieve thermoplastic polymers, and subsequently foamed by a gas foaming batch process. The effects of suitable plasticizing additives and melt-mixing process on the thermal and mechanical properties of the thermoplasticized proteins were evaluated to assess the thermoplastic characteristics of these materials. Furthermore, selected protein/plasticizers systems were foamed with mixtures of CO₂ and N₂ as blowing agents, in a batch foaming apparatus, at different temperatures, pressures and pressure drop rates, to evaluate the processing window and the final properties of the foams. Foams with densities of 0.1 g/cm³ and morphologies characterized by uniform distributions of cells with 10 μm diameters were obtained. Results indicated the suitability of zein and gelatin for being processed with classical thermoplastic processing technologies including melt mixing and foaming and their potentials as biodegradable polymers.

1 Introduction

Renewed interest in natural polymers like polysaccharides and proteins has been recently stimulated by waste disposal problems and environmental concerns, aiming at alternatives to petroleum-derived materials.

Within the polysaccharides, starch is the most important, since it is the most abundant in nature and relatively in expensive. Starch has been the subject of numerous papers reporting its plastic behaviour, for it can be processed with classical plastic processing technologies (e. g. extrusion, foaming and film blowing) and for the plastic-like properties of thermo-plasticized starch, that have promoted its use in some commodity application as substitute for petroleum based plastics (van Soest and Borger, 1997; Wiedmann and Srobel, 1991; Yu and Gao, 1996). The main limitation for starch is the hydrophilic nature, which limits its use in high moisture environments (Brouillet-Fourmann et al., 2002).

Zein, the prolamine of corn, is a natural protein with high resistance to water (it is insoluble in water) (Lai et al., 1997; Lai and Padua, 1998; Lawton, 2002; Momany et al., 2006; Padua

and Rakotoniraing, 2003; Shukla and Cheryan, 2001), due to the high portion of relatively hydrophobic amino acids present and better water vapour barrier properties (Cuq et al., 1998), if compared with other proteins like casein, or polysaccharides such as starch. Zein has been used in a number of applications since becoming commercially available in 1938 but its use as plastic materials is still very limited to high value added products (e. g. in pharmaceuticals) (Beck et al., 1996; Padua et al., 2002). This is mostly due to the complex, hierarchical, highly interactive structure which makes it very difficult to process. In particular, proteins are heteropolymers (differently from starch, which is a homopolymer) with amino acids as building blocks, arranged in secondary structures of helices and sheets, in turn packed to form globular units (Batterman–Azcona, 1999; Wang et al., 2005). These three dimensional structures are tightly bonded by hydrogen as well as disulfide bonds and have to be (at least partially) disrupted, to obtain separate, entangled macromolecules by a process called “denaturation”, in order to achieve plastic-like properties (de Graaf, 2000).

Denaturation can be induced both by temperature and by denaturants, often by both. Protein denaturation has been well studied in solutions with water content >90 % (wet denaturation) while little research has been performed on denaturation in systems at low or medium water content (dry denaturation), which is more interesting from a technological point of view (Ha and Padua, 2001; Wang et al., 2003; Wang et al., 2005). Several proteins have been thermoplasticized using very low water content, by direct extrusion, internal mixing or injection moulding, proving the high potential of these “bioplastics” for massive production (Azranitoyannis et al., 1998; Cuq et al., 1997; Jongjareonrak et al., 2007; Pomet et al., 2003; Redl et al., 1999a; Thièband et al., 1996; Vez et al., 2003). However, there is still need for additional fundamental information, such as the mechanism of thermoplasticization, the role and mechanisms of plasticizers and the influence of processing conditions (i. e. temperature, shear stress) on denaturation and on the final properties.

Gelatin is the result of the denaturation process of collagen, the major structural protein of most connective tissues (Bigi et al., 2004). Currently there is a wide interest in gelatin, for its low cost and biodegradability, in food, pharmaceutical and photographic industries. Its film forming ability, furthermore, generated interests in using gelatin in packaging applications (Padua et al., 2002). Gelatin films have been produced by casting while direct melt (dry) processing on gelatin has not been reported.

Foaming of natural polymers has been mostly studied in the context of food engineering, in the preparation of bread and

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cooked snacks (Glenn et al., 2001; Shogren et al., 2002) while other examples include ice creams, puff-dried fruits and vegetables, egg white and beer (Goof et al., 1999; Hagolle et al., 2000). The utilized technologies are different from the gas foaming technology used for thermoplastic polymers (e. g. bread and cooked snacks are produced via mixing (aeration) and fermentation with gas evolution processes). Classical polymer science (e. g., matrix rheology, matrix density, interfacial, strain hardening properties) has been successfully applied to optimize food final sensation and texture (de Cindio et al., 2002a, 2002b; Thièband et al., 1996). Recently, however, plastic processing technologies (steam-based extrusion) have been used to produce foams with different formulations including starch for different applications such as packaging and insulation (Willet and Shogren, 2002), while the gas foaming technology to produce foams from thermoplasticized proteins has never been reported in the scientific literature.

In this paper we analyzed the melt mixing process of zein and gelatin and the use of the batch foaming technology with nitrogen and carbon dioxide as the physical blowing agents to obtain foamed materials.

2 Materials and Methods

2.1 Materials

Maize zein (cod.: Z3625, batch: 101H0724) and gelatin from bovine skin type B (cod.: G9382, batch: 04K0004) were purchased from Sigma-Aldrich (Italy). In order to investigate the thermoplasticity of zein and gelatin, low molecular weight compounds with different chemical functions (alcohol and acid) and hydrophobicity degree (carbon chain length) were used as plasticizers (see Table 1). In particular, glycerol and lactic acid were used as plasticizers for gelatin while PEG 400, lactic acid, lauric acid and stearic acid for zein. N₂, CO₂ and their mixtures (Air Liquide, Italy) were used as physical blowing agents for gas foaming experiments.

2.2 Thermoplasticized Protein-based Materials Preparation

Zein powder or gelatin powder, as received by the supplier (moisture content, as determined by thermogravimetric analysis, equal to 7 and 11 wt.%, respectively), were mixed with the plasticizer in a beaker using a spatula to provide a crude blend. The blend was then subjected to temperature and shear stresses in a twin counter rotating internal mixer (Rheomix 600 Haake, Germany) connected to a control unit (Rheocord

9000 Haake, Germany) for thermoplasticization. Torque and melt temperature were recorded during the mixing process to provide the mixing process history. The mixing chamber (volume of 50 cm³) was filled with 50 g total mass for all experiments in approximately 3 min at 5 min⁻¹. Plasticizer contents of 20, 25 and 30 wt.% were used. Mixing temperature, T_{mix}, speed of rotation, N, and mixing time, t, were 60 °C, 60 min⁻¹ and 6 min, respectively for thermoplastic gelatin (TG) and 80 °C, 50 min⁻¹ and 10 min for thermoplastic zein (TZ).

A P300P hot press (Collin, Germany) was then used to prepare slabs with thickness of 1 mm. Materials were heated at the same temperature of mixing and pressed at 50 bar for 10 min and subsequently cooled to 30 °C under pressure. From the central region of the films, dog bone-shaped specimens for mechanical analysis and cylindrical samples of 10 mm in diameter for gas foaming experiments were cut.

2.3 Thermoplasticized Protein-based Materials Characterization

2.3.1 Thermal Analysis

Thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses were performed to evaluate the effect of the thermoplasticization on thermal properties of gelatin and zein and to select suitable foaming temperatures. TGA experiments were carried out on a TGA 2950 (TA Instruments, USA) over a temperature range of 30 °C to 600 °C at 10 °C/min under inert atmosphere. For DSC analyses (DSC Q1000, TA Instruments, USA), 15 mg samples were initially dried by heating to and held at 100 °C for 5 min and subsequently scanned at 5 °C/min from -80 °C to 200 °C.

2.3.2 Mechanical Properties

Tensile tests were performed at room temperature according to ASTM standard D1708-02 by using a 4204 Universal Testing Machine (Instron, USA) with 1kN load cell and at a displacement rate of 10 mm/min. Force and displacement were measured by the apparatus and recorded to evaluate Young's modulus (E), stress at break (σ_R) and elongation at break (ε_R). Because the mechanical properties of these films are known to be strongly affected by water content, samples were preconditioned at room temperature and 50% relative humidity for 48 h before testing. Mechanical characterization was performed within 3 days from sample moulding.

Plasticizer	Chemical formula	Mw g/mol	Supplier
Glycerol	OH-CH ₂ -CHOH-CH ₂ -OH	92.09	Sigma-Aldrich
Poly(ethylene glycol) 400 (PEG 400)	H-(OCH ₂ CH ₂) _n -OH	400	Fluka
Lactic Acid	CH ₃ -CH-OH-COOH	90.08	Sigma-Aldrich
Lauric Acid	CH ₃ -(CH ₂) ₁₀ -COOH	200.32	Sigma-Aldrich
Stearic Acid	CH ₃ -(CH ₂) ₁₆ -COOH	284.49	Sigma-Aldrich

Table 1. Physico-chemical characteristics of the different plasticizers used

2.4 Foaming of Thermoplasticized Protein-based Materials

2.4.1 Batch Foaming Experiments

Foaming experiments were carried out by using a batch process on disc-shaped samples (10 mm in diameter and 1 mm thick). The thermoplasticized protein samples were placed into the pressure vessel (Marrazzo et al., 2007) and kept with blowing agent mixture for six hours at 70 °C and at saturation pressure (P_{sat}) in the range 60 to 180 bar. After saturation, samples were cooled or heated to the desired foaming temperature with a controlled profile and finally pressure was reduced to atmospheric pressure to allow foaming. To stabilize the cellular structure, foams were immediately cooled down to ambient temperature and subsequently removed from the vessel. The processing parameters selected to control foam morphologies were (Di Maio et al., 2005; Hwang and Cha, 2002; Han et al., 2003; Park et al. 1995): N_2 - CO_2 vol.% of the blowing agent mixture in the range 0-100 to 100-0; foaming temperature (T_F) in the range 44 to 140 °C and pressure drop rate (PDR) in the range 250 to 700 bar/s.

2.4.2 Foam Characterization

Foamed samples were cross-sectioned, gold sputtered and analyzed by scanning electron microscopy (LEICA mod. S440). To evaluate the effect of gas foaming processing parameters on foam microstructures, mean cell diameter (D_C) was evaluated by image analysis. A minimum of 150 cells for each sample were selected from the micrographs and analyzed with Image J software. The cell diameter was calculated with the hypothesis of spherical shape, by correcting the software output with the factor $4/\pi$ (ASTM D3576) (Kumar and Suh, 1990).

3 Results and Discussion

3.1 Mixing

Fig. 1 shows the evolution of torque and melt temperature vs. time during the mixing process of zein with the four different plasticizers (stearic acid, PEG 400, lactic acid and lauric acid,

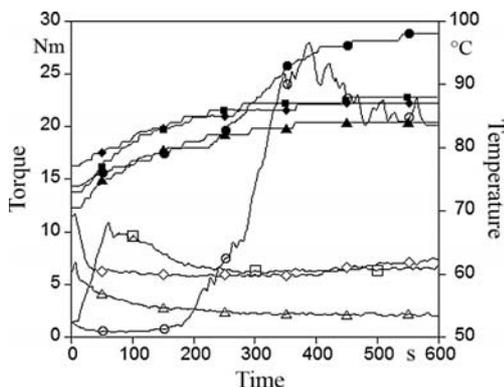


Fig. 1. Torque (open symbols) and melt temperature (closed symbols) evolution during the mixing process of zein with PEG 400 (\diamond , \blacklozenge), stearic acid (\circ , \bullet), lauric acid (\square , \blacksquare) and lactic acid (\triangle , \blacktriangle) (25 wt.% plasticizer content, $N = 50 \text{ min}^{-1}$, $T_{\text{mix}} = 80 \text{ }^\circ\text{C}$, $t = 10 \text{ min}$)

25 wt.%). As reported for other protein-plasticizer systems, torque evolution during thermoplasticization can be described as a three-step process (Redl et al., 1999b), characterized by a first horizontal plateau followed, after a certain induction time, by a steep increase of the torque to a maximum and then a continuous decrease to a rather stationary value, when also the melt temperature becomes constant. In our case, this behaviour was more evident in zein-stearic acid and zein-lauric acid systems, while for PEG 400 and lactic acid the torque increase was immediate, with the absence of the induction time.

The complexity of the thermoplasticization process is related to numerous phenomena, which bring the plasticizer in close contact with the protein macromolecules and, eventually, with the help of shear stresses, denature the hierarchical structure to achieve entangled molecules. Process variables and formulations that enhance the diffusion of the plasticizer and the shear stresses induce an improvement and a shortening of the whole thermoplasticization process. In particular it is fundamental the ability of the plasticizer to interact with the protein: it is known (Sothornvit and Krochta, 2001) that the efficiency of the plasticizer depends on several factors such as its size (molecular weight), shape and functionality (mostly, number of oxygen atoms). As a general rule, a good plasticizer should have a high content of available oxygen atoms and a small size. In this work all of the plasticizers were linear molecules, and they were different in content of oxygen atoms and size. In our case lactic acid and PEG 400 were better plasticizers for zein with respect to lauric and stearic acid. This is probably related to their smaller molecular size and/or higher amount of oxygen atoms.

Torque histories of the thermoplasticization process of gelatin are reported in Fig. 2, showing that, in this case, the lactic acid was more efficient than glycerol. Fig. 2 also reports the effect of plasticizer content (20 and 25 wt.%) on torque during gelatin mixing with lactic acid and glycerol, showing an increase of the induction time and a decrease of the maximum and final torque with the increase of the plasticizer amount. Same dependences have been observed by Selling et al. (2004) for zein plasticized with 5 to 30 wt.% of water and/or

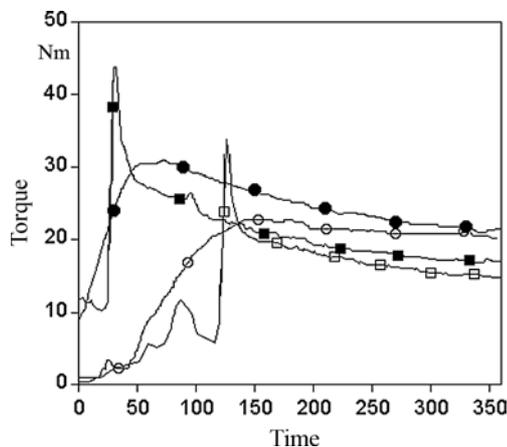


Fig. 2. Effect of type and plasticizer content on torque evolution during the mixing process of gelatin with glycerol (\bullet 20 wt.%, \circ 25 wt.%) and lactic acid (\blacksquare 20 wt.%, \square 25 wt.%) ($N = 60 \text{ min}^{-1}$, $T_{\text{mix}} = 60 \text{ }^\circ\text{C}$, $t = 6 \text{ min}$)

tri(ethylene) glycol, and by Redl et al. (1998) for gluten plasticized with 30 to 60 wt.% of glycerol. Observed dependencies can be related to the enhanced lubricant effect of the increased amount of plasticizer that reduced the viscosity of the system and consequently, the torque values measured during mixing. As a co-effect, shear stresses and melt temperature decreased, in turn reducing the diffusivity of the plasticizer molecules into the protein chains and, finally, determining the observed increase of the time lag.

3.2 Thermal Properties

Fig. 3 reports TGA and DSC results for pure gelatin and TG. TGA curve of pure gelatin showed a weight loss in the range 30 to 140 °C, associated to evaporation of water, while a steep weight decrease starts at 271 °C and can be associated to the degradation of the protein. Results of the TGA for TG show a similar water loss in the range 30 to 140 °C, while, in this case, both the evaporation of the plasticizer (glycerol) and protein degradation are responsible for the earlier steep weight loss at 221 °C (T_{ons} in Fig. 3). Moreover, the DSC curve for the TG showed a glass transition (T_g) at 50 °C, which is not present in

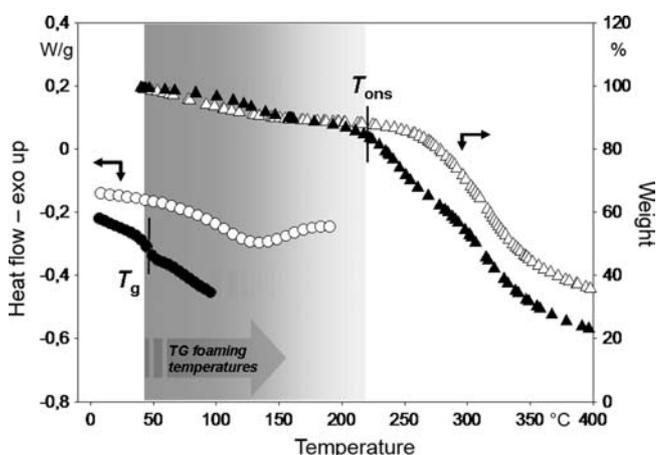


Fig. 3. TGA and DSC curves of pure (Δ , \circ) and thermoplasticized gelatin (\blacktriangle , \bullet) with the indication of T_g , T_{deg} and foaming temperature range of TG

the thermograms of the pure gelatin, while both TG and gelatin are characterized by an endothermic peak in the range 90 to 180 °C. Similar thermal transitions have been observed by Zheng et al. (2002) for dehydrated gelatin powder (attributed to the devitrification of α -amino acid-rich blocks) and by Vanin et al. (2005) for dehydrated gelatin-glycerol systems (attributed to the helix-coil transitions). Results of the thermal analysis on TG provide useful information for the selection of processing temperatures in foaming (e.g. solubilization and foaming temperatures). In effect, at temperatures below the T_g of the TG, foaming is hindered by the very high rigidity of the polymer/blowing agent solution while, at high temperatures, the protein is prone to degradation/loss of plasticizer. Gas foaming temperatures were hence selected with the minimum temperature close to T_g and with maximum temperature well below 221 °C.

TGA curves of pure and thermoplasticized zein showed a less pronounced differences in the T_{ons} (280.9 °C and 272.5 °C, respectively). Moreover, the DSC analyses of the pure zein revealed the presence of a thermal transition at 162 °C for the pure protein, which can be attributed to the T_g . Similar T_g values (162 to 165 °C) have been observed by Magoshi et al. (1992) for anhydrous zein. Beck et al. (1996) measured a T_g of 139 °C for pure zein and a T_g of 90 °C for zein-20 wt.% PEG 300 prepared via water-plasticization, compression moulding and drying. In view of the natural variability of the material source and of the different plasticization methods employed, these results can be considered in agreement with ours. Taking into account these results, foamability of TZ materials was investigated at T_F starting from 44 °C.

3.3 Mechanical Properties

The effect of the different plasticizers and their content on the tensile characteristics of plasticized zein and gelatin is reported in Table 2. Of the plasticizers studied, lactic acid-plasticized proteins resulted in the highest σ_R for both gelatin and zein, with minor differences observed in E and ϵ_R (see Table 2). This behaviour can be due to the smaller size of the lactic acid molecule with respect to the other plasticizers, allowing increased interaction with the protein molecules, facilitating, in turn, their movement in response to the applied stress (Donhowe

Protein	Plasticizer types	Plasticizer wt.%	σ_R MPa	E MPa	ϵ_R mm/mm
TZ	Lactic acid	25	11.5 ± 1.5	897.1 ± 150	0.043 ± 0.023
	Lauric acid	25	14.1 ± 1.1	820.3 ± 25	0.026 ± 0.007
	Stearic acid	25		Fragile material	
	PEG 400	20		Fragile material	
	PEG 400	25	11.8 ± 0.8	843.2 ± 110	0.028 ± 0.011
	PEG 400	30	0.721 ± 0.2	23.91 ± 9	0.75 ± 0.24
TG	Lactic acid	20	5.48 ± 0.29	241.2 ± 30	2.24 ± 0.23
	Glycerol	20	7.69 ± 0.69	198.5 ± 22	1.76 ± 0.1
	Glycerol	25	6.29 ± 0.31	114.8 ± 17.8	1.78 ± 0.03

Table 2. Effect of type and plasticizer content on the tensile properties of TZ and TG films

and Fennema, 1993; Sothornvit and Krochta, 2001). As expected, the increase of the plasticizer content resulted in materials with lower E and σ_R but with higher ϵ_R (see Table 2), in agreement with the studies of Masco-Arriola (1996) and Jongjareonrak et al. (2006).

Literature data on mechanical properties of plasticized zein and gelatin mostly deal with materials prepared by solution casting, revealing that samples obtained by casting show, generally, inferior mechanical properties with respect to melt mixed materials, mostly in terms of deformability. Tillekeratne et al. (2002) reported a value of ϵ_R of 1.5 % for zein plasticized with PEG 400 at 30 %, while we measured a ϵ_R of 75 %, with the same composition of PEG 400. Similar conclusions can be drawn on gelatin for which Jongjareonrak et al. (2006) reported an ϵ_R of 10.9 % for gelatin plasticized with 25 wt.% of glycerol, while we observed a ϵ_R of 180 %. Unfortunately data on E and σ_R were not reported by the cited references. The effect of the different film formation technologies has been reported by Lai and Padua (1997) which investigated the mechanical properties of zein films plasticized with 33 wt.% of oleic acid and prepared from casting solutions and stretched resins. They observed that, in general, stretched resin films showed better mechanical properties with respect to cast films in terms of deformability (fourfold increases in ϵ_R) at comparable E (18 % lower in the case of stretched resin) and σ_R (20 % higher in the case of stretched resin), proving, possibly, a lower plasticizing efficiency of the casting technique. Although results reported in Table 2 show that lactic acid provided the best mechanical properties to TZ, with PEG 400 slightly below, it has to be evidenced that lactic acid tends to migrate to the surface of gelatin and zein films, resulting in a loss of film flexibility (Tillekeratne and Easteal, 2002). For this reason, PEG 400 (at 25 wt.%) and glycerol (at 20 wt.%) were finally used for preparing TZ and TG, respectively, for the gas foaming experiments.

3.4 Foaming

The foamability of the thermoplasticized protein-based materials was studied by analyzing the effect of the gas foaming processing parameters on foam morphologies. In particular, the effects of blowing agent composition, T_F and PDR, on D_C and final density of TZ and TG foams were evaluated.

Test number	N_2-CO_2 vol.%	P_{sat} bar	T_F $^{\circ}C$	PDR bar/s
1	0–100	60	50	250
2	0–100	60	60	250
3	0–100	60	70	250
4	50–50	150	70	250
5	80–20	180	44	700
6	80–20	180	70	700
7	80–20	180	73	700
8	80–20	180	76	700
9	80–20	180	79	700
10	80–20	180	87	700
11	80–20	180	100	700
12	100–0	180	100	700

Table 3. Experimental conditions used for the preparation of TZ foams

3.4.1 Thermoplastic Zein

The test conditions used in TZ foaming experiments are listed in Table 3. SEM micrographs of selected TZ foams (#1, #9 and #12) are shown in Fig. 4 in order to illustrate the effect of the different blowing agents (pure CO_2 , 80–20 N_2-CO_2 vol.% mixture and pure N_2 ; Fig. 4A, B and C, respectively) on foam morphologies. The cell microstructure changed significantly by using CO_2 , N_2 , or their mixture. In particular, when foamed with CO_2 (Fig. 4A), the cells were separated from each other by thick walls (suggesting a high density of the foams) and they were characterized by pores with a D_C of 70 μm having highly irregular and rough pore surfaces. Similar morphologies were observed with the increase of the T_F (maintaining constant the other processing parameters, in test #2 and #3), which resulted in foams with pores characterized by greater and more dispersed values of D_C and lower foam densities (as low as 0.24 g/cm^3). Foams prepared from TZ with 80 to 20 N_2-CO_2 vol.% (Fig. 4B) showed a microstructure characterized by higher cell number densities, with smaller D_C (37 μm) and homogeneous cellular structures. The decrease of D_C is related to the different blowing mixture composition, but also to the higher P_{sat} and PDR (#9). It is important to note that, in the cited tests (compare #1 and #9, Fig. 4A and B) foaming temperatures were different. In effect, plasticization induced by observed in many polymeric systems, plasticization induced

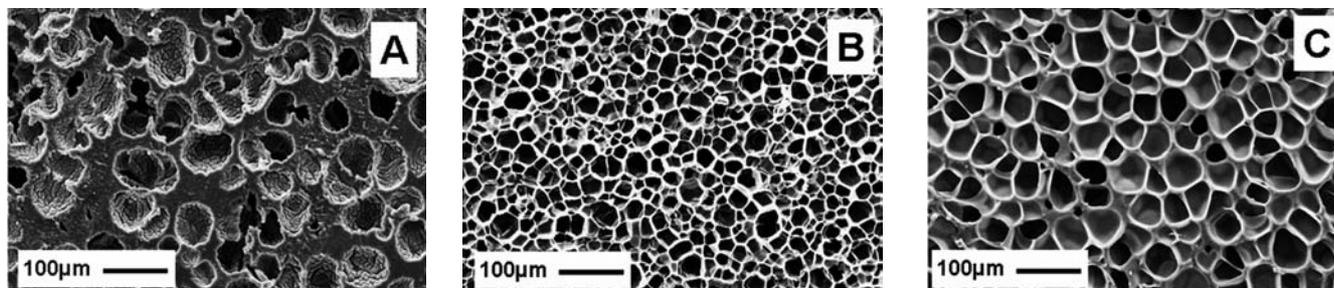


Fig. 4. SEM micrographs of TZ foams: (A) N_2-CO_2 0–100 vol.%, $T_F = 50^{\circ}C$, $P_{sat} = 60$ bar and PDR = 250 bar/s; (B) 80–20 vol.% N_2-CO_2 , $T_F = 79^{\circ}C$, $P_{sat} = 180$ bar and PDR = 700 bar/s; (C) 100–0 vol.% N_2-CO_2 , $T_F = 100^{\circ}C$, $P_{sat} = 180$ bar and PDR = 700 bar/s

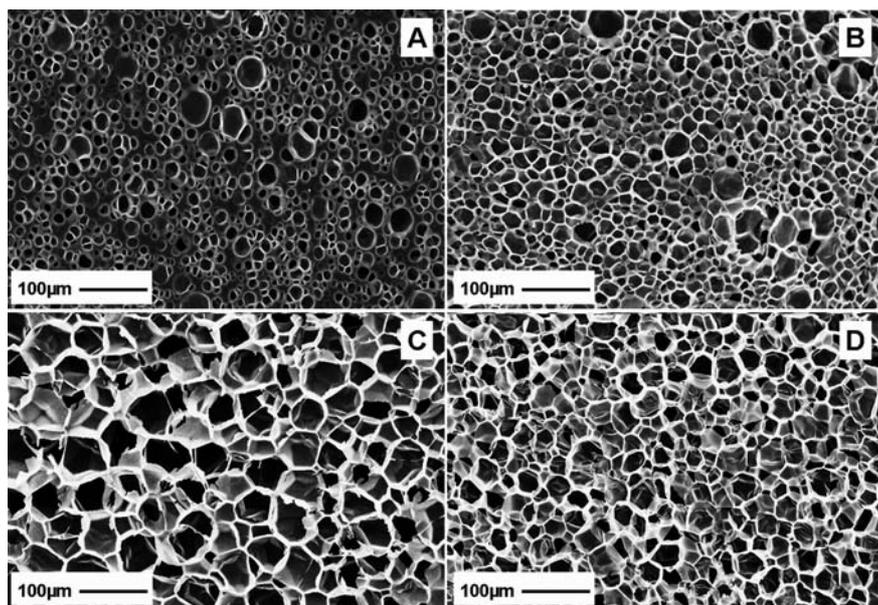


Fig. 5. SEM micrographs of TZ foamed with N_2-CO_2 80–20 vol.% at $P_{sat} = 180$ bar, $PDR = 700$ bar/s and $T_F = 44^\circ C$ (A), $70^\circ C$ (B), $76^\circ C$ (C) and $87^\circ C$ (D)

by CO_2 is more pronounced with respect to N_2 , resulting in lower foaming temperatures, as also observed also for other biodegradable polymers (Di Maio et al., 2005). Finally, Fig. 4C shows the cell microstructure obtained by using pure N_2 (#12), at a higher temperature ($100^\circ C$). The use of pure N_2 resulted in TZ foams characterized by a homogeneous porosity and D_C of $48\ \mu m$. As a general comment on the effect of blowing agent compositions on TZ foaming, there is evidence that the mixture 80 to 20 N_2-CO_2 vol% can be considered the best blowing agent. The reasons are related to the possibility of processing the material at higher temperatures compared with pure carbon dioxide and the use of higher pressures and higher pressure drop rates that favor the formation of a higher number of cells, thus leading to a structures characterized by cells of smaller size.

Fig. 5 reports the SEM micrographs of the TZ foams prepared with 80 to 20 N_2-CO_2 vol.% blowing gas mixture at

$P_{sat} = 180$ bar, $PDR = 700$ bar/s and different T_F from 44 to $100^\circ C$ (#5 to #11). Due to the wide foaming temperature range, it is possible to obtain foams with different morphologies and densities. At lower temperatures (Fig. 5A), the TZ foam is characterized by small cells separated by thick walls, with density of $0.65\ g/cm^3$. By increasing the T_F , the matrix stiffness decreased and density decreases accordingly, (Fig. 5B and Fig. 5C) down to $0.1\ g/cm^3$. At higher temperatures, Fig. 5D, TZ foams showed a slight decreases in pores dimension. The effect of T_F on cell size is shown in Fig. 6, where is seen that at T_F of $44^\circ C$ the D_C is $14\ \mu m$ and it increases with temperature up to a maximum value of $55\ \mu m$ attained at T_F of $76^\circ C$. By further increasing the T_F ($86^\circ C$ to $100^\circ C$) a “shrinking phenomenon” was observed, with an apparent reduction of D_C to $15\ \mu m$ (Fig. 6, #11). It is believed that the size of the cells decreased with increasing T_F because of excesses gas diffusion through the cell walls. The same behavior was observed when using a mixture 50 to 50 N_2-CO_2 vol.% but at lower temperatures ($T_F = 70^\circ C$, #4, SEM not reported) due to

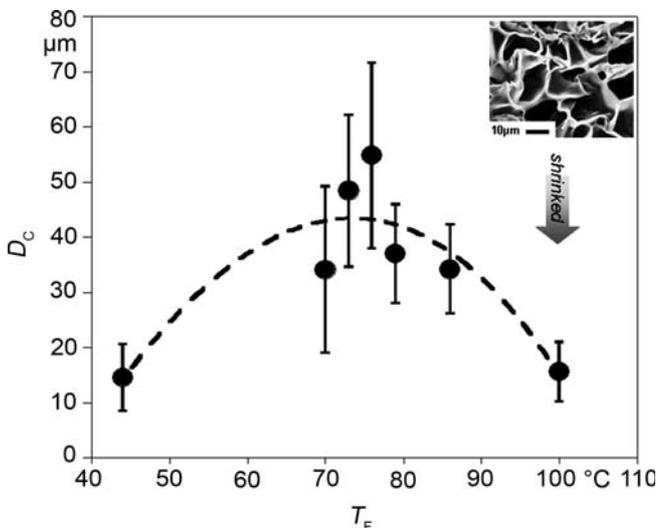


Fig. 6. Effect of T_F on D_C for TZ foamed with N_2-CO_2 80–20 vol.% at $P_{sat} = 180$ bar and $PDR = 700$ bar/s

Test number	N_2-CO_2 vol.%	P_{sat} bar	T_F °C	PDR bar/s
13	0–100	60	50	250
14	0–100	60	60	250
15	0–100	60	70	250
16	50–50	150	100	250
17	80–20	180	44	700
18	80–20	180	70	700
19	80–20	180	80	700
20	80–20	180	87	700
21	80–20	180	100	700
22	80–20	180	120	700
23	80–20	180	140	700
24	80–20	180	100	250

Table 4. Experimental conditions used for the preparation of TG foams

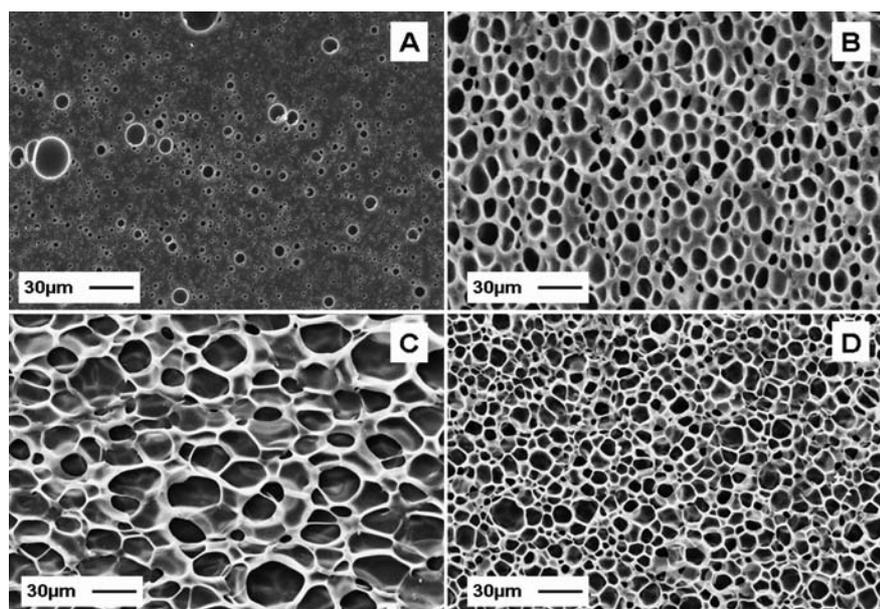


Fig. 7. SEM micrographs of TG foamed with N_2 - CO_2 80-20 vol.% at $P_{sat} = 180$ bar, $PDR = 700$ bar/s and $T_F = 44$ °C (A), 80 °C (B), 120 °C (C) and 140 °C (D)

the higher content of carbon dioxide in the gas blowing mixture. In more detail, with the increase of CO_2 content the processing temperatures shift downward, because of the enhanced plasticizing effect. In summary, the optimal foaming condi-

tions for zein thermoplasticized with 25 wt.% PEG 400 are: 80 to 20 N_2 - CO_2 vol.% blowing agent at $T_F = 70$ to 80 °C, $P_{sat} = 150$ to 200 bar, which resulted in foams characterized by pores with $D_C = 20$ to 50 μm and densities equal to 0.1 g/cm³.

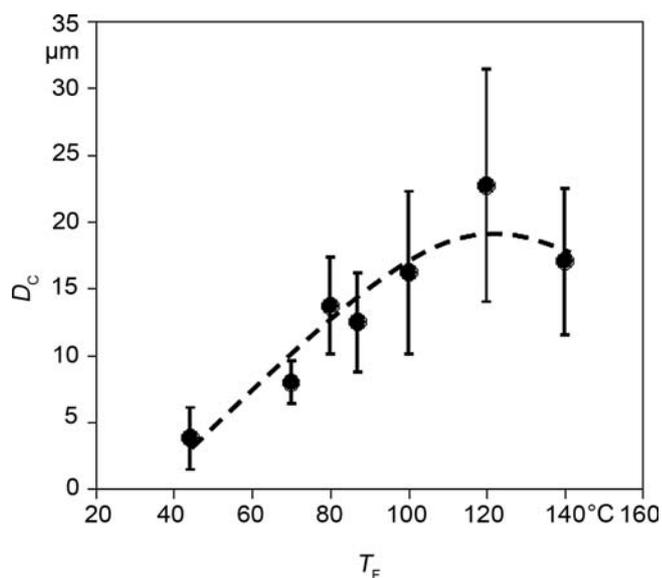


Fig. 8. Effect of T_F on D_C for TG foamed with N_2 - CO_2 80-20 vol.% at $P_{sat} = 180$ bar and $PDR = 700$ bar/s

3.4.2 Thermoplastic Gelatin

Table 4 reports the testing conditions used for TG foaming. The effect of T_F on the microstructures of TG foams (#17 to #23) is shown in Fig. 7. The reduction of the matrix stiffness associated to the increase of T_F resulted in foams with lower densities. In particular, as shown in Fig. 7A, at $T_F = 44$ °C (#17), foaming is limited and only tiny pores can be observed. By increasing the T_F to 80 °C and higher, uniform distributions of pores characterized by increased cell dimension could be observed (Fig. 7B and C), with foam densities in the range 0.7 g/cm³ to 0.55 g/cm³, respectively. When the TG was foamed at higher temperatures (e. g. $T_F = 140$ °C in Fig. 7D) degradation (browning) was evident (in fact, TGA results showed initial loss of plasticizer and/or protein degradation at $T_{ons} = 221$ °C under inert atmosphere). The variation of D_C with T_F is shown in Fig. 8. D_C increased from 3 μm at $T_F = 44$ °C to 16 μm at $T_F = 100$ °C and reached the maximum value at $T_F = 120$ °C (25 μm).

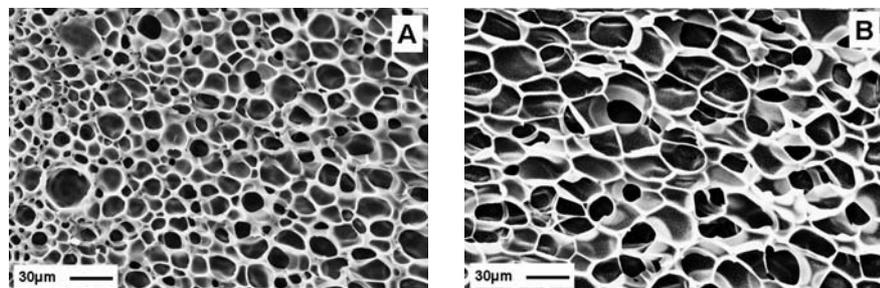


Fig. 9. SEM micrographs of TG foamed with: N_2 - CO_2 80-20 vol.% at $P_{sat} = 180$ bar, $T_F = 100$ °C and $PDR = 700$ bar/s (A); 50-50 N_2 - CO_2 vol.% at $P_{sat} = 120$ bar, $T_F = 100$ °C and $PDR = 250$ bar/s (B)

With the aim of modulating the morphology of TG foams, the effect of the blowing mixture composition and PDR was investigated on samples prepared at $T_F = 100\text{ }^\circ\text{C}$ (Fig. 9). A significant increase of the average cell size from $16\text{ }\mu\text{m}$ (Fig. 9A, #24) to $55\text{ }\mu\text{m}$ (Fig. 9B, #16) was obtained by raising the carbon dioxide concentration from 20% to 50% in the gas mixture while no remarkable effects were observed when decreasing PDR from 700 to 250 bar/s.

4 Conclusions

Natural polymers have much more complex molecular structures and lower thermal stability than common petrochemical based polymers and, for these reasons, they are mainly processed by using solvent based technologies. However, the preparation of thermoplastic bio-based materials by employing adequate plasticizers and mixing conditions allows the development of materials that can be processed by conventional thermoplastic technologies. Throughout this work it has been shown that selected zein/plasticizer and gelatin/plasticizer mixtures were suitable to be processed via gas foaming like common synthetic polymers, resulting in foams with fine morphologies and low densities. In particular, morphologies of foams prepared from thermoplastic zein and gelatin, utilized in this work, were mainly dependent on blowing agent composition and foaming temperature. The cellular morphology was finely modulated by controlling these basic foaming parameters and foams with density as low as 0.1 g/cm^3 and mean cell diameter of $10\text{ }\mu\text{m}$ were obtained.

References

- Azranitoyannis, I. S., et al., "Chitosan and Gelatin Based Edible Films: State Diagrams, Mechanical and permeation properties", *Carb. Polym.*, **37**, 371–382 (1998)
- Batterman-Azcona, S. J., et al., "Effect of Specific Mechanical Energy on Protein Bodies and α -Zeins in Corn Flour Extrudates", *Cereal. Chem.*, **76**, 316–320 (1999)
- Beck, M. I., et al., "Physico-Chemical Characterization of Zein as a Film Coating Polymer. A Direct Comparison with Ethyl Cellulose", *Int. J. Pharm.*, **141**, 137–150 (1996)
- Bigi, A., et al., "Relationship between Triple-Helix Content and Mechanical properties of Gelatin Films", *Biomat.*, **25**, 5675–5680 (2004)
- Brouillet-Fourmann, S., et al., "Evolution of Interactions between Water and Native Corn starch as a Function of Moisture Content", *J. Appl. Polym. Sci.*, **86**, 2860–2865 (2002)
- Cuq, B., et al., "Thermoplastic Properties of Fish Myofibrillar Proteins: Application to Biopackaging Fabrication", *Polymer*, **38**, 4071–4078 (1997)
- Cuq, B., et al., "Proteins as Agricultural Biopolymers for Packaging Production", *Cereal. Chem.*, **75**, 1–9 (1998)
- de Cindio, B., et al., "Filled Snack Production by Coextrusion-Cooking: 1. Rheological Modelling of the Process", *J. Food Eng.*, **52**, 67–74 (2002a)
- de Cindio, B., et al., "Filled Snack Production by Coextrusion-Cooking: 2. Effect of Processing on Cereal Mixtures", *J. Food Eng.*, **54**, 63–73 (2002b)
- de Graaf, L. A., "Denaturation of Proteins from a Non-Food Perspective", *J. Biotechnol.*, **79**, 299–306 (2000)
- Di Maio, E., et al., "Structure Optimization of Polycaprolactone Foams by Using Mixtures of CO_2 and N_2 as Blowing agent", *Polym. Eng. Sci.*, **45**, 432–441 (2005)

- Donhowe, I. G., Fennema, O., "The Effects of Plasticizers on Crystallinity, Permeability, and Mechanical properties of Methylcellulose Films", *J. Food Process. Preserv.*, **17**, 247–257 (1993)
- Glenn, G. M., et al., "Effect of Starch, Fiber and CaCO_3 on the Properties of Foams Made by a Baking Process", *Ind. Crops Prod.*, **14**, 201–212 (2001)
- Goof, H. D., et al., "A Study of Fat and Air Structures in Ice Cream", *Int. Dairy J.*, **9**, 817–829 (1999)
- Ha, T. T., Padua, G. W., "Effect of Extrusion Processing on Properties of Zein-Fatty Acids Sheets", *Trans. ASAE*, **44**, 1223–1228 (2001)
- Hagolle, N., et al., "Study of the Stability of Egg White Protein-based Foams: Effect of Heating Protein Solution", *J. Sci. Food Agric.*, **80**, 1245–1252 (2000)
- Han, X., et al., "Extrusion of Polystyrene Nanocomposite Foams with Supercritical CO_2 ", *Polym. Eng. Sci.*, **43**, 1261–1275 (2003)
- Hwang, Y. D., Cha, S. W., "The Relationship between Gas Absorption and the Glass Transition Temperature in a Batch Microcellular Foaming Process", *Polym. Test.*, **21**, 269–275 (2002)
- Jongjareonrak, A., et al., "Effect of Plasticizers on the Properties of Edible Films from Skin Gelatine of Bigeye Snapper and Brown-stripe Red Snapper", *Eur. Food Res. Technol.*, **222**, 229–235 (2006)
- Kumar, V., Suh, N. P., "A Process for Making Microcellular Thermoplastic Parts", *Polym. Eng. Sci.*, **30**, 1323–1329 (1990)
- Lai, H.-M., et al., "Properties and Microstructure of Zein Sheets Plasticized with Palmitic and Stearic Acids", *Cereal. Chem.*, **74**, 83–90 (1997)
- Lai, H.-M., Padua, G. W., "Water Vapour Barrier of Zein Films Plasticized with Oleic Acid", *Cereal. Chem.*, **75**, 194–199 (1998)
- Lawton, J. W., "Zein: A History of Processing and Use", *Cereal. Chem.*, **79**, 1–18 (2002)
- Magoshi, J., et al., "Structure and Physical Properties of Seed Proteins, Glass Transition and Crystallization of Zein Protein from Corn", *J. Appl. Polym. Sci.*, **45**, 2043–2048 (1992)
- Marrazzo, C., et al., "Process-structure Relationships in PCL Foaming", accepted on *J. Cell. Plast.* (2007)
- Masco-Arriola M. L., "Preparation and Physical Properties of Zein Based Films", MS. Thesis University of Illinois, Urbana-Champaign, IL (1996)
- Momany, F. A., et al., "Structural Characterization of α -Zein", *J. Agri. Food Chem.*, **54**, 543–547 (2006)
- Padua, G. W. et al., "Chapter 2 Formation and Properties of Corn Zein Films and Coatings", in *Protein-Based Films and Coatings*, Gennadios, A. (Ed.), CRC Press LLC, Boca Raton, p. 43–67 (2002)
- Park, C. B., et al., "Effect of the Pressure Drop Rate on Cell Nucleation in continuous Processing of Microcellular Polymer", *Polym. Eng. Sci.*, **35**, 432–440 (1995)
- Pommet, M., et al., "Thermoplastic Processing of Protein-based Bioplastics: Chemical Engineering aspects of Mixing, Extrusion and Hot Molding", *Macrom. Symp.*, **197**, 207–218 (2003)
- Redl, A., et al., "Extrusion of Wheat Gluten Plasticized with Glycerol: Influence of Process Conditions on Flow Behavior, rheological properties, and Molecular Size Distribution", *Cereal. Chem.*, **76**, 361–370 (1999a)
- Redl, A., et al., "Rheological Properties of Gluten Plasticized with Glycerol: Dependence on Temperature, Glycerol Content and Mixing Conditions", *Rheol. Acta*, **38**, 311–320 (1999b)
- Selling, G. W., et al., "Effect of Water and Tri(ethylene)glycol on the Rheological Properties of Zein", *Polymer*, **45**, 4249–4255 (2004)
- Shogren, R. L., et al., "Baked Starch Foams: Starch Modifications and Additives Improve Process Parameters, Structure and Properties", *Ind. Crops Prod.*, **16**, 69–79 (2002)
- Shukla, R., Cheryan, M., "Zein: The Industrial Protein from Corn", *Ind. Crops Prod.*, **13**, 171–192 (2001)
- Sothornvit, R., Krochta, J. M., "Plasticizer Effect on Mechanical Properties of β -Lactoglobulin Films". *J. Food Eng.*, **50**, 149–155 (2001)
- Thiéband, M., Dumay, E., Cheftel, C. C., "Influence of Process Variables on the Characteristics of a High Moisture Fish Soy Protein Mix Texturized by Extrusion Cooking", *Lebensm.-Wiss. u.-Technol.*, **29**, 526–535 (1996)

- Tillekeratne, M., Easteal, A. J., "Modification of Zein Films by Incorporation of Poly(ethylene glycol)s", *Polym. Int.*, **49**, 127–134 (2000)
- U.S. Patent 6 635 206 (2003) Padua, G. W., Rakotonirainy, A. M., Ha, T. T.
- van Soest, J. J. G., Borger, D. B., "Structure and Properties of Compression-Molded Thermoplastic Starch Materials from Normal and High Amylose maize Starches", *J. Appl. Polym. Sci.*, **64**, 631–644 (1997)
- Vanin, F. M., et al., "Effects of Plasticizers and Their Concentrations on Thermal and Functional Properties of Gelatin-Based Films", *Food Hydroc.*, **19**, 899–907 (2005)
- Vaz, C. M., et al., "Casein and Soybean Protein-based Thermoplastics and Composites as Alternative Biodegradable Polymers for Biomedical Applications", *J. Biomed. Mater. Res.*, **65A**, 60–70 (2003)
- Wang, Y., et al., "Effects of Processing on the Structure of Zein/Oleic Acid Films Investigated by X-Ray Diffraction", *Macr. Biosci.*, **5**, 1200–1208 (2005)
- Wang, Y., Rakotonirainy, A. M., Padua, G. W., "Thermal Behavior of Zein-based Biodegradable Films", *Starch*, **55**, 25–29 (2003)
- Wiedmann, W., Strobel, E., "Compounding of Thermoplastic Starch with Twin-Screw Extruders", *Starch*, **43**, 138–145 (1991)
- Willet, J. L., Shogren, R. L., "Processing and Properties of Extruded Starch/Polymer Foams", *Polymer*, **43**, 5935–5947 (2002)
- Yu, J., Gao, J., "Biodegradable Thermoplastic Starch", *J. Appl. Polym. Sci.*, **62**, 1491–1494 (1996)
- Zheng, J. P., et al., "Gelatin/Montmorillonite Hybrid Nanocomposite. I. Preparation and properties", *J. Appl. Polym. Sci.*, **86**, 1189–1194 (2002)

Acknowledgements

Authors wish to thank Mr. Mauro Politano for experimental support on thermoplasticization of gelatin. The work on thermoplastic gelatin was financed by CRdC "New Technologies", (Regione Campania) while the work on thermoplastic zein by the EU project Enviropak (INCO-DEV ICA4-CT-2001-10062).

Date received: May 2, 2007

Date accepted: July 25, 2007

Bibliography
 DOI 10.3139/217.2065
 Intern. Polymer Processing
 XXII (2007) 5; page 480–488
 © Carl Hanser Verlag GmbH & Co. KG
 ISSN 0930-777X

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