

Study of Wheat-Flour-Based Agropolymers: Influence of Plasticizers on Structure and Aging Behavior

R. Saiah,¹ P. A. Sreekumar,^{1,2} N. Leblanc,^{1,3} M. Castandet,³ and J.-M. Saiter^{1,4}

ABSTRACT

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Wheat-flour-based agropolymers are prepared using an extrusion method. The morphology of the native and extruded wheat flours are analyzed by scanning electron microscopy (SEM). During plasticization using water (9%, w/w) and glycerol (12.8%, w/w), a change in morphology of native wheat flour occurs. The structure of these materials was investigated by X-ray diffraction (XRD) with special reference to the amount of plasticizers used, such as water and glycerol molecules. The introduction of these plasticizers decreases the crystallinity rate and also

increases the average distance between chains in the remaining vitreous phase of the extruded wheat flour. Replacing water molecules with glycerol reduces the crystalline phase and diminishes the average size of crystalline structures. The plasticization effects were confirmed by mechanical investigations. Indeed, increasing the amount of glycerol from 12.8 to 20% decreases the stress at failure and the tensile modulus, while the strain at failure increases. Finally, aging studies show that the percentage of crystallinity increases with time.

During the last few decades, nonbiodegradable petroleum-based polymeric materials have produced some environmental concerns. The use of nonrenewable materials has increased our dependence on crude oil and also created plastic waste, causing environmental pollution that affects the human population as well as wildlife. Biodegradable polymeric materials, especially those prepared from readily available, renewable and inexpensive natural resources such as carbohydrates, starches, oils, lignocellulosic materials, and proteins have thus become increasingly important. The use of natural materials in composites is rising. Initially, these materials were chosen for environmental benefits but later it was found that these materials offer both processing and structural benefits. Investigation of the use of cereal extracts is very important. Cereal extracts are mixtures of starches, natural proteins, and other components. Wheat grain is one of the world's most obtainable crops and it is principally used as flour. Wheat flour is composed of starches and proteins (Ma et al 2005; Tang et al 2005). The other main sources of commercial starch are maize, potatoes, cassava, and waxy maize. As starch is obtainable from many sources (Petersen et al 1999; Copinet et al 2001), it has the advantages of being renewable and available in great quantities and it is cheap and highly biodegradable (Carvalho et al 2003). However, the cost of extracting starch is significant, limiting its profitability. Thus there is an interest in developing materials based on wheat flour starch. Each wheat starch granule consists of $\approx 25\%$ amylose and $\approx 75\%$ amylopectin (Miyazaki et al 2004). Native starch is a semicrystalline material with a crystallinity index of 15–45%, depending on the source (Zobel 1988). These starch granules exhibit the different types of crystalline structures under X-ray diffraction (XRD): A-type for cereal starches; B-type for tuber and amylose-rich starches (Katz and Van Italie 1930; Colonna et al 1982; Zobel 1988); C-type combines both A- and B-types (Sarko and Wu 1978; Wu and Sarko 1978; Gernat et al 1990, 1993; Biliaderis 1992). These crystalline structures characterize most legume starches (Colonna et al 1981), fruit starches (Jane et al 1999; Stevenson et al 2006), and cereals grown under specific temperature and hydration conditions (Buleon

et al 1998). Cereals can also have a V-type structure (Hinkle and Zobel 1968; Yamashita and Monobe 1971; Winter and Sarko 1974). This structure is obtained when amylose crystals are prepared by adding complexing agents to an amylose solution.

The main plasticizers used to prepare starch-based thermoplastic materials are water (Rindlav-Westling et al 1998; Follain et al 2006), glycerol (Poutanen and Forssell 1996; Rindlav-Westling et al 1998; Stepto et al 2003; Follain et al 2006), ethylene glycol (Poutanen and Forssell 1996; Smits et al 2003a), urea (Shogren et al 1992), and sugars (Poutanen and Forssell 1996; Rindlav-Westling et al 1998). Water is an excellent plasticizer but it has some disadvantages because it is very difficult to control the amount used during heat transformation. On the other hand, the hydrophilic nature of the material makes the water molecules dependent on the surrounding atmosphere such as outside humidity (Bangyekan et al 2006). The proportion of plasticizer and its chemical nature strongly influences the physical properties of processed starch, thereby affecting the final properties of the materials (Da Roz et al 2006).

The objective of this work was to produce new, fully biodegradable materials that exhibit physical characteristics comparable to standard thermoplastic materials. In other words, we are trying to produce ecofriendly new plastics from raw materials such as wheat flour. The effects of aging and the role played by plasticizers on the structure of wheat-flour-based extruded new materials was investigated.

MATERIALS AND METHODS

The wheat flour was provided by Grands Moulins de Paris (France). After a dry division of cereal, the flour was separated into two categories, one rich in protein that is used by the food industry and a second one with low protein content ($<12\%$, w/w) and 85% , w/w, starch. This second flour, which was used in this work, is often considered a by-product of wheat flour production. Additives used were glycerol (12.8%), water (9%), sorbitol (7.2%), silicon dioxide (1%), and magnesium stearate (1.8%) that were of laboratory quality. The different proportions for each constituent were chosen in agreement with previous work (Leblanc and Dubois 2001) to get film with reproducible characteristics through extrusion.

Sample Preparation

The wheat flour (68.2%) and the additives, except water and glycerol, were placed into a thermo-regulated turbo mixer (Kaiser, Germany) and mixed with a rotating speed of 750 rpm over 3 min. A mixture of water and glycerol (21.8%) was introduced slowly

¹ Laboratoire Polymères, Biopolymères et Membranes, Unité CNRS 6522, équipe LECAP, Institut des Matériaux Rouen, Université de Rouen, Faculté des Sciences, Avenue de L'université BP 12, 76801 Saint Etienne du Rouvray, France.

² National Institute of Technology Calicut, NITC P O, Calicut, Kerala-673601, India.

³ Laboratoire de Génie des Matériaux de (LGMA), Esitpa rue grande, BP 607, 27106 Val de Reuil Cedex, France.

⁴ Corresponding author. Phone: 33 (0)2 32955085. Fax: 33 (0)2 32955082. E-mail: jean-marc.saiter@univ-rouen.fr

through a valve fixed on the lid to a single-screw extruder (Scamex, S0262, France) that exhibits two heating zones. The extrusion conditions were heating up to 120°C (same temperature for each heating zone) and a screw rotating speed of 40 rpm. The glycerol and water allows the rupture of starch granules and plasticizes the materials. Silicium dioxide allows good dispersion of plasticizers in the formulation and facilitates passage of the formulation in the extruder. Magnesium stearate is used as a lubricant and sorbitol is the solid plasticizer. This method produces pellets. After that, stress relaxation and stabilization were performed by maintaining the pellets at room temperature for several hours. A second extrusion using the same temperature and screw speed was performed to get the final film, which was immediately put into desiccators and kept in controlled atmospheric conditions (75% relative humidity and room temperature). The additive chosen has been patented (Leblanc and Dubois 2001). This choice produces film of good quality. The wheat-flour-based material was used to prepare the samples and to analyze their characteristics. The thickness of extruded film was $\approx 400 \mu\text{m}$ and the width was $\approx 100 \text{mm}$.

Characterization Methods

Scanning electron microscopy (SEM) was performed (LEO 1530 FEG). Each sample was cryogenically fractured in liquid nitrogen and then coated with gold palladium. The thickness of the coating was $< 4 \text{nm}$. The principle of this technique was based on the use of a tungsten point covered with zirconium oxide heated to 1,850°C and subjected to a strong electric field, emitting electrons that are concentrated and accelerated on the sample.

The structures of the samples were tested with X-ray diffraction experiments using a Rigaku miniflex wide-angle X-ray diffractometer. The X-ray diffraction patterns were performed with the Cu K α radiations ($\lambda = 1.54 \text{Å}$) scanning 2θ angles from 5° to 35° with a step of 0.02° and a counting time of 5 sec.

Tensile tests of the films were conducted on a universal testing machine (Instron 4301). The tests were performed using a load cell of 1 kN (cell reference: 2518-806 Instron) at a crosshead speed of 2 mm/min. The samples were taken from the center of the film in the extrusion direction. The sample geometry is 100 × 10 × 0.4 mm. Determination of tensile modulus (E) is a tangent at the origin of the stress-stain curve. For each sample, the values of the mechanical characteristics were the arithmetic mean of at least five different specimens.

RESULTS AND DISCUSSION

Morphology of Native and Plasticized Wheat Flour

SEM showed the different structures for native and thermoplastic wheat flour. The native wheat flour has a granular structure. These granules are spherical or oval and have different domain sizes. The surfaces of these granules are rough due to the existence

of protein, lipid, and pentosan molecules that were not eliminated during the flour-milling extraction. For wheat flour there is a wide distribution of granular size, which is a common feature of cereal starches (Buleon et al 1998; Charles et al 2003). During plasticization (the transformation of granular morphology into a homogeneous polymeric film), the destruction of hydrogen bonds between the starch molecules occurs synchronously with the formation of the hydrogen bonds between the plasticizer and starch molecules (Yang et al 2006). The extrusion method is a combination of thermal and mechanical input.

During this process, wheat flour was plasticized and a homogeneous molten phase characteristic of thermoplastic polymeric material was obtained.

Structure of Native and Plasticized Wheat Flour

The molecular organization of the wheat granules was investigated by XRD. This powerful tool reveals the existence and quantity of crystalline and amorphous phases. The X-ray diffraction patterns for native and plasticized wheat flour (with 9% water and 12.8% glycerol) are displayed in Fig. 1A and B, respectively. The signal obtained for native wheat flour presents diffraction rays superimposed on a diffusion halo, proving the semicrystalline nature of this material. The diffraction peaks obtained for 2θ values are equal to 11.3, 15.2, 17.3, 18.1, 20.1, 23.3, and 26.7°, leading to the conclusion that these raw materials present A-type crystalline structure. This general characteristic of cereal starches was already observed in many other works (Katz and Van Italie 1930; Le Bail et al 1993; Krogars et al 2003). This double helix structure is organized in a monoclinic unit cell ($a = 2.124 \text{nm}$, $b = 1.172 \text{nm}$, $c = 1.069 \text{nm}$, $\gamma = 123.5^\circ$, space group B2) where eight water molecules are located between the double helices (Katz and Van Italie 1930; Imberty et al 1988, 1991). Different peaks can be observed for the extruded material. Extrusion seems to change the initial crystalline structure of native wheat flour. After extrusion, the diffraction peaks appear at $2\theta = 7.2^\circ$, 12.9° , 19.8° , and 22.6° (Fig. 1B); they are characteristics of a V_h-type structure (Le Bail 1995; Fanta et al 2002). This structure was obtained by complexation of amylose with lipids. The models suggest that the chain conformation consists of six left-handed residues per turn helix with a rise per monomer between 0.132 and 0.136 nm. This structure is characterized by an orthorhombic unit cell ($a = 1.37 \text{nm}$, $b = 2.37 \text{nm}$, $c = 0.805 \text{nm}$) with the space group P2₁2₁2₁ and 16 water molecules within the unit cell (Winter and Sarko 1974). However, another peak at $2\theta = 17.3^\circ$ was observed. This peak corresponded to an A-type structure. As a consequence, we find two types of crystalline plasticized structures for wheat flour material: V_h and A-type. In the plasticized material, the A-type residual crystallinity is due to incomplete deconstruction and fusion during the transformation (Van Soest et al 1996; Willett and Doane 2002).

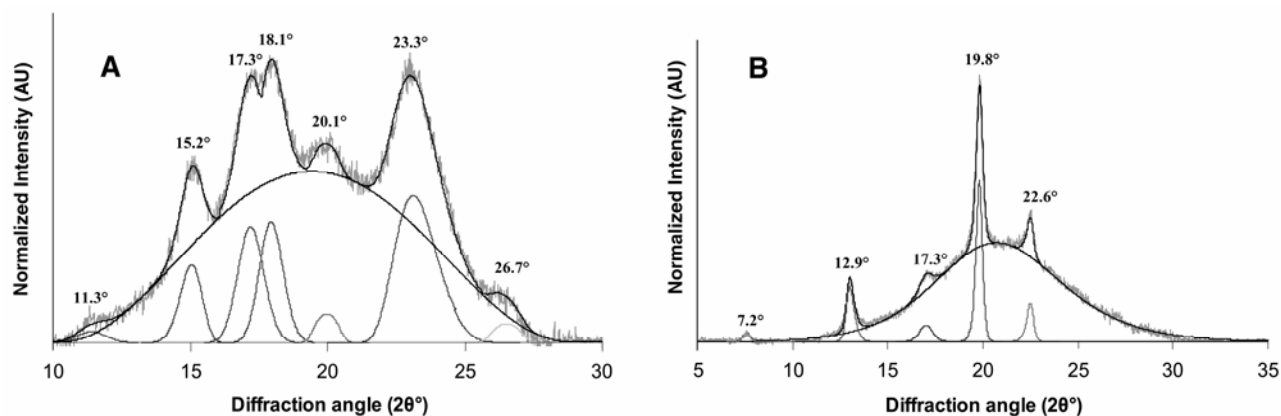


Fig. 1. X-ray diffraction (XRD) pattern of native (A) and extruded (B) wheat flour showing different contributions to rebuilding experimental signal.

A quantitative evaluation of each constitutive phase was obtained by fitting the X-ray signal. This fitting procedure can be performed by first subtracting the diffusion halo, then using a Gaussian law for each diffraction peak, and then superimposing all the curves to get the experimental data. The degree of crystallinity is calculated using equation (1)

$$X_c = \frac{S_c}{S_c + S_a} \quad (1)$$

where S_c and S_a are the area of the crystalline and amorphous peaks, respectively.

For native wheat flour, the degree of crystallinity is 30%. For the thermoplastic wheat flour, the crystallinity is 14%. It follows that the extruded films have a greater amorphous or vitreous phase content. As these amorphous or vitreous domains are characterized by the lack of structural order, the existence of molecular relaxations are allowed. In other words, it is probable that the physical properties of these extruded wheat flours will be time-dependent.

Effect of Plasticizers (Glycerol and Water) on Structure

For insight on the effect of plasticizers, the amount of one plasticizer was kept constant (i.e., water initially fixed at 9%), while the percentage of glycerol was modified (initially 12.8%) to 16.5%. For the final sample, a 20% content was used to study the effect of glycerol on the structure. This composition was limited by the extrusion ability of the mixture. For all these materials, we observed that XRD patterns (Fig. 2) showed peaks for the same 2θ values. As a consequence, a V_h crystalline structure and an A-type crystalline structure were present in these two films (16.5 and 20% glycerol, respectively). An increase in the intensity of the amorphous halo was observed when glycerol content was increased (Fig. 3). In other words, the increase in percentage of glycerol decreases the percentage of crystallinity of the material from 14 to 11% (calculated by equation 1). Table I gives the characteristics of the amorphous halo (the maximum diffraction angle [θ_m]), which allows calculation of an average intermolecular distance (d_m) according to the Bragg formula

$$2d_{hkl} \sin \theta = n\lambda \quad (2)$$

where λ is the wavelength of X-rays ($\lambda_{K\alpha Cu} = 1.54\text{\AA}$) and n is a positive whole number called order of diffraction. The amorphous halo shifts toward the smaller angles when the percentage of glycerol increases, which increases the average distance (d_m) between two molecular chains. The position of the amorphous halo reflects the average density (or specific volume) of the material (Arrighi et al 1998). When the average intermolecular distance (d_m) increases from 4.28 to 4.35 \AA , the average density (or the specific volume) decreases (Fig. 4).

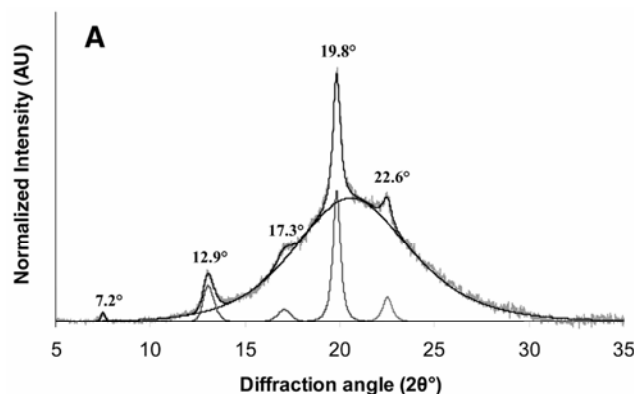


Fig. 2. X-ray diffraction (XRD) pattern of extruded wheat flour with 9% water and 16.5% glycerol (A) and 20% glycerol (B) showing different contributions to rebuilding the experimental signal.

As a consequence, it is expected that the amount of free volume linked to existence of an amorphous or a vitreous phase increases in the extruded materials.

Next we studied the relative effect of each plasticizer by varying the percentages of glycerol and water but keeping the sum of the plasticizers constant at 21.8%. The XRD patterns for these materials are shown in Fig. 5. For materials with different water contents (0, 5, and 9%), the characteristic 2θ values observed on the XRD pattern were the same. A V_h structure was observed for all compositions. But for material with no water (0%), the peak at $2\theta = 17.3^\circ$ does not appear. It is notable that when water content decreases, the intensity of all peaks decreases and peak broadening occurs as well. As water content decreases from 9 to 0%, the peak intensity at $2\theta = 17.3^\circ$ also decreases, and this peak vanishes when the water content is 0%. The lowering of crystallinity was in the order: 9% water and 12.8% glycerol (14%) > 5% water and 16.8% glycerol (11%) > 0% water and 21.8% glycerol (8%). The disappearance of the peak at $2\theta = 17.3^\circ$ in the material with 0% water and 21.8% glycerol was due to the complete granule destructure and to a crystalline phase fusion.

TABLE I
Values Characterizing Amorphous Halo Observed
by X-ray Diffraction (XRD)^a

Glycerol (% w/w)	θ_m	$\sin \theta_m$	d_m (\AA)
12.8	10.36 ± 0.02	0.1798	4.28 ± 0.008
16.5	10.30 ± 0.02	0.1788	4.31 ± 0.008
20.0	10.20 ± 0.02	0.1770	4.35 ± 0.008

^a Distance (d_m) is obtained with the Bragg formula from measurements of the maximum diffraction angle (θ_m).

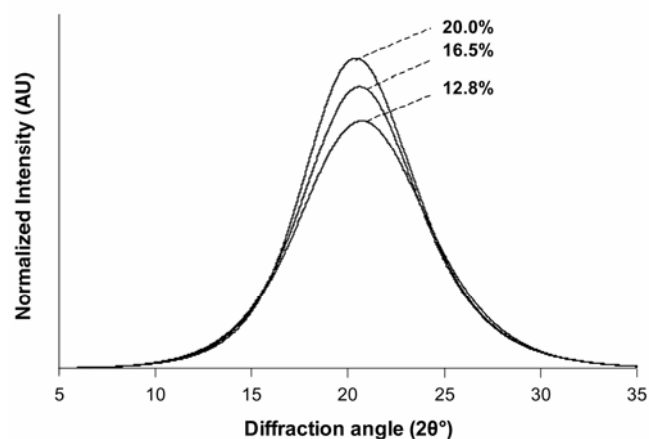
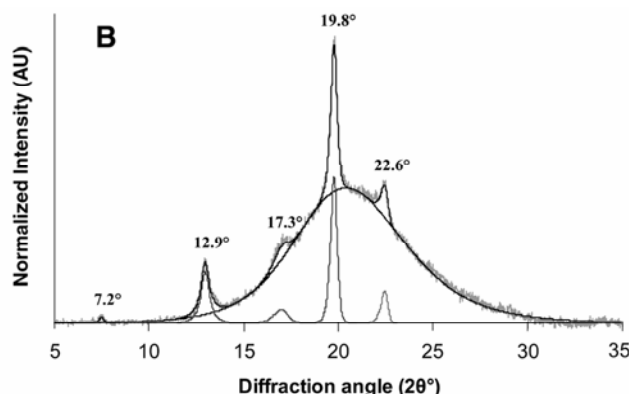


Fig. 3. X-ray diffraction (XRD) pattern showing variations in the amorphous halo when the glycerol content changes.



Both phenomena occurred during the sample preparation. This means that the glycerol contributes more to the destructure of crystals than the water molecules. The replacement of water by glycerol before extrusion led to the reduction of percentage of crystallinity and crystal size.

Effect of Plasticizers (Glycerol and Water) on Mechanical Properties

Mechanical testing measurements were performed to analyze these behaviors. Figure 6 shows the stress-strain average curves for samples with various glycerol contents (12.8, 16.5, and 20%). From these curves we determined the values of stress at failure, strain at failure, and tensile modulus. These data are regrouped in Table II. Adding glycerol decreases the stress at failure from 3.2 to 2.1 MPa and the tensile modulus from 125 to 57 MPa, while an increase from 17 to 22.9% in strain at failure is observed. These results indicate that the ductility of material increases and, as expected, a plasticization effect is obtained by introducing glycerol in the sample composition. These plasticization effects due to glycerol have been observed in materials made of starch (Mali et al 2006). In this latter system, introducing plasticizer reduces direct interaction between starch chains, thus facilitating movement of starch chains under tensile forces (Garcia et al 1999; Mali et al 2002). The same scenario occurs for wheat-flour-based materials.

Another material was prepared by replacing 9% of the water with glycerol. The average stress-strain curves for the materials (21.8% glycerol and 0% water) and (21.8% glycerol and 9% water)

are presented in Fig. 7. A small increase in the strain at failure from 17 to 19.7% was observed. On the other hand, stress at failure decreases from 3.2 to 2.4 MPa (which means a variation of 25%). The tensile modulus of material also decreases from 125 to 82 MPa (variation of 35%). This is consistent with the previous XRD data showing that incorporation of plasticizer increases the intermolecular distance between chains belonging to the vitreous phase. These results also show that a better plasticizing effect is reached when glycerol molecules are used.

Recrystallization of Starch (Retrogradation)

Aging studies were performed on a material with 9% water and 12.8% glycerol. Materials were kept at room temperature under a surrounding atmosphere with 75% relative humidity for different time periods (1 week, 1 month, 6 months, and 12 months). The XRD patterns for this material are shown in Fig. 8. It appears that

TABLE II
Values of Mechanical Characteristics of Wheat Flour Materials with Different Glycerol Content

Glycerol (%)	σ_{max} (MPa)	ϵ_{max} (%)	E (MPa)
12.8	3.2 ± 0.10	17.0 ± 1.0	125 ± 6
16.5	2.7 ± 0.20	19.4 ± 1.2	102 ± 6
20	2.1 ± 0.12	22.9 ± 0.5	57 ± 4

^a Values are average ± standard deviation (n = 5).

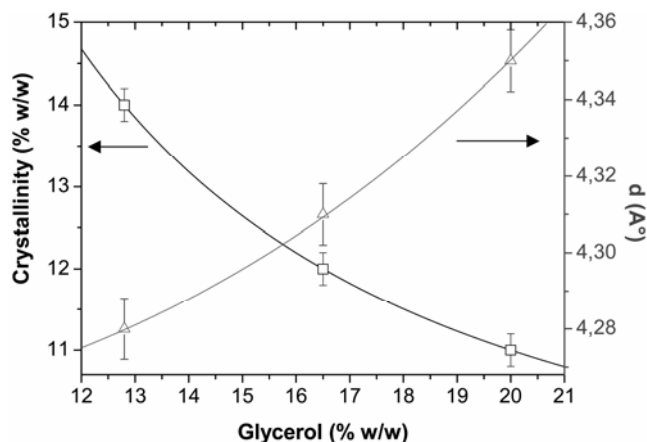


Fig. 4. Variations in crystalline fraction of samples and modification of average intermolecular distance in amorphous domains when glycerol content changes.

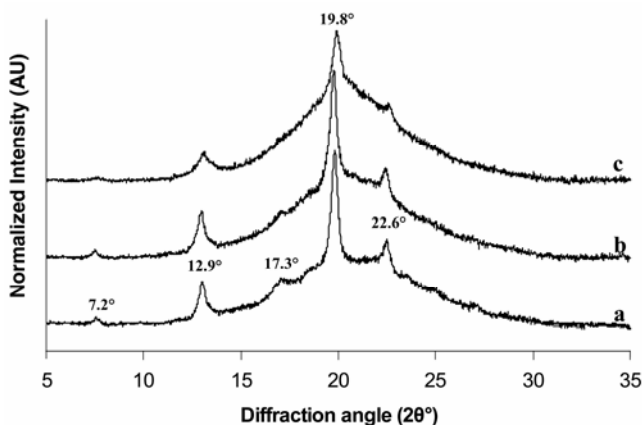


Fig. 5. X-ray diffraction (XRD) patterns obtained for extruded wheat flour with varying amounts of plasticizers: a) 12.8% glycerol and 9% water; b) 16.8% glycerol and 5% water; c) 21.8% glycerol and 0% water.

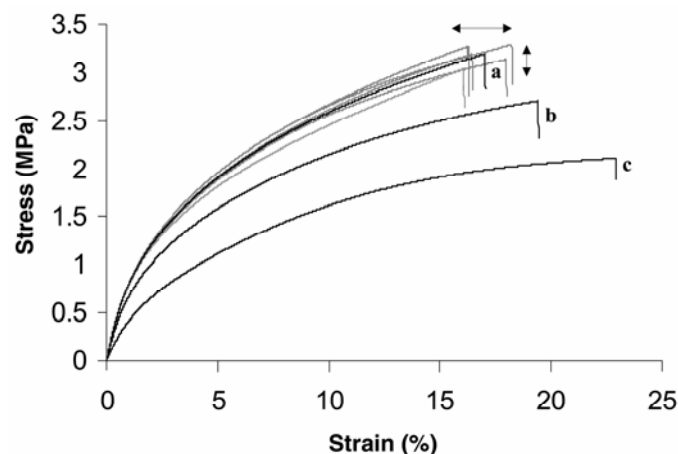


Fig. 6. Stress-strain curves calculated for wheat flour materials: a) 12.8% glycerol and 9% water; b) 16.8% glycerol and 5% water; c) 20% glycerol and 0% water. Sample (a) shows the full set of measurements where the data dispersion is relatively small.

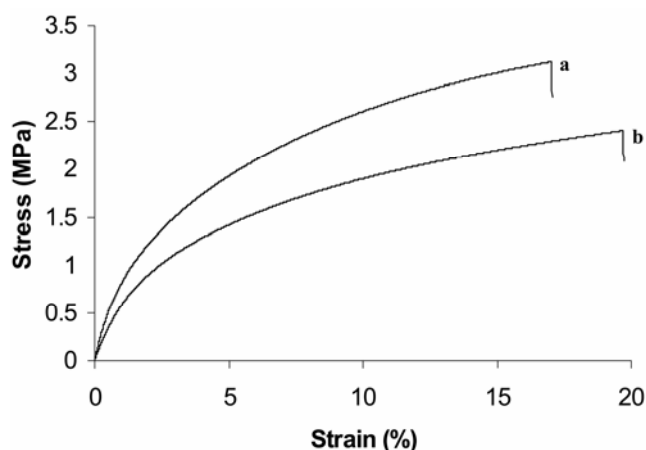


Fig. 7. Stress-strain curves calculated for wheat flour materials: a) 12.8% glycerol and 9% water; b) 21.8% glycerol and 0% water.

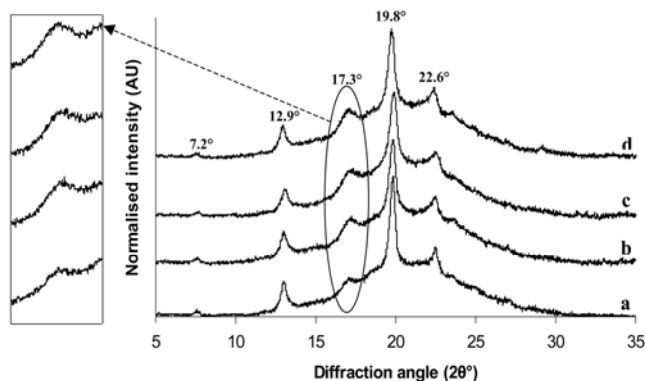


Fig. 8. X-ray diffraction (XRD) pattern of extruded wheat flour with a composition of a) 12.8% glycerol and 9% water for one week; b) one month; c) six months; and d) 12 months. Zoom of the domain $2\theta = 17.3^\circ$ shows the existence of residual A-type crystalline structure.

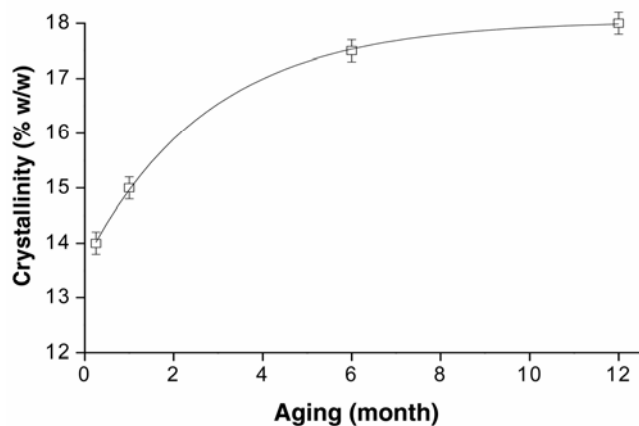


Fig. 9. Variations of crystallinity with duration of aging. Samples stored at room temperature under a controlled humidity atmosphere (75% rh).

aging for a long period (12 months) increases the intensity of the peak located at $2\theta = 17.3^\circ$. This peak corresponds to the A-type crystalline structure. Thus, after a long period of storage, the starch macromolecules of wheat flour film can be reorganized and undergo the phenomenon of retrogradation (recrystallization). During this period of storage, the V_h structure is not modified. Therefore, the percentage of crystallinity is modified during aging, increasing from 14 to 18% (Fig. 9). This retrogradation phenomenon depends on the nature of plasticizer used because smaller plasticizers favor crystallization by mobilizing the starch molecules, while larger particles prevent crystal propagation (Smits et al 2003b). It is also clear from Fig. 9 that the kinetics of crystallization observed during aging were not linear. Assuming in a first approximation, a value close to 18% crystallinity for an infinite aging duration, we find that 87.5% of possible recrystallization was done during the first six months.

CONCLUSIONS

The present study investigated the morphology of new agro-polymeric films obtained by extrusion of wheat flour. Scanning electron microscopy (SEM) shows that the films were homogeneous. X-ray diffraction (XRD) shows that the crystalline structure is very sensitive to the nature and amount of plasticizers. Indeed the XRD analysis for extruded wheat flour exhibits two types of crystallinity: V_h and A-type. The degree of crystallinity reaches 14% while the native material was at 30% crystallinity. When the percentage of glycerol was increased while keeping

percentage of water constant, the crystallinity of all materials decreased from 14 to 11%. We also observed modification in the amorphous phase. Indeed, the average intermolecular distance (d_m) increased as the glycerol content increased. When the relative percentage of glycerol and water were varied but the total content of plasticizers was kept constant, the crystallinity increased when the water content increased. The plasticizer molecules modify the mechanical behavior by decreasing stress at failure (variation of 34.4%) and tensile modulus (variation of 54.5%), while increasing strain at failure (variation of 26%) when the glycerol content varied from 12.8 to 20%. Finally, aging also leads to structural modifications by increasing the percentage of crystallinity.

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LITERATURE CITED

- Arrighi, V., Higgins, J. S., Burgess, A. N., and Floudas, G. 1998. Local dynamics of poly(dimethyl siloxane) in the presence of reinforcing filler particles. *Polymer* 39:6369-6376.
- Bangyekan, C., Aht-Ong, D., and Srikulkit, K. 2006. Preparation and properties evaluation of chitosan-coated cassava starch films. *Carbohydr. Polym.* 63:61-71.
- Biliaderis, C. G. 1992. Structure and phase transitions of starch in food systems. *Food Technol.* 6:98-109.
- Buleon, A., Colonna, P., Planchot, V., and Ball, S. 1998. Starch granules: Structure and biosynthesis. *Int. J. Biol. Macromol.* 23:85-112.
- Carvalho, A. J. F., Zambon, M. D., Curvelo, A. A. S., and Gandini, A. 2003. Size exclusion chromatography characterization of thermoplastic starch composites 1. Influence of plasticizer and fibre content. *Polym. Degrad. Stab.* 79:133-138.
- Charles, A. L., Kao, H. M., and Huang, T. C. 2003. Physical investigations of surface membrane-water relationship of intact and gelatinized wheat-starch systems. *Carbohydr. Res.* 338:2403-2408.
- Colonna, P., Buleon, A., and Mercier, C. 1981. *Pisum sativum* and *Vicia faba* carbohydrates: Structural studies of starches. *J. Food Sci.* 46:88-93.
- Colonna, P., Buleon, A., Mercier, C., and Lemaguer, M. 1982. *Pisum sativum* and *Vicia faba* carbohydrates. IV. Granular structure of wrinkled pea starch. *Carbohydr. Polym.* 2:43-59.
- Copin, A., Bliard, C., Onteniente, J. P., and Couturier, Y. 2001. Enzymatic degradation and deacetylation of native and acetylated starch-based extruded blends. *Polym. Degrad. Stab.* 71:203-212.
- Da Roz, A. L., Carvalho, A. J. F., Gandini, A., and Curvelo, A. A. S. 2006. The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydr. Polym.* 63:417-424.
- Fanta, G. F., Felker, F. C., and Shogren, R. L. 2002. Formation of crystalline aggregates in slowly-cooled starch solutions prepared by steam jet cooking. *Carbohydr. Polym.* 48:161-170.
- Follain, N., Joly, C., Dole, P., Roge, B., and Mathlouthi, M. 2006. Quaternary starch based blends: Influence of a fourth component addition to the starch/water/glycerol system. *Carbohydr. Polym.* 63:400-407.
- García, M. A., Martino, M. N., and Zaritzky, N. E. 1999. Edible starch films and coatings characterization: Scanning electron microscopy, water vapor transmission and gas permeabilities. *Scanning* 21:348-353.
- Gernat, C., Radosta, S., Damaschun, G., and Schierbaum, F. 1990. Supermolecular structure of legume starches revealed by X-ray scattering. *Starch/Stärke* 42:175-178.
- Gernat, C., Radosta, S., Anger, H., and Damaschun, G. 1993. Crystalline part of three different conformations detected in native and enzymatically degraded starches. *Starch/Stärke* 45:309-314.
- Hinkle, M. E., and Zobel, H. F. 1968. X-ray diffraction of oriented amylose fibers. III. The structure of amylose-*n*-butanol complexes. *Biopolymers* 6:1119-1128.
- Imberty, A., Chanzy, H., Pérez, S., Buléon, A., and Tran, V. 1988. The double-helical nature of the crystalline part of A-starch. *J. Mol. Biol.* 201:365-378.
- Imberty, A., Buléon, A., Tran, V., and Pérez, S. 1991. Recent advances in knowledge of starch structure (invited review). *Starch/Stärke* 43:375-384.
- Jane, J. L., Chen, Y. Y., Lee, L. F., McPherson, A. E., Wong, K. S., Rado-

- savljevic, M., and Kasemsuwan, T. 1999. Effect of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starches. *Cereal Chem.* 76:629-637.
- Katz, J. R., and Van Itallie, T. B. Z. 1930. The physical chemistry of starch and bread making. All varieties of starch have similar retrogradation spectra. *Physik. Chem.* A150:90.
- Krogars, K., Heinämäki, J., Karjalainen, M., Rantanen, J., Luukkonen, P., and Yliiruusi, J. 2003. Development and characterization of aqueous amylose-rich maize starch dispersion for film formation. *Eur. J. Pharm. Biopharm.* 56:215-221.
- Le Bail, P., Bizot, H., and Buléon, A. 1993. 'B' to 'A' type phase transition in short amylose chains. *Carbohydr. Polym.* 21:99-104.
- Le Bail, P., Bizot, H., Pontoire, B., and Buléon, A. 1995. Polymorphic transitions of amylose-ethanol crystalline complexes induced by moisture exchanges. *Starch/Starke* 47:229-232.
- Leblanc, N., and Dubois, M. 2001. Matériaux biodégradables. French patent 0115451.
- Ma, X. F., Yu, J. G., and Ma, Y. B. 2005. Urea and formamide as a mixed plasticizer for thermoplastic wheat flour. *Carbohydr. Polym.* 60:111-116.
- Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. M., and Zaritzky, N. E. 2002. Microstructural characterization of yam starch films. *Carbohydr. Polym.* 50:379-386.
- Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. M., and Zaritzky, N. E. 2006. Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources. *J. Food Eng.* 75:453-460.
- Miyazaki, M., Maeda, T., and Morita, N. 2004. Effect of various dextrin substitutions for wheat flour on dough properties and bread qualities. *Food Res. Int.* 37:59-65.
- Petersen, K., Nielsen, P. V., Bertelsen, G., Lawther, M., Olsen, M. B., Nilsson, N. H., and Mortensen, G. 1999. Potential of biobased materials for food packaging. *Trends Food Sci. Technol.* 10:52-68.
- Poutanen, K., and Forsell, P. 1996. Modification of starch properties with plasticizers. *Trends Polym. Sci.* 4:128-132.
- Rindlav-Westling, A., Stading, M., Hermansson, A. M., and Gatenholm, P. 1998. Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydr. Polym.* 36:217-224.
- Sarko, A., and Wu, H. C. H. 1978. The crystal structures of A-, B- and C-polymorphs of amylose and starch. *Starch/Starke* 30:73-78.
- Shogren, R. L., Swanson, C. L., and Thompson, A. R. 1992. Extrudates of cornstarch with urea and glycols: Structure/mechanical property relations. *Starch/Starke* 44:335-338.
- Smits, A. L. M., Kruiskamp, P. H., Van Soest, J. J. G., and Vliegthart, J. F. G. 2003a. Interaction between dry starch and plasticisers glycerol or ethylene glycol, measured by differential scanning calorimetry and solid state NMR spectroscopy. *Carbohydr. Polym.* 53:409-416.
- Smits, A. L. M., Kruiskamp, P. H., van Soest, J. J. G., and Vliegthart, J. F. G. 2003b. The influence of various small plasticisers and malto-oligosaccharides on the retrogradation of (partly) gelatinised starch. *Carbohydr. Polym.* 51:417-424.
- Stepo, R. F. T., Cail J. I., and Taylor, D. J. R. 2003. Predicting the modulus of end-linked networks from formation conditions. *Macromol. Symp.* 200:255-264.
- Stevenson, D. G., Domoto, P. A., and Jane, J. L. 2006. Structures and functional properties of apple (*Malus domestica* Borkh) fruit starch. *Carbohydr. Polym.* 63:432-441.
- Tang, H., Mitsunaga, T., and Kawamura, Y. 2005. Functionality of starch granules in milling fractions of normal wheat grain. *Carbohydr. Polym.* 59:11-17.
- Van Soest, J. J. G., Hulleman, S. H. D., De Wit, D., and Vliegthart, J. F. G. 1996. Crystallinity in starch bioplastics. *Indus. Crops Prod.* 5:11-22.
- Willett, J. L., and Doane, W. M. 2002. Effect of moisture content on tensile properties of starch/poly(hydroxyester ether) composite materials. *Polymer* 43:4413-4420.
- Winter, W. T., and Sarko, A. 1974. Crystal molecular structure of the amylose-DMSO complex. *Biopolymers* 13:1461-1482.
- Wu, H. C., and Sarko, A. 1978. The double-helical molecular structure of crystalline b-amylose. *Carbohydr. Res.* 61:7-25.
- Yamashita, Y., and Monobe, K. 1971. Single crystals of amylose V complexes. II. Crystals with 81 helical coniguration. *J. Polym. Sci.* 9:1471-1481.
- Yang, J. H., Yu, J. G., and Ma, X. F. 2006. Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). *Carbohydr. Polym.* 63:218-223.
- Zobel, H. F. 1988. Starch crystal transformations and their industrial importance. *Sarch/Starke* 40:1-7.

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