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Studies on the effect of storage time and plasticizers on the structural variations in thermoplastic starch

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ABSTRACT

Starch was combined with plasticizers such as glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blends by means of high shear extrusion process to prepare thermoplastic starch (TPS). Effect of storage time and plasticizers on the structural stability of melt processed TPS was investigated. Morphological observation, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy reveal that melt extrusion process is efficient in transforming granular starch into a plasticized starch for all plasticizer compositions. XRD analysis highlights major changes in the microstructure of plasticized starch, and dependence of crystalline type and degree of crystallinity mainly on the plasticizer composition and storage time. Dynamical mechanical analysis (DMA) yields a decrease of the peak intensity of loss factor with aging time. The effect of ageing on tensile strength also appears to be highly dependent on the plasticizer composition. Thus, through different plasticizer combinations and ageing, starch-based materials with significant differences in tensile properties can be obtained, which may be tuned to meet the requirements of a wide range of applications.

1. Introduction

In recent years, ecological awareness enormously increased within society due to the adverse effects from petroleum derived plastics as well as shrinking crude oil resources and rising prices. Much effort has recently been made to develop eco-friendly and biodegradable materials. In this context, the starch appears to be an alternative to synthetic materials because of its easy availability, low price and biodegradability.

The native starch is a semi-crystalline material mainly composed of amylose and amylopectine (98% of dried mass). Depending on the botanical origin of starch, different structure can be distinguished by X-ray diffraction namely A–C-type crystalline structures (Van Soest & Vliegenthart, 1997). The differences between the crystallinity A-type and B-type lies in the density of the envelope of the double helix and the water content related to the network. The A-type structure is described as a compact monoclinic envelope ($a = 2.124$ nm, $b = 1.172$ nm, $c = 1.069$ nm, and $\gamma = 123.5°$) containing 8 water molecules (Sarko & Wu, 197) (Imberty, Chanzy, Pérez, Bulèon, & Tran, 1988) while the B-type structure is described as a hexagonal unit cell ($a = b = 1.85$ nm and $c = 1.04$ nm) with 6 double helices and a column containing 36 molecules of water present in the centre of the hexagonal arrangement. The C-type, observed in legumes, is an intermediate structure between type A and B-type, in which the A-type surrounds B-type (Jiping et al., 2007).

Starch has poor processing ability and should be plasticized before processing and moulding (Van Soest, De Wit, & Vliegenthart, 1996). Plasticization process transforms the semi-crystalline granules into a homogeneous, rather amorphous material by the destruction of hydrogen bonds between the starch molecules, and synchronously the formation of hydrogen bonds between plasticizer and starch molecules (Pang et al., 2007). Granular disruption could be achieved in the presence of appropriate plasticizer by applying thermomechanical energy in a continuous process (Schmitt, Prashantha, Soulestin, Lacrampe, & Krawczak, 2012a; Schmitt et al., 2012b). This combination of thermal and mechanical inputs can be obtained by an extrusion process, which is a cost effective and common plastic processing technique (Yu & Christie, 2001).

The development of a plasticized starch requires the addition of high (25–30 wt.%) plasticizer content. Water remains the best natural plasticizer, but starch being very hydrophilic, its moisture content strongly depends on the storage conditions. This dependence can be partially limited by replacing part of water by a less volatile plasticizer, such as polyols (glycerol, sorbitol, xylitol, glycol ...) or sugars. The nature and the composition of the plasticizer

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system (including water) greatly affect the transformation of granular starch into a homogenous thermoplastic phase (Hulleman, Janssen, & Feil, 1998) but also the glass transition temperature (T_g) of the final material (Shi et al., 2007) and, consequently its mechanical properties and kinetics of crystallization at the temperature of service.

The amylose crystallizes in single helices called V-amylose (Buleon, Delage, Brisson, & Chanzy, 1990). Depending on the hydration or dehydration, crystalline structures are denoted as V_H ($V_{Hydrate}$) amylose for hydration and V_A ($V_{Anhydrous}$) amylose for dehydration (Winter & Sarko, 1974). The most frequently observed crystalline structure is found to be V_H-type, which is packed in an orthorhombic unit cell (Zobel, French, & Hinkle, 1967) or in a hexagonal unit cell (Brisson, Chanzy, & Winter, 1991). A second most observed crystalline structure is V_A-type which is indexed as an orthorhombic unit cell (Zobel et al., 1967). The third observed crystalline form is the B-type, which is due mainly to the crystallization of amylopectine.

During storage, water/polyols plasticized starch can undergo recrystallization phenomena, named retrogradation. The retrogradation is a practical issue because it effects the quality and self life of final products (Delville, Joly, Dole, & Bliard, 2003; Tako, Tamaki, & Konishi, 2008). For instance, it can lead to opacity and hardening of the material and eventually decreases the elongation, at break (Smits, Ruhnau, & Vliegenthart, 1998; Yu, Prashantha, Soulestin, Lacrampe, & Krawczak, 2013). The retrogradation is mainly due to internal stresses in the material caused by the difference in the rearrangement rate of starch molecules.

The rate of retrogradation depends on the plasticizer content and the glass-transition temperature. The recrystallization process involves two phenomena which do not take place at the same speed. Firstly, the rapid recrystallization of single helical structures of amylose occurs after processing. Secondly, a slower development of the crystallization of amylopectine occurs (Van Soest et al., 1997).

Urea can be used as plasticizer to limit the retrogradation (Zullo & Iannace, 2009; Ma, Yu, & Ma, 2005). In this case, amide groups of plasticizer have the ability to create hydrogen bonds with starch which are more stable than those between starch and polyols, thereby promoting the ageing resistance ability. However the use of the urea yields to poor mechanical properties (materials are rigid and brittle) (Stein & Greene, 1997). To overcome this problem, the urea is generally mixed with ethanolamine, which can increase the flexibility of the plasticized starch (Ma, Yu, & Ma, 2006).

Although many studies have been reported on the processing of starch using different plasticizers, most of them are devoted to the processing and properties of the plasticized starch but reports on the ageing-induced structural changes in the plasticized starch are very limited. Therefore, the present study aims at investigating the structural stability of melt processed thermoplastic starch based on wheat starch combined with polyols such as glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blends. As a control system, water plasticized starch will also be reported. The effect of ageing on the physical and mechanical properties of these materials will be investigated, and some new viewpoints on ageing-properties will be pointed out.

2. Experimental

2.1. Materials

Wheat starch (Roquette, France) was used in this study. It was stored at 23 °C with 50% relative humidity (RH) to limit the fluctuation of its humidity content. In these conditions, the native starch contains 12 wt.% of moisture. Glycerol (99% purity, Sigma Aldrich, France), sorbitol (ACROS organics, Belgium), and urea and ethanolamine (Fisher Scientific, Belgium) were used as plasticizers. A lubricant glycerol monostearate (Mosselman, Belgium) was also used to facilitate compounding.

2.2. Processing of thermoplastic starch

Thermoplastic starch was melt processed by mixing of starch, plasticizers composition and lubricants as follows. At first, 75 wt.% native starch, 24 wt.% plasticizer (glycerol, sorbitol, glycerol/sorbitol blend (ratio 1:1) or urea/ethanolamine blend (ratio 1:2)) with 1 wt.% glycerol monostearate (GMS) were physically blended in a mechanical mixer. As a control system, 75 wt.% native starch, 24 wt.% water with 1 wt.% GMS was also prepared. These mixtures were kept for 3 h at room temperature, then processed in a twin-screw extruder (screw diameter 16 mm, screw ratio L/D 40) (Haake Rheomex PTW 16 OS, Thermo Scientific, Germany) at a screw speed of 60 rpm. The temperature setting from the hopper to the die was 110–115–115 °C, 90–90–110 °C, 105–110–110 °C and 105–110–110 °C for the materials containing water, glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blend, respectively. In the following, the corresponding plasticized materials will be named, WS (reference) GS, SS, GSS and UES, respectively.

After pelletizing and conditioning at 23 °C and 50% RH during one week, each material was injection-moulded (Babyplast 6/10P, Cronoplast, Italy) into standard test specimen for tensile test, dynamic mechanical analysis (bars) and into discs(diameter = 50 mm) for X-ray analysis. The injection-moulding process was carried out at a flow rate of 1.3 $cm^3\ s^{-1}$ with a holding pressure of 50 bars and a holding time of 10 s, at 145 °C for SS and UES materials and at 150 °C for SS and GSS materials; the cooling time was set at 10 s for all the materials. The discs of SS material for X-ray analysis could not be manufactured because the material injection-moulding was impossible, mainly due to high viscosity of the material which lead incomplete filling of the mould. In case of water plasticized starch (WS), moulding of samples for X-ray analysis and tensile properties of WS samples was not possible due to very high brittleness of the samples. All samples were stored in controlled humidity chamber at 23 °C with a relative humidity (RH) of 53% using saturated solution of magnesium nitrate during the entire testing period.

2.3. Characterization

The moisture content of all the samples was determined using a Karl Fischer titrator (V30, Mettler-Toledo, France) coupled with an oven (Mettler Stromboli, France). The sample was placed in falcon tube inside the oven operating at 150 °C. For 30 min., the evaporated water was transported by nitrogen from the sample vessel to the reaction medium. Afterwards, the water was titrated with reactive Hydranal (Sigma Aldrich, France) and solvent Hydranal (Sigma Aldrich, France) with a theoretical titer of 1 mg H_2O/ml. The analysis was performed five times per sample.

The scanning electron microscopy (SEM) observations were performed under high vacuum with a SEM instrument (S-4300SE/N, Hitachi, Japan) operating at 5 kV, on injection-moulded cryofractured samples previously coated with a thin gold layer.

The structural change in the materials was monitored by Fourier transform infrared (FTIR) spectroscopy (Nicolet 380 FT-IR, Thermo Scientific, France). The FTIR spectra were recorded in transmission mode. The native starch was previously mixed with KBr pellets. The FTIR spectra of plasticized starches were recorded using FTIR coupled with a microscope on a 5 μm thick sample slices cut with a microtome (Leica RM2165, Switzerland). The spectra of all materials were recorded after at least 32 scans with 4 cm^{-1} resolution, in the spectral range of 4000–600 cm^{-1}. The native starch showed

several characteristic peaks: the peaks between 3600–3300 cm^{-1} was assigned to the —OH bonds; the peak around 2931 cm^{-1} was attributed to the —C—H_3 bond stretching of the anhydroglucose ring; the peak around 1647 cm^{-1} and 1300 cm^{-1} were assigned to water bonding vibration; the peaks between 1160 and 1080 cm^{-1} are characteristic of —C—O—H bonds, and the peaks between 1030 and 990 cm^{-1} were due to the —C—O bond stretching in the anhydroglucose ring.

The X-ray diffraction patterns of the materials were recorded using an X-ray diffractometer (D8 Advance, Bruker, Germany). The data collection was performed with a Co K_α cathode and a detector (Lynxeye, Brucker, Germany). The monochromator was used at a voltage of 40 kV and an intensity of 40 mA. The scattering angle (2θ) ranged from 5° to 40° at an interval of 0.02. The X-ray diffraction was used to determine the crystallinity degree and to identify the crystal structure of plasticized starches and their evolution during ageing. The crystalline signal was extracted from the X-ray pattern by subtracting the amorphous hallo. The amorphous fraction of the sample was estimated by the curve which passes through the base of each peak of the X-ray pattern, drawn using a commercial software package (Diffrac^{plus} basic assessment EVA12 Bruker, Germany) (Fig. 1). The crystallinity degree was calculated using by the following equation:

$$\text{relative crystallinity} = \frac{\text{crystalline area}}{(\text{crystalline+amorphous})\,\text{area}} \quad (1)$$

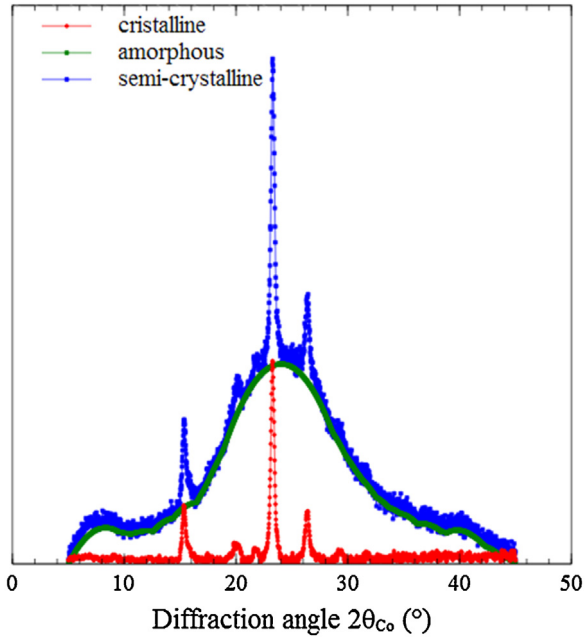

Fig. 1. X-ray diffractogram showing the method used to estimate amorphous and crystalline curves from the semi-crystalline curve.

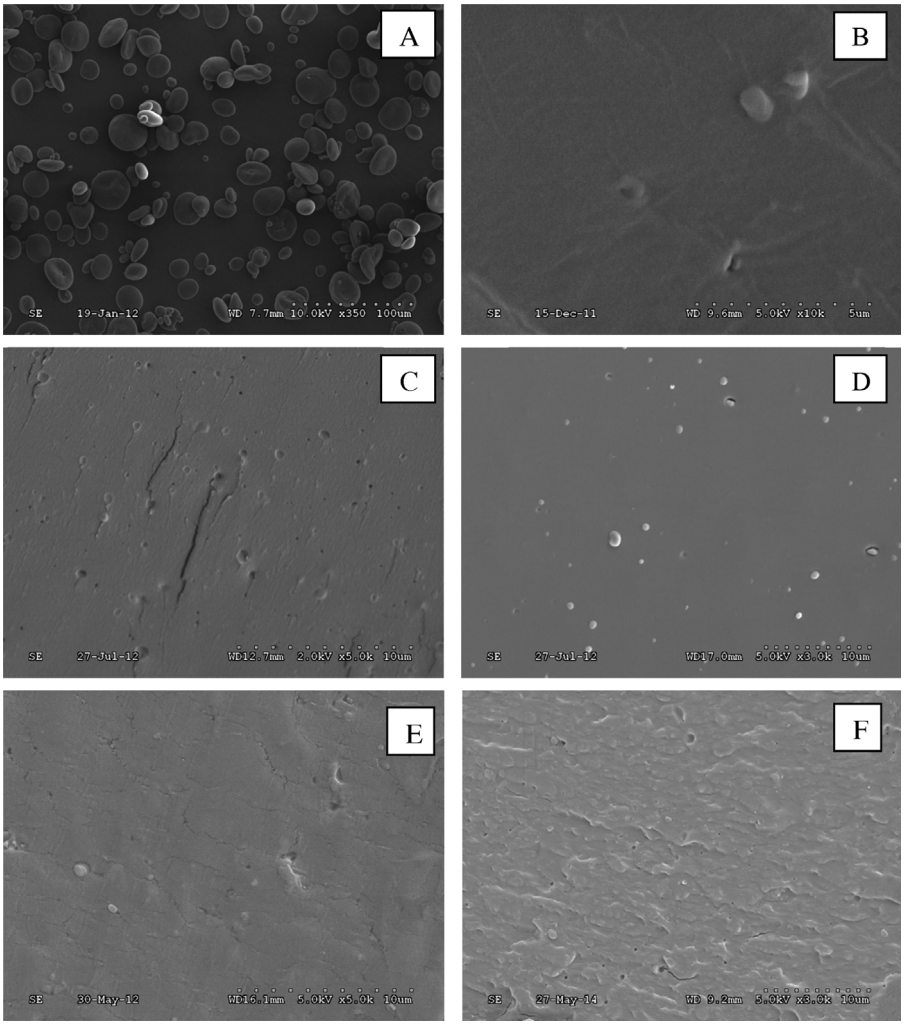

Fig. 2. SEM images of native starch (A) and differently plasticized starch GS (B), SS (C), GSS (D) UES (E) and WS (F) after 4 weeks of ageing.

Individual crystalline percentages (B-, V_A- and V_H-type) were calculated using the area of the peaks corresponding to a particular crystalline type in the crystal signal.

The viscoelastic behaviour was studied in tension by dynamic mechanical analysis (DMA + 150, MetraviB, France) at a frequency of 10 Hz. The displacement amplitude was 3.5 μm. Data were collected from −80 °C to 100 °C at a scanning rate of 2 °C min^{-1}. DMA specimens (4 mm × 10 mm × 15 mm) were cut from injection-moulded impact bar samples. At least three specimens of each composition were tested. It was not possible to track the effect of storage time in the case of SS samples, due to their brittleness (samples break during testing).

The tensile properties were evaluated from injection-moulded specimens using a tensile machine (Instron, Model 1185) equipped with a 1 kN force sensor at a crosshead speed of 10 mm min^{-1} at 23 °C and 50% HR according to the ISO 527 standard. At least five specimens of each composition were tested.

3. Results and discussion

3.1. Plasticization: Morphological and chemical characterization

Irrespective plasticizer a continuous phase of plasticized starch structure is observed (Fig. 2). No significant difference in the morphology is observed for the different plasticizer compositions. Each of them promotes the fragmentation and the dissolution of starch granules as it disrupts the intermolecular and intramolecular hydrogen bonds and plasticizes the native starch during high shear extrusion process. However, in case of WS sample (Fig. 2F), some starch granules are clearly visible, indicating an incomplete destructuration of starch granules in water plasticized starch.

The characteristic FTIR peaks of native starch and plasticized starch can be identified in the FTIR spectra (Fig. 3a).

The FTIR spectra of all plasticized materials show a similar hydroxyl absorption band intensity (2750–3750 cm^{-1}) which does not change with plasticizer composition.

During the plasticization process, added plasticizers and original water play a key role, by forming hydrogen bonding with starch in order to make plasticized starch (Hulleman et al., 1998) (Fig. 3b). The position of differently plasticized starch (WS, GS, SS, GSS and UES) peaks weakly shifts to lower wave numbers (1151 and 1077 cm^{-1}) compared to those of native starch (1158 and 1081 cm^{-1}). Appearance of peak at 1023 cm^{-1} in the FTIR spectra of the plasticized starches indicates stable hydrogen bonds between plasticizer and both of O in C—O—H and O in anhydroglucose ring O—C of starch molecules (Ma et al., 2006). Further, in case of UES material, a peak appears around of 1647 cm^{-1} which is attributed to N—H stretching bond. So here, FTIR clearly confirms the occurrence of plasticization and further supports the microscopic observation (Fig. 2).

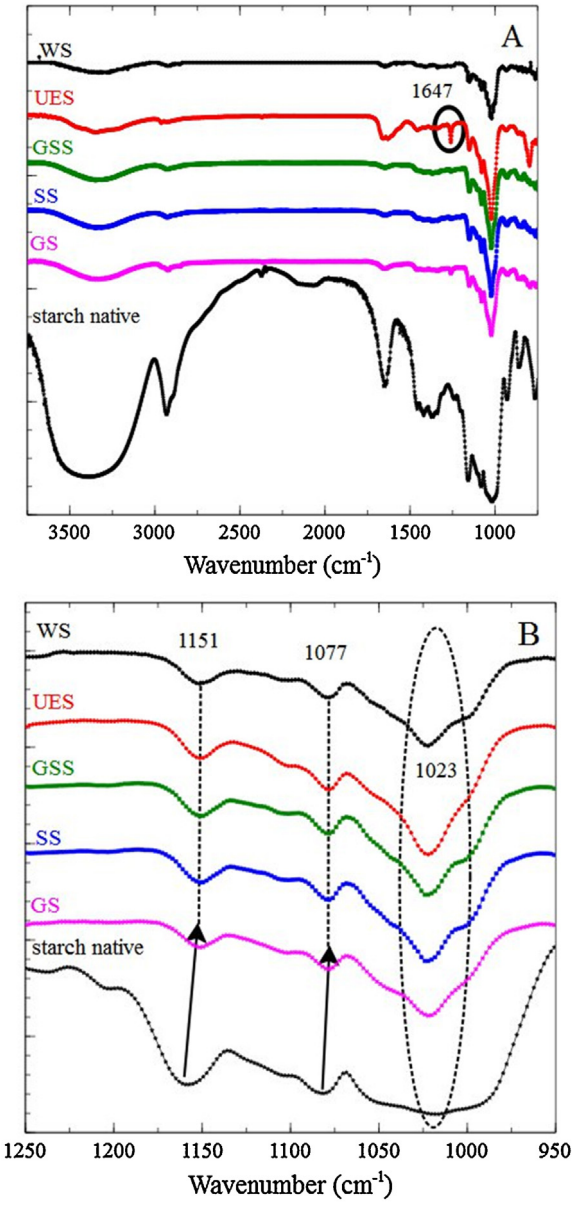

Fig. 3. FTIR spectra of native starch and differently plasticized starch (WS, GS, SS, GSS and UES) after 4 weeks ageing (A) and zoom on peaks showing the forming hydrogen bonding (B).

3.2. Effect of ageing and plasticizer on the properties of thermoplastic starch

3.2.1. Microstructure

Table 1 shows the influence of the plasticizers composition and storage time on the crystallinity degree and the crystalline types over eight weeks (56 days) after processing. One day after compounding, the crystallinity degree of GS and GSS materials is low (6 to 7%) and globally stable during ageing. UES materials initial crystallinity is very low (around 1%) and increases continuously during ageing to attain values comparable to those of GS and GSS materials after 56 days of storage time. These results confirm the efficiency of the extrusion process and the selected plasticizers systems for the destruction of the crystalline structure of the native starch and the formation of a rather amorphous material. The use of urea/ethanolamine blend and its associated extrusion parameters seem to be the most efficient system, just after compounding (lower crystallinity degree). Nevertheless, because the crystallinity degree of GS and GSS materials are rather stable during ageing whereas that of UES material increases, all the plasticized materials contain about the same crystallinity degree after 56 days of storage.

Further, XRD observations in Fig. 4 clearly indicate that, in all plasticized samples, the A-type crystalline structure of the cereal native starch which characteristic peaks are observed at 5.83 Å ($2\theta_{Co}$ = 17.78°), 5.18 Å ($2\theta_{Co}$ = 20.10°), 4.92 Å ($2\theta_{Co}$ = 21.21°), 4.48 Å ($2\theta_{Co}$ = 23.41°) and 3.90 Å ($2\theta_{Co}$ = 27.16°) is transformed into V-type (V_A: 4.29 Å ($2\theta_{Co}$ = 24.51°) and 6.51 Å ($2\theta_{Co}$ = 15.87°) and V_H: 4.51 Å ($2\theta_{Co}$ = 23.26°) and 6.76 Å ($2\theta_{Co}$ = 15.27°)) and B-type (4.03 Å ($2\theta_{Co}$ = 26.21°), 4.16 Å ($2\theta_{Co}$ = 25.33°) and 4.85 Å ($2\theta_{Co}$ = 21.53°).

V_A-type structure never exists in UES material. Its amount in GSS material after compounding is very low and decreases to zero

Table 1
Changes in the type of crystallinity (V_H-, V_A-, B-types) calculated from X-ray scattering area for differently plasticized starch (GS, GSS and UES) and native starch as a function of ageing (storage) time.

Sample	Crystallinity (%)	Percent crystallinity versus ageing time (days)					
		1	7	14	21	28	56
GS	Total	6.1	12.0	6.6	6.8	9.2	7.7
	B-type	6.5	4.6	2.8	12.3	17.3	28
	V_A-type	93.5	48.5	42.2	18.4	31.1	/
	V_H-type	/	46.9	53.5	69.3	51.6	72
GSS	Total	7.3	7.4	8.9	8.3	6.7	6.7
	B-type	19.3	21.2	21.6	19.2	24.6	26.6
	V_A-type	5.1	7.7	10.3	8.5	2.3	/
	V_H-type	75.6	71.1	68.1	72.3	73.15	73.4
UES	Total	1.1	1.0	4.9	4.9	3.8	6.7
	B-type	31	24.5	29.3	31.3	29	26.8
	V_A-type	/	/	/	/	/	/
	V_H-type	69	75.5	70.7	68.7	71	73.2

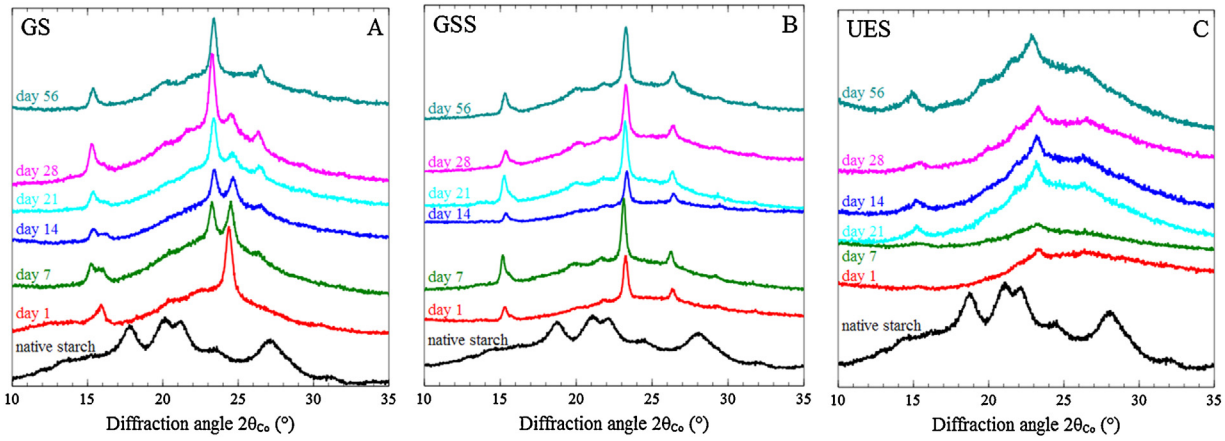

Fig. 4. XRD patterns of differently plasticized starch GS (A), GSS (B) and UES (C) as a function of ageing (storage) time.

after 56 days of storage. GS material contains mainly V_A-type structure after compounding but its amounts quickly decreases to zero after 56 days of storage. This evolution of V_A-type content can be, at least partially, explained by the transformation of V_A-type structure into V_H-type structure which depends on the hydrophilicity of the plasticizers systems (Buleon et al., 1990). Urea/ethanolamine blend and sorbitol are not very sensitive to moisture whereas glycerol is highly hydroscopic. That explains that the moisture content of GS increases significantly at the beginning of storage and remains high over the entire ageing time. Because glycerol content in GSS material is lower, the moisture content of GSS material is also lower and more stable during ageing (Fig. 5). Thus, V_A-type in GS material is quickly transformed into V_H-type. This transformation is slower in GSS material but the initial amount being lower; it attains a complete transformation after 56 days of storage. In case of water plasticized starch, the reported results on XRD analysis indicates that, retrogradation is strongly dependent on the water content of the sample and the storage temperature (Farhat, Blanshard, & Mitchell, 2000a; Aguirre, Osella, Carrara, Sanchez, & Buera, 2011). The observed crystalline pattern was that, at low water contents and at high storage temperatures, the A-type structure was obtained, while at high water contents and low storage temperatures, the B-type structure and a very fast retrogradation has been reported for water plasticized starch (Karim, Norziah, & Seow, 2000). But, in the present work for all the plasticized starch material the change of V-type (V_A- and V_H-type) into B-type is observed. This transformation is due to the slow retrogradation process of the material; Because of hydration of the material, the formation of B-type is promoted at the expense of A-type.

The kinetics of this transformation depends on the plasticizer system (Fig. 6), very fast for GS material, very slow for UES material and intermediate for GSS material. The urea/ethanolamine blend is an efficient plasticizer to prevent the retrogradation (Ma et al., 2006).

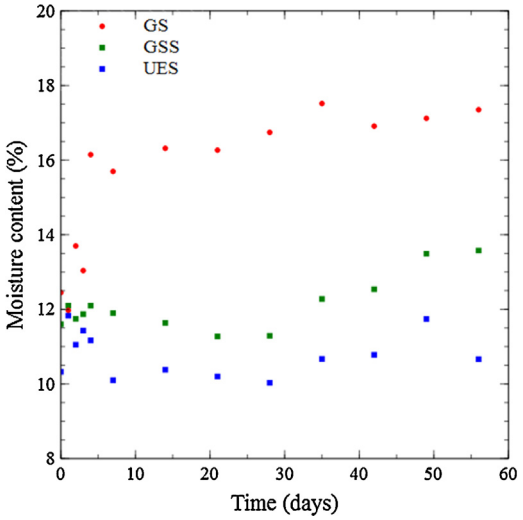

Fig. 5. Moisture content of differently plasticized starch such as GS, GSS and UES as a function of ageing (storage) time.

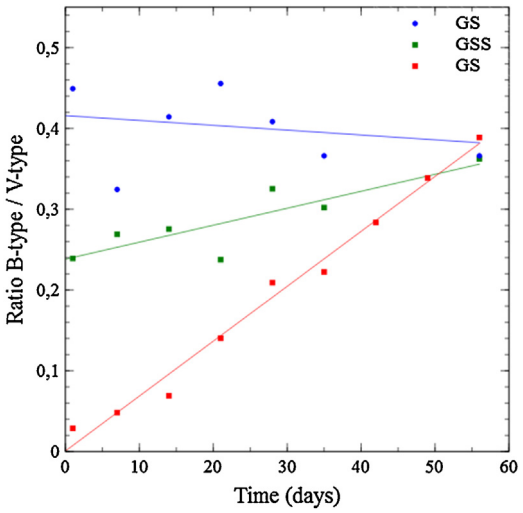

Fig. 6. B-type/V-type crystallinity ratio of differently plasticized starch GS, GSS and UES as a function of ageing (storage) time.

3.2.2. Viscoelastic behaviour

Two peaks appear on the loss factor of for GS, GSS and UES materials (Fig. 7a), the first one is observed in negative temperature range and the second in positive temperature range, whereas only one peak in positive temperature range is visible in case of SS material. But, control samples (WS) showed a small peak shoulder at 5 °C and an intense peak at 41 °C. As indicated by the Wunderlich (2005) literature, tan δ peak is commonly referred to relaxations of the polymer related to glass transition temperature (T_g) or secondary transitions. In the case of plasticized starch, the position of the upper transition is commonly associated to the glass transition of a starch rich phase ($T\alpha$), while the lower one is attributed to the glass transition of a plasticizer rich phase ($T\beta$) (Forsella, Mikkila, Moates, & Parker, 1997).

In case of SS material, appearance of only one relaxation peak associated to the glass transition of a starch rich phase indicates a more homogenous material, whereas other materials show heterogenous distribution of the plasticizer. The $T\alpha$ of the SS material is observed at higher temperature ($T\alpha_{SS}$ = 80 °C) that of GSS material slightly above the ambient temperature ($T\alpha_{GSS}$ = 40 °C), that of GS material around the ambient temperature ($T\alpha_{GS}$ = 25 °C), and that of UES material is well below the ambient temperature ($T\alpha_{UES}$ = 12 °C).

In GS material, the amplitude of the peak corresponding to the starch rich phase decreases significantly with the ageing of material (Fig. 7b) and for GSS material the amplitude peak decreases less significantly (Fig. 7c). In case of UES material, the height of tan δ peak decreases at the beginning of storage and attains saturation after 28 days of storage time (Fig. 7d). The decrease in the tan δ peak height may be due to the structural reordering of amylopectin (retrogradation), which results in decreasing amorphous ratio and thus in the ability of movement.

After one week of storage, two tan δ peaks are visible for WS sample, a shoulder peak and an intense peak appear at 5 and 41 °C, respectively (Fig. 7e). After 15 days of storage, the peaks shift to higher temperature and very intense two peaks are observed at 22 and 51 °C. Eventually, after 21 days of storage, the peak at lower temperature disappears and only one peak remains at 42 °C. The peak observed at lower temperature during the first two week of storage represents the structural relaxation processes due to increase in the mobility of water in the starch. The peak at higher temperature during the entire storage period is due to the equilibrium amorphous state of starch (Shogren, 1992). Appearance of only one peak after 3 weeks of storage is due to loss of moisture by evaporation, thereby showing only one peak corresponding to

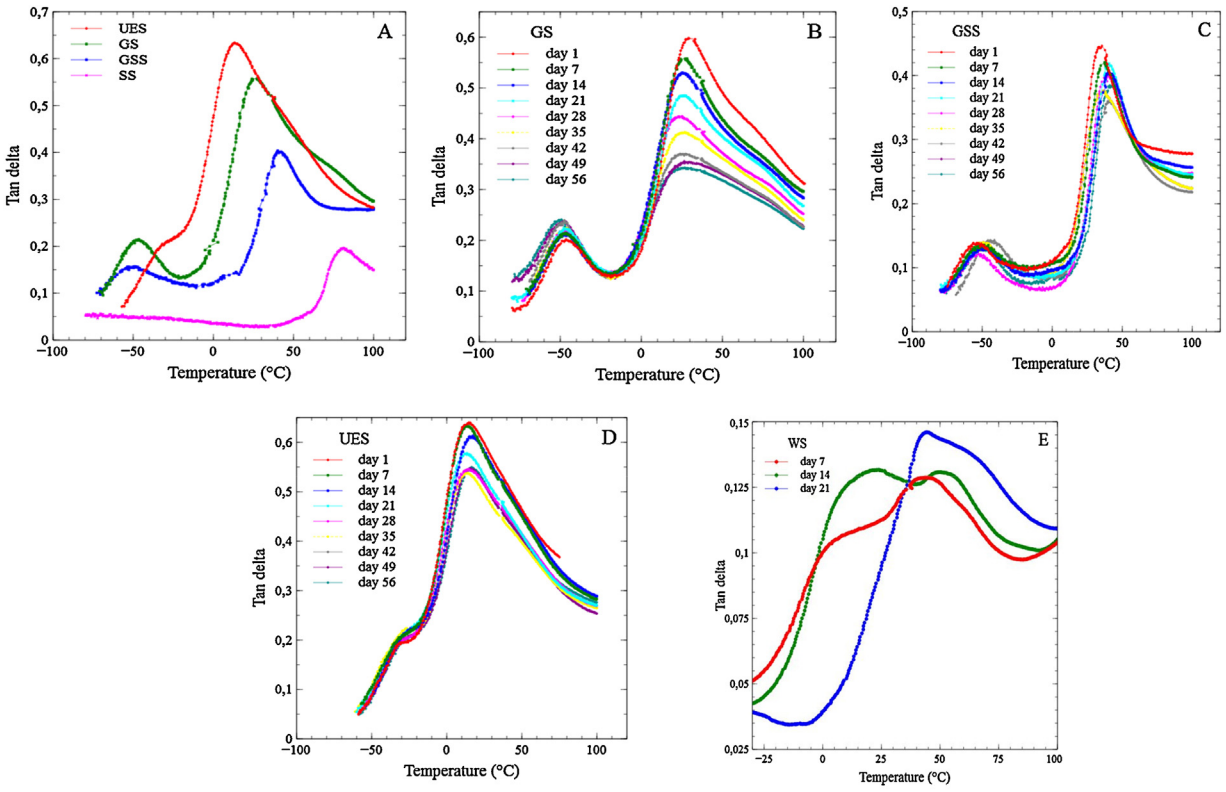

Fig. 7. Tan δ vs temperature curves for differently plasticized starch (GS, SS, GSS and UES) after one day ageing (A) and tan δ vs temperature as a function of ageing (storage) time GS (B), GSS (C), UES (D) and WS (E) samples.

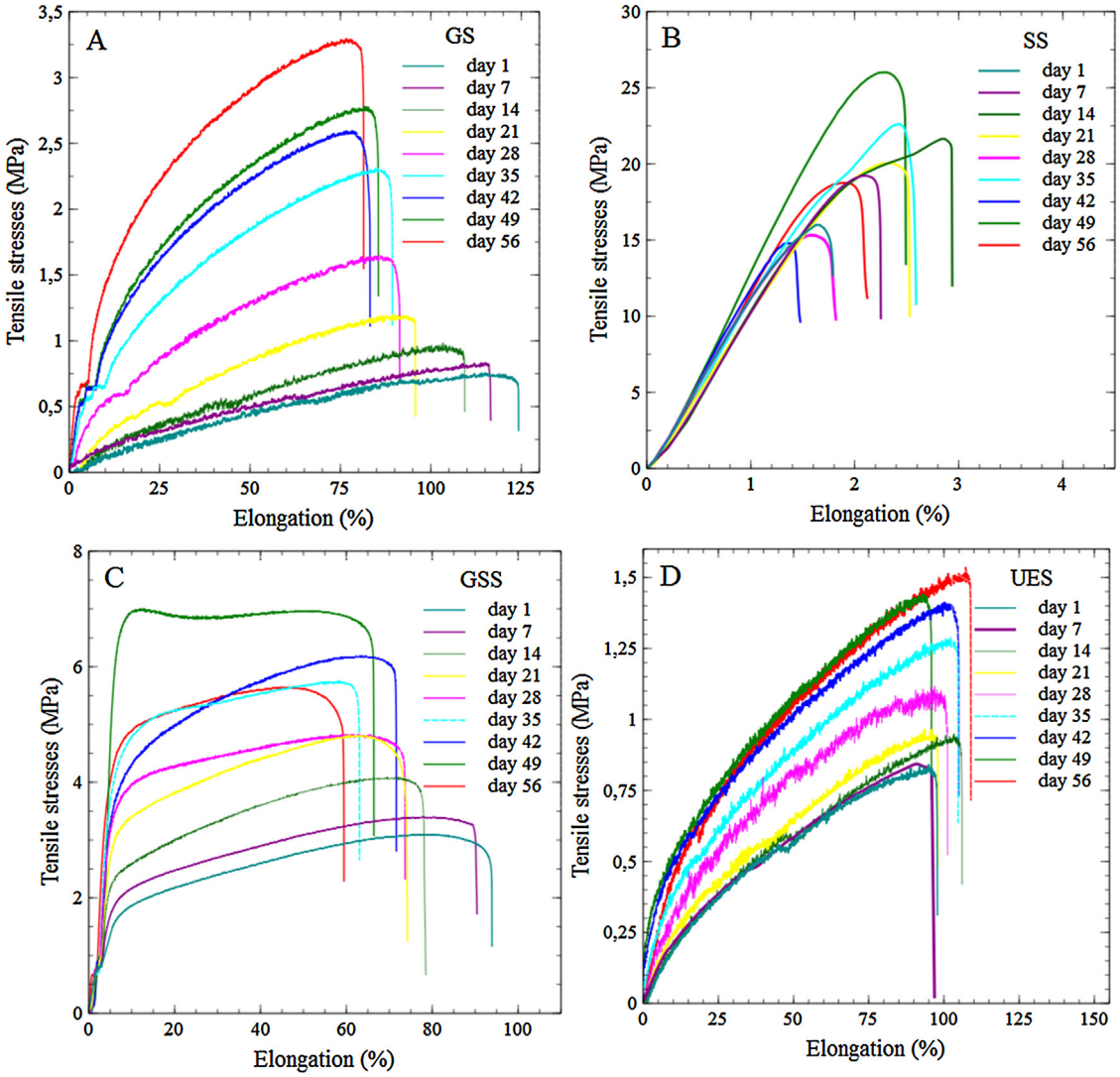

Fig. 8. Typical tensile stress-strain curves of differently plasticized starch GS (A), SS (B), GSS (C) and UES (D) as a function of ageing (storage) time.

plasticized starch. Subsequent analysis of WS samples after 21 days was not possible due to extreme brittle nature of the samples.

3.2.3. *Mechanical properties in tension*

The typical tensile stress-strain are recorded for different plasticizers (Fig. 8) and mechanical properties (modulus, strength, elongation at break) are computed (Table 2).

In case of GS and UES materials, stress increases continuously with strain without yield until fracture; considering the high elongation at break, the behaviour is typically referred as plastic behaviour. In the case of SS material, the behaviour is typically brittle (Fig. 8). Therefore, the results suffer from a high scattering and are therefore hardly significant.

The obtained mechanical properties (Table 2) clearly indicate that the mechanical properties of plasticized starch can be tuned by changing the plasticizer composition. For example after one week of storage, glycerol-based (GS) materials show very low tensile modulus (less than $E = 1.5$ MPa) and strength (less than 1 MPa) but high ductility (elongation elongation at break higher than 110%) (Fig. 8a), whereas sorbitol-based (SS) materials are characterized by very high modulus (more than 1100 MPa) and strength (almost 20 MPa) but a very low elongation at break (around 2%) (Fig. 8b). In between, when a glycerol/sorbitol mixture is used as plasticizer, the materials (GSS) with intermediate mechanical properties are obtained (modulus around 45 MPa, strength around 3.5 MPa and elongation at break reaching 90%) (Fig. 8c). In case of urea/ethanolamine mixture, the tensile properties of UES material is rather close to those of GS material, with slightly lower elongation at break, similar strength and modulus with comparable order of magnitude (Fig. 8d). The glycerol/sorbitol mixture provides a good balance between rigidity, strength and ductility. Finally any combinations could be utilized to tune either the tensile strength or tensile strain at break depending on the requirements. In case of urea/ethanolamine, the tensile properties are significantly balanced compared to that of GS and UES materials with modulus around 3 MPa, strength less than 1 MPa and elongation at break reaching 100%.

Regarding the effect of ageing, tensile strength and elastic modulus of GS material increases by up to +346% and +1280%, respectively, and the elongation at break decreases significantly (−32%) after 8 weeks of storage, indicating a progressive stiffening and embrittlement (Fig. 8a and Table 2). The stiffness of the material is due to the retrogradation caused by the recombination native helix structure (Table 1 and Fig. 6) which can regroup and form crystalline region in the material. Thus, reformation of native crystalline structure B-type is prevalent and leads to internal stresses at the

Table 2
Tensile properties of differently plasticized starch (GS, SS, GSS and UES) as a function of ageing (storage) time: Young's modulus (E), tensile strength (σ_R) and elongation at break (ε_R).

Material	Properties	Tensile properties versus ageing time (days)					
		1	7	14	21	28	56
GS	E (MPa)	1.5 ± 0.7	1.5 ± 0.2	2.4 ± 0.1	4.4 ± 0.3	7.9 ± 0.6	20.6 ± 5.2
	σ_R (MPa)	0.8 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	1.1 ± 0.1	1.7 ± 0.1	3.4 ± 0.1
	ε_R (%)	122.6 ± 7.0	114.8 ± 8.4	104.1 ± 5.0	91.8 ± 5.3	89.1 ± 6.0	77.6 ± 5.3
SS	E (MPa)	1126.7 ± 150.7	1153.1 ± 182.1	1185.7 ± 182.0	1147.8 ± 110.5	1131.5 ± 217.3	1284.5 ± 131.4
	σ_R (MPa)	15.7 ± 2.7	18.0 ± 1.9	19.3 ± 3.3	12.0 ± 0.5	13.3 ± 6.2	20.8 ± 7.8
	ε_R (%)	2.0 ± 0.5	2.1 ± 0.6	2.4 ± 0.6	1.6 ± 0.5	1.9 ± 0.6	2.2 ± 0.7
GSS	E (MPa)	35.0 ± 11.7	43.8 ± 12.1	57.4 ± 19.4	90.0 ± 13.3	114.0 ± 35.8	211.2 ± 57.9
	σ_R (MPa)	3.7 ± 0.2	3.5 ± 0.3	4.2 ± 0.3	4.7 ± 0.1	4.9 ± 0.2	5.9 ± 0.4
	ε_R (%)	93.7 ± 5.7	89.2 ± 4.9	80.5 ± 5.4	73.7 ± 8.0	72.4 ± 7.4	61.6 ± 1.8
UES	E (MPa)	2.2 ± 0.6	3.1 ± 0.5	2.4 ± 0.2	2.8 ± 0.4	3.9 ± 0.9	5.3 ± 1.0
	σ_R (MPa)	0.7 ± 0.1	0.8 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.5 ± 0.1
	ε_R (%)	98.9 ± 5.4	99.7 ± 2.9	106.2 ± 11.8	98.5 ± 3.9	100.7 ± 8.8	105.0 ± 6.3

junction zones between two crystalline amylopectine molecules (present just after compounding and arises after retrogradation), therefore material form cracks and reduces the strength and the elongation (Van Soest et al., 1996).

During ageing of GSS material, significant changes in mechanical properties are observed. Tensile strength and elastic modulus increase by up to +69% and +382% at the maximum, respectively, and the elongation decreases (−31%) during 8 weeks of storage (Fig. 8c and Table 2). The stiffness is less pronounced because the recombination the starch chains into the native form is lower (Table 1 and Fig. 6). The changes in mechanical properties of UES material during ageing are not the same as those observed for GS material. Actually, tensile strength and elastic modulus increase moderately by up to +86% and +74% only, respectively, and the material does not show only loss of elongation (+5%) after 8 week of storage (Fig. 8d and Table 2). The mechanical properties of UES material do not change during ageing time because the B-type/V-type ratio remains unchanged during ageing and the height of the tan δ peak corresponding to the starch rich phase does not significantly change during ageing; UES material is stable.

The reported literature on the effect of ageing on the mechanical properties of water plasticized starch indicates that, after 28 days of aging, the tensile strength and modulus of samples increases by 60% and 50%, respectively, while the elongation decreases from approximately 12 to 7% (Shogren, 1992). The tensile properties obtained in the present studies using glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine as plasticizer for starch are found to be better than those reported for water plasticized starch (Shogren, 1992).

3.2.4. *Modelling the retrogradation kinetics*

The retrogradation kinetics was studied by modelling using modulus data measured at different storage times using the Avrami equation. This model has been successfully applied to various starch-based systems to predict the variations in molecular reordering process (Farhat et al., 2000a; Farhat, Blanshard, Descamps, & Mitchell, 2000b; Noosuk, Hill, Farhat, Mitchell, & Pradipasena, 2005). The rates for retrogradation can be modelled by Avrami equation (Noosuk et al., 2005; Ottenhof, Hill, & Farhat, 2005).

$$Y(t) = Y_\infty - (Y_\infty - Y_0)\exp(kt)^n \quad (2)$$

The rate of retrogradation is given by, $G(s^{-1}) - = k^{1/n}$ where "n" represents the Avrami coefficient, which depends on the type of crystal nucleation and the dimensions in which growth takes place, "k" is the crystal growth rate. "Y_∞" is the value of the measured parameter (modulus in the present case) at the longest time and "Y_0" its initial value, and "$Y(t)$" is a physical parameter describing the crystallization dependency over time "t".

In this study, the experimental results were modelled with Eq. (2) using a least squares minimization fitting method. Retrogradation rate was found to be 1.372E − 4, 1.202E − 4 and 1.018E − 4 s^{-1} for GS, GSS and UES materials, respectively. The calculation of retrogradation rate for SS samples was not possible due to highly scattered data. The obtained values for GS, GSS and UES samples are similar in order of magnitude to those indicated in the literature for extruded starch-based systems (Farhat et al., 2000a; Ottenhof et al., 2005). The effects of different plasticizers such as glycerol, glycerol/sorbitol and urea/ethanolamine on the rate of retrogradation under storage are clearly in the following ranking: UES < GSS < GS. These observations are consistent with the XRD analysis.

4. Conclusions

The effect storage time on the structure and stability melt processed thermoplastic starch was investigated. X-ray diffraction was successfully used to monitor the evolution of the different crystalline types of starch (B-, V_A- and V_H-type) as a function of plasticizer type and storage time. Also, crystal modifications of plasticized starches during their ageing were related to the materials mechanical properties. The urea/ethanolamine mixture is the most effective plasticizer as it can limit the retrogradation process which results in a stiffening and a loss of ductility of the material. In case of polyols plasticizers, retrogradation phenomenon was observed, but these plasticizers showed better mechanical properties and therefore, the plasticizer combination and/or storage time can be chosen to achieve desired capabilities, from structural stability to mechanical strength. Dynamic mechanical analysis indicated that all plasticizers lead to better thermo-mechanical properties than those of water plasticized starch. Also, there is a clear glass transition temperature properly describing the rubber-like structure of the product at ambient temperature. The stiffening of the product during storage, indicated by an increase in the elastic modulus, was correlated to a reordering of amylopectin from the starchy component as indicated increasing the B-type crystallinity. These progressive changes in the thermoplastic starch indicate that, starch chains become less mobile during ageing. The obtained results indicate that using different combinations of plasticizers and aging, the starch-based materials show significant differences in terms of mechanical properties and each plasticizer may find an interest in very specific applications.

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