Electron-Beam Processing of Destructurized Allylurea–Starch Blends: Immobilization of Plasticizer by Grafting

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ABSTRACT: Allylurea (AU) was used as a reactive additive with poor aptitude to homopolymerization for obtaining grafted plasticized starch films with stabilized physical properties. Potato starch was mixed with AU (30-50 parts per hundred/pph) in a mixer operating at 125°C. Upon storage in well-defined hygrothermal conditions, the resulting thermoplastic material shows strong plasticizer migration revealed by AU crystals blooming at the samples surface and exhibits strong opacity assigned to phase separation of the organic additive inside the material. Freshly prepared thermoplastic films of appropriate thickness were exposed to a 175-kV electron beam (EB) radiation for inducing covalent grafting of AU by a free radical process. FTIR monitoring of the resulting chemical changes in thin films of AU-starch blends indicates unambiguously the transformation of AU allylic bond. High irradiation doses are required for achieving complete conversion of AU in the blend. However, no detectable AU migration was observed for intermediate AU conversion, probably as a consequence of higher plasticizer solubility in the grafted polysaccharide. Examination of the viscoelastic properties by dynamic mechanical thermal analysis shows that artificial aging by placing the films alternatively in high and low relative humidity (RH) atmosphere does not significantly alter the thermomechanical spectrum of the material reconditioned in a cell at 58% RH. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 409-417, 1999

Key words: starch; allylurea; EB grafting; starch plasticization; starch grafting

INTRODUCTION

Thermoplastic starch is an attractive biodegradable material with strong potential for the low-cost production of disposable packaging.¹ Intimate blends of starch with polymers and/or with low molecular weight additives are generally obtained by extrusion at temperatures of 120–180°C.² Several low molecular weight hydroxy or amido compounds (glycerol, urea), as well as some metal carboxylates (sodium lactate) and alcaline hydroxides, are mixed with starch to obtain destructurization and plasticization.³⁻⁶ These low molecular weight compounds can play an additional role as humectants.⁷

Phase separation of the plasticizer in the blend as well as its migration out of the material induce physical effects with adverse consequences on the desired mechanical properties.^{8,9} Reduction of plasticizer concentration in the amorphous material and possible recrystallization and retrogradation of the polysaccharide chains are two mechanisms generally invoked to account for the physical aging of plasticized starch.¹⁰

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In this context, there is obvious interest for developing selective modification processes yielding thermoplastic starch with immobilized plasticizers. Internal plasticization would result, with possible reduced efficiency compared with the free additive present at the same weight content. However, improved durability is expected, especially after wet aging.¹¹

The choice for a reactive plasticizer was based on structural similarity with commonly used additives. Particular attention was paid to the functional moiety intended to react with starch by a free radical mechanism. Vinyl and acrylic derivatives are known to yield homopolymers much more easily than the allylic homologues, especially in the case of monounsaturated reactants.¹² Allylurea is reported not to polymerize efficiently in the liquid state, although crystals of AU could be converted into high polymers upon γ -irradiation.¹³ It can be reasonably concluded that AU is sensitive to ionizing radiation, and exhibits a low reactivity for propagation and a high tendency to transfer when activated as an amorphous material. On the basis of its chemical structure and reactivity, AU seems well suited for producing shortchain branching onto starch.

Grafting unsaturated reactants onto polysaccharides can be performed by means of conventional thermally initiated radical chemistry, by a redox or by photochemical process, and by ionizing radiation. Among the latter, 60 Co γ -ray sources have been frequently used to graft reactive monomers onto gelatinized starch,^{14,15} producing presumably long-chain grafts at low rates of initiation.¹⁶ Accelerated electron beams (EB) are generally considered to induce the same type of radiochemical processes as obtained under γ -radiation. EB generators can deliver high-energy doses at high dose rates. This feature may be essential for developping economically viable processes. EB processing of starch containing material has already been used for achieving graft copolymerization¹⁷ and for improving the morphology of starch-EVA (ethylene vinyl alcohol copolymers) blends.^{18,19}

The objective of this work was to induce permanent grafting of AU onto potato starch by EB irradiation of intimate blends, and to assess the efficiency of the chemical modification for stabilizing the mechanical properties of the thermoplastic material.

EXPERIMENTAL

Materials and Sample Preparation

Potato starch (Roquette Frères, France) with ca. 13 wt % of moisture content was used for this work. Urea and allylurea (AU) were reagent grade chemicals supplied by Aldrich and used without further purification. Plasticized blends of starch with urea or with AU were prepared in an internal Brabender mixer at 125°C with a rotation rate of 50 cycles per min for 15 min. Films of $200-\mu m$ thickness were pressed with a Darragon hydraulic press at 120°C, with a pressure of 10 MPa maintained for 5 min. For transmission FTIR analysis, films of $20-40 \ \mu m$ were prepared by compression molding the thermoplastic material with a SPECAC filming apparatus heated to 120°C and placed in a Perkin-Elmer hydraulic press (5 MPa for 5 min). All films were stored in a closed cell having a relative humidity (RH) of 58% obtained in the presence of a saturated NaBr solution at 23°C. Reference starch films containing no synthetic additive were prepared by premixing 100 parts of starch with 28 parts of water and by pressing the mixture at 10 MPa and by heating up to 120°C. Cooling was conducted under pressure. Unless otherwise indicated, the materials were stored and equilibrated in a closed cell maintained at 58% RH.

Spectroscopic Characterization

Infrared spectra of the starch–urea (or AU) were recorded from a Perkin-Elmer System 2000 FTIR spectrophotometer. Analysis of crystalline migrating compounds collected at the film surface was performed by FTIR spectroscopy (KBr pellets) and by ¹H-NMR spectroscopy (deuterochloroform solutions) using a Bruker AC-300 spectrometer. AU conversion upon exposure to EB radiation was determined by monitoring the IR absorbance decrease of the two peaks at 927 and 1421 cm⁻¹ assigned to the allylic double bond.

Electron Beam Grafting

Thermoplastic starch samples containing AU were treated under the electron beam of an Electrocurtain CB150 generator operating at 175 kV. The irradiation chamber was placed under nitrogen flow to obtain oxygen concentration lower than 200 ppm. To ensure uniform energy deposition in the depth of films of thickness greater than 100 μ m, the two sides were treated consecutively.

Current intensity (8 mA) and conveyor speed were adjusted to yield a unit dose of 100 kGy per pass. Higher doses were obtained by increasing the number of passes in the chamber of the EB processor.

Mechanical Analysis

Mechanical properties of film samples (typically 5 \times 40 \times 0.2 mm) were determined by dynamic mechanical thermal analysis (DMA) using a Rheometrics RSA II solids analyzer. Storage modulus (E'), loss modulus (E''), and loss angle tangent were determined for temperatures ranging from -50 to $+50^{\circ}$ C (heating rate 5° C \cdot min⁻¹) at a frequency of 1 Hz.

Dry aging was accomplished by storing samples for 1 week in a closed cell containing $CaCl_2$ as a desiccating agent (ca. 22% RH). Wet aging was obtained by storing samples to constant weight in a closed cell containing a saturated aqueous KNO₃ solution at 92% RH.

RESULTS AND DISCUSSION

Preparation and Characterization of Starch Blends

Two series of plasticized starch blends including 20, 30, 40, and 50 parts of additive per hundred parts of starch (pph) were prepared by triturating in an internal mixer the powdery starting materials. Efficient transformation into molten thermoplastic material proceeded within 15 min of mixing at temperatures ranging from 120 to 150°C. A slight evolution of ammonia, and possibly of alkyl amines in the case of AU, was detected under these conditions, indicating that thermal degradation of the urea additives was present but limited when the process was conducted at 125-135°C. Elemental analysis of the mixtures allows quantitative determination of nitrogen content in the samples. The amount of urea additive in the blends was deduced from the data corrected for proteinic nitrogen,²⁰ assuming that the limited degradation of urea additives yields only volatile by-products. The results collected in Table I indicate actual urea nitrogen content ranging from 93 to 100% of the calculated value, thus confirming that thermal decomposition of urea (or AU) is kept at an acceptable level.

At the same weight concentration in the blend, urea and AU have similar activities for achieving destructurization and plasticization of starch. Addition of small amounts of water (5–10 pph)

Fable I 1 after Mixi	[heoretical (Feeding Comp. ng	osition) and Me	easured Nitrogen Cont	tent in the Urea or AU	Destructurized Sta	rch Blends Obtained
ء -	Feed Composition (Parts	Additive	$N ext{ Content}^{ ext{b}} (ext{wt } \%) ext{ in }$	n Urea–Starch Blends	N Content ^b (wt %)) in AU–Starch Blends
Parts of Additive ^a	in Weight) Dry Starch/ Additive/Water	Content (%) (Dry Basis)	Found	Calculated ^c	Found	Calculated ^c
20	72.5/16.5/11.0	17	8.34	8.30	4.86	5.18
30	66.9/23.1/10.0	25.5	10.96	11.24	6.63	6.93
40	62.1/28.6/9.3	31.5	13.39	13.77	8.06	8.44
50	58.0/33.3/8.7	36.5	15.72	15.96	9.07	9.74

wt-parts of urea or AU per hundred parts of native stock starch with 13% water content. Elemental analysis. Not corrected for water loss during mixing.

EB PROCESSING OF AU-STARCH BLENDS 411 makes the mixing process faster or permits to reduce the mixing temperature. However, for the present study, potato starch with an equilibrium water content of 13 wt % was used without additional water, the operating temperature of the mixer being set at 135°C.

The thermoplastic materials were transformed into films of thickness ranging from 100 to 200 μ m by pressing 2-g samples at moderate temperature (ca. 120°C) using a standard hydraulic press operating at 10 MPa.

Upon cooling at room temperature, the translucent thermoplastic films solidify and become brittle. Softening is observed by reheating the films at temperatures ranging from 40°C, for films containing 40 to 50 urea or AU pph, to 60°C, for films with lower plasticizer content (20-30 pph of urea or AU). Accurate determination of the influence of the blend composition on the glass transition by calorimetric or by mechanical measurements was, however, judged irrelevant because most of the thermoplastic starch films were not physically stable, urea or AU crystals blooming at the samples surface after a short aging time. The powder collected with a doctor's blade from the two series was identified by means of FTIR and ¹H-NMR spectroscopy as urea and AU, respectively, of purity equal to that of the used starting chemicals. In addition to the migration process, the films cleaned from the crystal powder covering the surface also presented strongly opaque zones in the depth, suggesting the presence of phase-separated crystalline microphase into the starch material. Similar behavior has already been reported for starch blends containing 60 pph of urea.²¹ Conditioning the samples at 58% RH cells was shown to accelerate opacification and blooming process. Absorbed water is indeed known to assist plasticizer migration or phase separation in the case of glycerol and other hydroxylic organic plasticizers.²²

Interestingly, physical aging revealed by AU blooming was not observed for the samples containing the lowest amount (20 pph) of urea or AU, suggesting that the maximum solubility of these two organic plasticizers at ambient temperature and for materials equilibrated at 45–58% RH was above but not far from this value. We focussed our study on samples derived from the starch blend containing 50 pph of AU, which give flexible films at moderate temperatures (30–40°C).

To avoid significant physical modifications prior to the EB treatment, the stock starch blends were stored at -17° C immediately after produc-



Figure 1 FTIR spectra of a water destructurized starch film (a), AU in KBr pellet (b), and film of starch plasticized with 50 pph of AU (c).

tion in the mixer, and the films were analyzed or processed as soon as obtained from the heating press. By comparison with the transmission FTIR spectra of cast films obtained from gelatinized water-starch blends, destructurized starch containing AU revealed the presence of the allylic double bond detected at 1421 (=CH₂ deformation) and 927 cm⁻¹ (=CH₂ wagging) (Fig. 1). The strong absorption peaks assigned to the urea moiety were observed at 1653 (carbonyl stretching), 1608, and 1599 cm^{-1} (NH deformation).²³ This corresponds to the superimposed infrared absorptions of separated constituents. It was concluded that the olefinic moiety of the additive is not measurably affected by the thermal and mechanical treatment in the mixer.

EB Treatment

The chemical effects of EB treatment onto freshly pressed starch films containing 50 parts of AU was monitored by FTIR spectroscopy (Fig. 2). The absorption peak at 1421 cm⁻¹ in the blends is only due to the AU double bond, whereas at 927 cm⁻¹ starch also has a small absorption band. The decrease of the peaks corresponding to allylic double bond was used to quantify the progress of AU conversion. Because the polymerizability of AU is low, especially in the dispersed and amorphous solid state,¹⁵ and because of the high concentration in secondary hydroxylic groups that



Figure 2 Changes in the FTIR spectra of an starch-AU (50 pph) film submitted to increasing EB doses.

favor transfer of propagating free radicals,²⁴ it is reasonably speculated that AU consumption is due to short-chain grafting (Scheme 1). The dependence of allyl conversion $\pi = 1 - [=]_D/[=]_0$ with the absorbed radiation dose D is plotted in Figure 3. Maximal AU conversion requires extremely high doses compared with the usual curing doses ranging between 50 to 100 kGy for crosslinking polymerization of acrylate-based formulations.²⁵ For a 200-kGy dose, the value for π is about 0.2, and maximal conversion with π approaching 0.98 is obtained for a dose of 1400 kGy. Strictly speaking, the plot of conversion π as a function of the dose is not a representation of AU transformation with time, because irradiation was performed in a discontinuous manner. However, if one examines the changes from a kinetic point of view, the very slight initial curvature of the conversion plot in Figure 3 is not consistent with the usual polymerization or grafting kinetics that generally follow, at least in initial conditions, a first order in reactant. The corresponding firstorder integral function $-\ln(1-\pi) = f(D)$ is apparently linear above a dose of ca. 400 kGy. It suggests that some induction phenomenon takes place at the beginning of the process, possibly caused by dissolved oxygen that can inhibit free radical grafting. This peculiar behavior requires further investigation.

The films exposed to EB radiation doses above 200 kGy do not exhibit AU migration even after prolonged aging in 58% RH cells. This observation was unexpected on the basis of the π vs. D dependence of Figure 3 that indicates limited AU conversion for the lowest doses ($\pi \approx 0.2$). AU immobilization by reaction with nitrogen atoms could explain the absence of migration at low double-bond conversion. There are actually no spectroscopic arguments supporting this possibility. In addition, higher reactivity for grafting of the urea moiety of AU compared with the allylic function is dubious. The increase of the AU-starch blend solubility in water with increasing dosage is discussed in the next section. It affords



Scheme 1 Possible sketch for the grafting reaction onto starch (AGU: anhydroglucose unit).



Figure 3 Progress of AU conversion in a starch–AU (50 pph) film with the absorbed EB dose.

a definitive objection to this hypothesis. If both functions were potentially reactive for grafting, crosslinking would indeed result. A reasonable explanation is based on the enhancement of AU compatibility with the polysaccharide as a consequence of AU grafting. The expected beneficial effects of radiation treatment on migration are, nevertheless, acquired at low AU conversion. The mechanical properties were shown to be affected as well. From a physical point of view, after EB treatment, all films loose some of their plasticity. After reconditioning in a cell at 58% RH, the samples treated by doses up to 400 kGy recover their original suppleness. The increase in rigidity can be explained partly by a loss of absorbed water due to temperature elevation in the sample during EB treatment and to the repeated exposure to strong flow of anhydrous nitrogen in the inerted irradiation channel. Films submitted to doses exceeding 400 kGy remain brittle after reconditioning, showing that other parameters than moisture content are responsible for the changes in viscoelastic properties.

Dynamic Mechanical Analysis

Dynamic mechanical analysis of EB treated starch films containing 50 parts of AU generally affords useful information for gaining deeper knowledge and understanding of the structure– physical properties of these complex blends. The storage modulus (E') and loss modulus (E'') are sensitive to the various compositional, structural, and morphological changes that take place as a consequence of blending, heating, (de)hydrating, and aging of the polysaccharide material. The upper limit of the temperature range was set at +50°C to reduce film dehydration during the experiments conducted in air. Repeated DMA scans on the same sample indeed showed poor reproducibility assigned to the decreasing plasticization with increasing water loss. DMA spectra were thus recorded on films conditioned at 58% RH and submitted to a single scan.

In accordance with the literature,²⁶ destructurized starch with its equilibrium moisture content (ca. 15% in the given conditions)⁹ does not exhibit any thermomechanical transition in the -50 to +50°C temperature range covered in our analyses (Fig. 4). The tan δ maximum observed at -68° C is assigned to β -relaxation of anhydroglucose units, as observed with amylose at comparable water content. The behavior of freshly prepared and conditioned AU plasticized samples exhibits a broad tan δ peak associated with a drop of storage modulus E' revealing the glassy transition located at about 40°C, in good agreement with the qualitative observation of rigid films that soften upon moderate heating. After treatment with 200 and 400 kGy doses, the samples show contrasting behavior (Fig. 5). The glass transition region for the samples treated with a 200 kGy dose is decreased to about 20°C, whereas the films treated with a 400 kGy dose exhibit a glass transition slightly above 25°C (Fig. 6). The latter result is consistent with the observed higher brittleness of heavily irradiated samples.

We cannot exclude that incipient phase separation of AU affects to some extent the thermomechanical behavior of the unirradiated films. However, if we consider that the measurements at zero dose are characteristic of the reference state, the changes after grafting reveal antagonistic effects. Under ionizing radiation, starch is a polymer of the degrading type that undergoes main chain scission, essentially by breaking glycosidic C—O bonds.^{27,28} This phenomenon is effective at low irradiation doses (20–100 kGy).¹⁸



Figure 4 Plot of the thermomechanical spectrum of water destructurized starch films from this study $(+, \diamond)$, from ref. 26 (\times, \bigcirc) compared to a freshly prepared starch film plasticized with AU-50 pph $(*, \square)$.



Figure 5 Changes in the thermomechanical spectrum of starch films plasticized with AU (50 pph) before (\diamond,\times) and after EB irradiation: 200 kGy $(\bigcirc,-)$, 400 kGy $(\bigcirc,+)$.

The progress of grafting in this dose range may be still too low for inducing structural and physical effects that would overcome degradation. The increase of T_g at higher doses for the degrading-type polymer main chain can result from chemical or physical crosslinking.

Gel fraction determination was performed to evaluate the net result of possibly competing scission and crosslinking induced by EB irradiation. The soluble fraction of irradiated starch blends in water at 25°C actually increases with the radiation dose (Fig. 7). This proves that radiation induces a larger number of main-chain scission compared with chemical crosslinks. Therefore, H bonding of grafted AU units to glycosidic units belonging to another chain is the proposed inter-



Figure 6 Changes of thermomechanical property tan δ for a starch film plasticized with AU (50 pph) before (\diamond) and after EB irradiation: 200 kGy (\bigcirc), 400 kGy (\square).



Figure 7 Decrease of the insoluble fraction in water of irradiated AU–starch blends as a function of absorbed EB dose.

pretation for T_g increase with the absorbed dose. In the solid state, this effect seems to overcome the antagonistic contribution of main-chain scissions. Consistently, the higher the dose, the smaller the drop in storage modulus E' from the vitrous to the rubbery state. The rough E' values measured at (T_g + 40°C), certainly affected to a slight extent by water content reduction at high temperatures, are 3, 30, and 60 MPa for films treated with a 0, 200, and 400 kGy dose, respectively.

Aging Experiments

Aging experiments on AU-grafted starch films in dry and in wet atmosphere were conducted to evaluate the stabilization of mechanical properties, which results from plasticizer immobilization. After 1 week in an atmosphere having a relative air humidity of ca. 22%, films become brittle, but after reconditioning for 1 week in an atmosphere with 58% RH, they regain their initial suppleness. After conditioning in a wet ambience for 1 week at 92% RH, the films become extremely flexible and soft. Reconditioning the samples at 58% RH restores their original aspect. The transparency of the samples was however unchanged. The same treatment applied to unirradiated starch blends of the same AU content accelerates phase separation and migration, as seen by simple optical examination. To quantitatively evaluate the effectiveness of AU grafting for obtaining permanent stabilization of the physical and mechanical properties of plasticized starch, a series of DMA experiments were conducted on a sample submitted to a 200-kGy EB treatment and then to the aging ambiences depicted in Scheme 2. Figure 8 shows that the viscoelastic behavior of the reconditioned films is



Scheme 2 Aging cycle applied to the starch–AU (50 pph) samples after 200 kGy EB irradiation for assessing stabilization of the thermomechanical behavior.

almost identical, despite the strong changes of moisture content that prove to have essentially reversible consequences in the reported conditions.

CONCLUSIONS

Urea and AU act as plasticizers of destructurized starch but exhibit limited compatibility with the polysaccharide. Phase separation is observed, and plasticizer blooming at the film surface is evidenced for urea or AU contents above 20 pph. AU is a radiation-sensitive additive that can be grafted onto the polymer. Radiation doses as high as 1400 kGy are required for approaching complete allyl group conversion. Interestingly, not



Figure 8 Effects of aging in various hygrometric conditions on the thermomechanical spectrum of reconditioned starch film plasticized with AU (50 pph) and treated by a 200 kGy dose at stage $1 (\Box), 2 (\bigcirc), \text{ or } 3 (\diamond)$ of scheme 2.

only is the migration aptitude of grafted AU molecules prevented by permanent immobilization, but also grafting seems to induce higher compatibility of free AU with the modified polysaccharide. Thus, efficient compatibilization can be acquired at a moderate radiation dose. Blended starch films containing 50 pph of AU do not show any sign of phase separation after a 200-kGy treatment. Aging experiments in wet and the dry ambiences have shown that the thermomechanical properties of the films are stabilized. Further experiments are currently in progress to elucidate the actual mechanism for AU grafting and to evaluate the extent of polymer degradation upon exposure to EB irradiation.

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