

Mechanical Properties of Starch-Based Materials. I. Short Review and Complementary Experimental Analysis

N. Follain,¹ C. Joly,² P. Dole,² C. Bliard¹

¹Formation de Recherche en Evolution, 2715, Centre National de Recherches Scientifiques, Laboratoire de Pharmacognosie, Bât 18 Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, France

²UMR-INRA FARE 614, Equipe EMOA, CPCB Moulin de la Housse, BP 1039, 51687 Reims, Cedex 2, France

Received 30 October 2003; accepted 5 October 2004

DOI 10.1002/app.21664

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this study was to review the mechanical properties (at break) of plasticized starch-based materials from the literature. The methodology relied on the use of a graphic tool allowing a direct comparison of the strength and strain at break. The mechanical properties of the materials were systematically compared with those of glycerol-plasticized starches at 57% relative humidity. Because all the systems were equivalent, whatever the strategies were, several starch development approaches were examined that depended on the required performance at

break. First, classical formulations described in the literature (under comparable conditions) were tested. A smoothing of the mechanical performances was obtained, and they were surprisingly similar to those of the simple glycerol-plasticized, starch-based material family. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1783–1794, 2005

Key words: ageing; mechanical properties; starch; PVA; biopolymers

INTRODUCTION

Starch-based materials have been widely studied,^{1–30} although few applications have been actually marketed. The reasons are numerous: the materials are hydrophilic, they undergo aging, and they have low mechanical properties, impact strength, and inappropriate chemical structures. In this article, the ultimate mechanical properties are highlighted to (1) summarize those of published materials and (2) reach useful conclusions on the development of new strategies necessary to improve low mechanical performances.

This work deals essentially with economically conceivable materials, that is, materials formulated with a great amount of renewable and low-cost native starch. Blends with low starch contents and high starch derivatives have been excluded.

The drawback of starch-based materials is the result of the structures of the two constitutive starch macromolecules, which are amylose and amylopectin.³¹ Amylose is often considered a linear structure, and amylopectin is often considered very branched.^{32–36} These macromolecules are able to create short interac-

tions (van der Waals and hydrogen forces) developed at a low distance between the macromolecules or functional groups (e.g., OH). If these forces are important, the associated strength (at a low elongation) will be high.

Long-distance interactions are typically macromolecular entanglements that develop if the macromolecules are long enough. If entanglements happen, the elongation at break can be higher.

Both polymers (amylose and amylopectin) create a system that does not develop enough long-distance interactions (e.g., entanglements) to present good ultimate mechanical properties: the starch-based systems are not cohesive enough. Moreover, a second characteristic is the presence of three hydroxyl groups per monomer; this leads to a large variation of physical properties as a function of the ambient relative humidity (RH). In addition, hydrophilicity also enables the system to partially crystallize (or retrograde) as a function of the water content.^{8,14,37–41}

Concerning the mechanical properties, two types of bibliographies have been identified. One is devoted to cognitive research based on model systems that do not fulfill the required conditions allowing potential applications in the field of materials. The second type includes much more realistic complex systems, but unfortunately it is difficult to objectively appreciate the actual improvements of these last systems. Indeed, the authors have omitted a systematic comparison of their materials with references nonintrinsically related

Correspondence to: C. Joly (catherine.joly@univ-reims.fr).

Contract grant sponsor: Europol'Agro (through a research program devoted to the development of materials derived from agricultural resources).

TABLE I
Characteristics of Selected Polymers for Starch-Based Blends

Polymer	M_w (g/mol)	Hydrolysis rate (%)	Designation
PVA	13,000–23,000	99	PVA _{13.99}
	13,000–23,000	88	PVA _{13.88}
	124,000–186,000	99	PVA _{124.99}
	124,000–186,000	88	PVA _{124.88}
Commercial name		Society	Designation
Biodegradable polyesters	BAK 1095	Bayer (Lyon, France)	BAK
	PCL Capa 680	Solvay (Paris, France)	PCL
	Biopol 401 GN	Monsanto (St. Louis, MO)	Biopol
	Bionolle 3001	Showa Highpolymer (Tokyo, Japan)	Bionolle

to their studies. For example, a simple variation in the water content can lead to a large variation (reaching several orders of magnitude) of mechanical characteristics.

Furthermore, the exploitation of mechanical properties can often be deceiving if the results are objectively presented: the increase of at least one of the properties (i.e., the strength) imposes (in the majority of cases) the reduction of the associated properties (i.e., the strain), and in this way, the material properties are not actually improved.

To be able to compare the different strategies employed to elaborate starchy materials, we propose a graphic tool allowing the direct evaluation of the mechanical properties of starch-based materials. Ultimate performances were gathered for the strength versus the strain with log–log scales. Young's modulus was not been selected because the elastic modulus is not considered a direct image of the cohesion of the system (at a high strain) but evidently is more related to its stiffness at a low strain. Moreover, ultimate strength and strain values are largely available in the literature. Thus, the log–log cartography was used throughout this study to evaluate the materials' performances from the literature and to list the main parameters influencing their mechanical properties at 50–60% RH.

When we considered the numerous tested strategies (e.g., chemical modifications, blends with other polymers, and formulations with different plasticizers or fibers or fillers), some intrinsic reference materials directly reproduced from literature were made to develop an experimental analysis of the bibliography. These reference materials were made with the same methodologies, from the elaboration to the testing method. The conclusion discusses new strategies that arose from this comparative analysis for designing materials in the future.

MATERIALS AND METHODS

Components

Native wheat starch (27% amylose and 73% amylopectin) was provided by Chamtor Co. (Pomacle, France)

and was stored under constant hygrometric conditions before use (57% RH). High-amylose maize starch or Eurylon 7 (70 wt % amylose) was purchased from Roquette (Lestrem, France). Amylose from potato starch was supplied by Sigma–Aldrich (Chemical Abstract Service Registry (CAS) 9005-82-7). Before use, the amylose was dissolved in dimethyl sulfoxide (DMSO) to remove as much complexed *n*-butanol as possible, and then it was intensively washed with water and ethanol to remove DMSO; this was followed by vacuum desorption at 40°C.

Poly(vinyl alcohol) (PVA), a water-soluble polymer, was obtained from Aldrich (Lyon, France). Different molecular weight ranges and hydrolysis rates were used (Table I).

Synthetic biodegradable polyesters were used, and their characteristics are listed in Table I. Glycerol and sodium benzoate were purchased from Avocado Research Chemical, Ltd. (La Tour Du Pin, France), and were used as a plasticizer and a photosensitive adjuvant, respectively. This last additive was used as a starch photocrosslinking agent⁴² in another part of this work.

Film preparation

Casting method

Aqueous starch suspensions (4 wt %) were heated in a high-pressure reactor at 120°C for 20 min, as described by Lourdin et al.⁹ Precise amounts of additives (the plasticizer and sensitizer) were added. The obtained solutions were spread on a hot antiadhesive-coated mold maintained at 60°C. This stage sped up water evaporation and avoided extensive starch retrogradation. The obtained films were transparent and had a regular average thickness of 80 μm .

A similar process was used for glycerol-plasticized starches containing 5 or 10 wt % PVA additive. PVA was first dissolved in water.

All films were stored until equilibrium at a convenient RH at 20°C before they were tested. The atmospheric humidity was controlled by saturated salt solutions at 20°C.⁴³

Extrusion process

Convenient amounts of starch and glycerol were pre-mixed and heated for 45 min at 170°C for plasticizer absorption and water evaporation (the starch water content was previously determined). The dry blend was stirred while the additives were added (water containing an adequate amount of the dissolved additives). The additives were typically water-soluble, that is, sodium benzoate and the selected PVA. The water concentration was 20% on a dried starch basis. The final mixture was then gelatinized into a ribbon by one run through a Scamia three-zone single-screw extruder (Scanex, Crosne, France) (heated at 100, 110, and 115°C) equipped with a slit die (2 cm × 1 mm) heated to 120°C. The mixing screw diameter was 2 cm and had a length/diameter ratio of 11; it was operated at 40 rpm. Because there was no zone of a high shear rate, the preplasticization step was necessary (as discussed previously).

For glycerol-plasticized thermoplastic starches in the presence of 5 or 20 wt % synthetic biodegradable polyesters (nonhydrosoluble polymers), the extrusion process required a preliminary step of polymer solubilization in appropriate solvents (CH₂Cl₂ for BAK and Biopol and tetrahydrofuran for Bionolle and PCL) followed by evaporation *in vacuo*. This polyester powder was then added to the dry blend and extruded under conditions imposed by the added polymer characteristics.⁴

Extruded ribbons were stored at a controlled RH and at 20°C before the mechanical testing.

Conditioning

Starch plates were stored at 57% RH and 20°C in closed chambers over a saturated salt solution (sodium bromide). Each sample was analyzed after 1 week of storage.

Accelerated aging

The aging of starch films was performed in the rubbery state at 20°C and at 80% RH (potassium bromide solution) for 10 weeks; this was followed by 7 days at 57% RH for subsequent tensile testing (water sorption equilibrium).

Mechanical analysis

A tensile test machine (Test 108 2kN, GT-Test Co., Ecoven, France) equipped with a load cell of 500 N was used for the tensile measurements. The strength and strain at break were measured at a crosshead speed of 10 mm min⁻¹ under constant conditions (57% RH and 20°C) in an environmentally controlled chamber. Dumbbell-shaped specimens of the H₃ type were

cut from the extruded or cast plates. Ten replicates were tested for each material, and the average value was reported. The tensile strength was calculated from the initial sample section, which was systematically measured before the mechanical testing.

Film designations

The film nomenclature is as follows. WSG17 was a wheat-starch film plasticized with 17 wt % glycerol. EurG17 was a high-amylose starch film (Eurylon 7) plasticized with 17 wt % glycerol. PVA_xy.z WSG17, where *x* is the percentage of PVA of an average molecular weight, *y* is equal to $M_w/1000$ (where M_w is the weight-average molecular weight), and *z* is the hydrolysis rate, was added to wheat-plasticized starch. The weight percentages of the additives were calculated on a starch basis at 57% RH and on a starch-glycerol basis for sodium benzoate.

SHORT LITERATURE REVIEW

Figure 1 summarizes the strength-strain cartography of numerous mechanical properties extracted from the literature¹⁻³⁰ devoted to plasticization, aging, starch origins, and grafting. A large legend has been required to relate the literature references to the collected experimental data. Figure 1 gathers model systems and complex systems, aged and not aged. Despite the great data dispersion, the majority of the systems are obviously located in the same diagonal area (see the dotted line), descending from stiff and brittle (short strain) materials to soft and noncohesive systems. In fact, all the systems have bad properties, the intermediate ones combining the bad properties of the extreme data, in comparison with the usual synthetic polymers, which are ideally located at both high strengths and strains. The existence of a common area for numerous and very different systems leads to the conclusion that only a few studies have provided actual original systems, with the exception of Zhao's team,^{28,29} whose works are focused on complex systems and are worth being discussed elsewhere.

To clarify the data analysis, we organized the values into different sections corresponding to the developed strategies; that is, the strength-strain figures were divided according to several parameters.

Plasticization and aging

Starch is most often plasticized with water and glycerol.^{2-4,7-9} Depending on the amounts of the added plasticizers, two well-known behaviors are identified in Figure 2(a). (The glycerol addition is followed by a bold arrow for different starch origins: amylose, amylopectin, and potato starch). First, there is an antiplasticization zone for a low additive content, which pre-

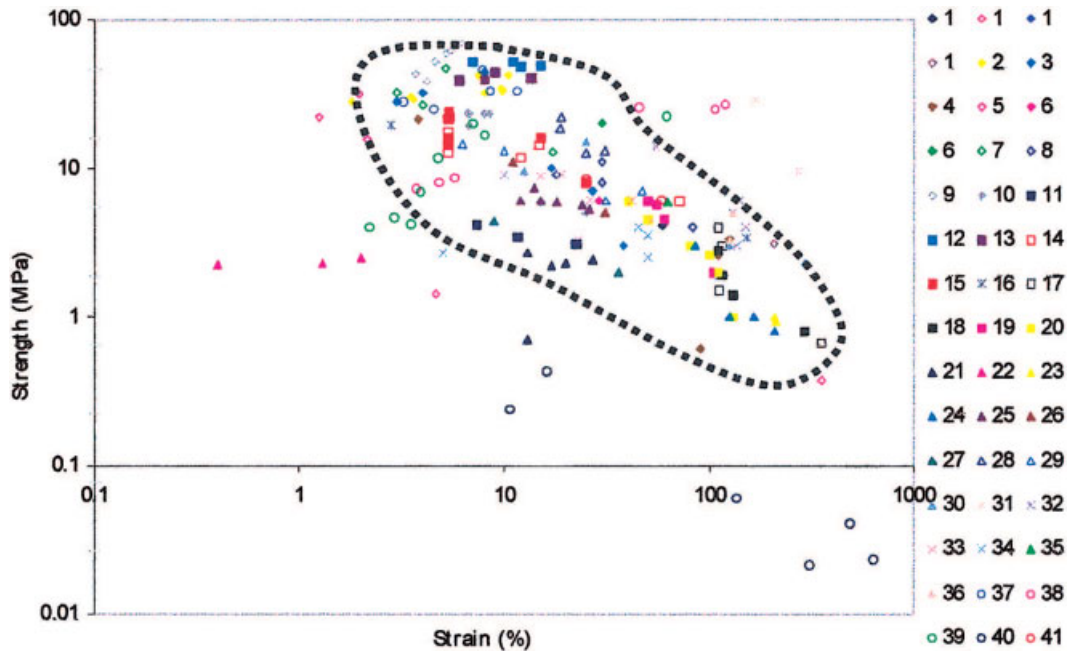


Figure 1 Mechanical properties (strength and strain) of starch-based materials at (1) 55% RH, 20°C, 14 days, and 10 mm/min;¹ (2) 30°C, 4 days, and 20 mm/min;² (3) 57% RH, 25°C, and 48 h;³ (4) 50% RH, 23°C, 50 mm/min, and 2 weeks;^{4,5} (5) 50% RH, 20°C, and 7 days;⁷ (6) 50% RH, 23°C, 2 days, and 10 mm/min;⁶ (7) 50% RH, 20°C, and 7 days;⁷ (8) 60% RH, 20°C, and 10 mm/min;⁸ (9) 57% RH, 25°C, and 2 mm/min;⁹ (10) 57% RH, 25°C, and 2 mm/min;⁹ (11) 57% RH, 25°C, and 2 mm/min;¹⁰ (12) 50% RH, 23°C, and 5 cm/min;¹¹ (13) 50% RH, 23°C, and 5 cm/min;¹¹ (14) 57% RH, 22°C, and 10 mm/min;¹² (15) 57% RH, 22°C, and 10 mm/min;¹² (16) 50% RH, 23°C, and 50 mm/min;¹³ (17) 80% RH, 22°C, and 10 mm/min;¹² (18) 80% RH, 22°C, and 10 mm/min;¹² (19) 50% RH and 20°C;¹⁴ (20) 50% RH and 20°C;¹⁴ (21) 58% RH, 25°C, 14 days, and 10 mm/min;¹⁵ (22) 58% RH, 25°C, 72 h, and 0.2 mm/min;¹⁶ (23) 57% RH, 25°C, 72 h, and 5 mm/min;¹⁷ (24) 57% RH, 25°C, 72 h, and 5 mm/min;¹⁷ (25) 43% RH, 25°C, 14 days, and 50 mm/min;¹⁸ (26) 43% RH, 22°C, 14 days, and 50 mm/min;¹⁹ (27) 50% RH, 23°C, 3 days, and 100 mm/min;²⁰ (28) 54% RH, 23°C, 6 weeks, and 50 mm/min;^{21,22} (29) 54% RH, 23°C, 6 weeks, and 50 mm/min;^{21,22} (30) 54% RH, 23°C, 6 weeks, and 50 mm/min;²² (31) 50% RH, 14 days, and 20 mm/min;²³ (32) 50% RH, 14 days, and 20 mm/min;²⁴ (33) 50% RH, 23°C, and 7 days;²⁵ (34) 50% RH, 23°C, and 7 days;²⁶ (35) 54% RH, 23°C, 6 weeks, and 50 mm/min;^{5,13} (36) 54% RH, 23°C, 6 weeks, and 50 mm/min;⁵⁴ (37) 65% RH, 20°C, 48 h, and 5 mm/min;²⁷ (38) 2.54 mm/min;^{28,29} (39) 2.54 mm/min;²⁸ (40) 65% RH, 21°C, and 10 days;³⁰ and (41) 57% RH, 22°C, and 7 days.¹² [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sents typical strengths of 20–80 MPa and a strain of less than 10%. The antiplasticization phenomenon shows both the strength and strain decreasing when the plasticizer concentration increases up to 10–15%^{3,44} and corresponds to a local macromolecular motion limitation.^{45,46} Second, for larger amounts of the plasticizer, a classical plasticization effect can be obtained that obviously governs the mechanical properties of unaged systems (Fig. 1). This zone can be observed whatever the starch origin is (amylopectin, potato, wheat, tapioca, corn, or amylose). Looking at more greatly plasticized materials [i.e., the long, dotted arrow in Fig. 2(a)], we find that a simple variation of the glycerol content allows a roughly whole description of the descending diagonal previously shown. Thus, very complex systems show approximately the same mechanical properties as the simplest ones (model systems) made only of starch, glycerol, and water. The diagonal previously reported could be considered a master curve and will be discussed again in the Experimental section.

Figure 2(b) shows the influence of physical aging on the properties (the strength increases and the strain decreases) for several systems.^{10–12} This figure also shows that aged materials have higher strength and lower strain whatever the starch origin is [wheat, potato, maize, or amylopectin; the arrows in Fig. 2(b) present the aging influence on the properties with time]. Thus, for lower plasticizer concentrations, the starch materials are glassy and are subjected to physical aging, which is explained by a progressive recovery of a thermodynamically favorable state with an increasing amorphous phase density.⁴⁷ This aging leads to a simple shift in the master curve. This aging is always reported as a problem for starchy materials, but this is undoubtedly of less importance when we consider mechanical property improvements. The aging of materials in the rubbery state leads to morphological modifications (retrogradation), the kinetics of which are increased if the macromolecular mobility is enhanced by the plasticizer contents. The initial mate-

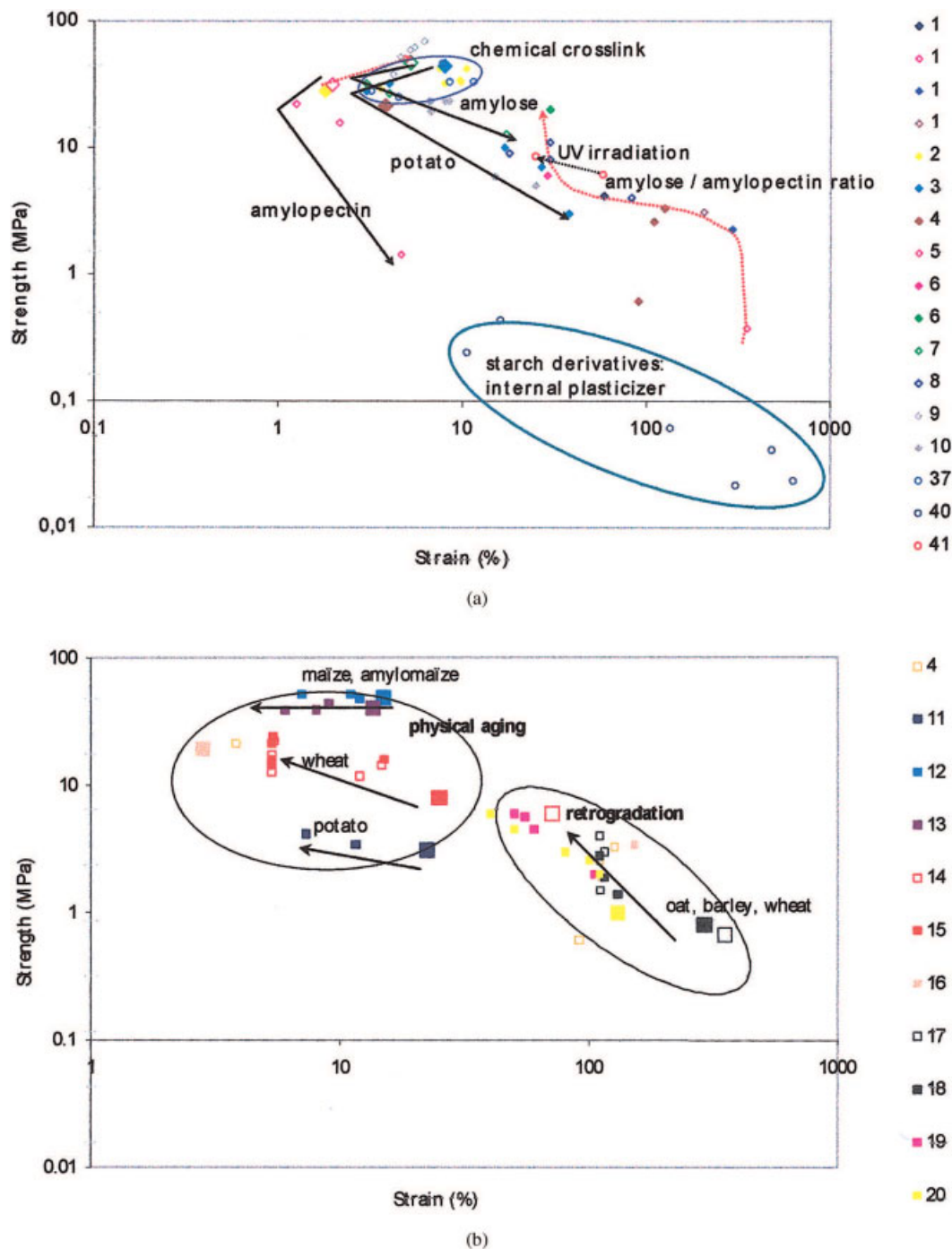


Figure 2 (a) Mechanical properties of starch films as a function of the plasticizer content for several starch origins and internal plasticization (starch derivatives). The added plasticizers are shown by bold arrows, and the increase in the amylose/amylopectin ratio is shown by dotted arrows for a low plasticizer content (small arrow) and for 30 wt % glycerol (long arrow). (b) Influence of aging on starch. The larger symbols represent unaged materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rials are supposed to be amorphous or partially amorphous. As aging occurs, mechanical reinforcement is achieved by crystallite development and is symbolized in Figure 2(b) by convenient arrows (an increase in the aging time).¹²⁻¹⁴ This phenomenon also appears as a simple displacement following the master curve toward less plasticized systems.

Starch derivatives

Chemically modified starch has been developed both to limit hydrophilicity and to graft alkyl chains able to act as internal plasticizers. This second property is an interesting solution to the problem of plasticizer localization, segregation,^{48,49} or migration.³⁰ Concerning

mechanical properties, we find that the literature only reports high grafting rates, which produce rubbery materials, as shown in Figure 2(a). Thus, the macromolecular interactions are weaker than those for more greatly plasticized unmodified starches.

Materials with low grafting rates are not represented in the literature (no mechanical tests), perhaps because they require specific plasticizer systems. Without convenient plasticizer systems, the materials are too brittle and cannot be tested. Highly grafted systems have been investigated to produce mainly hydrophobic starch materials (starch derivatives are mainly grafted with alkyl chains, esters, or ethers).

Crosslinked starch properties are reported in Figure 2(a) (see the UV irradiation arrow and the chemical crosslinking area);^{27,42,50} they are still located near the master curve.

Amylose/amylopectin ratio

A widely studied parameter is the amylose/amylopectin ratio. The idea is that amylose-enriched materials are often mechanically excellent. In the cartography proposed in Figure 2(a), this affirmation can be readjusted. First, two behaviors are reported as a function of the plasticizer content:^{1,7,9} (1) for lower plasticizer contents, an increase in the amylose/amylopectin ratio would improve both the strength and strain because of the linear structure [see the short, dotted line in Fig. 2(a)], and (2) for higher contents, the variation is different and comparable to that of a mechanical reinforcement (the strength increases and the strain decreases; see the long, dotted arrow) when the amylose content is increased. This last tendency is related to fast amylose crystallization in comparison with slower amylopectin retrogradation. Rindlav-Westling et al.⁵¹ reported that the crystallinity of amylose-enriched systems was higher than expected. Morphological and molecular effects are in fact not always clearly distinguished in the literature. The blended systems described by Hulleman¹ presented a surprisingly high strain (300%) for pure amylopectin (0/100), probably because of the specific elaboration conditions. The materials were made stiffer by the addition of amylose to reach, for the 100/0 blend, the common region in Figure 2(a).

In conclusion, the amylose/amylopectin ratio is not a determining parameter for mechanical property improvements (at break) because the data are again positioned undoubtedly close to the master curve.

Starch/polymer blends

Starch/polymer blends have been widely tested and more specifically with high contents of biodegradable polyesters or PVA. The strengths and strains have

generally been enhanced for starch blends containing more than 25 wt % non-starch polymer. In this case, starch or plasticized starch tends to reduce the intrinsic properties of the associated polymer. For lower polymer contents, three systems have been developed (Fig. 3, empty symbols; the arrows represent the increase in the added polymer content):

1. For very incompatible polymers (e.g., polyolefins), the properties are weaker or equal to those of the pure starch reference, even in the presence of a compatibilizing agent.^{52,53}
2. For more or less compatible polymers (e.g., biodegradable polyesters), the polymers act as fillers, the properties developing with a strength increase for an equivalent or lower strain according to the plasticizer content.^{5,13,54}
3. For hydrosoluble polymers (e.g., PVA), the properties are very dispersed. For 10–20 wt %, the properties are roughly equivalent to those from the addition of 25% polyesters at high glycerol rates. For lower plasticizer contents, the property gain is lower. Unfortunately, for these compatible systems, it is surprising to see the absence of studies at a very low concentration (<10 wt %).

In summary, the heterogeneous systems are characterized by interfacial compatibilization problems. The materials are then mechanically weak or are modestly improved for the most compatible associated phases. Only PVA seems to be slightly out of the master curve. This study excludes all systems containing more than 25% added polymer, and so the blend strategy remains deceiving because all the systems behave in the same region close to the master curve and thus can also be mimicked by a simple plasticizer action (Fig. 3).

Fillers and fibers

Other additives have been selected for their ability to develop specific interactions with the starch matrix. Cellulosic fibers and mineral fillers have been used.^{15,18–22} Generally, fillers or fibers at a concentration of 15–30 wt % are incorporated into starch materials (Fig. 3, full symbols; the arrows correspond to the increase in the filler and fiber contents). For cellulosic fibers and mineral fillers, a classical reinforcing effect has been observed, and most of the results follow a simple mixing law.^{19,21,22} The materials with a low cellulose whisker content¹⁵ show more promising behavior, with an increase in both the strength and strain; the system cohesion is improved, and the good quality of the created interface and fiber–fiber interaction effects are shown. Concerning mineral fillers, the obtained properties

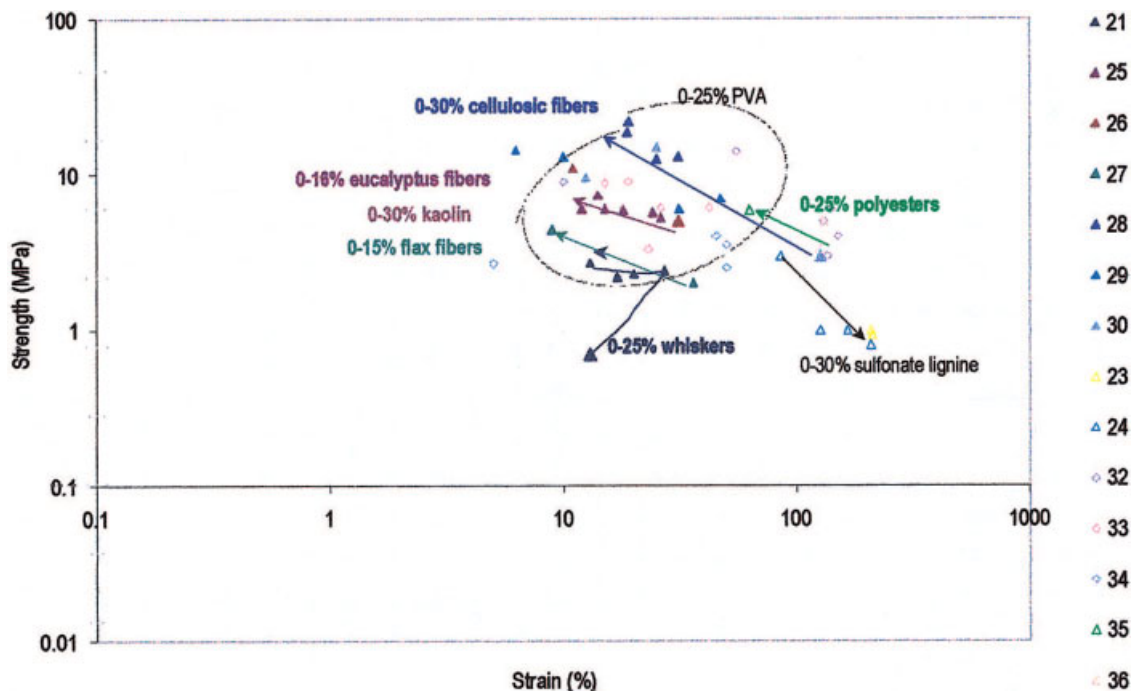


Figure 3 Mechanical properties of starch/additive blends. The PVA and biodegradable polyesters are indicated by empty symbols, and the mineral charges and fibers are indicated by filled symbols. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are sometimes inconsistent¹⁸ and will be discussed elsewhere, but they generally show a classical reinforcing effect.

Partial conclusion

Among the large number of strategies devoted to starch material development or more cognitive research, it is obvious that no ideal material has been proposed (actual strength–strain improvements). If the material formulations are sometimes very complex, no really original approach has been developed.

More amazingly, most of the systems show ultimate mechanical properties rather close to those obtained with a simple modulation of the plasticizer content, whatever the starch origin is. This result is important and merits development through experimental analysis.

Indeed, as the collected data shown in Figure 1 are very dispersed, it is worth wondering if this heterogeneity is due (1) to the strategies themselves, which are very numerous, leading effectively to slightly different mechanical systems, or (2) to the experimental methodology, which is extraordinarily varied in the literature.

To answer this point, we undertook an experimental analysis of the bibliography by scrupulously reproducing reference systems from the literature with the same methodology (e.g., same film-forming

processes, sample geometries, RH, and aging conditions).

EXPERIMENTAL

Reference curve of wheat-starch plasticization

Wheat-starch films were plasticized with glycerol (5, 17, 22, or 30 wt %) and were mechanically tested at two RH values (57 and 80%). The results are presented as log strength/log strain curves, which show a classical plasticization behavior at 57% RH [Fig. 4(a), dotted line]: a regular strength decrease and a strain increase. This dotted line curve is repeatedly used as the reference curve, and all others materials are compared to this curve, which is the internal reference of this work. A monotonous decrease can be observed even at a low plasticizer concentration (WSG5 data). The absence of an anti-plasticization effect, probably due to the film processing conditions,³ is discussed later.

The second curve (bold line) was obtained at 80% RH and was compared to the curve at 57% RH. Indeed, the whole plasticizer concentration (water and glycerol) increased at 80% RH. The observed turning point also occurred earlier than that at 57% RH. These results can be interpreted with the support of water sorption isotherms performed for pure starch and glycerol starch blends.^{7,49,55} It is known that glycerol addi-

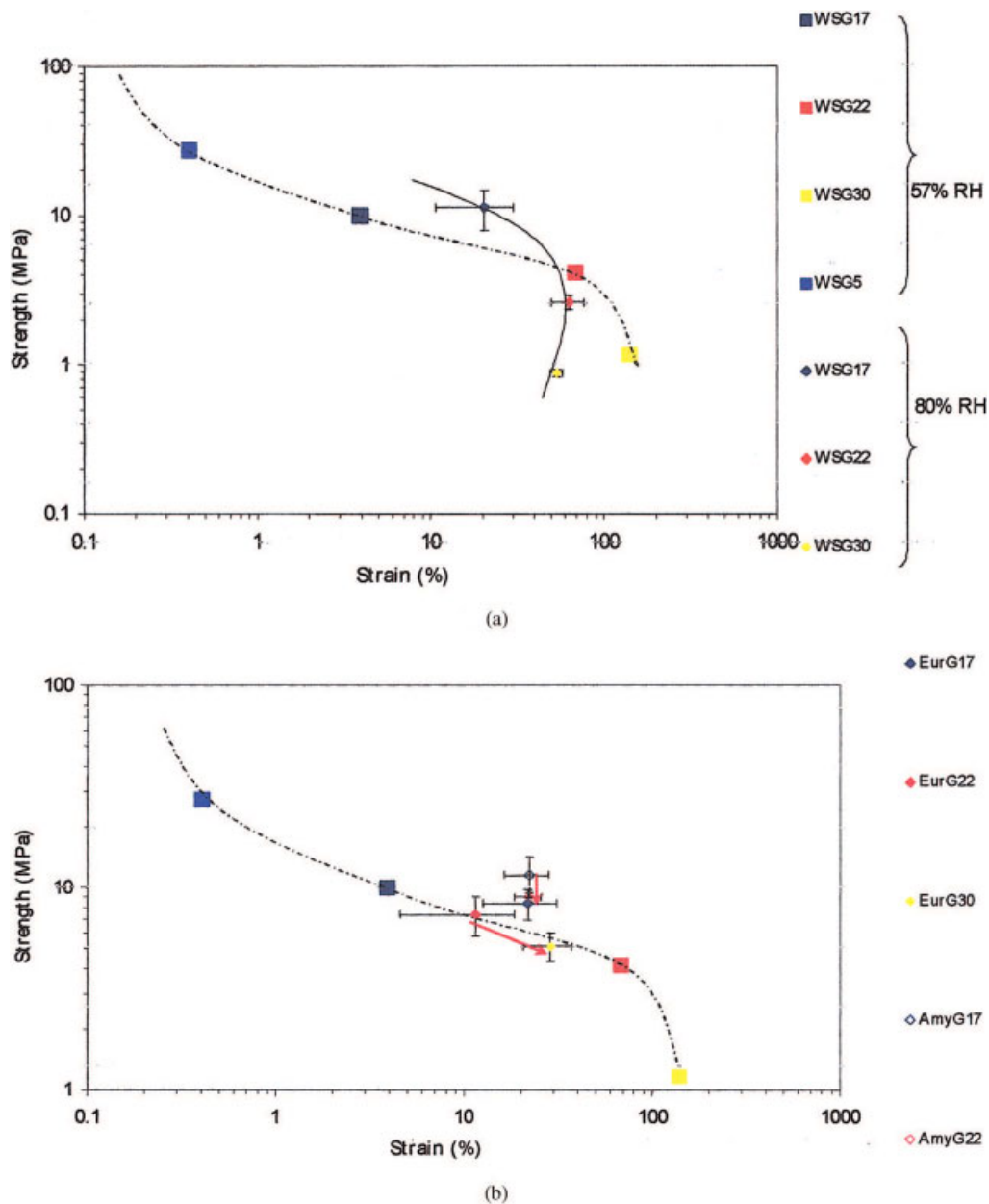


Figure 4 Mechanical properties of (a) wheat-starch-based films plasticized with 5, 17, 22, or 30 wt % glycerol and conditioned at (---) 57 or (—) 80% RH and (b) glycerol-plasticized, high-amylose starch films (70 or 100 wt %) conditioned at 57% RH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion reduce starch water uptake until around 60% RH because of the establishment of a competition between the water sorption sites. At a higher RH, glycerol is specifically hydrated, and the water uptake is then directly correlated to the amount of this hydrophilic plasticizer,^{49,51} which can be considered to be available. In fact, Lourdin et al.⁴⁸ previously reported the existence of phase separation in starch glycerol blends. More precisely, glycerol-enriched microdomains, able to be preferentially hydrated, have to be considered.^{7,55} The loss of mechanical properties can then be attributed to the presence of such microdomains, to the detriment of system

cohesion. The more hydrated the system is, the more premature the turning point.

Influence of the amylose/amylopectin ratio

The mechanical properties at 57% RH are described in Figure 4(b) for glycerol-plasticized, amylose-enriched systems [70 (Eurylon) or 100 wt % amylose]. The materials were plasticized with 17, 22, or 30 wt % for Eurylon and 17 or 22% for pure amylose. The plasticizing effect (shown by the arrows) was lower than that for the amylopectin-enriched systems that gave

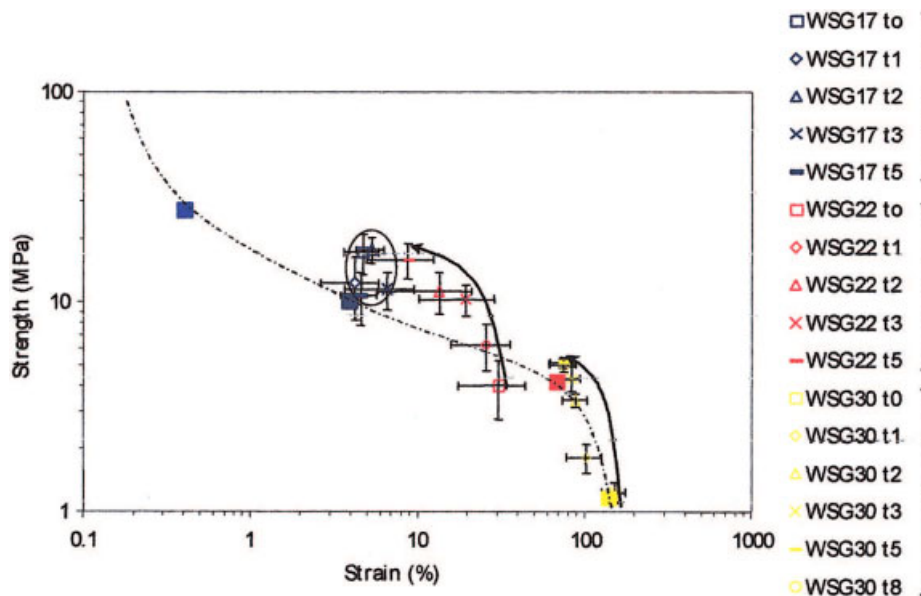


Figure 5 Mechanical properties of glycerol-plasticized, wheat-starch-based materials after 8 weeks of aging by retrogradation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the reference curve (superimposed dotted line). Two interpretations are possible: (1) the turning point for amylose is earlier because of higher glycerol phase separation^{51,55} and (2) amylose crystallization (also generating free glycerol) renders the materials less sensitive to plasticization.

Starch system retrogradation

The retrogradation impact on the mechanical properties is presented in Figure 5 for reference systems WSG17 to WSG30. As crystallization occurred (see the arrows), the strength increased and the strain decreased for all the systems (22 and 30 wt % glycerol), except that with 17% glycerol, which presented only a slight change with time after 5 weeks of aging. The WSG5 system is not shown because it was too brittle to be tested under good conditions. As previously observed in the first part of this study, the aged system properties followed the reference curve. Considering the experimental errors, we superimposed all data.

In Figure 6, the amylose-enriched systems show the same behavior with similar changes, in comparison with the reference curve. As for wheat starch, the system plasticized with 17 wt % glycerol showed no change; only the EurG22 and EurG30 systems are presented. The high-amylose starch systems were equivalent and are not shown.

As previously shown, the aged systems showed properties close to those of the reference curve.

Starch/polymer blends

The starch/polymer blends were reproduced from the literature, and the mechanical properties are displayed

in Figure 7. The amounts of the additive polymers, PVA and biodegradable polyesters (BAK, PCL, Biopol, and Bionolle; Table I), were chosen to be equal to 5 and 10 wt %. For PVA, several molecular weights and hydrolysis degrees were tested. In Figure 7, the data obtained for the polyesters and PVA are delimited and labeled. The tested polyester data are situated near the reference curve and thus are of limited interest. In contrast, for more compatible PVA (a water-soluble polymer), the systems seem to stand slightly apart from the reference curve. However, the properties were only moderately modified, and no evident correlations can be made as a function of the molecular weight or hydrolysis degree.

DISCUSSION

A comparison of the data from Figures 4–7 (obtained with the same methodologies and formulations found in the literature) with those of the same systems taken from Figure 1 is shown in Figure 8. The data dispersion observed in Figure 1 is solely due to the extraordinarily varied operating modes employed. This conclusion validates the ongoing conclusion, that the mechanical properties at break are entirely defined by a simple reference curve obtained by the variation of the glycerol content, whatever the studied system is. Although the methodology adopted in this study is also open to criticism (because other specific aspects of materials, e.g., the process, the initial crystallinity, and other RH values, are not explored), the obtained data clearly reveal that starch material development has been stagnant (for the majority of the authors, including us) and is well defined by plasticization action.

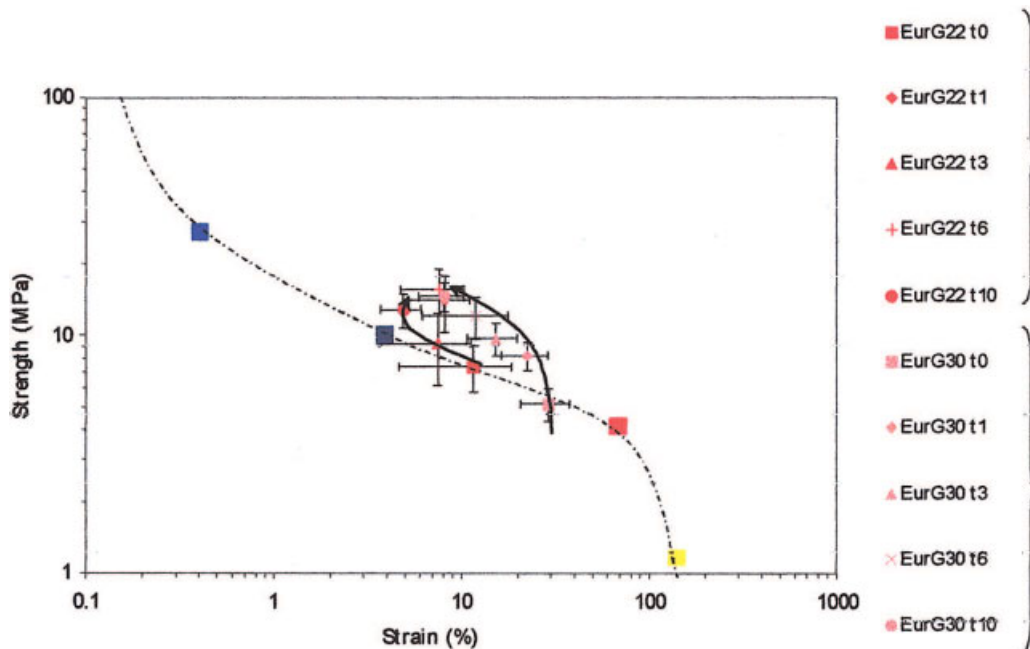


Figure 6 Mechanical properties of glycerol-plasticized, high-amylose, starch-based materials after 10 weeks of aging by retrogradation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This review and the complementary experimental section show that every strategy developed to improve the mechanical properties of starch has failed. However, data were only collected and recorded be-

tween 50 and 60% RH and could exclude interesting systems performed at higher or lower RH values.

The ultimate properties of every system are equivalent to those reported for very simple ternary systems

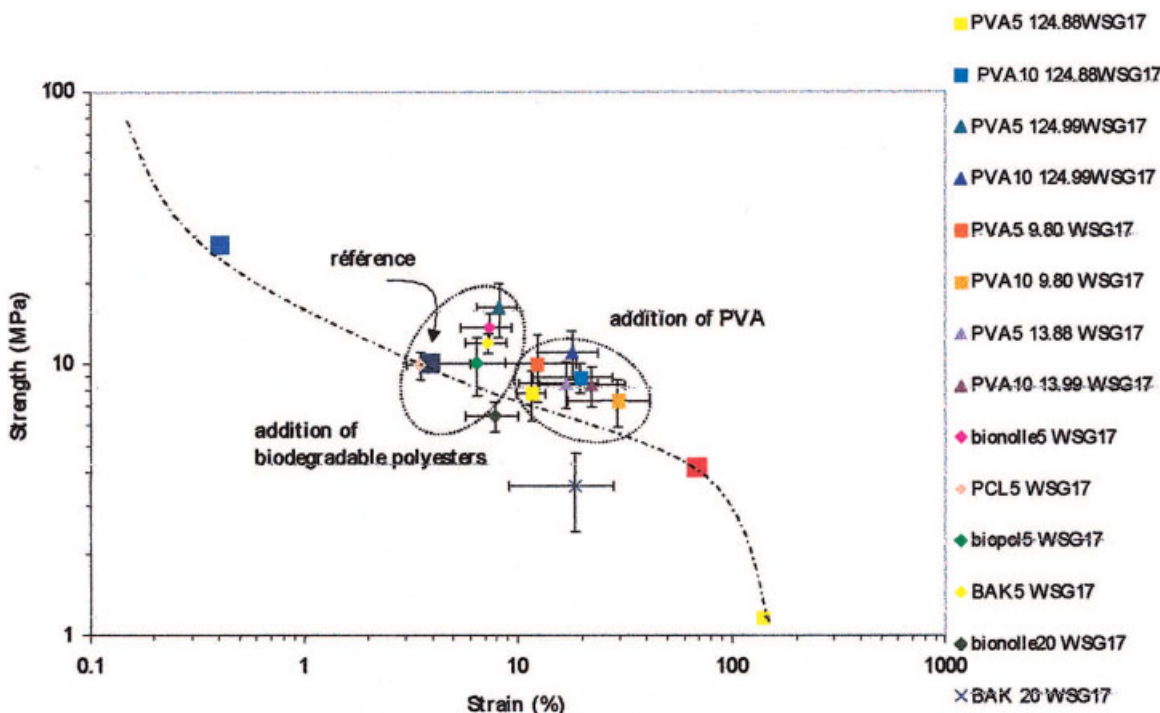


Figure 7 Mechanical properties of starch/PVA and starch/polyester blends at 57% RH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

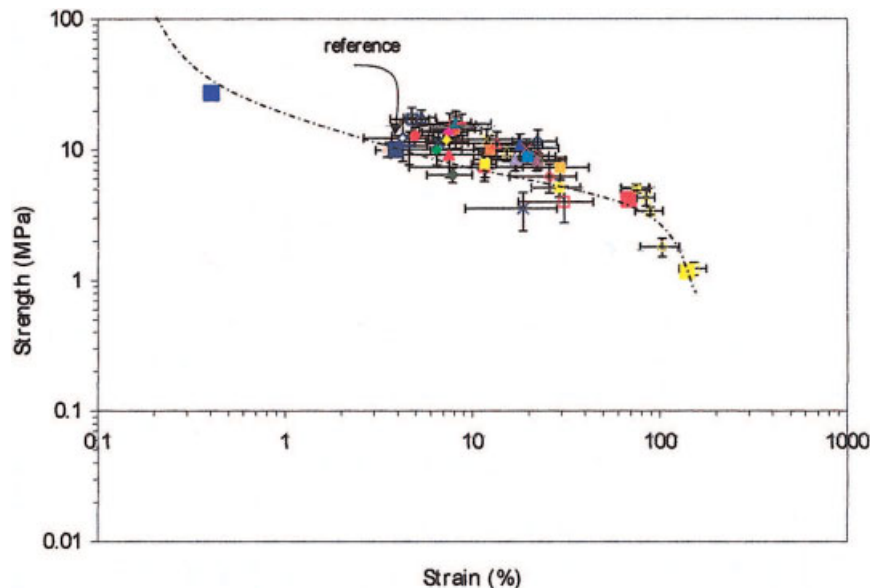


Figure 8 Mechanical properties with respect to a plasticization master curve of systems reproduced from the literature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(water, starch, glycerol), whatever the complexity is of the studied materials:

1. The addition of amylose and other polymers (except PVA) does not improve the mechanical properties.
2. The plasticizer system is a recurrent problem remaining to be solved to avoid fast phase separation and hydration at higher RH values.
3. Aged materials are similar to those with a plasticizer loss (note that the development of starch materials merits more attention than this secondary phenomenon).

The existence of a master curve is difficult to explain. This behavior could be related to a family of common break criteria (a common area of failure initiation).

Because of the great range covered by the strain at break over the whole reference curve, different types of failure criteria must be imagined before strategies of starch mechanical improvement can be envisioned. Figure 9 is a scheme drawn to propose strategies adapted for different zones of the reference curve.

Zone 1

Zone 1 concerns low plasticizer contents with a low strain at break. In this domain, no sollicitation of long-distance interactions between macromolecules occurs. Improving the mechanical properties is equal to modifying short-distance interactions. Some starch derivatives (e.g., hydroxyethyl derivatives) have been tested in this way by the grafting of spacer groups. PVA oligomers or oligosaccharides may correspond to this strategy with simple blends.

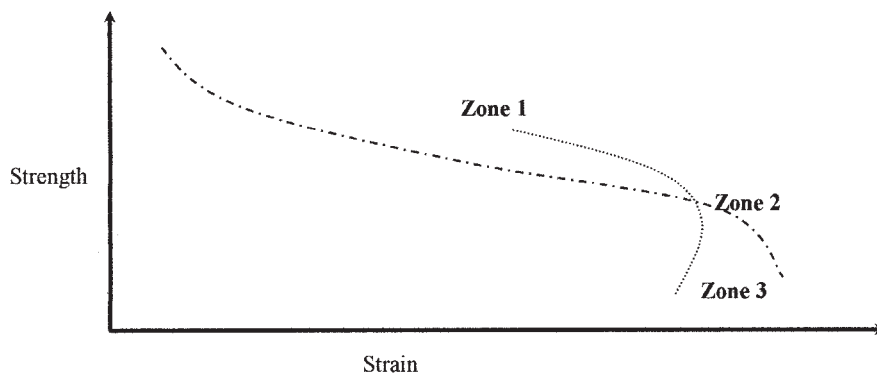


Figure 9 Characteristics of master curve domains.

Zone 2

The elongation in this zone is much higher, and long-distance interactions (entanglements) play a major role. In this area, the macromolecular geometry is deleterious. Starch macromolecule skeletons have to be modified to increase the ratio of the linear chain. The best way is not to lean toward pure amylose materials because (1) a high crystallinity rate is associated with a low strain, (2) entanglements can be favored by a slight branching rate, and (3) original strategies can be developed through a controlled crystallization process that cannot be achieved by rapid amylose organization. For example, the studies of Zhao et al.^{28,29,56} could be a starting point for such a strategy.

Zone 3

The turning point has been interpreted as property loss due to glycerol-enriched microdomains. A new family of plasticizer systems (e.g., polysaccharide oligomers) less sensitive to water and allowing delayed phase separation should be tested.

Testing these different perspectives (including chemical skeleton modification) should be helpful in developing the new strategies presented in the literature that consist of *in planta* starch modification.^{57,58}

References

- Hulleman, S. H. D.; Janssen, F. H. P.; Feil, H. *Polymer* 1998, 39, 2043.
- Chang, Y. P.; Cheah, P. B.; Seow, C. C. *J Food Sci* 2000, 65, 445.
- Lourdin, D.; Bizotand, H.; Colonna, P. *J Appl Polym Sci* 1997, 63, 1047.
- Averous, L.; Fringant, C. *Polym Eng Sci* 2001, 41, 727.
- Averous, L.; Moro, L.; Dole, P.; Fringant, C. *Polymer* 2000, 41, 4157.
- Rindlav-Westling, A.; Stading, M.; Hermansson, A.-M.; Gatenholm, P. *Carbohydr Polym* 1998, 36, 217.
- Myllärinen, P.; Partanen, R.; Seppala, J.; Forssell, P. *Carbohydr Polym* 2002, 50, 355.
- Van Soest, J. J. G.; Borger, D. B. *J Appl Polym Sci* 1997, 64, 631.
- Lourdin, D.; Della Valle, G.; Colonna, P. *Carbohydr Polym* 1995, 27, 261.
- Lourdin, D.; Colonna, P.; Brownsey Geoffrey, J.; Noel Timothy, R.; Ring Stephen, G. *Carbohydr Res* 2002, 337, 827.
- Shogren, R. L.; Jasberg, B. K. *J Environ Polym Degrad* 1994, 2, 99.
- Delville, J. Ph.D. Thesis, University of Reims, 2001; p 311.
- Martin, O.; Averous, L. *Polymer* 2001, 42, 6209.
- Forsell, P. M.; Hulleman, S. H. D.; Myllärinen, P.; Moates, G. K.; Parker, R. *Carbohydr Polym* 1999, 39, 43.
- Angles, M. N.; Dufresne, A. *Macromolecules* 2001, 34, 2921.
- Baumberger, S.; Lapiere, C.; Monties, B.; Della Valle, G. *Polym Degrad Stab* 1998, 59, 273.
- Baumberger, S.; Lapiere, C.; Monties, B.; Lourdin, D.; Colonna, P. *Ind Crops Prod* 1997, 6, 253.
- De Carvalho, A. J. F.; Curvelo, A. A. S.; Agnelli, J. A. M. *Carbohydr Polym* 2001, 45, 189.
- Curvelo, A. A. S.; De Carvalho, A. J. F.; Agnelli, J. A. M. *Carbohydr Polym* 2001, 45, 183.
- Wollerdorfer, M.; Bader, H. *Ind Crops Prod* 1998, 8, 105.
- Averous, L.; Fringant, C.; Moro, L. *Starch* 2001, 53, 368.
- Averous, L.; Fringant, C.; Moro, L. *Polymer* 2001, 42, 6565.
- Stenhouse, P. J.; Mayer, J. M.; Hepfinger, M. J.; Costa, E. A.; Dell, P. A.; Kaplan, D. L. In *Biodegradable Polymers and Packaging*; Ching, C.; Kaplan, D.; Thomas, E., Eds.; Technical: Lancaster, PA, 1993; p 151.
- Mao, L.; Imam, S. H.; Gordon, S. H.; Cinelli, P.; Chiellini, E. *J Polym Environ* 2000, 8, 205.
- Liu, Z.; Feng, Y.; Yi, X.-S. *J Appl Polym Sci* 1999, 74, 2667.
- Park, E. H.; George, E. R.; Muldoon, M. A.; Flammino, A. *Polym News* 1994, 19, 230.
- Rioux, B.; Ispas-Szabo, P.; Ait-Kadi, A.; Mateescu, M. A.; Juhasz, J. *Carbohydr Polym* 2002, 50, 371.
- Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B. *Chem Mater* 1998, 10, 804.
- Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B. *Chem Mater* 1998, 10, 794.
- Gros, A. T.; Feuge, R. O. *J Am Oil Chem Soc* 1962, 39, 19.
- Bertoft, E. *Carbohydr Res* 1991, 212, 229.
- Durrani, C. M.; Donald, A. M. *Polym Gels Networks* 1995, 3, 1.
- Gallant, D. J.; Bouchet, B.; Baldwin, P. M. *Carbohydr Polym* 1997, 32, 177.
- Gidley, M. J. In *Gums and Stabilizers for the Food Industry*; Phillips, G. O.; Williams, P. A., Eds.; Oxford University Press: New York, 1992; p 87.
- Hizukuri, S. *Carbohydr Res* 1986, 147, 342.
- Imberty, A.; Perez, S. *Biopolymers* 1988, 27, 1205.
- Goodfellow, B. J.; Wilson, R. H. *Biopolymers* 1990, 30, 1183.
- Inaba, H.; Hatanaka, Y.; Adachi, T.; Matsumura, Y.; Mori, T. *Carbohydr Polym* 1994, 24, 31.
- Keetels, C. J. A. M.; Oostergetel, G. T.; van Vliet, T. *Carbohydr Polym* 1996, 30, 61.
- Russell, P. L. *J Cereal Sci* 1987, 6, 133.
- Van Soest, J. J. G.; De Witand, D.; Vliegthart, J. F. G. *J Appl Polym Sci* 1996, 61, 1927.
- Delville, J.; Joly, C.; Dole, P.; Bliard, C. *Carbohydr Polym* 2002, 49, 71.
- Weast, R. C. *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1986.
- Jackson, W. J.; Caldwell, J. R. *J Appl Polym Sci* 1967, 11, 211.
- Benczedi, D.; Tomka, I.; Escher, F. *Macromolecules* 1998, 31, 3055.
- Lourdin, D.; Bizot, H.; Colonna, P. *Macromol Symp* 1997, 114, 179.
- Perez, J. *Physique et Mécanique des Polymères Amorphes*; Edition Tec & Doc: Paris, 1992.
- Lourdin, D.; Ring, S. G.; Colonna, P. *Carbohydr Res* 1998, 306, 551.
- Lourdin, D.; Coignard, L.; Bizot, H.; Colonna, P. *Polymer* 1997, 38, 5401.
- Delville, J.; Joly, C.; Dole, P.; Bliard, C. *Carbohydr Polym* 2003, 53, 373.
- Rindlav-Westling, A.; Stading, M.; Gatenholm, P. *Biomacromolecules* 2002, 3, 84.
- Raj, B.; Annadurai, V.; Somashekar, R.; Rajand, M.; Siddaramaiah, S. *Eur Polym J* 2001, 37, 943.
- Ramkumar, D. H. S.; Bhattacharya, M.; Vaidya, U. R. *Eur Polym J* 1997, 33, 729.
- Averous, L.; Fauconnier, N.; Moro, L.; Fringant, C. *J Appl Polym Sci* 2000, 76, 1117.
- Follain, N. Ph.D. Thesis, University of Reims, 2003; p 350.
- Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B. *Chem Mater* 1998, 10, 784.
- Gérard, C.; Planchot, V.; Colonna, P.; Bertoft, E. *Carbohydr Res* 2000, 326, 130.
- Planchot, V.; Gérard, C.; Colonna, P. *Biofutur* 1999, 192, 40.