

Thermoplastic Starch/PVAI Compounds: Preparation, Processing, and Properties

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ABSTRACT: As a renewable and native polymeric material, thermoplastic starch is gaining increased acceptance because of resource and environment concerns. This study reports the formulation design of native starch/polyvinyl alcohol (PVAI) compounds; the preparation technology to make them available for thermoplastic processing; and their rheological, mechanical, and degradation properties. Among various plasticizers investigated, a mixture of glycerin and water (50/50 wt %) is found to be the best one for the compounds in terms of rheological behavior, mechanical properties, and environmental stability. The mechanical properties do not increase with the PVAI content to an expected extent, mainly due to the poor interface adhesion between the fibrous PVAI structure and the starch matrix. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2667–2673, 1999

Key words: starch; PVAI; thermoprocessing; rheological behavior; mechanical properties

INTRODUCTION

There is currently a revival of worldwide interest in the use of biopolymers for applications in which synthetic polymers have traditionally been the materials of choice. Materials of interest include different synthetic or biosynthetic polymers,¹ as well as plant-based polymers such as starch and pectin. Such polymers may be biodegradable and recyclable and, therefore, may help satisfy increasing consumer and regulatory demands for materials with these properties.

Physical incorporation of granular starch as a functional additive or filler into synthetic poly-

mers by plastic processing is well known as the first generation of starch compounds. In the 1990s, technology began to focus on thermoprocessing of starch-based compounds without any petrochemical polymers with conventional equipment. Thus, thermoplastic starch (TPS), cited as the second generation of starch plastics, has been developed.^{2–4} Commercially available products of this kind of plastics include Novon and Mater-Bi.^{5–9} In addition to starch, the latter serial products marketed by Novamont may contain polycaprolactone, poly(ethylene vinyl alcohol), as well as cellulose acetate, depending on the specific application. The presence of these less-moisture-sensitive biopolymers, at least, can prevent the material from becoming soft or brittle in changing atmospheric conditions.^{10,11}

PVAI, a water-soluble and biodegradable polymer, has three distinct chain configurations: iso-

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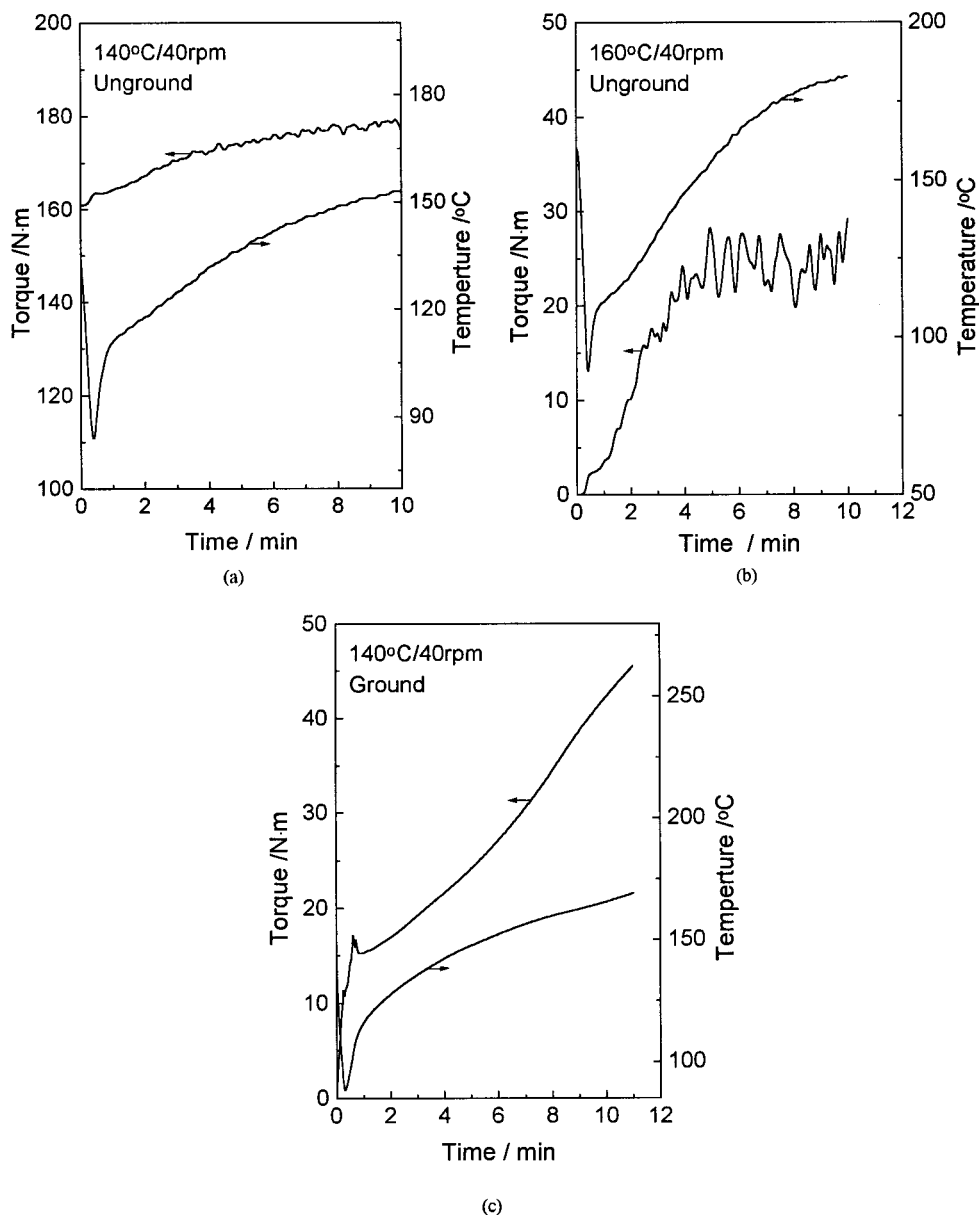


Figure 1 Plastographs of SPVA (20% PVAL, 12% glycerin): (a) unground mixture, 140°C/40 rpm; (b) unground mixture, 160°C/40 rpm; (c) ground mixture, 140°C/40 rpm.

tactic, heterotactic, and syndiotactic, which determine the melting point of the polymer ranging from 224 to 246°C. Basically it is hard to melt-process PVAL because its thermodegradation temperature is slightly higher than its melting temperature. Therefore, PVAL has frequently been used in solution form as, for example, in soluble gel and solution spinning. Since the 1980s, thermoplastic starch/PVAL has been studied primarily for producing films by means of casting and calendaring,¹²⁻¹⁶ and starch-based loose-fillers or foam plates as a replacement for expanded polystyrene.^{17,18} In general, the presence of PVAL im-

proves mechanical strength, weatherability, and water resistance of the starch/PVAL material. However, from an economic viewpoint, solution processing is likely unacceptable mainly due to the additional high processing cost and low efficiency in comparison to thermoplastic processing.

Our work presents the preparation, characterization, and properties of a starch/PVAL (SPVA) compound. The objective of the work is to develop an economic and ecological technology to prepare and melt-process the compound through conventional processing techniques.

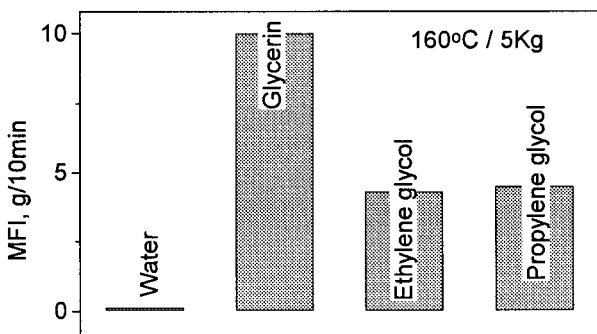


Figure 2 Effect of various plasticizers on the MFI of SPVA (15% PVAI, 12% plasticizer).

EXPERIMENTAL

Wheat starch; PVAI (17-99F), which had a degree of polymerization of 1700 and a degree of saponification 99 mol %; and LLDPE (DNDA 7144) were supplied by domestic companies (Xiaoshan Starch Plant, Jianxi Chemical Co., and Qilu Petrochemical Co., China, respectively). Glycerin, ethylene glycol, propylene glycol, and distilled water were used as received.

Starch, PVAI, and plasticizer were first mixed using a high-speed mixer (GH-1000, Beijing Plastics Device Co., China), and the mixtures were then immediately sealed in polyethylene bags. The thermoprocessability was studied using a HAAKE Rheocord 90 (HAAKE, USA) with a rotating speed of 40 rpm for the ground and ungrounded mixtures. The grinding was done at 130–135°C for approximately 10 min using a double-roller (Shanghai Machinery & Mold Co.,

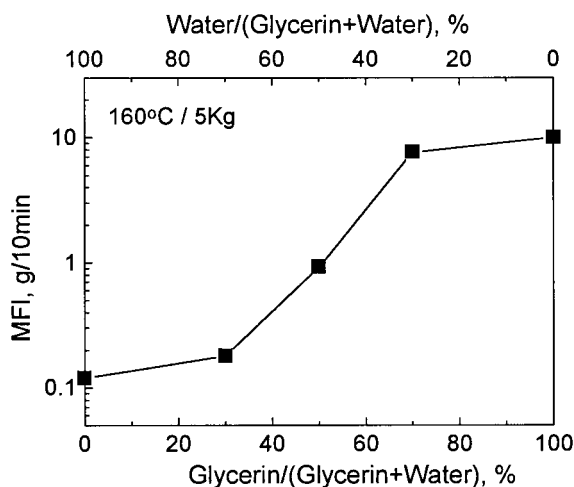


Figure 3 Effect of the water/glycerin ratio on the MFI of SPVA (15% PVAI, 12% mixed plasticizer).

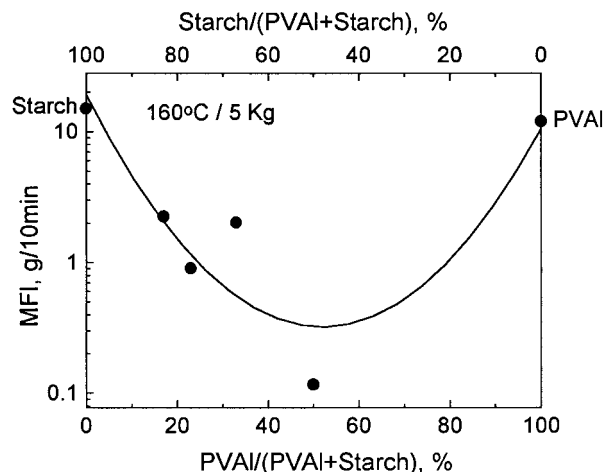


Figure 4 Effect of the PVAI/starch ratio on the MFI of SPVA (12% mixed plasticizer of 50/50 water/glycerin).

China) with a space of 0.5–2 mm. Next, the prepared powders were extruded and pelletized using a degassing single screw extruder line (SJ20A×25, $\phi = 20$ mm, length/inside diameter (L/D) = 25 (Shanghai Machinery & Mold Co., China)) at a barrel temperature profile of 160–180°C. The as-processed pellets were sealed immediately, also in polyethylene bags. Compounding starch with 19% LLDPE was implemented through extrusion and pelletization under the same conditions.

Melt flow index (MFI) was measured at 160°C with XRZ400 equipment (Scientific Instruments Co., Jilin University, China) using a load of 5 kg,

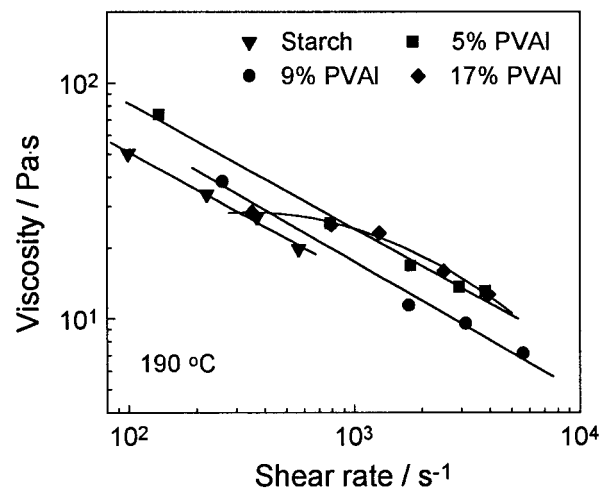
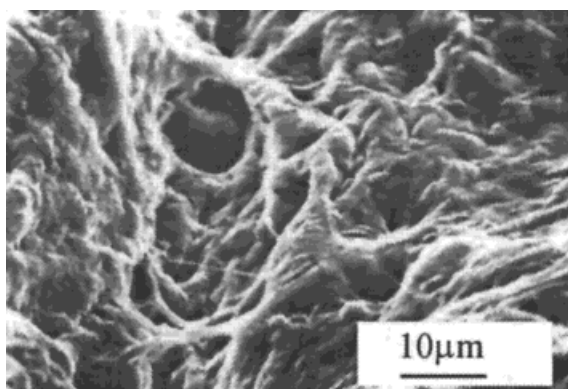


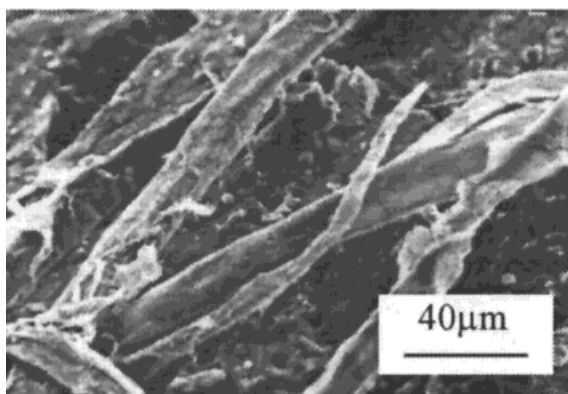
Figure 5 Effect of the PVAI content on the melt viscosity of SPVA (12% mixed plasticizer of 50/50 water/glycerin).

according to ASTM D 1238-86. Rheological measurements were carried out using a capillary rheometer equipped with a capillary of an inside diameter (D) of 1 mm and a length (L) of 5 mm, giving an L/D value of 5. Three other capillaries with the same diameter, but with L/D values of 10, 20, and 40, were used for Bagley correction for the end effect and Weissenberg–Rabinowitsch correction.¹⁹ A temperature profile of 150/170/190°C, with an accuracy of 0.5°C, was adopted with the barrel for all the formulations to be measured.

Tensile tests were performed with a WSM-2000 digital test machine (Changchun, Institute of Applied Physics, China) at ambient environment (23°C, 70% relative humidity), according to ASTM D 638-87. The standard tensile specimens were injection-molded using an SZ-60/40 injection molding machine (Zhejiang Plastics Machinery Co., China). The melt and the mold temperatures were kept at 175 and 35°C, respec-

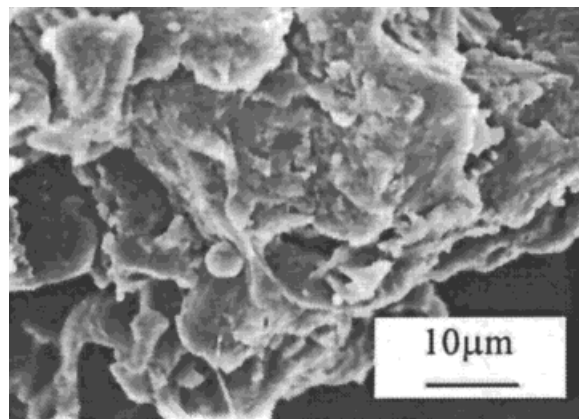


(a)

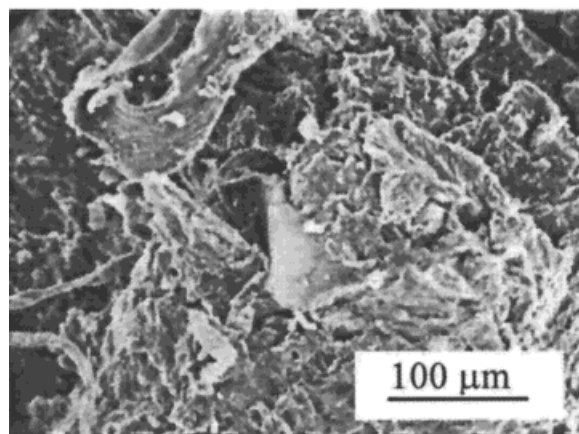


(b)

Figure 6 SEM photographs of SPVA containing 13% PVAL: (a) skin section; (b) core section.



(a)



(b)

Figure 7 SEM photographs of SPVA containing 19% PVAL: (a) skin section; (b) core section.

tively, for all the moldings. The as-processed moldings were immediately sealed in polyethylene bags and stored at ambient temperature for more than 1 week prior to further tests.

A JSM-T20 scanning electron microscope (JEOL Co., Japan) was used to examine phase morphology evolution in the extruded strands of SPVA and starch/LLDPE compounds. Fracture surfaces were prepared in liquid nitrogen. The direction of the fracture was perpendicular to the flow direction. Gold coating the fracture surfaces was implemented using a JFC-1100 ion sputter (JEOL Co., Japan).

The environmental stability of the tensile specimens was measured by weight gain at ambient environment (23°C, 70% relative humidity). The moisture sorption was restricted to the weight on the dry base, regardless of the original water in the plasticizers used for the specimens.

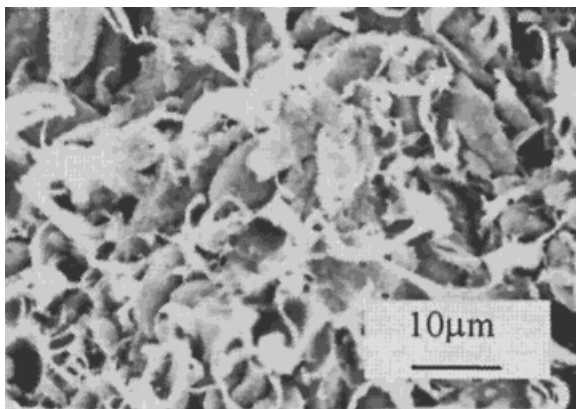


Figure 8 SEM photograph of starch/LLDPE (19% LLDPE).

RESULTS AND DISCUSSION

Figure 1 illustrates the plastographs of an SPVA compound having 20% PVAI. It is found that the ungrounded mixtures cannot be well plasticized and molten either at 140°C or at 160°C [Fig. 1(a) and (b)], although the processing at 160°C does reduce the input energy. However, for the mixture preground by a double-roller, the torque curve becomes smoother and exhibits a viscosity improvement effect [Fig. 1(c)]. The strong shear stress during the grinding, although apparently useful to compress plasticizers into both PVAI and starch, in the meanwhile destroys portions of their crystalline structures.

Flow Ability

Figure 2 reports the effect of various plasticizers on the melt flow index (MFI) values at 160°C. Obviously, of the investigated plasticizers, good flow ability is best promoted by glycerin, and least by water, which is mainly due to the different numbers of hydroxyl groups on their molecules. Using the mixtures of water and glycerin as plas-

Table I Effect of Various Plasticizers on Mechanical Properties of SPVA^a

Plasticizer	Tensile Strength (MPa)	Strain at Break (%)
Water	10.0	12
Ethylene glycol	2.0	22
Propyl glycol	3.0	22
Glycerin	6.2	29

^a At 15% PVAI, 12% plasticizer.

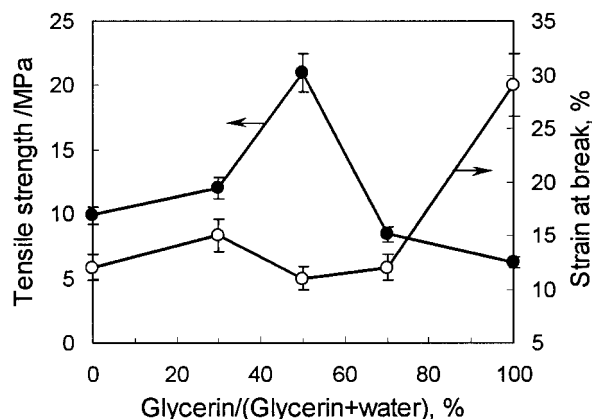


Figure 9 Effect of the water/glycerin ratio on the tensile properties of SPVA (15% PVAI, 12% mixed plasticizer).

ticizers resulted in a relatively complicated flow behavior. The plot of MFI against the glycerin content in the mixed plasticizer looks like a leaning S-shaped curve, as shown in Figure 3. The 50/50 ratio of the water/glycerin plasticizer falls on the intermediate point by the superposition rule. Compounds for further studies, therefore, were all prepared with this mixed plasticizer.

Figure 4 shows the MFI values of the SPVA compounds against the PVAI content. Either adding PVAI into starch or starch into PVAI decreases the MFI value, indicating a lowering effect on flow behavior. This negative deviation effect suggests a phase-separation behavior in the system.²⁰

The viscosity increment, due to the presence of PVAI, is also demonstrated in Figure 5. All the PVAI-loaded flow curves indicate higher viscosity

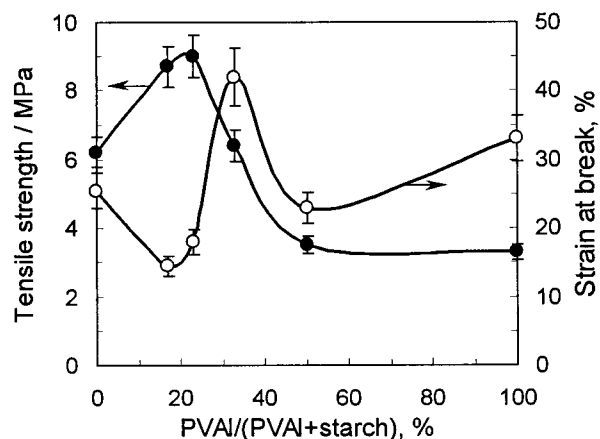


Figure 10 Effect of the PVAI/starch ratio on tensile properties of SPVA (12% mixed plasticizer of 50/50 water/glycerin).

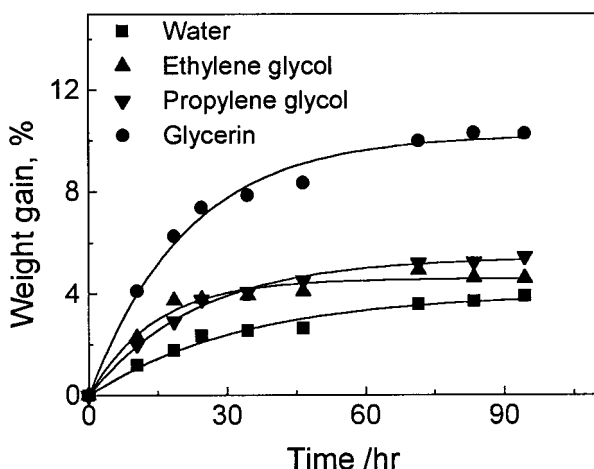


Figure 11 Effect of various plasticizers on the weight gain of SPVA (15% PVAL, 12% plasticizer).

levels than those of the starch. However, the influence of the PVAL content on the viscosity increment is complicated. The consistency study of the rheological data (which for the sake of brevity is not presented here) tells that the PVAL thickening effect will be altered for the SPVA compound containing PVAL higher than 9%. Nevertheless, flow behavior of the compound does not follow power law, probably due to alternation in the continuous/discrete phase composition.²⁰

Morphology

SEM micrographs in Figure 6 and Figure 7 reveal that the phase structure in the compounds seems to be less changed for the PVAL content of both 13% and 19%. The starch component still forms the continuous phase and the PVAL still forms the discrete, networklike phase, particularly in the skin area [Fig. 6(a)]. The cavities were probably formed during the processing. In the center area [Fig. 6(b)], relatively long PVAL fibers of approximately 18 μm diameter are found. They were apparently poorly embedded in the starch matrix, which should be responsible for the poor mechanical properties. An apparently homogeneous structure occurred for the compound containing 19% PVAL both in the skin and center areas. Interestingly, the morphology evolution in our investigations is opposed to that reported of the surface of starch/PVAL foams,¹⁸ in which swollen starch granules were embedded in a matrix of PVAL.

In comparison to the starch/polyethylene compound, in which intact granular starches (gray ellipsoidal particles) were embedded in the poly-

ethylene matrix (Fig. 8), it is conceivable that PVAL may be partially compatible with starch. This can also be confirmed by the comparable affinity of their solubility parameters: $23.4 (\text{J}/\text{cm}^3)^{1/2}$ for PVAL and $22.8 (\text{J}/\text{cm}^3)^{1/2}$ for starch.

Tensile Properties

Table I presents the tensile properties of the SPVA compounds with various plasticizers. It is clear that water causes high stiffness and glycerin leads to high ductility. Thus, it can be expected that the tensile properties can be balanced by using a mixed plasticizer of water and glycerin.

Investigations on compounds using the water/glycerin plasticizers show that both the tensile strength and the strain at break deviate from the superposition rule, negatively for the strain and positively for the strength (Fig. 9). A maximum strength is found at a water/glycerin ratio of 50/50. Moreover, it is noticed that the strain at break hardly varies with the glycerin ratio lower than 70%. This may suggest that the antiplastication effect of the water/glycerin mixture on TPS²¹ disappears in the presence of PVAL.

The effect of the PVAL content on the tensile properties of the compounds is shown in Figure 10. The compound is quite brittle at a PVAL level of 18% and becomes comparably ductile at a PVAL level of 26%. In between, a maximum strength value exists at a PVAL level of 20%. According to these curves, a suitable composition for required tensile properties can be chosen.

Environmental Stability

Figure 11 shows weight gains of the specimens exposed to an open ambient environment. Obvi-

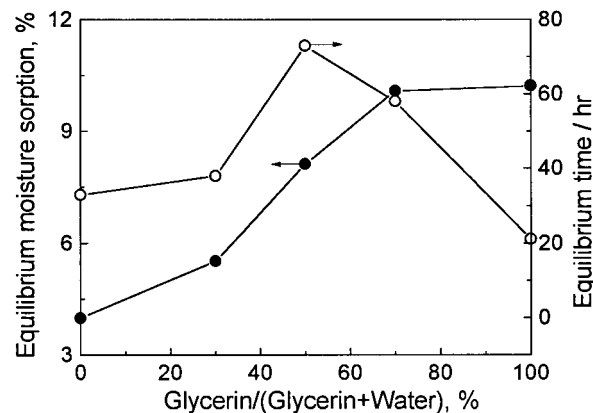


Figure 12 Effect of the water/glycerin ratio on the equilibrium moisture sorption and equilibrium time of SPVA (15% PVAL, 12% mixed plasticizer).

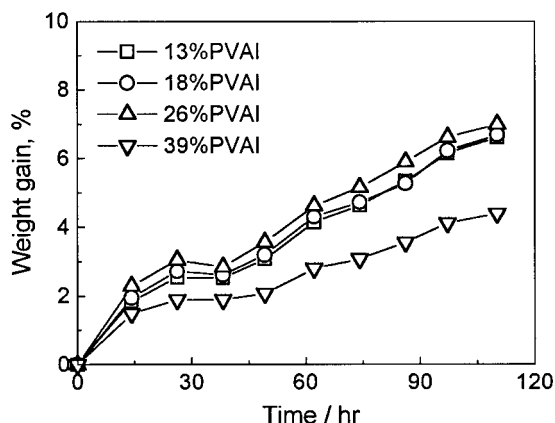


Figure 13 Effect of the PVAL content on the weight gain of SPVA (12% mixed plasticizer of 50/50 glycerin/water).

ously, the moisture take-up behavior depends significantly on the type and the content of the plasticizer used. Glycerin is well known to be much more moisture sensitive than other plasticizers studied, because it has many more hydroxyl groups per units.

Using the mixed plasticizer, the moisture sensitivity depends in turn on the water/glycerin ratio (Fig. 12). It is supposed that neither water nor glycerin in the mixed plasticizer is free due to the hydrogen-bonding interaction between their molecules.²² The bound molecules may function like a plasticizer with large molecular weight, thereby making the plasticizer easier to hydrogen bond with starch. As a result, improvements in the plasticating efficiency and the equilibrium moisture sorption may be achieved. By the positive deviation of the equilibrium time from the superposition rule, Figure 12 also reveals that the moisture sensitivity can significantly decline by using the water/glycerin plasticizer.

The initial objective of incorporating PVAL into starch was to improve the mechanical properties and minimize the moisture sensitivity. In this study, the latter has been reached. Figure 13 shows a relatively low moisture take-up (less than 10%) in the SPVA compounds. The PVAL content seems to have little effect on the moisture take-up, due to the promising effect of the plasticizer.

CONCLUSIONS

To obtain good processability, glycerin is much more effective than water as a plasticizer for the SPVA compounds, but it sacrifices tensile strength and water barrier properties. To balance these

properties, a mixture of glycerin and water (50/50 in weight) was hence suggested as the optimum plasticizer for the compound. Incorporation of PVAL into starch can enhance the mechanical properties, although the melt viscosity is increased as well. However, improvement in the mechanical properties is limited, mainly due to the poor interface adhesion between the fibrous PVAL structure and the starch matrix. Using the mixed plasticizer, compound composition can be preliminarily designed and balanced regarding both the processing condition and rheological and mechanical properties.

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