Properties of Fatty-Acid Esters of Starch

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SYNOPSIS

This work examines the properties of starch esters for their possible application as environmentally degradable thermoplastics. The rheological, thermal, and mechanical properties of a series of fatty-acid esters of high-amylose starch (as well as the effects of adding plasticizer on some selected properties) were evaluated. The ester group acts like an internal plasticizer, with an increase in the size of the fatty-acid chain, resulting in greater internal plasticization. This is reflected in the rheological and thermal measurements as well as in the mechanical properties. Overall, larger ester groups and the addition of external plasticizer make these starch-based materials more processable and more ductile. However, comparing their properties and cost to commodity thermoplastics leads us to believe that their commercial applications are likely to be limited, at least in the near future. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Starch or its components have been generally found to be unsuitable for use by themselves in applications requiring reasonable mechanical integrity. For example, even though films of pure amylose (prepared by a solvent-casting procedure) were found to be self-supporting and to possess a high tensile modulus, they were only somewhat flexible and displayed a very low ultimate tensile extension.[1] In addition, due to the hydrophilic nature of amylose, the wet strength of these films was also found to be quite low. Addition of amylopectin was found to adversely affect the flexibility, tensile strength, and elongation to break.

Because the derivatization of the glucosidic hydroxyl groups can be carried out with relative ease, various kinds of chemical modifications of starches have been attempted along this route in order to modify their chemical and physical properties. Changes in these properties are highly dependent upon the nature of the chemical group that is appended to the hydroxyl groups, and the extent of the derivatization. This has found diverse applica-

tions such as the modification of the gelatinization behavior of granular starches, control of the gelling and retrogradation of amylose-containing starches, and increasing the hydrophilicity of starches as well as imparting hydrophobic or ionic character through incorporation of suitable moieties.[2] The modification of the interaction of starch–solvent interactions, and concomitantly, the solution properties of starch (or its components) is relatively easily achievable with the addition of a small number of chemical groups. In fact, for many industrial applications, only a low level of chemical modification is generally needed to suitable alter the properties of starch; most commercially used starches generally have a degree of substitution (D.S.) less than 0.2.[2] (D.S. is defined as the moles of substituents per D-glucopyranosyl structural unit of the starch polymer; with three hydroxyl groups per unit, the theoretical maximum D.S. is 3). High levels of substitution, on the other hand, can completely transform the character of starch. This is true not only of starch but of most polysaccharides; for example, a variety of highly substituted cellulose esters have been used for various applications since the last century.[3,4]

A number of reports exist in literature pertaining to the preparation of esters of starch or its components with high degrees of substitution with the ultimate aim of significantly modifying the physical—

chemical properties of starches, and imparting suitable mechanical characteristics such as to render them more useful as engineering materials than the pure precursors. Reactions on starches to prepare highly substituted derivatives are not easy, mainly because of the almost impossible proposition of dissolving granular starch in a suitable medium without significant degradation. Among the various methods of ester preparation that have been attempted to overcome this hurdle are the gelatinization pretreatment of starch,[5] dispersion in inert solvents at elevated temperatures,[6,7] and at room temperatures.[8] The addition of the ester group is carried out by employing the appropriate acid anhydride or the acid chloride (with the latter generally being more effective for the higher esters) in the presence of pyridine, which serves the dual purpose of catalyst as well as solvent.

Mullen and Pacsu[9] briefly evaluated the properties and potential industrial applicability of some corn starch esters. They found that although starch esters such as the butyrate and caproate can be molded, their general mechanical properties were not very satisfactory. Addition of plasticizer was found to remedy the situation somewhat. Wolff et al.[10,11] prepared triesters of amylose, amylopectin, and corn starch and evaluated some of their physical characteristics in greater detail. The properties of the molded products or cast films from amylopectin and starch esters were found to be generally unsatisfactory, consistent with the work of Mullen and Pacsu.[9] On the other hand, it was found that the amylose esters could be molded quite easily at elevated temperatures and pressures, with reasonably strong and tough products; these esters also gave satisfactory films upon casting from solution. Wolff et al. also observed that the melting points of amylose esters were higher than that of their amylopectin counterparts, with the respective whole starch esters falling in between. It was also seen that the esters were amorphous as prepared, but heating the amylose esters, or orienting them by stretching at an elevated temperature, resulted in some crystallinity as detected by x-ray diffraction. (In fact, properties of fibers prepared from amylose triacetate were found to be significantly improved by secondary drawing,[12,13] presumably due to increased crystallinity.) The ultimate tensile strength of fatty-acid esters of amylose decreased with increasing length of the acyl group, a trend similar to that observed for cellulose. However, the amylose esters were found to be consistently weaker than the respective cellulose esters. The ultimate tensile extension of these

derivatives displayed a fluctuating, but generally increasing trend. The water permeability of the amylose esters also decreases with increasing size of the ester group, which is attributable to the higher hydrophobicity of the higher esters.[7] Mixed esters of amylose were also found to be promising in terms of manipulation of their physical and chemical properties.[14] This body of literature suggested that the properties of pure amylose esters approach those of the cellulose esters, but the properties of the esters based on unfractionated starches were clearly inferior to their cellulose counterparts. This was attributed to the presence of a significant amount of branched amylopectin present in most commercial starches (for example, up to 70% or 100% in corn starches). For this reason, industrial utilization of highly substituted starch esters was deemed undesirable; amylose esters did show some promise but the high costs of amylose fractionation from starch precluded its use as a raw material for derivatization, especially given its lack of advantage over cellulose.

The increasing emphasis on environmentally degradable polymers coupled with recent work indicating that highly substituted polysaccharides can be degraded (albeit slowly) in the natural environment under the action of microorganisms[15,16] has caused a renewed interest in starch derivatives. Among the various derivatives of starch, starch esters probably merit the closest reexamination, because they seem to be suitable candidates for potentially replacing nondegradable thermoplastics for certain applications. Keeping in mind the past work in this area, it seems clear that amylopectin is undesirable as a fraction in the starch due to its adverse impact on mechanical and physical properties of these derivatives. Pure amylose seems to be the most desirable precursor for the starch–ester-based thermoplastics, though the expensive steps involved in the fractionation and purification of amylose would add substantially to the cost of these materials. However, a compromise is offered by the availability of high-amylose varieties of starch that contain dominant fractions of amylose. Utilization of these raw starch materials could provide suitable properties for the resulting esters, yet the high amylose content should obviate the need for any major purification steps. Moving along this line of thought, this work focuses on fatty acid esters of a high-amylose starch. C_4–C_6 esters were utilized in this study, because they have been shown to be easily moldable, and reasonably tough as opposed to the more brittle lower esters. The esters were prepared by an acid chloride reaction route. Subsequently, the rheolog-

ical properties of the neat esters, and the thermal and mechanical properties of the neat as well as plasticized esters were evaluated.

EXPERIMENTAL

Preparation of Esters

The basic material used in this study was a purified high-amylose starch (Sigma Chemical Co., A-7043), consisting approximately of 70% amylose and 30% amylopectin. The esterification of this starch was carried out by the method of Gros and Feuge.[7] This method was used in preference to the others reported in literature, because it allowed a larger scale of synthesis, with almost complete derivatization, i.e., approaching D.S. = 3, and was claimed to lead to minimal degradation. The general method of synthesis was as follows: 0.1 mol of starch (on a repeat unit basis, i.e., 16.2 grams) was dried overnight in a vacuum oven at about 80°C to minimize its moisture content. This starch was then placed in an Erlenmeyer flask, and 200 mL of dioxane and 50 mL of pyridine were added. This flask was then placed in an oil bath at 100°C, with a magnetic stirrer being used for continuous vigorous mixing. Two hundred milliilters of toluene mixed with 0.45 mol of the corresponding acid chloride was then added to the flask. The flask was sealed after fitting it with a condenser, and flushing it with nitrogen. The reaction was allowed to continue for 6 h at constant temperature.

While allowing the reaction mixture to cool down, part of the volatiles were removed by stripping under low pressure. After the remaining mixture had cooled down, it was poured with vigorous stirring into a dish containing a mixture of ethanol and ice water. The derivatized starch (generally yellowish in color, probably partly due to pyridine impurities) eventually floated to the surface, and was removed subsequently. To purify the polymer, it was immersed in an ethanol bath for a few days, and finally washed thoroughly with hot water. (The ethanol, though not a solvent for these esters, does swell them.)

These materials were utilized as such in the rheological studies, while thin films of the samples were cast from suspension of these polymers in chloroform for all the other studies. For plasticized samples, dibutyl phthalate (10% by weight of the polymer) was added to the solution before casting. The cast films were placed in an air stream for at least 48 h before all testing to allow the residual solvent to evaporate.

Characterization of the Esters

The extent of the derivatization was measured using elemental analysis to obtain the carbon and nitrogen content of the product, as well as by saponification according to the alcoholic–alkali saponification procedure described by Genung and Mallatt.[17]

Rheological Measurements

The rheological measurements on the esters were obtained with a capillary viscometer (Instron Model 3210 Rheometer coupled with a Model 4505 series Universal Testing Instrument) where the material was molten in a barrel. The barrel assembly was then moved upwards at a fixed velocity and the force exerted by a plunger at the top pushed out the material through the capillary. The Rabinowitsch correction factor was applied to account for the non-Newtonian velocity profiles of the molten blends. The true shear rate at the capillary wall was obtained from the product of this correction factor and the apparent shear rate. The ratio of the wall shear stress and shear rate yielded the melt viscosity at that shear rate. A stainless steel capillary (internal diameter, D, 0.762 mm and length, L, 50.8 mm; L/ D = 66.7) was used in this study. The viscosity of each of the esters was measured at three temperatures in order to get an estimate of their flow activation energy.

Thermal Analysis

The calorimetric studies on the neat and plasticized esters were carried out on a differential scanning calorimeter (Perkin–Elmer DSC 7 with subambient operation capability). The tests were carried out on about 5–10 mg of the sample (cast films) placed in standard crimpable aluminum pans. The first heat for the samples was initiated at −10°C at a heating rate of 10°C/min. At the end of the heating run, the sample was cooled at a rate of 10°C/min until the temperature of the sample was brought down back to −10°C, at which point the second heat was initiated (with the same parameters as the first heat). Additional runs were also carried out with just the first heat for most samples, as were some simple annealing experiments for the unplasticized esters.

Dynamic Mechanical Analysis

The tensile dynamic mechanical analyses were carried out an a Seiko DMS 200 instrument. Films of the neat and plasticized esters of thickness 0.2–0.3

mm, cut to a width of 0.6–0.7 mm approximately, were utilized in the testing (thinner samples tended to slip from the grips). The distance between the grips was set at 10 or 15 mm, depending upon the cross-sectional area of the sample such that the ratio of the testing length to the film cross-sectional area was at least 5. The amplitude of the elongation was 5 μm, and the measurements were made at frequencies of 1, 2, 5, and 10 Hz. The testing was initiated at −100°C with the temperature being ramped up at 2°C/min; the test was continued until failure or significant necking of the sample. This generally happened in the region of 80–120°C for the unplasticized esters, and 60–100°C for the plasticized films.

Mechanical Testing

For the tensile mechanical testing, films of the esters (both plasticized and unplasticized) of thickness of the order of 0.1–0.2 mm were utilized. Strips of the films were cut using a razor blade; these strips were then mounted on rectangular cardboard frames using cyanoacrylate adhesives or epoxy (the former is preferable because it is less viscous and easily spreads; however, the cyanoacrylate ester monomer seemed to dissolve the starch butyrate). For the testing, the frames were held at the top and bottom in pneumatic grips such that the length of the polymer strip was along the direction of extension. Subsequent to this, lateral cuts were made in the vertical sides of the frame, such that the load would be borne only by the sample during the tensile testing. The eventual testing was carried out at a constant rate of grip separation on an Instron Model 4505 Universal Testing Machine, with a load cell of 2000 g. The data were collected using the Instron Mechanical Testing Series IX program, and reanalyzed using a graphics program (Kaleidagraph 3.0.1, Abelebeck Software) to account for the initial variations in the stress due to any slight misorientation or slack in the films. The nominal gauge length of the samples was 25.4 mm, and the extension rate was 2.54 mm/min for the modulus determination (as indicated in ASTM D 882-91[18]). Grip speeds of 2.54 and 12.7 mm/min were used to examine the ultimate tensile strain, and maximum nominal stress values as a function of the strain rate. At least five specimens were utilized for measurements at each condition.

RESULTS AND DISCUSSION

After purification, the esters were white or slightly off-white in color. As mentioned earlier, these esters do not form true solutions in solvents such as trichloroethylene, chloroform, and trichloroethane, but result in stable suspensions instead. This has also been noted by a number of other workers for various higher amylose esters (e.g., Mullen and Pacsu,[5] Gros and Feuge[7]).

The films of the starch butyrate ester were quite smooth and lustrous, and very stiff. However, these films were also very brittle, and displayed easy and rapid crack propagation. The starch valerate and hexanoate films were less shiny and slightly less brittle by comparison, but sometimes these films (especially if they were thicker, approximately 0.3 mm) also exhibited a tendency to snap while being bent or cut. Addition of the dibutyl phthalate plasticizer resulted in a significant increase in the pliability of all the starch ester films, though the plasticized butyrate ester was still noticeably stiffer than the other two plasticized esters.

Extent of Conversion

The results from the elemental analysis and the alcohol alkali saponification procedure matched reasonably, although the alcoholic alkali saponification procedure indicates slightly higher levels of conversion. These results indicate that almost complete conversion was reached for all the three esters (D.S. > 2.8).

Rheological Behavior

The viscosity data for the starch esters are shown in Figures 1(a–c). These indicate that for the range of shear rates covered by the capillary viscometer the molten esters are in the power-law regime. It is only for the starch hexanoate at 170°C that the appearance of a possible constant-viscosity regime is seen (though it should be noted at these higher temperatures and the low shear rates, the viscosity of the starch hexanoate melt is very low, and the shear stress is at the limits of experimental measurements achievable with the capillary rheometer). As the size of the hydrophobic side group is increased, for any given shear rate at a given temperature, the viscosity drops quite dramatically. The slopes of the viscosity vs. shear rate plots for the butyrate and valerate esters are close to each other, though greater than that of the hexanoate ester. Because the derivatization procedure was the same for the three esters (same temperature, duration, concentration of reagents), we assume that the amount of degradation of the starch during the reaction is similar. This would indicate that the changes in the behavior of
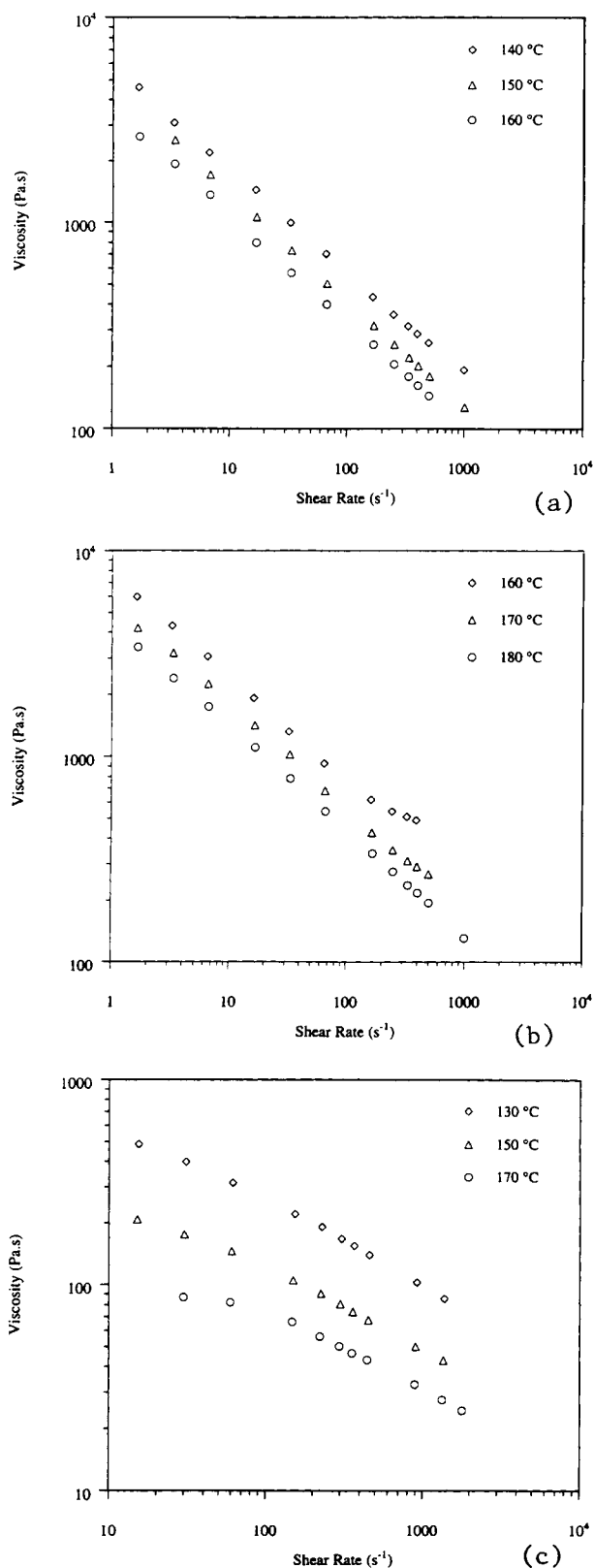
Figure 1   Viscosity as a function of shear rate for high-amylose starch esters: (a) starch butyrate; (b) starch valerate; (c) starch hexanoate.

Table I   Flow Activation Energy for Starch Esters, and for Plasticized, Neat High-Amylose (Hylon VII) Starch

Sample	$\Delta H/R$ (K)
Starch butyrate	5480
Starch valerate	4750
Starch hexanoate	5350
Hylon 7	4250

the esters melts (especially the gross differences in their viscosities) is mainly attributable to the internal plasticization provided by these esters, as well as due to the changes in the conformation of the starch molecules caused by these bulky side groups.

The viscosity, η, of plasticizer-containing starches has been found to have power law dependency on the shear rate, γ, and an Arrhenius dependence on the temperature, T.[19] (Studies have also showed a dependence on the moisture content, but that is not relevant for these hydrophobic ester.) The general form of this relationship is:

$$\eta = m\dot{\gamma}^{(n-1)}\exp(\Delta H/RT)$$

where m is the consistency index, n is the power-law exponent, and ΔH is the flow activation energy. In our case, because the measurements indicated that we were operating in the power-law regime, the flow activation energy could be obtained from a series of measurements at different temperatures for the same material. The average values of the flow activation energy for the three esters are shown in Table I, along with the value for neat high-amylose (Hylon VII) starch pellets that were prepared through extrusion processing with addition of external plasticizers (glycerin and water) (see Villar et al. 1994[19]). (To be more specific, the starting material for that experiment was a physically modified Hylon VII, but we expect it to be quite similar to the starch precursor for our derivatization reaction.) It can be seen that the overall values of the flow activation energy of the starch esters do not change much with the ester-group size; the values are also close to those of the neat Hylon VII, which seems to indicate that the flow activation energy is relatively insensitive to the plasticizer type and level.

Thermal Behavior

The data for the neat and plasticized starch esters are given in Table II, while the salient features of the thermal behavior of the neat and plasticized

Table II   DSC Data for Neat and Plasticized Starch Esters

	First Heat			Second Heat	
Sample	Melting Point (°C)	T_{g1} (°C)	T_{g2} (°C)	Melting Point (°C)	T_g (°C)
Starch butyrate	—	74	48	—	65
Starch butyrate (plasticized)	∼ 117	∼ 39	—	∼ 116	∼ 26
Starch valerate	124	64	42	—	63
Starch valerate (plasticized)	∼ 95	∼ 35	—	∼ 95	∼ 18
Starch hexanoate	91	49	41	—	50
Starch hexanoate (plasticized)	∼ 72	∼ 36	—	∼ 72	∼ 20

starch esters are best illustrated by the DSC plots for starch valerate shown in Figure 2. [For brevity, only figures from starch valerate (the middle ester in our series) are shown for the thermal, dynamic mechanical, and mechanical behavior since the results of the data are tabulated for these measurements.] The starch valerate and hexanoate esters were found to display an endothermic peak (at about 124 and 92°C, respectively), though the starch butyrate does not display any endotherm. Other studies in literature on pure amylose esters have indicated the presence of some crystallinity for all three of these derivatives. In addition, the melting point observed in our studies are lower than the ones reported for the pure amylose counterparts.[20,21] These differences between our starch esters and those based on pure amylose may be attributable to the long-chain branching in the amylose fraction in our sample, and the presence of a significant fraction (≈ 30%) of amylopectin. This should lead to a reduction in the ability to form crystals, as well as the formation of less perfect crystals. It is also possible that the butyrate ester does not provide enough of an internal plasticization to allow crystal formation during the casting of films from solution. It was also found that the crystalline structure does not reappear in the second heat of our heat-cool-heat experimental cycle. However, annealing (subsequently to melting) at temperatures above the glass transition point, and below the melting point led to reappearance of the starch valerate and hexanoate endotherms.

The glass transition temperatures for these materials also display a curious behavior. For the first heat, the glass transitions for films of the unplasticized esters (cast from solution) display two distinct glass transitions close to each other, the one at the higher temperature generally also being of a larger magnitude. As with the melting points, the glass transition temperatures for our esters are lower

than those reported by Cowie et al.[20] for the corresponding amylose esters. It is possible that the derivatized amylopectin and amylose molecules might be phase-separating to some extent in the cast films. Given that the (almost) linear amylose molecules have an architecture very different from the amylopectin (the latter composed almost exclusively of branches, generally only 15–30 repeat units long), there could very well be a difference in their glass transition temperatures. However, this cannot be proved conclusively from these data, and further experiments to test this hypothesis were not carried out at this time. In the second heat, in contrast, only one glass transition was observed for the esters at a temperature close to the larger transition observed in the first heat.

In comparison to the neat esters, the plasticized esters displayed smaller, and much broader transitions [see Fig. 2(b)]. Since these transitions almost abutted each other, it was difficult to interpret them as clearly as for the neat esters. The lower temperature transition was attributed to a broad, single glass transition, and the second transition to a broad melting endotherm. (During the second heat, the melting endotherm was preceded by what seemed to be a small crystallization exotherm.). The behavior of the plasticized esters was also different from that of the neat esters in that the sequence of melting, cooling, and subsequent reheating generally resulted in the reappearance of the endotherm at about the same peak temperatures as the first heat. The temperatures of these transitions could be estimated only in a very rough fashion, given their broad, smeared nature. The overall data indicate that a large fraction of the plasticizer allows enough molecular mobility for some crystallization, but is also responsible for smearing the transitions. The difference between the glass transition temperatures observed in the first and second heat of the plasticized esters could possibly be due to some aging effect
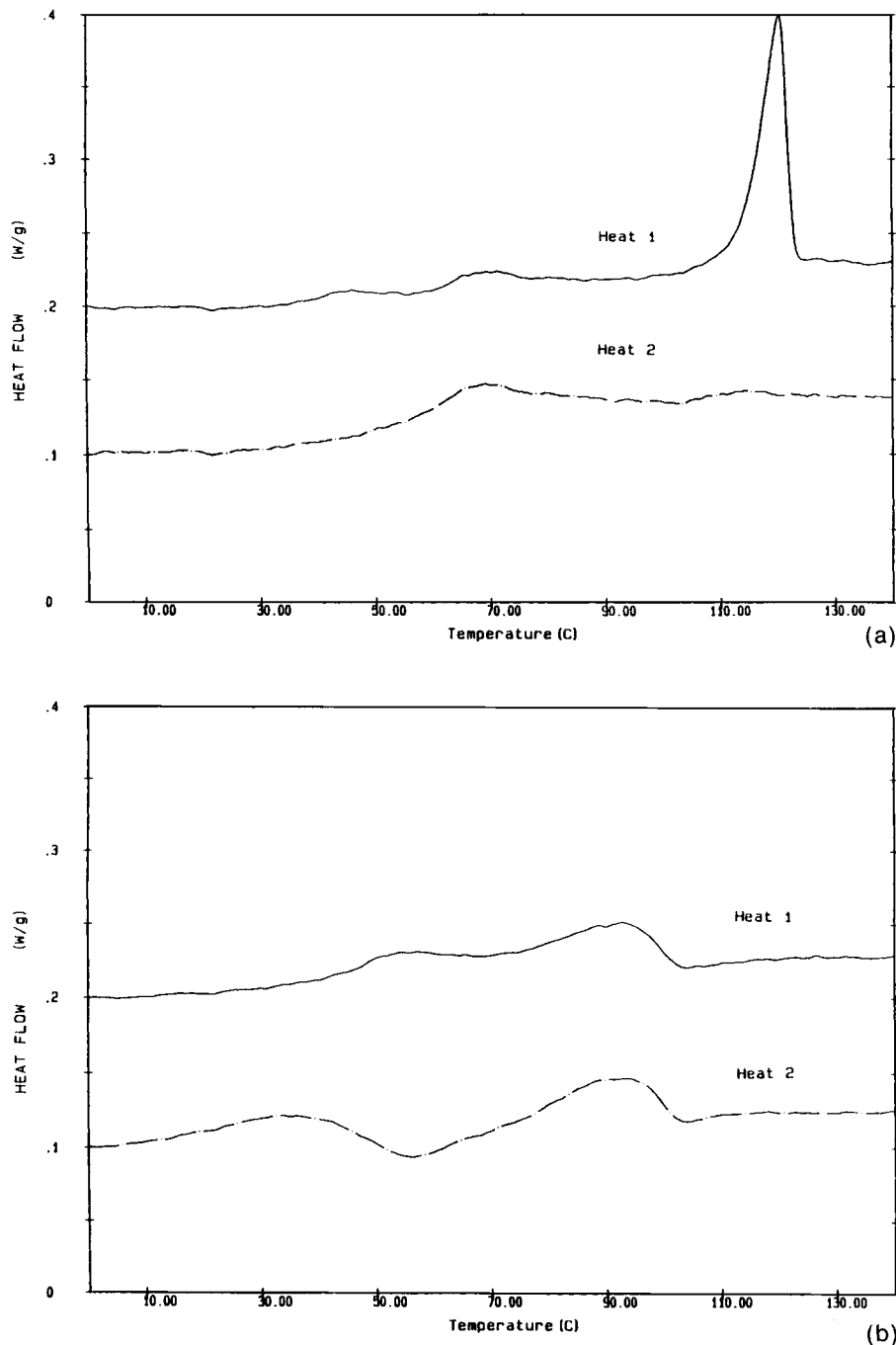
Figure 2   Thermal behavior of neat and plasticized starch esters illustrated by the DSC plots for (a) starch valerate—neat; (b) starch valerate—plasticized.

(such as some phase separation between the plasticizer and polymer) because the films were utilized in tests a few days after they were cast. This might also be responsible for the variations sometimes observed between different runs for the same plasticized esters.

Dynamic Mechanical Behavior

Figure 3(a,b) illustrate the storage modulus (E') and the loss factor (tan δ) behavior for the neat and plasticized starch valerate esters. The highest temperature at which the tan δ peak appears is reported
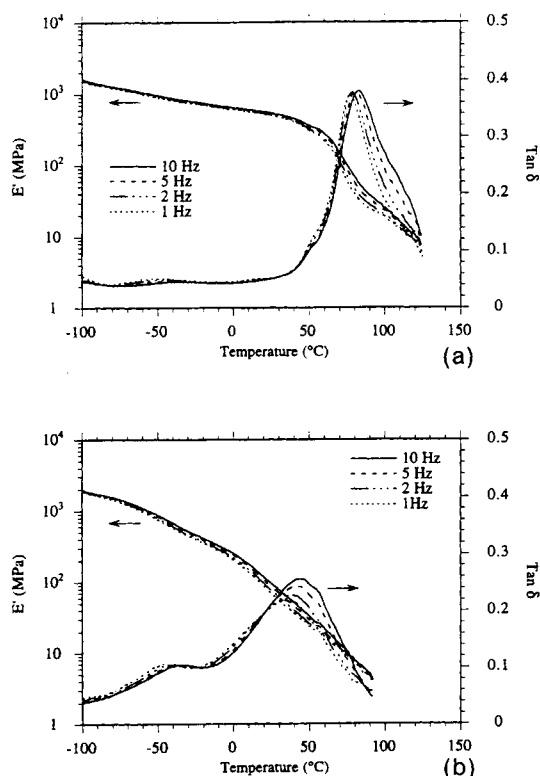
Figure 3 Dynamic mechanical behavior of neat and plasticized starch esters illustrated by the DMA plots for: (a) starch valerate—neat; (b) starch valerate—plasticized.

as the DMA α-transition (or the glass transition temperature); the second (local) maximum observed in the tan δ curves at a lower temperature is reported as the DMA β-transition (probably due to some side-chain motions). The transition temperatures at the lowest measured frequency (i.e., 1 Hz), and the values of E' at 2 Hz (and corresponding to a temperature of 21°C) are reported in Table III. (E' is tabulated for the measurement at 2 Hz, because this corresponds the closest to a strain rate of 0.1 min^{-1} which is the strain rate used for the modulus mea-

surements on the Instron. Also, the tensile testing on the Instron was carried out at 21°C, and therefore, the value of E' is reported for this temperature to allow comparison between the modulus values from the DMA and the Instron.)

For the neat esters, it can be seen that the α-transition temperature moves to lower temperatures, and the corresponding tan d peak becomes broader as the size of the esters group is increased. The α-transition temperatures are slightly higher than that for the larger glass transition in the DSC first heat (T_{g1}), although it should be noted that the heating rate during the DMA was much lower than that in the DSC experiment. A sharp drop in E' coincides with the tan δ peak, which is as expected for these mainly amorphous polymers. The β-transition is much less prominent, although for the higher neat esters, the presence of this transition is clear at a temperature of about −45°C.

For the plasticized starches, the α-transition shifts to a much lower temperature, as expected, and the peak is also much broader, consistent with the observations on the DSC. Also, for these materials, there is no sharp drop in E' at any temperature, just a gradual decline. Compared to the neat esters, however, the plasticized esters show a significant drop in E' at almost all temperatures as expected (except at very low temperatures where the plasticizer presumably cannot contribute to chain motion). The β-transition peak also becomes much more pronounced with the addition of plasticizer, though it does not significantly shift position on the temperature axis.

Mechanical Properties

Table IV lists the numerical values of the mechanical properties for the neat and plasticized esters, and Figure 4(a) and (b) show representative stress-strain curves for starch valerate. Addition of the es-

Table III Transition Temperatures (1 Hz), and the Storage Modulus, E' at 21°C (2 Hz), for the Neat and Plasticized (10% DBP by Weight) Starch Esters as Obtained by Tensile Dynamic Mechanical Analysis

Sample	α Transition (°C)	β Transition (°C)	E' (MPa)
Starch butyrate	85	−44	736
Starch butyrate (plasticized)	56	−33	310
Starch valerate	77	−50	488
Starch valerate (plasticized)	35	−43	83.3
Starch hexanoate	65	−48	243
Starch hexanoate (plasticized)	33	−44	42.3

Table IV   Mechanical Properties of Neat and Plasticized Starch Esters

Sample	Strain Rate = 0.1/min			Strain Rate = 0.5/min	
	Initial Modulus (MPa)	Ultimate Strain (Percent)	Maximum Nominal Stress (MPa)	Ultimate Strain (Percent)	Maximum Nominal Stress (MPa)
Starch butyrate	594 ± 15	36.7 ± 23	15.9 ± 0.4	7.33 ± 4.3	17.9 ± 2.5
Starch butyrate (plasticized)	275 ± 14	40.9 ± 5.4	6.60 ± 0.1	48.0 ± 5.5	9.86 ± 0.7
Starch valerate	495 ± 17	20.2 ± 4.8	12.7 ± 0.6	11.0 ± 6.4	14.1 ± 0.7
Starch valerate (plasticized)	93.7 ± 12	44.4 ± 17	2.72 ± 0.2	57.6 ± 27	3.17 ± 0.2
Starch hexanoate	191 ± 16	74.9 ± 36	5.48 ± 0.3	28.1 ± 12	8.10 ± 1.2
Starch hexanoate (plasticized)	52.8 ± 15	59.2 ± 18	1.75 ± 0.3	119 ± 33	1.50 ± 0.2

ter group modifies the mechanical properties of the starch significantly, as mentioned earlier. This can be attributed to the internal plasticization provided by the ester groups. The tensile mechanical tests on these materials showed the general expected trends in the response of these materials, but also showed some unexpected results at the lower strain rate. At the lower strain rate, the neat starch hexanoate displayed the formation of a stable neck that propa-

Figure 4 Representative nominal stress vs. nominal strain curves for neat and plasticized starch esters: (a) starch valerate; strain rate 0.1/min; (b) starch valerate; strain rate 0.5/min.

gated with increasing strain. The starch valerate also formed a neck, which, however, did not propagate; the localized neck resulted in comparatively early failure. The behavior of the butyrate ester was contrary to expectation, though. These samples necked significantly, and displayed strain-to-break values larger the valerate samples.

The plasticized samples all necked clearly, but their overall extensibility was not very different from that of their neat counterparts. The plasticized samples, however, failed due to the propagation of cracks from the edges of the film as it was pulled. It is not clear if these cracks were initiated from flaws formed during the cutting of the films. In any case, the plasticized films did not seem to show much tear resistance. A wide variation in the strain-to-break values for different specimens for any given material was generally also seen, leading to the larger ranges indicated in Table IV.

At the higher strain rate, the behavior of the neat esters changed significantly. The starch butyrate samples displayed an almost brittle failure, and shattered at comparatively low strains. The valerate esters necked locally and then fractured shortly thereafter as the test proceeded. The starch hexanoate also necked, but in a more stable fashion, allowing a reasonable extension before failure. Overall, the neat starch butyrate showed the greatest dependence upon the strain rate. The plasticized esters, on the other hand, showed a much smaller sensitivity to the strain rate; in fact, they displayed a slight increase in the values for the ultimate tensile strains as compared to those for the lower strain rate.

The values for the initial tensile modulus for the neat and plasticized esters indicate that, as expected, plasticization causes a significant drop in the modulus of the esters. The overall trends and values also correspond well with those obtained from the DMA.
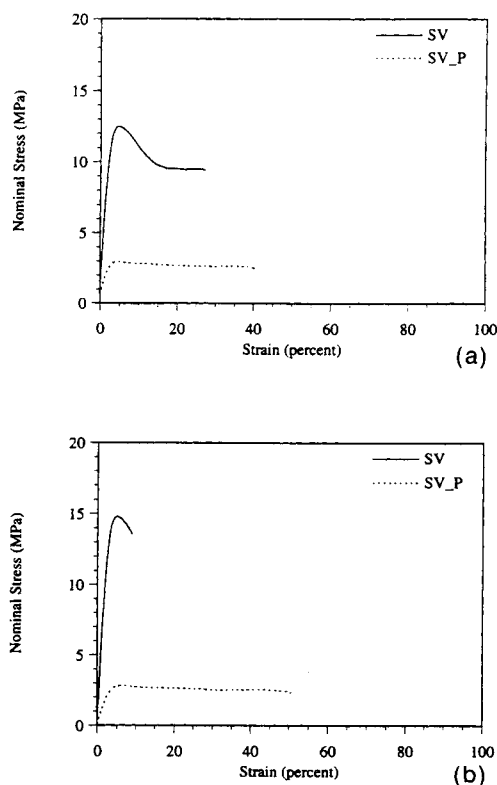
The mechanical tests also indicate that the maximum nominal stress for these starch derivatives drops monotonically with increasing size of the ester group, and also with plasticization. Both the neat and the plasticized starches generally displayed an increase in the maximum nominal stress at the higher strain rate (except for the plasticized starch hexanoate). (The nominal stress, i.e., the load per unit initial cross-sectional area, and nominal strain, i.e., extension relative to overall initial length, are reported here because the specimens neck locally during the test leading to nonuniform strain over the sample. The films were too thin to mount strain gauges to measure real strains. Therefore, it was not possible to estimate the true stress and strain in the polymer as the test proceeded.)

CONCLUSIONS

As with pure amylose, chemical modification of high-amylose starch with fatty-acid esters is achievable through dispersion in an inert solvent and by reaction with the appropriate acid chloride in the presence of pyridine. The resulting starch esters are hydrohobic, thermoplastic materials that can be shaped, handled, and processed with much greater ease than the starch precursor. At least some of the higher esters of high-amylose starch (such as the valerate and hexanoate) are semicrystalline. These materials possess reasonable mechanical properties in terms of their tensile modulus and load-carrying capacity, although their ultimate tensile extension is much lower than commodity thermoplastics such as polyolefins. [Mechanical tests on the neat starch esters indicate elastic modulii ranging from 200 to 600 MPa, maximum nominal stress from 5 to 18 MPa, and ultimate tensile strain from 10 to 75% as we span the range from starch butyrate to starch hexanoate. In comparison, for example, representative values of these parameters for low density polyethylene (LDPE) are as follows: tensile modulus ranging from 55 to 172 MPa, tensile strength from 15 to 79 MPa, and elongation at break from 150 to 600%.[22]] The starch esters are also quite susceptible to propagation of cracks and, therefore, their tear strength is low. The butyrate ester seems to be too brittle to use neat, though the addition of plasticizer does ameliorate the situation somewhat. The unplasticized starch valerate and hexanoate films were less brittle than their butyrate counterpart; plasticization rendered them more flexible. It is conceivable that such higher esters of high-amylose starch could eventually find use in some applications where biodegradability is required, but the mechanical property requirements are not very demanding.

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