Blends of Thermoplastic Starch and Polyesteramide: Processing and Properties

L. AVEROUS,[1] N. FAUCONNIER,[1] L. MORO,[1] C. FRINGANT[2]

[1] Packaging Engineering School, ESIEC, Centre d'Etudes et de Recherche en Matériaux et Emballage, CERME, B.P. 1029, 51686 Reims cedex 2, France

[2] Agro industry Research and Development, ARD, Route de Bazancourt, 51110 Pomacle, France

ABSTRACT: The blending of thermoplastic starch (TPS) with other biodegradable polyesters such as polyesteramide could be an interesting way to produce new biodegradable starch-based materials. Different mixes of wheat starch and polyesteramide (BAK) were melt blended by extrusion. After pelletization, granules were injection molded to produce test specimens. A range of blends was studied with glycerol (plasticizer)/starch content ratios varying from 0.14 to 0.54. BAK concentrations were up to 40 wt %, TPS remaining as the major phase in the blend. Various properties were examined with mechanical, thermomechanical (dynamic mechanical thermal analyzer) and thermal (differential scanning calorimetry) analysis. Hydrophobicity was determined with contact angle measurements. Thanks to the knowledge of the properties of each polymeric system, we analyzed the blends' behavior by varying each component concentration. The material aging was also studied. We showed that structural changes occurred during several weeks after injection. We noticed a certain compatibility between both polymeric systems. The addition of BAK to TPS matrix allowed us to overcome the weaknesses of pure thermoplastic starch: low mechanical properties, high moisture sensitivity, and high shrinkage in injection, even at 10 wt % BAK. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1117–1128, 2000

Key words: blend; thermoplastic starch; polyesteramide; mechanical properties; hydrophobicity

INTRODUCTION

The litter problem with regard to the environment pollution has created an urgent need to develop new biodegradable materials that have comparable properties with today's polymeric materials at an equivalent cost. An important number of biodegradable polymers, biopolymers, exist that are derived from both synthetic and natural sources,[1–3] but most of them are quite costly. The use of agricultural products in plastics applications is considered as an interesting way to reduce surplus farms products and to develop nonfood applications. Starch-based materials are low-cost biopolymers and are obtained from renewable agricultural resources. Several authors[4,5] have shown the possibility to transform native starch into thermoplastic materials under destructuring and plasticization conditions. Thermoplastic starch (TPS) is processed like synthetic plastics by extrusion and injection molding. Unfortunately, TPS is a very hydrophilic product. Some authors[6] tried to modify the starch structure, for example by acetylation, to reduce the hydrophilic character of the chains; this chemical way results in inferior mechanical properties and greater product cost.[7]

Table I   Starch Formulations

TPS Formulation	Starch Contents (wt %)	Glycerol Contents (wt %)	Water Contents (wt %)	Glycerol/ Starch Ratio
S74G10W16	74	10	16	0.135
S70G18W12	70	18	12	0.257
S67G24W9	67	24	9	0.280
S65G35	65	35	0	0.538

Some authors[8,9] have described changes in the mechanical properties of TPS in relation with the crystallinity and the contents of plasticizer and water, during aging. Moisture sensitivity and aging have led to the necessity to associate TPS with another biopolymer, to maintain the biodegradability of the final blend. Association between polymers can be as blends or multilayers products. Multilayers can be obtained by a coating[10] or coextrusion[11] process. However, in each case it is necessary to determine the compatibility between the different biopolymers. Blend analysis is a good way to appraise such a property.

Blending of TPS with other polymers has been widely used.[2–5,12–25] Research groups[2–5,12] have developed blends with synthetic polymers such as polyethylene, leading to nonfully biodegradable materials. Some starch-based blends have been commercialized, such as Mater-Bi[13] (Novamont-Italy) or Bioplast[14] (Biotec-Germany). To maintain the biodegradability of the blend, biopolymer components such as aliphatic polyesters—for example polycaprolactone[15–22] (PCL) or polyhydroxybutyrate-co-valerate[15–17,23–25] (PHBV)—have been used.

Polyesteramides are copolymers of polyamide and aliphatic ester. Available since 1996, the commercial products are represented by the BAK grades from Bayer AG. According to Grigat et al.,[26] BAK is completely biodegradable under composting conditions. BAK provides lower water sensitivity than starch and seems to be suited for our purpose as the hydrophobic component.

Various plasticizers have been tested with starch.[4,5,9,27,28] Under shearing and thermopressure conditions, water and glycerol act as a good destructuring-plasticizer agent. Several papers[4,28,29] have been published on the effect of plasticizer on the glass transition of TPS. It is possible to adjust the properties of TPS, from a soft material (high plasticizer level) to a brittle material (low plasticizer level) according to moisture and glycerol contents.

The aim of this paper is to report on various properties of TPS/BAK blends without using compatibilizers. Different TPS/BAK ratios were tested. In order to develop economically viable biodegradable materials, TPS was kept as the major phase in the blend (>50%). Different starch formulations with various glycerol and moisture contents were analyzed. Water sensitivity was determined through the surface contact angle. Mechanical properties (tensile and impact tests), thermomechanical and thermal behaviors (dynamic mechanical thermal analyzer [DMTA] and differential scanning calorimetry [DSC]) were evaluated.

EXPERIMENTAL

Materials

Wheat starch was obtained from Chamtor (France). According to the supplier, the amylose and amylopectin contents were 25% and 75% respectively; the residual protein content was less than 1%. Polyesteramide BAK1095 was kindly provided by Bayer (France). This product is based on caprolactam, butanediol, and adipic acid. This is a semicrystalline polymer, whose melting point is close to 125°C and whose density is 1.07. The chemical structure of this copolymer is given by the following formula:

$$—[CO—(CH_2)_4—CO–O—(CH_2)_4—O—]_x$$
$$—[CO—(CH_2)_5—NH—]_y—.$$
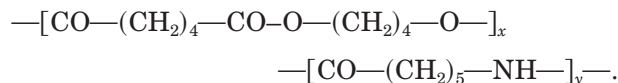
The glycerol used has a purity close to 99.5%. Magnesium stearate (99% purity) from Aldrich was used as a demolding agent in injection molding: less than 1 wt % is used for each blend.

Table II   Different Blends Tested[a]

TPS/BAK Blends	BAK 40 wt %	BAK 25 wt %	BAK 10 wt %
S74G10W16 (TPS density: 1.38)	× (0.46)	× (0.30)	
S70G18W12 (TPS density: 1.37)		× (0.30)	
S67G24W9 (TPS density: 1.35)		× (0.30)	
S65G35 (TPS density: 1.42)	× (0.47)	× (0.31)	× (0.13)

[a] BAK volumic ratios are given between brackets.

Table III Shrinkage (%) for Different TPS/BAK Blends

BAK wt %	S74G10W16	S70G18W12	S67G24W9	S65G35
0	6,2	14,2	13,1	9,3
10	—	—	—	4,9
25	1,8	6,8	6,9	4,1
40	0,7	—	—	3,5

Sample Preparation

Blends preparation

Granules of TPS were prepared according to the following procedure. Native starch was weighed and introduced in a turbo-mixer. Glycerol was then added slowly while the starch was slowly mixed. After completion of glycerol addition, the mixture was dispersed at high speed to obtain a homogeneous dispersion. The mixture was then placed in a vented oven at 170°C for 45 min and occasionally stirred, allowing vaporization of water and diffusion of glycerol into the starch granule. After cooling, the proper amount of water was added to the mixture that was once more dispersed at high speed in the mixer. The powder was then extruded and granulated. Various TPS formulations (Table I) with different plasticizer/starch ratios were prepared.

After equilibration at 65% RH (Relative Humidity) during 8 days, TPS and BAK pellets were mixed. Various compositions were extruded and granulated after cooling and equilibrated at 65% RH for 8 days before injection molding. The TPS/BAK blends which were tested are presented in Table II.

The blends are denoted as follows; S75G15W10/BAK25 means that the TPS comprises 75 parts of starch (dry basis), 15 parts of glycerol, and 10 parts of water. The blend was prepared by mixing 25 wt % of BAK and 75 wt % of thermoplastic starch pellets.

Processing conditions

Blends were extruded on a single screw extruder (SCAMIA S 2032, France) equipped with a coni-

Table IV Mechanical Properties of Thermoplastic Starch-BAK Blends[a]

% Wt BAK	Aging Time = 2 Weeks				Aging Time = 6 Weeks		
	Modulus (Mpa)	Max. Tensile Strength (Mpa)	Elongation at Break (%)	Impact Strength (kJ/m^2)	Modulus (Mpa)	Max. Tensile Strength (Mpa)	Elongation at Break (%)
			Polyesteramide BAK 1095				
100	262 (12)	17.2 (5.2)	420 (59)	No break	262 (12)	17.2 (5.2)	420 (59)
			Starch 74/Glycerol 10/Water 16				
0	997 (59)	21.4 (1.0)	4 (0)	0.79 (0.09)	1144 (42)	21.4 (1.7)	3 (0)
25	716 (16)	10.2 (0.5)	2 (0)	2.93 (0.34)	825 (22)	11 (0.6)	2 (0)
40	556 (23)	8.7 (0.5)	3 (0)	3.98 (0.63)	609 (34)	9 (0.2)	3 (0)
			Starch 70/Glycerol 18/Water 12				
0	52 (9)	3.3 (0.1)	126 (2)	No break	116 (11)	4.0 (0.1)	104 (5)
25	60 (4)	5.0 (0.1)	130 (13)	No break	133 (12)	6.3 (0.1)	79 (17)
			Starch 67/Glycerol 24/Water 9				
0	26 (4)	2.6 (0.1)	110 (11)	No break	45 (5)	3.3 (0.1)	98 (5)
25	32 (2)	3.6 (0.1)	146 (8)	No break	69 (6)	4.6 (0.1)	73 (17)
			Starch 65/Glycerol 35				
0	2 (1)	0.6 (0.2)	91 (5)	No break	11 (1)	1.4 (0.1)	60 (5)
10	3 (1)	0.8 (0.0)	105 (7)	No break	9 (1)	1.5 (0.1)	85 (5)
25	18 (1)	2.1 (0.1)	162 (12)	No break	31 (5)	2.4 (0.1)	66 (7)
40	41 (4)	4.8 (0.2)	311 (23)	No break	59 (8)	4.6 (0.1)	267 (12)

[a] Standard deviations are given between brackets.

Table V   Estimations of Modulus with Model on 6 Weeks Aging Modulus Results

Formulations	Modulus (MPa)	E_{upper} (MPa)	E_{lower} (MPa)
S74G10W16/BAK 25	825	877	567
S74G10W16/BAK 40	609	735	447
S70G18W12/BAK 25	133	159	139
S67G24W9/BAK 25	69	97	60
S65G35/BAK 10	9	36	12
S65G35/BAK 25	31	82	16
S65G35/BAK 40	59	124	20

cal-shaped element (see description in Onteniente et al.[30]). This design is suitable to provide high shearing. The extruder has two heating zones situated at the conversion zone and at the die. A die was used to obtain strands that were then pelletized after air cooling. An injection molding machine DK Codim NGH 50/100 (France) with a clamping force of 50 tons was used to mould standard dumbbells (tensile bars). The screw is regulated in temperature along the barrel between 100°C and 130°C, from the hopper to the nozzle. Injection pressure was 1500 bars. Holding pressure and time were 1000 bars and 15 s respectively. Cooling time was set at 15 s. The uniaxial shrinkage is defined by the eq. (1).

$$Sh = (1 - (L/L_0)) * 100 \qquad (1)$$

L is the length of the specimen after cooling and L_0 is the length defined by the mold.

Dumbbell specimens produced have an active portion 10-mm wide and 4-mm thick (according to French standard NFT 51-034 1981). The Charpy test samples were cut out from the central part of the dumbbells to get samples without notches whose dimensions were $10 * 4 * 60$ mm (according to French standard NFT 51-035 1983).

Mechanical Properties

Tensile test

Tensile strength measurements, Young's modulus, and elongation at break were performed on a mechanical tensile tester (Instron 4204-G.B.). A cross-head speed of 50 mm/min was used. Ten samples for each blend composition were tested after a 2-week period conditioning at 23°C, 50% RH. The influence of ageing on the mechanical

properties was determined after 6 weeks conditioning in the same conditions.

Impact test

A mechanical impact tester (JPS -France) with a 1 J pendulum was used for Charpy tests. For each blend composition, 10 specimens were tested after 14 days conditioning at 23°C and 50% RH. Impact strength is usually quoted as energy per unit area.

Contact angle measurements

The contact angle formed between a water droplet placed at the surface of a material and the kinetics of spreading is related to the hydrophobicity of the material. Contact angle measurements were performed with a Kruss G23 (Germany) apparatus. A water droplet was dropped on the surface of a dumbbell specimen. The evolution of the droplet shape was recorded. A CCD video camera and image analysis software were used to determine the contact angle evolution. Due to variations in the surface smoothness, a large dispersity in the results is obtained in this type of analysis between different kind of materials. Results must be taken into account as trends in a comparison approach on the same type of material.

Thermal Analysis

The thermal characteristics of the blends were determined using a modulated DSC (Universal

Table VI   Contact Angle Measurements of Thermoplastic Starch-BAK Blends

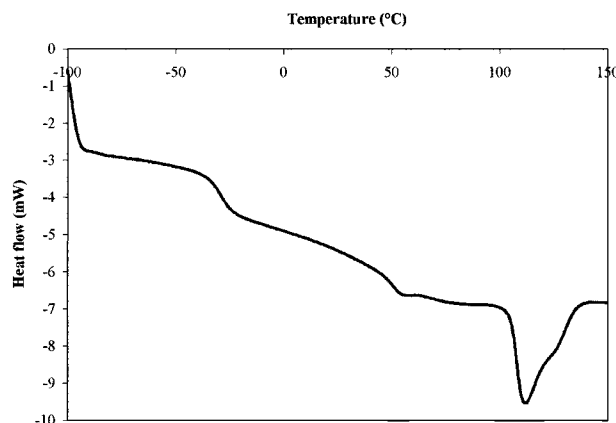| % BAK	Initial Value (degree)	Slope at Origin (degree/s)
	BAK	
100	63	−0.15
	Starch 74 Glycerol 10 Water 16	
0	51	−4.20
25	57	−1.00
40	66	−0.84
	Starch 70 Glycerol 18 Water 12	
0	40	−2.02
25	66	−0.74
	Starch 67 Glycerol 24 Water 9	
0	50	−3.22
25	69	−0.28
	Starch 65 Glycerol 35	
0	32	−3.95
10	61	−0.96
25	62	−0.72
40	71	−0.41

Figure 1   BAK-DSC thermogram.

V1.9D TA instrument, USA) cooled with liquid nitrogen circulation. Samples (15–20 mg) were cut from a dumbbell specimen after conditioning and placed in sealed aluminum pans. The pan is closed hermetically to prevent water evaporation during scanning. A first scan was performed between ambient temperature and 100°C; the sample was then cooled rapidly at -100°C and rescanned until 150°C. Scanning rate was 10°C per min. An empty pan was used as reference. The glass transition temperature was computed as the midpoint of heat capacity increase. The thermal effects were recorded during the second heating run. The first scan allowed removal of thermal history of the material.

Thermomechanical Analysis

Thermomechanical properties of the different blends were determined with a dynamic thermomechanical analyzer (TA instrument-DMA 2980, USA). Samples were cut from the central part of the dumbbells to get specimens whose dimensions were $4 \times 10 \times 27.3$ mm. They were tested by applying a bending constraint using the dual cantilever geometry. The displacement amplitude was set to 14.5 μm. The measurements were performed at the frequency of 1 Hz. The range of temperature was from -100°C to 140°C at the scanning rate of 1.5°C/min. Samples were coated with silicone wax to preserve water evaporation during scanning.

RESULTS AND DISCUSSION

Shrinkage Analysis

Shrinkage values are reported on Table III. The shrinkage obtained for thermoplastic starch is

clearly observed. Addition of BAK leads to a significant reduction of shrinkage to acceptable values. BAK can be considered as a dimensional stability enhancer.

Mechanical Properties

Complete mechanical properties obtained from tensile and impact strength measurements on injection molded bars are presented in Table IV. The results obtained after, respectively, 2 and 6 weeks aging at 50% RH and 23°C are presented.

BAK is a ductile polymer with a relatively high elongation at break, a high-impact strength resistance, and a medium Young's modulus. The behaviour of the pure TPS is similar to that reported by many workers[9]: Young's modulus and tensile strength are seen to decrease while increasing the glycerol content. Depending on the plasticizer content, the elongation at break increases and then decreases for the highest glycerol concentrations. This phenomena could be due to a phase separation between starch and glycerol as described by some authors.[29] The maximum of elongation at break seems to be at a glycerol/starch ratio close to 0.2. Two kinds of material behaviors can be defined. The S74G10W16 formulation is a glassy material, whereas the other formulations lead to rubbery material with high-impact strength (no break of the samples during testing).

For BAK-based blends, two kinds of behavior are observed. For the S74G10W16 formulation, the addition of BAK results in an improvement of impact properties. The impact strength is improved, as when blending with a highly flexible material. Young's modulus and the maximum strength decrease when the BAK content increases. But for more flexible TPS formulations (S70G18W12, S67G24W9, and S65G35), the addition of BAK increases all the mechanical characteristics (modulus, maximum strength, and elongation at break). For these TPS formulations, BAK provides higher mechanical properties.

Modulus results (see Table V) are in rather good agreement with the classical rule of mixtures. The mechanical model is based on two boundaries. The upper boundary is described by the additivity law described by the eq. (2), where E_{upper} is the upper modulus estimation of a blend based on polymeric systems 1 and 2. E_1 and E_2, V_1 and V_2 are respectively the modulus and the volumic ratio of each polymeric system. The lower
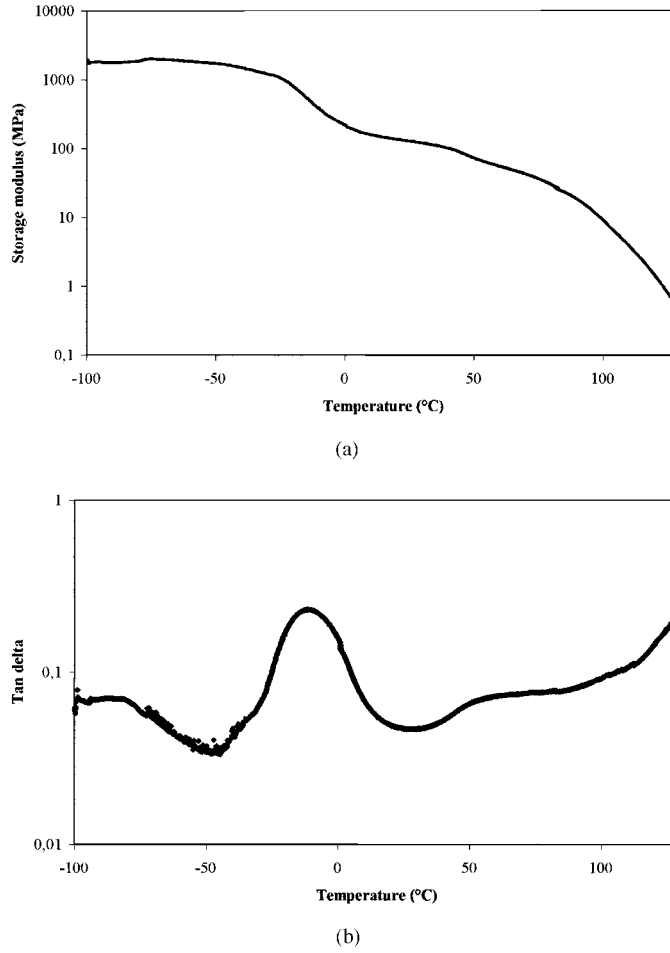
(a)

(b)

Figure 2 (a) BAK-storage modulus curve; (b) BAK- tan delta curve.

boundary is given by the eq. (3): Equations 2 and 3

$$E_{\text{upper}} = E_1 \cdot V_1 + E_2 \cdot V_2 \qquad (2)$$

$$1/E_{\text{lower}} = V_1/E_1 + V_2/E_2 \qquad (3)$$

For all the formulations, the aging of the samples results in increased rigidity of the material:

Table VII   BAK and TPS Thermal (DSC) and Thermomechanical (DMTA) Properties

	Secondary Relaxation		Glass Transition			Melting
	$T_{\beta(\text{DMA})}$	$T_{\sec(\text{DSC})}$	$T_{\alpha(\text{DMA})}$	$T_{g(\text{DSC})}$	ΔCp	$T_{m(\text{DSC})}$
	in °C		in °C		in Jg^{-1} K^{-1}	in °C
BAK	None		-11	-29	0.5	112°C
S74G10W16	-55	Invisible	63	43	0.4	None
S70G18W12	-54	-67	31	8	0.4	None
S67G24W9	-58	-72	17	-7	0.4	None
S65G35	-62	-77	1	-20	0.2	None

$T_{\beta(\text{DMA})}$ and $T_{\alpha(\text{DMA})}$ are determined at the maximum of the tan δ peak; $T_{\sec(\text{DSC})}$ and $T_{g(\text{DSC})}$ are determined at the midpoint of heat capacity increase.
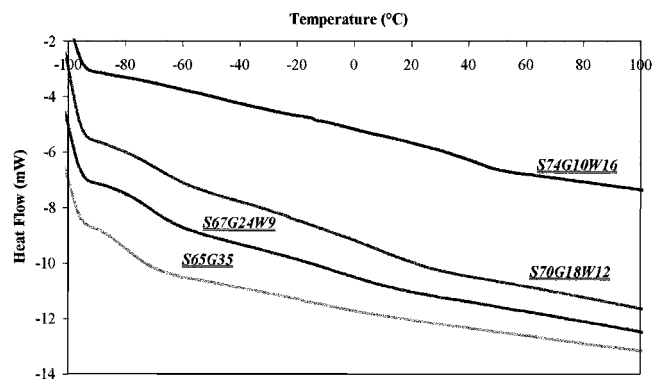
Figure 3 DSC thermograms for TPS formulations: S74G10W16, S70G18W12, S67G24W9, and S65G35.

higher modulus and maximum strength, and lower elongation at break after 6 weeks. This behavior is well known by people skilled in the TPS area. It is partially due to crystallization of starch chains and water content modification. It is noteworthy that the presence of BAK is not sufficient to prevent aging.

Contact Angle Measurements

The results of contact angle measurements are presented in Table VI. The material behaviors are quantitatively illustrated by measurement of the initial values of contact angle just after deposition of the droplet and by the value of the slope that illustrates the kinetics of absorption. In a pure TPS case, the water droplet is rapidly absorbed, because of the hydrophilic nature of the material. When BAK is blended with thermoplastic starch, the evolution of contact angle with time is slower and more constant. In all cases, the presence of

BAK leads to a significant improvement of the material hydrophobicity. The initial contact angle value is higher than that of pure TPS, the kinetics of absorption decreases. These trends are more pronounced for higher amount of BAK in the blends. The interesting fact of these results is that the introduction of BAK at a level as low as 10 wt % leads to a significant improvement of water resistance of the materials.

During the injection molding process, a thin skin of BAK rich material is formed at the surface of the sample. This layer is observed after breaking of the samples. BAK in this case acts as a processing aid, like stearate or wax in injection formulation. During the mold filling phase, we have a preferential migration of BAK toward the cold surface of the mold producing a kind of multilayer structure with a thin BAK skin.

Some samples of TPS formulations with and without BAK have been immersed in liquid wa-
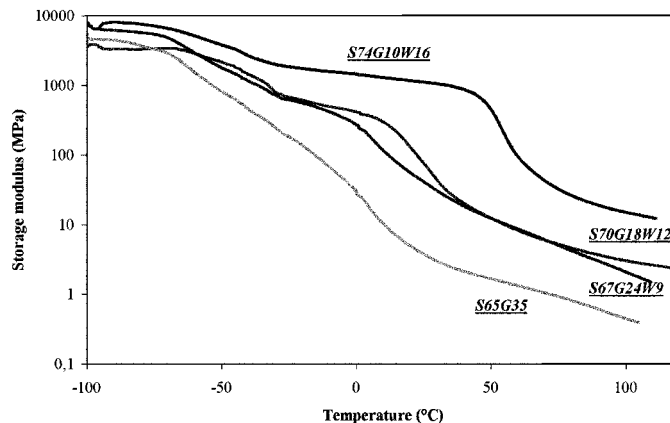

Figure 4 Storage modulus curves for TPS formulations(DMTA): S74G10W16, S70G18W12, S67G24W9, and S65G35.
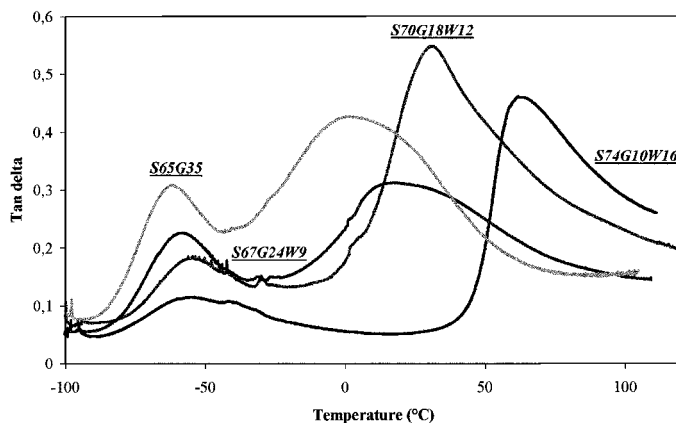
Figure 5 Tan delta curves for TPS formulations(DMTA): S74G10W16, S70G18W12, S67G24W9, and S65G35.

ter. The pure TPS samples rapidly become sticky and gummy, and begin to dissolve slowly. On the contrary, the blends with BAK retain their integrity for several weeks. No noticeable swelling was observed. However, the mechanical properties remained water sensitive. Blending BAK with starch is an efficient way to increase the hydrophobicity.

Thermal and Thermomechanical Properties

Characteristics of pure BAK

The DSC and DMTA curves obtained with pure BAK are presented in Figures 1 (DSC) and 2 (DMTA). The temperatures associated with thermal events are reported in Table VII. Different thermal events are observed: the heat capacity increase at $-29°C$, attributed to the glass transition of the polymer; a small endothermic peak around 55°C; and a more pronounced endotherm around 115°C. The enthalpy of the peaks was impossible to determine accurately because the peaks were too overlapped and no straight baseline was observed. The endothermic peaks are attributed to the melting of the crystalline area of the polymer. The reason why two melting endothermic peaks can be observed is not clearly established. It is expected that the copolymer (polyesteramide) can crystallize with different structures depending on the processing conditions (cooling kinetics) and these different crystalline systems have two melting points. The thermal events seen on the DSC curves can be also observed through DMTA measurements, as can be noticed in Figure 2. The evolution of the storage modulus presents a marked decrease around $-15°C$ that is related to the glass transition observed by DSC and correlates with a large peak of the tan delta signal. A small decrease of the storage modulus is observed around 50°C that correlates with a small increase of tan delta. This is probably attributed to the small first melting
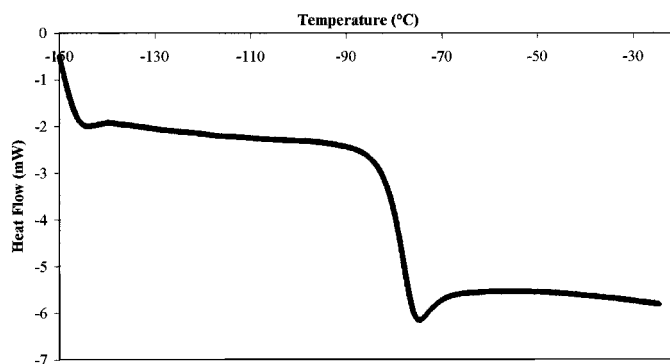

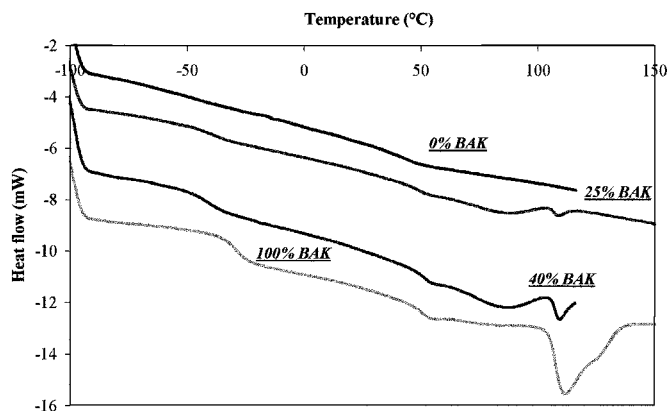**Figure 6** DSC thermogram for glycerol.

Figure 7 DSC thermogram for S74G10W16-based blends (0, 25, 40, and 100 wt % of BAK, from top to bottom).

peak observed by DSC. Then, a sharp decrease of the modulus is observed over 100°C, whereas the tan delta curve increases, that correlates with the melting of the polymer observed by DSC.

Characteristics of pure thermoplastic starch

The DSC and DMTA curves obtained with TPS are presented in Figures 3 (DSC), 4, and 5 (DMTA). The temperatures associated with the different thermal events are reported in Table VII. The DSC curves present two changes of heat capacity for most of the TPS compositions. The position of the one at highest temperatures is strongly dependent on the amount of glycerol: the higher it is, the lower the temperature of the heat capacity change. This observed decrease in temperature at the heat-capacity change can be attributed to a glass transition temperature shift, due to increasing amounts of plasticizer. More-

over, the experimental values are in good agreement with the glass transition temperature reported in the literature.[9,28,29] This glass transition is also demonstrated by DMTA where the curves show a loss of modulus and a tan delta peak in the same temperature range. The second change of heat capacity is not detected by DSC for the less plasticized formulations. But for the others, a change of the heat capacity drop is correlated to the glycerol content. The glycerol DSC curve (Fig. 6) presents a heat capacity drop in the same temperature range as for TPS formulations. We can attribute the observed transition to the glycerol glass transition. Similar results have been obtained by Lourdin and al.[29] According to this study, this relaxation seems to be due to the glycerol and a phase separation for glycerol/starch ratio higher than 0.2 is observed. The relaxation is also observed by DMTA between −50
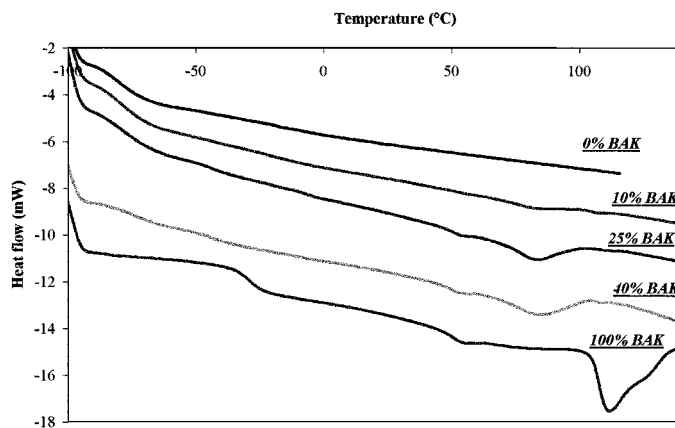
Figure 8 DSC thermogram for S65G35-based blends (0, 10, 25, 40, and 100 wt % of BAK, from top to bottom).
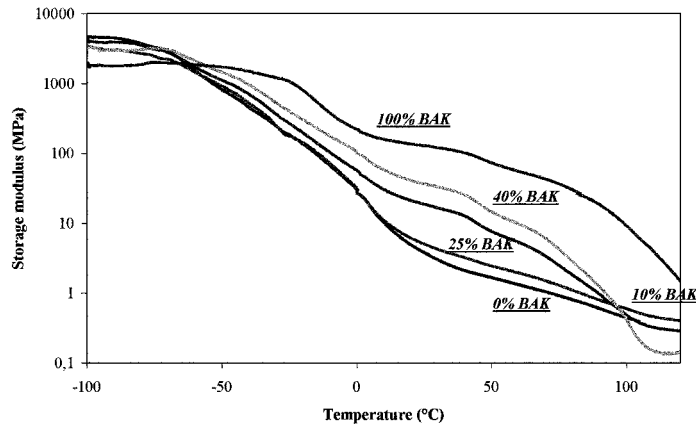
Figure 9   Storage modulus curves (DMTA) for S65G35-based blends (0, 10, 25, 40, 100 wt % of BAK).

and −60°C. The magnitude of the tan delta peak is strongly dependent on the glycerol content that is also consistent with a relaxation linked to glycerol glass transition.

Characteristics of the blends

The DSC and DMTA curves are presented only for some blends (S74G10W16- and S65G35-based blends) in Figures 7–11. Figures 7 and 8 present DSC curves and the Figures 9–11 present DMTA curves (tan delta and storage modulus).

For the S74G10W16-based blends, DMTA results show that the modulus moves between both pure components according to the formulation, the BAK content. The same kind of result is observed by tensile tests on modulus values. It can be noticed that, for temperatures between the alpha relaxation of pure TPS (50°C) and the melt-

ing of BAK (100°C), the modulus is increased by BAK in the blend. This is observable on the transition associated with the relaxation of the starch that seems to be shifted toward higher temperatures by BAK. On the contrary, the peak that could be related to the alpha relaxation of BAK in the blends is shifted toward lower temperatures by the presence of TPS. The presence of these two relaxations, which do not differ strongly from the ones of pure components, indicates that the morphology of the blend does not consist, probably, of a monophase. However, the shift of the transitions could indicate that some interactions between the two components of the blend exist.

For the S70G18W12-based blends, the curve of tan delta versus temperature allows one to separate four relaxations for which maximum temperature are respectively −57°C, −29°C, +27°C, and
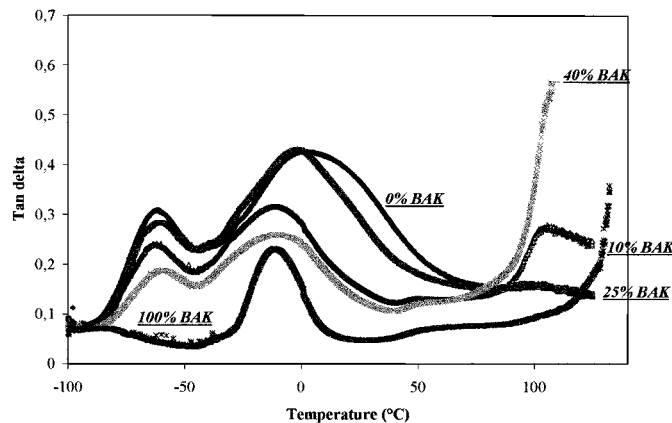

Figure 10   Tan delta curves (DMTA) for S65G35-based blends (0, 10, 25, 40, 100 wt % of BAK).
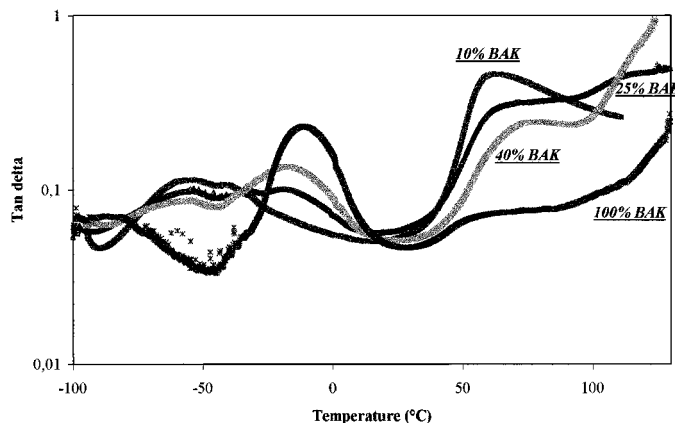
Figure 11   Tan delta curves (DMTA) for S74G10W16-based blends (0, 25, 40, 100 wt % of BAK).

+112°C. The comparison with the curves obtained for pure components shows that all the characteristics of each component are present in the blend: glycerol glass transition, BAK alpha relaxation, TPS alpha relaxation, and melting of BAK. The starch relaxations in the blend are slightly shifted toward lower temperature, whereas the ones for BAK are shifted significantly (around 20°C lower). The same evolution can be observed for the blends based on the S67G24W9 TPS formulation. The only difference lies in the shift observed for the alpha relaxation of starch that is higher for the more plasticized formulation than in the previous case (shift of −12°C instead of −4°C). This seems to indicate a better degree of compatibility for both components of the blend. In the case of the most highly plasticized blend (Fig. 10), three relaxations instead of four are observed, but the one at intermediate temperature is very large and it is difficult to state whether or not it can be attributed to a single relaxation.

CONCLUSIONS

The thermal and thermomechanical characteristics of the blends show a phase separation in the blend as it is the case for nonmiscible polymers. However, the relaxations attributed to the different phases of the blend are slightly different from the ones of pure components. This difference is probably due to a partial compatibility between the polymeric systems.

By blending BAK with TPS, even with a BAK content as low as 10 wt %, the dimensional sta-

bility of TPS was improved. The hydrophobicity of the blends was much more important than the one of TPS, leading to better water resistance. The association of TPS with BAK is an interesting way to overcome the most important weakness of thermoplastic starches: moisture sensitivity, poor mechanical properties, and so on. The different combinations between the TPS formulations and BAK give a wide range of mechanical behavior that can fit different applications. This kind of blend is an interesting approach to produce cheaper biodegradable materials.

REFERENCES

1. Kaplan, D. J.; Mayer, J. M.; Ball, D.; McMassie, J.; Allen, A. L.; Stenhouse, P. In Biodegradable Polymers and Packaging; Ching, C.; Kaplan, D. L.; Thomas, E. L., Eds.; Technomic Publication: Basel, 1993; Chap. 1.
2. Chiellini, E.; Solaro, R. Adv Mater 1996, 8, 305.
3. Amass, W.; Amass, A.; Tighe, B. Polym Int 1998, 47, 89.
4. Tomka, I. Adv Exp Med Biol 1991, 302, 627.
5. Swanson, C. L.; Shogren, R. L.; Fanta, G. F.; Imam, S. H. J Env Polym Deg 1993, 1, 155.
6. Fringant, C.; Desbrières, J.; Rinaudo, M. Polymer 1996, 37, 2663.
7. Avérous, L.; Moro, L.; Fringant, C. Properties of plasticized starch acetates. In ICBT Conference, Coimbra, Portugal, 28–30 September, 1999.

8. Van Soest, J. J. G.; Knooren, N. J Appl Polym Sci 1997, 64, 1411.

9. Van Soest, J. J. G.; Starch plastics structure-property relationships. Utrecht university (Netherland), P&L Press: Wageningen, 1996.

10. Koening, M. F.; Huang, S. J. Polym Deg Stab 1994, 45, 139.

11. Avérous, L.; Fringant, C.; Martin, O. In Biopolymer science: Food and non food applications; Colonna, P.; Guilbert, S., Eds.; INRA Editions: Paris, 91, 207, 1999.

12. Jasberg, B. K.; Swanson, C. L.; Shogren, R. L.; Doane, W. M. J Polym Mater 1992, 9, 163.

13. Bastioli, C. Polym Deg Stab 1998, 59, 263.

14. Lörcks, J. Polym Deg Stab 1998, 59, 245.

15. Koening, M. F.; Huang, S. J. Polym Mater Sci Eng 1992, 67, 290.

16. Huang, S. J.; Koening, M. F.; Huang, M. In Biodegradable Polymers and Packaging; Ching, C.; Kaplan, D. L.; Thomas, E. L., Eds.; Technomic Publication: Basel, 1993, Chap. 6.

17. Koening, M. F.; Huang, S. J. Polymer 1995, 36, 1877.

18. Narayan, R.; Krishnan, M. Polym Mater Sci Eng 1995, 72, 186.

19. Bastioli, C.; Cerrutti, A.; Guanella, I.; Romano, G. C.; Tosin, M. J Env Polym Deg 1995, 3, 81.

20. Pranamuda, H.; Tokiwa, Y.; Tanaka, H. J Env Polym Deg 1996, 4, 1.

21. Myllymäki, O.; Myllärinen, P.; Forssell, P.; Suortti, T.; Läteenkorva, K.; Ahvenaien, R.; Poutanen, K. Packag Technol Sci 1998, 11, 265.

22. Avérous, L.; Moro, L.; Dole, P.; Fringant, C. Polymer 2000, to be published.

23. Ramsay, B. A.; Langlade, V.; Carreau, P. J.; Ramsay, J. A. Appl Env Microbiol 1993, 59, 1242.

24. Verhoogt, H.; St-Pierre, N.; Truchon, F. S.; Ramsay, B. A.; Favis, B. D.; Ramsay, J. A. Can J Microbiol 1995, 41, 323.

25. Knotnis, M. A.; O'Brien, G. S.; Willett, J. L. J Env Polym Deg 1995, 3, 97.

26. Grigat, E.; Koch, R.; Timmermann, R. Polym Deg Stab 1998, 59, 223.

27. Shogren, R. L. In Biodegradable Polymers and Packaging; Ching, C.; Kaplan, D. L.; Thomas, E. L., Eds.; Technomic publication: Basel, 1993, Chap. 10.

28. Lourdin, D.; Coignard, L.; Bizot, H.; Colonna, P. Polymer 1997, 38, 5401.

29. Lourdin, D.; Bizot, H.; Colonna, P. J Appl Polym Sci 1997, 63, 1047.

30. Onteniente, J. P.; Etienne, F.; Bureau, G.; Prudhomme, J. C. Starch 1996, 48, 10.