Biodegradable polymers by reactive blending trans-esterification of thermoplastic starch with poly(vinyl acetate) and poly(vinyl acetate-co-butyl acrylate)

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Abstract

Wheat starch was reacted with poly(vinyl acetate) and with poly(vinyl acetate-co-butyl acrylate) in an internal mixer at 150 °C in the absence of catalyst, and in the presence of sodium carbonate, zinc-acetate and titanium(IV) butoxide. The resulted blends were pressed into film and characterized by ^{1}H NMR–^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), mechanical testing, dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), and water absorption. Partial trans-esterification took place between wheat starch and the polymers. The blends appeared as homogenous, translucent films with one glass transition temperature range, between that of starch and of the polymer. The presence of wheat starch in the blends improved the mechanical strength of the polymers, although elongation at break severely decreased, which is disadvantageous for processability. Zinc-acetate improved the tensile strength of the blends of starch with PVAC, while all catalysts resulted in an increase in strength of the blends of starch with poly(vinyl acetate-co-butyl acrylate) compared to the strength of the blends without catalyst. Water absorption of wheat starch/copolymer blends was between 150% and 250%, higher than that of the blends with the homopolymer, which was between 100% and 150% after soaking in water. The onset temperature of thermal decomposition was between 290 and 300 °C for all the blends, although the presence of sodium carbonate resulted in a decrease in the onset temperature of thermal decomposition by about 60 °C.
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1. Introduction

Thermoplastic starch would be an ideal matrix for packaging material or one-use articles, because it is a renewable resource material, and biodegradable [1].

Inherent in the chemical structure of starch [2,3], however, the products made from thermoplastic starch are inclined to retrogradation, are sensitive to water, and since water is plasticizer of starch, their performance is unstable, and depends on the moisture content being in equilibrium with the ambient relative humidity. Trommsdorff and Tomka [4] studied the structure of dry amorphous starch on a molecular level by applying an atomistic model, which was in good correlation with experimental results. They extended the model to starch containing different amount of water [5]. Benczedi et al. [6] applied the lattice-fluid hydrogen-bonding (LFHB) model, in order to study the volumetric properties of starch–water mixtures. The experimental data were correlated with the LFHB model, which is able to describe satisfactorily the volumetric behavior of both pure components and of water–starch mixtures. Benczédi et al. [7,8] studied the thermodynamics of amorphous starch–water systems. Their work enables the estimation of the essential properties of amorphous starch, such as glass transition temperature or gas barrier properties.

For extending practical utilization of starch-based products, reinforcement [9] or modification [10,11] of starch is essential. Among the many possibilities of modification, esterification is one of the most important one. Direct esterification [12,13] seems to be the simplest route, although degradation of starch chains is unavoidable resulting in inferior mechanical performance of the end product [14]. Starch–poly(vinyl acetate) materials have been prepared via in situ polymerization of vinyl acetate in the presence of starch by using ferrous ammonium sulfate-hydrogen peroxide redox initiator system [15]. Other methods include melt blending of starch with synthetic polymers, such as poly(ethylene-co-vinyl acetate) and polyethylene with anhydride functionality [16,17].

Goal of this work is to modify thermoplastic starch by reactive blending with polymers containing functional groups, which may react with starch OH groups during the blending procedure via polymeranalog reaction. For this purpose poly(vinyl acetate) and poly(vinyl acetate-co-butyl acrylate) have been selected. The reason for the choice of PVAC was first of all the partial trans-acetylation of starch with this polymer, in order to reduce its moisture sensitivity. As a result, the formation of a compatible interpenetrating polymer network of starch, of starch acetate and of poly(vinyl alcohol-co-acetate) is expected. The internally plasticized PVAC, i.e. poly(vinyl acetate-co-butyl acrylate), would serve to decrease the glass transition temperature range of the resulting blend. Both polymers are sold as biodegradable

by the supplier, and the forming OH groups would enhance their biodegradability. There are three important aspects for attaining positive results via reactive blending. Complete destructurization (gelatinization) of starch, molecular homogenization of the polymeric chains, and adequate energy for the polymeranalog reaction. Therefore gelatinization of starch has been carried out in excess water in the presence of the polymer emulsion in a reaction flask. The homogenous starch–polymer emulsion was dried and the trans-esterification reaction was carried out in the internal mixer in the absence of water at elevated temperature. Experiments have been carried out without using catalyst and in the presence of sodium carbonate, zinc-acetate and titanium(IV) butoxide. Sodium carbonate has been selected for promoting gelatinization of starch, from zinc-acetate and titanium(IV) butoxide catalytic effect to trans-esterification was expected. The blends were tested for chemical structure by ^{1}H NMR and ^{13}C NMR spectroscopy, for mechanical strength, for thermal stability by TGA analysis, for relaxational transitions by DSC and dynamic mechanical spectroscopy, and for swelling in water.

2. Experimental

2.1. Materials

Native wheat starch "A" a product of Szabolcs Starch Ltd. (H-4700 Mátészalka-Vágóháza Hungary) is a white powder of neutral taste, typical odor, with light binding capacity. Amylose content is about 25%. Specifications are the following:

Moisture content:	max. 15% by mass
Ashes:	max. 0.3%
Protein content:	max. 0.5%
SO_2:	max. 0.5%
Acid degree:	max. 20 cm³ (0.1 mol NaOH necessary to neutralize 100 g starch)
pH-value:	5–6
Microbiology:	Salmonella/25 g: negative
	E. coli/g: <10⁴
	Enterobacteriaceae/g: <10³
	quantity of microbe/g: <10⁶
	mould fungus/g: <10⁴
Storability:	in case of proper storing in dry space unlimited

The polymer emulsions are manufactured by DUS-LO Rt. Bratislava, Slovakia and marketed by Enviro-chem Rt., Budapest, Hungary.

Duvilax® *B* is an unplasticized poly(vinyl acetate) emulsion in water with solids content of min. 48.5 mass%, pH 3–5, viscosity (Brookfield, 23 °C) 3–8 Pa s and minimal filmforming temperature of 18 °C.

Duvilax® *BD20* is poly(vinyl acetate) emulsion containing poly(vinyl alcohol) as protective colloid and 20% diisooctyl phthalate plasticizer. The solids content: is min. 53.5 mass%, pH: 3–5, viscosity (Brookfield, 23 °C): 6–15 Pa s, and the minimal filmforming temperature: +2 °C.

Duvilax® *KA11* is an emulsion copolymer of vinyl acetate and butyl acrylate. Its solids content is min. 51.5 mass%, pH 4–6, viscosity (Brookfield, 23 °C) 1–8 Pa s, and minimal filmforming temperature +5 °C.

Duvilax® *KA4* is an emulsion copolymer of vinyl acetate and butyl acrylate forming a self-adhesive film. Solids content is min. 50 mass%, pH 4–7, viscosity (Brookfield, 23 °C) 6–30 Pa s, and minimal filmforming temperature 0 °C.

Sodium carbonate and *zinc-acetate* are products of Reanal Finechemical Co., Hungary, *titanium(IV) butoxide* is supplied by Sigma Aldrich Ltd. They were used as received.

2.2. Preparation of the materials for reactive blending

Natural wheat starch, polymer emulsion (and catalyst) were weighed in a three-necked round bottom flask equipped with a water bath, mechanical stirrer, reflux condenser and thermometer. The ratio of components was selected so, that two OH groups in the repeat unit of starch should be transesterified by the polymer. For trans-esterification with poly(vinyl acetate), e.g. 215.8 g 38% suspension of natural wheat starch (corresponding to 82 g (0.51 mol) of dry starch granules) and 180.62 g 48.5% Duvilax® B dispersion (corresponding to 87.6 g (1.02 mol) of dry poly(vinyl acetate)) were weighed in. If catalyst was used, its quantity was 0.01 mol/mol PVAC, the quantity of sodium carbonate was 0.1 mol/mol starch. Sodium carbonate and zinc-acetate have been dissolved in water and added to the starch suspension in the form of solution before the PVAC emulsion was added. Titanium(IV) butoxide was added during reactive blending.

The temperature of water bath is raised to boiling, the content of the flask is stirred at elevated temperature (ca. 80 °C) until gelatinization of the starch component is attained. The formed homogenous gel is poured to a tray, dried at 60 °C in a drying oven and ground.

2.3. Reactive blending

Reactive blending was carried out in a Brabender W 50EH internal mixer of a Haake Rheocord EU 10V plastograph at a rate of 50 min^{-1}, at 150 °C for 20 or 60 min. The volume of the mixer was 48 cm^3. From the blends sheets of 1 mm thickness were pressed with a Fontijne SRA 100 for the investigations.

2.4. Methods of characterization

The blends were analysed without purification by ^{1}H NMR, and ^{13}C NMR spectroscopy with a Bruker DRX-500 in deuterated dimethyl sulfoxide in 10 mg/ml concentration at 80 °C. Thermogravimetric analysis was carried out by using a Perkin Elmer TGA-6 on 10 mg sample from 30 to 600 °C at a rate of 10 °C/min in purging nitrogen (40 ml/min). For DSC analysis served a Perkin Elmer DSC 7. Measurements were carried out on 3–5 mg sample in purging nitrogen in the temperature range of −60 to 220 °C at a rate of 10 °C/min. Dynamic mechanical thermal analysis was carried out with the dynamic mechanical analyzer DMTA MkII of Polymer Laboratories. The temperature range was −100 to 180 °C, frequency 1 Hz, strain x4 and the heating rate 3 °C/min. Type of load was single cantilever bending. Mechanical properties of samples have also been tested with an Instron mechanical tester with a measuring cell of 500 N and a rate of 10 mm/min. The clamp distance was 40 mm. The width of the test samples was 10 mm, the thickness 1 mm. Swelling the samples in water has also been tested.

3. Discussion of results

3.1. Chemical reactions during reactive blending

Reactive blending of starch with poly(vinyl acetate) gives chance for a trans-esterification reaction between the two polymers resulting in the acetylation of some of the OH groups of the starch repeat unit with simultaneous formation of OH groups on poly(vinyl acetate) chain:
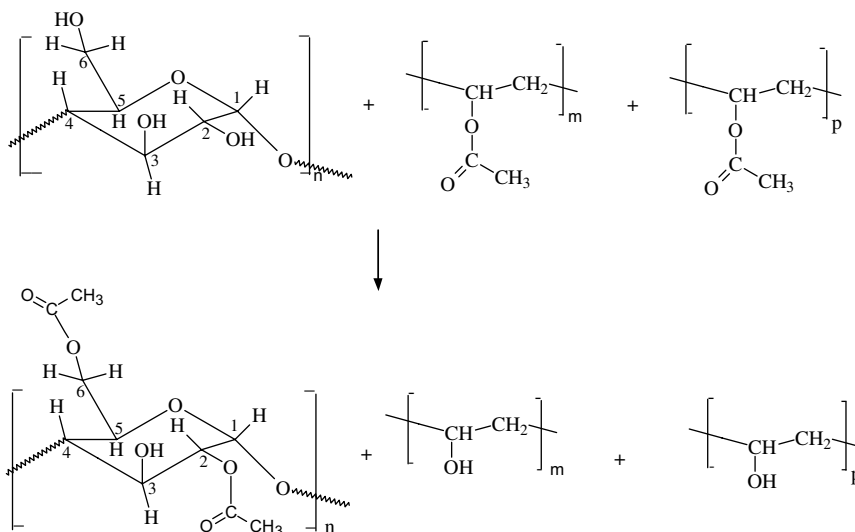
This presumes the formation of an in situ blend of unreacted starch, of starch mono- and diacetate, of poly(vinyl acetate) and of poly(vinyl acetate-co-vinyl alcohol).

In case of poly(vinyl acetate-co-butyl acrylate) transesterification between the pendant butylester groups and starch OH groups is also possible enabling the formation of chemical bonding between the starch and the copolymer with simultaneous release of n-butanol:

and of their copolymers is expected. Results of both ^{13}C NMR, and ^{1}H NMR spectroscopy proved that reaction took place between starch and the selected polymers.

3.2. Results of ^{13}C NMR spectroscopy

In order to ease the evaluation of the reactive blends, wheat starch acetate has been synthesized and character-
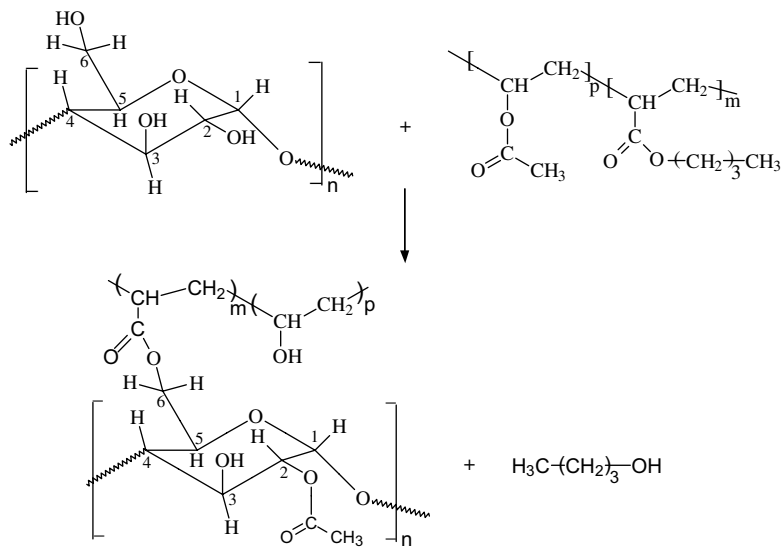
As a result the formation of an interpenetrating polymer network of starch, of partially acetylated starch, poly(vinyl acetate-co-vinyl alcohol-co-butyl acrylate)

ized together with wheat starch by ^{13}C NMR and ^{1}H NMR spectroscopy. The results of ^{13}C NMR spectroscopy of poly(vinyl acetate), of poly(vinyl acetate-co-

butyl acrylate) and of their blends with wheat starch after reaction at 150 °C for 20 min are summarized in Table 1.

In starch acetate resonance of the carbonyl C=O groups appear at 205.95 ppm, at 169.59 and at 168.93 ppm. Compared to starch new resonances could be detected for C-3 and C-6 in the range of 71–60 ppm, and for the formed methyl groups at 30.68 ppm and at 20.49 ppm.

It is difficult to prove the formation of starch acetate from wheat starch and poly(vinyl acetate) by ^{13}C NMR spectroscopy due to the same resonance of the C=O carbon atoms as well as of the CH_3 carbons in both polymers. The resonance at 39.93 ppm in the reaction product may refer to trans-esterification between starch and PVAC.

In the reactive blend of poly(vinyl acetate-co-butyl acrylate) and wheat starch the appearance of the signals of the formed CH_2 groups at 60.43 and at 63.83 ppm, and the shifting of starch carbon signals refer to trans-esterification between the copolymer and wheat starch.

3.3. Results of ^1H NMR spectroscopy

The proton assignments of wheat starch, acetylated wheat starch, poly(vinyl acetate), poly(vinyl acetate-co-butyl acrylate) and of their blends with wheat starch after reaction at 150 °C for 20 min are shown in Table 2.

Table 1
Chemical shifts of carbon atoms in poly(vinyl acetate), in poly(vinyl acetate-co-butyl acrylate) and in their reaction product with wheat starch (starch/polymer 1/1 m/m) after reactive blending at 150 °C for 20 min in the internal mixer [18–22]

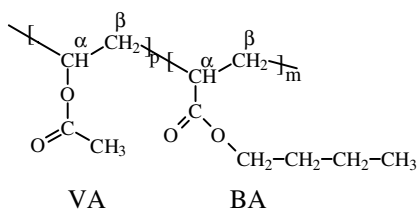| Carbon atom	Chemical shift (ppm)			
	Duvilax® B	Duvilax® B/wheat starch	Duvilax® KA11	Duvilax® KA11/wheat starch
C=O	206.45	205.97	205.93	205.94
	169.76	169.36	169.25	169.25
	169.67	169.27		
1 (starch)		99.84		99.80
4 (starch)		78.56		78.56
5 (starch)		73.04		73.03
2 (starch)				71.81
3 (starch)		71.45		71.42
CH	69.77	69.67	69.67	69.67
	67.88	67.79	67.75	67.88
	66.99	66.89	66.88	66.97
	66.64	66.57	66.55	
	66.27	66.18		**63.83 (formed)**
	65.90		63.75	63.76
6 (starch)				**60.43 (formed)**
		60.33		60.32
CH_2	40.01	40.01		
		39.93 (formed)		
	39.85	39.84		
	39.68	39.68		
	39.51	39.51		
	39.35	39.34		
	39.18	39.18		
	39.01	39.01		
	38.75			
	38.51	38.50		
	38.35		30.68	30.68
	38.02	38.04	30.05	30.00
CH_3	30.67	30.70	20.70	20.75
	20.78	20.79	18.64	18.64
	20.73		13.55	13.55
	20.64			

Table 2
Chemical shifts of protons of wheat starch, of acetylated wheat starch, poly(vinyl acetate), poly(vinyl acetate-co-butyl acrylate) and of their blends with wheat starch after reaction at 150 °C for 20 min in the internal mixer [20–24]

Proton	Wheat starch	Wheat starch acetate		Duvilax® B	Duvilax® B/wheat starch	Duvilax® KA11	Duvilax® KA11/ wheat starch
		DS = 1.16	DS = 2				
H-6	5.465	5.470	5.478		**5.488**		**5.483**
	5.387		5.443		**5.479**		5.474
		5.380			5.389		**5.439**
							5.427
							5.386
		5.250	5.253				
		5.170	5.178				
		5.110	5.104		**5.104**		**5.105**
			4.975				
			4.955				
H-1	5.098	4.880	4.840				
		4.740	4.737				
Hα				4.770	4.775	4.769	4.767
OH				4.020	4.020		
CH₂– OCO						3.979	3.979
						3.507	
H-4	4.561		4.563		4.563		4.559
			4.476				4.510
		4.310	4.303				
		4.240	4.234				
		4.030					
		3.950	3.951				
			3.848				
		3.840	3.841				
			3.753				
H-2, H-3	3.649	3.650	3.656		3.651		3.652
H-5	3.578	3.590	3.598		3.582		3.584
			3.587		3.506		**3.507**
							3.477
							3.420
							3.409
							3.350
Hα				3.510	3.487		–
					3.466		
					3.380		
					3.350		
CH₃			2.358				
			2.243				
		2.210	2.209				
			2.178				
		2.080	2.146				
			2.119		**2.114**		
			2.084	2.080	2.084		**2.084**
			2.062	2.040	2.026		**2.051**
			2.055	2.030	2.001		**2.024**
			2.028				
			2.009				
			1.995				
			1.980				
			1.955				

Table 2 (*continued*)

Proton	Wheat starch	Wheat starch acetate		Duvilax® B	Duvilax® B/wheat starch	Duvilax® KA11	Duvilax® KA11/ wheat starch
		DS = 1.16	DS = 2				
		1.950	1.947			1.940	1.940
			1.842				
		1.230	1.235		**1.235**		
			1.147				
H_β				1.970	1.971	2.113	
				1.940	1.944	2.084	
				1.930	1.932	2.082	
				1.910	1.922	2.054	
				1.750	1.912	1.970	1.970
					1.899	1.931	1.932
					1.746	1.909	1.908
						1.746	1.748
							1.626
							1.613
						1.541	1.541
						1.351	
						1.337	1.337
						1.325	1.326
							1.236
CH_3 (BA)						0.903	0.903
						0.888	0.888
						0.873	0.874

VA   BA

Repeat unit of poly(vinyl acetate-co-butyl acrylate)

The ^1H NMR spectrum of the blend of PVAC with wheat starch proves the formation of starch acetate by the appearance of H-6 resonances at 5.488, at 5.479, and at 5.104 ppm. Resonances at 2.114 and at 1.235 ppm refer to the methyl groups of the formed starch acetate. The Hα resonances in the range of 3.487–3.350 ppm support the formation of poly(vinyl acetate-co-vinyl alcohol).

The blend of poly(vinyl acetate-co-butyl acrylate) with wheat starch also shows resonances supporting trans-esterification at 5.483, at 5.439 and at 5.427 ppm. Together with the resonance at 3.584 ppm (H-5) new resonances appear at 3.507, at 3.477, at 3.420, at 3.409 and at 3.350 ppm referring to chemical reaction of the CH_2OH group of starch. Formation of acetate groups are proven by the appearance of new CH_3 signals at 2.084, 2.051 and 2.024 ppm.

3.4. Homogeneity, relaxational transitions

The DSC measurements served to determine the relaxational transitions of the reactive blends. From the relaxational transitions we could conclude to the homogeneity of the blend, and could compare the T_g with that of the components. DSC in itself would not be a sufficient evidence for reactive blending, together with DMTA and NMR, however, it supported the success of the process. The determination of the T_g range of the blends is very important for the performance of the material.

All the blends prepared gave a translucent homogenous film. The films were elastic except those prepared with the unplasticized poly(vinyl acetate) Duvilax® B. One glass transition range was detected for each blend. The glass transition ranges revealed by DSC analysis are given in Table 3.

The glass transition temperature of natural wheat starch is 131 °C as determined by the inflection temperature of the transition. Thermal treatment at 150 °C for 20 min did not effect the glass transition temperature range of the polymers. It has been observed, that the glass transition of the pure polymers was detected in a temperature range somewhat higher by DSC 1st heating, than by the second heating. This has no more been observed for their blends with wheat starch. The glass transition range of the blends has increased compared to

Table 3
Glass transition range of the polymers and of their blends with wheat starch determined by DSC analysis

Material	DSC 1st heating			DSC 2nd heating		
	T_{onset} (°C)	$T_{infl.}$ (°C)	T_{endset} (°C)	T_{onset} (°C)	$T_{infl.}$ (°C)	T_{endset} (°C)
Wheat starch	Overlapped by gelatinization peak			86.84	130.63	148.84
Duvilax® BD20 no treatment	4.97	12.74	30.18	0.73	9.12	22.71
Duvilax® BD20 150 °C 20 min	3.35	12.8	30.17	1.69	7.43	23.47
Starch:BD20 1:1 150 °C 20 min (no catalyst)	7.25	15.0	18.91	10.5	16.0	27.7
Starch:BD20 1:1 150 °C 60 min (no catalyst)	8.0	17.3	21.0	13.5	21.0	24.0
Starch:BD20 1:1 150 °C 60 min (Na$_2$CO$_3$)	3.0	13.3	20.0	8.0	16.9	22.0
Starch:BD20 1:1 150 °C 60 min (Ti(OBu)$_4$)	7.0	15.3	21.0	10.5	17.7	22.3
Starch:BD20 1:1 150 °C 60 min (Zn-acetate)	6.1	13.6	18.5	9.7	16.8	22.2
Duvilax® B no treatment	36.15	44.13	48.92	30.35	39.71	45.51
Duvilax® B 150 °C 20 min	35.84	44.52	49.28	31.43	40.45	46.00
Starch:Duvilax® B 1:1 150 °C 60 min (no catalyst)	27.9	38.7	45.8	35.7	43.5	50.0
Duvilax® KA11 no treatment	14.97	21.26	35.23	8.20	15.43	26.94
Duvilax® KA11 150 °C 20 min	14.34	21.31	34.13	8.96	14.94	20.99
Starch:Duvilax® KA11 1:1 150 °C 60 min (no catalyst)	15.0	22.7	29.0	18.9	26.3	30.0
Starch:Duvilax® KA4 1:1 150 °C 60 min (no catalyst)	−32.5	−22.4	−22.7	−30.0	−23.3	−19.0

that of the polymers. The glass transition range of the blend of wheat starch with plasticized poly(vinyl acetate) (Duvilax® BD20) is in the range of 8–24 °C, with non-plasticized poly(vinyl acetate) (Duvilax® B) of 28–50 °C. The presence of catalysts used did not significantly effect the glass transition range of the blends.

Wheat starch blended with poly(vinyl acetate-co-butyl acrylate) (Duvilax® KA11) has a glass transition range between 15 and 30 °C, while with copolymer of higher butyl acrylate content (more internal plasticizer) (Duvilax® KA4) between −33 and −19 °C.

Results of DMTA analysis are in accordance with those of DSC. Glass transition temperature of starch/externally plasticized poly(vinyl acetate) (Duvilax® BD20) blend is 22 °C (Fig. 1), of starch/poly(vinyl acetate-co-butyl acrylate) (Duvilax® KA11) blend is 29 °C as determined by the peak temperature of the maximum of the tan δ curve.
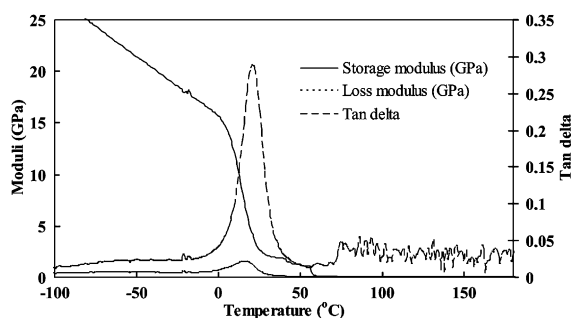

Fig. 1. Results of DMTA analysis of the reactive blend prepared from wheat starch and externally plasticized poly-(vinyl acetate) (Duvilax® BD20) at 150 °C for 60 min (starch/polymer 1/1 m/m).

It should be noted that the blends have their glass transition temperature range at or near ambient temperature, which is disadvantageous for practical use. For further experiments shifting the glass transition temperature range from ambient is an essential issue.

3.5. Mechanical behavior

The mechanical strength of the blends of wheat starch with the homopolymer was rather low. The unplasticized poly(vinyl acetate) (Duvilax® B) resulted in such a rigid blend with wheat starch, that the mechanical strength could not be measured, the test specimen broke at once before putting them into the clamps. The films prepared from blend of wheat starch and plasticized poly(vinyl acetate) (Duvilax® BD20) were soft, elastic, the test probes easily stick together, the modulus could not always be measured. In order to elucidate the reason for the low mechanical performance of the blends, the homopolymer has also been tested before and after thermal treatment in the internal mixer. The results are summarized in Table 4.

The homopolymer poly(vinyl acetate) has a rather high tensile strength of 10.54 ± 1.51 MPa. The strain at break is 216.70 ± 55.48%. This means that the molecular mass of the homopolymer might have exceeded the entanglement molecular mass. The polymer, however, undergoes a severe change during the thermal treatment in the internal mixer at 150 °C for 20 min. While the strength practically does not change, the strain at yield and at break decreases dramatically. This may be due to the lack of plasticizing effect of moisture, which is lost during thermal treatment of the homopolymer. The presence of external plasticizer (i.e. 20% diisooctylphthalate) in the homopolymer resulted in a decrease in

Table 4
Results of mechanical tests of PVAC homopolymers and their blends with wheat starch before and after thermal treatment at 150 °C without catalyst (rate of measurement 10 mm/min)

Mechanical properties	Material					
	Non-plasticized PVAC (Duvilax® B)[a]		Externally plasticized PVAC (Duvilax® BD20)		Starch/Duvilax® BD20 1/1 m/m mol starch/mol PVAC = 0.60	
	No treatment	150 °C 20 min	No treatment	150 °C 20 min	150 °C 20 min	150 °C 60 min
Tensile stress (MPa)	10.54 ± 1.51	12.28 ± 4.30	2.77 ± 0.24	0.31 ± 0.04	0.53 ± 0.04	1.21 ± 0.13
Strain at break (%)	216.70 ± 55.48	0.77 ± 0.28	61.02 ± 9.10	816.07 ± 83.29	66.70 ± 11.41	71.09 ± 13.72
Stress at yield (MPa)	10.62 ± 1.22	13.17 ± 4.86	2.92 ± 0.29	0.37 ± 0.01	2.05 ± 0.03	1.99 ± 0.06
Strain at yield (%)	3.53 ± 0.45	0.74 ± 0.29	56.41 ± 8.67	520.27 ± 53.78	11.30 ± 0.27	17.67 ± 1.13
Modulus (Young's 0.1–0.3%) (GPa)	2.78 ± 0.43	2.61 ± 0.21	0.06 ± 0.01	0.02 ± 0.01	0.12 ± 0.02	0

[a] Breaks at the clamp.

strength by an order of magnitude and in an increase in the elongation at break and at yield. After thermal treatment in the internal mixer at 150 °C for 20 min the strength decreased by an order of magnitude and the elongation at break and at yield enormously increased. Wheat starch did not significantly improve the mechanical performance, which may be due to the presence of the plasticizer. Increasing the reaction time, however, advantageously effected the mechanical performance of the blend as a result of chemical reaction between starch, PVAC and plasticizer. Table 5 shows the effect of the increase of the concentration of wheat starch on the mechanical performance of the blend with plasticized PVAC. The increase in the amount of starch up to 0.60 mol/mol PVAC resulted in the improvement of the mechanical strength after thermal treatment at 150 °C for 60 min. Elongation at break, however, decreased with increasing amount of starch. The overall strength is very low due to the presence of high amount of external plasticizer.

Table 5
The effect of the amount of wheat starch to plasticized poly(vinyl acetate) (Duvilax® BD20) on the mechanical performance of the blend (after reaction at 150 °C for 60 min in the presence of Na_2CO_3) (rate of measurement 10 mm/min)

Mechanical properties	Mole wheat starch/mol PVAC		
	0.30	0.40	0.60
Tensile stress (MPa)	1.12 ± 0.17	1.48 ± 0.18	1.73 ± 0.16
Strain at break (%)	174.46 ± 31.68	79.06 ± 13.23	42.19 ± 5.86
Stress at yield (MPa)	1.49 ± 0.06	1.81 ± 0.06	2.3 ± 0.04
Strain at yield (%)	73.75 ± 2.94	36.36 ± 1.27	15.92 ± 1.3
Modulus (Young's 0.1–0.3%) (GPa)	0.1 ± 0.04	0	0

Table 6
Results of mechanical tests of the film of poly(vinyl acetate-co-butyl acrylate) (Duvilax® KA11) before and after thermal treatment in the internal mixer at 150 °C for 20 min and of its blend with wheat starch after reaction at 150 °C for 20 min (rate of measurement: 30 mm/min)

Mechanical properties	Poly(vinyl acetate-co-butyl acrylate) (Duvilax® KA11)		Starch/Duvilax® KA11 0.5/1 molar blend
	No treatment	150 °C 20 min	150 °C 20 min
Tensile stress (MPa)	[a]0.30 ± 0.10	0.93 ± 0.19	2.46 ± 0.72
Strain at break (%)	1033.84 ± 0.02	959.37 ± 101.25	23.29 ± 1.66
Stress at yield (MPa)	0.52 ± 0.13	1.01 ± 0.13	5.76 ± 0.73
Strain at yield (%)	426.45 ± 45.41	857.62 ± 122.42	10.16 ± 2.49
Modulus (Young's 0.1–0.3%) (GPa)	0.02 ± 0.00	–	0.52 ± 0.15

[a] Does not break.

Catalysts had no effect on the strength of the blends with the homopolymer, except zinc-acetate, in the presence of which there was some increase in strength.

The comonomer butyl acrylate serves as an internal plasticizer for PVAC. Table 6 shows the results of mechanical tests of the copolymer (Duvilax® KA11) before and after thermal treatment in the internal mixer, as well as of its blend with wheat starch. The copolymer has very low strength, it does not break during the measurement. Thermal treatment of the copolymer in the internal mixer does not adversely effect its mechanical properties, it results in a decrease in the elongation at break, but not as severe, as in case of the homopolymer. The relatively high strength of the blends may be due to chemical reactions between starch and the copolymer and due to compatibility of the resulted blend. Since chemical reaction between starch and the copolymer involves the elimination of butanol, the lack of plasticizing effect resulted in a decrease in the elongation at break and at yield. Prolonged reaction time resulted in the improvement of the mechanical properties. This may be due to the proceeding of chemical reactions between starch and the copolymer. Catalysts further increased the strength of the films.

The copolymer of vinyl acetate and butyl acrylate with higher butyl acrylate content, Duvilax® KA4 resulted with wheat starch in a blend too soft to measure mechanical properties.

3.6. Swelling of the prepared films

Fig. 2 shows the water uptake of films prepared from blends of wheat starch and polymers without catalyst. The maximum of water uptake is attained within 8–10 days, and it is the highest, almost 200%, with poly(vinyl acetate-co-butyl acrylate), Duvilax® KA11. Blends of wheat starch with the copolymer with higher butyl acrylate content, Duvilax® KA4 and with poly(vinyl acetate) had lower degree of swelling in the range of 100–150%. The presence of diisooctyl phthalate plasticizer in poly(vinyl acetate) did not effect the water uptake of the blends. Prolonged soaking time caused a decreasing tendency of water uptake, which may be due to dissolution of material from the blends.
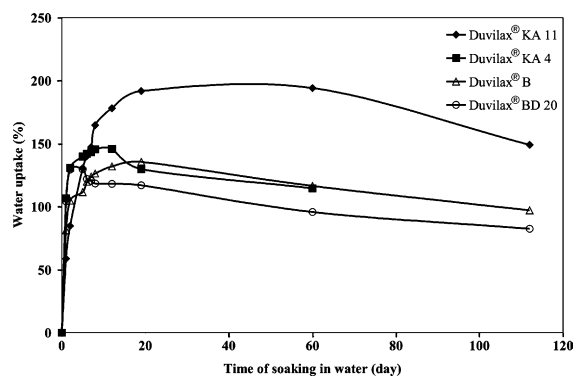

Fig. 2. The degree of swelling of the reactive blends prepared from wheat starch and different polymers at 150 °C for 60 min in the absence of catalyst (starch/polymer 1/1 m/m).

The presence of Ti(OBu)$_4$ catalyst had no effect on the water uptake of the samples. In the presence of zinc-acetate the water uptake was somewhat higher, and sodium carbonate resulted in the highest degree of swelling. The same effect of catalysts was observed for the blends prepared with all the polymers.

3.7. Thermal stability

Results of thermogravimetric analysis of wheat starch/polymer reactive blends are represented by Table 7.

All the reactive blends have rather high thermal stability with an onset temperature of thermal decomposition between 290 and 300 °C. The blend of wheat starch with plasticized poly(vinyl acetate) Duvilax® BD20 has the lowest temperature of thermal decomposition of 290 °C.

In the presence of sodium carbonate the onset temperature of thermal decomposition decreased by about 60 °C, and also the mechanism of decomposition changed, as could be concluded from the derivative thermogravimetric curves. Catalysts of titaniumtetrabutoxide and zinc-acetate did not have a significant effect on the thermal decomposition of the reactive blends.

Table 7
Results of thermogravimetric analysis of wheat starch/polymer 1/1 m/m blends after reaction at 150 °C for 60 min in the internal mixer

Modifying polymer	Δm at 170 °C (%)	T_{onset} (°C)	Δm at T_{onset} (%)	T_{endsat} (°C)	Δm at T_{endset} (%)	Residual mass at 600 °C (%)
Duvilax® B	3.74	300.16	5.39	485.14	84.49	14.17
Duvilax® BD20	3.87	289.48	11.13	478.21	86.08	13.15
Duvilax® KA11	3.05	294.90	5.90	479.53	91.00	8.49
Duvilax® KA4	3.12	289.61	4.88	444.58	88.96	10.02

4. Summary

An attempt was made to prepare new biodegradable polymers by reactive blending of wheat starch with poly(vinyl acetate) and poly(vinyl acetate-co-butyl acrylate). Homogenization of natural starch powder with the polymer emulsions took place with simultaneous gelatinization of starch in a laboratory reactor at 80 °C. Trans-esterification was carried out in an internal mixer at 150 °C in the absence of catalyst, as well as in the presence of sodium carbonate, titanium-tetrabutoxide and zinc-acetate. The reaction products were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, DSC analysis, dynamic mechanical thermal analysis (DMTA), thermogravimetry, mechanical testing, and swelling in water. Partial trans-esterification of wheat starch took place, as proven by NMR spectroscopy. The resulted blends gave homogenous, translucent films with one glass transition temperature range. The glass transitions revealed by DSC were in accordance with DMTA measurements. Wheat starch blended with non-plasticized poly(vinyl acetate) had a glass transition of 44 °C, with plasticized poly(vinyl acetate) of 22 °C, and with poly(vinyl acetate-co-butyl acrylate) of 29 °C.

The mechanical performance of the blends with plasticized homopolymer was rather poor due to the high plasticizer content. The blend of wheat starch with copolymer of vinyl acetate and butyl acrylate (Duvilax® KA11) resulted in improved mechanical strength compared to that of the copolymer. The presence of starch in the blend, however, decreased the elongation at yield and at break, which is disadvantageous for processability. Swelling of wheat starch blends with poly(vinyl acetate-co-butyl acrylate) in water was 150–250%, higher than that of the blends with poly(vinyl acetate), which had the degree of swelling of 100–150%. The blends have rather high thermal stability, the starting temperature of thermal decomposition was in the range of 290–300 °C. The blend of wheat starch with plasticized poly(vinyl acetate) had the lowest starting thermal decomposition temperature of 290 °C due to high plasticizer content. The presence of sodium carbonate decreased the starting thermal decomposition temperature of each polymer blend by about 60 °C.

Acknowledgments

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