Environmentally Friendly Biocomposites Based on Waste of the Dairy Industry and Poly(vinyl alcohol)

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ABSTRACT: Environmentally friendly polymeric biocomposites based on whey powder, a waste material of the dairy industry, and fully or partially hydrolyzed poly(vinyl alcohol) were prepared and characterized with optical microscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry, and stress–strain analysis, and their biodegradation was evaluated with the modified Zahn–Wellens method and the spectrophotometric determination of poly(vinyl alcohol). In addition, the ability of the biocomposites to absorb moisture and its consequent influence on the mechanical properties were investigated under different storage conditions. The structural differences of the two types of poly(vinyl alcohol) matrices had a significant effect on all the mentioned characteristics. Possible molecular interactions between the polymer matrix and modifier, due to hydrogen bonding, were also examined. First-order kinetics were applied for the biodegradation data. The two-phase character of the biodegradation was shown. The results indicated that whey powder is suitable for the modification of polymers, and this is important for the production of biodegradable polymer materials and the consequent reduction of the environmental load. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1869–1879, 2007

Key words: biodegradable; biomaterials; composites

INTRODUCTION

Biodegradable polymers, materials that can be decomposed by the action of living organisms, represent one possibility for solving the problem of the annually increasing amount of plastic waste and the consequent environmental load. These materials survive for a markedly shorter time in the environment in comparison with nonbiodegradable polymers.[1,2]

Generally, biodegradable polymers can be divided into three groups.[3] Biopolymers, polymers of natural origins (polysaccharides, proteins, and microbial polyesters), belong to the first group. The second group consists of synthetic biodegradable polymers, that is, mostly oil-based polymers with a hydrolyzable backbone chain (some polyesters, polyamides, and polyurethanes and also some vinyl polymers may be mentioned here). The last group includes modified polymeric materials; this means polymers (synthetic or natural) that undergo some kind of modification (physical or chemical) to achieve biodegradability and/or changes in the material properties and costs.

Economic factors are actually the main reason for the relatively slow introduction of biodegradable polymers into areas (e.g., the packaging industry) in which nonbiodegradable plastics have been used so far.[4] The conjunction of ecological and economical demands has led to the idea of waste utilization for the production of biodegradable polymeric materials. A number of studies describing the uses of waste from the leather industry, agriculture, and mineralogy have been already reported. For instance, Saha et al.[5] showed a way to produce biodegradable materials through the combination of synthetic polymers and protein hydrolysates isolated from chrometanned solid leather waste. On the other hand, Ozaki et al.[6] presented a biodegradable composite from waste wood. This composite displayed good mechanical properties and even higher durability than solid wood. Inorganic industrial wastes have also been used for the preparation of low-cost biodegradable polymer composites with semiconducting and superparamagnetic properties, which can be useful in the production of microelectronic devices.[7]

This work is focused on the waste of the dairy industry: whey. Liquid whey is a byproduct appearing in cheese production in large quantities, and its annual production is continuously rising. Although whey is used in several applications, such as food supplements and animal feedstuffs, a lot of whey is still wasted, and this means a potential environmen-

tal hazard. Consequently, there is significant interest in finding new applications for it.[8]

According to the aforementioned division of biodegradable polymers, poly(vinyl alcohol) (PVA) belongs to the group of synthetic biodegradable polymers. It is a water-soluble material employed in many practical applications, including the binding of pigments, dip coating, and the production of detergents, adhesives, paints, and solution-cast films. PVA has good mechanical properties in the dry state and chemical resistance to various chemical agents. In addition, the properties of PVA can be tailored during its preparation through the degree of hydrolysis.[9,10]

In this article, we propose a new biodegradable polymeric material based on dried whey waste and two sorts of PVA with different degrees of hydrolysis. The optical, mechanical, thermal, and structural properties and biodegradability of the material were investigated via optical microscopy, stress–strain analysis, differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and biodegradation tests in an aquatic environment.

EXPERIMENTAL

Materials

Two types of PVA (Sloviol P 98-14 and Sloviol P 88-08) were obtained from Nováké Chemické Závody (Nováky, Slovak Republic). Their detailed characteristics are shown in Table I. Liquid whey, waste from the dairy industry, was kindly provided by Dairy Kromilk, Ltd. (Kroměříž, Czech Republic).

Preparation of the polymeric films

First, liquid whey was sterilized in steam at 121°C for 15 min with a Tuttnaner 3870 M autoclave. The sterilized whey was then poured into a Petri dish and dried at 50°C for 48 h. The resulting material was mechanically ground and sieved on a Retsch AS 200 sieving machine. Whey powder (WP) with a particle diameter in the range of 250–500 μm was used for further experiments. It was determined that the content of organic carbon in WP was 35.29%.

The samples were prepared in the following way. An aqueous solution of the polymer (either Sloviol P 98-14 or Sloviol P 88-08) was prepared through the dissolution of polymer granules with a relevant part of WP at 80°C for 30 min under continuous stirring. The concentrations of WP in the investigated systems were 0, 10, 20, 30, 40, and 50 wt %. The solutions were then poured into an acrylic mold and dried at 35°C in a temperature-controlled incubator for 48 h. The thicknesses of the prepared transparent films were in the range of 150–200 μm.

TABLE I
Characteristics of the PVA Matrices

Characteristic	Sloviol P-9814	Sloviol P-8808
Molecular weight (g/mol)	61,000–100,000	34,000–72,000
Degree of hydrolysis (mol %)	98.80	87.20
Viscosity in a 4% water solution (mPa s)	13.20	9.30
Volatile substances (wt %)	2.80	2.10
pH in a 4% water solution	6.50	5.1
Ash content (wt %)	0.51	0.38

The information was taken from the supplier, Novacke Chemické Závody.

Conditioning of the samples

The samples were divided into two groups. The first set was dried in a vacuum drier at 40°C and 30 kPa for 24 h and was stored in a desiccator containing silica gel. The second group was placed in a conditioning chamber, in which a constant relative humidity (50%) and temperature (25°C) were maintained. The influence of the conditioning method on the moisture content and mechanical properties of the samples was investigated after 2 weeks.

Methods

Optical microscopy

To study the mixing nature of the PVA matrices and their biocomposites with WP, optical microscopy (CX 31, Olympus) was used. The images of the samples were taken with an Olympus C4000 digital camera, and their conversion into a black-and-white form was performed in Adobe Photoshop 6.0 CE.

FTIR spectroscopy

To identify the physicochemical structures of pure PVA, WP, and their mixtures, an FTIR spectroscopy analysis was carried out. Attenuated total reflectance/Fourier transform infrared (ATR–FTIR) spectroscopy was conducted on powder and thin films with a Nicolet 320 FTIR instrument equipped with an attenuated total reflectance accessory using a Zn–Se crystal and software package OMNIC over the range of 4000–650 cm^{-1} at room temperature. A resolution of 2 cm^{-1} was maintained in all cases. The differential spectra were obtained by the subtraction of the polymeric mixture spectra and pure PVA film. All samples were conditioned at 50°C for 24 h to avoid the moisture effect on the ATR–FTIR spectra.

DSC

For the determination of the glass-transition temperature (T_g), DSC was used. A small piece of a sample

(ca. 4 mg) was placed in a steel pan and analyzed on a PerkinElmer Pyris 1 DSC instrument calibrated for the temperature and heat flow with indium. The experiments were performed according to the following program:

- Initial temperature, $-10°C$.
- First heating cycle, heating to $200°C$ ($20°C/\text{min}$).
- Holding at $200°C$ for 15 min.
- Cooling to $0°C$ ($20°C/\text{min}$).
- Holding at $0°C$ for 1 min.
- Second heating cycle, heating to $200°C$ ($20°C/\text{min}$).

The value of T_g was determined in the second heating cycle at the midpoint stepwise increase of the specific heat associated with the glass transition.

Determination of the water content

The water content in the polymeric films of pure PVA and PVA modified with WP was determined by the gravimetric method. The initial weight (W_i) of the samples was determined ($25 \times 50\ \text{mm}^2$) before drying. This was carried out in a vacuum oven at $50°C$ and 30 kPa up to a constant weight (W_d). The water content (W) was then calculated:

$$W(\%) = \frac{W_d - W_i}{W_i} \times 100 \qquad (1)$$

Static tensile measurements

The mechanical properties (Young's modulus, tensile strength, and strain at break) of samples based on PVA and WP were investigated with an Instron 8871 tensile testing machine at $23°C$ and 40% relative humidity. The samples were initially 50 mm long, 25 mm wide, and about 150–200 μm thick. The speed of the moving clamp was 50 mm/min, and Young's modulus was determined according to EN 10002 and ASTM E 8 standards. Five specimens were studied in each case.

Biodegradability

The laboratory tests of biodegradability were carried out in Erlenmeyer flasks (500 mL) under continuous shaking at 160 rpm at room temperature ($25°C$). Activated sludge from a municipal wastewater treatment plant (Zlin-Malenovice, Czech Republic) was used as a source of mixed microorganisms. The sludge was filtered, decanted, centrifuged (3000 rpm for 10 min), and resuspended in a mineral medium. It was aerated for not less than 24 h before the test.[11] The polymer samples were dissolved in distilled water, and an equivalent volume of the solution [the

initial total organic carbon concentration (TOC) was up to 100 ppm] was introduced into the reactor.

The environmental impact of the PVA and PVA WP polymeric materials was investigated in two ways: first according to the Zahn–Wellens method (ISO 9888) on the basis of measurements of TOC and second by the spectrophotometric determination of PVA.

TOC was measured on a Shimadzu 5000 A, and the biodegradation of the samples was calculated:

$$D_{\text{TOC}}(\%) = \left[1 - \frac{(C_t - C_b)}{(C_a - C_{ba})} \right] \times 100 \qquad (2)$$

where D_{TOC} is the biological degradation at time t (%); C_t and C_b are TOC values (mg/dm^3) in the test mixture and blank at the time of sampling, respectively; and C_a and C_{ba} are the TOC values in the test mixture and blank 3 h after the beginning of the test, respectively.

The methodology of the spectrophotometric determination of PVA was described in detail by Joshi et al.[12] In principle, PVA forms a blue complex with triiodide in the presence of boric acid. This complex absorbs in the visible wavelength area, and it is dependent on the concentration of PVA. The samples for the determination of the PVA concentration were collected regularly from the reactors, and after filtration through filter paper, they were spectroscopically analyzed at 670 nm and room temperature. The percentage of PVA biodegradation (D_{PVA}) was calculated in analogy with eq. (2).

The experimental data obtained from both TOC and spectrophotometric methods were evaluated with simple first-order kinetics [eq. (3)] and regression-processed by the least-squares method; the SOLVER subprogram of Microsoft Excel 7.0 was applied:

$$D = D_{\text{MAX}}(1 - e^{-k(t - t_{\text{LAG}})}) \qquad (3)$$

where D (%) is TOC (D_{TOC}) or PVA (D_{PVA}) removal at time t (h) of biodegradation, D_{MAX} (%) is the maximum removal of TOC or PVA (limit value), k (h^{-1}) is the rate constant, and t_{LAG} (h) is the lag phase of biodegradation.

RESULTS AND DISCUSSION

Morphology

Films of pure Sloviol P 98-14 are transparent and yellowish. On the other hand, pure Sloviol P 88-08 creates colorless films. Polymeric biocomposites become yellowish with an increasing content of WP. The effect of changing the WP concentration is shown in Figure 1 in more detail. In the Sloviol P
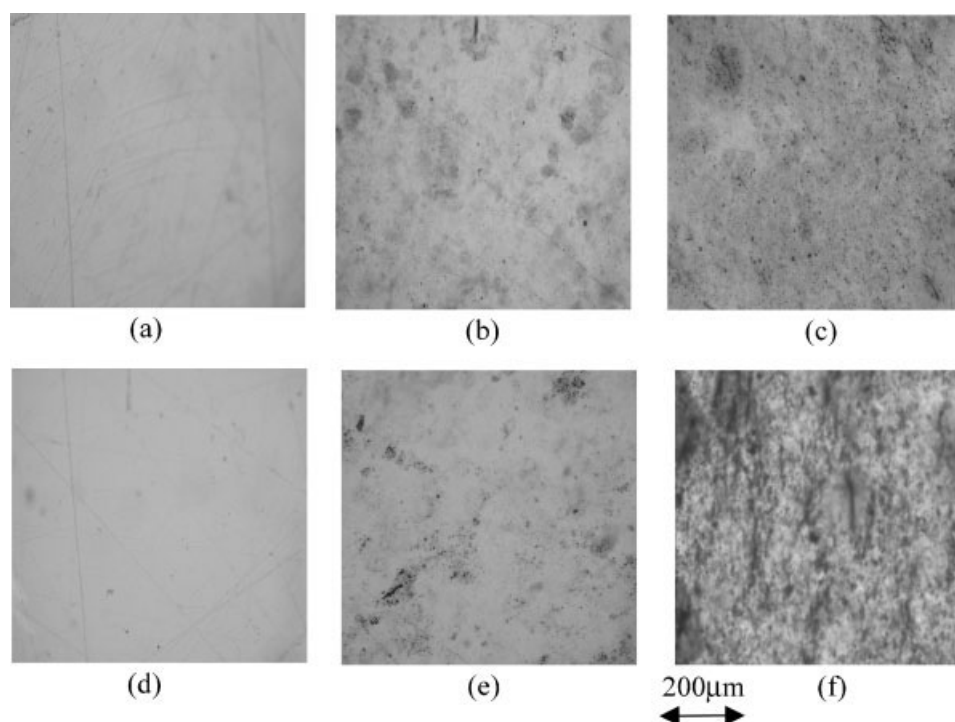
Figure 1 Optical micrographs of PVA and its composites with WP: (a) pure Sloviol P 98-14, (b) Sloviol P 98-14/20 wt % WP, (c) Sloviol P 98-14/50 wt % WP, (d) pure P 88-08, (e) Sloviol P 88-08/20 wt % WP, and (f) Sloviol P 88-08/wt % WP.

98-14 matrix [Fig. 1(a–c)], the particles of WP create agglomerates already at a concentration of 20 wt % [Fig. 1(b)]. This effect is even more visible at 50 wt %. On the contrary, the distribution of WP within Sloviol P 88-08 seems to show a certain uniformity, as can be noticed in Figure 1(d–f). The difference in the WP distributions within various types of PVA is especially obvious from a comparison of Figure 1(c,f).

The reason for these differences can be found in the characteristics of the polymer matrices (see Table I and Fig. 2). Although the degree of hydrolysis and viscosity of Sloviol P 98-14 are 98.8 mol % and 13.2 mPa s, respectively, these properties are lower for Sloviol P 88-08 (87.2 mol % and 9.3 mPa s). The pH probably also plays a considerable role here.

Effect of moisture on the mechanical properties

PVA and WP are supposed to be moisture-sensitive materials.[13,14] Thus, this work also studies the effects of different ways of conditioning and the resultant various contents of absorbed water on the mechanical properties of the biocomposites. As noted in the Experimental section, the samples were stored under two different sets of conditions before the tensile properties were tested. The water contents of the pure PVAs and their composites are shown in Figure 3. Generally, the water content increases with an increasing concentration of WP. Furthermore, the conditioning of samples at 50% relative humidity

increases the water content more than twofold in comparison with the dried samples. Interestingly, although the water content in the conditioned samples is more or less the same for both sets of biocomposites, there is a discrepancy in the case of the dried samples. Sloviol P 98-14 may interact more strongly with molecules of water because of its molecular structure than Sloviol P 88-08 does, and so a higher water content is present in the former biocomposites.

The effects of moisture on the mechanical properties of PVA/WP films are shown in Figures 4–6. A significant influence of the conditioning on the values of the Young's modulus, tensile strength, and strain at break can be seen from the graphs.

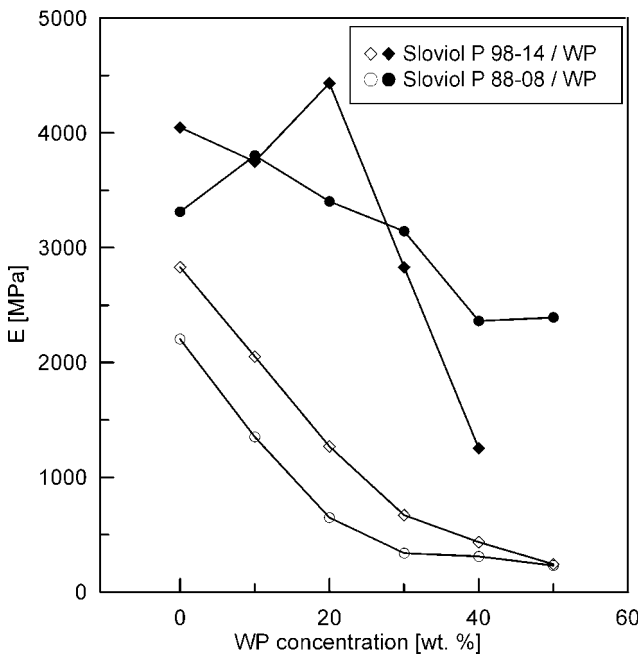In the conditioned samples, a gradual decrease in Young's modulus is observed with an increasing
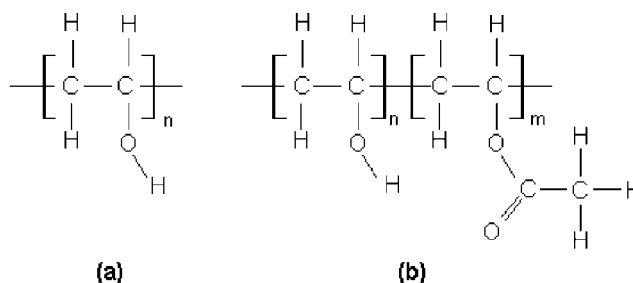
Figure 2 Chemical structures of the two types of researched PVA: (a) fully hydrolyzed and (b) partially hydrolyzed.
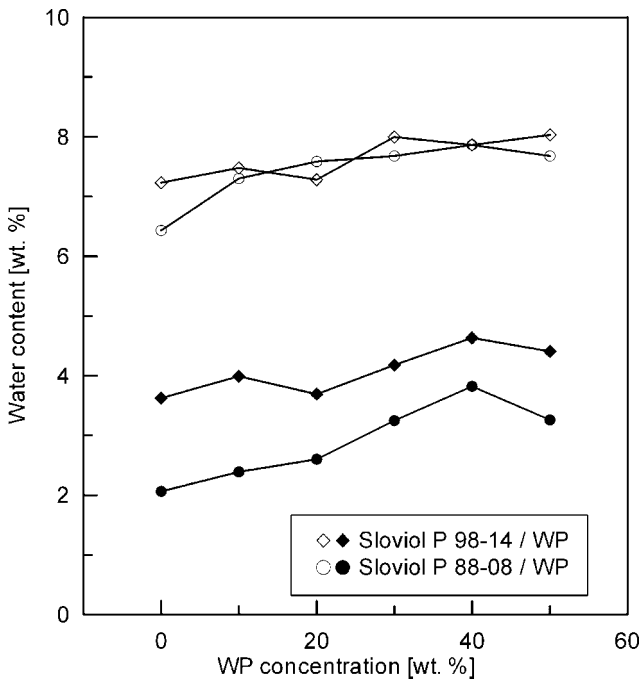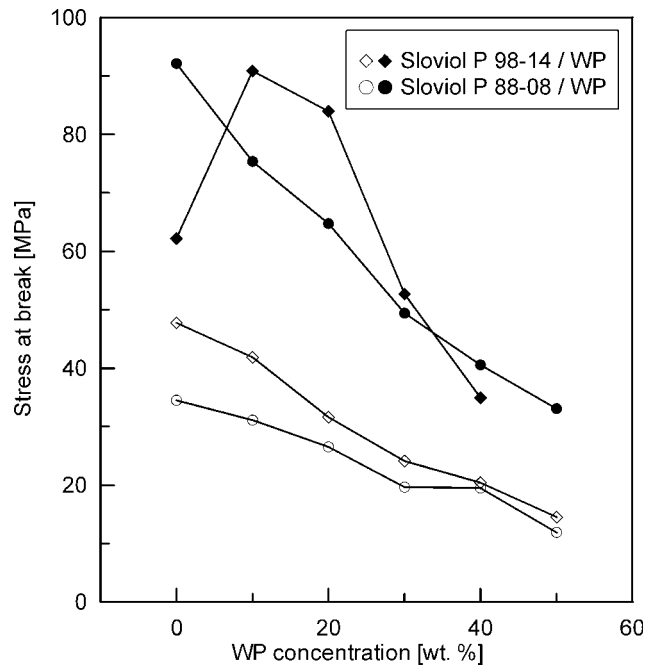
Figure 3 Water content versus the WP concentration in biocomposites based on Sloviol P 98-14 and Sloviol P 88-08/WP. The full symbols represent dried samples; the empty symbols represent moisture-exposed samples.

concentration of WP (Fig. 4). This decrease amounts to almost 90% at 50 wt % WP for both sets. As can be expected, the Young's modulus values of the dried samples are higher. An enhancement of
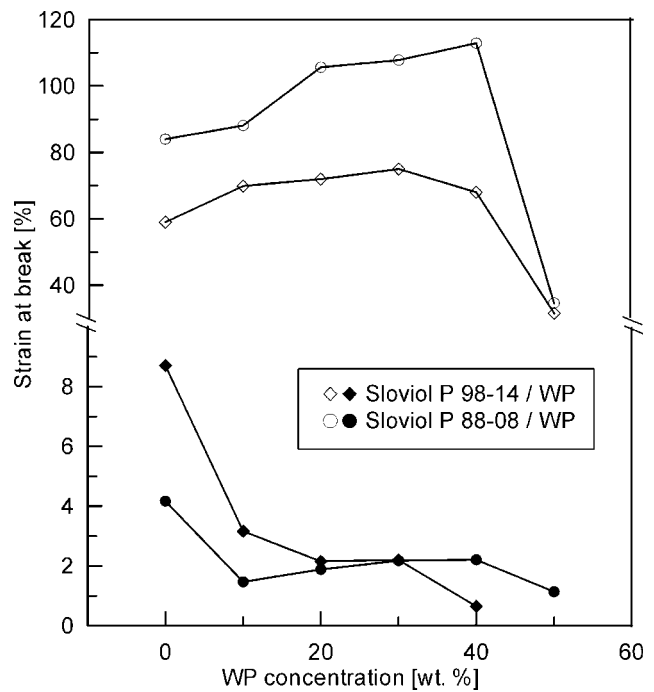

Figure 5 Stress at break as a function of the WP concentration in biocomposites of Sloviol P 98-14 and Sloviol P 88-08. The full symbols represent dried samples; the empty symbols represent moisture-exposed samples.

Young's modulus is achieved at 20 wt % WP (4430 MPa, Sloviol P 98-14) and 10 wt % WP (3800 MPa, Sloviol P 88-08). Further increasing the WP content leads to a steep decrease in Young's modulus. The

Figure 4 Effect of the WP concentration on Young's modulus (E) of Sloviol P 98-14 and Sloviol P 88-08. The full symbols represent dried samples; the empty symbols represent moisture-exposed samples.

Figure 6 Strain at break as a function of the WP concentration in biocomposites of Sloviol P 98-14 and Sloviol P 88-0. The full symbols represent dried samples; the empty symbols represent moisture-exposed samples.

specimens of Sloviol P 98-14 and WP 50 wt % have mechanical properties too low to be measured.

The results for the stress at break (Fig. 5) are analogous to the previous results. Conditioned samples show a gradual decrease in the tensile strength as the content of WP rises. Dry Sloviol P 88-08 with 20 wt % WP does not show any enhancement, unlike Young's modulus. On the contrary, its stress at break starts to diminish already at 10 wt % WP. The interactions of WP and Sloviol P 98-14, however, cause a trend of the curve similar to that in the case of Young's modulus.

The increase in Young's modulus as well as the tensile strength may also indicate intermolecular hydrogen bonding between lactose, which is present in whey, and the PVA matrix, as suggested by Fan et al.[10] According to the results presented here, this idea could be applied only to biocomposites of Sloviol P 98-14 and WP. The other PVA matrix used here does not demonstrate any improvement in the tensile properties caused by WP, most likely because of the physicochemical nature of the given polymers.

The influence of moisture on the strain at break is shown in Figure 6. It is well known that molecules of water can act as plasticizers to reduce chain interactions of PVA.[10] This is noticeable in the different strain-at-break results for the conditioned and dried samples. Low contents of water in the dried samples cause their relatively low maximum elongation (8.7% for pure Sloviol P 98-14 and 4.2% for pure Sloviol P 88-08); furthermore, it is reduced by the addition of WP. On the other hand, the conditioned samples show significantly higher elongations (59% for pure Sloviol P 98-14 and 84% for pure Sloviol P 88-08). The rising concentration of WP increases the values of the strain at break of both types of biocomposites up to 30 (Sloviol P 98-14) and 40 wt % (Sloviol P 88-08). Further exceeding the WP content causes a drop in the maximum elongations below the initial values of the unmodified PVA films. These facts are in agreement with the results obtained from the water content determination (Fig. 3). The drop, which appears at higher concentrations of WP, can be a result of decreased concentrations of PVA matrices.

Thermal properties

The effect of moisture on the observed values of T_g could be logically considered crucial. However, the settings of our DSC experiments (2 heat cycles) ensure a reduction of the moisture influence. This has been proved by the testing of dried and moisture-exposed samples with hardly noticeable variations of T_g.

DSC thermograms of both PVA polymeric matrices and WP are shown in Figure 7. Pure Sloviol P 98-14 (track a) exhibits its T_g at 74°C. The structural
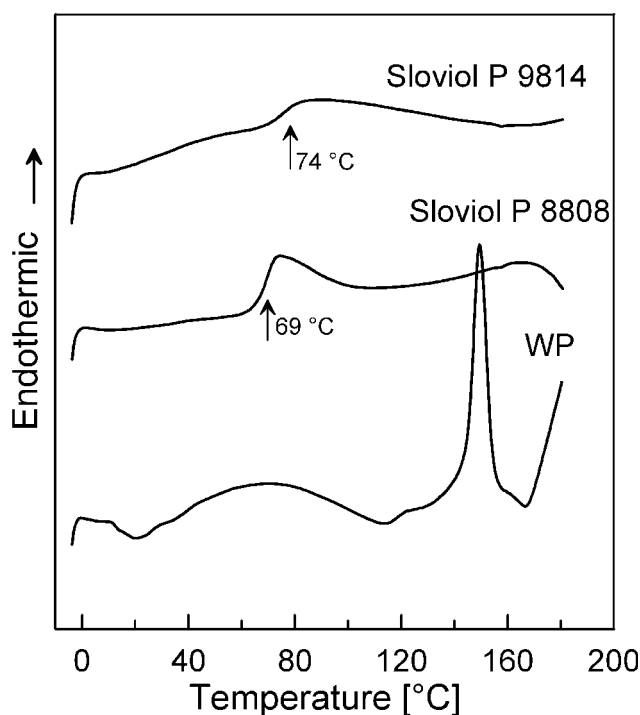

Figure 7 DSC curves of (a) Sloviol P 98-14, (b) Sloviol P 88-08, and (c) WP.

difference and lower molecular weight of Sloviol P 88-08 (track b) are responsible for the decreased T_g value, which is located at 69°C. The peaks that could indicate the melting point (T_m) of both polymers were not monitored within the studied temperature range (−10 to 200°C). The published literature confirms that T_m of PVA is strongly dependent on the nature of the polymer. For instance, Park et al.[9] reported T_m of fully hydrolyzed PVA (weight-average molecular weight = 89,000–98,000) at 230°C. Another study investigating a similar material showed its T_m at 200°C.[15] On the other hand, T_m below 200°C was determined for partially hydrolyzed PVA with a weight-average molecular weight of 124,000.[10] Nevertheless, some sources assert that T_m of the PVA crystals is above the thermal degradation temperature.[16]

The DSC curve (first scan) of the third researched material, WP (Fig. 7, track c), shows a broad endothermic peak around 60°C. This is probably connected to denaturation of the whey protein.[17] Another sharp endothermic peak appears at 149°C. Because whey contains a considerable amount of lactose, as mentioned previously, this peak can be interpreted as a melting peak of lactose present in WP. Similar results were reported also by Fan et al.,[10] who studied interactions between PVA and lactose. The second heating scan in our measurements did not show any thermal response.

The dependence of T_g on the content of WP in PVA-based biocomposites is depicted in Figure 8.
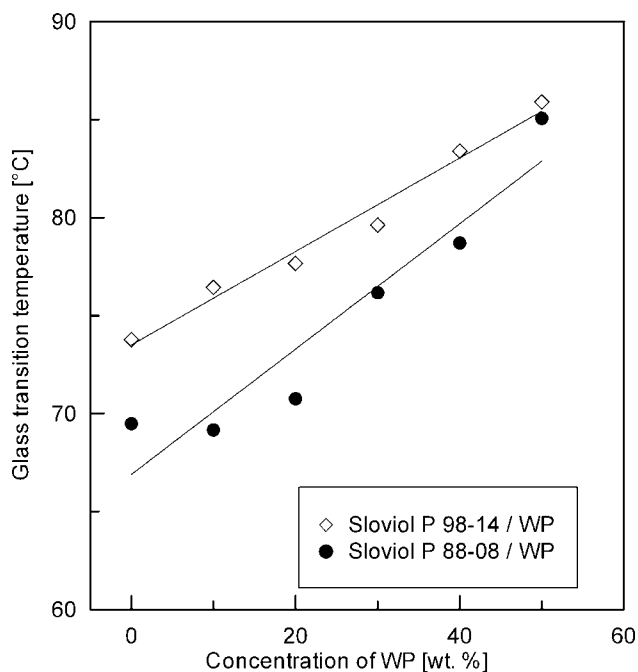
Figure 8 T_g values of pure PVA films and their composites with WP.

Evidently, the T_g values of both systems increase with an increasing concentration of WP. Although the total increase in T_g at 50 wt % WP is 12°C in the case of Sloviol P 98-14, 16°C was detected for biocomposites with Sloviol P 88-08. This can refer to better interactions between the WP particles and polymeric matrix of the latter. This assumption is also supported by optical micrographs (Fig. 1). In addition, these results may reveal some intermolecular reactions between PVA and WP, such as hydrogen bonding. The hydrogen bonds could be created between carbonyl moieties from residual acetyl groups of PVA and amino groups from peptide bonds of proteins present in WP. Another possibility is intermolecular shearing of hydrogen by two atoms of oxygen (carbonyl–hydroxyl interactions). These interactions should be noticeable from FTIR results. Their discussion follows.

Physicochemical properties

The FTIR spectra of pure PVA (Sloviol P 98-14 in this case) and WP and differential spectra of their biocomposites, which were obtained by the subtraction of biocomposite and pure PVA film spectra through OMNIC software, are presented in Figure 9. Although the differential spectra do not give exact information on the quantities of the constituent elements, they can be useful for the consideration of qualitative changes inside the investigated systems. In addition, they provide semiquantitative information about the trends in absorption. The ATR–FTIR

spectra of pure Sloviol P 98-14 show a broad absorption peak at 3245 cm^{-1}, which corresponds to O—H bond stretching. Other interactions of O—H groups can be found at 1014 cm^{-1}, and two other peaks, at 1081 and 1260 cm^{-1}, correspond to the stretching of C—O bonds. The response of C—H bonds is presented by absorption peaks at wave numbers of 1321 and 2902 cm^{-1}. These results are in agreement with the observations reported by Yang et al.[18]

One of the main components of whey is lactose.[19,20] Thus, the ATR–FTIR spectrum of WP (Fig. 2) is similar to the spectrum of pure lactose, which was already reported in one of our previous articles.[21] It is represented by very intensive absorption in the range of 1200–950 cm^{-1}, with a maximum at 1030 cm^{-1}, and three peaks at 3319, 2918, and 1734 cm^{-1}, which can mean interactions of O—H, C—H bonds, and aliphatic esters, respectively. The occurrence of the protein component in WP obtained from the waste of the dairy industry is proved by the absorption peak at 2844 cm^{-1}.

The differential spectra of the polymeric biocomposites based on Sloviol P 98-14 and WP are shown in tracks a–e. With the changing content of WP, the peaks corresponding to pure WP appear in the spectra, and the intensity of these peaks gradually increases with the rising concentration of WP. On the other hand, the downward peaks, related to the decreasing concentration of PVA, can be noticed (e.g., 804 cm^{-1}).

The spectra of the other type of matrix, Sloviol P 88-08, WP, and their biocomposites are shown in
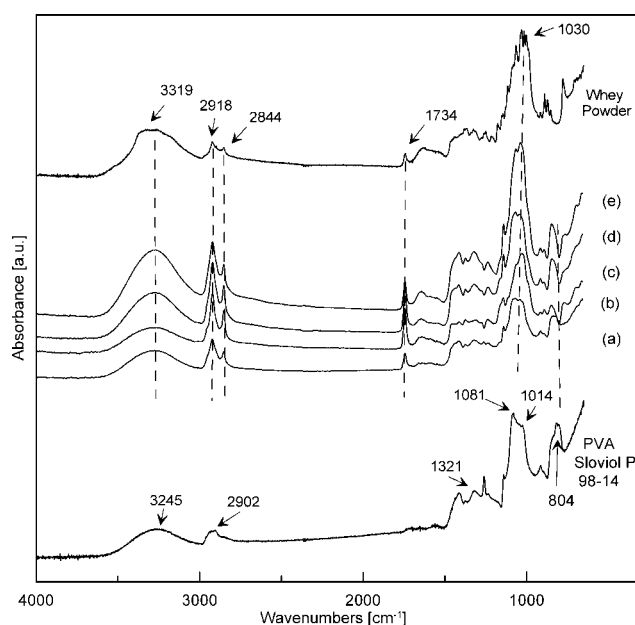
Figure 9 ATR–FTIR spectra of PVA (Sloviol P 98-14) and WP and differential spectra of their biocomposites with (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 wt % WP.
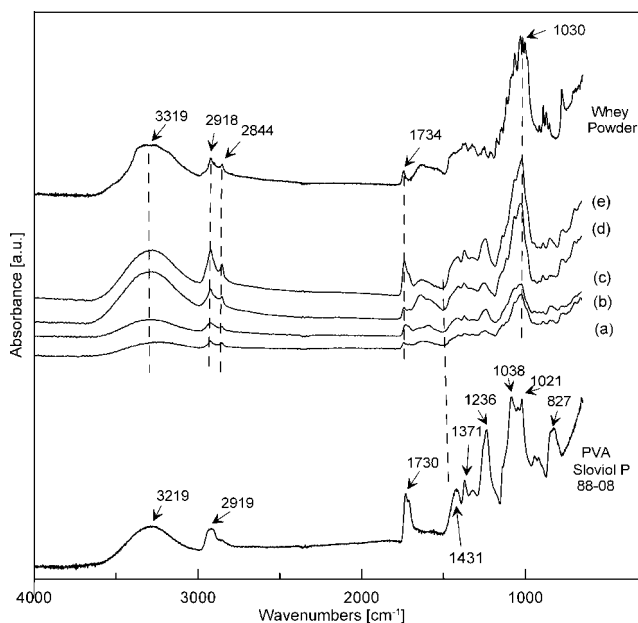
Figure 10 ATR–FTIR spectra of PVA (Sloviol P 88-08) and WP and differential spectra of their biocomposites with (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 wt % WP.

Figure 10. The description of the Sloviol P 88-08 ATR–FTIR spectrum is similar to that of Sloviol P 98-14. However, there are some differences caused by the various degrees of hydrolysis of both polymers. Generally, the distinction between partially (87–89 mol %) and fully (97–99 mol %) hydrolyzed PVA (Fig. 2) is caused by the number of residual acetyl groups present in the polymer backbone.[22] Thus, a higher number of residual acetyl groups is responsible for the absorption at wave numbers of 1730 and 1236 cm^{-1} (Fig. 10).

The ATR–FTIR differential spectra of partially hydrolyzed Sloviol P 88-08 and WP biocomposites are depicted in tracks a–e. The changing concentrations of WP and PVA in the biocomposites have the same effect as that described previously. An example of a downward peak with decreasing PVA concentration can be found at 1431 cm^{-1}.

The nature of both the polymeric matrix and modifier begs the question of possible interactions between these two components, such as hydrogen bonding. However, because of the complexity and relatively high moisture content in all the prepared films (Fig. 3), we were not able to confirm the suppositions suggested previously.

Biodegradation

Many investigations concerning the biodegradability of PVA-based materials in aqueous environments have been conducted. Generally, significant levels of biodegradation are reached only in the presence of acclimated (adapted) PVA-degrading microorgan-
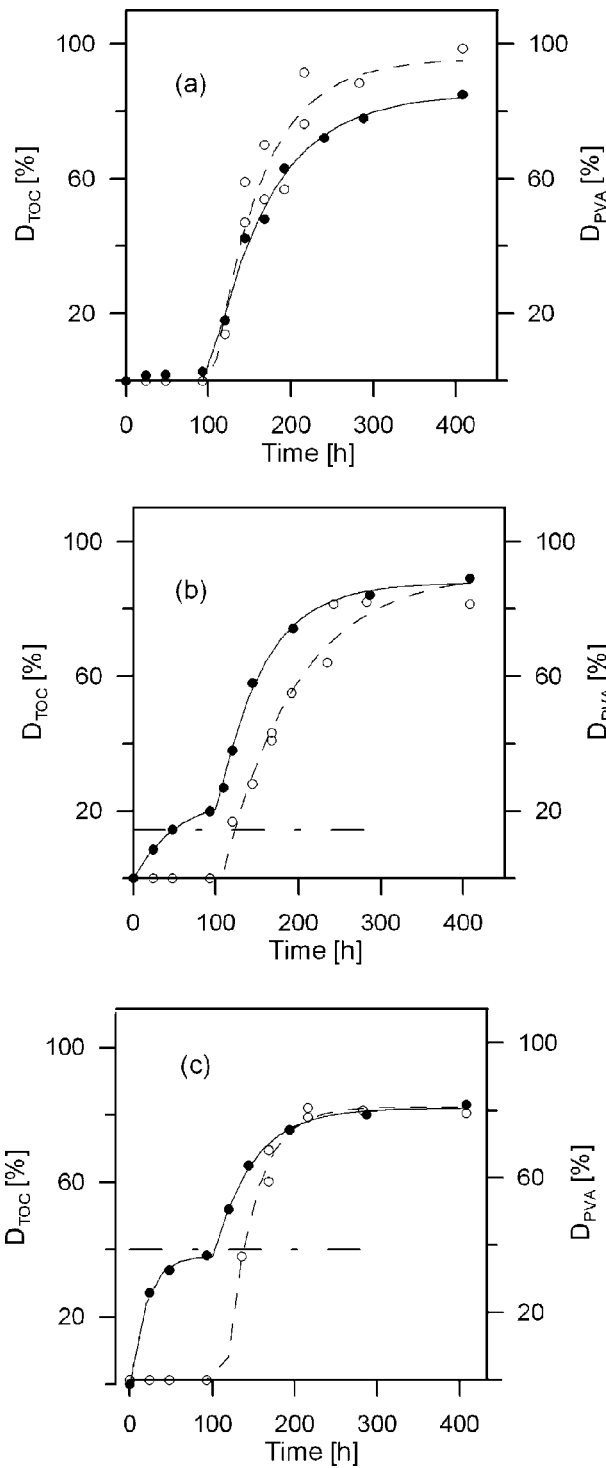
isms.[11,23] In our studies, unadapted activated sludge from a wastewater treatment plant was used as an inoculum. The absence of an acclimation time, during which the required enzymatic systems could be developed within the microorganisms that are able to degrade PVA, prolongs the total time of biodegradation. Nevertheless, this method simulates real conditions in an environment in which PVA does not occur naturally.

The biodegradability test of the PVA/WP-based materials shows satisfactory results. The samples made of partially hydrolyzed PVA Sloviol P 88-08 show full biodegradability after about 400 h of testing. On the other hand, fully hydrolyzed Sloviol 98-14 proves incomplete biological degradation (ca. 90%) after the same time. The time dependences of the biodegradation of both PVAs and their biocomposites with WP (20 and 50 wt %) are presented in Figures 11 (Sloviol 98-14) and 12 (Sloviol P 88-08). They were obtained by the application of first-order kinetics. All the samples are characterized by an approximately 100-h lag phase caused by the absence of PVA-degrading enzyme secretion by the bacteria present in the reaction mixture. This is especially evident from the trends of D_{PVA}, which describes solely the changes in the PVA concentration. On the other hand, trends of D_{TOC} should involve a decrease in all organic carbonaceous matters. This comparison is important for the investigation of multicomponent materials, such as PVA/WP-based polymeric films. These materials evidently show two-phase biodegradation, as shown in Figures 11(b,c) and 12(b,c). This reveals that the easily degradable component (WP) is consumed preferentially by microorganisms. Similar results were reported by Hoffmann et al.,[11] who studied the biological degradability of PVA films containing protein hydrolysate and glycerol.

The assumption of preferential utilization of WP is supported by theoretical calculations of the organic carbon, which is represented by the modifier present in the biocomposites. It can be expressed as a percentage of D_{TOC} at the complete degradation of WP and is shown in Figures 11 and 12 (dotted–dashed horizontal line). This theoretical value more or less corresponds to the first phase of the biodegradation course. The exception makes Sloviol P 88-08 with 50 wt % WP [Fig. 12(c)], for which the theoretical degree of biodegradation is about 10% lower in comparison with experimental data.

The rate constant ($-k$) of the first phase increases with the rising content of WP, as can be seen in Table II. The same response is detected also for the values of D_{TOC}. This is in agreement with the increasing content of the easily biodegradable substrate (WP), which shows a zero leg phase (t_{LAG}). The metabolic activity of the present microorganisms

Thus, no noticeable trend of the biodegradation course can be distinguished.

The spectroscopic method is solely PVA-sensitive. Thus, only a single-phase degradation course is

Figure 11 Biodegradation of (a) pure Sloviol P 98-14 and its composites with (b) 20 and (c) 50 wt % WP. D_{TOC} is shown by the full symbols fitted with a solid line, and D_{PVA} is shown by the empty symbols fitted with a dashed line. The calculated TOC in WP is shown by a dotted–dashed line.

is limited mainly by the WP concentration. On the other hand, the second phase of biodegradation involves polymer utilization. The values of the kinetic constant fluctuate around a certain mean value.
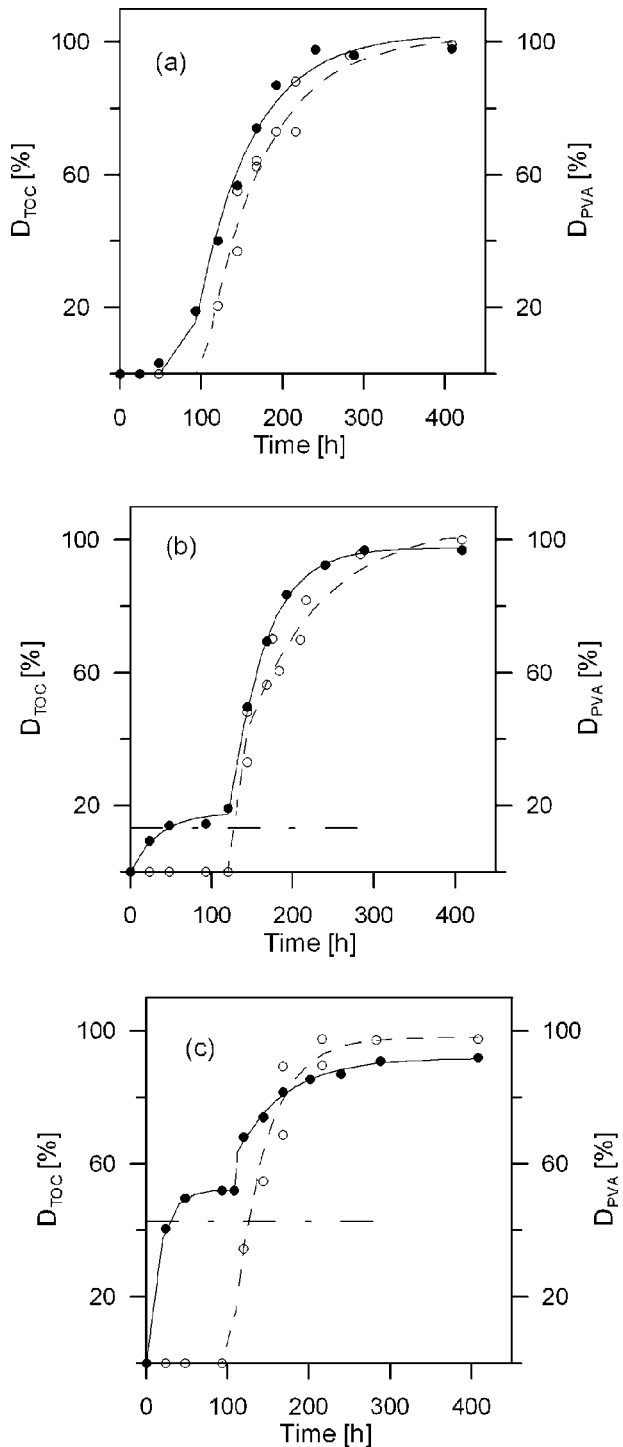

Figure 12 Biodegradation of (a) pure Sloviol P 88-08 and its composites with (b) 20 and (c) 50 wt % WP. D_{TOC} is shown by the full symbols fitted with a solid line, and D_{PVA} is shown by the empty symbols fitted with a dashed line. The calculated TOC in WP is shown by a dotted–dashed line.

TABLE II
Kinetic Constants of the First-Order Equation Describing the Biodegradation Course of PVA/WP Biocomposites (Modified Zahn–Wellens Method)

PVA	WP (wt %)	D_{TOC} (%)		$-k$ (h^{-1})		t_{LAG} (h)	
		First phase	Second phase	First phase	Second phase	First phase	Second phase
Sloviol P 98-14	0	—	85.1	—	0.014	—	81.4
	10	—	82.8	—	0.016	—	83.2
	20	24.41	87.8	0.019	0.018	0	87.9
	30	27.06	97.2	0.027	0.013	0	79.8
	40	27.69	93.7	0.043	0.009	0	78.8
	50	38.23	81.9	0.050	0.022	0	72.9
Sloviol P 88-08	0	—	102.5	—	0.014	—	81.6
	10	—	93.6	—	0.018	—	78.3
	20	17.95	97.7	0.029	0.024	0	84.7
	30	34.04	90.9	0.027	0.018	0	73.6
	40	36.18	92.1	0.039	0.013	0	76.6
	50	52.18	91.8	0.062	0.017	0	71.3

observed.[24] Table III shows kinetic constants describing the biodegradation. These calculations, performed with a first-order kinetic equation, provide slightly increased values of the constants (especially in the case of $-k$ and t_{LAG}) in comparison with the previous method. These discrepancies can have several reasons: the spectrophotometric method does not detect the other carbonaceous compounds that can affect the results of the TOC determination, the two phases can influence each other (modified Zahn–Wellens method), and the potential inaccuracy of the spectroscopic measurements should be considered here as well. Nevertheless, it can be assumed that these two methods correspond to each other, as also shown in Figures 11 and 12.

In agreement with the results, it can be supposed that the biodegradation course of PVA is not affected by the presence of a modifier (WP), and the decisive factor in this process is the degradation of the polymer. However, the easily biodegradable modifier replaces part of the oil-based polymer and thus reduces the potential environmental load.

TABLE III
Kinetic Constants of the First-Order Equation Describing the Biodegradation Course of PVA/WP Biocomposites (Spectroscopic Determination of PVA)

PVA	WP (wt %)	D_{PVA} (%)	$-k$ (h^{-1})	t_{LAG} (h)
Sloviol P 98-14	0	95.62	0.017	105.9
	10	94.63	0.011	90.77
	20	91.10	0.011	107.7
	30	82.61	0.031	110.7
	40	91.33	0.034	92.41
	50	80.96	0.031	117.2
Sloviol P 88-08	0	100.0	0.014	102.1
	10	96.60	0.018	100.8
	20	100.0	0.011	95.78
	30	100.0	0.009	75.32
	40	98.52	0.016	117.8
	50	98.15	0.020	103.3

CONCLUSIONS

Environmentally friendly polymeric composites containing WP, a waste material of the dairy industry, and fully (Sloviol P 98-14) or partially (Sloviol P 88-08) hydrolyzed PVA have been characterized.

The micrographs show a better distribution of the WP particles within partially hydrolyzed PVA (at higher concentrations of WP) in comparison with the fully hydrolyzed polymer. More detailed studies of PVA/WP properties, which were carried out with FTIR spectroscopy and differential scanning spectroscopy, reveal possible molecular interactions between PVA and the used biomaterial (hydrogen bonding). However, no clear evidence of this has been found because of the considerable complexity of the systems.

The investigated biocomposites are highly sensitive to moisture absorption. This is proved by significant differences in the mechanical properties of the materials, which were stored under various conditions. An enhancement of the tensile properties was reached only for unconditioned samples of Sloviol P 98-14 containing up to 20 wt % WP. A decrease in the mechanical properties was otherwise observed with an increasing content of WP. However, the materials based on partially hydrolyzed PVA (Sloviol P 88-08) show better compactness at a higher concentration of WP (>40 wt %).

Two methods were used for the investigation of the biodegradability: the assay of TOC and the spectrophotometric determination of PVA. For quantifying and comparing these methods and consequently the course of biodegradation, a first-order kinetic equation was used. The results from these two methods correspond with each other and reveal that the decisive role in the biodegradation of these materials is played by PVA. This means that an overall improvement in the biodegradability has not been

achieved because of the modification of PVA with WP. Nevertheless, the addition of the modifier to the polymeric matrix means a lower amount of the oil-based polymer is used, and thus the potential environmental load is reduced. The use of WP has another advantage. It is prepared from waste of the dairy industry and is relatively cheap. The use of such a material is therefore convenient from both economic and environmental points of view.

References

1. Jakubowicz, I. Polym Degrad Stab 2002, 80, 39.
2. Scott, G. Polym Degrad Stab 2000, 68, 1.
3. Schink, B.; Nanesen, P. H.; Frings, J. FEMS Microbiol Rev 1992, 103, 311.
4. Selke, S. E. M. In Packaging and the Environment, Alternatives, Trends and Solutions; Selke, S. E. M., Ed.; Technomic: Lancaster, PA, 1994; Chapter 1.
5. Saha, N.; Zatloukal, M.; Saha, P. Polym Adv Tech 2003, 14, 854.
6. Ozaki, S. K.; Monteiro, M. B. B.; Yano, H.; Inamura, Y.; Souza, M. F. Polym Degrad Stab 2004, 87, 293.
7. Saha, N.; Sedlarik, V.; Saha, P.; Kazantseva, N.; Kar, S.; Banthia, A. K. Polym Compos 2005, 26, 739.
8. Olabarrieta, I.; Forsstrom, D.; Gesce, U. W.; Hedenquist, M. S. Polymer 2001, 42, 4401.
9. Park, J. S.; Park, J. W.; Ruckenstein, E. Polymer 2001, 42, 4271.
10. Fan, X. D.; Hsien, Y. L.; Krochta, J. M. J Appl Polym Sci 2002, 83, 929.
11. Hoffmann, J.; Reznickova, I.; Kozakova, J.; Ruzicka, J.; Alexy, P.; Bakos, D.; Precnerova, L. Polym Degrad Stab 2003, 79, 511.
12. Joshi, D. P.; Lan-Chun-Fung, Y. L.; Pritchard, J. G. Anal Chim Acta 1979, 104, 153.
13. Mazzobre, M. F.; Soto, G.; Aguilera, J. M.; Buera, M. P. Food Res Int 2001, 34, 903.
14. Sedlarik, V.; Saha, N.; Kuritka, I.; Saha, P. Plast Rubber Compos 2006, 35, 355.
15. Shao, C.; Kim, H. Y.; Gong, J.; Ding, B.; Lee, D. R.; Park, S. J. Mater Lett 2003, 57, 1579.
16. PolymerProcessing, http://www.polymerprocessing.com/polymers/ PVOH.html (accessed December 2005).
17. Ellepola, S. W.; Ma, C. Y. Food Res Int 2006, 39, 257.
18. Yang, J. M.; Su, W. Y.; Leu, T. L.; Yang, M. C. J Membr Sci 2004, 236, 39.
19. de Wit, J. N. J Dairy Sci 1981, 81, 597.
20. Sedlarik, V.; Saha, N.; Saha, P. Polym Degrad Stab 2006, 91, 2039.
21. Sedlarik, V.; Saha, N.; Kuritka, I.; Saha, P. Polym Compos 2006, 27, 147.
22. Shuman, T. Thesis, Chalmers University of Technology, Gothenburg, Sweden, 2002.
23. Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. Prog Polym Sci 2003, 28, 963.
24. Sedlarik, V.; Saha, N.; Kuritka, I.; Saha, P. Int J Polym Anal Char 2006, 11, 253.