

Polyvinyl alcohol and starch blends: properties and biodegradation behavior

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Abstract. In this paper, polyvinyl alcohol (PVA)/starch blends films were prepared using the melting technique. The effect of starch content on the biodegradability of the tested blends was investigated by the variation of mechanical properties (tensile strength and elongation to break %) and the determination of weight loss of specimens buried to soil until 30 days. Firstly, the results from the initial tensile strength and elongation at break tests showed as the starch content increased, the tensile properties decreased. After exposure of specimens to soil action, the tensile strength increased and elongation to break dramatically decreased. It was noticed that the weight loss increased with increasing of starch content. Finally, chemical structure by FTIR and optical properties of PVA/starch blends were investigated.

Key Words: polyvinyl alcohol, starch, properties, polymers, biodegradable.

Introduction. In recent decades the production of polymers has been recorded a real explosion. This is due to the wide spectrum of properties covered by macromolecular compounds, which make their use to be indispensable in various fields (Tudorachi et al 1997). Polymeric materials are used in various areas for a short period of use (in the packaging industry, agriculture, domestic use) after which they are discarded into the environment as waste, thus contributing to its pollution. Environmental degradation is one of the biggest problems facing mankind today and shows a multitude of regional and national issues.

Researchers bear a great responsibility in the discovery of new synthetic biodegradable polymers and modification of some of existing polymers in order to increase their susceptibility to biodegradation, without affecting their physical and mechanical characteristics. The advantages of synthetic polymers are obvious, including adequate physical and mechanical properties and low-cost. Natural polymers present in abundance in the environment, are totally biodegradable and show lower physical and mechanical properties.

Polyvinyl alcohol (PVA) is a synthetic polymer, non-toxic, flexible, soluble in water and biodegradable. PVA exhibits excellent mechanical and barrier properties and is compatible with the starch. The physical properties of PVA, such as resistance, water solubility, thermal characteristics and gas permeability vary with the degree of crystallinity, which is highly dependent on the degree of hydrolysis and average molecular weight of the polymer. The amount of crystalline material present in the compounded PVA is dependent on the plasticizer and/or water incorporated into the compound, the synthesis (acid or alkaline catalysis), the degree of hydrolysis and molecular weight. PVA with a partially degree of hydrolysis contains residual acetate groups and for this reason can be considered as a copolymer that reduces the total level of crystallinity, while homopolymers show the total degree of hydrolysis. PVA is high-cost, which has to compete with low-cost thermoplastic materials like polyethylene, polypropylene, and poly (vinyl chloride) in practical applications. Hence, a potential solution to enhance the biodegradation rate and to decrease the cost of PVA lies in preparing of composites with more biodegradable, cheaper, and easily processed by adding fillers or polymers.

Among the natural polymers, starch is a totally biodegradable polymer, has a low-cost, is renewable and can be a promising candidate for the development of sustainable materials (Nawrath et al 1995). Starch is an important polysaccharide. 75% of the total organic matter on the soil is present in the form of polysaccharides (Stevens 2002). World production of corn starch in 2012 was estimated at about 158,253 metric tons and the price for starch obtained from cereal was around 0.60 USD/kg (estimated from the total volume and value of exports). The largest amount of starch is produced in USA, then in Europe and Asia (De Bragança & Fowler 2004).

It have been made many efforts to develop starch-based polymers, in order to conserve petrochemicals resources, to reduce environmental impacts and to search new applications for short term in order to replace the synthetic thermoplastic polymers (Park et al 2004; Schwach & Avérous 2004; Stepto 2006; Cinelli et al 2008). For example, blends based on starch/polyvinyl alcohol (PVA) films (3:1) and glycerol (0-20% wt) are used for biomedical field (Shi et al 2008), starch-g-poly (vinyl alcohol) is used as encapsulated agrochemical for slow release (Zhu & Zhuo 2001), potato starch, corn fibers and poly(vinyl alcohol) blends are investigated for foamed tray production (Cinelli et al 2006; Iriani et al 2012).

Most of PVA/starch blends are prepared by solution cast method using glutaraldehyde (GA) (Pal et al 2006), irradiation by microwave with doses ranging from 10 to 30 kGy (Wongsuban et al 2003; Jelinska et al 2008), freeze-thaw method (Bagri et al 2011) as crosslinking agents.

The aim of this paper is to prepare biodegradable blends based on PVA and starch by melting technique and to investigate the mechanical parameters variation (tensile properties and weight loss) by exposure to soil during 5 days, 10 days, 15 days, 22 days and 30 days. Chemical structure and optical properties were carried out using FTIR and UV/VIS methods.

Experimental part

Materials. In order to achieve biodegradable formulations were used the following raw materials:

- PVA type ELVANOL 71-52 (DU PONT) having a degree of hydrolisis in the range of 99.0 – 99.8%. It was used as thermoplastic matrix. Its characteristics are shown in Table 1;
- starch type AMYZET 100 (AMYLUM România); it has acidity 22%, pH 4.9, water content 10-13.5 % and crystallinity degree 32%. It was used as biodegradation agent;
- glycerol (SIGMA-ALDRICH), having density of 1.267 g/cm³; it was used as plasticizer in order to decrease the glass-transition temperature (T_g) and to increase the flexibility and workability of starch and PVA since starch is only partially compatible with PVA.

Table 1

Characteristics of PVA type ELVANOL 71-52

<i>Characteristics</i>	<i>UM</i>	<i>Value</i>
Appearance	-	Granules
Color	-	White
Hydrolysis degree	%	99.0–99.8
Viscosity	Cp	12–15
PH solution	-	5.0–7.0
Volatile, max.	%	5
Ash, max.	%	0.7
Weight	g/cm ³	0.398

Preparation of the PVA/starch blends. It was carried out four formulations coded: PSG9, PSG17, PSG25 and PSG30 containing starch from 9 to 30 wt.%, as it is shown in Table 2. The starch, before use was dried for 4 hours at 105°C.

Table 2

Compositions of biodegradable blends

Code sample	PVA, wt. %	Starch, wt. %	Glycerol, wt. %	PVA/Starch, wt./wt.	DS [*] / Plasticizer, wt./wt.
PSG9	62	9	29	6.88	2.44
PSG17	37	17	46	2.17	1.17
PSG25	29	25	46	1.16	1.17
PSG30	30	30	40	1.00	1.50

* DS means dried substances (PVA and starch).

The melting of blends was performed using a BRABENDER Plastograph, in the following conditions: cuvette of 30 cm³, temperature 175±5°C, mixing time 10 minutes, speeds of rotors 40/70 rpm.

Films and sheets with thickness of 0.1 mm and respectively 1 mm were obtained by pressing in the following conditions: temperature: 170±5°C; preheated time: 10 min respectively 20 min; pressing time: 5 min respectively 10 min; cooling time: 40 min; pressure: 250 bar.

Characterizations

Fourier-transform infrared (FT-IR) spectroscopy. Analyses were carried out with a FTLA 2000-104 spectrophotometer (ABB Canada) in the range of 3500 cm⁻¹ - 770 cm⁻¹, resolution 4 cm⁻¹, in transmission mode. PVA film obtained by casting method (PVA 20 % sol. w/v) was used as control.

Tensile properties. The tensile strength and elongation at break of the blends were measured on a universal testing machine (FP10 DINAMOMETER) at room temperature with cross-head speed of 50 mm min⁻¹. An average value of five replicates for each sample was taken, according to SR EN ISO 527-2:2000. Tensile properties were carried out on sheets of 1 mm both initial and after exposure to soil at the following period: 5 days, 10 days, 15 days, 22 days and 30 days.

Determination of changes in physical and mechanical characteristics (tensile strength and elongation at break) was performed by exposure of specimens to a mixture of fertile land (manufacturer SC HM NUTRIPLANT SRL) recommended for fertilizing of vegetable crops and flowers in greenhouses and field crops, organic soil conditioner with following characteristics: plant nutrient easily accessible; high content of organic matter; improver of the soil characteristics; increased water retention capacity. It contains: pH 6.0–7.55; CaO 85-180 mg/100 g sol.; MgO 30-40 mg/100 g sol.; P₂O₅ 150-250 mg/100 g sol.; K₂O 270-500 mg/100 g sol.; Fe 40-45 mg/100 g sol.

Weight loss. Biodegradability of the blends was assessed by evaluating of weight loss over time in a fertile land previously described. Three specimens of (30 mm x 30 mm x 1 mm) from each sample were weighed and then buried in boxes of soil. Soil was maintained at 20 % moisture in weight and specimens were buried at a depth of 15 cm, following the EN ISO 846. The buried samples were removed from the soil at 5 days, 10 days, 15 days, 22 days and 30 days, were washed in distilled water, were dried in an oven at 50±8°C for 24 h and equilibrated in a desiccator for at least a day, before being weighed and then returned to the soil. Dried films were weighed in order to calculate the weight loss. The evaluation of the weight loss was performed by using the formula:

$$\text{Weight loss, \%} = \frac{(m_f - m_i)}{m_i} \times 100$$

where:

m_f is the final weight of tested samples;
 m_i is the initial weight of tested samples.

This ratio is, generally, negative due the weight loss.

Light transmittance testing. The light transmittance (Tr) of the films with a thickness of max. 0.14 mm was measured using an ultraviolet–visible (UV–Vis HELIOS ALPHA) spectroscope (Thermo Spectronic) at the wavelength from 200 to 800 nm.

Results and Discussion

Fourier-transform infrared (FT-IR) spectroscopy. The FTIR spectra of PVA/starch blends are depicted in Figure 1 and Table 3.

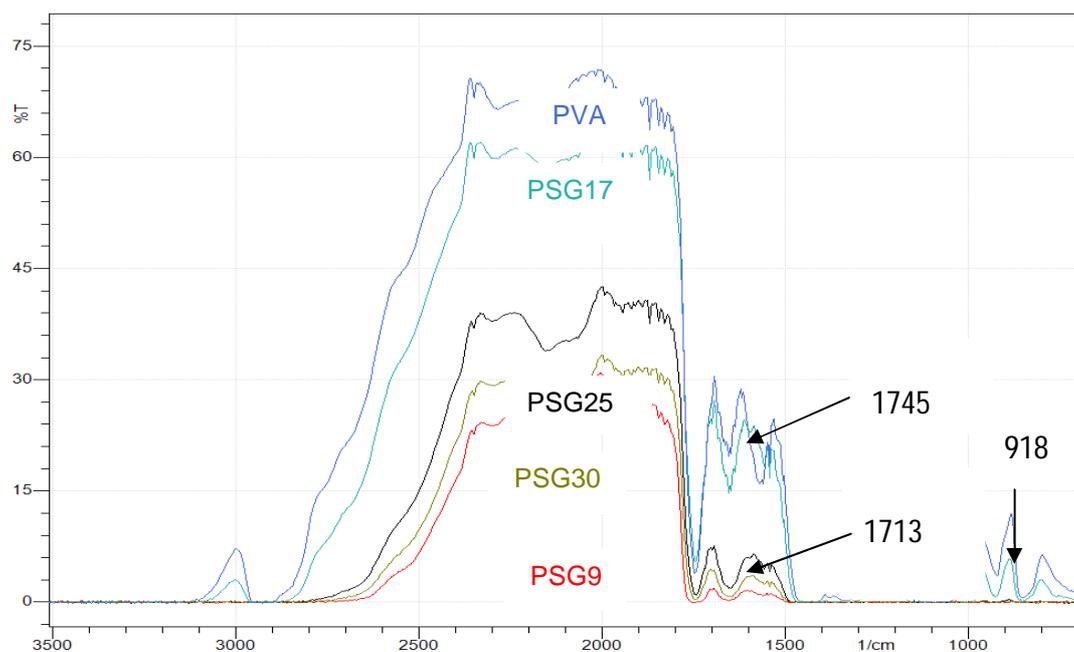


Figure 1. FTIR spectra of PVA and PVA/starch films.

Table 3

Peak assignment in the FTIR spectra of PVA/starch films

Peak assignment	PVA	PSG9	PSG17	PSG25	PSG30
C-O bending C-O-C ring vibration due to starch	-	790-775	758	789-775	789-775
CH rocking	918	916	926	916	943
C-O stretching in C-O-C	1055	1013	1022	1043	1022
C-O stretching in C-O-H	-	1143	1146	1148	1149
	-	1063	1087	1067	1022
C-H wagging	1430-	1433-	1433-	1433-	1433-
	1275	1205	1205	1205	1205
CH bend of CH ₂	1456	1460	1460	1460	1485
-OH bending	1653	1653	1656	1653	1653
C=O stretching	1745	1742	1744	1742	1745
characteristics carbonyl vibration in the residual acetate in PVA	1713	1712	1712	1712	1712
C-H stretching	2955	2850	2964	2964	2947
-OH stretching	3500-	3500-	3500-	3500-	3500-
	3200	3200	3200	3200	3200

The stretching and bending vibration of the hydrogen bonding -OH group of PVA and PVA/starch blends occurred at 3500-3200 cm⁻¹ and 1653 cm⁻¹, respectively. The

stretching vibration of C-O bond in C-O-C group in the anhydrous glucose ring appeared at $790\text{-}775\text{ cm}^{-1}$. The characteristic peaks at 1745 and 1713 cm^{-1} in PVA are attributed to the residual acetate groups due to the manufacture of PVA from hydrolysis of polyvinyl acetate. All spectra exhibit the characteristic absorption bands of pure PVA which are $3500\text{-}3200$, 2955 , 1745 , 1456 and $1430\text{-}1275\text{ cm}^{-1}$. The vibrational peaks are assigned to O-H stretching, C-H stretching, C=O stretching, C-H bend of CH_2 , and C-H wagging of PVA and they existed in the FTIR spectra of PVA/starch blends, indicating the success of blending of PVA with starch. The C-H rocking mode of PVA was appeared at 918 cm^{-1} and is shifted to 916 , 926 , 916 and 943 cm^{-1} . Similar types of characteristic peaks were also observed by other researchers (Chen et al 2008).

Tensile properties. The tensile properties provide an indication of the strength and elasticity of the films which can be reflected by strength and strain-at-break. Tensile strength and elongation at break up to 30 days during soil burial are presented in Figure 2 and Figure 3.

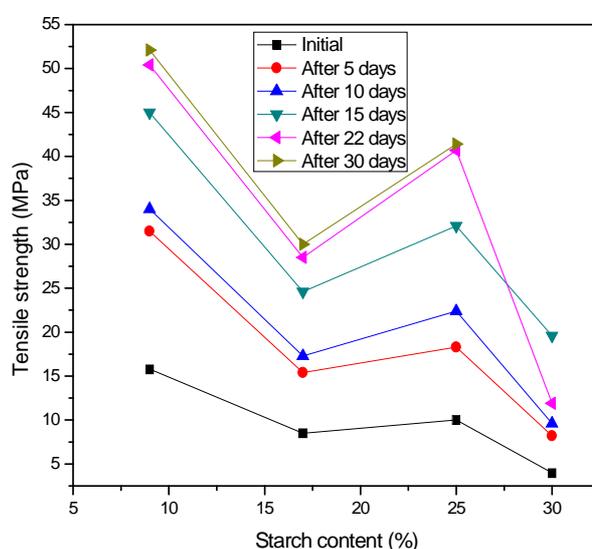


Figure 2. Effect of starch content on tensile strength during soil burial.

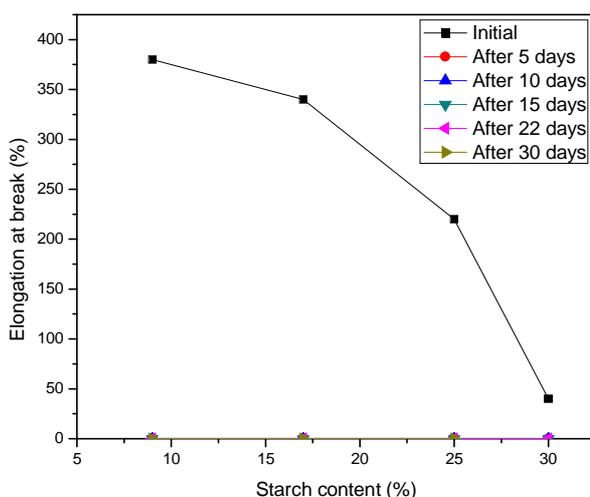


Figure 3. Effect of starch content on elongation at break during soil burial.

The initial results show that the increasing amount of starch in blends leads to decrease both tensile strength and elongation at break. A similar behavior was also observed by other researchers (Parvin et al 2010) which found the tensile strength of starch/PVA films began decreasing steadily with the increasing percentage of starch in the blend films. It could be due to increased crystallization of the blend films.

PSG30 shows a decrease of tensile strength of about 34% against PSG9. Also, it records a decrease of elongation at break about 15% against PSG9. This is probably due to a smaller mobility of starch macromolecules although the amount of glycerol in the blends was enhanced. Adding of glycerol into the blends decreases the tensile strength, and does not improve their plasticity and flexibility. However, too high of glycerol content causes the decrease of elongation at break. Also, a decrease of the amount of PVA from 62 wt% to 30 wt% leads to a decrease both of tensile strength and elongation at break. This behavior is probably due to the unreactivity of the non-polar PVA matrix, and the polar surface of the thermoplastic starch. This is in accordance with the results of other researchers (Widiarto 2005).

Analyzing the variation of the mechanical parameters over time from Figures 2 and 3 it can observe the followings:

- after exposure of samples to the action of microorganisms from soil, the tensile strength shows high value compared with initial blends; PSG25 shows the higher value of strength than PSG17. After 30 days, all specimens show visible holes on their surfaces; the tensile properties of PSG30 could not be recorded (Figure 2);
- the elongation at break dramatically decreased, all blends going to 0% after 5 days of exposure to the soil burial (Figure 3).

This behavior can be explained by the fact that starch was consumed by soil's microorganisms and migration of plasticizer into soil. Also, this phenomenon of increasing of tensile strength and decreasing of elongation at break was observed in the case of photochemical crosslinking of materials based on starch and PVA (Follain et al 2005). As a result of tested in burial soil, the formulations have undergone major changes under the influence of environmental factors (humidity, temperature), they were underwent to the partial crosslinking of the macromolecules.

Weight Loss (%). The weight loss during soil burial up to 30 days is presented in Figure 4.

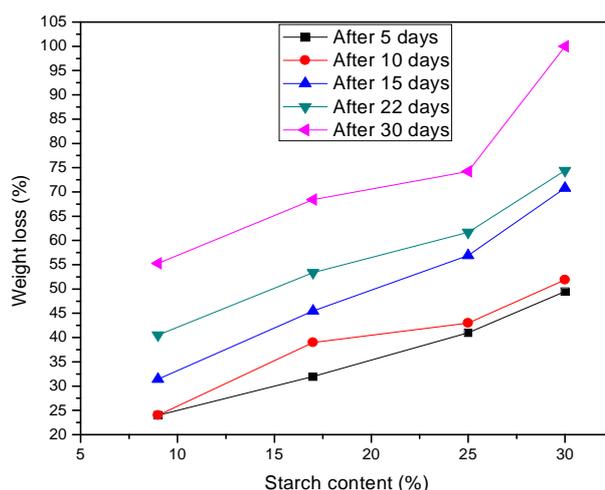


Figure 4. Effect on starch on loss mass during soil burial.

From the results showed in Figure 4 it is found that weight loss of formulations increased with increasing of starch content and exposure time into soil. PSG30 blend had the highest weight loss at all times of exposure. Thus, PSG30 (containing PVA and starch ratio of 1:1) recorded weight loss of 49.5% after 5 days and respectively 51.9% after 10 days;

meanwhile PSG9 lost 24% after 5 days of exposure to soil burial. Han et al (2009) investigated the biodegradability in the soil from blend composed by starch and PVA (ratio starch:PVA 7:3) crosslinked by formaldehyde content 10 wt%. This formulation was biodegraded in soil environment after 50 days of exposure, and the ultimate weight loss exceeded 50%. The highest values of weight loss were recorded for films with a high content of starch in mixture. Răpă et al (2010) studied biodegradable blend based on polyethylene (LDPE) and starch 30 wt% in content and found that after 3 months exposure by soil burial, the sample recorded a weight loss of about 18%. This demonstrates the use of LDPE for LDPE/starch blend leads to the blends partially biodegradable, the weight loss being assigned only to starch content. The high weight loss assigned to PVA/starch blends are due to both starch and PVA content. Starch is a biodegradable agent and PVA is soluble in water. Also, after removing from soil, PSG30 specimen showed development of fungi, spots and holes more pronounced than PSG9, PSG17 and PSG25 specimens. Weight loss and holes indicate the starting of a degradation process due to the metabolic activity of microorganisms. As it is known, this process leads to chemical modifications caused by assimilation processes in which the fungi use the constituents of the degraded material, as nutrients.

Light transmittance testing. The light transmittance (T_r) of PVA, PSG7, PSG15, PSG25 and PSG30 films at the wavelength from 200 to 800 nm is shown in Figure 5.

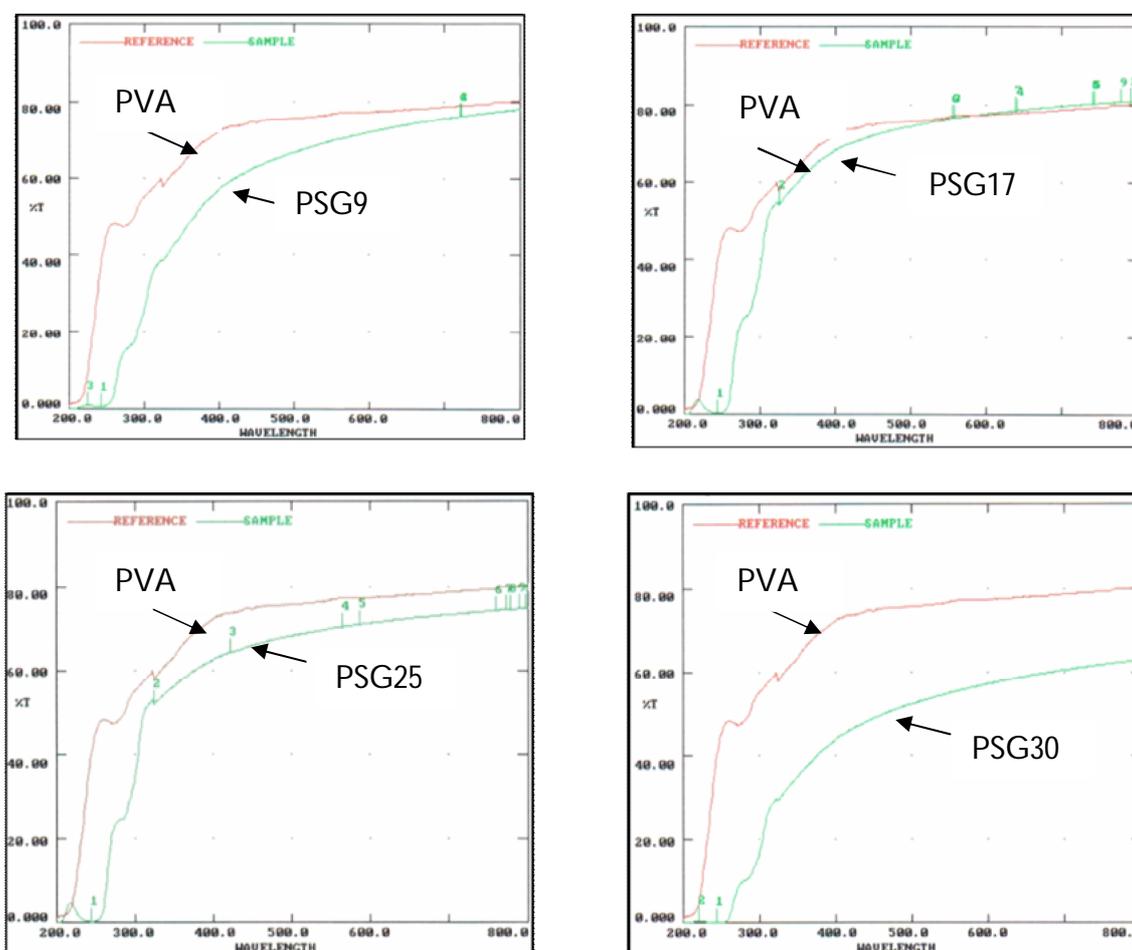


Figure 5. Dependence of the light transmittance (T_r) of PVA and PSG films on the wavelength from 200 to 800 nm.

The films obviously showed higher T_r values at the range of visible light (400–800 nm) than that at the range of ultraviolet light (200–400 nm). The T_r values of PVA, PSG9, PSG17 and PSG25 films are about 60% at the wavelength from 400 to 800 nm, indicating their good transparency in nature. At the same wavelength, the T_r of PSG17 is the

highest among the selected films, due to the homogeneous dispersion of starch and strong interactions with PVA. With an increase of starch (PSG25 and PSG30), the T_r values of the composite films decreased significantly. This is due to the different interactions with PVA and resulted in different effects on the optical properties of the composite films.

Conclusions. Four formulations coded: PSG9, PSG17, PSG25 and PSG30 containing starch from 9 to 30 wt% were prepared by melting technique.

The effect of starch content on the biodegradability of the tested blends was investigated by the variation of mechanical properties (tensile strength and elongation to break %) and the determination of weight loss up of specimens buried to soil until 30 days.

The vibrational peaks are assigned to O–H stretching ($3500\text{--}3200\text{ cm}^{-1}$), C–H stretching (2955 cm^{-1}), C=O stretching (1745 cm^{-1} , 1713 cm^{-1}), C–H bend of CH_2 (1456 cm^{-1}), and C–H wagging of PVA ($1430\text{--}1275\text{ cm}^{-1}$) and they existed in the FTIR spectra of PVA/starch blends, indicating the success of blending of PVA with starch.

Initially, the increasing amount of starch in blends leads to decrease both tensile strength and elongation at break. After exposure of samples into microorganisms from soil, the tensile strength shows high value compared with initial blends meanwhile elongation at break dramatically decreased, all blends going to 0%.

Weight loss of formulations increased with increasing of starch content and exposure time into soil indicating the starting of a degradation process.

Light transmittance values of formulations are about 60% at the wavelength from 400 to 800 nm, indicating their good transparency in nature.

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