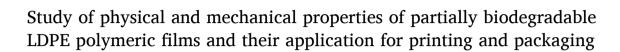
Contents lists available at ScienceDirect

# **Polymer Testing**





Edmundas Kibirkštis<sup>a</sup>, Volodymyr Mayik<sup>b</sup>, Roksolyana Zatserkovna<sup>b</sup>, Kestutis Vaitasius<sup>a,\*</sup>, Anna Stepanenko<sup>c</sup>, Rasa Kandrotaitė-Janutienė<sup>a</sup>, Ingrida Venytė<sup>a</sup>, Paulius Pavelas Danilovas<sup>d</sup>

<sup>a</sup> Kaunas University of Technology, Department of Production Engineering, Studentų St. 56, 51424, Kaunas, Lithuania

<sup>b</sup> Ukrainian Academy of Printing, Department of Media Printing Technologies and Packaging, Pidholosko St., 19, 79020, Lviv, Ukraine

<sup>c</sup> Velikomorskaja Str. 30-60, 220028, Minsk, Belarus

<sup>d</sup> Polymer Competence Center, Gradauciznos K. 7, 60430, Raseiniu R., Lithuania

ARTICLE INFO

Keywords: Thermal stability Tensile strength Heat seal strength Optical density Printability Packaging

## ABSTRACT

Potato starch, glycerine, itaconic acid and molasses of different physical state (dry and liquid) were used for manufacturing partially biodegradable low density polyethylene (LDPE) films. The mechanical, physical properties of new polymeric films with different physical state were investigated using these test methods: scanning electron microscopy, FTIR spectroscopy, thermogravimetric analysis, tensile testing, heat seal testing and printability testing. Investigated film properties were determined and compared with the properties of the pure LDPE film. It was determined that thermal stability did not changed significantly with the addition of biode-gradable additives. The tensile strength and elongation of LDPE films containing potato starch, glycerine and itaconic acid were about 50% lower than pure LDPE film but of the film containing dry molasses and glycerine - was only 25% lower. The heat seal strength of film containing dry molasses was the closest to pure LDPE film at 115 °C. The other tested films required a higher temperature range to form a seal of sufficient strength. The SEM microphotographs have shown the particles of biodegradable additives randomly oriented on the surfaces of some LDPE films, thus, the values of optical density of only one LDPE film containing potato starch and glycerine were the closest to pure LDPE film. LDPE with molasses has been found to be the most suitable film for printing and packaging processes.

## 1. Introduction

Flexible polymeric packages made of synthetic polymers are very durable during their all life cycle and present serious environmentally problems. Thus, one option to solve such problems is to use pure biodegradable polymeric films made of renewable resources or combine blends with synthetic polymers to obtain partially biodegradable films. However, the use of biopolymers is still limited by a higher price and worse chemical, physical and mechanical properties [1–3].

The other option is to use combined partially biodegradable blends of raw materials (starch, molasses, chitosan, glycerine and others) and pure polymeric films. The first researches [4–11] reported on preparation of LDPE compositions with various content of starch and analysed mechanical, physical characteristics and properties of these materials. The authors have concluded that higher content of starch leads to the adverse effect on the mechanical and physical properties.

The mechanical properties, gas and water permeability, and biodegradability before and after storage of LDPE and rice or potato starch mixtures were investigated [5]. The presence of high starch contents (30 w%) had an adverse effect on the mechanical properties of LDPE/starch blends. Gas permeability and water vapor transmission rate increased proportionally to the starch content in the blend. The biodegradability rate of the blends was enhanced when the starch content exceeded 10 w %. The mechanical properties of LDPE blends were investigated to test the effectiveness of Surlyn starch treatment. The strength of LDPE and treated starch blends was found to be lower than that of the original LDPE [6]. Mechanical properties (percent elongation, tensile, bursting, and tear strength), as well as barrier properties (water vapor and oxygen

https://doi.org/10.1016/j.polymertesting.2022.107646

Received 18 February 2022; Received in revised form 28 April 2022; Accepted 23 May 2022 Available online 28 May 2022





<sup>\*</sup> Corresponding author.

*E-mail addresses*: edmundas.kibirkstis@ktu.lt (E. Kibirkštis), maik@uad.lviv.ua (V. Mayik), zatserkovna.r@gmail.com (R. Zatserkovna), kestutis.vaitasius@ktu.lt (K. Vaitasius), anna-stepanenko@mail.ru (A. Stepanenko), rasa.kandrotaite-janutiene@ktu.lt (R. Kandrotaite-Janutiene), ingrida.venyte@ktu.lt (I. Venyte), p. danilovas@gmail.com (P.P. Danilovas).

<sup>0142-9418/© 2022</sup> The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

transmission rate) of the filled LDPE film with different quantities of starch, were studied [7]. It can be observed that with the incorporation of 1% starch, there was a marginal decrease in the mechanical properties of LDPE films. However, in the case of 5% starch filled LDPE film, mechanical properties such as percent elongation, tensile, tear, bursting, and seal strengths decreased by19.23, 33.65, 3.88, 10.8, and 22.12%, respectively. The physical and thermal mechanical properties of corn starch/LDPE composites were investigated [8]. It was found that increasing the amount of starch increases biodegradability, but gradually decreases the tensile strength and elongation at break several times. In [9] study it was investigated the incorporation of different starches, such as sago starch, corn starch, potato starch, tapioca starch, and wheat starch, in a low-density polyethylene matrix (LDPE). It was found that tensile strength and elongation at break of LDPE/starch blends decreased as the starch content increased (tensile strength to 3 times and elongation at break to 10 times, when 30% starch was added). Also, the samples containing sago starch showed good mechanical properties compared with other types of starch. Modified linear low-density polyethylene (LLDPE) blended with corn starch and nonfunctional LLDPE with the starch was investigated [10]. Tensile strength and modulus increased and percentage elongation decreased as the starch content increased in the blends. Water absorption of the blends increased with an increase in starch content. Blends exposed to a soil environment are degraded more than fungi alone. The authors [11] studied films obtained by using starch from potato, oat, maize, tapioca, and rice and found that starch-based films made from oat and tapioca have been found to have the lowest tensile strength. The highest values of tensile strength were observed for films made from potato starch. Furthermore, the oat and tapioca films exhibited the highest contact angle values and, simultaneously, the lowest values for the polar component of the surface free energy, which is related to lower wettability and lower hydrophilicity. Wettability for the maize film was found to be the highest and that of oats the lowest.

The other authors [12-21] continued to develop the new LDPE and starch blends using different types and content of starch and other renewable materials in order to make a partially biodegradable polymeric film with good mechanical and physical characteristics. Paper [12] presents an approach to preparing polyethylene/thermoplastic starch blends with unique properties. Under certain conditions, a film of the LDPE polymer/TPS blend was developed, which was characterized by high elongation at break, modulus, and strength in the machine direction (at a composition level of 71:29 PE/TPS containing 36% glycerol, the blend retains 96% of the elongation at break and 100% of the modulus of polyethylene). The elongation at break in the cross direction of these materials is lower than the machine direction properties. In work [13] it was investigated the incorporation of different starches, such as native, adipate, acetylated, and cassava starch, in low-density polyethylene matrix (LDPE). Starch addition usually caused a negative impact on mechanical resistance and elongation at break, if compared with pure LDPE. However, the compounds with low starch content (5 and 10 wt%), presented Young modulus values above the ones for pure LDPE. Samples containing adipate and cassava starches presented better results for mechanical and biodegradation tests. In [14] work, biodegradability, morphology, and thermomechanical properties of LDPE/modified starch blends and LDPE/starch blends were compared. The substitution of starch by starch phthalate in the blends with LDPE showed an increase in mechanical and thermal properties with increasing starch content. In [15] work the mechanical properties (tensile strength, elongation, melt flow index, and burst strength) of the films that were prepared by blending corn starch, cross-linked starch, or glycerol modified starch in LDPE were studied. It was found that the tensile strength, elongation at break, and melt flow index of LDPE blend with 7.5% native starch decreased, but burst strength increased (compared to pure LDPE film). The tensile strength, elongation and melt flow index of the films containing cross-linked starch was considerably higher than those containing native starch but the burst strength showed

a reverse trend. For native starch and cross-linked starch modified with glycerol, the elongation and melt flow index of the films increased but burst strength decreased. Mechanical properties of composites made from sago starch (SS) and LLDPE were investigated in the work [16]. Yield strength, tensile strength, and elongation at break reduced with an increase in filler content but the modulus increased. The optimum filler content was found to be 15%, above which a sharp drop in the mechanical properties occurred. In [17] work is studied the influence of biodegradability on mechanical properties of polymer film based on low-density polyethylene and cassava starch. It was observed, that elastic modulus and yield stress of blends before the biodegradability test are slightly increased with increasing TPS contents but at high TPS concentration (50% (w/w)) the yield stress and elongation are remarkably decreased. The tensile properties of PES40 films are significantly decreased after the biodegradability test (burial in natural soil or compost soil for 150 days). Sugar cane bagasse (SB)-low density polyethylene composites with different mechanically treated SB were investigated in the work [18]. The studies found that the elongation at break was fairly constant. Thermal stability decreased in the presence of SB and linearly increased concerning with respect to the treatment times. Heat sealing property of films based on corn starch and amylose (AM), methylcellulose (MC), or hydroxypropylmethylcellulose (HPMC) was evaluated in [19]. Films sealed at temperature <143 °C showed peeling mode failure attributing to weak seal strength, while that at 144 °C showed tearing mode failure indicating good seal strength. The heat sealability of laminated films with linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) was investigated [20]. It was found that laminated films made from the extrusion lamination process provided a lower level of achievable heat seal strength when compared with the laminated films made from the dry-bond lamination process. The blend properties were found to depend not only on composition but also on the generated morphology [21].

There are works in which the authors study the flammability of composites derived from recycled polymers, the dependence of their mechanical properties on the composition of the composite [22]; the effect of polymer degradation on the chemical and physical properties of polymer films [23,24]; the biodegradability of polymers [25] or the antibacterial activity of polymer composites with zinc oxide nanoparticles [26].

In order to decide on the application of polymer packaging with bioscale additives to packaging technologies and to estimate the everincreasing flows of polymer packaging in the world, it is important to determine the temperature of film degradation, their aging process, as well as to investigate the distribution of biodegradable particles in the material.

In addition, it is necessary to investigate other physical properties of these materials, such as the value of the tear strength of the weld, the tensile strength and elongation, the quality of the print on the surface of the material, and the suitability of these films for packaging technologies.

Thus, the aim of this paper is to investigate the physical and mechanical properties of the proposed polymer films (based on LDPE) with bioscale additives and their suitability for printing and packaging technologies.

## 2. Experimental details

## 2.1. Materials

The materials for testing were manufactured at Belarusian National Technical University and Ukrainian Academy of Printing using a single screw film blowing extruder SJM35-400 that screw diameter was 35 mm and length to screw diameter ratio L/D = 30:1. Five newly developed low density polyethylene (LDPE) polymeric films containing potato starch and molasses were obtained with the following compositions – see Table 1.

#### Table 1

Polymeric films with following compositions.

Polymeric film	Compositions of polymeric films
LDPE	pure low density polyethylene (referred as LDPE);
LDPE1	LDPE + 3% potato starch + 1% glycerine (referred as LDPE1);
LDPE2	LDPE + 3% potato starch $+ 1%$ glycerine $+ 10%$ itaconic acid
	(referred as LDPE2);
LDPE3	LDPE + 5% potato starch + 1% glycerine + 10% itaconic acid
	(referred as LDPE3);
LDPE4	LDPE + 2% molasses (dry) + 1% glycerine (referred as LDPE4);
LDPE5	LDPE+2% molasses (liquid) $+$ 1% glycerine (referred as LDPE5).

All tested LDPE samples can be divided into two groups. The first one - polymeric films containing varying content of potato starch and constant glycerine and itaconic acid. The blowing pressure of all these polymeric films was 24516.6 kPa and the temperature was 160 °C. The films of the second group contained molasses of different physical states and glycerine. The blowing pressure of these films was the same but the temperature was 190 °C.

## 2.2. Research methods

For experimental studies of LDPE1-LDPE5 polymeric films were used the following research methods: scanning electron microscopy, FTIR spectroscopy, thermogravimetric analysis, tensile testing, heat seal testing, printability testing.

## 2.2.1. Scanning electron microscopy

The images of the LDPE films containing biodegradable additives were taken using scanning electron microscopy. The microphotographs were taken using FEI Quanta 200 electron microscope (more details see Fig. 1).

## 2.2.2. FTIR spectroscopy

FTIR spectra analysis of the polymeric films was carried out by using a Perkin–Elmer Frontier spectrophotometer with a Universal ATR Accessory. The data were recorded in the spectral range from 655 to  $4000 \text{ cm}^{-1}$  by accumulating 5 scans with a resolution of 1 cm<sup>-1</sup> (more details see Fig. 2).

## 2.2.3. Thermogravimetric analysis

The thermogravimetric analysis was carried out using a PerkinElmer (TGA 4000) instrument. The values of temperature of thermal destruction have been calculated using the tools of "Pyris software" (onset method) of a PerkinElmer (TGA 4000) instrument. The measurements were carried out at the heating rate of  $20 \, ^\circ \text{C} \cdot \text{min}^{-1}$  under nitrogen atmosphere (flow rate  $20 \, \text{cm}^3 \, \text{min}^{-1}$ ). About 10.0 mg of sample was loaded in the ceramic pan during the test (see Fig. 3).

## 2.2.4. Tensile testing

LDPE/starch/molasses polymeric films were tested according to the standard LST EN ISO 527-3:2019 in the machine direction (MD) and across the direction (CD) of extrusion. A universal tensile/compression machine Tinius Olsen H10KT was used to determine the tensile force and elongation at break. Using "Twhings - Albert JDC Precision Sample Cutter" the samples were cut into strips ( $15 \times 150$  mm), the load cell was 500 N and cross-head speed 100 mm/min (see Fig. 4).

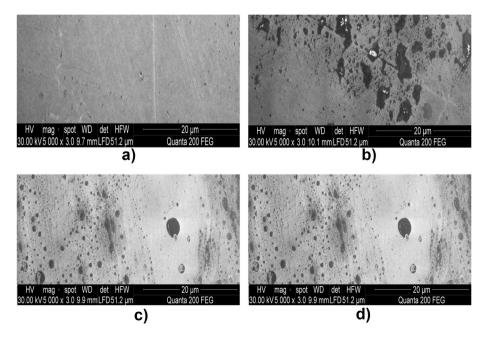
## 2.2.5. Heat seal testing

The heat sealing tests were carried out according to the standard ASTM F88 – 07. "Labthink Instrument Heat Seal Tester HST-H3" was used for welding the polymeric films. The welding parameters were set as follows: dwell time – 0.8 s, pressure – 257 kPa, temperature range – 115 ÷ 145 °C. Welded samples were cut into strips perpendicular to the seal direction in size of 15 × 100 mm. The seal was peeled apart using the peel tester "Twhings – Albert Instrument FP-2255" at a constant velocity – 15 cm/min, recording the peak-force (N) and noting the visual evaluation of the character of seal failure (see Table 5).

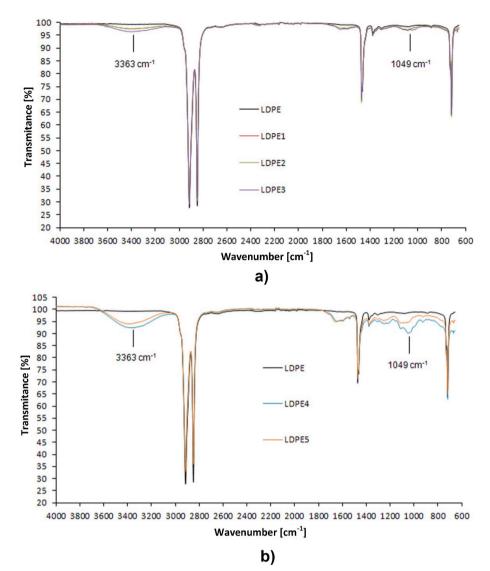
## 2.2.6. Printability testing

"Flexiproof 100/UV" printing tester was used to print the 100% ink color patches on polymeric films. Equal printing parameters were maintained for LDPE1-LDPE5 samples: speed, inks, UV lamp, anilox roller (see Table 2).

Proof printing was carried out for samples without additional surface treatment (virgin surface tension) and with additional treatment by setting the power at 70 W/min/m<sup>2</sup>. Such value was set considering to the recommendations of flexographic printing and packaging specialists from Lithuanian flexographic printing houses. The corona discharge



**Fig. 1.** SEM microphotographs of partially biodegradable LDPE films: (a) LDPE (pure); (b) LDPE3 ((LDPE + 5% potato starch + 1% glycerine + 10% itaconic acid); (c) LDPE4 (LDPE + 2% molasses (dry) + 1% glycerine); (d) LDPE5 (LDPE + 2% molasses (liquid) + 1% glycerine).



**Fig. 2.** FTIR spectra of partially biodegradable LDPE films: (a) LDPE (pure); LDPE1 (LDPE + 3% potato starch + 1% glycerine); LDPE2 (LDPE + 3% potato starch + 1% glycerine + 10% itaconic acid); (b) LDPE (pure); LDPE4 (LDPE + 2% molasses (dry) + 1% glycerine); LDPE5 ((LDPE + 2% molasses (liquid) + 1% glycerine).

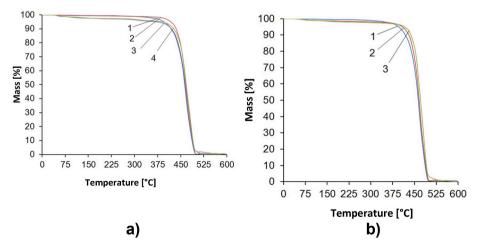


Fig. 3. TGA curves of partially biodegradable LDPE films: (a) 1 - LDPE; 2 - LDPE1; 3 - LDPE2; 4 - LDPE3; (b) 1 - LDPE; 2 - LDPE4; 3 - LDPE5.

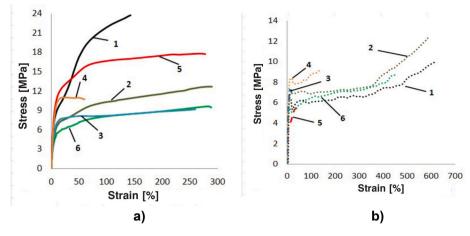
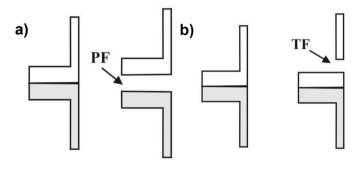


Fig. 4. Stress - strain curves of tested LDPE films: (a) machine direction MD; (b) across direction CD; 1 – LDPE; 2 – LDPE1; 3 – LDPE2; 4 – LDPE3; 5 – LDPE4; 6 – LDPE5.



**Fig. 5.** Simplified schemes of heat sealing failures: (a) PF - peeling failure (layers of film separate and the interface of seal); (b) TF - tearing failure (film tears in the near region of seal) [19].

Table 2	
---------	--

Parameters of printing process.

Printing speed [m/min]	50
Anilox roller	
Cells, lines/cm	160
Volume, cm <sup>3</sup> /m <sup>2</sup>	6
UV lamp, W/cm	160
Printing ink	Flexocure Gemini cyan

## Table 3

Results of temperature of thermal destruction of tested polymeric films.

Polymeric film	Temperature of thermal destruction [°C]
LDPE	456.2
LDPE1	455.5
LDPE2	456.7
LDPE3	452.3
LDPE4	454.4
LDPE5	453.9

device "Vetaphone Corona-Plus" was used to increase the surface tension of polymeric materials. The wetting angle was measured according to the standard ASTM D5946 and using the "Pocket Goniometer PG2". Later the values of wetting angle were converted to surface tension (ST) values (dyn/cm). The quality of printed images was assessed by measuring the optical density of 100% ink color patches (see Table 6) and applying microscopic analysis of samples. Optical density was measured using the spectrodensitometer "X-Rite Colour" and microscopic analysis was carried out using optical microscope Nikon equipped

Table 4
Results of tensile strength and elongation at break measurements of tested LDPE
polymeric films.

Polymeric film	Tensile strength [MPa] MD/ CD	Relative to LDPE [%] MD/CD	Elongation at break Δl <sub>0</sub> [mm] MD/CD	Relative to LDPE [%] MD/CD
LDPE	23.76/10.04	-	128.65/591	-
LDPE1	12.7/12.36	54/123	266/556	207/94
LDPE2	9.9/7.25	42/72	262.7/23.9	204/4
LDPE3	11.01/9.12	46/91	63.8/107.3	50/18
LDPE4	17.82/5.59	75/55	286.8/25.86	223/4
LDPE5	9.66/8.77	40/88	233.7/260.2	182/44

Results of seal strength of tested polymeric films.				
Polymeric film	Peel force [N]	Welding temperature [°C]	Evaluation of seal	
LDPE	11.41	115	Tearing failure	
LDPE1	4.23	135	Peeling failure	
LDPE2	4.31	115	Peeling failure	
LDPE3	9.76	145	Tearing failure	
LDPE4	8.91	115	Tearing failure	
	16.45	125	Tearing failure	
LDPE5	1.95	115	Peeling failure	
	4.45	125	Peeling failure	

Та	ble	6	

Table 5

Values of printability testing.

Polymeric film	Corona discharge [W/min/m <sup>2</sup> ]	Wetting angle [°]	Surface tension [dyn/ cm]	Optical density [–]
LDPE	0	72	39	1.23
	70	69	40	1.28
LDPE1	0	76	38	1.22
	70	71	40	1.27
LDPE2	0	92	32	1.03
	70	80	37	1.16
LDPE3	0	97	29	0.83
	70	86	34	1.12
LDPE4	0	99	29	0.78
	70	85	34	0.94
LDPE5	0	87	34	0.95
	70	79	37	1.14

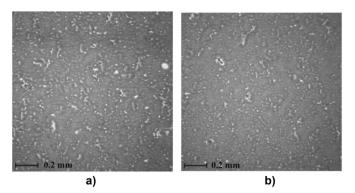


Fig. 6. View of 100% color patch of LDPE1 sample: (a) without surface treatment (38 dyn/cm); (b) 70 W/min/m<sup>2</sup> (40 dyn/cm).

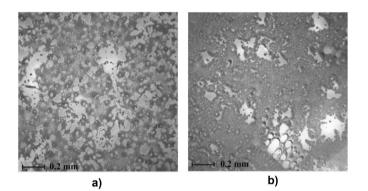


Fig. 7. View of 100% color patch of LDPE3 sample: a) without surface treatment (29 dyn/cm); b) 70 W/min/m<sup>2</sup> (34 dyn/cm).

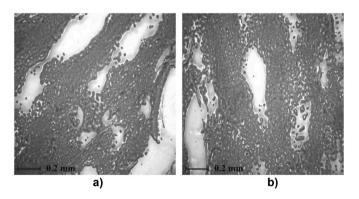


Fig. 8. View of 100% color patch of LDPE4 sample: a) without surface treatment (29 dyn/cm); b) 70 W/min/m<sup>2</sup> (34 dyn/cm).

with video camera Nikon DS-2 16 MP and objectives Nikon TU Plan Fluor  $10 \times /0.30$  and Nikon TU Plan Fluor 100x/0.90 (see Fig. 6 – Fig. 9).

## 3. Results and discussions

## 3.1. Scanning electron microscopy

The SEM microphotographs of pure LDPE film and other tested partially biodegradable films are shown in Fig. 1.

Fig. 1b, c and 1d depicted the particles of biodegradable additives randomly oriented on the surfaces along the machine direction during manufacturing. In the case of LDPE3 and LDPE5 polymeric films the shape of additives' particles is irregular and having average diameter of

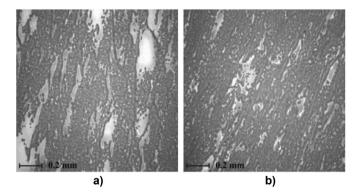


Fig. 9. View of 100% color patch of LDPE5 sample: a) without surface treatment (34 dyn/cm); b) 70 W/min/m<sup>2</sup> (37 dyn/cm).

 $20 \ \mu$ m. Meanwhile, the shape of additives at the LDPE4 surface is similar to an ellipse and the diameter is less than  $20 \ \mu$ m. It could be stated that additives were not melted sufficiently during the manufacturing of the samples and were concentrated at the surface. Also the SEM microphotographs of LDPE1 and LDPE2 surfaces were similar to the pure LDPE.

## 3.2. FTIR spectroscopy

The FTIR spectra of LDPE, LDPE1, LDPE2, LDPE3, LDPE4 and LDPE5 polymeric films are shown in Fig. 2.

The FTIR spectrum of pure LDPE polymeric film has shown all expected peaks according to the work [27]. The similar peaks at the same wavenumbers of tested biodegradable polymeric films have been also determined, however, with two different peaks at  $3363 \text{ cm}^{-1}$  (hydroxyl group) and  $1049 \text{ cm}^{-1}$  (C–O–C, C–O–H bending) which may be detected because of the presence of various additives (glycerine, starch, molasses). Regarding the FTIR spectra, the peak intensity at  $3363 \text{ cm}^{-1}$  and  $1049 \text{ cm}^{-1}$  increased with an increasing number and concentration of additives at the surface of tested samples, especially for LDPE3, LDPE4, and LDPE5 polymeric films.

## 3.3. Thermogravimetric analysis

The TGA curves of LDPE, LDPE1, LDPE2, LDPE3, LDPE4 and LDPE5 polymeric films are shown in Fig. 3. Table 3 presents the results of the temperature of thermal destruction of tested polymeric films.

As expected, LDPE starts degrading above 400 °C and produces gaseous phase compounds, with no solid mass remaining above 500 °C. Determined onset decomposition temperature of LDPE is 456.2 °C (see Table 3). LDPE1 film, containing starch and glycerol, exhibited a similar one-step pattern of decomposition with no significant weight loss below 400 °C. LDPE2 and LDPE3 films, additionally containing relatively large amount of itaconic acid, lose mass in two clearly differentiated stages; the first one occurs in a wide temperature interval approximately between 60 and 370  $^\circ\text{C}$  and that corresponds to  ${\approx}3\%$  of the mass for both samples. Such mass loss can be attributed to the release of volatile compounds, formed due to decomposition of thermally non-stable ingredients of films or evaporation of volatile compounds formed during reactive extrusion process. The second and main stage of thermal decomposition begins above 400 and ends near 500 °C. LDPE4 and LDPE5 also exhibit two-step mass loss pattern, the first one occurring above 75 °C due to the release of volatile compounds, formed during decomposition of thermally non-stable ingredients of films. The mass loss at 370 °C was  $\approx$ 1.5% and is therefore, very insignificant. As in the case of all previously described films, the main thermal decomposition stage of LDPE4 and LDPE5 begins above 400 °C. This main thermal destruction stage represents a weight loss of more than 90% for all samples and is undoubtedly related to decomposition of polyethylene, which is the main component of all films. Table 3 shows determined onset decomposition temperature values of polyethylene in different samples. As one can see, polyethylene thermal destruction temperature values are very similar for all films ranging from 452.3 to 456.7 °C. Hence, it can be concluded that neither additives used in production of all multicomponent films nor the decomposition products of such additives do not reduce thermal decomposition temperature values of polyethylene and therefore, do not initiate its premature thermal decomposition.

## 3.4. Tensile testing

The results of tensile measurement are listed in Table 4 and Fig. 4. For comparison of tensile properties and their changes of polymeric films containing various additives, a calculation relative to the pure LDPE sample has been made and shown in columns 3 and 5 of Table 4.

The measurements have shown that the value of tensile strength (MD) of LDPE film was 23.76 MPa and it was higher than of all other tested polymeric films. The tensile strength of polymeric films containing potato starch/glycerine/itaconic acid was similar and about 50% lower compared to LDPE film. The addition of liquid molasses has reduced the tensile strength by 60% of the LDPE film and was the lowest among all tested polymeric films. But the tensile strength of LDPE4 film containing dry molasses was only about 25% lower than LDPE film. A completely different result was observed of tensile strength in CD. The tensile strength of most tested films was close to LDPE film (70  $\div$  90%). The tensile strength of LDPE1 film was even 23% higher than that of LDPE film, meanwhile, for the LDPE4 film it was 45% lower.

The values of elongations at break in MD were mostly 2 times higher than the ones of LDPE films except for LDPE3 film that elongation at break was only 50%. Therefore, in CD all elongations were lower than LDPE films especially for LDPE2 and LDPE4 films that elongations were about 95% lower.

#### 3.5. Heat seal testing

The results of polymeric films seal strength testing are presented in Table 5. It was determined that the sealing of tested LDPE films containing various additives occurred in the temperature range of  $115 \div 145$  °C. For evaluation of seal strength according to previous M. Das and T. Chowdhury researches of starch based polymeric films heat sealing [19], two characters of seal failure were distinguished: peeling failure (Fig. 5 a) or tearing failure (Fig. 5 b). In case of peeling failure, the layers of polymeric films tear in the near area of seal that shows a sufficient seal strength.

The initial welding temperature was 115 °C. LDPE, LDPE2, LDPE4 and LDPE5 polymeric films were welded at this temperature. At this temperature, it was impossible to form a seal for LDPE1 and LDPE3 films. The highest peel force (11.41 N) and tearing failure character was observed for pure LDPE film. According to the flexographic printing and packaging specialists, for successful packaging processes a sufficient value of peel force is about 10 N under that no disentanglements can be observed in the sealed area. Thus the peel force (8.91 N) of LDPE4 polymeric film was sufficient and tearing failure was observed at the temperature of 115 °C. The peeling failure character was observed for LDPE5 film and the peel force was about 4.5 times lower than LDPE4 film.

In the next step of testing the temperature was increased up to 125 °C. Similar to the first test, it was impossible to form a seal for LDPE1 and LDPE3 films. The LDPE and LDPE2 films have melted and also it was impossible to form a seal. Meanwhile, the peel force of LDPE4 and LDPE5 films increased 1.8 and 2.2 times, respectively. The heat sealing failure of both these films was identical as in the first test. In the third test, the temperature was increased up to 135 °C. In this case, LDPE and LDPE2 films were not tested because of melting at 125 °C

temperature. The peel force of LDPE1 film at this temperature was only 1.9 N. For LDPE3 film, again it was impossible to form a seal. At this temperature, LDPE4 and LDPE5 films have melted and it was impossible to form a seal. In the fourth test the temperature was increased up to 145  $^{\circ}$ C. The LDPE3 film has formed a seal at sufficient force (9.76 N) and a tearing failure character was observed at this temperature.

## 3.6. Printability testing

The following results were obtained after the determination of wetting angle and optical density analysis (see Table 6).

Obtained data shows that only LDPE1 film has sufficient surface tension for printing. The other four samples containing potato starch, dry or liquid molasses and glycerine additives have lower ST without the additional treatment and were not suitable for qualitative flexography printing.

The microphotographs have shown the biodegradable additives on the surface of LDPE3, LDPE4 and LDPE5 polymeric films, thus, it could cause worse surface tension and printing quality. Comparing with other LDPE films having different compositions, the value of optical density of 100% color patch printed on LDPE1 polymeric film was the highest (D = 1.22). Additional surface treatment increased this value only up to 4%. Similar values of optical density were observed for LDPE film, as well. The microphotographs of 100% color patch show that the surface was coated qualitatively by UV inks (see Fig. 6).

The measured values of optical density of LDPE3, LDPE4 and LDPE5 polymeric films were insufficient as recommended for UV flexography printing (see Table 6). As can be seen from microphotographs shown in Figs. 6–9, the inking quality of surfaces was worse than LDPE1 or LDPE. The UV inks did not form a solid layer but were tended to contract itself into the shape of an irregular uncoated area (Figs. 6–9, bright areas). Such behaviour caused the distortion of optical characteristics and made worse the value of optical density. Additional surface treatment increased the optical density – 13% for LDPE2 film and 35% for LDPE3 film. Also, the layer of inks at the surfaces was more solid than it was before treatment (see Fig. 7 b). The values of optical density of LDPE4 film containing dry molasses before and after additional treatment were about 22% worse than LDPE5 containing liquid molasses (see Figs. 8 and 9).

## 4. Conclusions

The paper investigated the physical and mechanical properties and characteristics of LDPE based polymer films with bioscale additives and their suitability for printing and packaging technologies.

Thermal destruction temperatures of polymer films LDPE 1–5 with bioscale additives were determined, and compared with the decomposition temperature of the base LDPE film.

Pure LDPE film and LDPE films, containing starch and glycerol, showed no significant mass loss below 400 °C. Multicomponent films, containing 10% of itaconic acid, showed  $\approx$ 3% of mass loss mass between 60 and 370 °C due to release of volatile compounds, formed due to decomposition of thermally non-stable ingredients of films or evaporation of volatile compounds formed during reactive extrusion process. Multicomponent films, containing 2% of mollases showed  $\approx$ 1.5% of mass loss between 60 and 370 °C due to release of volatile compounds, formed during decomposition of thermally non-stable ingredients of films.

The TGA analysis has showed that the addition of biodegradable materials to the pure LDPE polymeric film practically does not affect thermal degradation temperature of polyethylene (456.2 °C), since thermal decomposition temperature values of polyethylene in multi-component films are very similar ranging from 452.3 to 456.7 °C.

The SEM microphotographs showed the particles of biodegradable additives randomly oriented at the surfaces along the machine direction during manufacturing of the LDPE3, LDPE4 and LDPE5 polymeric films. Thus, the values of optical density of polymeric films of first group (LDPE1-LDPE3) were higher and closer to the LDPE film values than molasses/glycerine (LDPE1–99%, LDPE2–86%, LDPE3–69%, LDPE4–64%, LDPE5–77% of LDPE film).

The tensile strength of polymeric films containing potato starch/ glycerine/itaconic acid was similar and about 50% lower compared to LDPE film. The addition of liquid molasses reduced the tensile strength 60% of LDPE film and was the lowest between all tested polymeric films. Therefore, the tensile strength of LDPE4 film containing dry molasses was only about 25% lower of LDPE film. A completely different result was observed of tensile strength in CD. The tensile strength of most tested films was close to LDPE film (70  $\div$  90%). The tensile strength of LDPE1 film was even 23% higher than of LDPE film, meanwhile, for the LDPE4 film it was 45% lower.

The insertion of bioscale additives into the structure of polymer films had no significant effect on the value of the wetting angle and the surface tension of the surface of the studied films. Prototypes of all studied polymer films had good hydrophilic properties, therefore, these films could be used for printing as well. LDPE 3 and LDPE 4 films were found to be more suitable for packaging technologies (the peel force of the welding seam of the packages of these films was sufficient). The investigated materials are intended for the production of disposable materials and short-term packaging.

Most of the commercially available biodegradable materials are fully biodegradable and compostable. Such materials are usually composed of a significantly large amount of starch blended with biodegradable aliphatic polyesters. The materials investigated in our study are of different types (only partially biodegradable) and unfortunately, would not be suitable for composting process. However, the matrix material we used in this study (LDPE) is at least several times cheaper than the matrix, used in commercially available compostable products. Therefore, LDPE-starch blends have an advantage in terms of price.

#### Author statement

Conceptualization: Edmundas Kibirkštis and Volodymyr Mayik, methodology: Edmundas Kibirkštis, Roksolyana Zatserkovna, Kęstutis Vaitasius, preparation of specimen: Roksolyana Zatserkovna and Anna Stepanenko, SEM and optical photographs: Rasa Kandrotaitė-Janutienė, FTIR spectroscopy: Paulius Pavelas Danilovas, thermogravimetric analysis: Paulius Pavelas Danilovas, printability testing: Ingrida Venytė, heat seal testing: Kęstutis Vaitasius, tensile testing: Kęstutis Vaitasius, writing – original draft preparation: Ingrida Venytė, writing – review and editing: all; funding acquisition: Edmundas Kibirkštis, All authors have read and agreed to the published version of the manuscript.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was supported by Research Council of Lithuania (Agreement No. TAP LB-02/2015). Also this work is supported by JSC "Aurika" (support agreement No. SV8-0067).

### References

- N. Peelman, P. Ragaert, B. De Meulenaer, et al., Application of bioplastics for food packaging, Trends Food Sci. Technol. 32 (2) (2013) 128–141, https://doi.org/ 10.1016/j.tifs.2013.06.003.
- [2] J. Langley, N. Turner, A. Yoxall, Attributes of packaging and influences on waste, Packag. Technol. Sci. 24 (3) (2011) 161–175, https://doi.org/10.1002/pts.924.

- [3] B. Laycock, M. Nikolic, J.M. Colwell, et al., Lifetime prediction of biodegradable polymers, Prog. Polym. Sci. 71 (2017) 144–189, https://doi.org/10.1016/j. progpolymsci.2017.02.004.
- [4] G.J.L. Griffith, US Patent 4 021 388, 1977.
- [5] I. Arvanitoyannis, C.G. Biliaderis, H. Ogawa, N. Kawasaki, Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications. Part 1, Carbohydr. Polym. 36 (2–3) (1998) 89–104, https://doi.org/10.1016/S0144-8617(98)00016-2.
- [6] Y.J. Kim, H.M. Lee, O.O. Park, Processabilities and mechanical properties of Surlyn treated starch/LDPE blends, Polym. Eng. Sci. 35 (20) (1995) 1652–1657.
- [7] J.H. Jagannath, S. Nadanasabapathi, A.S. Bawa, Effect of starch on thermal, mechanical, and barrier properties of low density polyethylene film, J. Appl. Polym. Sci. 99 (6) (2006) 3355–3364, https://doi.org/10.1002/app.22358.
- [8] A.R. Oromiehie, T. Taherzadeh lari, A. Rabiee, Physical and thermal mechanical properties of corn starch/LDPE composites, J. Appl. Polym. Sci. 127 (2) (2013) 1128–1134, https://doi.org/10.1002/app.37877.
- [9] S. Kormin, F. Kormin, M.D.H. Beg, M.B.M. Piah, Physical and mechanical properties of LDPE incorporated with different starch sources, IOP Conf. Ser. Mater. Sci. Eng. 226 (2017), 012157, https://doi.org/10.1088/1757-899X/226/1/ 012157.
- [10] R. Chandra, R. Rustgi, Biodegradation of maleated linear low-density polyethylene and starch blends, Polym. Degrad. Stabil. 56 (2) (1997) 185–202.
- [11] Z. Zołek-Tryznowska, A. Kałuza, The influence of starch origin on the properties of starch films: packaging Performance, Materials 14 (2021) 1146, https://doi.org/ 10.3390/ma14051146.
- [12] F.J. Rodriguez Gonzalez, B.A. Ramsay, B.D. Favis, High performance LDPE/ thermoplastic starch blends: a sustainable alternative to pure polyethylene, Polymer 44 (5) (2003) 1517–1526, https://doi.org/10.1016/S0032-3861(02) 00907-2.
- [13] E.M. Nakamura, L. Cordi, G.S.G. Almeida, N. Duran, L.H.I. Mei, Study and development of LDPE/starch partially biodegradable compounds, J. Mater. Process. Technol. 162 (2005) 236–241, https://doi.org/10.1016/j. imatprotec.2005.02.007.
- [14] I.M. Thakore, S. Desai, B.D. Sarawade, S. Devi, Study on biodegradability, morphology and thermomechanical properties of LDPE/modified starch blends, Eur. Polym. J. 37 (1) (2001) 151–160, https://doi.org/10.1016/S0014-3057(00) 00086-0.
- [15] S. Garg, A. Jana Kumar, Studies on the properties and characteristics of starch-LDPE blend films using cross-linked, glycerol modified, cross-linked and glycerol modified starch, Eur. Polym. J. 43 (9) (2007) 3976–3987, https://doi.org/ 10.1016/j.eurpolymj.2007.06.030.
- [16] R. Nawang, I.D. Danjaji, U.S. Ishiaku, H. Ismail, Z.A. Mohd Ishak, Mechanical properties of sago starch-filled linear low density polyethylene (LLDPE) composites, Polym. Test. 20 (2) (2001) 167–172, https://doi.org/10.1016/S0142-9418(00)00018-0.
- [17] D.M. Nguen, T. Vi Vi Do, A.C. Grillet, H. Ha Thuc, ChN. Ha Thuc, Biodegradability of polymer film based on low density polyethylene and cassava starch, Int. Biodeterior. Biodegrad. 115 (2016) 257–265, https://doi.org/10.1016/j. ibiod.2016.09.004.
- [18] T. Motaung, M. Mochane, T. Makhetha, et al., Effect of mechanical treatment on morphology and thermal and mechanical properties of sugar cane baggasse-lowdensity polyethylene composites, Polym. Compos. 38 (2017) 1497–1503, https:// doi.org/10.1002/pc.23717.
- [19] M. Das, T. Chowdhury, Heat sealing property of starch based self-supporting edible films, Food Packag. Shelf Life 9 (11) (2016) 64–68, https://doi.org/10.1016/j. fpsl.2016.05.002.
- [20] C.S. Yuan, A. Hassan, M.I. Ghazali, A.F. Ismail, Heat-seal strength analysis of laminated films with LLDPE and LDPE sealant materials in bar sealing application, J. Appl. Polym. Sci. 104 (6) (2007) 3736–3745, https://doi.org/10.1002/ app. 25863
- [21] P. Matzinos, V. Tserki, C. Gianikouris, E. Pavlidou, C. Panayiotou, Processing and characterization of LDPE/starch/PCL blends, Eur. Polym. J. 38 (9) (2002) 1713–1720, https://doi.org/10.1016/S0014-3057(02)00061-7.
- [22] K.M. Zadeh, D. Ponnamma, M.A. Al-Maadeed, Date palm fibre filled recycled ternary polymer blend composites with enhanced flame retardancy, Polym. Test. 61 (2017) 341–348, https://doi.org/10.1016/j.polymertesting.2017.05.006.
- [23] M.C. Antunes, J.A.M. Agnelli, A.S. Babetto, B.C. Bonse, S.H.P. Bettini, Correlating different techniques in the thermooxidative degradation monitoring of highdensity polyethylene containing pro-degradant and antioxidants, Polym. Test. 69 (2018) 182–187, https://doi.org/10.1016/j.polymertesting.2018.05.008.
- [24] S.G. Hirsch, B. Barel, D. Shpasser, E. Segal, O.M. Gazit, Correlating chemical and physical changes of photo-oxidized low-density polyethylene to the activation energy of water release, Polym. Test. 64 (2017) 194–199, https://doi.org/ 10.1016/i.polymertestine.2017.10.005.
- [25] S.A. da Silva, E.W. Hinkel, T.C. Lisboa, V.V. Selistre, A.J. da Silva, L.O.F. da Silva, D.J.L. Faccin, N.S.M. Cardozo, A biostimulation-based accelerated method for evaluating the biodegradability of polymers, Polym. Test. 91 (2020), https://doi. org/10.1016/j.polymertesting.2020.106732.
- [26] R. Galli, M.C. Hall, E.R. Breitenbach, G.L. Colpani, M. Zanetti, J.M.M. de Mello, M. Josiane, L.L. Silva, M.A. Fiori, Antibacterial polyethylene - ethylene vinyl acetate polymeric blend by incorporation of zinc oxide nanoparticles, Polym. Test. 89 (2020), https://doi.org/10.1016/j.polymertesting.2020.106554.
- [27] D.J. da Silva, H. Wiebeck, Using PLS, iPLS and siPLS linear regressions to determine the composition of LDPE/HDPE blends: a comparison between confocal Raman and ATR-FTIR spectroscopies, Vib. Spectrosc. 92 (2017) 259–266, https:// doi.org/10.1016/j.vibspec.2017.08.009.