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Effects of blow molding ratio on mechanical properties of polylactide nanocomposite films

Summary — The results of the investigations of the effect of blow-up ratio of nanocomposite poly(lactic acid) (PLA) films on the mechanical properties determined under static tension are discussed. Investigated films contain additives in the form of a montmorillonite (MMT) nanofiller (LC sample) or MMT and poly(methyl methacrylate) (PMMA) as a modifier (LCM sample) or MMT and poly(ethylene glycol) (PEG) as a plasticizer (LCG sample). Using the X-ray diffraction (XRD) method, it was found that the screw shape of the co-rotating twin-screw extruder, applied to prepare a granulated nanocomposite, significantly influenced the dispersion of MMT within the PLA matrix. The PLA film containing the additives and subjected to a proper extrusion blow molding have better mechanical properties as compared to those of a neat PLA (L sample) film. These properties were found to be the best when the blow-up ratio (R) of the nanocomposite films was equal to 4. The images obtained by means of the transmission electron microscopy (TEM) confirmed that ordering of the MMT platelets within the PLA matrix occurred during the film blowing, which induced an improvement in the film mechanical properties. The presented results prove usefulness of the extrusion blow molding as a method of manufacturing nanocomposite films based on the PLA matrix.
Keywords: poly(lactic acid), nanocomposites, montmorillonite, blown film, mechanical properties.

WPŁYW STOPNIA ROZDMUCHANIA NA WŁAŚCIWOŚCI MECHANICZNE NANOKOMPOZYTOWYCH FOLII POLILAKTYDOWYCH

Streszczenie — W artykule przedstawiono wyniki badań wpływu stopnia rozdmuchania nanokompozytowych folii polilaktydowych (PLA) na właściwości mechaniczne wyznaczane podczas próby statycznego rozciągania. Badane folie zawierały dodatki w postaci: nanonapełniacza montmorillonitowego (MMT) (próbka LC), MMT i modyfikatora, którym był poli(metakrylan metylu) (PMMA) (próbka LCM), MMT i poli(glikolu etylenowego) (PEG), spełniającego rolę plastyfikatora (próbka LCG) (tabela 1). Metodą dyfrakcji rentgenowskiej (XRD) stwierdzono istotny wpływ kształtu ślimaków wytłaczarki dwuślimakowej współbieżnej (rys. 1), stosowanych do wytworzenia granulatu nanokompozytowego, na rozproszenie MMT w osnowie PLA (rys. 2—4). Wykazano również, że folia PLA, zawierająca wymienione składniki dodatkowe i odpowiednio rozdmuchana podczas wytłaczania, ma właściwości mechaniczne znacznie lepsze niż folia PLA bez dodatków (próbka L) (rys. 5—7, tabela 2). W przypadku badanych folii nanokompozytowych właściwości mechaniczne były najlepsze, gdy stosowano stopień rozdmuchania $R = 4$ (tabela 3 i 4). Metodą transmisyjnej mikroskopii elektronowej (TEM) potwierdzono tezę, że podczas rozdmuchiwania folii następuje uporządkowanie ułożenia płytek MMT w osnowie PLA, co ma wpływ na poprawę jej właściwości mechanicznych (rys. 8 i 9). Wyniki przeprowadzonych badań potwierdziły przydatność wytłaczania z rozdmuchiwaniem, jako metody wytwarzania folii nanokompozytowych o osnowie z PLA, charakteryzujących się korzystnymi właściwościami mechanicznymi.
Słowa kluczowe: polilaktyd, nanokompozyty, montmorillonit, folia rozdmuchiwana, właściwości mechaniczne.

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A known maxim "There's plenty of room at the bottom", expressed some fifty years ago by a famous American physicist Richard Feynman, Nobel Prize laureate in 1964, is considered as a main impulse giving rise to the development of nanotechnology. These days, investigations of nanoscale objects constitute a vast area of interdisciplinary scientific research. Achievements of many fundamental sciences, such as physics, chemistry, mathematics, mechanics and materials engineering, are successfully adopted into the nanotechnology practice. The nanoscale research deals not only with the engineering materials and objects, but it is very important also in biology, medicine and pharmacology. Nanomaterials, including polymeric nanocomposites, constitute a significant part of the nanotechnology and create a group of the most prospective materials with very wide application possibilities [1—4].

The nanocomposite materials, based on a matrix made of biodegradable aliphatic polyesters originating from renewable resources, have in recent years become a subject of an extensive scientific research and industrial application. Biodegradability under conditions of industrial composting and possibility to be produced from vegetable (*e.g.* starch obtained from various plants) or animal (*e.g.* whey) resources are basic advantages of these polyesters and nanocomposites, which enable to save fossils, first of all crude oil. Packaging is a prospective application area of these materials, especially of nanocomposite films that can be used for food packaging. The films are being modified by introducing inorganic nanofillers, mostly montmorillonite (MMT), in order to enhance mechanical properties and reduce permeation of water vapor, nitrogen, and carbon dioxide [5—8].

Poly(lactic acid) (PLA), or polylactide, is one of biodegradable aliphatic polyesters with many potential applications. In spite of its advantages, including total biodegradability under conditions of industrial composting, this polymer is rigid and fragile, which is its serious disadvantage, especially when used as a packaging material. To increase impact strength and lower glass transition temperature, PLA is being modified by blending with other polymers or introducing various plasticizers, like poly(ethylene glycol), poly(propylene glycol), poly(propylene oxide), polyoxyethylene, polycaprolactone, oligomers of lactic acid, and citrate esters. By incorporation of small amounts of MMT (up to 5 %), a nanocomposite with enhanced mechanical strength and improved barrier properties can be obtained [9—12].

A possibility to process PLA with the use of machinery commonly applied to the processing of thermoplastics, including manufacture of polylactide films (10—150 μm thick) by the method of extrusion blow molding, is a significant advantage of this material. Because PLA in a plasticized state is of less tensile strength than *e.g.* polyolefins, it is necessary to apply modifiers, like styrene compounds or methyl methacrylate, which increase this property. The technological waste of PLA, occurring during processing of this polymer, can be reused to a great extent, which is an important advantage of polylactide [13, 14].

Most of the publications on investigation of nanocomposite polymeric films deal with the polyolefin films [15—21]. The majority of the studied films have been manufactured from granulated nanocomposites containing various compatibilisers, which had been prepared with the use of twin-screw extruders or special blenders while the blow-up ratio of the films was 2—6. Also the influence of a shape and/or rotational rate of the extruder screws on various film properties was analyzed [18, 19]. From the results of these investigations it can be concluded that the MMT nanofiller and proper film blowing cause:

— enhancement of mechanical properties, mostly a longitudinal modulus of elasticity,

— large improvement in barrier properties (reduction in permeation of water vapor and other gases),

— increase in film crystallinity with respect to that of a relevant granulated material,

— improvement in thermal stability.

The nanocomposite polyolefin films gain a better quality due to the modifications and therefore can be used effectively as a packaging material.

The blowing effects of the PLA films containing MMT are largely similar to the above mentioned ones of the polyolefin films [22, 23]. However, determination of quantitative relations between composition and blow molding conditions of these films requires further investigations.

The aim of this work was to study the influence of the blow-up ratio of the PLA films containing a montmorillonite (MMT) nanofiller, or MMT and poly(methyl methacrylate) (PMMA) as a modifier, or MMT and poly(ethylene glycol) (PEG) as a plasticizer, on the mechanical properties of these films determined under static tension. Evaluation of usefulness of the extrusion blow molding as a technique for manufacturing nanocomposite PLA films was another purpose of this work. These issues are closely related to the development of novel techniques for processing and applying the nanocomposite PLA films as food packaging materials.

EXPERIMENTAL

Materials

The studied nanocomposite films contained the following components:

— poly(lactic acid) (PLA), type 2002D (NatureWorks®, USA) used as a polymer matrix, characterized by the melt flow rate (*MFR*) equal to 5—7 g/10 min (2.16 kg, 210 °C) and density $d = 1.24$ g/cm^3;

— montmorillonite (MMT) nanofiller modified by ion exchange, type Cloisite 30B (Southern Clay Products, USA);

— poly(methyl methacrylate) (PMMA), type PLEXPOL SC (HEKO®, Poland) used as a modifier, characterized by *MFR* = 2.3 g/10 min (3.8 kg, 230 °C) and *d* = 1.19 g/cm^3, intended to improve the film mechanical strength and barrier properties;

— poly(ethylene glycol) (PEG), type PEG 6000 (Sigma-Aldrich GmbH, Germany) used as a plasticizer, with *MFR* = 2.2 g/10 min (2.16 kg, 60 °C) and *d* = 1.05 g/cm^3, intended to enhance the film flexibility.

The above mentioned nanofiller, modifier, and plasticizer are also referred to as additives. The selected additives were mainly supposed to improve barrier properties as well as to enhance impact strength and flexibility of the studied PLA nanocomposite films.

Preparation of granules and blown films of PLA nanocomposite

To prepare blends of PLA and additives in the form of granulated materials the gravimetric dosing system type VIP 6100 (Inno-Plast, Germany) for precise metering of the individual components into the feed hopper of an extruder and co-rotating twin-screw extruder type TSK 20 (Bühler, Germany), equipped with four types of screws 20 mm in diameter and length/diameter ratio equal to 40 were used. PLA and the additives were dried for 12 h at 110 °C before use. The feed rate was controlled by measuring the mass loss of the nanocomposite components placed in individual containers. Possible correction of the feed rate was performed by changing the rotation rates of the dosing screws. The final blending of the components and homogenization of the granulated products were carried out in the extruder barrel. The granulating process was performed at the ambient temperature and the granulated products were cooled in the air at 25 ± 3 °C.

T a b l e 1. Symbols and compositions of the studied films (for details see text)

Sample symbol	Sample composition, wt. %			
	PLA	MMT	PMMA	PEG
L	100	0	0	0
LC	95	5	0	0
LCM	85	5	10	0
LCG	85	5	0	10

To produce flat or extrusion blown nanocomposite films a single-screw extruder, type PlastiCorder PLV 151 (Brabender, Germany), with the screw diameter equal to 19.5 mm and length/diameter ratio equal to 25 were applied. The extruder with a flat head, 170 mm wide and with a controlled gap size as well as a set of planishing and cooling rolls were used to obtain 75 μm thick nanocomposite films. The same extruder, equipped with an angle head with die 13.3 mm in diameter, was applied to form blown films. The blow-up ratio (*R*) was defined as a ratio of the perimeters of the blown film sleeve and angle head die, being equal to the ratio of the diameters of these objects. Both flat and blown films were extruded under the same conditions, *i.e.* at the same temperatures of individual zones of the barrel and head and same rotational rates of the screw and rolls of the extruder. Designations and compositions of the film samples are listed in Table 1.

Methods of testing

X-ray diffractometer, type DRON-2 with high-voltage generator PW 3830 (Philips Analytical X-Ray B.V., Holland) were applied for evaluation of dispersion of the MMT platelets within the PLA matrix. In order to avoid the effect of ordering of the MMT platelets on the XRD results, the granulated LC, LCM, and LCG nanocomposites were ground in a knife mill at the liquid nitrogen temperature. The resulting powder with no distinguished orientation of the MMT platelets was placed in a container in which a 1.5 mm thick powder layer was formed. Dispersion of the MMT platelets within the PLA matrix was estimated from the powder particles by the XRD method over the range of diffraction angles $2\theta = 1—9°$, at the accelerating voltage of 50 kV and anode current of 30 mA.

For determination of the Young's modulus (E), tensile strength (σ_M), tensile stress at break (σ_B), tensile strain at tensile strength (ε_M), and tensile strain at break (ε_B) of the PLA material under static tension, a tensile testing machine type Tiratest 27025 (TIRA Maschinenbau GmbH, Germany) was used. The samples meant for the tensile test were dumbbell-shaped in accordance with an appropriate standard (PN-EN ISO 527-2:1998). The velocity for testing each sample was 50 mm/min (according to PN-EN ISO 527-1:1998). The values of E, σ_M, σ_B, ε_M, and ε_B were determined using 12 individual samples. Then the arithmetic means of 10 results were derived (two extreme ones being discarded).

Dispersion and arrangement of the MMT platelets within the PLA matrix were evaluated using a transmission electron microscope (TEM), type BS 500 (Tesla, Germany). A proper preparation of the samples, which should have constant thicknesses, not larger than 150 nm (this determines the image quality), is the most challenging task in the TEM investigations. Thus, the film pieces of the size 4 × 4 × 10 mm were covered on both sides with epoxy resin. When the resin hardened at the ambient temperature, the samples 60 nm thick were cut out from the prepared film pieces, using an ultramicrotome type PowerTome PC (Boeckeler, USA) equipped with diamond cutters. Then, the samples were placed on standard copper grids of the transmission electron microscope. The accelerating voltage was 90 kV.

RESULTS AND DISCUSSION

Influence of the screw shape of twin-screw extruder on exfoliation of the produced nanocomposite

In order to prepare a granulated exfoliated nanocomposite, an influence of the shape of four screw pairs of a co-rotating twin-screw extruder on the dispersion of the MMT platelets within the PLA matrix was initially examined. The screw pairs used were denoted as S1, S2, S3 and S4. They included various numbers of different segments presented in Fig. 1 and were described in detail in the literature [4, 5]. Compared to S1, the S2 screws exhibited less plastifying and blending ability, S3 — less plastifying ability, and S4 — less blending ability.

The XRD patterns of the LC, LCM, and LCG nanocomposites prepared using the individual screw pairs are shown in Figs. 2, 3, and 4, respectively. As follows clearly from these figures, the dispersion of the MMT platelets depends on both the screw shape and the nanocomposite composition. The nanocomposites formed with the use of the S2, S3, and S4 screw pairs exhibit mostly a mixed nanostructure, *i.e.* intercalated and exfoliated. The XRD patterns of LC show one minor peak with its maximum at $2\theta \approx 2.4°$, whereas those of LCM and LCG, two peaks with

Fig. 1. Exchangeable screw segments: transporting (1), suppressing (2), neutral (3), and kneading (4)

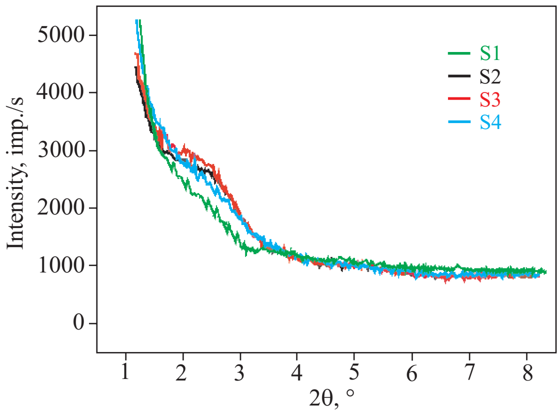

Fig. 2. XRD patterns of the LC nanocomposite prepared using the S1, S2, S3, and S4 screws

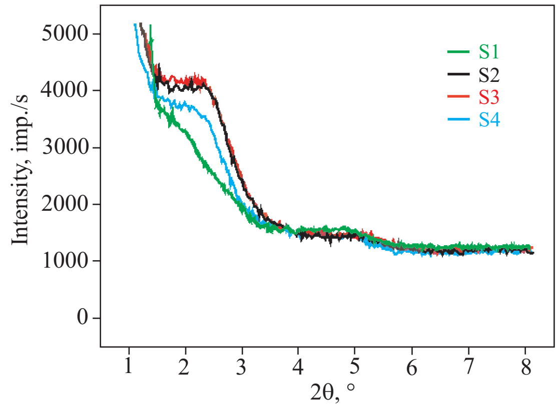

Fig. 3. XRD patterns of the LCM nanocomposite prepared using the S1, S2, S3, and S4 screws

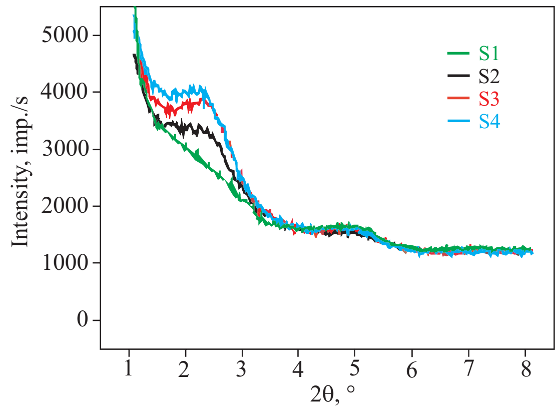

Fig. 4. XRD patterns of the LCG nanocomposite prepared using the S1, S2, S3, and S4 screws

their maxima at $2\theta \approx 2.4°$ (the larger peak) and $2\theta \approx 5°$. The larger peak is associated with the partly exfoliated nanocomposite while the smaller one is attributed to the intercalated fraction of MMT. The XRD patterns of the nanocomposites prepared using the S1 screw pairs show no peak for LC and a minor peak at $2\theta \approx 5°$ for the LCM and LCG samples.

Thus, the XRD results indicate that the PLA/MMT nanocomposite exfoliated to a great extent can be prepared with the use of screws of a proper shape. The PMMA or PEG additives hinder the MMT dispersion within the PLA matrix, when the screws of an improper shape (S2, S3, or S4 — see Figs. 2—4) are used. The greatest exfoliation of the nanocomposites studied was achieved using the S1 screw pair. The latter was then applied to form film samples utilized in the measurements.

Effect of blow-up ratio on mechanical properties determined under static tension

The E, σ_M, and σ_B values for the studied films, measured in the direction parallel to the machine direction (MD), are shown in Figs. 5—7. The bar symbols (2, 3, 4, 5, and 7) stand for value of the blow-up ratio (R) of indivi-

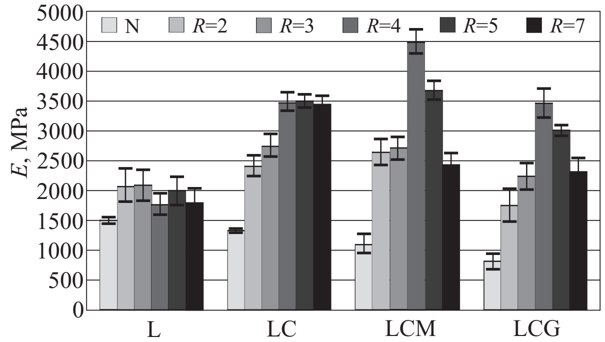

Fig. 5. Effect of the blow-up ratio (R) of the studied films on longitudinal modulus of elasticity (E)

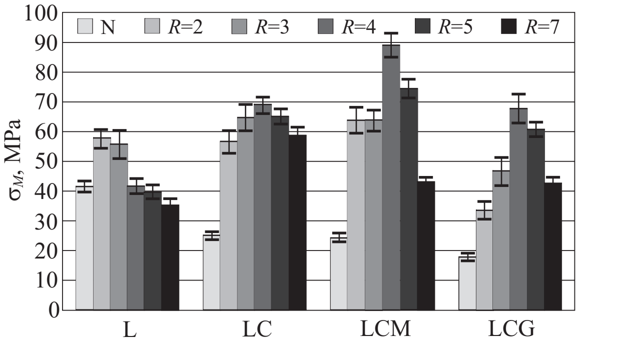

Fig. 6. Effect of the blow-up ratio (R) of the studied films on tensile strength (σ_M)

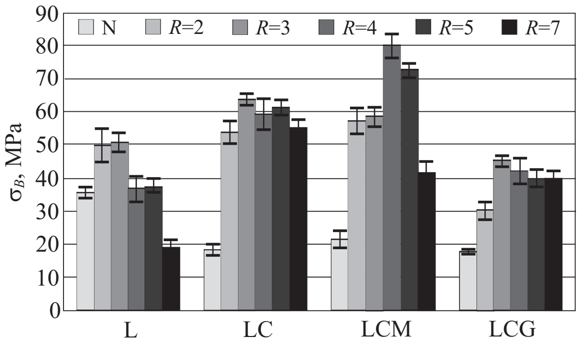

Fig. 7. Effect of the blow-up ratio (R) of the studied films on tensile stress at break (σ_B)

dual film samples, N relating to a non-blown film. As can be seen, the additives (MMT, PMMA, and PEG) cause a decrease in the *E* values for the non-blown LC, LCM, and LCG samples by *ca*. 12, 27 and 45 %, in the σ_M values by 39, 41 and 57 %, and in the σ_B values by 48, 40, and 50 %, respectively, in relation to the relevant values for the neat PLA. These results indicate a non-uniform dispersion of the MMT platelets within the PLA matrix and formation of MMT clusters, which has been confirmed by the TEM results discussed below.

T a b l e 2. Effect of the blow-up ratio (*R*) on mechanical properties of the studied films as related to those of the non-blown films (for details see text)

R	Δ*E*, %			$\Delta\sigma_M$, %			$\Delta\sigma_B$, %		
	LC	LCM	LCG	LC	LCM	LCG	LC	LCM	LCG
2	+81	+99	+112	+126	+154	+91	+183	+96	+69
3	+107	+107	+169	+161	+156	+163	+236	+167	+152
4	+162	+312	+317	+176	+256	+267	+216	+264	+133
5	+163	+236	+263	+160	+200	+239	+226	+232	+122
7	+160	+123	+179	+136	+72	+139	+189	+91	+122

By a proper PLA film blowing (*R* = 2 or 3), the values of *E*, σ_M, and σ_B can be increased by *ca*. 33—40 %, possibly due to enlargement of contribution of the crystalline phase of the polymer. For larger blow-up ratios ($R \geq 3$) these values become smaller, probably because of cracking of PLA macromolecules due to excessive elongation. The effect of the blow-up ratio on the properties of the LC, LCM and LCG nanocomposite films, illustrated in Figs. 5—7, is summarized in Table 2. The percentage increases in individual values (Δ*E*, $\Delta\sigma_M$, and $\Delta\sigma_B$) were calculated in relation to the relevant values for the non-blown films. As follows from the table, the blow-up ratio influences the examined mechanical properties qualitatively in a similar way for all the nanocomposite films, although quantitatively the changes clearly differ. In most cases, the largest changes occur for *R* = 4. Thus, the film blowing should be carried out in the range of $3 \leq R \leq 5$, in order to improve the mechanical properties of the nanocomposite films.

The effects of the additives introduced into the PLA matrix and of the film blowing (*R* = 4) are presented in Table 3. The values of individual quantities, measured for the blown nanocomposite films, are related to the relevant values for the non-blown PLA film. As can be seen, the additives and proper film blowing cause a significant increase (2.3—3.0 times) in the *E* value. Slightly smaller growths, by 62—112 % and 26—77 %, are observed for σ_M and σ_B, respectively.

T a b l e 3. Mechanical properties of the studied films with the blow-up ratio *R* = 4 as compared to those of the non-blown PLA film (for details see text)

Quantity	L	LC	LCM	LCG
E, MPa	1509	3488	4527	3476
Δ*E*, %	–	+131	+200	+130
σ_M, MPa	42	69	89	68
$\Delta\sigma_M$, %	–	+64	+112	+62
σ_B, MPa	36	64	59	42
$\Delta\sigma_B$, %	–	+77	+63	+17

The best mechanical properties of the PLA film were obtained for *R* = 2. In this case, the *E*, σ_M, and σ_B values increased by 38, 38, and 39 %, respectively, with respect to the relevant values for the non-blown PLA film. Thus, it is interesting to compare these values with those for the nanocomposite films blown at R = 4, which is shown in Table 4. As follows from the table, introduction of 5 wt. % of MMT into PLA (LC sample) and blowing at R = 4 the film obtained from the resulting nanocomposite caused growths in the E, σ_M, and σ_B values by 67, 19 and 28 %, respectively. Incorporation of PMMA into the LC nanocomposite (sample LCM) increased the E and σ_M values by 50 and 34 %, correspondingly, and reduced the σ_B value by 10 %. Introduction of PEG into the same nanocomposite did not change the values of E and σ_M but it decreased the σ_B value by 16 %. The PEG plasticizer exerts a positive effect on the material properties, consisting in a significant increase in flexibility of the LCG film in relation to that of the L, LC and LCM films.

T a b l e 4. Mechanical properties of the studied films with the blow-up ratio R = 4 as compared to those of the PLA film with R = 2 (for details see text)

Quantity	R = 2	R = 4		
	L	LC	LCM	LCG
E, MPa	2085	3488	4527	3476
ΔE, %	—	+67	+117	+68
σ_M, MPa	58	69	89	68
$\Delta\sigma_M$, %	—	+19	+53	+17
σ_B, MPa	50	64	59	42
$\Delta\sigma_B$, %	—	+28	+18	-16

The values of ε_M for all the examined films were comprised in the range of 1—4 % and were independent of the blow-up ratio of the films. The ε_B values in turn decreased from 14 to 4 %, from 6 to 3 %, from 8 to 4 %, and from 15 to 8 % for the L, LC, LCM, and LCG samples, respectively, with the rising blow-up ratio. Quality of the nanocomposite films meant as a packaging material is determined mostly by the values of E, σ_M, and σ_B as well as by flexibility. Thus the presented results justify the use of PMMA and PEG as additives to PLA in order to manufacture adequate packaging films.

The E, σ_M, and σ_B values measured in the transverse direction (TD) are affected by the film blowing similarly as those measured in MD. They are however smaller, which is presented in Table 5. The values measured in TD are expressed as percentages of the relevant values measured in MD and denoted as E', σ'_M, and σ'_B. As follows from this table, the reduction in the E value is the smallest: in 15 out of 24 cases, the decrease in E is not greater than 20 % and in 3 cases only greater than 30 %. The values of σ_M and σ_B diminish to a much greater extent: for more than a half of the samples, the decrease in these values is comprised in the range of 30—50 %. The larger film strength measured in MD may be caused by the greater ordering of the PLA macromolecules and the ordering and exfoliation of the MMT platelets. The latter phenomenon could enlarge the surface area of the direct contact between the MMT platelets and PLA macromolecules. Such a fact is commonly known and characteristic of many extruded polymeric objects.

T a b l e 5. Mechanical properties of the studied films with different blow-up ratios, determined in TD expressed as percentages of relevant values measured in MD (for details see text)

Sample	R	E′, %	σ'_M, %	σ'_B, %
L	N	99	96	93
	2	84	60	50
	3	63	59	53
	4	79	66	73
	5	64	64	66
	7	85	77	82
LC	N	85	90	86
	2	74	51	52
	3	80	53	54
	4	86	63	64
	5	87	87	82
	7	79	67	64
LCM	N	99	97	71
	2	54	73	66
	3	71	51	69
	4	70	56	59
	5	95	65	59
	7	97	79	67
LCG	N	95	93	76
	2	80	87	80
	3	95	75	73
	4	87	66	98
	5	79	52	67
	7	93	70	57

The values of ε_M for all the films stretched in TD are comprised in the range of 1—3 % and are essentially independent of the blow-up ratio. The σ_B values, in turn, vary from 3 to 12 %, but no clear relation between the film elongation and the blow-up ratio was observed. The only regularity found is that the LCG films exhibit larger tensile strain at break compared to that for the remaining films.

Arrangement of nanofiller platelets within the polylactide matrix

During blowing of the film containing MMT, ordering of the nanofiller platelets within the polymeric matrix occurs, which mostly induces changes in mechanical properties and improvement in barrier properties of the film. To evaluate the variation in the arrangement of the platelets, the TEM method was applied. While analyzing the TEM images, a three-step color scale (dark, grey, and light) is generally being adopted for evaluation of the ordering. The dark color corresponds to the areas in which clusters of non-oriented MMT platelets or single MMT platelets ordered perpendicularly to the incident electron beam are present. The grey color relates to the domains in which MMT platelets are non-ordered, *i.e.* arranged at various angles with respect to the direction of the incident electron beam. The light color corresponds to the areas in which traces or no MMT platelets are present. In addition to the TEM method, assessment of the dispersion and ordering of the MMT platelets in the polymeric matrix and of the conditions for separation of single MMT platelets from their clusters may be performed with other techniques [21, 26, 27].

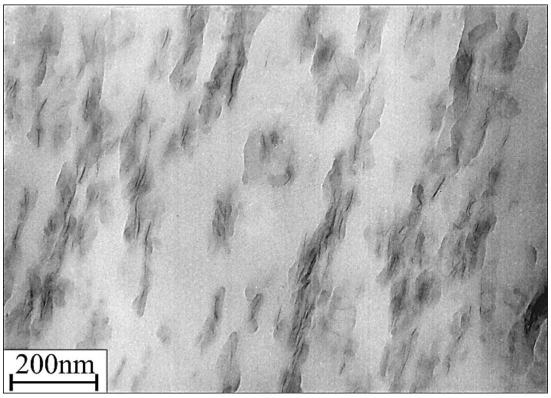

Fig. 8. TEM image of non-blown LC film

Since the most beneficial mechanical properties of the studied films were achieved at the blow-up ratio $R = 4$, the TEM images of the samples of the non-blown (N) and blown at $R = 4$ LC films were analyzed. The image of the non-blown film (Fig. 8) is dominated by light domains, containing traces or no MMT platelets. Grey areas, attributed to the MMT platelets that are dispersed and oriented in various directions, constitute a slightly smaller contribution. Dark longitudinal domains, clearly oriented in MD, contribute the least. They correspond to the MMT clusters formed during the flow of the nanocomposite through the extruder head. What is characteristic of this image, there is almost total lack of single MMT platelets. One can assume that the arrangement of the MMT platelets within the PLA matrix is not uniform on the molecular level, which confirms the hypothesis that blending of MMT and PLA is not complete. This is the reason for worsening of the mechanical properties of the nanocomposite film compared to those of the neat PLA film. In order to increase miscibility of these components, a proper compatibiliser should be used, which will be a subject of our further research.

An image of the film cross-section parallel to MD is shown in Fig. 9. There are clearly visible the MMT platelets that are straightened, rather uniformly arranged, and oriented in MD. When comparing Figs. 8 and 9 with each other, one can state that blowing of the PLA film containing MMT significantly changes the film inner structure: the MMT platelets become more oriented and uniformly arranged within the PLA matrix while most of them straighten out to a great extent. The MMT clusters, seen in Fig. 8, vanish whereas single MMT platelets appear in a great number. One can conclude that, during the LC film blowing, individual MMT platelets separate from the clusters as well, which has already been noticed by other authors [26, 28, 29].

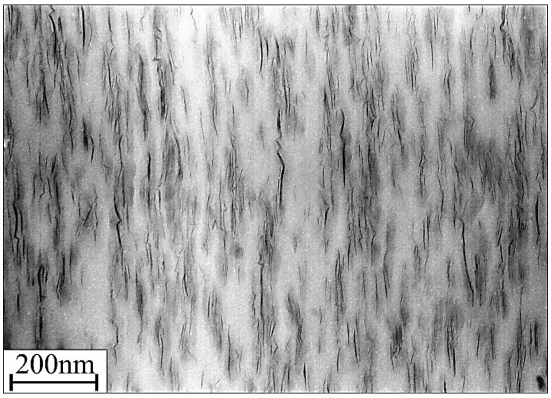

Fig. 9. TEM image of LC film with the blow-up ratio R = 4

The presented TEM images suggest that blending MMT with the plasticized PLA using a co-rotating twin-screw extruder with properly designed screws, producing this way a granulated nanocomposite, and then manufacturing and blowing the film formed from that nanocomposite is a good method to achieve a uniform arrangement of the MMT platelets within the PLA matrix. The nanocomposite film prepared in this manner exhibits generally an exfoliated ordered structure with uniformly arranged and oriented MMT platelets.

CONCLUSIONS

It is possible to prepare a nanocomposite film exhibiting mechanical properties much improved in relation to those of a neat PLA film. This can be achieved by selecting a proper shape of a screw pair of a co-rotating twin-screw extruder used to form the granulated nanocomposite containing 5 wt. % of MMT (LC sample) and by applying an adequate blow-up ratio of the film. A further improvement of these properties can be obtained by adding 10 wt. % of PMMA (LCM sample), which increases mainly the longitudinal modulus of elasticity and tensile strength. On the other hand, addition of 10 wt. % of PEG (LCG sample) does not worsen the film mechanical properties, except for a slight reduction in tensile stress at break, but it significantly improves flexibility of the film containing this component.

Under the applied investigation conditions, the best results were obtained when the blow-up ratio $R = 4$, and slightly worse results, when $R = 3$ or 5. In relation to the non-blown PLA film, the nanocomposite films with $R = 4$ exhibited the longitudinal modulus of elasticity increased *ca*. 2.3—3.0 times, mechanical strength 1.6—2.1 times, and tensile stress at break 1.3—1.8 times.

The observed improvement of the film mechanical properties is caused by a more uniform and parallel arrangement of the MMT platelets within the PLA matrix and partial straightening of macromolecules of this polymer, induced by the film blowing. The ordered and uniformly arranged MMT platelets constitute a phase that strengthens the film and transfers a significant part of mechanical stresses while the straightened PLA macromolecules form a quasi-crystalline phase that also increases the film mechanical strength.

The presented results of experimental investigations confirm effectiveness of the blow molding extrusion as a method to form the PLA matrix-based nanocomposite films, whose mechanical properties can be favorably modified. The obtained materials offer many potential applications.

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