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Thermoforming of polylactide nanocomposite films for packaging containers

RAPID COMMUNICATION

Summary — Experimental results of thermoforming of two kinds of polylactide containers of similar capacity but differing in shape were used to determine the basic parameters of this process. The films made of both pure polylactide or polylactide nanocomposites, the latter including a montmorillonite nanofiller (5 wt. %) and poly(ethylene glycol) (10 wt. %) or poly(methyl methacrylate) (10 wt. %), were applied to forming these containers. These three kinds of films were 250 or 400 μm thick. It was found that the containers could be thermoformed in the temperature range of 75–90 $^{\circ}\text{C}$ and that the film thickness affected the dispersion of the container wall thicknesses. Thus, it has been confirmed that a thorough experimental study is necessary before the manufacturing of a specific type of container thermoformed from pure polylactide or its nanocomposites could be implemented. The study should be aimed mainly at a reduction in the dispersion of the container wall thickness.

Key words: polylactide, nanocomposites, thermoforming, packaging.

TERMOFORMOWANIE POJEMNIKÓW OPAKOWANIOWYCH Z NANOKOMPOZYTOWYCH FOLII POLILAKTYDOWYCH

Streszczenie — Na podstawie wyników badań określono główne parametry procesu termoformowania dwóch typów pojemników polilaktydowych o różnych kształtach i zbliżonej objętości. Do wytwarzania tych pojemników zastosowano folię polilaktydową oraz folie z nanokompozytu polilaktydowego zawierającego 5 % mas. nanonapełniacza montmorillonitowego i 10 % mas. glikolu poli(oksy)etylenowego lub 10 % mas. poli(metakrylanu metylu). Badane pojemniki wytwarzano z tych trzech rodzajów folii o dwóch różnych grubościach wynoszących 250 lub 400 μm . Stwierdzono, że te pojemniki można termoformować w temperaturach od 75 do 90 $^{\circ}\text{C}$. Zauważono wpływ grubości zastosowanych folii na rozrzut grubości ścianek pojemników. Tym samym potwierdzono konieczność przeprowadzania, przed wdrożeniem do produkcji konkretnego typu pojemnika termoformowanego z polilaktydu lub z jego nanokompozytów, szczegółowych badań eksperymentalnych, których głównym celem byłoby dobranie warunków procesu dających zmniejszenie rozrzutu grubości ścianek pojemnika.

Słowa kluczowe: polilaktyd, nanokompozyty, termoformowanie, opakowania.

Application of polylactic acid (PLA), also known as polylactide, and its nanocomposites as packaging materials implies a necessity to adapt the techniques commonly used for manufacturing of plastic packaging to processing conditions relating to an applied polymer [1, 2]. Vacuum thermoforming, called further simply thermoforming, is one of important methods of manufacturing of plastic containers designed for packing of food, medicines, some cosmetics as well as paints, glues and pastes. Implementation of this technique goes back to the fifties of the 20th century; therefore, it is well recog-

nized from both scientific and practical points of view. However, the number of scientific and scientific-technical publications devoted to this method is much lower than that of the papers on technology of *e.g.* extrusion or injection molding [3, 4, 5, 6].

The process of thermoforming of polylactide and its composites depends largely on a proper selection of temperature to which these materials should be heated. The value of this temperature influences quality as well as manufacturing costs of the products. If the temperature is too low, then the mold cannot be adequately filled and the achievement of an appropriate distribution of the container wall thickness is significantly hindered. On the other hand, if the temperature is too high, the energy consumption is excessive, deformation of the container shape occurs, and the optical properties of the container material change due to *e.g.* polylactide crystallization.

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Generally, it is assumed that, prior to the thermoforming the polylactide film should be heated to temperature in the range 80–110 °C, what is much lower than that for common-use polymer films [1, 6, 7].

Proper wall thickness is one of the most important qualitative criteria of thermoformed containers. An appropriate distribution of these thicknesses in specific sites of the container walls depends not only on the correct mold design and thermoforming technology but also on the kind of a material used for that purpose. The sites in which walls change their shape *e.g.* an area where a side wall transforms into a bottom, are critical points to obtain the containers of good quality. In general, one can assume that the molds used in the thermoforming of poly(ethylene terephthalate) or polystyrene can be applied also to the thermoforming of polylactide. However, the time necessary for cooling the PLA containers is longer due to a lower heat conductivity of this polymer. On the other hand, the molds used in the thermoforming of polypropylene cannot be applied to thermoforming of polylactide because of a significant difference in the coefficients of thermal expansion of these polymers [1].

The aim of this work was to recognize in more detail the conditions and effects of thermoforming of polylactide films for making packaging containers of two typical kinds and to determine experimentally the temperature to which these films should be heated prior to the thermoforming. The films were selected taking into account the results of our previous investigations [8–10]. There were studied the films of pure polylactide and polylactide nanocomposites including a modifier — poly(ethylene glycol) or poly(methyl methacrylate) in addition to a montmorillonite nanofiller. The films samples were of two different thicknesses.

EXPERIMENTAL

Materials

The studied materials contained the following components:

— polymer matrix *i.e.* polylactide (denoted by L), type 2002D (NatureWorks®, USA), of the melt flow rate $MFR = 5\text{--}7$ g/10 min (2.16 kg, 210 °C) and density $d = 1.24$ g/cm³;

— montmorillonite nanofiller *i.e.* Cloisite 30B (denoted by C) modified by ion exchange (Southern Clay Products, USA);

— modifiers — poly(ethylene glycol) (denoted by G), type PEG 6000 (Sigma-Aldrich GmbH, Germany), with $MFR = 2.2$ g/10 min (2.16 kg, 60 °C) and $d = 1.05$ g/cm³; poly(methyl methacrylate) (denoted by M), type PLEXPOL SC (HEKO®, Poland), with $MFR = 2.3$ g/10 min (3.8 kg, 230 °C) and $d = 1.19$ g/cm³.

The above additives (the nanofiller and modifiers) were mainly supposed to improve barrier properties

(C and M) and to enhance impact strength (G) of the materials studied [8–10].

Instruments

The following instruments were used:

— gravimetric dosing system type VIP 6100 (Inno-Plast, Germany), intended for a precise metering of the individual components of the material studied into the feed hopper of an extruder;

— concurrent double-screw extruder, type TSK 20 (Bühler, Germany), of the screw diameter equal 20 mm and length/diameter ratio equal 40, equipped with a segmented plastifying system, designed to obtain the granulated material;

— single-screw extruder, type PlastiCorder PLV 151 (Brabender, Germany), of the screw diameter equal 19.5 mm and length/diameter ratio equal 25, intended for producing the films of the material to be thermoformed;

— stand for investigation of thermoforming of polymer films, equipped with two molds: one (I) with a cavity of 120 mm diameter, 30 mm depth, circular cross-section, and rounded edges between the bottom and side walls, and the other (II) with a cavity of the dimensions 120×100×30 mm, rectangular cross-section, and rounded edges;

— digital thermometer type Testo 925 (Testo GmbH & Co, Germany);

— digital thickness gauge type 547-401 (Mitutoyo, Japan).

Methods

The gravimetric dosing system and double-screw extruder were used to prepare the blends of PLA and additives in the form of granulated materials. The feed rate was controlled by measuring of the mass loss of the nanocomposite components placed in individual containers. The final blending of the components and homogenization of the granulated products carried out in the extruder cylinder. The granulating process was performed at the ambient temperature and the granulated products were cooled in an air at 25 ± 3 °C. Two kinds of the granulated materials were prepared:

— LCG, including 85 wt. % of L, 5 wt. % of C, and 10 wt. % of G;

— LCM, containing 85 wt. % of L, 5 wt. % of C, and 10 wt. % of M.

The single-screw extruder with a flat head, 170 mm width, controlled gap size, and set of planishing and chill rolls was used to obtain 250 and 400 μm thick nanocomposite films. The film samples to be thermoformed were denoted similarly as the parent granulated materials, with the addition of a digit "1" or "2" in case of the sample thickness of 250 or 400 μm, respectively.

The results of preliminary investigation indicated that the studied films should be heated up to temperature in the range 70–95 °C prior to the thermoforming. During the present investigations, the samples were heated by infrared radiators up to 70, 75, 80, 85, 90 or 95 °C, while the temperature of a sample surface was constantly measured by direct contact method. The samples were placed on the mold outer surface (directly above the cavity) and the heating time was 5–15 s, depending on the final temperature and film thickness. Once the assumed temperature of the film was attained, the thermoforming process was initiated by activating a vacuum pump to remove an air from the mold cavity covered with the heated film. The pressure inside the cavity was reduced down to 0.06 MPa, which induced formation of a container. Thermoforming time was assumed as the time of the duration of reduced pressure inside the mold cavity. The containers formed in the air-cooled molds I and II were denoted with the symbols A and B, respectively.

Quality of the containers obtained (presented in Figure 1) was assessed by measuring of the wall thickness in various sites of the products (indicated in Figure 2) and by visual examination while taking into account mainly the shape, smoothness, and color of the container walls. The wall thickness in a specific container site was assumed as an arithmetic mean of the results of five measurements performed for different points of this site.



Fig. 1. General view of the thermoformed container with circular cross-section

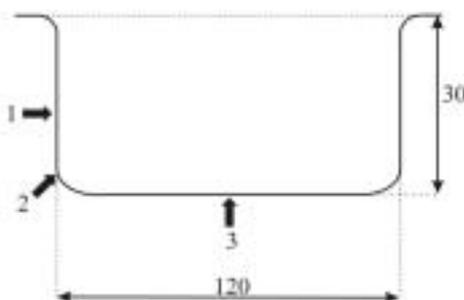


Fig. 2. Approximate sites of the measurements of the wall thickness of the containers studied: 1 — side wall, 2 — area of transition between the side wall and the bottom, 3 — bottom

RESULTS AND DISCUSSION

The results of selection of basic parameters of the thermoforming process, for which the best quality containers were obtained, are summarized in Table 1. These values were mainly determined upon the visual examination of the containers thermoformed at various temperatures (70–95 °C). During this examination, surface smoothness, wall transparency and stability of the containers were analyzed. According to these criteria, the containers produced under the conditions specified in Table 1 fulfil the standards provided for products designed for food storage.

As follows from Table 1, a contribution of poly(ethylene glycol) (10 wt. %) in the polylactide nanocomposite enables to reduce the heating temperature *i.e.* to decrease the heating time of the film being subjected to the thermoforming. On the other hand, the thicker the thermoformed film, the longer the time of heating and processing of the film.

Table 1. Basic parameters of thermoforming of the containers studied

Symbol of sample	Heating temperature, °C	Heating time, s	Thermoforming time, s
L1	80	10	2
LCG1	75	5	2
LCM1	85	10	3
L2	85	15	3
LC5G2	80	10	3
LCM2	90	15	4

Table 2. Wall thicknesses (in μm) of the containers studied; numbers of the measurement sites as in Fig. 2

Symbol of sample	Container A			Container B		
	1	2	3	1	2	3
L1	127	90	96	113	81	93
LCG1	135	93	102	105	88	98
LCM1	130	87	95	103	83	93
L2	193	177	183	165	142	160
LCG2	207	187	203	175	145	170
LCM2	190	170	185	190	159	175

The results of measurements of the wall thicknesses of the containers A and B are presented in Table 2. Independently on the film kind and container shape, a side wall (Fig. 2, site 1) is of the largest thickness, a bottom (Fig. 2, site 3) is of the medium, and area of the transition between the side wall and the bottom (Fig. 2, site 2) of the smallest thickness. The side wall thickness of each container is approximately identical. The walls of the container A are thicker than those of the container B in analogous sites, which results from different film stretch occurring during the thermoforming. The values of the extent of the film stretch, defined as the ratio of the total

surface area of the container walls and the surface area of the film fragment used to form this container, are equal to 2.0 and 2.1 for the containers A and B, respectively.

Table 3. Relative wall thicknesses of the containers studied; numbers of the measurement site as in Fig. 2

Symbol of sample	Container A			Container B		
	1	2	3	1	2	3
L1	1.00	0.71	0.76	1.00	0.72	0.82
LCG1	1.00	0.69	0.76	1.00	0.84	0.93
LCM1	1.00	0.67	0.73	1.00	0.81	0.90
L2	1.00	0.92	0.95	1.00	0.86	0.97
LCG2	1.00	0.90	0.98	1.00	0.83	0.97
LCM2	1.00	0.89	0.97	1.00	0.84	0.92

Considering the thickness of the side walls of the studied containers as a reference (Fig. 2, site 1), the values of relative wall thicknesses in the remaining sites of the containers (Fig. 2, sites 2 and 3) were calculated (Table 3). From the presented data, it results that:

— The greatest differences in the wall thickness occur for the container A thermoformed using the 250 μm thick film. In relation to site 1 (being the thickest), the walls are thinner by 28—33 % in site 2 and by 24—27 % in site 3 (Fig. 1). Analogous differences for the container B are much smaller: 19—28 % (site 2) and 10—18 % (site 3).

— The containers thermoformed from the 400 μm thick film differ relatively less in the wall thickness. The differences in the wall thicknesses in site 1 and site 3 do not exceed 8 % and those for the relevant values in site 1 and site 2 do not exceed 17 %.

— The kind of a film does not distinctly influence the differences in the thicknesses of the container individual walls; the obtained results are not conclusive.

In general, one can assume that the process of thermoforming of A and B containers runs stably and similarly for each film kind.

CONCLUSIONS

The presented results of the investigations confirm that the thermoforming of containers from polylactide and its nanocomposites can be performed at temperatures much lower than those characteristic for the thermoforming of containers from common-use polymers.

Designing both a specific container and relevant mold should be preceded by experimental studies aimed at a reduction in dispersion of wall thicknesses of this container. Also, the effect of the thickness of the film used in the thermoforming process on that dispersion should be taken into account.

ACKNOWLEDGMENT

The work has been supported by the Polish Ministry of Science and Higher Education with the funds of 2006—2009 as a research project No. DWM/9/EUREKA/2006.

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Received 22 XII 2008.