Assessing the thermoformability of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) / poly(acid lactic) blends compatibilized with diisocyanates

Jennifer González-Ausejo[1], Estefania Sanchez-Safont[1], Jose Maria Lagaron[2], Richard T. Olssson[3], Jose Gamez-Perez[1], Luis Cabedo [1*]

[1] Polymers and Advanced Materials Group (PIMA), Universitat Jaume I, 12071, Castelló, Spain.

[2] Novel Materials and Nanotechnology Group, IATA-CSIC, Paterna (Valencia), 46980, Spain

[3] Department of Fibre and Polymer Technology, KTH-Royal Institute of Technology, Stockholm, Sweden

* Correspondence to: Luis Cabedo Mas (E-mail: lcabedo@uji.es)

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[2] Novel Materials and Nanotechnology Group, IATA-CSIC, Paterna (Valencia), 46980, Spain

[3] Department of Fibre and Polymer Technology, KTH-Royal Institute of Technology, Stockholm, Sweden

* Correspondence to: Luis Cabedo Mas (E-mail: lcabedo@uji.es)

Abstract

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a renewable alternative to conventional barrier packaging polymers due to its thermoplastic properties, biodegradability and gas barrier performance but its potential industrial applications are limited by its high price and difficult processability. A thorough study concerning the thermoforming ability of PHBV, and blends with poly(lactic acid) (PLA) incorporating three different diisocyanates as compatibilizers (hexamethylene diisocyanate, poly(hexamethylene) diisocyanate and 1,4-phenylene diisocyanate) is herein presented after component melt blending. A straightforward universal qualitative method is proposed to assess the thermoformability, based on a visual inspection of a thermoformed specimen and the ability to reproduce the mold shape, and the thermoforming window of the material. The results reveal a significant improvement in the thermoforming capacity and a widening of the thermoforming windows as the correct amounts of diisocyanates are incorporated. The barrier properties and the biodisintegrability of the blends was also studied, confirming a predictable slight decrease of the barrier performance when PLA is added, but without negatively affecting the disintegrability under composting conditions with respect to pristine PHBV.

1. INTRODUCTION

Many of the most widely used rigid packaging products (such as trays, containers, cases or blister packages) are obtained by thermoforming thin thermoplastic sheets. The process is also widely used for preparation of multilayer polymer materials, which are commonly used as high barrier materials in the food packaging industry. Polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) are the most widely used polymers for such applications. However, these materials are derived from non-biodegradable fossil fuel resources, which entails environmental problems derived from the large amounts of discarded plastic and their waste management. Biopolymers here arise as a good alternative to replace those commodities, with a special interest in those that come from renewable resources. Poly(lactic acid) (PLA) and some polyhydroxyalkanotates (PHAs), specifically poly(hydroxybutirate-co-valerate) (PHBV), provide a good alternative to PVC, PP or PET, with the advantage of being 100% biodegradable, and compostable [1–3]. These biopolymers are already being commercialized for packaging applications, such as cosmetic containers, shampoo bottles, covers, milk cartons, among others (reviewed by Keshavarz et al. [4] and Aditi et al. [5]). Nevertheless, these biopolymers still present a number of drawbacks that limit their use in the packaging sector.

PHBV has interesting properties compared to other biopolymers, such as being thermoplastic, presenting high tensile strength, high service temperature (similar to that of PP) [6] and barrier properties to oxygen (close to those of PET and much higher than PLA) [7] [8]. However, its high crystallinity, which is responsible of the excellent barrier performance, restricts its processability by thermoforming. In fact, PHBV can be thermoformed only within a very narrow range of temperatures close to the melting point of the polymer, which leads to sagging phenomenon of the sheet prior to the drawing process, which stems from the sudden loss of mechanical stability. This characteristic limits the geometries and its suitability for thermoformed products in comparison with other conventional polymers, and despite of the importance of the thermoforming process in the packaging sector, few works address this issue in the scientific literature. Among them, Gimenez et al. [9,10] improved the thermoformability of ethylene-vinyl alcohol copolymer (EVOH) by means of blending it with an amorphous polyamide and a compatibilized-ionomer. The ternary

blend resulted in an improved forming capacity with a much wider forming window than neat EVOH due to a blend composition showing improved dimensional stability during the thermoforming and reduced sensitivity towards sagging.

In the same vein of that reported by Gimenez et al., in the present work, blending PHBV with an amorphous biopolymer (PLA) is presented as an approach for fostering the thermoformability of PHBV. PLA shows an excellent thermoformability because of its amorphous state at normal processing conditions [11]. However, the PHBV/PLA blends have some disadvantages: the two biopolyesters exhibit an immiscible behavior when melt blended [12–14] thus yielding to a drop-in-matrix morphology with a poor interface adhesion, and the gas barrier properties decrease by incorporating PLA into PHBV, especially when the PLA content exceeds 25% [13]. These detrimental drawbacks limit the PLA blends for application in high barrier thermoformed packages, which currently are manufactured from PET [15].

In a previous work [16], blends of PHBV with PLA were compatibilized by reactive extrusion blending using three diisocyanates as compatibilizer agents (hexamethylene diisocyanate (HMDI), poly(hexamethylene) diisocyanate (PolyHMDI) and 1,4-phenylene diisocyanate (PDI)). PolyHMDI and PDI resulted in a higher compatibilizing effect, when compared with HMDI. Besides, the rheological behavior of the compatibilized blends suggested that the thermoformability of such systems could improve that of PHBV. In light of those results, the aim of this work is to assess the effect of blending PHBV with 25 wt.% PLA while using the different diisocyanates as compatibilizers, on the thermoforming processability, service properties (barrier to oxygen and water vapor) and biodisintegrability, as compared to neat PHBV.

2. EXPERIMENTAL

2.1. Materials

PHBV with 3 mol.% hydroxyvalerate content was purchased from the Tianan Biologic Material Co. (Ningbo, P.R. China) in pellet form (ENMAT Y1000P). PLA IngeoTM Biopolymer commercial grade 2003D was supplied by the NatureWorks® Co. LLC, USA. The three compatibilizers used, hexamethylene diisocyanate

(HMDI), poly(hexamethylene) diisocyanate (PolyHMDI) and 1,4-phenylene diisocyanate(DPI) were supplied by Sigma Aldrich.

2.2. Blend preparation

The PHBV and PLA used in this study were dried at 80 ºC for 2 h before using by a Piovan DPA 10 (Santa Maria di Sala VE, Italy), while the compatibilizers were used as received. Considering the limited gas barrier properties of PLA with respect to PHBV and in agreement with our previous works [10,11], a fixed PHBV/PLA ratio of 75/25 in weight was kept in all the samples. The PHBV blends were obtained by mixing different amounts of pellets of both polymers and the compatibilizer in an internal mixer (Rheomix 3000P ThermoHaake, Karlsruhe, Germany). To avoid thermal degradation of the biopolyesters during blending, the mixing time was done in less than 4 min, the temperature was set at 180 ºC and the rotor speed at 100 rpm. According to the melt temperature sensor during mixing, the polymers were always at temperatures below 195 ºC.

The batches were subsequently processed into thin sheets (thickness of 200 and 300 µm) by compression molding, using a hot-plate hydraulic press (Carver 4122, USA) at 180ºC, 3 MPa and 4 min. The 300 µm sheets were prepared the same day as they were used in the thermoforming study. In contrast, the 200 µm films were stored in a vacuum desiccator at ambient temperature for 2 weeks to allow full crystallization to take place [17] and subsequently used for full characterization.

Samples of both neat PHBV and PLA were processed under identical conditions as the blends, for the sake of comparison. The nomenclature used for the blends is as follows: PHBV/PLA for the blend system without compatibilizer, and HMDI, polyHMDI and PDI for the compatibilized blends. The compatibilizer content was adjusted to 1:20 molar ratio between the functional polymer reactive sites (end groups) and the compatibilizer ones (isocyanates) [18], according to the available Mn and molecular weight data of polymers and isocyanates. Table I summarizes the nomenclature and compositions of all the samples studied.

2.3. Characterization

Scanning Electron Microscopy (SEM) of all the samples was conducted using a high-resolution field-emission JEOL 7001F microscope. The samples were fractured in liquid nitrogen and then were coated by

sputtering with a thin layer of Pt prior to SEM observation. The size of the dispersed phase (i.e. diameter of the spheres) was measured in the SEM microphotographs by using Fiji® software (the number of spheres measured for each sample was never below 400).

The oxygen permeability (OP) of the films was measured in duplicate by using Oxtran 100 equipment (Modern Control, Minneapolis, MN) at 80% relative humidity (RH) and 24 °C. RH was generated by a built-in gas bubbler and was checked with a hygrometer placed at the exit of the detector. Prior to the measurements, the samples were purged with nitrogen for a minimum 20h in the previously relative humidity equilibrated samples. The oxygen flow during the experiments was fixed at 10 ml/min. the measurements were performed through a 5cm2 samples area by using an in-house development mask. To obtain the oxygen permeability, film thickness was considered in each case.

The water vapor permeability (WVP) of the PHBV/PLA blends was measured according to the ASTM E96 (2011) gravimetric method, using Payne permeability cups (Elcometer SPRI, Hermelle/s Argenteau, Belgium). Measurements were taken in duplicates. The samples were placed between the aluminium top (open O-ring) and bottom part (deposit for the permeant) with a Viton rubber ring between the film and the top part of the cups to ensure their complete sealing. The cups were placed inside a desiccator at 0% RH and the water weight loss through a film area of 0,001 m^2 was monitored and plotted as a function of time. Water vapor permeability rate was estimated from the slope of the linear part of this plot, thus ensuring the steady-state conditions. Cups with aluminum films were used as control samples to estimate water vapor losses thought the sealing. Water weight loss was calculated as the total cell loss minus the loss through the sealing. Water vapor permeability was obtained multiplying the water vapor permeability by the average film thickness.

Disintegrability of films of neat PHBV, neat PLA and PHBV/PLA compatibilized blends and non-compatibilized blend was assessed by means of a disintegration test under lab scale composting conditions according to the ISO 20200 standard, “Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test” [19]. For the preparation of solid synthetic waste, 10% of activated mature compost (VIGORHUMUS H-00, purchased from Buras Professional, S.A., Girona, Spain) was mixed with 30% rabbit food, 10% starch, 5% sugar, 1% urea, 4% corn oil and 40% sawdust.

The water content of the substrate was around 55 wt% and the aerobic conditions were guaranteed by gently mixing the compost and periodically adding water according to the standard. The samples were cut from hot pressed plates (10x10x0.2 mm^3) and buried inside plastic mesh bags to simplify their extraction and allow the contact of the compost with the specimens, and were incubated at 58 °C for 31 days. At different composting times samples were recovered for analysis, washed with distilled water, dried at 40 °C under vacuum for 24 h, and weighed. The degree of disintegration was calculated by normalizing the sample weight, at different days of incubation, to the initial weight with Equation (1), where m_i is the initial dry mass of the test material and m_f is the dry mass of the test material recovered at different incubation stages.

$$D = \frac{m_i - m_f}{m_i} \times 100 \quad (1)$$

The disintegration study was completed by photographs for visual evaluation of the samples and their morphologies were further inspected by SEM analysis.

2.4. Thermoforming setup

The thermoforming pilot plant facility (SB 53c, Illig, Helmut Roegele, Germany) presented in Figure 1 was used for the vacuum assisted thermoformability study. The heating device is a platform equipped with 15 long waves infrared emitters which slides forward upon the thermoforming chamber during the heating step prior to the forming (see Figure 1b). For all the experiments the emitters were set to 600°C, while the heating time was changed in order to control the temperature of the polymer sheet. The sheet surface temperature was measured at different locations (both in the upper and the lower surface) as function of heating time, thus obtaining relation between the heating time and the sheet temperature (Figure 1d). As shown in Figure 1d, the temperature of the sheet follows a logarithmic trend with respect to the heating time, therefore the dependence of the sheet temperature with the heating time is much higher for lower times, being almost constant for times beyond 50 min, reaching a maximum temperature of ca. 130°C with the current setup.

Sheets having 300 μm thickness were used for the thermoforming study. Before the thermoforming of the sample specimen, a square grid pattern (1x1 cm) was stamped on each sheet in order to track the deformation of the sheet occurring during its mold conformation. The mold used was a female rectangular tray having 40 x 60 x 20 mm (width x length x depth) (see Figure 1c). Thus the maximum draw ratio of the

mold was determined by the ratio between the final and the initial area of the stamped squares, resulting in a maximum value of 5.2. A minimum of three trays were obtained for every heating time in order to obtain representative information from their thermoforming ability.

3. RESULTS AND DISCUSSION

3.1. Morphology

Figure 2 presents SEM micrographs of all the PHBV/PLA blends studied as a function of the diisocyanate type. The micrographs reveal that the blends present a two-phase morphology microstructure can be described as PLA homogeneously dispersed within a PHBV continuous matrix, thus revealing a characteristic discrete-phase structure (DPS, or drop-in matrix). This microstructure proves that the PHBV/PLA blends prepared with high molecular weight commercial polymer grades are immiscible and not fully compatible. The addition of isocyanates to the PHBV/PLA blend was previously studied by our group and we showed that their addition to the blend leads to a decrease in the droplet size of the dispersed phase, as well as decrease on the amount of detached particles.[18] The high compatibilization effect by adding small amounts of diisocyanates, with an improvement in the interfacial adhesion between the two biopolyesters, was herein confirmed.

Image analysis of cryo-fractured specimens was performed to reveal the average droplet size of the PLA droplets in the blends. These results summarized in the histogram plots of Figure 2.e. The average droplet diameter for the uncompatibilized PHBV/PLA blend is 1.15 μm with a clear detachment phenomenon between both phases, as can be seen in Figure 2.a. However, the incorporation of diisocyanates to the blend (in a 1:20 molar ratio of isocyanates with respect to polymer end-groups) led to a reduction in the PLA domains, with most pronounced results for polyHMDI and PDI. Hence, an average PLA domain size of 0.84, 0.45 and 0.57 μm was determined for the HMDI, polyHMDI and PDI blends, respectively. A similar trend was also found considering the amount of completely detached PLA particles from the matrix, which is in agreement with an increase in the interfacial adhesion and compatibility between PLA and PHBV in the samples containing HMDI, polyHMDI and PDI.

3.2. Barrier performance

The assessment of the barrier performance of the polymers and their blends in this work is of utmost interest, since one of the main advantages of the PHBV copolymer is its higher barrier performance, particularly to oxygen, when compared to other biopolyesters such as PLA. The gas barrier properties to water and oxygen of neat PHBV, neat PLA and the PHBV/PLA blends are summarized in Figure 3. The best barrier performance corresponds to PHBV, whereas the incorporation of 25 wt.% PLA results in a drop in oxygen and water vapor barrier performance by more than 85 % (86 and 89 % for water and oxygen, respectively). This can be attributed to the lower barrier properties of the PLA, derived from its amorphous state, in agreement with previous studies performed by Zembouai et al. [13], and to some extent the formation of phase interfaces in the two-phase morphology microstructure. The incorporation of the different isocyanates only altered the barrier properties to a small extent in relation to the uncompatibilized blend of PHBV/PLA (see Fig. 3). However, the values of the obtained blends, compatibilized and non-compatibilized, were still in the same order of magnitude than those of the neat PHBV.

3.3. Thermoforming study

The present work is framed in a project that aims improving the thermoformability of the PHBV while keeping both the gas barrier performance and the biodisintegrability. For doing so, blends of PHBV with PLA and compatibilization agents were obtained and their barrier performance, thermoformability and disintegrability assessed and compared to that of the pristine PHBV.

To evaluate the thermoforming ability of the compositions prepared, the setup and mold shown in Figure 1 was employed. To the best of our knowledge, no standard procedure for assessing thermoformability has been published and/or is being widely used. Generally, the assessment of the thermoformability consist only of a simple visual inspection or, in some cases, in a thickness distribution measurement [20–24]. The absence of a standardized method to compare the thermoformability and process window of the materials has led us to develop a thermoformability evaluation procedure by screening different heating times (i.e. different sheet temperatures), while keeping constant the other processing parameters, which were independently optimized for the specific mold and sheet thickness. Visual inspection of the thermoformed structures was performed and photographs taken for the record.

3.3.1 Assessment of the thermoformability and thermoforming window of the PHBV.

We herein define thermoformability as the ability of a material to be successfully thermoformed into a specimen with the shape of the mold and reproducible and controlled thickness distribution. The thermoforming process window is further related to the combination of parameters that allows good thermoformability, being the temperature range the most critical for a particular material. The thermoformability and the determination of the thermoforming temperature range (process window) for PHBV (and all the blends) were accordingly assessed based on screening of the process conditions, visual inspection of the obtained samples, and comparison with the original mold. The method consisted firstly of thermoforming the sheets with the grid drawn on them. After this process, with the aid of the deformed grid, three parameters were related to the reproducibility of the mold's shape, and the thickness distribution of the molded specimen was assessed (both local and overall). These three parameters are summarized in Figure 4.a) and described as follows:

a) Edge inspection: it assesses the linearity in the joint section between the flat surface of the original sheet and the onset of the deformation (for the particular case of a tray-shaped mold, this would be the line defined by the intersecting planes of the original flat sheet and the vertical sides of the tray).

b) Corner inspection: it provides information about the mold reproducibility at the corners of the tray.

c) Thickness inspection: in evaluates the uniformity in the path and span of the squares in the grid (the shape of the grid elements are related to the local draw ratio and to the thickness distribution; high draw ratios result in high span and low thickness. On the other hand, even square-grid deformation is related to a uniform thickness distribution).

As a comparison, Figure 4.b presents two thermoformed trays from PLA and PHBV under the most optimal conditions for each biopolyester. It can be appreciated that PLA reproduces accurately the mold's geometry and keeps a regular thickness distribution. On the other hand, the PHBV specimen exhibits an irregular final shape, which differs from that of the mold. With respect to the thickness distribution, the PHBV presents a non-symmetric and completely irregular path in the grid, in agreement with a random thickness distribution. In order to determine the thermoforming temperature range of PHBV, identical sheets of PHBV were

thermoformed varying the heating time. The resulting trays were observed, paying attention to the "edge", "corners" and "thickness" (as stated previously). Each parameter was classified as "bad" (red color, cross sign), "intermediate" (blue color, wave sign) or "good" (green color, tick mark), as depicted in Figures. 4b and 4c. The upper and lower limits of the temperature range (that is, the heating time range) were established as those at which all the studied compositions resulted in a poor thermoformability. For the present setup, they were 30 and 44 seconds, respectively, using a step of 2s for the screening (see inset Fig. 1.d). When evaluating the thermoformability of the neat PHBV, according to the method proposed in this work, none of the conditions yielded in a good thermoformed tray, as shown in Figure 4.c. Thus, it could be concluded that neat PHBV showed poor thermoformability. The overall poor thermoforming behavior of the PHBV, including its narrow thermoforming temperature range, can be ascribed to its high crystallinity, which results in an abrupt loss of mechanical stability when the softening temperature is reached, thus leading to sagging effect prior to the thermoforming step [9,10]. The sagging effect results in considerable redistribution of material within the molded sheet. Nevertheless, a slight improvement in the shape of the samples was accounted for heating times of 36 and 38s. Under these conditions, the so-obtained thermoformed trays are considered as intermediate (blue color). Figure 4.d summarizes the thermoformability of the PHBV trays (represented by the color code) as a function of the thermoforming temperature within the analyzed time range.

3.3.2 Thermoformability of the PHBV/PLA blends

Figure 5 summarizes the evaluation of the thermoforming ability for all the PHBV/PLA blends studied (with and without the compatibilizers) as a function of the heating time, including representative pictures of the thermoformed trays. From the figure, it can be deduced that the incorporation of the PLA to the PHBV resulted in a slight improvement with respect to the thermoformability of the PHBV. However, neither a more limited thickness variation nor an increase in the thermoforming temperature range could be observed. The limited effect of the addition of the PLA was assigned to the lack of compatibility between the two

polymers. The absence of compatibility was reported in a previous work [18] by SEM observations as well as by DSC and DMA, where two independent glass transition temperatures were clearly observed. However, as the compatibilizers were added to the blend, it greatly improved the thermoformability of the PHBV/PLA, with thermoforming enhancements as a function of the used compatibilizer.

The incorporation of HMDI to the PHBV/PLA blend resulted in a wider thermoforming temperature window, although the overall thermoformability of the blend was still classified as intermediate even in the best temperature range (30 to 40s heating). All the HMDI thermoformed trays showed poor reproducibility in the round corners of the mold. A small improvement in the thickness distribution, as determined from a more homogenous and predictable path of the square-grid, was observed. With respect to the samples containing polyHMDI and PDI, both compositions allowed a wider thermoforming temperature window, when compared to the neat PHBV and PHBV/PLA. Moreover, a good thermoformability (green color) was achieved for the first time in the samples obtained in the temperature range from 112 to 122 and from 112 to 124 °C for the polyHMDI and PDI, respectively. The samples processed at the limits of the studied temperature range showed however intermediate thermoforming compliance, according to the methodology used. Interestingly, the thickness distribution of the obtained samples was repetitive for all the samples and compositions, thus being predictable and controllable, and the samples resulted in trays that perfectly reproduced the geometry of the mold.

The positive outcome in terms of thermoformability when PLA with the compatibilizers were incorporated to the PHBV, and the expanded thermoforming temperature range can be ascribed to two phenomena: 1. an enhancement in the sheet stability during heating prior to thermoforming and, 2. an increase in the elasticity of the molten blend during the thermoforming. The former phenomenon is attributed to an improved interaction between the dispersed amorphous phase and the continuous crystalline phase. Such interactions are important at temperatures close to the softening point of the crystalline phase, and leads to an increase in the overall viscosity of the system [18]. This higher viscosity results in a reduction of the sagging effect and therefore, a better control of the thickness distribution during the distribution of the thermoplastic in the mold. Increasing thermoformability of highly crystalline polymers

by blending them with amorphous polymers was previously reported by Gimenez et al. [9,10]. The increase in the stability of the polymer system during the heating stage, prior to the deformation, and an increase in the elasticity of PHBV blends when compared to the pure PHBV was also reported for processing of PHVB blends in injection molding [25,26]. The higher elasticity, on the contrary, enables more extensive deformation of the sheet and therefore better definition of the geometry of the mold used.

Overall, both the enhanced stability and the improved elasticity are positive for the thermoforming outcome. Thus, the improvement in the thermoformability and in the thermoforming process windows in this work was a combined effect of enhanced sheet stability, counteracting a sudden drop in viscosity during thermoforming, and an improved phase interaction due to the use of diisocyanates.

3.4. Degradation in composting conditions

PHBV and PLA are well known for undergoing biodegradation in composting conditions within a short time, being this one of the main advantages of these materials for short time applications, such as packaging. Therefore, the melt blending of both polymers should, in principle, result in a completely biodegradable material. However, as in this work the blends of the two biopolyesters have been compatibilized with diisocyanates, the possibility of the isocyanates to interfere with the biodegradation was explored. Disintegration tests under composting conditions of all the compositions were therefore performed, monitoring the weight loss of the samples over time according to the ISO 20200 standard [19]. Results are summarized in Figure 6.

Figure 6.a shows the evolution of disintegration (% of weight loss vs. time) for neat PHBV, neat PLA, PHBV/PLA and the compatibilized blends (HMDI, polyHMDI and PDI). All tests were performed in lab-scale composting conditions. When compared the Neat PLA and Neat PHBV curves, some differences arise. Neat PLA shows a very short induction time in combination with fast disintegration, being fully disintegrated within the first two weeks. Neat PHBV, on the other hand, did not undergo significant weight variations during the first 8 days, in agreement with other reported works performed with the same grade of PHBV [27,28]. Additionally, although both disintegration vs. time curves present an exponential trend, the maximum slope of the Neat PLA is higher than the Neat PHBV one. To visually assess the impact over time of the composting

process on the tested samples, images of the studied blends were taken at different time points (Figure 6.b). The first sample of Neat PLA taken out from the compost reactor at the 8th day was already broken into pieces showing loss of transparency. According to Arrieta et al. and Fortunati et al. [29,30], this effect is the result of changes in the refraction index, water sorption and/or the presence of hydrolytic products during bacterial biodegradation. With respect to the PHBV-based materials, a noticeable surface roughness can be observed for composting times over 15 days. This surface roughness indicates the onset of the disintegration, since the biodegradation of PHAs takes place by means of a surface erosion by the microorganisms[31,32].

The differences in biodegradation onset time and rate of disintegration for PLA and PHBV can be ascribed to the accessibility of the microorganism involved in the biodegradation to the available amorphous polymer chains, which act as nourishment. Accordingly, the biodegradation takes place in the amorphous fraction of the biopolyesters rather than on the crystals. Therefore, the biodegradation of the amorphous PLA is favored over the highly crystalline PHBV as reported by Arrieta et al. [33]. This reasoning is consistent with the behavior observed for the PHBV/PLA blends, where the degradation takes place in two steps. The first one, with a weight loss up to 25%, is the fastest one and can be ascribed mostly to the PLA content of the blend, whilst the second one would correspond mainly to the PHBV fraction. On the other hand, during the step attributed to the PHBV fraction, an increase of the disintegration rate is detected when compared with the neat PHBV, which can be related with an increase in the specific surface derived from the voids resulting from the disintegration of the PLA droplets. The differences observed among the biodesintegration curves of the blends can be explained by the accessibility of the microorganisms to the PLA fraction, which results in a delay in the degradation onset with respect to neat PLA and also in variations in the initial disintegration rate, which in turn is faster as is larger the average size of the dispersed phase (c.f Fig. 2).

In order to corroborate all the above reasoning, a morphological study of the samples after 20 days in composting conditions has been carried out. Figure 6.c presents SEM micrographs of the surface of PHBV and PHBV/PLA blends. The neat PHBV sample shows a uniform rough surface, but the blends show some voids in the surface. The size of these voids is bigger for the uncompatibilized PHBV/PLA blend, following the same order for the rest of the blends as their average particle size decrease. According to our previous assumptions

based on weight loss, after 20 days most of the PLA phase should have been already biodegraded, leaving those voids in the samples. In Figure 6.d and 6.e it is presented a higher magnification detail of the surface of the neat PHBV and the PDI samples, respectively, where the voids in the PDI sample are clearly visible. Indeed, the bacterial growth and the surface erosion of the samples are noticeable in these images. All of the above leads us to the conclusion that the incorporation of diisocyanates as compatibilizers in PHBV/PLA blends in the present dosage does not negatively affect the biodisintegrability, with only small variations related with the size of the dispersed PLA domains within the PHBV matrix.

4. CONCLUSIONS

PHBV is a potential good candidate to replace petroleum-based polymers in the packaging sector due to its excellent barrier properties and biodisintegrability. However, PHBV copolymers present some shortcomings for its direct implementation in this sector. One of the main shortcoming arises from its poor thermoformability (defined as the ability to be successfully reproduce the shape of a mold with a controlled thickness distribution) and its narrow thermoforming window (defined as the temperature range at which good thermoformability is achieved). In this work, blends of PHBV with PLA and three different compatibilizers (hexamethylene diisocyanate, (HMDI), poly(hexamethylene) diisocyanate (polyHMDI) and 1,4-phenylene diisocyanate (PDI)) diisocyanates have been obtained by melt blending. The thermoformability, barrier properties and biodisintegrability of the so-obtained were investigated. In order to assess the thermoformability of the materials, a simple method for assessing qualitatively the thermoforming capacity of any polymeric film is proposed. Slight enhancement in the thermoforming capacity of PHBV is observed when HMDI is incorporated to the PHBV/PLA blend. On the other hand, good mold reproducibility is accomplished for a wide range of temperatures for both the polyHMDI and PDI blends, being the best ones obtained with PDI. Besides, the addition of diisocyanates did not substantially change the barrier properties of the PHBV/PLA blends, nor does negatively affect the biodisintegration with respect to PHBV. Overall, the use of diisocyanate-type compatibilizers has proven to be a convenient approach to improve thermoformability of PHBV/PLA blends, thus extending the usability of PHBV in thermoformed packaging applications.

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REFERENCES

[1] S. Khanna, A.K. Srivastava, Recent advances in microbial polyhydroxyalkanoates, Process Biochem. 40 (2005) 607–619. doi:10.1016/j.procbio.2004.01.053.

[2] L.S. Serafim, P.C. Lemos, R. Oliveira, M.A.M. Reis, Optimization of polyhydroxybutyrate production by mixed cultures submitted to aerobic dynamic feeding conditions., Biotechnol. Bioeng. 87 (2004) 145–60. doi:10.1002/bit.20085.

[3] M.A.M. Reis, L.S. Serafim, P.C. Lemos, A.M. Ramos, F.R. Aguiar, M.C.M. Van Loosdrecht, Production of polyhydroxyalkanoates by mixed microbial cultures., Bioprocess Biosyst. Eng. 25 (2003) 377–85. doi:10.1007/s00449-003-0322-4.

[4] T. Keshavarz, I. Roy, Polyhydroxyalkanoates: bioplastics with a green agenda., Curr. Opin. Microbiol. 13 (2010) 321–6. doi:10.1016/j.mib.2010.02.006.

[5] S. Aditi, D.S. Shalet, N. Manish, R. Pranesh, T. Katyayini, Microbial production of polyhydroxyalkanoates (PHA) from novel sources : A Review, Int. J. Res. Biosci. 4 (2015) 16–28.

[6] D.Z. Bucci, L.B.B. Tavares, I. Sell, PHB packaging for the storage of food products, Polym. Test. 24 (2005) 564–571. doi:10.1016/j.polymertesting.2005.02.008.

[7] D. Cava, E. Gimenez, R. Gavara, J.M. Lagaron, Comparative Performance and Barrier Properties of Biodegradable Thermoplastics and Nanobiocomposites versus PET for Food Packaging Applications, J. Plast. Film Sheeting. 22 (2006) 265–274. doi:10.1177/8756087906071354.

[8] Y.-M. Corre, S. Bruzaud, J.-L. Audic, Y. Grohens, Morphology and functional properties of commercial polyhydroxyalkanoates: A comprehensive and comparative study, Polym. Test. 31 (2012) 226–235.

doi:10.1016/j.polymertesting.2011.11.002.

[9] E. Giménez, J.M. Lagarón, M.L. Maspoch, L. Cabedo, J.J. Saura, Uniaxial tensile behavior and thermoforming characteristics of high barrier EVOH-based blends of interest in food packaging, Polym. Eng. Sci. 44 (2004) 598–608. doi:10.1002/pen.20054.

[10] E. Giménez, J. Lagaron, R. Gavara, L. Cabedo, J.J. Saura, Study of the thermoformability of ethylene-vinyl alcohol copolymer based barrier blends of interest in food packaging applications, J. Appl. Polym. Sci. 96 (2004) 3851–3855.

[11] R.M. Rasal, A. V. Janorkar, D.E. Hirt, Poly(lactic acid) modifications, Prog. Polym. Sci. 35 (2010) 338–356. doi:10.1016/j.progpolymsci.2009.12.003.

[12] I. Zembouai, S. Bruzaud, M. Kaci, A. Benhamida, Y. Corre, Y. Grohens, J.-M. Lopez-Cuesta, Synergistic Effect of Compatibilizer and Cloisite 30B on the Functional Properties of Poly (3-hydroxybutyrate- co -3-hydroxyvalerate)/ Polylactide Blends, Polym. Eng. Sci. 54 (2014) 2239–2251. doi:10.1002/pen.

[13] I. Zembouai, M. Kaci, S. Bruzaud, A. Benhamida, Y.M. Corre, Y. Grohens, A study of morphological, thermal, rheological and barrier properties of Poly(3-hydroxybutyrate-Co-3-Hydroxyvalerate)/polylactide blends prepared by melt mixing, Polym. Test. 32 (2013) 842–851. doi:10.1016/j.polymertesting.2013.04.004.

[14] S. Modi, K. Koelling, Y. Vodovotz, Miscibility of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with high molecular weight poly(lactic acid) blends determined by thermal analysis, J. Appl. Polym. Sci. 124 (2012) 3074–3081. doi:10.1002/app.35343.

[15] R.A. Auras, B. Harte, S. Selke, R. Hernandez, Mechanical, Physical, and Barrier Properties of Poly(Lactide) Films, J. Plast. Film Sheeting. 19 (2003) 123–135. doi:10.1177/8756087903039702.

[16] J. González-Ausejo, E. Sánchez-Safont, J.M. Lagarón, R. Balart, L. Cabedo, J. Gámez-Pérez, Compatibilization of poly(3-hydroxybutyrate- *co* -3-hydroxyvalerate)-poly(lactic acid) blends with diisocyanates, J. Appl. Polym. Sci. 134 (2017). doi:10.1002/app.44806.

[17] H. Alata, T. Aoyama, Y. Inoue, Effect of Aging on the Mechanical Properties of Poly(3-hydroxybutyrate-co -3-hydroxyhexanoate), Macromolecules. 40 (2007) 4546–4551. doi:10.1021/ma070418i.

[18] J. Gonzalez-Ausejo, E.L. Sanchez-Safont, J.M. Lagarón, R. Balart, L. Cabedo, J. Gamez-Perez, Compatibilization of PHBV/PLA blends with diisocyanates, J. Appl. Polym. Sci. (n.d.) Under revision.

[19] UNE-EN ISO, UNE-EN ISO 20200 Determinación del grado de desintegración de materiales plásticos bajo condiciones de compostaje simuladas en un laboratorio, (2006).

[20] A. Guinault, A.S. Nguyen, G. Miquelard-Garnier, D. Jouannet, A. Grandmontagne, C. Sollogoub, The Effect of Thermoforming of PLA-PHBV Films on the Morphology and Gas Barrier Properties, Key Eng. Mater. 504–506 (2012) 1135–1138. doi:10.4028/www.scientific.net/KEM.504-506.1135.

[21] R. McCool, P.J. Martin, The role of process parameters in determining wall thickness distribution in plug-assisted thermoforming, Polym. Eng. Sci. 50 (2010). doi:10.1002/pen.21718.

[22] D. Marathe, D. Rokade, L. Busher Azad, K. Jadhav, S. Mahajan, Z. Ahmad, S. Gupta, S. Kulkarni, V. Juvekar, A. Lele, Effect of plug temperature on the strain and thickness distribution of components made by plug assist thermoforming, Int. Polym. Process. 31 (2016). doi:10.3139/217.3060.

[23] M. Buntinx, G. Willems, G. Knockaert, D. Adons, J. Yperman, R. Carleer, R. Peeters, Evaluation of the Thickness and Oxygen Transmission Rate before and after Thermoforming Mono- and Multi-layer Sheets into Trays with Variable Depth, Polymers (Basel). 6 (2014) 3019–3043. doi:10.3390/polym6123019.

[24] R.E. Lee, Y. Guo, H. Tamber, M. Planeta, S.N.S. Leung, Thermoforming of Polylactic Acid Foam Sheets: Crystallization Behaviors and Thermal Stability, 55 (2016) 560–567. doi:10.1021/acs.iecr.5b03473.

[25] H. Zhao, Z. Cui, X. Sun, L.-S. Turng, X. Peng, Morphology and Properties of Injection Molded Solid and Microcellular Polylactic Acid/Polyhydroxybutyrate-Valerate (PLA/PHBV) Blends, Ind. Eng. Chem. Res. 52 (2013) 2569–2581. doi:10.1021/ie301573y.

[26] I. Zembouai, S. Bruzaud, M. Kaci, A. Benhamida, Y.-M. Corre, Y. Grohens, A. Taguet, J.-M. Lopez-Cuesta, Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Polylactide Blends: Thermal Stability, Flammability and Thermo-Mechanical Behavior, J. Polym. Environ. 22 (2013) 131–139. doi:10.1007/s10924-013-0626-7.

[27] A. Martínez-Abad, J. González-Ausejo, J.M. Lagarón, L. Cabedo, Biodegradable poly(3-

hydroxybutyrate-co-3-hydroxyvalerate)/thermoplastic polyurethane blends with improved mechanical and barrier performance, Polym. Degrad. Stab. (2016). doi:10.1016/j.polymdegradstab.2016.03.039.

[28] E.L. Sánchez-Safont, J. González-Ausejo, J. Gámez-Pérez, J.M. Lagarón, L. Cabedo, Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Purified Cellulose Fiber Composites by Melt Blending: Characterization and Degradation in Composting Conditions, J. Renew. Mater. 4 (2016) 123–132. doi:10.7569/JRM.2015.634127.

[29] M.P. Arrieta, J. López, E. Rayón, a. Jiménez, Disintegrability under composting conditions of plasticized PLA–PHB blends, Polym. Degrad. Stab. (2014) 1–12. doi:10.1016/j.polymdegradstab.2014.01.034.

[30] E. Fortunati, D. Puglia, C. Santulli, F. Sarasini, J.M. Kenny, Biodegradation of Phormium tenax/poly(lactic acid) composites, J. Appl. Polym. Sci. 125 (2012) E562–E572. doi:10.1002/app.36839.

[31] D. Puglia, E. Fortunati, D. a. D'Amico, L.B. Manfredi, V.P. Cyras, J.M. Kenny, Influence of organically modified clays on the properties and disintegrability in compost of solution cast poly(3-hydroxybutyrate) films, Polym. Degrad. Stab. 99 (2014) 127–135. doi:10.1016/j.polymdegradstab.2013.11.013.

[32] K. Iggui, N. Le Moigne, M. Kaci, S. Cambe, J.-R. Degorce-Dumas, A. Bergeret, A biodegradation study of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organoclay nanocomposites in various environmental conditions, Polym. Degrad. Stab. 119 (2015) 77–86. doi:10.1016/j.polymdegradstab.2015.05.002.

[33] M.P. Arrieta, J. López, A. Hernández, E. Rayón, Ternary PLA–PHB–Limonene blends intended for biodegradable food packaging applications, Eur. Polym. J. 50 (2014) 255–270. doi:10.1016/j.eurpolymj.2013.11.009.

Figure captions:

Fig. 1: Image of the a) thermoforming facility, b thermoforming chamber, c) mold and d) Sheet temperature as a function of the heating time.

Fig. 2: SEM micrographs of a) PHBV/PLA blend, b) HMDI, c) polyHMDI, d) PDI and e) diameter distribution of PLA domains of PHBV/PLA blend and compatibilized blends.

Fig. 3: a) Water vapor and b) oxygen permeability of the neat materials and their blends.

Fig. 4: a) parameters defined in the method on a thermoformed PLA tray, b) an example of the thermoformed trays for PLA and PHBV, c) thermoformed PHBV trays at different heating times evaluated according to the method and d) thermoforming temperature range according to the method.

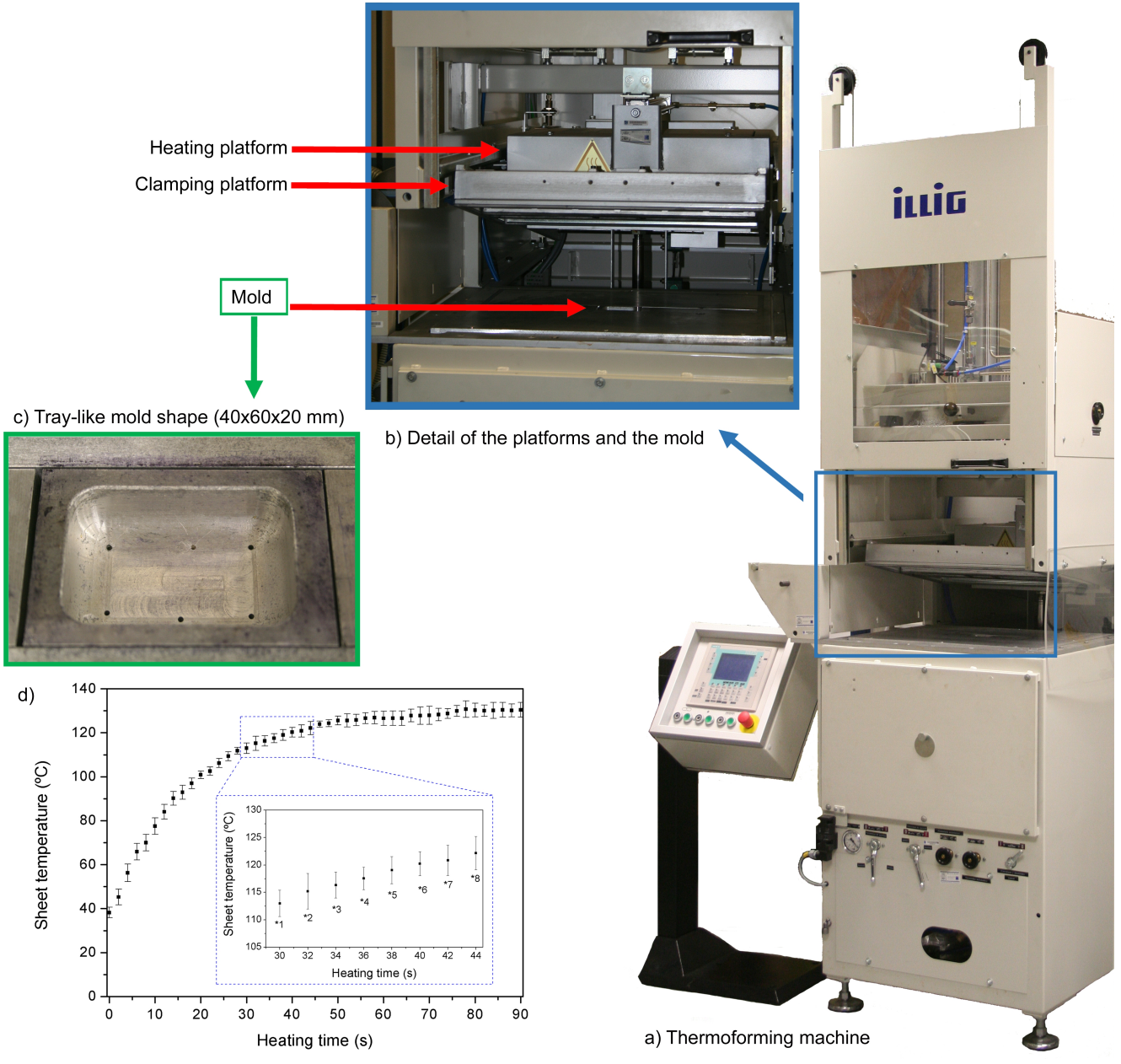
Fig. 5: Photographs of the thermoformed structures depending on the processing temperature and thermoforming temperature range for Neat PHBV, PHBV/PLA blend and the PHBV/PLA compatibilized blends.

Fig. 6: a) Disintegration curve, b) photographs of the disintegrated samples at different times, c) SEM micrographs of eroded surfaces after 20 days under composting conditions, d) and e) SEM micrographs of bacteria colonies after 20 days of composting of PHBV/PLA blend and PDI, respectively.

1 Table 1: Nomenclature and composition of studied PHBV, PLA and PHBV/PLA blends.

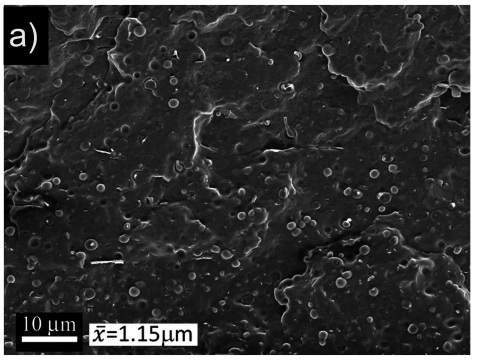
SAMPLE	Weigh percentage		Molar ratio			Compatibilizer (phr)
	PHBV	PLA	HMDI	polyHMDI	PDI	
Neat PHBV	100					
Neat PLA		100				
PHBV/PLA	75	25				
HMDI	75	25	1:20			1,26
polyHMDI	75	25		1:20		2,27
PDI	75	25			1:20	1,20

2

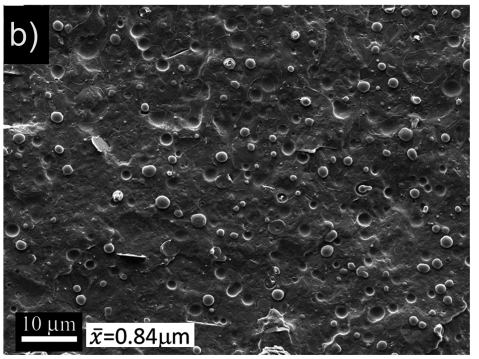

Heating platform
Clamping platform
Mold
c) Tray-like mold shape (40x60x20 mm)
b) Detail of the platforms and the mold
a) Thermoforming machine
ILLIG
d)
Sheet temperature (ºC)
Heating time (s)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
60
70
80
90
105
110
115
120
125
130
30
32
34
36
38
40
42
44
*1
*2
*3
*4
*5
*6
*7
*8

PHBV

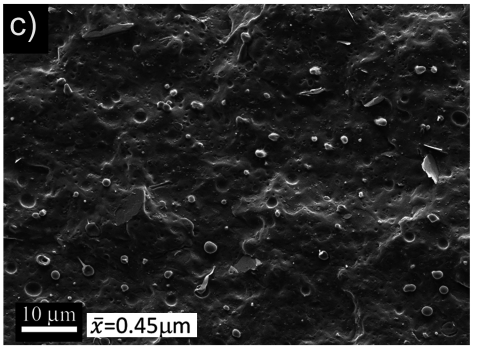
PLA



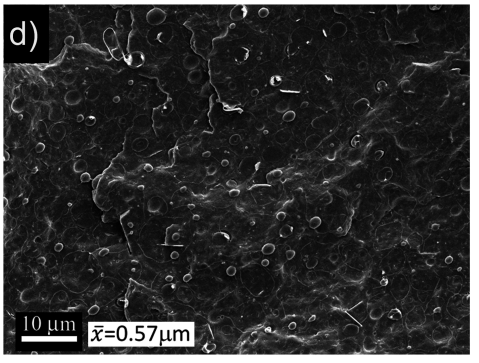
HDMI

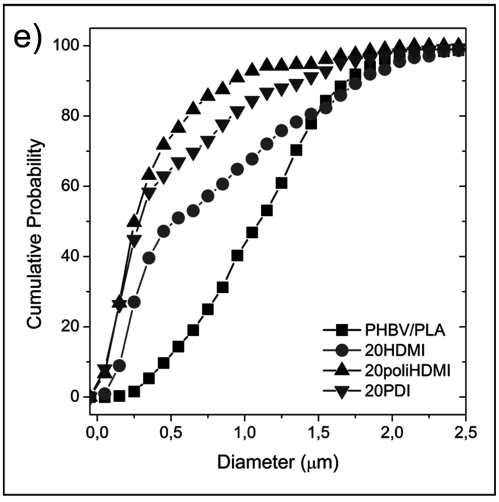


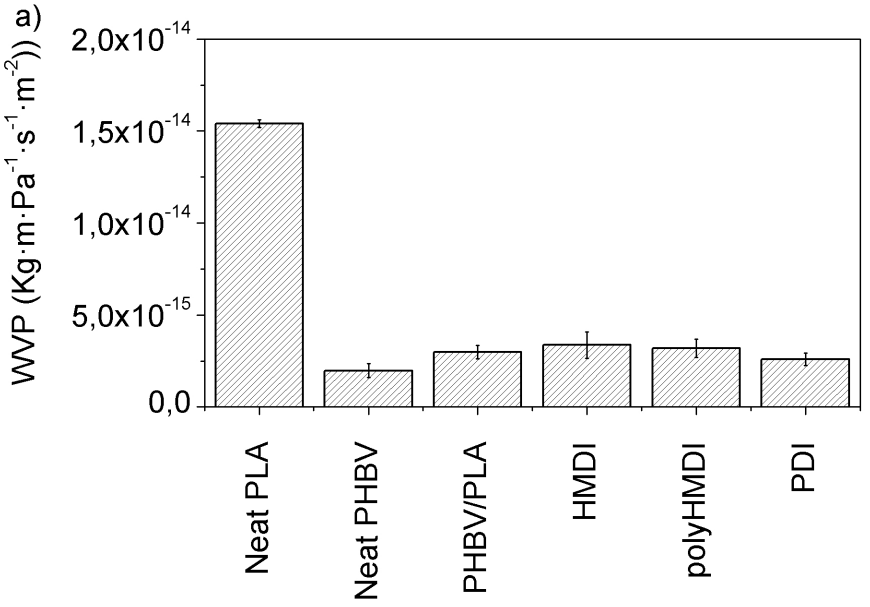
poliHDMI

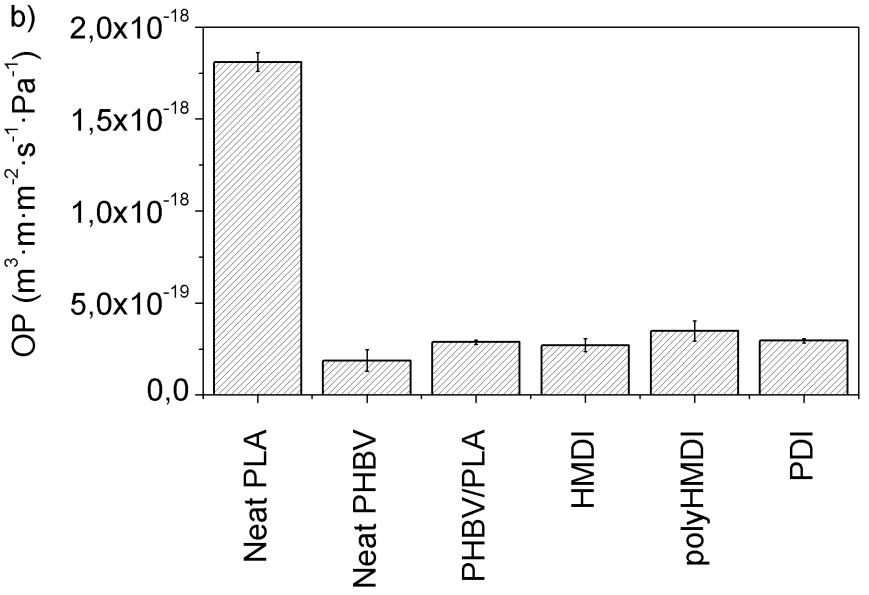


PDI

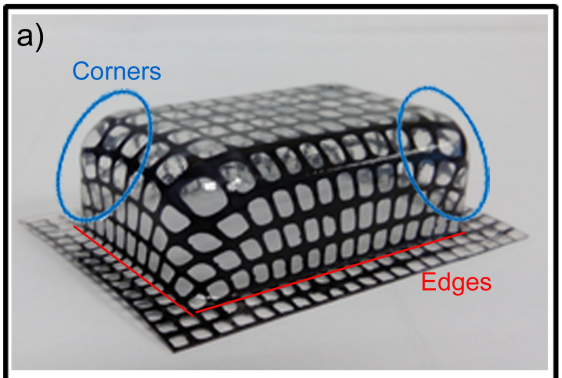





a)
WVP (Kg·m·Pa-1·s-1·m-2))
2,0x10-14
1,5x10-14
1,0x10-14
5,0x10-15
0,0
Neat PLA
Neat PHBV
PHBV/PLA
HMDI
polyHMDI
PDI


b)
OP (m3·m·m-2·s-1·Pa-1)
2,0x10-18
1,5x10-18
1,0x10-18
5,0x10-19
0,0
Neat PLA
Neat PHBV
PHBV/PLA
HMDI
polyHMDI
PDI

a)



Paramethers to define a good thermoformed structure:

* mold reproducibility

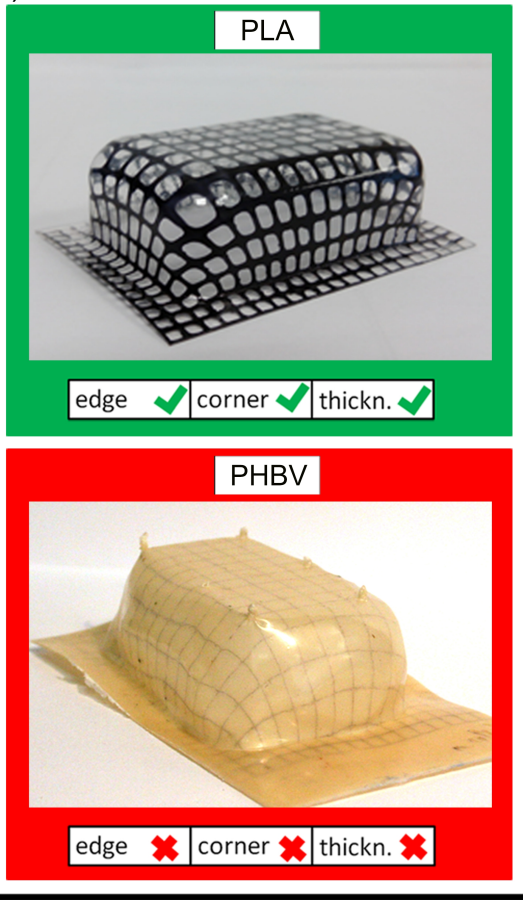
  - linearity in the junction area between the horizontal and vertical sides of the mold

  - curvature in the rounded corners

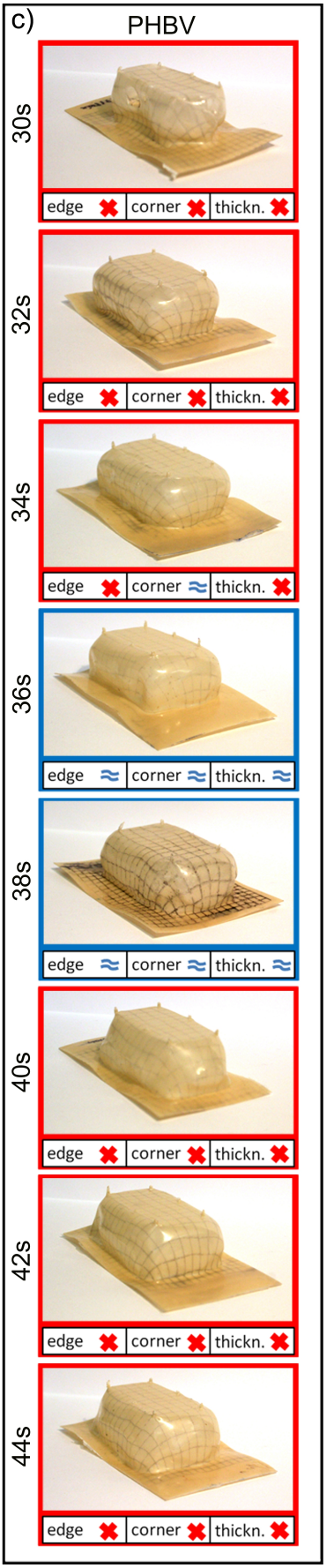
* distribution of thickness

  - path of squares stamped

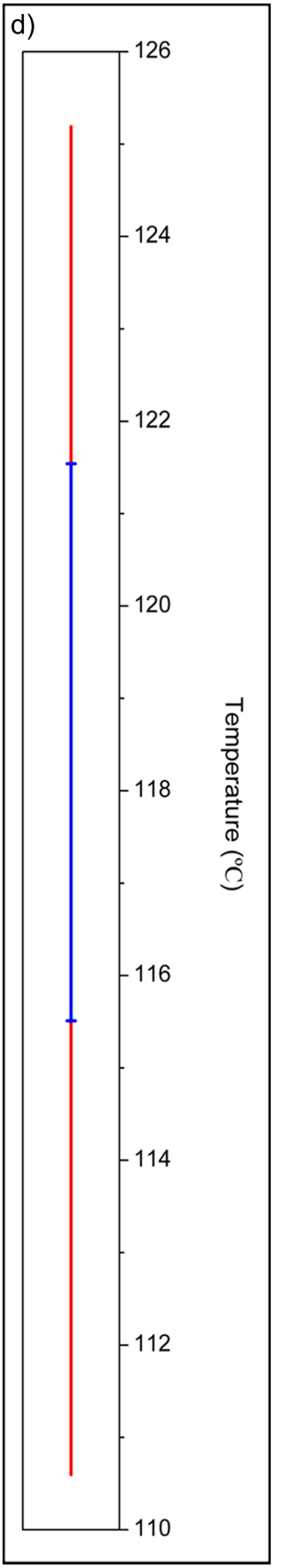
b)

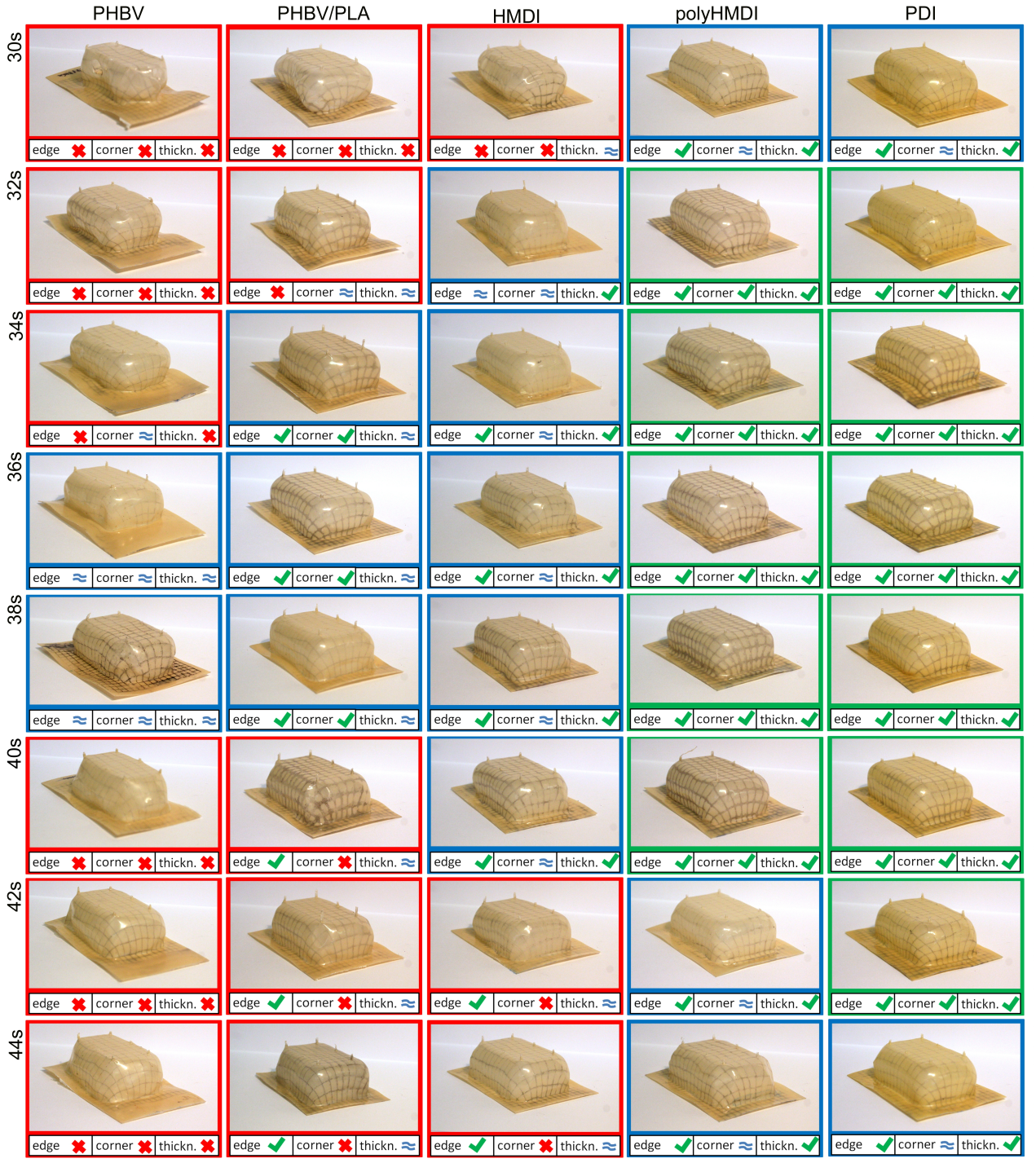


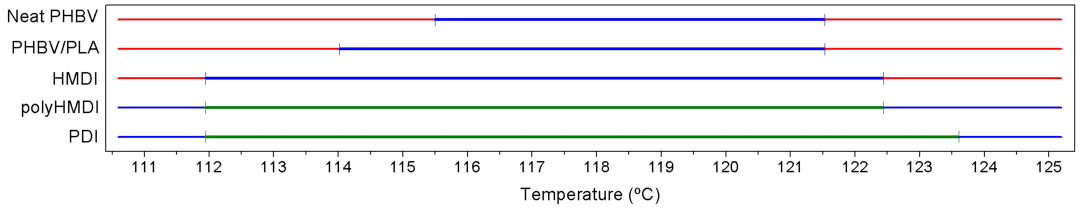
c)

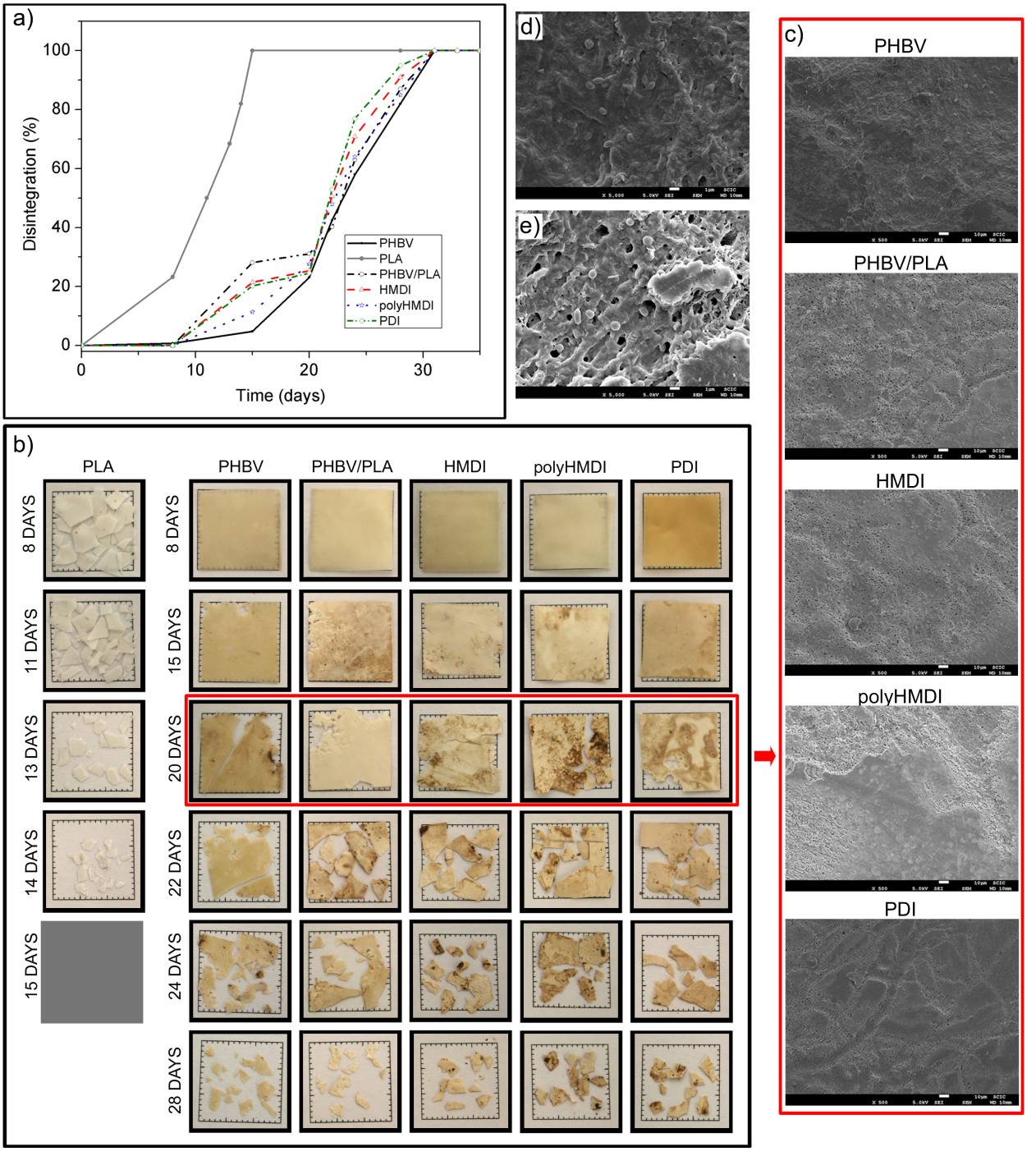


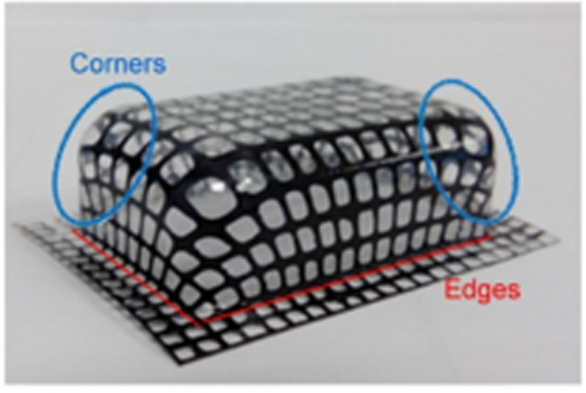
d)

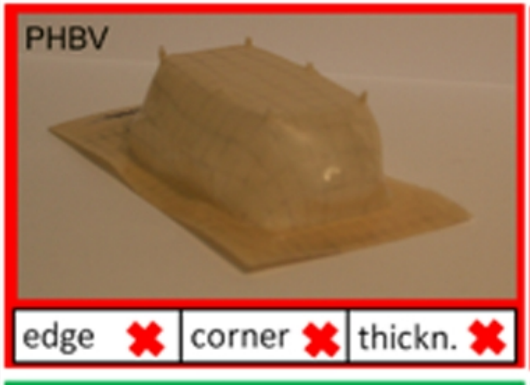
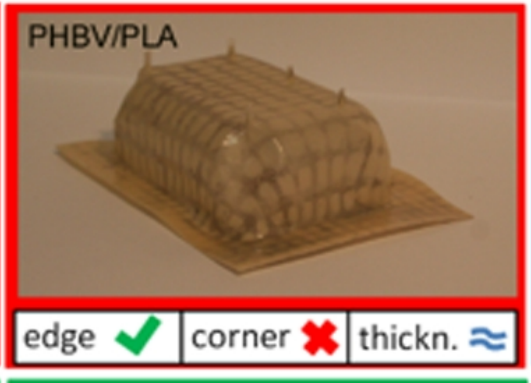
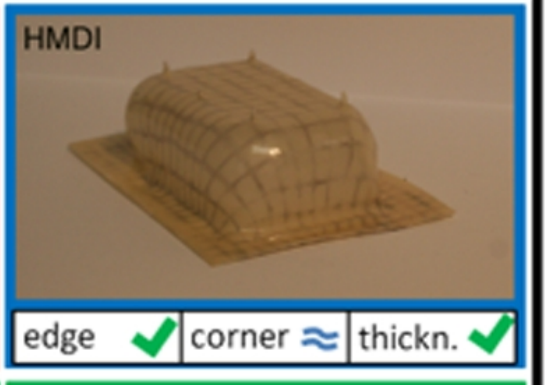
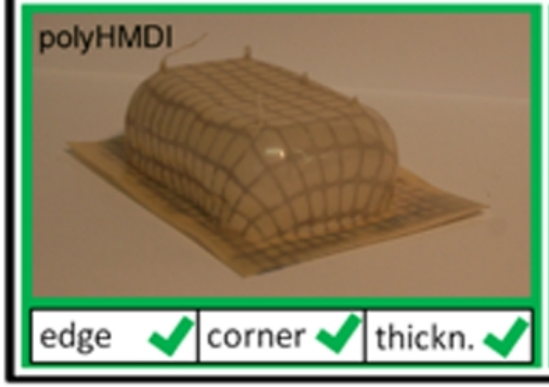
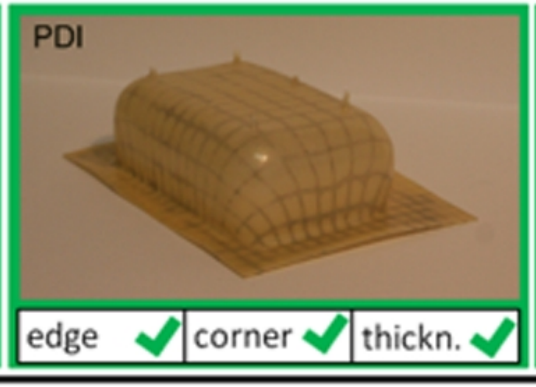
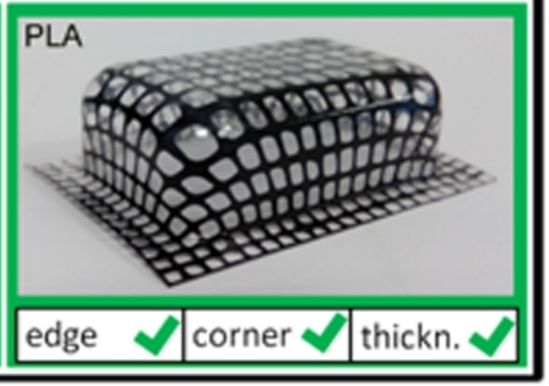



PHBV
PHBV/PLA
HMDI
polyHMDI
PDI
30s
32s
34s
36s
38s
40s
42s
44s
edge
corner
thickn.


Neat PHBV
PHBV/PLA
HMDI
polyHMDI
PDI
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
Temperature (ºC)


a)
Disintegration (%)
Time (days)
PHBV
PLA
PHBV/PLA
HMDI
polyHMDI
PDI
d)
e)
c)
PHBV
PHBV/PLA
HMDI
polyHMDI
PDI
b)
PLA
PHBV
PHBV/PLA
HMDI
polyHMDI
PDI
8 DAYS
11 DAYS
13 DAYS
14 DAYS
15 DAYS
8 DAYS
15 DAYS
20 DAYS
22 DAYS
24 DAYS
28 DAYS



Paramethers to define a good thermoformed structure:

* mold reproducibility
  - linearity in the junction area between the horizontal and vertical sides of the mold
  - curvature in the rounded corners
* distribution of thickness
  - path of squares stamped