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Research Article

Structural Foams of Biobased Isosorbide-Containing Copolycarbonate

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Isosorbide-containing copolycarbonate (Bio-PC) is a partly biobased alternative to conventional bisphenol A (BPA) based polycarbonate (PC). Conventional PC is widely used in polymer processing technologies including thermoplastic foaming such as foam injection molding. At present, no detailed data is available concerning the foam injection molding behavior and foam properties of Bio-PC. This contribution provides first results on injection-molded foams based on isosorbide-containing PC. The structural foams were produced by using an endothermic chemical blowing agent (CBA) masterbatch and the low pressure foam injection molding method. The influence of weight reduction and blowing agent concentration on general foam properties such as density, morphology, and mechanical properties was studied. The test specimens consist of a foam core in the center and compact symmetrical shell layers on the sides. The thickness of the foam core increases with increasing weight reduction irrespective of the CBA concentration. The specific (mechanical) bending properties are significantly improved and the specific tensile properties can almost be maintained while reducing the density of the injection-molded parts.

1. Introduction

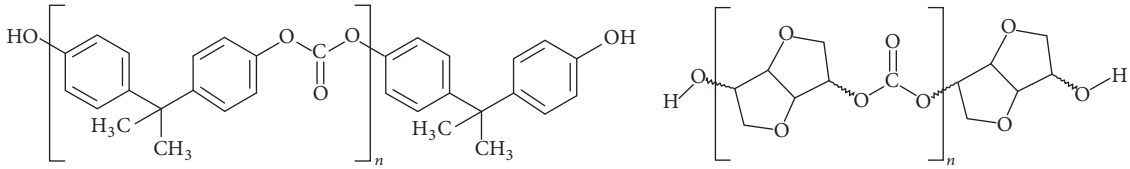
Polycarbonates (PC) are widely used in injection molding and extrusion including foaming technologies. However, conventional PC is based on nonrenewable resources and bisphenol A (BPA), which is still in discussion due to its toxicological effects [1–5]. Isosorbide-containing PC is a copolymer obtained by polymerization of isosorbide in presence of diphenyl carbonate and other dihydroxy components as comonomers. Figure 1 shows the molecular structures of conventional PC with bisphenol A as diol monomer component (Figure 1(a)) and of a polycarbonate composed of solely isosorbide as monomeric diol (Figure 1(b)).

Isosorbide-containing copolycarbonate is partly biobased and nondegradable with main mechanical and optical properties comparable to conventional PC (Table 1).

Because isosorbide-containing Bio-PC has been on the market for less than five years, most available literature and patents are focused on chemical aspects such as the synthesis of Bio-PC as well as on structural analysis of the polymer [6–11]. Only few patents and no detailed scientific investigations concerning foaming and foam properties of Bio-PC were published [12].

Thermoplastic foam injection molding (FIM) is a special injection molding process being practiced for many decades. The thermoplastic melt is loaded with a blowing agent which results in foaming of the plastics material after being injected into the cavity of the mold. The cavity is filled only partially in order to allow the melt to expand. Diffusion of the blowing agent and gas bubble formation lead to the formation of a structural foam and the complete volume of the mold is filled out. This structural foam is characterized in general by a compact skin layer and a foamed core. While the foam structure can be influenced directly by process parameters, the mechanical properties depend on the resulting foam structure, the thermoplastic material used and the part design [13–16].

This contribution characterizes basic properties of structural Bio-PC foams in a nutshell. The foams were produced by foam injection molding using an endothermic chemical blowing agent (CBA). Physical foam properties, morphology,



(a) (b)

Figure 1: Molecular structures of conventional PC with bisphenol A as diol monomer component (a) and of a polycarbonate composed of solely isosorbide as monomeric diol (b).

Table 1: Comparison of properties of Bio-PC and a conventional bisphenol A based PC (for both types supplier data from Mitsubishi Chemical Company).

	Bio-PC Durabio D 7340 R	Conv. PC Xantar 24 R
Tensile modulus (MPa)	2700	2300
Tensile strength (MPa)	79	60
Elongation at break (%)	72	>50
Flexural modulus (MPa)	2700	2400
Flexural strength (MPa)	116	90
HDT @ 1,80 MPa (°C)	106	130
Light transmission (%)	92	89
Refractive index (-)	1.50	1.58
Density (g/cm^3)	1.37	1.20
Biobased carbon content	60%	0%

and mechanical properties obtained from tensile test and bending test were analyzed. Specific mechanical properties were also calculated and discussed in conjunction with the CBA concentration, shell layer thickness, and morphology.

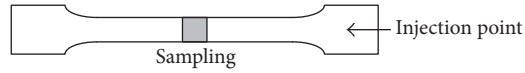


Figure 2: Sample position for morphology analysis and density measurement.

2. Materials and Methods

2.1. Materials. Isosorbide-containing PC was obtained as granules from Mitsubishi Chemical Holdings, formerly Mitsubishi Chemical Corporation, Tokyo (Japan), under the trade name Durabio D 7340 R. The melt flow rate at 230°C and 5 kg load is 19 g/10 min. The neat density is 1366 kg m^{-3} and the heat deflection temperature according to ISO 75 method B is 114°C [17, 18].

Palmarole MB.BA.16 from Adeka Palmarole SAS, Mulhouse (France), was used as an endothermic CBA masterbatch for the thermoplastic foam injection molding tests. The carrier polymer of the CBA masterbatch is a low-density polyethylene (LDPE). The active gas concentration of MB.BA.16 is 20% and the decomposition starts at 180°C [19]. Two concentrations of MB.BA.16 were used, namely, 2 wt.% and 3 wt.%. Bio-PC and CBA masterbatch resins were dry-blended in an internal mixer and this mixture was fed into the injection molding machine.

2.2. Foam Injection Molding. Multipurpose test specimens of type 1B were produced as foam parts according to DIN EN ISO 3167 by using an injection molding machine IntElect 100–340 from Sumitomo Demag Plastics Machinery GmbH, Schwaig, Germany. Low pressure foam injection molding technology, wherein the cavity is only partially filled, was applied to achieve two different weight reductions of the specimens, namely, 5% and 10%. The injection molding processing temperature was set to 220°C and the mold temperature was fixed at 50°C. The injection speed and maximum injection pressure were kept constant at about 35 cm^3 s^{-1} (screw diameter: 30 mm, volume flow rate 25 cm^3 s^{-1}) and 2000 bar, respectively. The back pressure was set to 120 bar which is high enough to prevent formation of gas bubbles in the screw vestibule.

2.3. Foam Characterization. Foam morphology was investigated in transverse direction to the melt flow by means of scanning electron microscopy (SEM). The samples were taken from the middle part of the multipurpose test specimen as shown in Figure 2 by cryogenic fracturing. Shell layer thickness and foam core thickness were measured.

The foam density was calculated from the specific volume and weight of five different samples. Tensile properties according to ISO 527 and bending properties according to

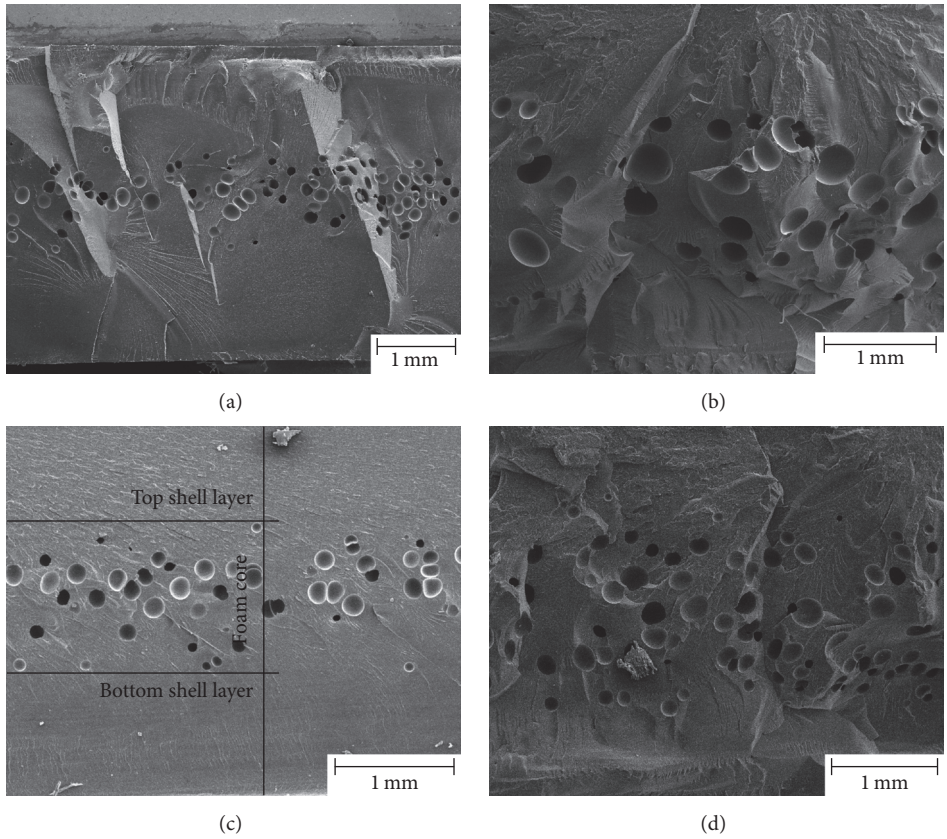


Figure 3: Morphology of injection-molded Bio-PC foams (cryogenically fractured surfaces transverse to melt flow): (a) 2 wt.% MB.BA.16, 5% weight reduction; (b) 2 wt.% MB.BA.16, 10% weight reduction; (c) 3 wt.% MB.BA.16, 5% weight reduction; (d) 3 wt.% MB.BA.16, 10% weight reduction.

ISO 178 (three-point bending test) were determined each using five samples.

3. Results and Discussion

Both CBA concentrations, 2 wt.% and 3 wt.%, proved to be suitable for achieving the desired weight reductions of 5% and 10% without any loss in specimen quality, that is, a fully filled specimen without sink marks, evaluated by visual inspection of the parts. The nonfoamed specimens are transparent due to the amorphous character of Bio-PC. The foamed parts are nontransparent and white caused by light scattering at the gas bubble polymer interfaces. The density of the nonfoamed Bio-PC specimens was measured at 1363 kg m^{-3} ± 1 kg m^{-3}, well matching the supplier data. From this, the density of the foamed Bio-PC specimens can be calculated taking the partial filling of the mold into account to 1295 kg m^{-3} for 5% weight reduction and 1227 kg m^{-3} for 10% weight reduction. These values should be independent from the CBA content in case that sufficient gas is produced for filling the mold completely.

Figure 3 shows representative morphologies of the cryogenically fractured surfaces of the injection-molded Bio-PC foams.

No significant differences with respect to the morphologies of the structural foam due to a compact shell layer and foamed core can be observed between 2 wt.% and 3 wt.% CBA concentration. The foam core is homogeneous, irrespective of the CBA concentration. The determination of the nonfoamed shell layer thicknesses and foam core thickness is shown exemplarily in Figure 3(c). The ratio between the top and bottom shell layer thicknesses (mean values for five specimen) ranges from 0.97 to 1.07 for the different experimental conditions. This indicates that the top and bottom shell layers have nearly identical thicknesses and the cross sections are almost symmetrical showing that the foam core is located right in the center. Contrary to the CBA concentration, significant influence is observed for the desired weight reduction. With increasing weight reduction from 5% to 10%, the shell layer thickness decreases and the foam core thickness increases from around 30% to 60% of the total cross-sectional area. By using the low pressure foaming method, the shot volume and therefore the injected amount of Bio-PC decrease with increasing weight reduction. This leaves more space in the cavity for foaming causing thicker foam cores. Similar results can be found in the literature [20–22].

Mechanical properties were measured in terms of tensile and three-point bending behavior, which is presented in Figure 4. The nonfoamed Bio-PC behaves ductile, similar to conventional BPA-based PC. In Figure 4(a), a strong decrease of the tensile elongation is found for the injection-molded Bio-PC foams in comparison to the nonfoamed Bio-PC.

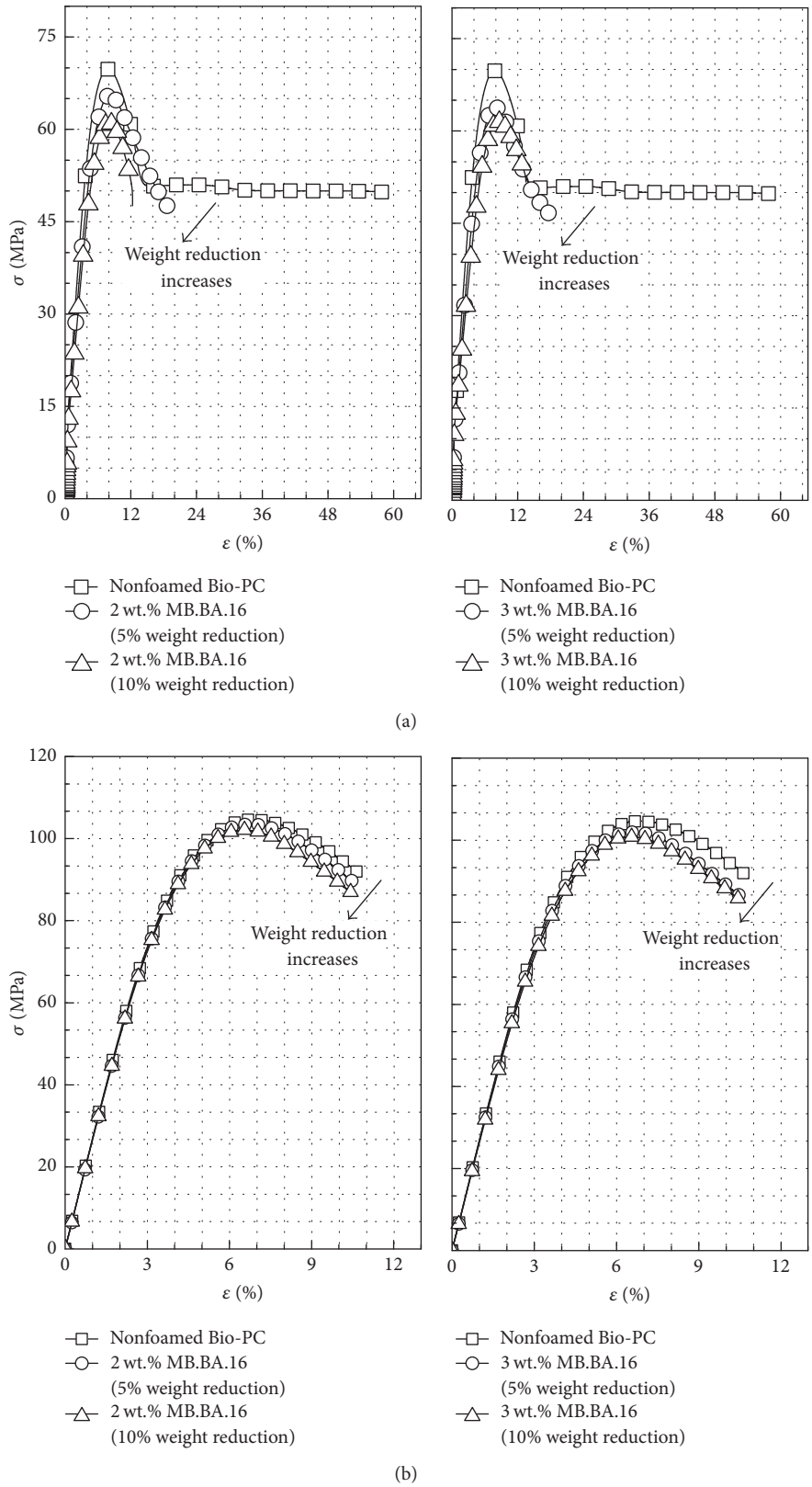


Figure 4: (a) Tensile curves of nonfoamed Bio-PC and foamed Bio-PC and (b) three-point bending curves of nonfoamed Bio-PC and foamed Bio-PC (2 wt.% and 3 wt.% CBA; 5% and 10% weight reduction). Graphs show the mean values recorded from five specimens tested.

Table 2: Specific mechanical tensile and bending properties of nonfoamed and foamed Bio-PC (the weight of the nonfoamed Bio-PC multipurpose test specimen is 13.53 g).

Property		Bio-PC	Bio-PC foams			
CBA concentration	(wt.%)	0	2	2	3	3
Weight reduction	(%)	0	4.9	11.2	5.1	10.6
Density	($kg\,m^{-3}$)	1363 ± 1	1296 ± 3	1211 ± 18	1293 ± 6	1219 ± 10
Specific tensile modulus	($MPa/(kg\,m^{-3})$)	1.98 ± 0.05	1.95 ± 0.07	1.92 ± 0.10	1.97 ± 0.10	1.91 ± 0.05
Specific tensile strength	($kPa/(kg\,m^{-3})$)	52.0 ± 0.4	50.0 ± 0.4	49.1 ± 1.3	49.4 ± 0.3	49.3 ± 0.8
Specific bending modulus	($MPa/(kg\,m^{-3})$)	1.96 ± 0.01	2.03 ± 0.01	2.13 ± 0.03	2.03 ± 0.01	2.12 ± 0.01
Specific bending strength at F_{max}	($kPa/(kg\,m^{-3})$)	77.0 ± 0.0	79.5 ± 0.0	83.1 ± 0.9	78.3 ± 0.4	82.1 ± 0.5
Specific bending strength at 3.5%	($kPa/(kg\,m^{-3})$)	60.1 ± 0.3	62.4 ± 0.2	66.0 ± 0.4	62.2 ± 0.2	64.9 ± 0.3

In addition, tensile strength and tensile stiffness as well as bending strength and bending stiffness decrease slightly. The reduction is less pronounced in case of bending (Figure 4(b)) due to higher resistance of the nonfoamed shell layers against deformation. There is no significant influence of the CBA concentration on the tensile and bending behavior. This is in good agreement with the morphologies observed in Figure 3, which show no significant difference between 2 wt.% and 3 wt.% MB.BA.16.

However, the achieved weight reduction clearly affects the mechanical properties due to the determination of the amount of nonfoamed material in the specimen. With increasing weight reduction from 0% over 5% to 10% the stiffness and strength as well as the ductility decrease continuously. In other words, the higher the degree of foaming, the lower the absolute mechanical properties.

On the other hand, it is well known that structural foams, for example, produced by injection molding, have excellent stiffness to weight and strength to weight ratios. That means the weight-related mechanical properties in terms of stiffness and strength are higher for the structural foam than for the nonfoamed part. Lots of studies have been conducted which confirm the excellent weight-related mechanical performance for many different polymeric structural foams [20, 23–26]. For example, Müller et al. [25] obtained 95% increase in relative flexural stiffness for 30 wt.% glass fiber reinforced PP while decreasing the density by about 28%. In addition, Müller [26] reported an increase in specific flexural stiffness of PP from about 25 $(N/mm^2)/(g/cm^3)$ to 40 $(N/mm^2)/(g/cm^3)$ while the density is reduced by about 49%. This typical result for structural foams also holds true for the Bio-PC foams, as can be seen from the specific tensile properties and specific bending properties summarized in Table 2. The density of the Bio-PC can be reduced by foam injection molding while maintaining or even increasing the specific mechanical properties in comparison to the nonfoamed parts. In particular, the specific bending properties steadily improve along with the density reduction and are noticeably better than the nonfoamed Bio-PC. In case of bending deformation, the nonfoamed shell layers are responsible for stiffness and strength whereas the centered foam core is close to the neutral axis. Therefore, the specific bending properties are significantly improved. In case of tensile load, the whole cross section of the specimen is uniformly deformed. Thus, the relatively large foam cells in the foam core act as voids causing a reduction in the specific tensile properties.

4. Conclusions

This contribution summarizes the first results on foam injection molding of isosorbide-containing copolycarbonate (Bio-PC) as potential long-term alternative to bisphenol A based polycarbonate (PC). The structural foams were produced by using the low pressure foam injection molding method. Two weight reductions, namely, 5% and 10%, and two concentrations of the chemical blowing agent (CBA), namely, 2 wt.% and 3 wt.%, were investigated. The weight reduction has a higher influence on the foam properties than the CBA concentration investigated in this study. All specimens consist of a central foam core with top and bottom shell layers of nearly identical thickness. A higher weight reduction leads to a higher degree of foaming, which is expressed in terms of increasing thickness of the foam core and decreasing thickness of the compact surface layers. The specific tensile and specific bending properties of the injection-molded Bio-PC are on the same level as the nonfoamed Bio-PC parts or even slightly higher. These results are in good agreement with the theory where structural foams provide excellent stiffness to weight and strength to weight ratios.

Further studies will be conducted using state of the art foam injection molding technologies such as the core-back technique or gas counterpressure method to guarantee a constant foam structure in the cross section of the foamed tensile bar over flow length. Impact properties and stress relaxation properties of Bio-PC foams will also be investigated.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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