Learnings about *design from recycling* by using post-consumer polypropylene as a core layer in a co-injection molded sandwich structure product

Markus Gall,⁎, Georg Steinbichler, Reinhold W. Lang

Institute of Polymeric Materials and Testing, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria

Institute of Polymer Injection Moulding and Process Automation, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria

**HIGHLIGHTS**

- Plastic crates with sandwich-structured multi-layer walls comprising a post-consumer recyclate core were made.
- Compositional analysis revealed foreign polymer contamination within the recyclate core resulting in incompatible inclusions.
- Despite contamination issues, incorporation of recycled content may improve short-term mechanical product performance.
- Defects in the recyclate core control impact performance of the entire sandwich structure regardless of tough skin layers.
- Design-from-recycling is discussed in the context of co-injection molded sandwich structures.

**ABSTRACT**

In pursuit of a circular economy of plastics, there is a need to use more recycled plastics for new products. Polypropylene (PP) constitutes a major fraction of post-consumer plastic wastes, and mechanical recycling is currently the most sustainable recovery strategy. Sandwich-structured multi-layer products with recyclate cores are a seemingly easy way to satisfy demands for recyclate utilization without compromising on product aesthetics. We present the case of a reusable plastic transport box with a recycled content of 45 wt% manufactured by a co-injection molding process. The box was characterized by spectroscopic and thermo-analytical methods. Mechanical performance was tested on both specimen and product levels. A comparison was made to transport boxes fabricated entirely from virgin or entirely from recycled PP, respectively. A number of contaminants including foreign polymers were identified within the recyclate core layer of the sandwich-structured material. While these contaminants had no deteriorative effect on stiffness-controlled performance, a strong influence on strength-controlled and impact-related properties was observed. We argue that the presence of inclusions of both polymeric and inorganic nature is an intrinsic quality characteristic of post-consumer recyclates. These need to be considered in any design-from-recycling philosophy to guarantee functionality, reliability, and safety of products with recycled content.

© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
1. Introduction

It is the declared goal of the European Commission to promote the transition to a circular economy of plastics [1,2] and to boost the utilization of recycled plastics for new products. By the year 2025, the annual amount of recyclates finding their way into new products produced in the EU should reach at least 10 million tons [1], up from about 4 million tons in 2018 [3]. In addition, the Commission has announced to propose mandatory recycled content requirements for specific product groups such as packaging, construction materials, and vehicles [2].

In 2018, 29.1 million tons of post-consumer plastic waste were collected in the EU28 + 2, i.e. the EU (including the UK at that time), Norway, and Switzerland. About 9.4 million tons (32.5%) of this amount were sent to recycling facilities and roughly 4 million tons of recyclates were used to make new products in the EU28 + 2 [3]. These plastic recyclates were predominantly used in the building and construction sector, for packaging applications, and for agricultural purposes with regards to tonnages processed [3]. However, the average recycled content, i.e. the ratio of recycled post-consumer plastics to virgin plastic resins used in a given year in a specific economic sector is still very low. With the notable exceptions of the agricultural sector (20%) and the building and construction sector (14%), the share of recyclate use in other market segments such as automotive, household and leisure goods, and packaging is at 5% or even lower [3]. Hence, recyclates will have to enter new applications and markets in order to meet the EU's declared goal of the European Commission to promote the regenerative use of recycled plastics is promoted by regulatory action, corporate marketing strategies, and public pressure, many of these new markets for recyclates pose more stringent performance requirements [12,13], demand adherence to tight technical specifications [14], and might even require compliance with specific regulations such as in food-contact applications [4,15,16]. Recycled plastics, however, often suffer from deteriorated properties [17]. Putting recycled content into the core layer of sandwich-structured multi-layer products is a seemingly easy way to satisfy demands for recycle utilization without compromising on product aesthetics and other surface-related performance characteristics [18-23].

1.1. Co-injection molding as a means to incorporate recycled content

Co-injection molding is a technique that allows to produce plastic parts with a sandwich structure composition where one material forms the core and the other material the skin layers [23]. The process which is also known as dual injection molding or sandwich molding may be performed in a sequential manner where the skin material is injected first, filling the mold only partially. Then the core material follows and completes the mold filling and compaction by displacing the skin and pressing it against the cavity walls. In another version, the two melts may be injected simultaneously during the filling phase to avoid switch-over marks that might arise from sudden changes in volumetric melt flow. The higher complexity of co-injection compared to conventional injection molding confers a number of consequences for the performance of the manufactured part. Seldén [20] analyzed the influence of different molding parameters including skin and core temperature as well as core content during co-injection of polyamide 6 and polybutylene terephthalate. While a strong correlation of mechanical properties such as flexural and impact strength with the skin-core distribution was observed, the prime determinant for a constant core thickness was found to be the core temperature [20]. Different combinations of PP and short glass fiber reinforced polypropylene (PP-GF) in co-injection molding were investigated by Messaoud and co-workers [21]. They found higher flexural modulus values for co-injected specimens with both skin and core made of PP-GF than compared to conventionally injection molded PP-GF specimens. This was attributed to enhanced orientation of the fibers in co-injection molding. Nagaoa and co-workers [22] investigated the influence of processing parameters such as injection speed, cylinder temperature (of the core material), and mold temperature on tensile and flexural strength of co-injection molded specimens made of PP homopolymer and copolymer pairings. They concluded that the temperatures of core and mold could be used to influence the mechanical properties of such co-injected sandwich moldings, while the importance of the injection speed was found to depend on the material combination used [22]. Karger-Koci et al. [23] conducted instrumented falling weight impact tests with co-injection molded plaques made of different combinations of PP grades and polymorphs in terms of α and β-crystalline phases. Furthermore, they underlined the potential gains in toughness due to using PP block copolymer skin layers [23]. While investigations on the influence of molding parameters, material pairings, and material modifications on co-injection molded sandwich structures are obviously available, this is not the case for recycled plastics. Despite the frequent referencing of co-injection molding being a solution for incorporating recycled content into products [18-23] an adequate investigation into the consequences of doing so is still lacking. Hence, it was the goal of this work to conduct a comparative study of a typical plastic product made from virgin PP, recycled PP, and a co-injected virgin/recycled sandwich structure respectively, and to discuss the findings from a design-from-recycling [24,25] perspective.

2. Materials & methods

2.1. Materials

The virgin plastic used in this study was a polypropylene (PP) block copolymer specifically designed for making transport packaging and technical parts. It contains a nucleating agent and anti-static additives and has a melt flow rate (MFR) of 12 g/10 min (2.16 kg, 230 °C), a density of 0.905 g/cm³, a tensile modulus of 1200 MPa. The material used for the recylate boxes was a recycled polypropylene (rPP) granulate derived from post-consumer collection via the yellow bag/yellow bin system. This PP recylate is of greyish color, has an MFR of 12 g/10 min (2.16 kg, 230 °C), a density of 0.920 g/cm³, a maximum ash content of 3 wt%, and a tensile modulus of 1200 MPa. Melt filtration with a mesh size of 250 μm was applied to this recylate.

Rectangular shaped solid wall boxes with integrated handles and stiffening ribs (see Fig. 1 (a) and Fig. 11) were made from virgin PP (virgin boxes) and mechanically recycled PP (recyclate boxes) by conventional injection molding. The boxes with sandwich-structured walls were produced by a specific co-injection molding process to generate a layered structure combining a PP recylate core (the same material that was used for the recylate boxes) and virgin PP skin layers. The skin layers were made from the virgin PP
described above with the addition of a white pigment master batch to increase skin layer opacity. The average wall thickness of all types of boxes was 2.5 ± 0.1 mm.

2.2. Sample preparation

All three types of boxes (virgin, recyclate, and sandwich) were produced with the same ENGEL duo 3660H/1560 W/450 combi injection molding machine. This hydraulically driven two-platen machine with a maximum clamping force of 4500 kN comprises two vertically stacked injection units for two-component injection molding. The machine producer’s proprietary process [30] was used for the production of the sandwich boxes, which is a co-injection molding process that was specifically developed to increase core content and eliminate switch-over marks on the part surface. A detailed process description can be found elsewhere [26,27]. The injection parameters used included a total shot volume of 1400 cm³ consisting of 608 cm³ core material and 792 cm³ skin material (resulting in a recycled content of 43.4% by volume), an injection time of 4.75 s, a holding time of 2 s, and a maximum holding pressure of 500 bar. The mold temperature was kept at 20 °C and the residual cooling time was 20 s. The overall cycled time was 48 s.

All specimens were punched out of the longer-side lateral walls of the boxes using a manually operable knee lever punch with a steel cutting die. The specimen geometry used was the type 5A specimen according to ISO 527-2 [28], which is a proportionally scaled miniaturized version of the typical dumb-bell-shaped multipurpose specimen (see Fig. 1(b)). These miniature specimens had an overall length of 76 mm, a width at the clamping ends of 12.5 mm, a length of the central narrow section of 26 mm, and a width of the narrow section of 4 mm. The specimen thickness was equivalent to the crate wall thickness of 2.5 mm.

2.3. Methods for compositional analysis

Compositional characterization was carried out by means of Fourier-Transform infrared (FTIR) spectroscopy and microscopy and complementary thermal analysis including differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA).

2.3.1. Infrared spectroscopy (ATR-FTIR)

Infrared spectra of the sample surfaces were acquired in the attenuated total reflection (ATR) mode using a Spectrum 100 spectrometer (PerkinElmer) equipped with a UATR module containing a ZnSe-coated diamond. The spectra were collected within a wavenumber range of 4000 cm⁻¹ to 650 cm⁻¹, using a resolution of 4 cm⁻¹, and a contact force of approximately 100 N. For each sample, 16 spectra were averaged. Cleaning with isopropanol and atmospheric background correction was done between measurements.

2.3.2. Infrared scanning microscopy

FTIR imaging of specimen cross-sections was carried out in the ATR mode using a Spotlight 400 FTIR microscope (PerkinElmer) equipped with a Germanium crystal and coupled with a Spectrum 100 FTIR spectrometer (PerkinElmer). Sections of 5A specimens of the co-injected sandwich material were fixed in transparent embedding resin and polished such that the individual layers of the sandwich structure became visible. Arbitrary locations within the recyclate core layer were selected and images with lateral dimensions of 100 × 100 μm² were recorded using a spectral resolution of 16 cm⁻¹, a spatial resolution of 1.56 μm, and two scans per pixel.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out with a DSC 8500 (PerkinElmer). Samples of 5 to 7 mg were cut out from 5A specimens such that they represented a full cross-section of the crate wall. They were placed in aluminum pans with holes and a lid. Triplicates were done for each material and an empty pan was used for baseline correction. The temperature program included an initial isothermal of 2 min at 20 °C, a first heating scan from 20 °C to 290 °C, a cooling scan from 290 °C to 20 °C, and a subsequent second heating scan from 20 °C to 290 °C. The heating and cooling rates were set to +10 K/min and −10 K/min, respectively [29]. Nitrogen was used as a purge gas at a flow rate of 20 ml/min.

2.3.4. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) was carried out using an STA 6000 (PerkinElmer). Samples of approximately 15 mg were cut out from 5A specimens such that they represented a full cross-section of the crate wall and were placed in ceramic crucibles. Triplicates were done for each material. After an initial isothermal of 2 min at 30 °C, a heating rate of 20 K/min [29] was applied between 30 °C and 775 °C and nitrogen was used as a purge gas at a flow rate of 20 ml/min.

2.4. Methods for mechanical characterization

Mechanical characterization included surface hardness measurements, monotonous tensile tests, and tensile impact tests. All tests were conducted with small-sized type 5A specimens according to ISO 527-2 [28]. The mechanical characterization on specimen level was complemented by a component-level investigation in the form of a simple box compression test that served as an indicator of overall product performance.
2.4.1. Hardness measurements

Surface indentation hardness was measured by means of a Shore durometer according to ISO 868 [30]. The Shore D setup was used. Hardness values were recorded 15 s after contact between indenter and specimen surface. Measurements from 5 randomly chosen locations on the specimen ends (the wide sections used for clamping) were averaged for each specimen and 3 specimens were tested for each material, i.e. virgin, recylcate, and sandwich.

2.4.2. Tensile tests

Tensile tests according to ISO 527-2 [28] were performed at a temperature of 23 °C and a relative humidity of 50% using a Z005 universal testing machine (ZwickRoell) equipped with hydraulic clamps and tactile strain gauges. A strain rate of 1%/min was applied for tensile modulus determination between 0.05 and 0.25% strain. Then the tests were continued with a strain rate of 50%/min until rupture. The specimens were stored under the testing conditions for at least 96 h prior to testing and 6 specimens were used per material and orientation.

2.4.3. Tensile impact tests

Tensile impact tests were carried out using a HIT 25P impact tester (ZwickRoell) following method A outlined in ISO 8256 [31] where the specimen is fixed in a clamping unit at the lower end of the pendulum trajectory. For the virgin PP samples, a 25 J pendulum and a 60 g anchor were used, whereas a 7.5 J pendulum and a 30 g anchor were used for both the recylcate and co-injected sandwich samples due to their lower impact strength. The tests were performed at a temperature of 23 °C and a relative humidity of 50%. Type 5A specimens according to ISO 527-2 [28] were used and no notches were introduced. The specimens were stored under the testing conditions for at least 96 h prior to testing. Five specimens were used per material and orientation.

2.4.4. Box compression tests

The produced crates were subjected to a simple box stacking and compression test without adhering to any specific standard. Three identical boxes were stacked on top of one another and placed between two horizontal parallel support surfaces in a compression testing machine. A compressive load was applied with a constant speed of 10 mm/min. The tests were conducted at room temperature of 23 °C. Force and displacement signals were recorded.

3. Results & discussion

3.1. Material composition

The ATR-FTIR spectra plotted in the upper part of Fig. 2 are typical PP spectra, however, they reveal some subtle differences between virgin PP, PP recylcate, and the skin layer of the sandwich structure material. The virgin PP resin (blue line in Fig. 2) exhibits a very broad absorption band above 3000 cm$^{-1}$ that appears together with another band at around 1600 cm$^{-1}$ (see magnification of region 1 in Fig. 2). In conjunction, these bands are indicative of water [32,33]. Anti-static and demolding additives which are present in this resin, are binding humidity from the ambient air owing to their polar chemical structure [34]. This explains the detection of surface-bound water. The spectra of the PP recylcate (black line in Fig. 2) and the skin layer of the sandwich structure specimen (red line) are rather pure PP spectra without adherent water. However, some peculiarities can be observed in wavenumber region 1 and 2 depicted in Fig. 2. In region 1, small peaks at around 1740 cm$^{-1}$ and 1650 cm$^{-1}$ can be observed in all spectra. The latter might indicate low-level contamination with polyamide [32] on the one hand. However, precise identification of the type of polyamide (e.g. PA6) in polyolefin recyclates requires more specific analytical methods such as liquid chromatography [35]. On the other hand, bands at around 1650 cm$^{-1}$ can sometimes be attributed to the presence of surface-bound additives such as fatty acid amide compounds that are frequently used as slip agents in PP film applications [36] or in plastic bottle screw caps [37]. For the latter, the transfer of legacy additive slip agents from post-use PE and PP bottle caps into recyclates made thereof is documented [38,39]. The absorption bands located between 1720 cm$^{-1}$ and 1750 cm$^{-1}$ are often actually the sum of several overlapping peaks [40] that originate from various compounds containing carbonyl groups such as aldehydes, ketones, and esters [32] that may be formed in the process of polyolefin oxidation [33,41]. Furthermore, if oxidative degradation can be ruled out as a source, ester group containing additives such as antistatic agents (e.g. glycerol monostearate
and related compounds [34]) may be the reason for such signals [42]. This is the case with the virgin PP skin layers of the sandwich structure material.

In region 2, the recyclate spectrum shows a pronounced doublet with maxima at 720 cm$^{-1}$ and 730 cm$^{-1}$, which is indicative of methylene rocking vibrations typically found in PE [32,43]. This indicates the presence of PE contamination, a commonly observed phenomenon in post-consumer polyolefin recyclates [44–49]. The spectrum representing the sandwich skin layer differs from the virgin PP spectrum especially in the spectral range below 750 cm$^{-1}$, where a strong and broad absorption band is found in the former. This is attributed to a titanium dioxide white pigment [42] of the master batch used to increase the opacity of the skin layer [34] in order to cover up the dark greyish recyclate core material underneath.

The in-depth spectroscopic analysis by means of ATR-FTIR scanning microscopy revealed the presence foreign polymer inclusions within the PP recyclate core of sandwich structure specimens. Sample images are shown in Fig. 3. Among those inclusions that were large enough for identification, mainly PE, polyamide (PA), and polyethylene terephthalate (PET) were found.

All of these polymers form discrete particles within the surrounding PP material due to the inherent incompatibility of most polymers [50]. In the present investigation the size of most disperse particles found ranged from 10 to 100 μm. However, this was an explorative characterization not aiming at statistically representative quantification of particle counts or size distributions. The DSC thermograms are depicted in Fig. 4, whereas the heat flow curves resulting from the second heating run are shown on the left (a) and those resulting from the cooling scan are shown on the right (b). Only one out of three curves is shown per material for reasons of simplicity and the curves have been shifted arbitrarily along the vertical axis to improve visibility. The virgin PP material, represented by the blue curve, reveals a single endothermal melting event with a peak temperature of 168 °C, which fits to a typical PP block copolymer [29]. The corresponding melting enthalpy was between 82 J/g and 89 J/g for three individual samples and indicates a degree of crystallinity of 40 to 43% for PP [29]. The recyclate samples, represented by the grey curve, revealed two distinct endothermal melting events with peak temperatures of 128 °C and 163 °C in the second heating run. These correspond to the melting of PE-HD and PP, respectively [29]. On average, a total enthalpy of melting of 97 ± 3 J/g was
measured in the temperature range between 60 °C and 170 °C, whereas the smaller peak of PE-HD accounted for about 7 J/g of these 97 J/g. Assuming a moderate degree of crystallinity of 60% for PE-HD and a value of 293 J/g for a hypothetically 100% crystalline PE [29], the measured value of 7 J/g would translate into roughly 4% PE-HD content in the recyclate samples. Polyolefin cross-contamination, i.e. a certain amount of PE in PP recyclates or vice versa, is a frequently reported phenomenon in post-consumer polyolefin recyclates [3,8,44–46,49]. Both PE and PP are used for a vast range of consumer products and packaging applications and they hence represent the major fraction of post-consumer plastic wastes [3,8–11]. Precise separation of PE and PP is not straightforward due to similar behavior in float-sink separation units [44,50].

The co-injection molded sandwich material, represented by the red curve in Fig. 4(a), exhibited a very similar pattern of two distinct melting peaks with average peak temperatures of 127 °C and 163 °C for the PE-HD and the PP phase, respectively. In addition, however, the PE-HD peak is somewhat smaller and the PP melting peak of the sandwich samples contains a shoulder at about 167 °C indicating overlapping peaks. The situation becomes clearer upon inspection of Fig. 4(b) which depicts the cooling curves. The recyclate sample exhibits a prominent PP crystallization peak at 124 °C next to a smaller peak at 116 °C, which is attributed to the crystallization of the PE-HD phase [29]. Contrary to that, the sandwich structure sample shows three exothermic crystallization events. The cooling and crystallization curve of the sandwich structure sample is hence a superposition of the virgin and the recyclate curves and the corresponding average peak temperatures are 130 °C, 124 °C, and 116 °C. The higher recrystallization temperature of 130 °C of the virgin PP fraction can be attributed to the presence of a nucleating agent that tends to shift crystallization to higher temperatures [29].

The TGA curves depicted in Fig. 5 illustrate the pyrolysis process of samples of virgin PP, PP recyclate, and the co-injection molded sandwich structure material. Again only one representative curve is plotted per material. All curves exhibit a single decomposition step with pronounced loss of mass starting at temperatures above 300 °C. There are no signs of premature degradation or significant emissions of volatiles. However, upon completion of polymer degradation at above 500 °C, those samples with recycled content, i.e. the PP recyclate and the sandwich structure material, exhibit a pyrolysis residue of up to 2 wt%. In contrast, the virgin PP produces significantly less pyrolysis residue. This indicates a small amount of inorganic contamination which might be assigned to the presence of legacy fillers in the recyclate and the sandwich samples. This interpretation is in line with the ash content and the density value of the PP recyclate used in this work which are stated with up to 3% and 0.92 g/cm³, respectively [51]. These values are somewhat higher than typically expected for a neat, unfilled PP resin [29,52]. Traces of legacy additives and fillers are a characteristic feature of many post-consumer recyclates [38,44,48,53]. The fact that the level of inorganics is even higher in the sandwich structure sample than in the recyclate alone is attributed to the use of an inorganic white pigment master batch for the virgin skin layer of the sandwich structure material (see materials section and discussion of ATR-FTIR results).

3.2. Mechanical performance

In this section, selected indicators of mechanical performance are discussed. The sections 3.2.1, 3.2.2, and 3.2.3 deal with mechanical properties determined at the specimen level, whereas section 3.2.4 deals with mechanical performance on the product level.

3.2.1. Surface hardness

The Shore D surface hardness values of specimens taken from the walls of boxes made from virgin PP and the co-injected sandwich structure material showed essentially identical hardness values. They are 58 ± 1.5 for virgin PP and 59 ± 1.2 for the sandwich structure, respectively. The recyclate samples reached an average value of 63 ± 1.2 indicating higher surface hardness. The typical range of Shore D hardness values of virgin PP resins extends from 62 to 74 for many commercial grades according to one source [54]. However, the precise value depends strongly on the molecular morphology such as the amount of isotactic segments and the degree of crystallinity of the respective PP grade [52]. In the present case, the investigated virgin PP is a block copolymer with a moderate degree of crystallinity of about 40%. Furthermore, Shore D hardness values reported for PP recyclates are typically somewhat lower and may range from 52 to 64 [54]. A graphical representation of the values measured is depicted in Fig. 5 in the supplementary materials.

3.2.2. Mechanical performance under monotonic tensile load

The tensile test results are summarized in Fig. 6. All stress-strain-curves are plotted together in Fig. 6(a), where solid lines denominated with ° represent specimens that have been punched out such that their longitudinal axis was oriented parallel to the main melt-flow direction inside the box wall during injection molding. Dashed lines denominated...
with 90° represent specimens oriented perpendicular to the main melt-flow direction inside the box wall. Numerical values of tensile modulus, tensile strength (here equivalent with the yield stress), and strain-at-break are compiled in Fig. 6 (b), (c), and (d), respectively.

The stress-strain curves in Fig. 6 (a) demonstrate the higher tensile strength of the PP recyclate compared to both the virgin PP and the sandwich structure specimens. On the other hand, the virgin PP specimens achieved by far the highest strain values, regardless of the specimen orientation. Specimens with recycled content, i.e. both the recyclate and the sandwich structure specimens, differed from the virgin PP specimens in two key aspects. First, the overall amount of strain that can be accommodated is significantly lower and the relative magnitude of the corresponding scatter bands of the strain-at-break values (Fig. 6 (d)) is much higher. The second aspect relates to the shape of the stress-strain curves in the post-yield regime. While all curves of virgin PP extend to high strain values and even exhibit a slight tendency towards strain hardening, i.e. increasing stress values with increasing strain in the post-yield regime, the specimens with recycled content showed no such behavior. In fact, the stress-strain-curves of recyclate and sandwich structure specimens tend to decline relatively rapidly after passing the yield point, occasionally with a short plateau.

Furthermore, the tendency towards high scatter and especially an inhomogeneous deformation behavior of PP recyclate and sandwich structure specimens is evident in Fig. 6 (a). Several grey and red stress-strain-curves exhibit a step-wise, gradual decline in the post-yield regime that is macroscopically associated with fibrillation of the necked-in specimen section and progressive rupture of highly strained thin-layer-like ligaments (see Fig. S2 in the supplementary materials). Fibrillation and formation of layer-like fracture surface has been connected with the presence of PE inclusions in specimens made of recycled PP [48]. Similar observations are reported by van Belle et al. [55] with regards to pure virgin PE-HD, pure virgin PP, and blends of PE-HD and PP with PP being the dominant component and PE-HD acting as a model contaminant. This could be the case in the present study as well, since cross-contamination with PE was detected (see Figs. 2, 3, and 4).

The tensile modulus of all tested materials is roughly around 1200 MPa. Any differences that are bigger than the scatter bands indicate a very small tendency towards higher modulus values of 0°-specimens that are oriented in melt-flow direction. Furthermore, slightly higher modulus values were obtained for the PP recyclate specimens. Interestingly, the modulus of the sandwich structure specimens does not follow a simple rule of mixture [49] of virgin PP and PP recyclate values. This may be a consequence of the more complex evolution of the temperature profile inside co-injection molded sandwich structures compared to conventional injection molding. Moreover, the obvious differences in re-crystallization behavior of skin and core and the associated differences in temporal and spatial release of crystallization enthalpy might add to this observation.

The strength values depicted in Fig. 6 (c) draw a more concise image of the differences between virgin PP, PP recyclate, and the sandwich specimens. The recyclate reached the highest tensile strength values with up to 28 MPa, while virgin PP and sandwich structure specimens achieved values up to 23 MPa and 24 MPa, respectively (also compare Fig. 6 (a)). Again, a moderate tendency towards higher tensile strength of 0°-specimens can be observed.

3.2.3. Mechanical performance under impact tensile load

The results of the tensile impact tests are depicted in Fig. 7. While orientation of the specimens generally seems to have no significant
fluence on toughness, there is a pronounced difference between the materials. Specimens taken from the virgin PP boxes achieved an unnotched tensile impact strength of over 900 kJ/m². Specimens with recycled content, i.e. both the PP recyclate and the sandwich structure specimens, fell considerably short of that value with a tensile impact strength between 175 and 200 kJ/m² only. Low or moderate toughness is per se not surprising for post-consumer recyclates [56], although other authors have reported beneficial effects on notched impact strength of PP with a certain amount of PE-HD content [57]. However, it is striking that the sandwich structure specimens showed no advantage over the PP recyclate despite having skin layers of rather tough virgin PP copolymer. Hence, there seems to be no benefit of using rather tough virgin skin layers, at least in terms of tensile impact performance. The fact that the average sandwich structure values are actually even lower than the average PP recyclate values is neglected due to the fact that the corresponding scatter bands greatly overlap.

Another relevant observation concerns the relative standard deviation of the tensile impact strength. For virgin PP, this parameter is between 11% and 15% of the nominal value for the 0° and 90° orientations, respectively. Contrary to that, the relative standard deviations for PP recyclate and the sandwich structure material are substantially higher and range from 41% to 43% and from 31% to 56%, respectively. The reason for this pronounced difference is most likely the presence of impurities and defects inside the PP recyclate. This holds true for both the actual PP recyclate specimens and the core layer of the sandwich structure specimens. In every single instance, the fracture of PP recyclate as well as sandwich structure specimens occurred in a quasi-brittle manner leaving behind rather flat fracture surfaces and exposing major inclusions in the recyclate layer. On the other hand, the virgin PP specimens exhibited clear signs of plastic deformation such as stress whitening, neck formation, and fringed fracture surfaces. All of these are associated with energy dissipation resulting in higher toughness. Examples of the specimens after testing are shown in Fig. 8 and fracture surfaces with inclusions are depicted in Fig. 9.

Intriguingly, inclusions that are significantly larger than the stated melt filter mesh size of 250 μm [51] were found. The scale bar depicted in the individual images shown in Fig. 9 (a) to (d) is 500 μm long. The inclusions present in these fracture surfaces are roughly about that size. Furthermore, the images Fig. 9 (a) and (b) as well as (c) and (d) each show the complementary fracture surfaces of the same PP recyclate or sandwich structure specimen, respectively. Evidently, the inclusions not only worked as crack initiators due to stress concentration and incompatibility with the surrounding PP matrix. In the two cases depicted in Fig. 9 (a) and (b) and in Fig. 9 (c) and (d) it was actually the inclusion itself that broke apart since complementary pieces are embedded in the facing fracture surfaces.

3.2.4. Mechanical performance in monotonous box compression tests

The box compression test is a standard product test for rigid transport packaging items and it is a simple way to illustrate the vertical loading capacity of stacked boxes as well as typical failure mechanisms. A photograph of stacked sandwich structure boxes under compressive load close to the end of the test is shown in Fig. 11. The individual boxes exhibit a loss of stability through buckling of the lateral walls and buckling and crimping of the stiffening ribs including beginning localized plastic deformation. All tested types of boxes showed the same deformation behavior. The corresponding load-displacement curves are depicted in Fig. 10 (a). Interestingly, the recyclate boxes reached an average maximum load of 16.2 kN, thereby clearly outperforming both the virgin PP boxes and the sandwich structure boxes, which achieved 13.5 kN and 13.7 kN, respectively (see Fig. 10 (b)). This finding is in good agreement with the results of monotonous tensile tests.
discussed in Fig. 6. There, recyclate specimens showed significantly higher tensile strength and load carrying capacity in the pre-yield and yield regime than virgin and sandwich specimens (acknowledging the fact that the response of polymeric materials to compressive and tensile loads is not equivalent).

A potential drawback of the recyclate boxes, however, is their tendency to produce higher standard deviations. While the load-displacement curves of three separately conducted compression tests with virgin boxes are essentially congruent, the curves of the recyclate boxes demonstrate great variability in the peak load region and the deformation behavior after surpassing the peak load (compare Fig. 10 (a)). This behavior is also reflected in the magnitude of the standard deviation values depicted in Fig. 6 (c) and Fig. 10 (b). Interestingly, this is the case despite the fact that the amount of the core layer material in locations such as the stiffening ribs of the boxes is typically very low. The specific cavity filling behavior in co-injection molding leads to a dominance of skin material at flow path ends [19]. Nevertheless, these tests demonstrate that the combination a recyclate core layer with a skin material that would otherwise constitute the entire crate can lead to comparable or even improved product performance in terms of stacked load carrying capacity.

3.3. Aspects of design from recycling

When it comes to product design in the context of a circular plastics economy, a strong emphasis is typically put on the concept of design for recycling, an approach that intends to optimize a product’s recyclability in the end-of-life phase [58]. However, in order to sustainably promote the use of recycled plastics and to increase the recycled content in new plastic products in the long run, it is necessary to elaborate complementary concepts of design with recyclates [24,25] or design from recycling.

Only when the distinctive features and peculiarities of recycled post-consumer plastics are adequately accounted for during product and process design, it will be possible to bring recyclates into more diverse and more demanding applications. Accordingly, the data on material composition and mechanical performance discussed above were summarized into two aspects that are of relevance for co-injection molded skin-core sandwich structures with recycled content.

3.3.1. Aspects regarding processing behavior

The thermal analysis discussed in conjunction with Fig. 4 revealed differences in melting and crystallization behavior of virgin and recycled PP as well as the presence of a certain fraction of PE-HD within the...
recycled PP material. This implies some consequences for processing compared to manufacturing the same part from virgin PP alone. In the present case, the total enthalpy of melting of the PP recyclates was already markedly higher than that of the virgin PP, despite the fact that the degree of contamination with PE-HD was not extensively high. Since PE-HD has a high melting enthalpy compared to PP [29], this contamination issue has the potential to increase the energy demand of the plasticizing unit of the injection molding machine. This might not be a very significant problem, because adequate equipment and processing parameters can be chosen. However, the inherent variability of PCR materials including varying levels of PE contamination might negatively affect efforts in energy efficient processing. Furthermore, a high level of PE-HD (or other low-melting polymers) might lead to longer cycle times in (co-)injection molding by elongating the cooling time and postponing earliest possible demolding. As seen in Fig. 4 (b), PE-HD typically crystallizes at lower temperatures than PP. In addition, PE-HD releases more crystallization enthalpy than PP on a mass normalized base [29] generating a higher demand for cooling. Moreover, it has a lower heat deflection temperature [54] leading to later demolding, and a higher shrinkage than PP [52,54]. None of these factors necessarily hampers quality production, especially when polyolefin cross-contamination is at a low level. Nevertheless, each of these factors at least has to potential to cause troubles when part designers and producers are not aware of them. Again, the tendency of feedstock and property variability in post-consumer recyclates has to be emphasized. In addition to efforts of running part production with quality assured PCR materials [6,7,12,13], strategies of material modification could be pursued to adjust processing properties. Nucleation of post-consumer PP is possible with additive loadings significantly below 1% and polymorphic modification is seen as a promising strategy in high value
3.3.2. Aspects regarding the criticality of defects

It has been highlighted that the utilization of a PCR material as the core layer of a co-injection molded sandwich structure can have very diverse effects on the mechanical performance of the respective part. Direction, i.e. positive or negative, and magnitude of these effects depend on the nature of the mechanical property in question. With regards to stiffness-controlled performance characteristics, such as tensile modulus or the product performance in a box compression test, the use of a PCR material may have a positive effect leading to higher nominal values. In fact, even performance improvement can be achieved by way of incorporating a suitable PCR grade in cases where a stiffness-related material parameter, or more generally speaking, the material response to monotonous and quasi-static loads is prime design and dimensioning factor. However, in the case of strength-controlled and especially toughness-controlled performance characteristics, the situation is not that clear. It was shown here, that the tensile impact strength was essentially controlled by the presence of defects alone. Whether tough virgin PP skin layers were present or not did not considerably change the poor tensile impact strength of samples with recycled content. It can be argued that the presence of inclusions that act as defects has to be thoroughly considered for any scenario in which the material behavior in the post-yield regime and the response to dynamic, cyclic, long-term or even superimposed loads is of relevance [60]. Due to the presence of inclusions and the potentially significant size of such defects, further research work, perhaps based on concepts of fracture mechanics, is needed to properly deal with the consequences for ultimate structural performance in terms of strength, toughness, and durability.

4. Conclusion

Globally, but especially in the European Union, considerable efforts are being made to promote the use of recycled post-consumer plastic wastes for the manufacturing of new products. For many applications, adequate strategies of design-from-recycling have to be found to guarantee safety, reliability, and functionality of the resulting product with recycled content. This requirement even extends to cases where post-consumer recylcate is put into the core layer of sandwich structure materials with virgin material skin layers. Besides a number of aspects that are relevant from a consumer experience point of view or from a processing point of view, it is the mechanical properties that deserve special attention. The present case of a co-injection molded sandwich structure transport box demonstrated that the use of recycled content in the core layer can lead to improvements in certain performance categories that go hand in hand with the deterioration of other properties. While increased stacked load carrying capacity was realized by incorporation of recycled PP into the core layer, the presence of defects and inclusion in that very same core layer led to a dramatic reduction in tensile impact strength. Future work should focus on ways to generate recyclates that are less affected by contamination and incompatibility issues. Specific emphasis should be put on developing adequate design approaches, including fracture mechanical methods, that can cope with defects and lead to safe and efficient plastic products with recycled content.

Declaration of Competing Interest

Georg Steinbichler has been working for Engel Austria GmbH who developed the proprietary injection molding process that was used to fabricate the multi-layer boxes analyzed in this work.

Acknowledgements

The authors express their gratitude to the Transfercenter für Kunststofftechnik GmbH (TCKT, Wels, Austria) for conducting box compression tests. The efforts of Cornelia Marchfelder and Ing. Alexander Lovas (both Johannes Kepler University Linz, Austria) in preparing FTIR-microscopy images and in assisting with tensile impact tests, respectively, were highly appreciated. This research did not receive any grant from funding agencies in the public, commercial, or not-for-profit sectors. The publication was supported by Johannes Kepler Open Access Publishing Fund.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2021.109576.

References


M. Gall, G. Steinbichler and R.W. Lang Materials and Design 202 (2021) 109576

M. Gall, G. Klammer, R. Rathner, R.W. Lang, G. Steinbichler, Recycling that gets under the skin, Kunststoffe International 05 (2020) 30–33.


