

Differential scanning calorimetry—a powerful tool for the determination of morphological features of the recycled polypropylene

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Abstract

In order to be recycled, polymers with different molecular masses, designed to be initially processed by different technologies such as thermoforming, injection or blow molding, are collected together. The melt viscosity of this material mixture will depend on the ratio of polymers having different molecular characteristics. The possibility of re-processing implies the use of higher range of temperature or the use of different additives to adjust the melt viscosity. In these conditions, the quality of recycled goods could be affected. This study presents the results obtained by differential scanning calorimetry analysis of some polypropylene-based samples coming from the real waste stream collection (conventional samples) as well as of selected polymers from this stream based on the processing technology and of different brand packages from each of the above-mentioned classified fractions. Based on the thermal data ($T_{\rm m}$, $T_{\rm c}$, $\Delta H_{\rm m}$, $\Delta H_{\rm c}$ and the melting and crystallization curve characteristics), morphological features of the recycled polypropylene, such as crystallinity degree of the initial recycled and re-crystallized polymers (X_m, X_c) , melting and crystallization rates (v_m, v_c) , lamellae thickness, and number of tie molecules, were determined, and the prediction of the maximal Young's modulus was made. This study evidenced that processing technology of the polymers in fresh state or as recycled material strongly influenced the product morphology and, as a consequence, the predicted mechanical properties. By comparing the conventional recycled polymers with the injection-molded mix of virgin polymers, the first one exhibited a lower crystallinity with about 22%, approximately the same lamella thickness, the crystals' polydispersity higher with about 10% and the Young's modulus lower with about 22%.

Keywords Polypropylene · Wastes · Processing technologies · DSC · Crystallinity · Lamella thickness · Young's modulus

Introduction

Recycling of polypropylene (PP) packages is a very complex and difficult task, due to the very large number of variables affecting the recycled polymer properties. The

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high differences between the properties of the initial polymer used in products obtaining, related to the molecular masses and their distribution, the crystallinity degrees, the type of the dominating crystalline form, the lamellae thickness, the spherulites' number and dimension, the amorphous phase characteristics, the number of tie molecules, the entanglements, as well as the proportion of the recycled products mixed in the separated fraction, have a strong influence on the recycled polymer features [1].

Also, polymer processing by extrusion, blow molding, thermoforming or injection molding, at different temperature ranges and under different shear or compressive forces, will determine supplementary alteration of the polymer features: change in the crystallinity degree and crystallization form (cylindritic crystal formation) and possible thermal degradation evidenced by carbonyl,

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carboxyl groups and double-bond formation [2–4]. The obtaining products have also required specific features depending on the type of the packaged goods and in correlation with the different brand characteristics. This means that some packages have to be transparent, other have to be dyed in different colors, other have to be resistant to microwaves and temperature, other have to be resistant to oily, aqueous or alcoholic contacts, other have to be resistant to UV irradiation, other must exhibit high impact or strength resistance. To obtain the requested properties, additives addition (dyes, pigments, thermal or antioxidant stabilizers, nucleating agents), PP copolymerization or blending of PP with random (RPP) or block (CPP) copolymers with ethylene or butylene in different proportions are necessary [5].

Furthermore, the impact of the life cycle on the polymer features has to be taken into account. This means we have to consider its possible degradation under the following factors: UV–Vis and/or microwaves irradiation, temperature and moisture variation, shelf period, the period between the waste drops and collection, fungal and microbial attacks.

Separation of the polypropylene fraction from the polymer waste stream, even in a narrow density range, or well selected by near-infrared (NIR) sensors, will include the results of all the above-mentioned factors that affected the polypropylene packages.

Further, the polymer re-processing will contribute to an extra polymer feature alteration by modification of the mix composition (mixture of PP homopolymer with different types of copolymers, mixtures of additives, mixtures of PP with different molecular masses and distribution), by a partial oxidation of the polymer, by the possible cross-linking reaction between the functional groups resulted from the degradation processes, by modification of the crystallinity degree and the crystallization types, by possible phase separation and also by additives concentration change (mainly their dilution or possible reaction between them).

All these aspects will be reflected in the recycled polymer properties.

A lot of efforts were devoted to study the influence of the initial polymer features on the product characteristics, on the environmental factors affecting the properties of the recycled polymer and on the methods of collection, selection and separation of the polymeric fraction on the recycled product quality but no or very low attention was paid to check the influence of the mixing of polymers (PP) processed by different technologies on the final properties of the recycled product.

Processing by different technologies means in fact different initial properties of the polymer (different molar mass: lower for injection molding and higher for thermoforming and blow molding), different additives and different thermal and mechanical regimes are applied.

This study presents the results obtained by differential scanning calorimetry (DSC) analysis of some types of polypropylene (PP) samples obtained from the real waste stream collection (conventional samples) as well as of selected polymers from this stream based on the processing technology (blow-molding mix, injection-molded mix and thermoforming mix) and of different brand packages from each of the above-mentioned classified fractions. The conventional sample was analyzed before and after labels' and impurities' separation. Also, the sample in pellet form or extruded in granule form was analyzed. Based on the thermal data, morphological features of the recycled polypropylene were determined, and the prediction of the maximal Young's modulus was made.

Materials and methods

Materials

Conventional sorted post-consumer PP was provided by SITA Suez Environnement Company, Rotterdam, the Netherlands, in 2015. This fraction was separated from household plastic waste by using NIR identification technique. After sorting by using a NIR sensor, the material streams were inspected manually, and impurities and films were removed from the stream.

Based on the specific characteristics of the package forms, the obtained conventional PP fraction was classified in sub-fractions depending on the processing technology.

The average distribution of the different types of PP was determined to be: 58% thermoformed and blow-molded PP; 42% injection-molded PP from which 52% was white PP, 29% was transparent PP and 19% had other colors.

In the separated sub-fractions, there were identified packages with different compositions (mixture among PP and PP copolymers having ethylene groups, block or random distributed on the chain) that were coded as it is specified in Fig. 1.

After separation from post-consumer stream, the conventional PP fraction was cleaned by washing with water and a small amount of liquid detergent (Persil for colored clothes, to avoid the presence of peroxides), at 90 °C, for 50 min, by using a household washing machine of type Indesit WIA 121, using the standard washing program number 1 and stopping the washing process before centrifugation. The polymer fraction was washed within a jute bag to prevent the ingress of small pieces of plastic to the water exhaust system of washing machine.



After washing, the products were manually cut, having the possibility to separate the labels. Also, aluminum residues were removed during this step.

Then, the fractions were shredded at 10-mm particles size, this one being optimal for the second cleaning step. Washing process is more effective at the flake level by comparing with the product level. An industrial mixer-type Hobart A200 was used. One-kilogram plastic flakes, 4 L of water at 80 °C, 30 mL detergent (neutral, containing sodium lauryl sulfate) were used for washing process, at a rotation speed of 107 rpm for 10 min. After mixing, a supplementary portion of 10 L of water was added into the washing machine, facilitating the separation process of PP, and impurities are still present in the fraction. The impurities were separated by sieving with a 2-mm mesh size, and then, the flakes were rinsed by water at 80 °C and dried overnight in the laboratory.

Aiming to eliminate the impurities, as much as possible, the polymeric flakes were then introduced into a spinning machine (Hermion BV, Waalvijk, the Netherlands) that allows elimination of smaller particles than 2 mm, by using a sieve of 2 mm mesh and 3000 rpm rotation speed. After this, the polymeric fraction was dried in an oven at 60 °C for 22 h, including ventilation.

A second size reduction was performed by using the same shredder and a sieve with mesh size of 6 mm, in order to easily homogenize the mixture of polymers.

Homogenizing step was carried out by using a co-rotating twin screw extruder (ZSK 18 MEGAlab from Coperion) to obtain granules. These make easier injection molding. The temperature profile for compounding process is presented in Table 1.

The reference samples were obtained following the producers' recipe, starting from the virgin polymers as it is presented in Table 2, by injection mold with or without extrusion. The composition was similar to packages obtained both by injection mold and by thermoforming, and the composition of the mix of these fractions was similar to the conventional post-consumer stream (Table 1).

Methods of analysis

DSC method was used to determine the thermal features of the conventional PP fractions and sub-fractions and to compare them with those of the reference samples.

Netzsch DSC 200 F3 Maia[®] instrument, with a heat flux system sensor, the measurement range from 0 to \pm 600 mW, temperature accuracy < 0.1 K, enthalpy accuracy < 1%, was used. The thermal regime applied during sample analysis was as follows: (1) cooling from the room temperature to -20 °C with a rate of 10 °C/min, (2) maintaining the sample at -20 °C, for 5 min to equilibrate it, (3) heating up to 230 °C with a rate of 10 °C/min, (4) maintaining the sample at 230 °C, for 5 min to equilibrate it; (5) cooling the sample up to -20 °C with the rate of 10 °C/min; (6) heating with the same rate of heating up to the room temperature. The measurements were taken in nitrogen flowing atmosphere.

Samples with an average mass of 6 mg were used in DSC analysis, and the scans were made in triplicate.

Fraction	Type of fraction	<i>T</i> 1/°C	<i>T</i> 2/°C	<i>T</i> 3/°C	<i>T</i> 4/°C	<i>T</i> 5/°C	<i>T</i> 6/°C	<i>T</i> 7/°C	<i>T</i> 8/°C	<i>T</i> 9/°C	Rotation speed/ rpm
80% HP + 20% CP	Recycled pure product										
	Recycled pure product + Labels/ink										
77% HP + 19.4% CP + 3% white	Recycled pure product										
	Recycled pure product + Labels/ink	155	170	170	175	175	180	180	185	190	120
50% HP + 50% CP	Extruded virgin										
	Recycled pure product										
	Recycled pure product + Labels/ink										
70% HP + 30% CP white	Extruded virgin										
	Recycled pure product (microwave)										
	Recycled pure product										
70% HP + 30% random CP blue	Extruded virgin	155	170	180	190	200	210	220	230	240	150
50% injection (50% HP + 50% CP) + 50% thermoformed) 70% HP + 30% random white)	Extruded virgin										
Persil bottles	Recycled pure product										

Table 1 Temperature profile for compounding process for reference samples

Table 2 Reference sample codes, composition and processing

Sample code	Sample characteristics
4A	PP100% (HP)
6A	70% HP + 30% RCP blue
7A	70% HP + 30% RCP white extruded
8A	70% HP + 30% RCP white not-extruded
9A	50% HP + $50%$ BCP extruded

Results and discussion

Starting from the idea that mixing the polymers with different molar masses will strongly affect the thermal characteristics of the sample, the following data were collected from the DSC curves:

- the melting and re-crystallization temperatures ($T_{\rm m}$ and $T_{\rm c}$),
- the melting and crystallization curve characteristics (onset, endset, width at 37% and height)
- the heat of melting and crystallization $(\Delta H_{\rm m}, \Delta H_{\rm c})$

By using these data, the following polymer features and transition characteristics were calculated:

• the crystallinity degree of the initial recycled polymer (from the melting curve) (X_m) and that of the re-

crystallized polymer (from the crystallization curve) (X_c) ,

- melting and crystallization rates $(v_{\rm m}, v_{\rm c})$
- lamellae thickness
- number of tie molecules
- predicted maximum Young's modulus calculated both from the melting and from crystallization curves.

From these data, the following information can be drawn:

The melting temperature indicates the crystallites' type of the polymer. Industrial polypropylene is generally i-PP [6–8]. It was noted that stable α -PP melts at around 155–160 °C [9–11]. The reaching of different equilibria between α and α' crystalline forms leads to the increase in the DSC curve width. The unstable β -crystalline form melts at around 120–130 °C [12–14]. So, the dominating crystalline form present in the sample can be identified by checking the melting temperature (peak temperature). Polymorphic modification affects both stiffness and strength of the polymer. The impact resistance of the β form is higher than that of the α -PP. Determination of the melting temperature gives information on PP polymorphism, and this is helpful in mechanical properties prediction.

Analyzing the DSC melting and crystallization curves, it can be noted that as in the general case of the polymers, the crystallization peak temperature of PP is always lower than that of its melting peak. This is due to both thermodynamic and kinetic reasons: (1) the possibility of the polymer crystallization only below the melting temperature when the free energy of the crystalline phase becomes smaller than that of the amorphous material and (2) the large size and consequently the low mobility of the polymer molecules, that kinetically hindered the crystallization. Crystallites cannot form immediately below $T_{\rm m}$, but at much lower temperature [15].

From Fig. 2, it can be noted that recycled PP obtained both by injection molding and by thermoforming exhibit quite similar melting and, respectively, crystallization peak temperatures. They are also close to the melting and crystallization temperatures of the conventional recycled polymers. Blow-molded polymers show the lowest melting temperature, with up to 26 °C lower, by comparing with the other samples. This could be due to the highest molecular mass of polymers used in blow-molding technology (MFI = 3) by comparing both with that obtained by thermoforming (MFI = 15) and with injection-molding technologies (MFI = 70). Injection-molded virgin samples show the highest melting temperature for nucleated PP, but lower melting temperatures for virgin polymers containing block heterophasic copolymer and white pigment, both of them acting as nucleating agents [16]. It could be stated that the presence of both copolymers and white pigment has the dominating influence on the melting temperatures, by comparing with the influence of the molar mass (Fig. 3).

The difference between $T_{\rm m}$ and $T_{\rm c}$ can give information concerning the nucleation agents' presence. So, it was stated that if $\Delta T = T_{\rm m} - T_{\rm c} \approx 50$ °C the polymers are nonnucleated. β -Nucleated samples exhibit lower ΔT values as in the case of blow-molded samples, as well as in that of



Fig. 2 Melting and crystallization temperatures for recycled and virgin samples obtained by different processing technologies

the injected virgin PP containing different percents of RCP and white pigment. The mix of the virgin PP-s exhibits a melting temperature close to the conventional recycled polymers, probably due to the dilution of the nucleating agents by mixing with un-nucleated PP.

The heat of melting can be correlated with the crystallinity degree of the recycled polymer. It can be calculated by using the formula (1):

$$X_{\rm m}(\%) = \frac{\Delta H_{\rm m}}{\Delta H_{\rm o}} \cdot 100 \tag{1}$$

where $X_{\rm m}$ is the crystallinity degree of the polymer; $\Delta H_{\rm m}$ is the melting enthalpy determined by integration of the surface under the DSC curve in the domain of melting process; and $\Delta H_{\rm o}$ is the melting enthalpy of the 100% crystallized i-PP (207 kJ/g [17, 18]).

The crystallization heat was calculated by determination of the area under the DSC curve of crystallization, in the crystallization temperature domain. The crystallinity degree of the re-crystallized sample was calculated by using a similar formula with Eq. (1), where ΔH_m was replaced by ΔH_c that is the crystallization enthalpy.

From Fig. 3, it can be observed that crystallinity degree of PP-based materials, calculated by using both melting and crystallization DSC curves, can be correlated with the transition temperature and with the technology type of the polymers processing. The higher the crystallinity degree, the higher the transition temperature. The eye guide lines from Fig. 4 evidenced that variation slope of the crystallinity as a function of the transition temperature is higher when the crystallization transition was used for crystallinity degree calculation and lower in case of the melting transition use. In the case of melting process, the crystallinity degree of samples was spread on a higher temperature interval, due to the higher polymorphism of the



Fig. 3 DSC melting and crystallization curves for virgin nucleated white extruded PP, virgin nucleated white not-extruded PP, recycled injection-molded mix and pure non-nucleated PP

initial mixed polymers. Re-crystallization led to more homogeneous morphology, and the influence of the molecular mass (used in different types of polymer processing) on the crystallinity degree and on the transition temperature was better evidenced:

 $X_{\text{Blow (MFI=3)}} < X_{\text{Conventional}} \le X_{\text{Thermoforming (MFI=15)}}$ $< X_{\text{Injection (MFI=70)}} < X_{\text{Virgin}}$

From Fig. 5, it can be noted that the highest crystallinity degree corresponds to the nucleated injected virgin PP. The addition of the RCP, and of the white pigment, determined a dramatic decrease in the materials' crystallinity. But the lowest crystallinity degree belongs to the blow-molded polymer, due to the highest molecular mass of the polymer and to the highest viscosity of the polymer's melt that hinders its crystallization. The crystallinity of the recycled fractions increases in the following series:

$X_{\text{Blow mold}} < X_{\text{Conventional polymers}} \le X_{\text{Thermoformed polymers}}$ $< X_{\text{Injected mold polymers}}$

It can be noted that the crystallization degree of the conventional recycled polymers is closer to that of the higher molecular mass fractions.

Crystallinity degree determined from the melting and crystallization curves exhibits the same trend, but a clearer selection of the polymers obtained by different processing technologies can be made by using the crystallization curve. The last one seems to be better related to the structural ability of the polymers to crystallize, due to the constant cooling regime applied during DSC analysis.

The samples obtained by waste collection are more heterogeneous from morphological point of view, due to their different origins. It is well known that sometimes, at



Fig. 4 Correlation between the samples' transition temperature and their crystallinity degree for samples obtained by different technologies



Fig. 5 Crystallinity degree and the width of the transition curve in melting (m) and crystallization (c) processes, as a function of the samples processing technology

industrial level, the product is cooled rapidly in order to increase the productivity. The fact that crystallization occurs under no equilibrium conditions was clearly demonstrated by the skin-core morphology of injection-molded polymers [19]. This aspect was evidenced in our study too, in case of the injection-molded polymers that exhibit a supplementary melting (endothermic) peak at 121–143 °C, characterized by a low peak height and attributed to β -PP crystals formation. Interesting, the presence of the injection-molded polymers in the conventional recycled mix can be identified by this secondary melting process evidenced at 133 °C (Fig. 6).

Characteristics of the melting or crystallization curve (onset, endset, width and height) can be correlated with the multiple crystallization melting equilibria, meaning the presence of different forms of crystallites or crystals perfection processes. These values were obtained by using the instrument software for all the analyzed samples. They were graphically represented as a function of the processing type to allow a better comparison between the data.

The higher width of the DSC curves in the case of the high molecular mass polymers (blow-molded ones) and in the case of the virgin white nucleated injection-molded polymers is more pronounced in the melting curve. In the crystallization curve, the same trend is maintained, but the differences are lower (Fig. 3). The crystallinity degree shows similar behavior of the conventional fraction with the thermoformed polymers, as in case of the melting temperature. Also, the conventional sample exhibits lower crystallinity by comparing with that of the injection-



Fig. 6 DSC curves for melting and crystallization of different fractions of recycled PP obtained by different processing types

molded virgin mix, evidencing possible degradation of the polymers during the life cycle. The formed OH, carbonyl or carboxyl groups hinder the crystallization.

Melting and crystallization rates are calculated by using formula (2):

$$v_{\rm m} \left[J \ {\rm g}^{-1} \ {\rm min}^{-1} \right] = \frac{\Delta H_{\rm m}}{\Delta t} \tag{2}$$

where Δt is the length of the melting process, calculated as ΔT /heating rate.

The obtained data were plotted as a function of the processing technologies and compared to the DSC curve width, as shown in Fig. 7.

From Fig. 7, it can be noted that the rate of melting is correlated with the dispersity of the crystallite types. Higher-type numbers of crystallites and lower melting rate are due to the multiple simultaneous equilibria. Crystallization rate shows the same trend as the melting rate, but the differences between samples obtained by different technologies are better evidenced by the last one.

The main goals of development in nowadays industry are both to increase the stiffness of PP above current levels and to improve the impact resistance or even more, to prepare materials having simultaneously large stiffness and fracture resistance. Large impact resistance is usually achieved by copolymerization and blending but rarely by nucleation.

Lamella thickness is a very important parameter, directly correlated both with modulus, meaning the polymer stiffness, and with its fracture (impact) resistance. While the polymer impact resistance depends only on the lamella thickness [19–22], modulus depends both on lamella thickness and on crystallinity.



Fig. 7 The rate of melting (ν_m) and crystallization processes $(\nu_c),$ correlated with the DSC curve width and processing type of the samples

Each lamella can be built up from several macromolecular chains, and one chain can participate to the formation of different lamellae. The number of tie molecules (chains connecting lamella) is inversely proportional to lamella thickness [23, 24] and influences the strength and fracture resistance of the polymer too.

Lamellae thickness can be calculated from the thermal DSC melting data, by using Gibbs–Thompson Eq. (3):

$$1 - \frac{2 \cdot \sigma_{\rm e}}{\Delta H_{\rm v}^{\rm o} \cdot l} = \frac{T_{\rm m}}{T_{\rm m}^{\rm o}} \tag{3}$$

where $T_{\rm m}$ is the melting temperature; $T_{\rm m}^{\rm o}$ is the temperature at the melting equilibrium (418 K); $\Delta H_{\rm v}^{\rm o}$ is the equilibrium enthalpy of fusion per unit volume expressed in this equation in kJ cm⁻³ (136.6 kJ m⁻³); *l* is the lamella thickness (nm); and $\sigma_{\rm e}$ is the free energy of the folded surface of lamella (0.122 J m⁻²) [15, 25–27]. The obtained values are presented in Table 3.

It can be observed that the thinner lamellae were obtained in the case of polymers obtained by blow-molding technology and in the case of the reference samples containing RCP and white pigment. The other samples have a lamellae thickness around 20–23 nm. Correspondingly, the tie molecules number is higher in case of the lowest thickness lamellae. This morphology can be correlated with the mechanical properties of the polymers.

The maximum modulus value can be predicted by using the melting DSC data [28–30], by applying Eq. (4) [27] and where the lamella thickness is calculated by using Eq. (3) and is presented in Table 3:

$$E_{\rm m} = 0.082 \cdot l + 0.025 \cdot \Delta H_{\rm m \ max} - 2.15 \tag{4}$$

Sample code	Type of samples obtaining	l _{max/} nm	$1/l/\mu m^{-1}$
10A	Conventional + impurities	20.90	47.83
11A	Conventional-impurities granulated	20.40	49.00
12A	Conventional-impurities flakes	21.53	46.43
13A	Blow mix	13.61	73.44
14A	Persil	13.17	75.88
15A	Injection-molded mix	20.90	47.83
16A	Injection-molded 50% HPP-50% RPP	21.16	47.25
17A	Injection-molded 80% HPP-20% RPP	23.22	43.06
18A	Thermoforming mix	21.69	46.09
19A	Thermoforming 70% HPP-30% RPP microwave	20.31	49.232
20A	Thermoforming 70% HPP-30% RPP aq	20.16	49.58
4A	HPP 100% virgin	22.91	43.64
6A	70% HPP-30% RPP blue virgin	20.31	49.23
7A	70% HPP-30% RPP white extruded virgin	14.53	68.78
8A	70% HPP-30% RPP white not-extruded virgin	14.94	66.92
9A	50% HPP-50% RPP virgin	22.55	44.34
5A	Mix virgin 50% (70% HPP-30% RPP) + 50% (50% HPP-50% RPP)	20.60	48.53

Table 3 Lamella thickness and number of tie molecules (proportional with 1/l)

where $E_{\rm m}$ is the maximum stiffness achievable (determined the melting data); *l* is lamella thickness; and $\Delta H_{\rm m max}$ is the maximum enthalpy of fusion per volume unit. We used the density of crystalline part as 936 kg m⁻³ [31].

Maximal modulus value can be calculated also from the crystallization data, by using the empirical Eq. (5) [32]:

$$E_{\rm c} = 0.02 \cdot T_{\rm c} + 0.025 \cdot \Delta H_{\rm c} - 3.2 \tag{5}$$

where E_c is the maximum stiffness achievable (determined from the crystallization data); ΔH_c is the crystallization heat.

From Fig. 8, it can be observed that the increase in the crystallinity degree determines the increase in the Young's modulus, meaning the increase in the polymer stiffness.

It could be noted also that the values of modulus calculated from the melting DSC curves are higher than those calculated by using crystallization DSC curves with up to 20%, but the same trend of variation was obtained.

Also, considering the influence of the processing technology on the modulus values, the following hierarchy was noted:

$E_{\text{Blow molding}} < E_{\text{Conventional}} < E_{\text{Thermoforming}}$ $\approx E_{\text{Injection molding}} < E_{\text{Virgin injection molding}}$

Not only the crystallinity degree influenced the maximal values of the Young's modulus but also the crystallite-type distribution described the DSC curve width.



Fig. 8 Maximal Young's modulus predicted by using DSC data both for melting (E_m) and for crystallization (E_c) processes versus the samples crystallinity and processing technology

From Fig. 9, it can be seen that the higher the dispersity of the crystallites is, the lower the Young's modulus values are. The highest dispersity was noted for packages obtained by blow molding and the lowest one for that obtained by injection molding. The conventional waste exhibits values in between, both for modulus values and for the crystallites dispersity, being closer to the thermoformed polymers.



Fig. 9 Maximal predicted Young's modulus as a function of the crystallization curve width at 37%

Conclusions

DSC measurements are very useful tools to determine materials' thermal and morphological characteristics and based on them to predict the mechanical and optical properties.

This study evidenced that the processing technology of the polymers in fresh state or as recycled material strongly influenced the product morphology and, as a consequence, the predicted mechanical properties.

Blow-molded recycled polymers are characterized by the lowest melting and crystallization temperatures, the lowest crystallinity, the highest polydispersity, the thinner lamellae, the highest number of tie molecules and the lowest maximal predicted Young's modulus.

On the contrary, injection-molded virgin polymers are the highest crystalline, with the lowest polydispersity, showing the highest melting and crystallization temperature, the highest lamellar thickness, the lowest tie number molecules and the highest maximal predicted Young's modulus.

Both injection-molded recycled polymers and thermoformed recycled polymers are in between, by comparing with the blow-molded recycled polymers and injectionmolded virgin polymers, from all the above-mentioned points of view.

Conventional recycled polymers, containing approximately 58% thermoformed and blow-molded PP and 42% injection-molded PP, behave very similar to the recycled thermoformed polymers from both thermal and mechanical points of view. By comparing the conventional recycled polymers with the injection-molded mix of virgin polymers, the first one exhibited a lower crystallinity with about 22%, approximately the same lamella thickness, the crystals' polydispersity higher with about 10% and the Young's modulus lower with about 22%.

The predicted properties will be correlated with the measured ones, and the morphological determined features will be used to explain the other properties of the recycled materials.

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References

- Satilla C, Cafiero L, De Angelis D, La Marca F, Tuffi R, Vecchio Ciprioti S. Thermal and catalytic pyrolysis of a mixture of plastics from small waste electrical and electronic equipment (WEEE). Waste Manag. 2016;54:143–52.
- Costiuc L, Tierean M, Baltes L, Patachia S. Experimental investigation on the heat of combustion for solid plastic waste mixtures. Environ Eng Manag J. 2015;14(6):1295–302.
- Costiuc L, Baltes L, Patachia S, Tierean M, Lunguleasa A. Influence of reprocessing by melt-mixing and thermo-formation of polyolefin fractions, separated from wastes, on their calorific power. Bulg Chem Commun. 2018;50:165–71.
- Stromberg E, Karlsson S. The design of a test protocol to model the degradation of polyolefins during recycling and service life. J Appl Polym Sci. 2009;112:1835–44.
- Blanco I, Siracusa V. Kinetic study of the thermal and thermooxidative degradations of polylactide-modified films for food packaging. J Therm Anal Calorim. 2013;112(3):1171–7.
- Maddah HA. Polypropylene as a promising plastic: a review. Am J Polym Sci. 2016. https://doi.org/10.5923/j.ajps.20160601.01.
- Zhang C, Yi X-S, Asai S, Sumita M. Morphology, crystallization and melting behaviors of isotactic polypropylene/high density polyethylene blend: effect of the addition of short carbon fiber. J Mater Sci. 2000;35(3):673–83.
- Bourbigot S, Garnier L, Revel B, Duquesne S. Characterization of the morphology of iPP/sPP blends with various compositions. Express Polym Lett. 2012. https://doi.org/10.3144/expresspo lymlett.2013.21.
- Varga J. Crystallization, melting and supermolecular structure of isotactic polypropylene. In: Karger-Kocsis J, editor. Polypropylene: structure, blends and composites. London: Chapmann&Hall; 1995. p. 56–115.
- Varga J. β-Modification of isotactic polypropylene: preparation, structure, processing, properties, and application. J Macromol Sci B. 2002;41:1121–71. https://doi.org/10.1081/MB-120013089.
- Padden FJ, Keith HD. Evidence for a second crystal form of polypropylene. Jpn J Appl Phys. 1959;30:1479–84. https://doi. org/10.1063/1.1734985.
- Natta G, Corradini P. Structure and properties of isotactic polypropylene. Nuovo Cimento. 1960;15:40–51. https://doi.org/ 10.1007/BF02731859.
- Meille SV, Ferro DR, Bruckner S, Lovinger AJ, Padden FJ. Structure of beta-isotactic polypropylene-a long-standing structural puzzle. Macromolecules. 1994;27:2615–22.

- Lotz B, Wittmann JJ, Lovinger AJ. Structure and morphology of poly(prolylenes): a molecular analysis. Polymer. 1996;37:4979–92.
- 15. Wunderlich B. Macromolecular physics: crystal nucleation, growth, annealing. London: Academic Press Inc.; 1979.
- Eagan JM, Xu J, Di Girolamo R, Thurber CM, Macosko CW, LaPointe AM, Bates FS, Coates GW. Combining polyethylene and polypropylene: enhanced performance with PE/*i*PP multiblock polymers. Science. 2017. https://doi.org/10.1126/science. aah5744.
- 17. Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR. Polymer handbook. 4th ed. New York: Wiley; 2005.
- Perrin-Sarazin F, Ton-That MT, Bureau MN, Denault J. Microand nano-structure in polypropylene/clay nanocomposites. Polymer. 2005;46:11624–34. https://doi.org/10.1016/j.polymer.2005. 09.076.
- Karger-Kocsis J, Csikai I. Skin-core morphology and failure of injection-molded specimens of impact-modified polypropylene blends. Polym Eng Sci. 1987;27:241–53.
- Wang SW, Yang W, Xu YJ, Xie BH, Yang MB, Peng XF. Crystalline morphology of beta-nucleated controlled-rheology polypropylene. Polym Test. 2008;27:638–44. https://doi.org/10. 1016/j.polymertesting.2008.04.004.
- Addink EJ, Beintema J. Polymorphism of crystalline polypropylene. Polymer. 1961;2:185–93.
- Phillips PJ, Mezghani K. Polypropylene, isotactic (polymorphism). In: Salamon JC, editor. The polymeric materials encyclopedy. Boca Raton: CRC Press; 1996. p. 6637–49.
- Nitta KH, Takayanagi M. Role of tie molecules in the yielding deformation of isotactic polypropylene. J Polym Sci, Part B: Polym Phys. 1999;37:357–68.
- 24. Nitta KH, Takayanagi M. Tensile yield of isotactic polypropylene in terms of a lamellar-cluster model. J Polym Sci, Part B: Polym Phys. 2000;38:1037–44.

- 25. Wunderlich B. Thermal analysis of polymeric materials. Berlin: Springer; 2005.
- 26. Furushima Y, Nakada M, Murakami M, Yamane T, Toda A, Schick C. Method for calculation of the lamellar thickness distribution of not-reorganized linear polyethylene using fast scanning calorimetry in heating. Macromolecules. 2015;48(24):8831–7.
- 27. Horváth Z. Correlation between molecular architecture and properties in semicrystalline polypropylene. PhD thesis, Published by Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest; 2014.
- Horváth Z, Menyhárd A, Doshev P, Gahleitner M, Tranninger C, Kheirandish S, Varga J, Pukánszky B. Effect of molecular architecture on the crystalline structure and stiffness of iPP homopolymers: modeling based on annealing experiments. J Appl Polym Sci. 2013;130:3365–73.
- Menyhárd A, Suba P, László Z, Fekete HM, Mester ÁO, Horváth Z, Vörös G, Varga J, Móczó J. Direct correlation between modulus and the crystalline structure in isotactic polypropylene. Express Polym Lett. 2015;9:308–20.
- Molnár J, Jelinek A, Maloveczky A, Móczó J, Menyhárd A. Prediction of tensile modulus of semicrystalline polymers from a single melting curve recorded by calorimetry. J Therm Anal Calorim. 2018;134:401–8.
- Clark EJ, Hoffman JD. Regime Ill crystallization in polypropylene. Macromolecules. 1984;17:878–85.
- Pukánszky B, Mudra I, Staniek P. Relation of crystalline structure and mechanical properties of nucleated polypropylene. J Vinyl Addit Technol. 1997;3:53–7.

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