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A Study on the Thermodynamic Changes in the Mixture of Polypropylene (PP) with Varying Contents of Technological and Post-User Recyclates for Sustainable Nanocomposites

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ABSTRACT

The use of recycled materials can address some of the issues associated with the cost and environmental implications of non-renewable materials. So the prime aim of this work was to determine the thermodynamic changes in the polypropylene (PP) mixtures depending on the percentage amount of different origin recyclates for sustainable nanocomposites. In this study, different polypropylene mixtures with the addition of PP recyclates from a selective waste collection system and in-plant recycling system have been subjected to detailed analysis. It was obvious that recyclates from technological waste were of higher quality than post-user recyclates obtained from a selective waste collection system. The influence of the source of the recyclates on the different properties of the processed materials has been studied in detail. The content of the repeatedly processed material in the technological recyclates was found to explain the unexpected influence of the recyclates content on the properties of the final product. A mathematical model was also formulated to calculate the content of the material with certain amount of recirculations in the in-plant recycling system since no analyses concerning the content of the repeatedly processed material in the technological recyclates added to the original material were found in the literature.

Key words: Polypropylene; nanocomposites, recycling; recyclates; thermal properties; processing properties

INTRODUCTION

Various types of polymers have been widely used in a number of household and industrial application such as agricultural, automobile, electrical, medical, pharmaceutical, packaging, etc. [1] [2] [3] [4] [5] . Some of the most important commodity polymers include polypropylene (PP), high density polyethylene (HDPE) and low-density polyethylene (LDPE)

[6] [7][8] [9]. All of these polymers are derived from petrochemical resources and have long chains of hydrogen and carbon atoms. In terms of the production volume, polypropylene (PP) ranks third place and this indeed causes a large amount of post-consumer waste of this polymer. The very low cost, high molecular weight, easy processability and good mechanical properties make polypropylene as one of the most valuable polymer for commercial applications [10]. Among various types of polypropylene, isotactic polypropylene has the greatest technical significance. This is partially crystalline polymer of high tensile strength, quite rigid and efficient toughness. Polypropylene is processed via different techniques that include injection moulding, extrusion, press moulding and vacuum forming, blowing extrusion, fluidization coating and flame spraying [11]. The PP fibres have been prepared using electro spinning technique, and polypropylene based foam products have also been produced for various industrial applications[12] [13]. This polymer has a large number of applications, the continuous fibres are used to manufacture cords, fishing nets, packing tapes and filter materials used in many industries [14]. It is commonly used as construction material including the production of pipes and films. It is a non-bio-degradable polymers and is highly stable to the most of the environmental effects [15]. Generally, it takes many years for the degradation of such commodity polymers and causes serious environmental concerns [16]. Recycling of such polymers is one of the best solution, however the resulting products exhibit materials with inferior properties compared to their pristine counterpart. PP and its recyclates are common components of wood-polymer composites WPC [17] [18] [19]. In polypropylene processing methods such as injection, extrusion and extrusion blow moldings, it is common to add up to 30 % of recyclates to the virgin matrix material [20]. Additives have been reported to affect the different properties of polymeric materials [21] [22] [23] [24]. Adding plastic recyclates to the original material is an important issue in terms of managing growing amounts of various polymer waste materials [25] [26] [27]. Recently a great attention is

being paid on the use of different polymers based materials including recycled polymers as matrices for reinforcement with nanomaterials to develop innovative nanocomposite materials[28] [29] [30] [31] [32]. Several types of nanocomposites have been reported for their applications ranging from energy storage to structural components[33] [34] [35] [36]. Nanocomposites are prepared using different processing technologies and each has its own advantages as well as disadvantages [37] [38]. One of the prime reason for using different types of nanomaterials being their high surface area that results in improvements in different properties, such as tensile strength and modulus (highly desired for structural application) and lower coefficient of thermal expansion to name a few [39] [40] [41]. Different types of recycled polymers exhibit a high potential to be used as novel matrices for nanocomposites applications.

In this work, the recyclates of the polypropylene (rPP) were added to the pristine matrix material polypropylene (PP). The recyclates content was varied from 0 to 100 %. The recyclates were collected from two different sources: municipal waste (post-user) and post-production waste (in-plant recycling system). In the case of post-production waste, the knowledge about the composition and the origins of the processed material is quite adequate while on the other hand, in the case of municipal waste, this kind of knowledge is very limited. Municipal waste contains both polypropylene and its mixtures with different fillers [14] [42]. Neither the proportions of the components content, the types of fillers used in the mixtures processing, nor the impurities and degradation products are known. So this research was carried out to determine the changes in the material properties with the change in the content of the recyclates depending on their origin. On the basis of this study it has been possible to define an optimum amount of the recyclates added to the pristine polymer material in order to obtain a final product with suitable properties. The main aim of this work was to

determine the changes in thermodynamic properties of polypropylene mixtures depending on the increasing percentage content of (different origin) multi processed PP recyclates.

MATERIAL AND TEST METHODS

The research material

The mixtures used in this work, contained the following raw materials: the pristine polypropylene (PP) under a trade name Moplen HP456J of Basell Orlen with the seat in Płock whose properties are presented in **Table 1 (Fig. 1a)**; the polypropylene post-production waste - rPPp (in-plant recycling system) **(Fig. 1b)** whose properties are presented in **Table 2** and post-user waste (municipal waste) - rPPo **(Fig. 1c).** The post-user (municipal) waste was segregated, washed and grinded via a slow-speed recycling grinder TYPE T4SW produced by TRYMET Ltd. Metal Products Plant. Grain size fractions were found to be about 5 mm (defined on the basis of the sieve analysis). Ten mixtures were obtained through mixing these materials in the mixing drum. The share of the particular mixture components is presented in **Table 3**. Subsequently, particular mixtures were extruded using a co-rotating twin-screw extruder type Bühler BTSK 20/40D and granulated in a pellet mill. The aim of this process was to homogenise the mixtures and get the base material for film processing. The parameters of pellet extrusion are presented in **Table 4**. Screws with the diameter of 10 mm, whose configuration diagram is presented in **Fig. 1 (d)**, were installed in the twin-screw extruder. Double degassing was applied in this configuration: free and vacuum degassing to eliminate by-products and process the material containing the least amount of internal defects. The processed research material was then subjected to:

a) Differential scanning calorimetry (DSC) analysis,

b) Tested to determine the processing characteristics: melt mass-flow rate (MFR) and melt volume rate (MVR).

Thermal analysis method

The processed material was subjected to the differential scanning calorimetry using a Mettler Toledo DSC822e STARe instrument. The parameters of the test were the following: temperature range 25-250°C, heating rate $\beta = 10°C/min$, the weight of the sample about $m_p \approx$ 8 mg, the weight of the crucible approximately $m_t \approx 49$ mg. The sample was placed in a 40 µl alumina crucible with pin. The weight of the sample was determined via a Mettler Toledo XS 105 analytical balance accurate to 0.01 mg. The test was carried out according to the PN-EN ISO 11357:2009 Standard. The highest melting temperature of crystallites - Tm, the degree of crystallinity - Xc, the enthalpy - ΔHm, the temperature of transformation beginning and end - Onset, Endset, the value of the heat flow - Q were determined on the basis of the thermograms [43].

Test method for rheological characteristics

The test was carried out according to the ISO 1133 (PN-93/C-89069) Standard with the use of the REO-100 Plastometer produced by Zakłady Budowy Maszyn HYDRAPRES S.A **(Table 5).** Piston load and measuring temperature were set taking the type of analyzed material and its properties into account. The parameters were the following: T = 230°C, the load 2160 g. The melt mass-flow rate (MFR [g/10min]) and the melt volume rate (MVR [cm^3/10min]) were determined on the basis of the test. The density of the tested material ρ [g/cm^3] is presented in **Table 6.** Each material underwent three series of tests and each series

consisted of five measurements from which the tester automatically determined the average value.

RESULTS AND DISCUSSION

The analysis of the tested material was initiated by defining its thermodynamic properties. Thermal analysis with differential scanning calorimetry (DSC) was performed as the first determination. The findings are presented in the thermogram **(Figs. 2 & 3)** and six graphs which successively represent the changes of the particular values of thermal parameters of the mixtures with the increase of the recyclates content (**Figs. 4**). In both cases, as the recyclates content in the mixtures increases, the height of the transition peak also slightly rises. This phenomenon indicates the consumption of more energy for the transition phase. The increasing recyclates content does not cause any significant changes of shape nor the maximum height of the transition peak in both cases. In the case of the post-user propylene P1 - **Figure 2a** - with the recyclates content, an additional small rising transition peak is clearly visible at about 130°C, which most likely indicates that the mixture contains a small amount of high-density polyethylene (HDPE). It may be due to the presence of HDPE packaging films in the PP waste or perhaps because of the wrong material information on some packages from selective waste collection, and as a result they were processed with the polypropylene. In both cases, the decomposition temperature of the recyclates (especially, the technological one) is lower than the original PP. This behaviour can be attributed to the presence of the repeatedly processed, thermally and mechanically degraded material [42] . On the basis of charts (**Fig. 4b**) it is possible to conclude that the film which contains 100 % of post-user recyclates absorbs about 20% more energy than technological recyclate, which certainly results from the greater structural diversity and impurity of the post-user recyclates.

On the basis of thermogram ascending curves trend of mixtures containing 10 and 20% of P1 and P2 recyclates (**Fig. 3a and 3b**) and 30 % of P2 recyclates (**Fig. 3c**) it can be concluded that they need less energy for plasticization (transition phase). The thermogram lines of the mixtures containing the recyclates tend to rise from the beginning of the test, indicating that they absorb less energy in preheating than the original material. The thermogram lines of pure - original PP clearly descend, which indicates regular energy absorption till the beginning of the transition peak reaching its maximum point at about 170°C. Thermographs of mixtures containing more than 50% of both recyclates (**Fig. 3d and 3e**) and 30% of P1 recyclates (**Fig. 3c**) show decreasing lines, as well as the thermograph curve of the original material. The thermogram curves were subjected for detailed analysis and the different values of thermal and structural properties were determined: Tm - the highest melting temperature of crystallites (**Fig. 4a**), Xc - the degree of crystallinity (**Fig. 4b**), Onset/Endset - the temperature of transformation beginning (**Fig. 4c**) and end (**Fig. 4d**), ΔHm - the enthalpy (**Fig. 4e**), Q - the value of the heat flow (**Fig. 4f**).

The degree of crystallinity is an important parameter in the recycling of contaminated, difficult to separate plastics [42] [44]. The graph of the highest melting temperature of crystallites Tm presented in **Figure 4a** suggests that the addition of the recyclates, regardless of their origin, slightly increases the value of this parameter. The increase is only about 2 %. On the other hand, the value of the degree of crystallinity of the mixtures descends with the increase of recyclates content regardless of its origin (**Fig. 4b**). The decrease of Xc material which contains 10 and 20% of P1 post-user recyclates is 6 %, the increasing of recyclates content up to 30 % causes a further 9% decline of crystallinity degree. Compared to the original material, the addition of 100% of P1 recyclates causes a 22% Xc declines. The decline in the crystallinity degree can be attributed to the decrease in the density of the tested material which causes the increasing of branching so the agglomerates are not created. It is

different in the case of the addition of P2 recyclates. The addition of up to 50 % of the recyclates improves the crystallinity by about 4 %, but the material processed solely from the recyclate indicates a 2% Xc decline compared to the original material. The dynamics and the difference of Xc decline between the materials containing P1 and P2 may result from the fact that P1 recyclates is more degraded and impure, which probably interferes with material crystallization during the stage of cooling down. On the Analysis of the impact of the recyclates addition on the transformation beginning and end temperature (Onset and Endset temperature - **Figs. 4c &d,** respectively), no significant differences were noticed, regardless of the waste origin.

On the basis of the analysis of enthalpy results, a decreasing trend was found irrespective of type and amount of the recyclates content. In the case of the material with P2 recyclates content, this decline is small and is only 1%. On the other hand, in the mixtures with P1 post-user recyclate share the decline is 16 % compared to the material with no recyclate share. The stream of heat (**Fig. 4e**) increases with the content of both recyclates. 100 % post-user recyclates absorbs about 30 % more energy than technological recyclates during melting. It is related to its inhomogeneity, degradation and impurities.

Another imperative task was to determine the melt mass-flow rate (MFR - **Fig. 5a**) and the melt volume rate (MVR - **Fig. 5b**). The changes in the values of both tested indexes depend on the percentage recyclate share in the tested mixtures. Simultaneously, the values of both studied indicators increases with the recyclates content and reach 31.11 g/10min (MFR) and 33.82 cm^3/10min (MVR) in material with 100 % recyclates share processed from municipal waste and 87.31 g/10min (MFR), 95.94 cm^3/10min (MVR) in material with 100% recyclate share processed from post-production waste. This value gap between the materials results from the fact that a significant part of municipal polypropylene waste, to different degrees, consists of degraded material and polypropylene composites with different filler

content, which causes the decline of the indicators value. The waste may also contain multilayer materials which are difficult to separate as well as laminated products. In the case of post-production waste, it may appear that we deal with some "pure" polymer i.e. slightly degraded (usually after one recycling) polypropylene with no fillers.

Plants engaged in the mass production of polymeric articles generally practice the so-called inner-recycling, based on the adding of about 30 % of its own recyclates to the processed original raw material in order to dispose the production waste (ingots, flash), which reduces the production costs. In the first processing, when its own recycled plastic is added to the original material, it is entirely made of polymer after the first processing (injection molding or extrusion plus grinding process). The processing results in further technological waste which is shredded again and added to the original material. Thus, after the second such procedure, the obtained recyclate will consist of the polymer after the first processing and polymer after the second processing (30 % of the added recyclates contains 21 % of the material after the first processing and 9 % after the second processing). Each successive step will increase the share of repeatedly processed polymer. The share of first recycled plastic decreases for the share of repeatedly processed material. This effect can be expressed in the following equation (1):

$$Z_k^n = (1 - dk - n - 1) \cdot \prod_{i=k-n}^{k-1} d_i \cdot 100\% \tag{1}$$

where:

Z_k^n is the percentage share in the k-th cycle of the raw material previously used n-times, assuming that $Z_1^0 = 100\%$ (in the first cycle only the original granulate is used). For k ≤ n:

$Z_k^n = 0\%$ (in the k-th cycle the recyclate, which was processed the greatest number of times,

was plasticised and shredded k-1 times, that is why it is sensible to consider the issue only for k > n, dk – the ratio of the residuals after the k-th production cycle, which can be used in the k + 1 cycle, to the total amount of the raw material used in one cycle, then for k=0, d_0=0.

Assuming that we always add 30 % of recyclates, the calculation of the percentage of the recyclate, which was previously processed three times, in the fourth production cycle will take the form as follows:

$$Z_4^3 = (1 - d0) \cdot d_1 \cdot d_2 \cdot d_3 \cdot 100\% = (1 - 0) \cdot \frac{3}{10} \cdot \frac{3}{10} \cdot \frac{3}{10} \cdot 100\% \tag{2}$$

On the basis of the equation form (1) it is possible to calculate the composition of the material processed in the fourth production cycle. It will comprise 70 % of the original material and 30% of the technological recyclates. Based on the calculations - (the equation form 2) it can be concluded that in the fourth production cycle the recyclates contains 18.3 % of the material after the first processing, 9% after the second processing and 2.7% after the third processing. The amount of the repeatedly processed material significantly increases, of which we are not usually aware. Such large values of both indicators in the case of 100 % of in-plant recyclates result from the share of the repeatedly produced material in the recyclates.

CONCLUSIONS

The current work explores the different properties of the recycled thermoplastic materials procured using extrusion procedures for developing sustainable nanocomposites. On the basis of the results, it was found that the percentage of the recyclates and their sources have a significant impact on the thermodynamic and processing properties of the material and recyclates from post-production waste (P2) are of higher quality than post-user recyclates (P1)

obtained from a selective waste collection system. Satisfactory thermodynamic and processing properties were noticed in material produced to 50 % post-production waste recyclates P2 content. Furthermore, in addition to the first processing material, significant amounts of the repeatedly processed material also occur in technological recyclates, which has a clear impact on the product properties.

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Table 1

Moplen HP456J characteristics

No.	PARAMETERS	UNITS	VALUE
1.	Melt flow index (230°C, 2,16 kg)	g/10 min	3,05
2.	Density	g/cm^3	0,91
3.	Tensile yield stress	MPa	34
4.	Elongation at yield (point)	%	10
5.	Break elongation	%	>50
6.	Vicat softening point (A50/B50)	^{o}C	154/92

Table 2

Post-user rPPo and post-production rPPp polypropylene characteristics

No.	PARAMETERS	UNITS	rPPo	rPPp
1.	Melt flow index (230°C, 2,16kg)	g/10 min	39,51	25,7
2.	Density	g/cm^3	0,92	0,90

Table 3

Mixtures of rPPo+PP and rPPp+PP (rPPo - polypropylene post-user waste (P1), rPPp - polypropylene post-production waste (P2), A-10%, B=20%, C=30%, D=50%, E=100%, PP - original polypropylene)

No.	SHARE OF MIXTURE COMPONENTS, [%]		SYMBOL
	rPP	*PP*	
P1 – PP Mixture + rPP post-user			
1.	10	90	P1A
2.	20	80	P1B
3.	30	70	P1C
4.	50	50	P1D
5.	100	0	P1E
P2 – PP Mixture + rPP post-production			
6.	10	90	P2A
7.	20	80	P2B
8.	30	70	P2C
9.	50	50	P2D
10.	100	0	P2E

Table 4

Technological parameters in extrusion granulation process

PARAMETER	UNITS	VALUE
Zone temperatures	°C	$t_1=195$
		$t_2=200$
		$t_3=200$
		$t_4=195$
Head temperature	°C	190
Temperature of the material inside the head	°C	190
The pressure of the material inside the head	bar	11
Rotational speed of screw	rpm	250

Table 5

Basic technical characteristics of REO-100 Plastometer

PARAMETER	UNITS	VALUE
Max. heater power	W	1050
Temperature range	°C	30-300
Temperature stabilization	°C	±0,2
Time measurement accuracy	ms	10
Route measurement accuracy	μm	5
Route measurement	mm	100

3

Table 6

The density of the tested mixtures

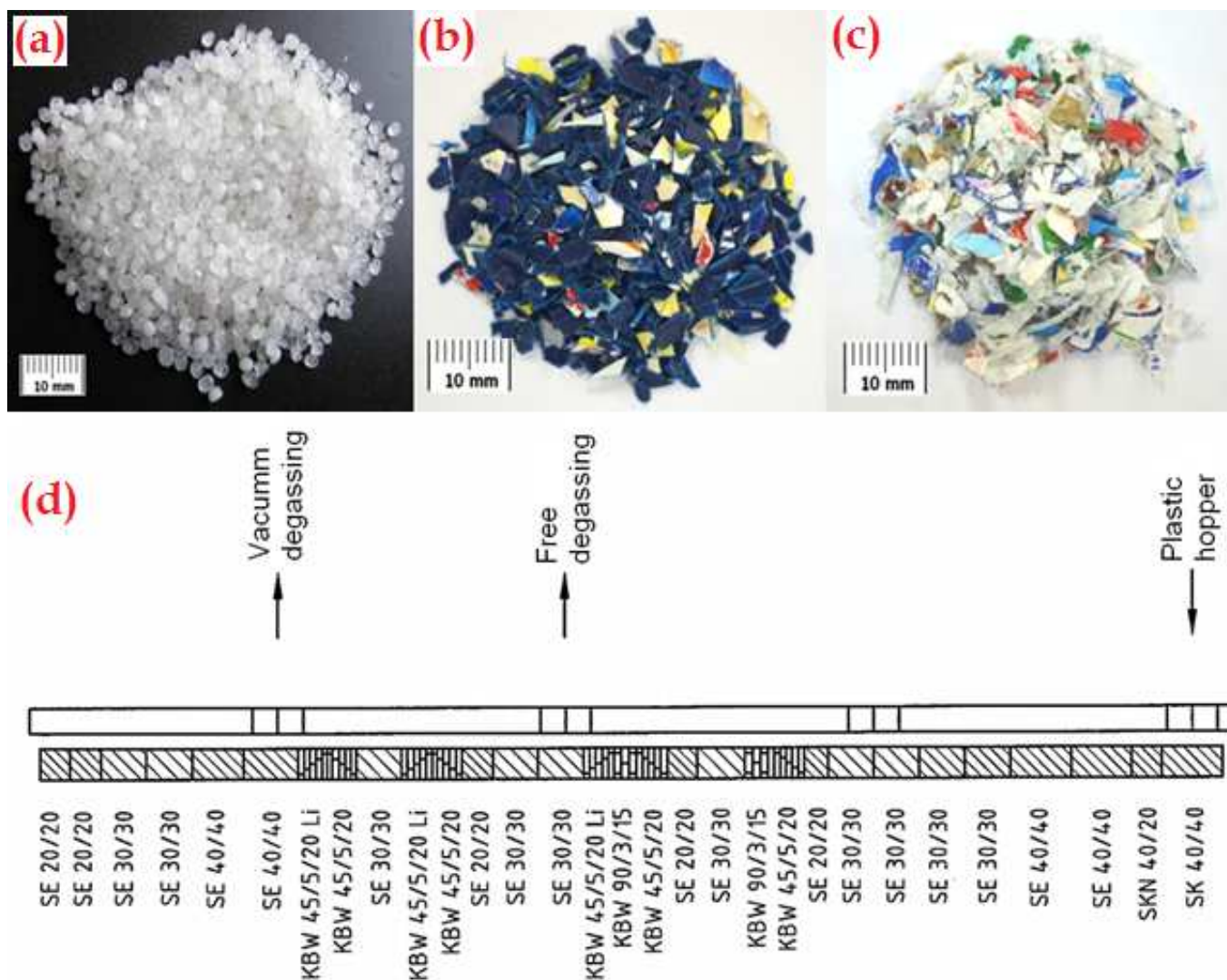|	A	B	C	D	E
	The recyclates content, %				
	10	20	30	50	100
P1	0,93	0,93	0,93	0,93	0,92
P2	0,93	0,93	0,92	0,92	0,91

Table 6

Fig. 1 a) View of the mixture components of original polypropylene (PP), b) post-production milling (rPPp), c) post-user waste (rPPo) and (d) K3 configuration of the screw applied to extrude mixtures PP+rPP
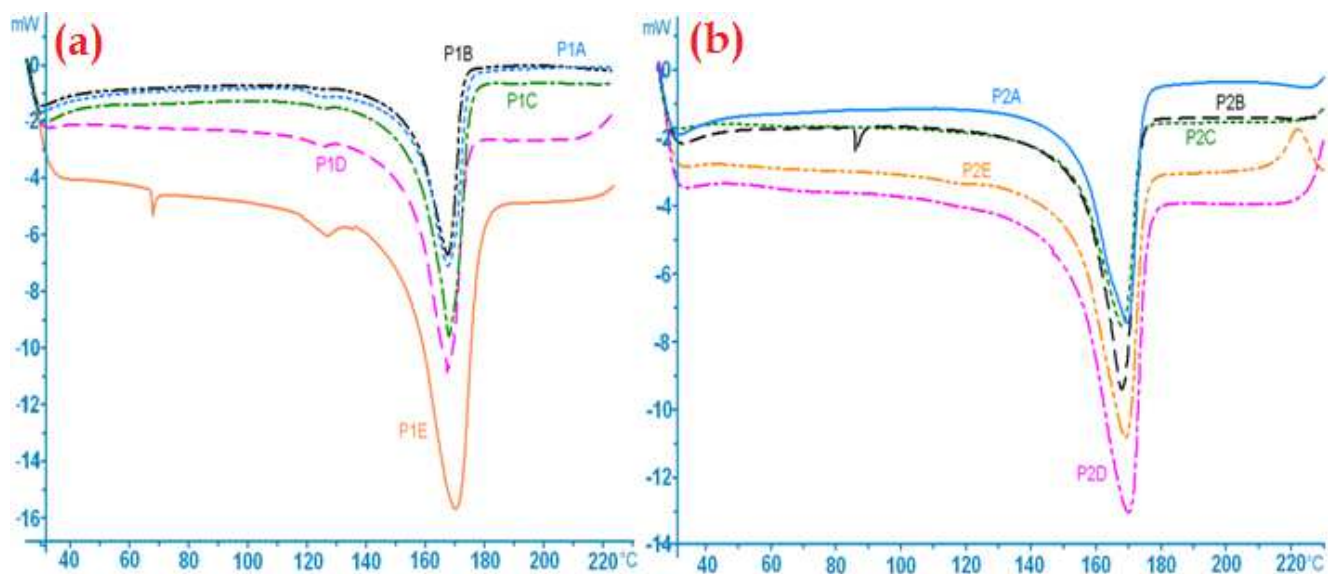
1

Fig. 2 DSC thermogram of the polypropylene mixtures: a) post-user P1, b) postproduction P2; *Signs*: 10% of polypropylene: post-user P1A, postproduction P2A; 20% of polypropylene: post-user P1B, postproduction P2B; 30% of polypropylene: post-user P1C, postproduction P2C; 50% of polypropylene: post-user P1D, postproduction P2D; 100% of polypropylene: post-user P1E, postproduction P2E
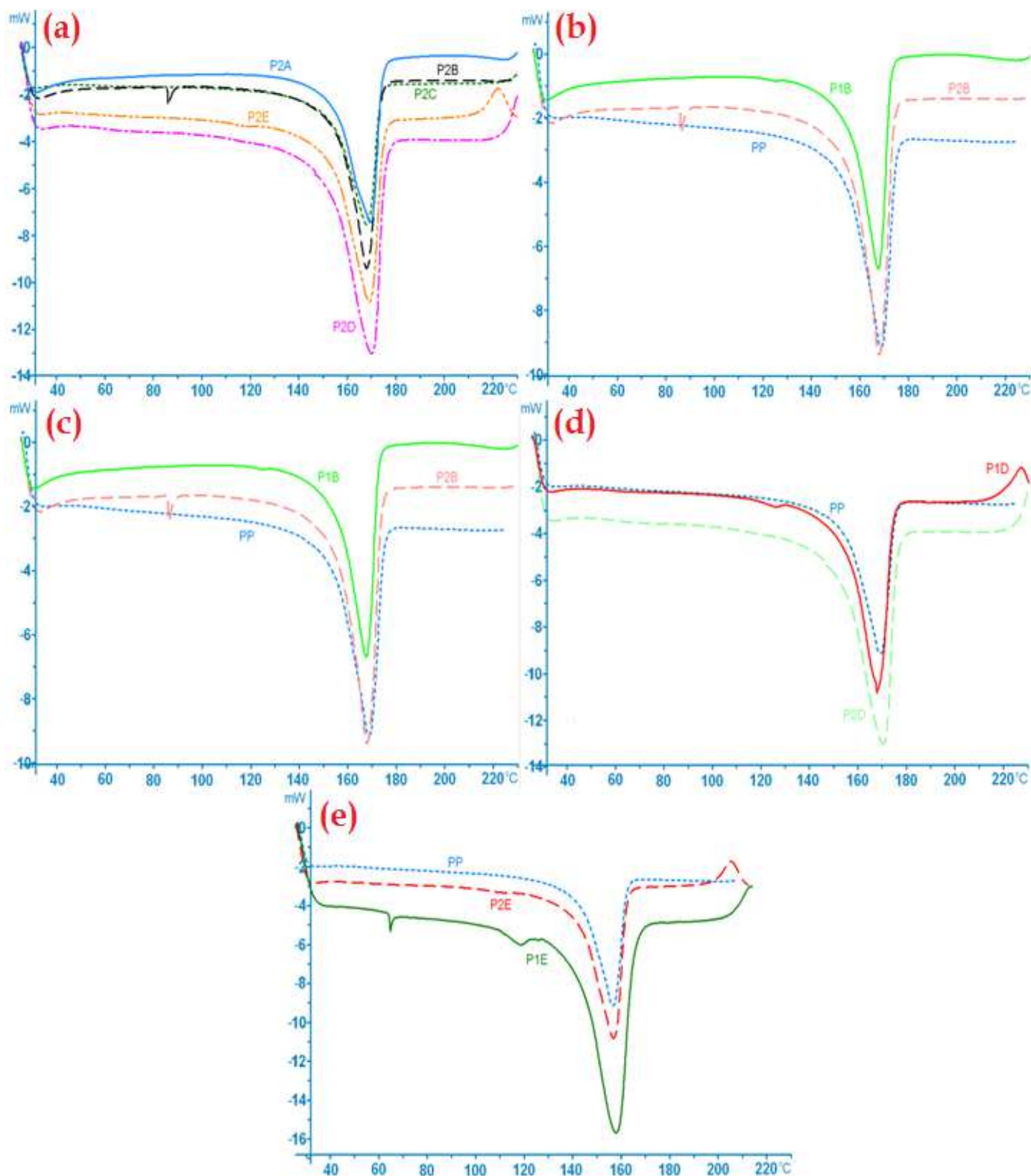
Fig. 3 DSC thermograms of PP mixtures containing: a) 10% of polypropylene: post-user P1A, postproduction P2A and thermogram of original PP, b) 20% of polypropylene: post-user P1B, postproduction P2B and thermogram of original PP, c) 30% of polypropylene: post-user P1C, postproduction P2C and thermogram of original PP, d) 50% of polypropylene: post-user P1D, postproduction P2D and thermogram of original PP, e) 100% of polypropylene: post-user P1E, postproduction P2E and thermogram of original PP
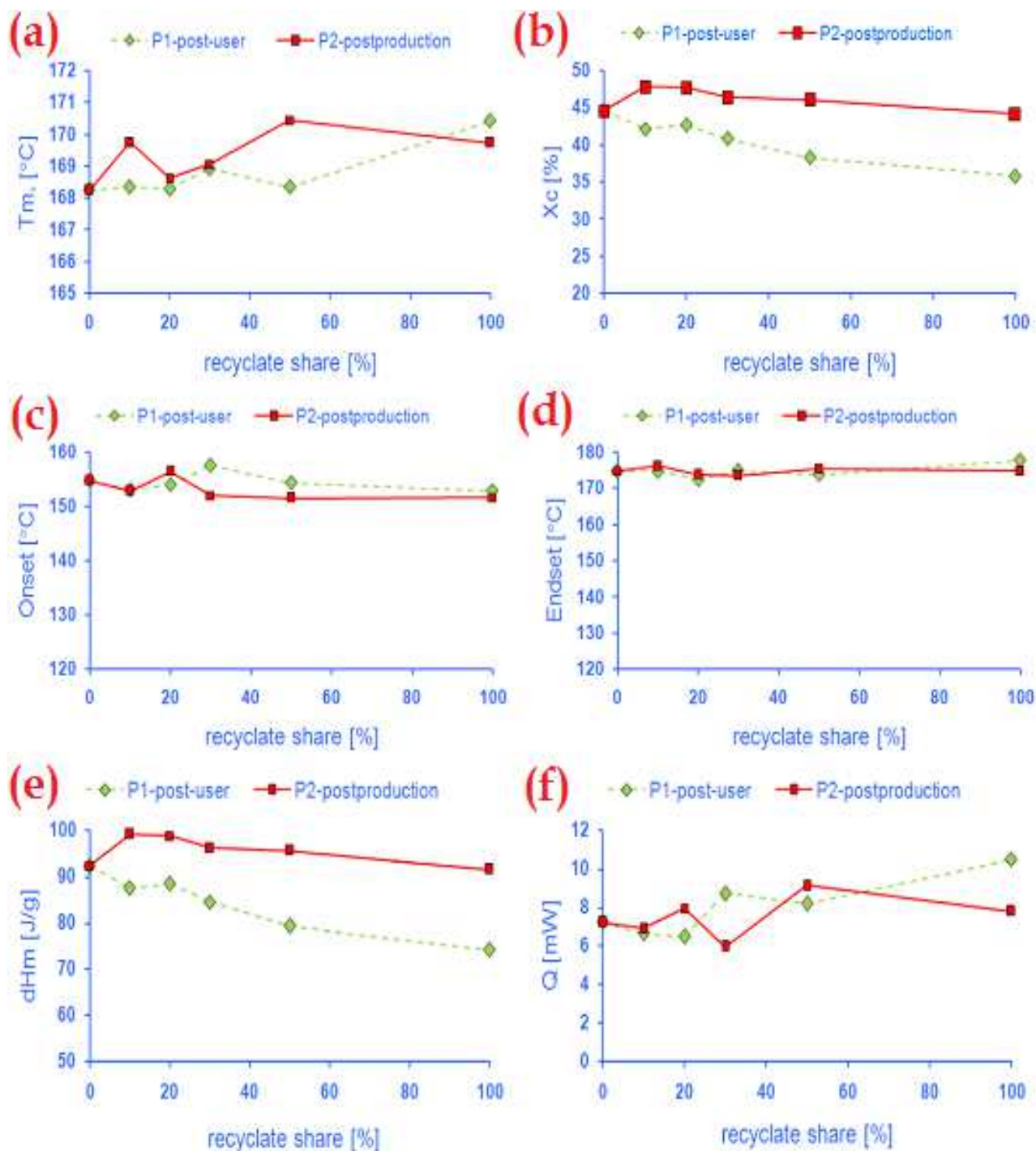
3

Fig. 4 Changes with the increasing share of P1 and P2 recyclate: a) Tm - the highest melting temperature of crystallites, b) Xc - the degree of crystallinity**;** c) Onset temperature, d) Endset temperature ; e) ΔHm - the enthalpy and f) Q - the value of the heat flow
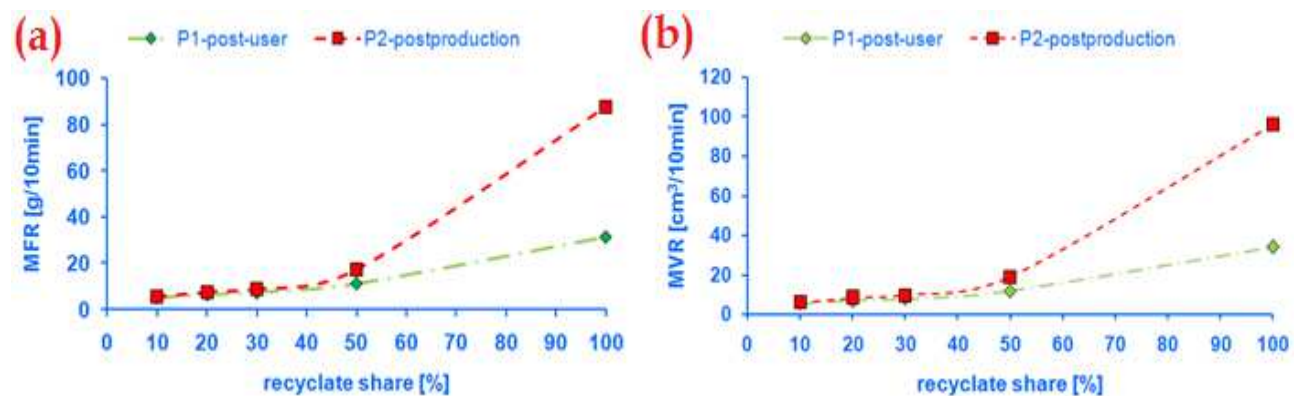
Fig. 5 Melt flow index change depending on P1 and P2 recyclates share: a) the melt mass-flow rate (MFR), b) the melt volume rate (MVR)

Highlights

- Recycled blend of polypropylene (PP) using twin-screw extruder.

- Thermal properties analysis of different recycled blends

- Examination of melt flow index changes

- Suitable for sustainable nanocomposites