Reprocessability and melting behaviour of self-reinforced composites based on PP homo and copolymers

Tamás Bárány · András Izer · Alfréd Menyhárd

Abstract In our present study, the reprocessability of a self-reinforced PP composites (SRPPC) prepared by compression molding was studied. The composite materials (handled separately, based on the related matrix material) were ground, then extruded five times and injection molded after the first and fifth cycle in order to investigate the behaviour of the material during reprocessing. As a reference, the matrices of the composites were also reprocessed and injection molded similarly to the composites. On the manufactured specimens, static (tensile and flexural) and dynamic mechanical tests (Charpy) were performed. The melting and crystalline characteristics were studied by Differential Scanning Calorimetry (DSC). The probable decomposition caused by multiple extrusions was followed by the Melt Volume Rate (MVR). The results indicated that in case of commercial materials there is no significant degradation even after multiple reprocessing cycles; therefore, the reprocessability of SRPPC products has no hindrance. The presence of α-iPP reinforcement in the rPP-based composites after reprocessing results in increased inclination for crystallization and consequently leads to improved mechanical stiffness compared to rPP neat matrices.

Introduction

The recyclability of polymers and their blends and composites has become very important issue nowadays. Its importance is represented by the European Union directive on the end-of-life of vehicles (ELV) [1]. In the automotive industry, isotactic polypropylene (iPP) is one of the most used polymeric materials. iPP has excellent price/performance ratio, it has to be filled and/or reinforced to compete with engineering plastics. Glass fibre (GF) is commonly used to improve the properties of iPP. Nevertheless, the recycling of the PP–GF composites is difficult. In order to fulfil the aforementioned directives, two possibilities are open: to improve the recycling technologies to be able to recycle more difficult systems or to develop materials which can be reprocessed easily. For the latter, a very promising alternative is to develop self-reinforced polymer composites (SRPC—the reinforcement and the matrix belong to the same polymer family but differing in their melting temperatures), because these composites may be used after reprocessing as a one-component material. SRPCs have been prepared form many polymers, although iPP has become widespread in SRPC applications yet. Any kind of polymer is available for producing SRPCs, which can be processed in fibrous form.

To produce SRPCs, suitable processing window (melting temperature difference between matrix and reinforcement) is necessary. It can be obtained by moulding the polymer fibres themselves (first only the skin of the fibre melts to become matrix and the core (reinforcement) remains oriented), called hot compaction, as developed by

T. Bárány (✉) · A. Izer
Department of Polymer Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, 1111 Budapest, Hungary
e-mail: barany@pt.bme.hu

A. Menyhárd
Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Műegyetem rkp. 3, 1111 Budapest, Hungary

Ward and Hine [2–4]. This is a really one-component system, so it can be reprocessed without any difficulties. The processing window during composite manufacturing can further be increased by selecting matrix materials having lower melting temperature than the reinforcement (but differing only slightly in the chemical composition—random PP copolymer (rPP)). This is the basis of the consolidation of coextruded tapes, developed by the group of Peijs [5–7]. This combination of iPP and rPP materials can also be processed by film-stacking method [8–15]. As a result of reprocessing of these two-component systems an iPP/rPP blend is obtained, so its homogeneity and morphology is to be determined [16]. Since iPP is a polymorphic polymer, it has three crystalline modifications: monoclinic (α), trigonal (β) and orthorhombic (γ) forms [17–19]. Commercial grades of iPP crystallize essentially in the α-form [20]), however, β-PP can be prepared easily in the presence of highly active β-nucleating agents [20, 21]. The melting temperature of β-form is lower than that of the commercial α-PP, which provides possibility to broaden the processing window of self-reinforced iPP composite (SRPPC) products, if α-PP is embedded as reinforcement in β-PP matrix. This kind of composite is really a homocomposite, because of the reinforcement and the matrix differ only in their crystalline forms [13, 14, 22, 23] (Note that analogous approach was also used for polyamide (PA6) based self-reinforced composites [24]). Therefore, the expected recyclability of these composites shall be similar to the hot compacted composites.

The reprocessability of polypropylenes was studied by several authors. After several injection molding cycles, the reprocessing may resulted in chain scission, which is mainly caused by heat loading and mechanical shearing [25]. However, no significant change in the molecular architecture occurs during several reprocessing cycles of well-stabilized commercial iPP grades. With increasing number of cycles or with increasing reprocessing temperature, only a little reduction can be observed in the average molecular mass [26, 27]. Many studies have been reported no change or only a slight decrease in the tensile strength and in molecular mass of the material [28–30]. The impact properties and the elongation at break are improved, however, as a consequence of the decreasing stiffness after reprocessing. Additionally, the melt viscosity and the elongation at break also decrease [31].

After reprocessing of reinforced polypropylenes, the mechanical properties (impact strength, flexural strength and modulus) were decreasing due to mainly the fibre breakage. These phenomenons were investigated in the literature [25, 28, 31]. The rheological tests showed the decrease of the viscosity. This is caused by chain scissions and reinforcing fibre breakage induced by reprocessing and grinding.

Since the reprocessing of iPP and its composites have been widely published but there are no studies for the reprocessing of SRPPCs according to the author's knowledge. Therefore, the goal of this work is to study the reprocessability of the SRPPCs. The composite materials (handled separately based on the related matrix material) were ground, than extruded five times and the properties were studied after the first and fifth extrusion, respectively, to investigate the melting characteristics and mechanical properties of the samples during reprocessing. From the granulated materials, different specimens were produced by injection molding and tested.

Materials, their processing and testing

Materials

Composite specimens prepared and tested previously [13, 14] and cutting scraps were used in our present study. The composite sheets are composed of a plain woven fabric as reinforcement (presented in our earlier study [14], composed of highly stretched split PP yarns) and three kinds of PP as matrix material (β form of isotactic PP homopolymer (H388F); random PP copolymer (R351F), and β form of the latter. The non-nucleated iPP grades were provided by TVK Co. (Tiszaújváros, Hungary) and exhibited a melt flow index of 8 g (10 min)$^{-1}$ (at 230 °C and 2.16 kg of load). 0.15 wt% of calcium salt of suberic acid (Ca-sub) was introduced into iPP as a selective β-nucleating agent to prepare β-nucleated samples [32]. The detailed processing method of all SRPPC specimens was described in our earlier studies [13, 14]. Thin film was extruded as matrix material and a woven fabric composed of highly stretched iPP tapes was applied as reinforcement. Table 1 contains the melting temperature of the components.

Composite sheets with a thickness of 2.5 mm and a nominal reinforcement (i.e. α-PP fabric) content of 50 wt% were produced by compression moulding of a film-stacked package at 7 different processing temperatures. They are selected at 5, 10, 15, 20, 25, 30 and 35 °C above the relevant matrix melting temperature. For the latter, the Differential Scanning Calorimetry (DSC) melting peak was

Table 1 The melting temperature of the materials

Type	Melting temperature, T_m/°C
α-PP tape	172.4
α-PP	164.4
β-PP	151.5
α-rPP	142.5
β-rPP	131.3

considered (cf. Table 1). Due to the different processing temperatures, the consolidation quality of the resulting composites was also different. The tested (failed) specimens and cutting scrap were collected separately according to the matrix material.

Grinding and extrusion

The collected tested composite specimens and cutting scrap were ground with Plastics Machinery Granulatore GRS 152_302 grinder. The ground composite material was inhomogeneous; significant amount of reinforcement material from the poorly consolidated SRPPCs was debonding from the matrix. Therefore, the particle size distribution was also inhomogeneous.

The ground material was extruded five times with a Brabender Plasti-Corder PL 2100 twin screw extruder and then granulated. The extrusion temperatures were set to 190, 195, 200 and 200 °C from the feeder to the die. The screw revolution 8 min^{-1} for the ground material (first cycle) and 25 min^{-1} for the granulated material (2–5th cycle) and for matrix materials were set. In order to compare, the original matrix materials were also extruded five times.

Injection molding

From the granulated materials after the first and fifth extrusion different (tensile and Charpy) specimens were manufactured on an Arburg Allrounder 320C 600-250 injection molding machine. Table 2 contains the injection molding parameters. The temperature zones were set to 185, 195, 200, 205 and 210 °C from the feeder to the nozzle. The injection molded materials are listed in Table 3. Note that the composite materials with random PP copolymer matrix (regardless of its crystalline form) became a blend due to the reprocessing at higher temperature (considerably higher than the melting temperature of the reinforcement). However, referring to the initial materials, we will further designate it as composite.

Specimens and their testing

In order to obtain the flowability and the degradation, Melt Volume Rate (MVR) test were performed on the materials after each process cycle on CEAST Modular Melt Flow 7027.000 machine. The test parameters were as follows: load: 2160 g, holding time: 240 s, temperature: 230 °C, sample mass: 8 g.

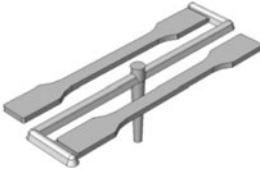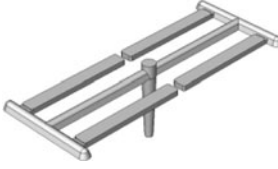**Table 2** The injection molding parameters

Parameter	Tensile specimen	Charpy specimen
Injection volume	44 cm^3	40 cm^3
Injection rate	50 cm^3 s^{-1}	50 cm^3 s^{-1}
Switch over point	12 cm^3	11 cm^3
Holding pressure	400 bar	300 bar
Holding time	20 s	20 s
Screw speed	15 m min^{-1}	15 m min^{-1}
Cooling time	15 s	15 s
Decompression	5 cm^3	5 cm^3
Mould temperature	50 °C	50 °C
Real pressure	540 bar	440 bar

Table 3 The injection molded materials

	α-PP matrix	β-PP matrix	α-rPP matrix	β-rPP matrix	β-PP composite	α-rPP composite	β-rPP composite
Neat material	x		x				
1× extruded	x	x	x	x	x	x	x
5× extruded	x	x	x	x	x	x	x

The crystallization and melting characteristics of the specimens were studied by DSC. The melting curves were recorded by a Perkin Elmer DSC 7 apparatus. Sample mass was between 3 and 5 mg and the scanning rate was 10 °C min^{-1} during heating (v_h) and cooling (v_c) as well. In order to erase thermal and mechanical history, the samples were heated up to 220 °C and held there for 5 min. Since β-form of iPP samples cooled to below 100 °C, recrystallized into the α-form during the partial melting of the β-phase [33], the end temperature of cooling (T_R) was set to 100 °C during non-isothermal crystallization. This setting prevents $\beta\alpha$-recrystallisation, so the polymorphic composition of the blends can be determined accurately from the melting curves [20, 21].

Static tensile tests were performed on dumbbell specimens (according to standard ISO 527:1999) using a Zwick Z020 universal testing machine with a crosshead speed of 5 mm min^{-1}.

Charpy impact tests were performed on Type 1 notched rectangular specimens (according to standard ISO 179:2001) on a Ceast Resil Impactor Junior P/N 6963.000 using the following settings: starting angle of the hammer: 150°; maximum energy: 15 J.

All mechanical tests were performed at room temperature and at least five specimens were tested.

Results and discussion

MVR

The MVR of the materials processed once and five times can be seen on Fig. 1. One can observe that MVR does not change significantly with increasing of the processing cycles. The more or less constant MVR values hint that the stability of the polymer is good and no thermal degradation occurs during the multiplied processing cycles. In case of ground SRPPCs tested prior to first extrusion, the flowability has considerably higher scatter than after extrusion. The reason is that the particle size of the ground material was inhomogeneous. The fluidity of the extruded SRPPCs is lower than that of matrices, since the fluidity of the neat material of the reinforcing tape production (foil extrusion grade) is much lower.

Melting and crystallization characteristics

Effect of blending

The rPP-based SRPPC is a 'two-component' system, because the copolymer matrix contains ca. 3–5 wt% ethylene co-monomers distributed randomly. As a result of the melt reprocessing, it is important to know the resulting
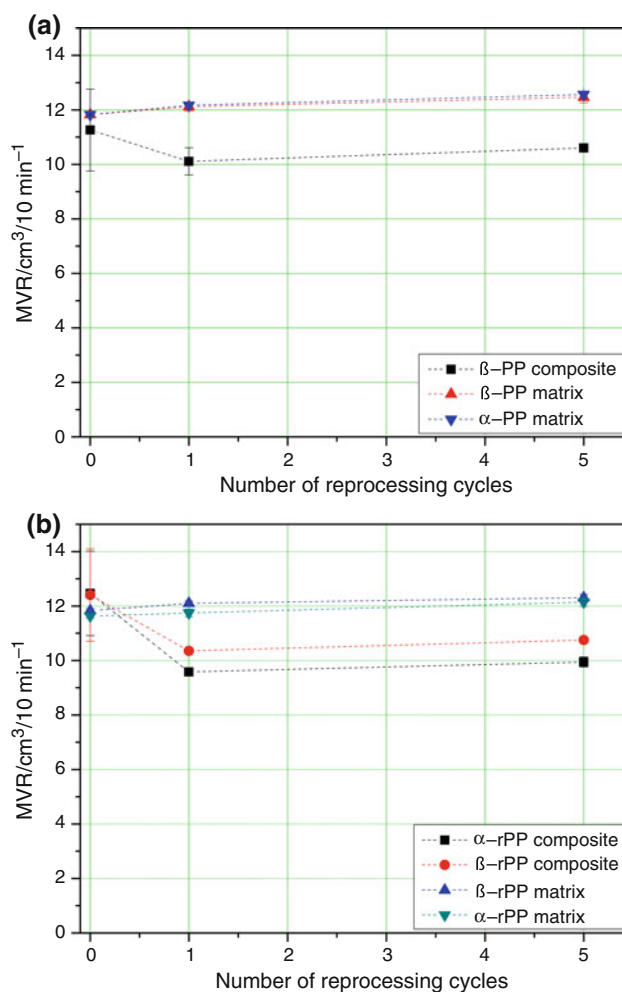

Fig. 1 The MVR index in case of iPP homopolymer (**a**), and random PP copolymer (**b**) systems

structure of iPP/rPP blend. The melting curves of α-PP (the neat material of α-PP reinforcement) and α-rPP matrices and the blend of α-rPP matrix and α-PP tapes (α-PP composite-based sample) are displayed in Fig. 2. The calorimetric traces indicate clearly that one peak appears during the melting and crystallization of composite materials indicating the miscibility of iPP and rPP in the reprocessed α-PP composite-based sample. The melting peak at 164 °C relates to α-PP and, α-rPP matrix melts in the vicinity of 145 °C. The melting of the blend consists of these two PPs (ca. in 50–50 wt%) is around at 155 °C and its melting is reflected by one melting peak. The iPP component has advantageous effect on the crystallization of rPP. iPP and rPP are miscible polymer pair in molten state and the crystallization of the components take place simultaneously. Consequently, only one crystallization peak can be observed during the crystallization of iPP/rPP blends and the higher the iPP content is, the higher is the peak temperature of crystallization.
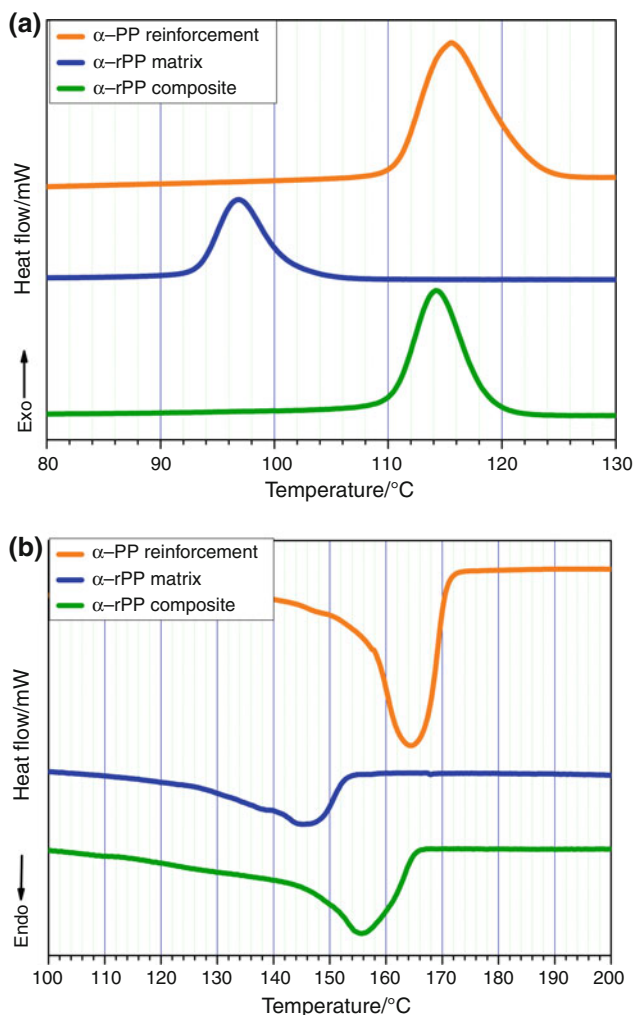
Fig. 2 The cooling (1st cool—**a**) and melting curves (2nd heat—**b**) of the α-PP, α-rPP matrix and the reprocessed α-rPP composite

Fig. 3 The cooling (1st cool—**a**) and melting curves (2nd heat—**b**) of the α-PP, β-rPP matrix and the reprocessed β-rPP composite

The melting and crystallization characteristic of β-rPP composite-based material after reprocessing is demonstrated in Fig. 3. The peak temperature of crystallization (T_{cp}) of the α-reinforcement, the β-matrix and the composites are in the vicinity of 112, 104 and 114 °C respectively. The T_{cp} of β-rPP matrix is significantly higher than that of the non-nucleated rPP matrix (see in Fig. 2a), which unambiguously indicates the presence of the highly active nucleating agent. The presence of Ca-sub results in even higher T_{cp} of the β-rPP composite as well compared to the α-PP reinforcement. The β-nucleated matrix and composites have complicated melting peaks. The double melting peak at lower temperatures refers to the β-form, however, the melting peak duplication hints at structural instability [33]. A perfection process within the unstable β-phase results in a ββ′-recrystallization. Similar characteristics are represented by the melting trace of β-rPP composite-based specimen, although the melting peaks are shifted towards
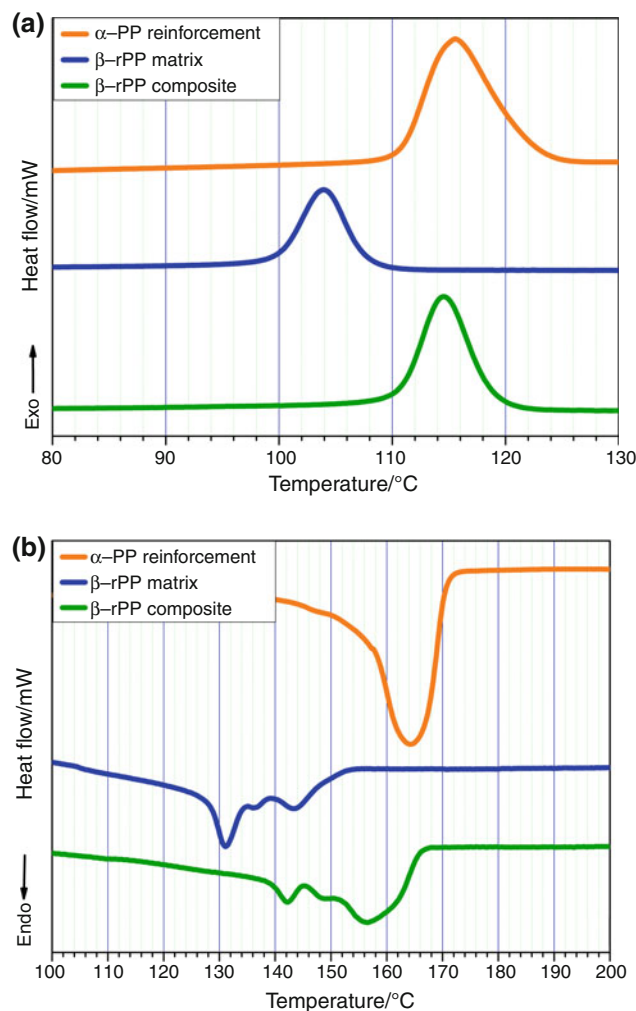
higher temperatures, because of the presence of iPP in the composites. The doubled melting peaks at 142 and 148 °C can be attributed to the ββ′-recrystallization as well, but it has to be pointed out that the intensities of the melting peaks of β-form are less pronounced because of the decreased amount of the nucleating agent. The β-rPP matrix contains 0.15 wt% Ca-sub, while the content of β-nucleating agent in the β-rPP composite-based material is only the half of that in the β-rPP matrix.

The effects of number of reprocessing cycles

Figure 4 shows the melting and cooling curves of β-PP matrix and β-PP composite-based material after reprocessing once and five times. When comparing samples reprocessed once and five times, one can see that there was no considerable difference due to the cyclic reprocessing for both matrix and composite-based specimen.
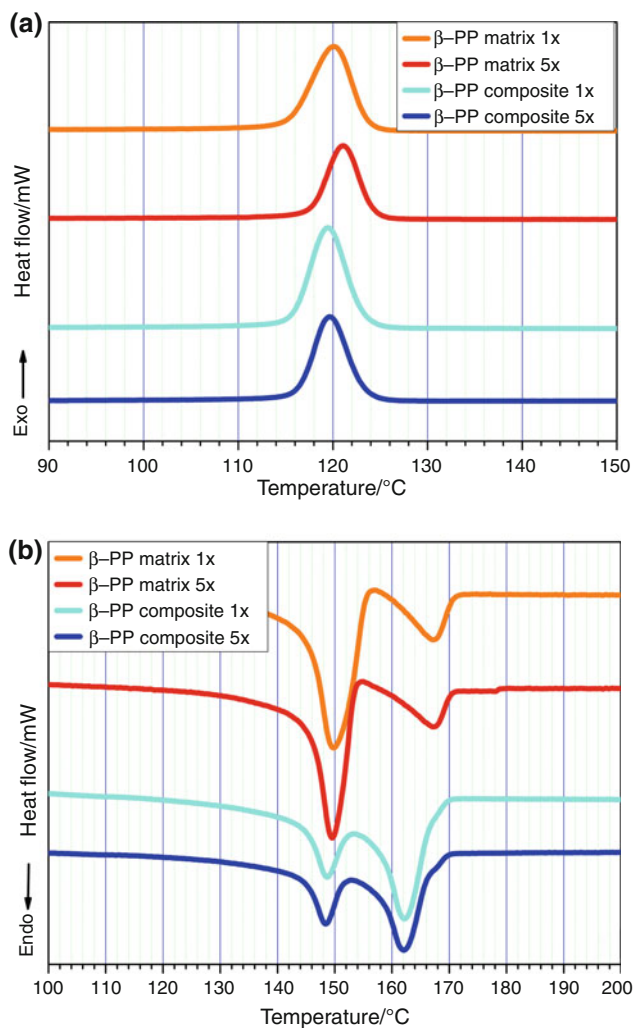
Fig. 4 The cooling (1st cool—**a**) and melting curves (2nd heat—**b**) of the β-PP materials reprocessed once and five times

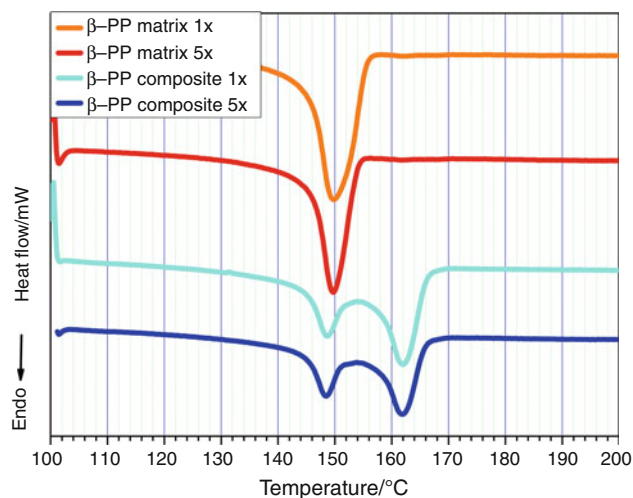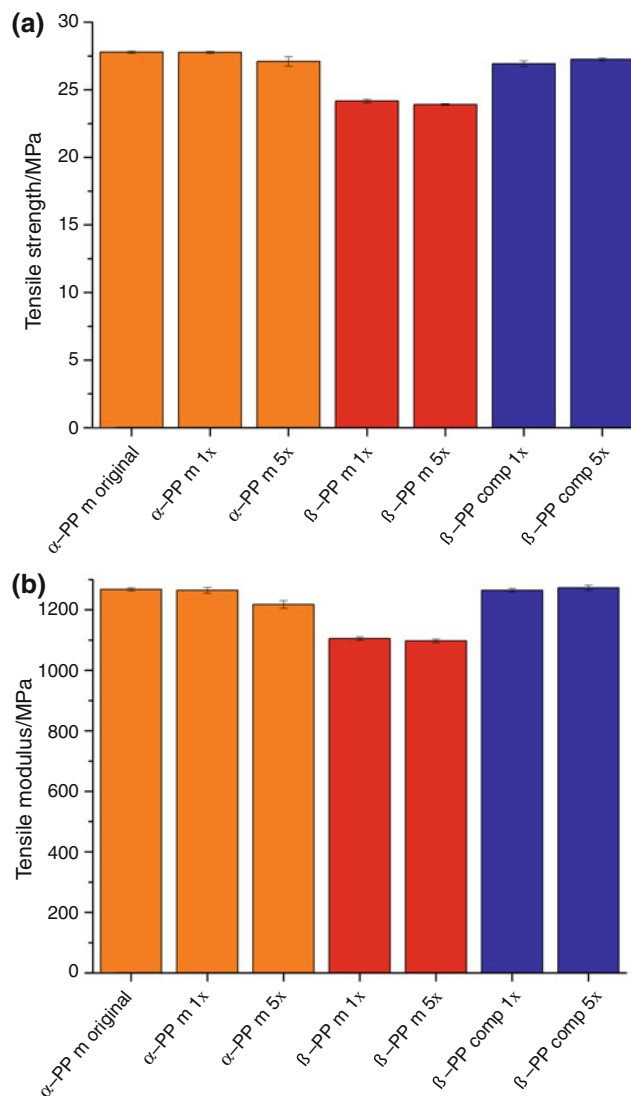Fig. 5 The melting curves (3rd heat) of the β-PP materials reprocessed once and five times

Fig. 6 Tensile strength (**a**) and modulus (**b**) of the PP homopolymer based systems

The β-nucleating agent is still efficient even after five reprocessing steps, because of its good thermal stability, although during injection moulding the related standard for PP was followed, parameters of which did not support the formation of the β-crystals. The crystallization temperatures are at around of 120 °C, which is characteristic for nucleated iPP. Pronounced βα-recrystallization process is reflected on the melting traces (see in Fig. 4b) indicating the presence of the β-form. The βα-recrystallization can be eliminated if the samples are not cooled below 100 °C [33]. The melting traces recorded after limited recooling step are represented in Fig. 5. One can see that the β-nucleated matrix materials crystallized fully in β-form, but the composites also contain significant amount of α-form due to considerably lower β-nucleating agent content. The reprocessability of the β-nucleating agent is

shown only on β-iPP composite-based samples due to the higher β-content of the matrix. The same tendency can be observed in case of β-rPP materials. The melting curves do not indicate any degradation after multiplied processing in good agreement with MVR data.

Mechanical properties

Static tensile tests

The tensile strength (a) and modulus (b) values of iPP- and rPP-based systems are shown in Figs. 6 and 7, respectively. When comparing the results of once and five times processed materials, the mechanical properties of the specimens

do not modify considerably, which indicates that no pronounced degradation takes place during multiplied reprocessing. Comparing the non-nucleated and β-nucleated matrix materials (both homo- and copolymer), it can be stated that the β-nucleation resulted in a slight decrement in tensile strength and in the Young's modulus, because of the presence of β-form. It should be noted that the β-nucleated matrix material have the lowest stiffness and tensile strength and the properties of the composite-based ones are closer to that of the non-nucleated matrix material in case of iPP-based materials. The relatively large stiffness and tensile strength of the α-iPP composite-based specimens can be explained by the large α-iPP content of the samples (See in Fig. 5). This is also true when comparing α- and β-rPP
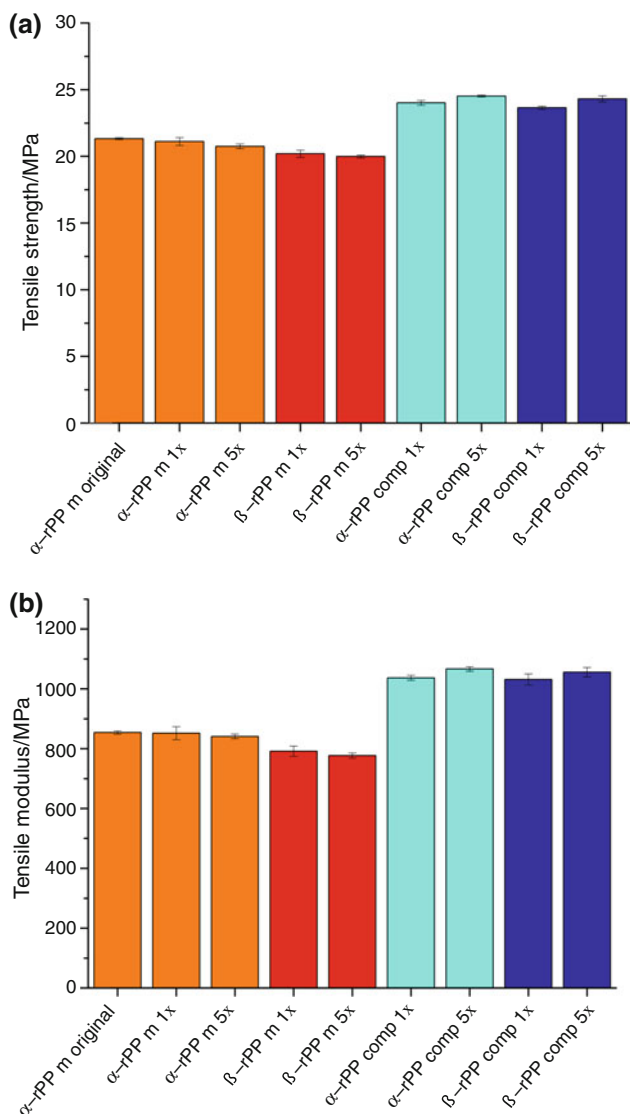

Fig. 7 Tensile strength (a) and modulus (b) of the random PP copolymer based systems
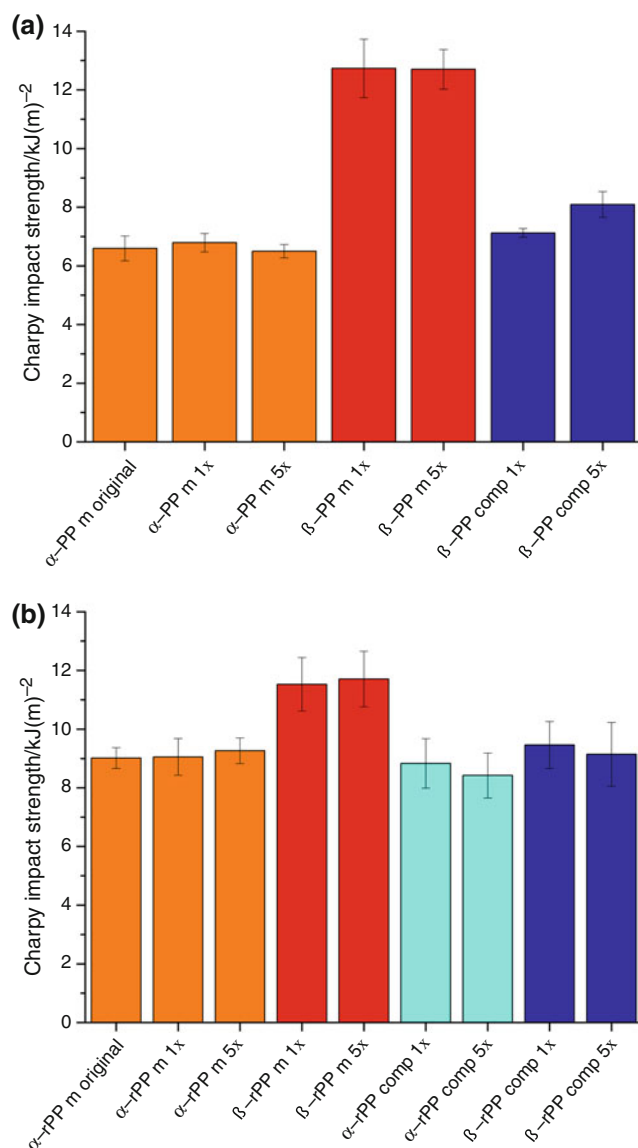

Fig. 8 Charpy impact strength of the PP homopolymer (a) and random PP copolymer (b) based systems

SRPPC-based materials. The modulus and tensile strength of rPP composite-based specimen (iPP/rPP blends) were significantly higher than those of related matrix material, because of the presence of iPP phase.

From the result, it can be stated further that there was no considerable change in the tensile properties if comparing the material processed once and five times.

Charpy impact tests

Figure 8 shows the Charpy impact strength results for iPP (a) and rPP (b) based systems. Based on the results, it can be seen that the β-modification has improved the Charpy impact strength in case of matrix materials. The increasing of impact resistance is more pronounced in case of homopolymer [20], because the rPP contains elastomers (PE), which improves the impact resistance as well. In the case of β-PP composites, efficiency of the lower amount of β-nucleating agent may be more sensitive for the processing parameters, so the impact resistance did not increase significantly. In case of rPP composite-based samples, the lower toughness is resulted by the approximately 50 wt% of α-iPP content (see Fig. 8a). It can also be concluded from the test results that with increasing number of reprocessing, the Charpy impact strength did not decrease considerably.

Conclusions

The goal of this article was to study reprocessability and the melting behaviour of the self-reinforced PP composite composed of fabric, woven from highly stretched split iPP yarns as reinforcement and α and β crystal forms of isotactic PP homopolymer and random PP copolymer as matrix materials. From the granulated materials, different specimens were produced by injection molding and they were tested (MVR, DSC, tensile, Charpy).

Based on the results the following conclusions can be drawn:

- self-reinforced PP composites can well be reprocessed without any loss of properties related to the properties of the matrix materials, thereby it is an excellent candidate for upcycling,
- the cyclic reprocessing (once and five times) did not result in considerable deterioration of the mechanical properties,
- based on the DSC results it can be stated that the used β-nucleating agent (Ca-sub) is still efficient after even five reprocessing cycles. However, it is necessary to apply suitable settings of injection molding.

- the random PP copolymer-based SRPPCs (reinforced with PP homopolymer) became a one-phase blend after reprocessing. Their melting temperature and mechanical properties are between those of random copolymer and homopolymer.

References

1. Directive 2000/53/EC of European Parliament and of the Council of 18 September 2000.
2. Ward IM. Developments in oriented polymers, 1970–2004. Plast Rubber Compos. 2004;33:189–94.
3. Ward IM, Hine PJ. Novel composites by hot compaction of fibers. Polym Eng Sci. 1997;37:1809–14.
4. Ward IM, Hine PJ. The science and technology of hot compaction. Polymer. 2004;45:1413–27.
5. Alcock B, Cabrera NO, Barkoula NM, Reynolds CT, Govaert LE, Peijs T. The effect of temperature and strain rate on the mechanical properties of highly oriented polypropylene tapes and all-polypropylene composites. Compos Sci Technol. 2007;67:2061–70.
6. Alcock B, Cabrera NO, Barkoula NM, Spoelstra AB, Loos J, Peijs T. The mechanical properties of woven tape all-polypropylene composites. Compos Pt A Appl Sci Manuf. 2007;38:147–61.
7. Alcock B, Cabrera NO, Barkoula NM, Wang Z, Peijs T. The effect of temperature and strain rate on the impact performance of recyclable all-polypropylene composites. Compos Pt B Eng. 2008;39:537–47.
8. Houshyar S, Shanks RA, Hodzic A. Influence of different woven geometry in poly(propylene) woven composites. Macromol Mater Eng. 2005;290:45–52.
9. Houshyar S, Shanks RA, Hodzic A. The effect of fiber concentration on mechanical and thermal proverties of fiber-reinforced polypropylene composites. J Appl Polym Sci. 2005;96:2260–72.
10. Houshyar S, Shanks RA. Morphology, thermal and mechanical properties of poly(propylene) fibre-matrix composites. Macromol Mater Eng. 2003;288:599–606.
11. Bárány T, Izer A, Czigány T. On consolidation of self-reinforced polypropylene composites. Plast Rubber Compos. 2006;35:375–9.
12. Bárány T, Izer A, Czigány T. High performance self-reinforced polypropylene composites. Mater Sci Forum. 2007;567–538:121–8.
13. Bárány T, Izer A, Karger-Kocsis J. Impact resistance of all-polypropylene composites composed of alpha and beta modifications. Polym Test. 2009;28:176–82.
14. Izer A, Bárány T, Varga J. Development of woven fabric reinforced all-polypropylene composites with beta nucleated homo- and copolymer matrices. Compos Sci Technol. 2009;69:2185–92.
15. Houshyar S, Shanks RA, Hodzic A. Modelling of polypropylene fibre-matrix composites using finite element analysis. Express Polym Lett. 2009;3:2–12.
16. Menyhárd A, Varga J, Liber Á, Belina G. Polymer blends based on the beta-modification of polypropylene. Eur Polym J. 2005;41:669–77.

17. Padden FJ Jr, Keith HD. Spherulitic crystallization in polypropylene. J Appl Phys. 1959;30:1479–84.
18. Varga J, Ehrenstein GW, Schlarb AK. Vibration welding of alpha and beta isotactic polypropylenes: mechanical properties and structure. Express Polym Lett. 2008;2:148–56.
19. Varga J. Beta-modification of isotactic polypropylene: preparation, structure, processing, properties, and application. J Macromol Sci Phys. 2002;41:1121–71.
20. Menyhárd A, Varga J, Molnár G. Comparison of different beta-nucleators for isotactic polypropylene, characterisation by DSC and temperature-modulated DSC (TMDSC) measurements. J Therm Anal Calorim. 2006;83:625–30.
21. Abraham TN, Wanjale SD, Bárány T, Karger-Kocsis J. Tensile mechanical and perforation impact behavior of all-PP composites containing random PP copolymer as matrix and stretched PP homopolymer as reinforcement: effect of [beta] nucleation of the matrix. Compos Pt A Appl Sci Manuf. 2009;40:662–8.
22. Bárány T, Karger-Kocsis J, Czigány T. Development and characterization of self-reinforced poly(propylene) composites: carded mat reinforcement. Polym Adv Technol. 2006;17:818–24.
23. Bhattacharyya D, Maitrot P, Fakirov S. Polyamide 6 single polymer composites. Express Polym Lett. 2009;3:525–32.
24. Martins MH, De Paoli MA. Polypropylene compounding with post-consumer material: II. Reprocess. Polym Degrad Stab. 2002;78:491–5.
25. González-González VA, Neira-Velázquez G, Angulo-Sánchez JL. Polypropylene chain scissions and molecular weight changes in multiple extrusion. Polym Degrad Stab. 1998;60:33–42.
26. Xiang Q, Xanthos M, Mitra S, Patel SH, Guo J. Effects of melt reprocessing on volatile emissions and structural/rheological changes of unstabilized polypropylene. Polym Degrad Stab. 2002;77:93–102.
27. Incarnato L, Scarfato P, Acierno D. Rheological and mechanical properties of recycled polypropylene. Polym Eng Sci. 1999;39:749–55.
28. Ramírez-Vargas E, Navarro-Rodríguez D, Blanqueto-Menchaca AI, Huerta-Martínez BM, Palacios-Mezta M. Degradation effects on the rheological and mechanical properties of multi-extruded blends of impact-modified polypropylene and poly(ethylene-co-vinyl acetate). Polym Degrad Stab. 2004;86:301–7.
29. Rust N, Ferg EE, Masalova I. A degradation study of isotactic virgin and recycled polypropylene used in lead acid battery casings. Polym Test. 2006;25:130–9.
30. da Costa HM, Ramos VD, de Oliveira MG. Degradation of polypropylene (PP) during multiple extrusions: thermal analysis, mechanical properties and analysis of variance. Polym Test. 2007;26:676–84.
31. Varga J, Mudra I, Ehrenstein GW. Highly active thermally stable beta-nucleating agents for isotactic polypropylene. J Appl Polym Sci. 1999;74:2357–68.
32. Varga J. Melting memory effect of the beta-modification of polypropylene. J Therm Anal. 1986;31:165–72.
33. Horváth Z, Sajó I, Stoll K, Menyhárd A, Varga J. The effect of molecular mass on the crystallization tendency and supermolecular structure of the polymorphic modifications of isotactic polypropylene. Express Polym Lett. 2010;4:101–14.