



Budapest University of Technology and Economics
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Theses Booklet

**DEVELOPMENT AND INVESTIGATION OF SELF-REINFORCED
POLYPROPYLENE COMPOSITES BASED ON THE POLIMORPHISM OF
PP**

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The referees' opinion and the minutes of the PhD examination can be inspected at the Deans Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics.

1. INTRODUCTION

Nowadays one of the key issues in materials development is the recyclability of products after their lifecycle. This aim is supported (especially in the automotive industry) even by the European Union directive on the end-of life vehicles (ELV). This directive states that no later than 2015 the reuse and recovery of all vehicles shall be increased to a minimum of 95% and recycling shall be increased up to 85% by an average weight per vehicle and year. A lot of problems arise because the newest vehicles should also perform this request. Considering the commercial aspects, one of the most used polymeric materials in the automotive industry is polypropylene (PP), which is usually reinforced with glass fibre (GF) and rarely with natural fibre (NF). The properties of PP based composites can compete with engineering plastics, but their reprocessing is difficult therefore the requirements of the above mentioned directive cannot be fulfilled without an accompanied decrease in the mechanical properties. In the last 15 years considerable efforts have been devoted to develop more environmental-friendly engineering materials which show similar mechanical performance, however, far better recyclability.

One of the suitable ways to achieve the above mentioned goal is the application of natural fibres (hemp, sisal, flax) as reinforcement. These fibres can be found in great amount in nature, therefore they are ecofriendly and cheap. Several investigations show however, that a coupling agent is needed to achieve good mechanical properties (only the specific values of these composites can compete with the properties of GF-PP). Therefore matrix-reinforcement debonding is also an unsolved problem of recycling.

On the other hand self-reinforced polymer composites (SRPC) seem to be a viable alternative to GF-PP composites, where the matrix and the reinforcement are from the same polymer family thereby easy recycling is ensured. The concept was first presented by Capiati and Porter for high-density polyethylene (HDPE). Later on the concept was adapted to several polymers. The use of PP for self-reinforced composites (SRPPC) seemed to be the best way because of its favourable properties and commercial aspects.

The basis of all SRPC techniques is to set a suitable processing window, which exploits the difference in the melting temperature (T_m) of the reinforcement and the matrix. The wider the processing window is, the cheaper the processing of the composite can be. This temperature difference can be widened in various ways, such as using fibres of different orientation

(stretch ratio) or difference in the composition like random PP copolymer for matrix, and PP homopolymer for reinforcement.

There are three main research trends to produce SRPC: hot compaction, consolidation of coextruded tapes and film-stacking method. Each method yields a great alternative material to GF-PP in cases where composites are shaped by thermoforming. The disadvantage of the first two processes is the relatively high manufacturing cost due to the precise technique in case of hot compaction and the additional step in the technique of coextruded tapes. To eliminate these drawbacks new research has been started to produce SRPPC from commercial products and to process it by a simple technique which can be competitive in price with GF-PP.

Great advantages of these composites are the full recyclability, good mechanical properties, excellent fibre-matrix adhesion without any help of a coupling agent and the approx. 30% lower weight compare to GF-PP.

2. AIMS OF THE THESIS

The composition of the matrix and reinforcement is done every case by hot pressing (compression moulding). The processing parameters (processing pressure, temperature, time) have great influence on the consolidation quality of the composite. The increasing consolidation quality means that the melted matrix wets the reinforcement better and the void content in the composite is decreased. Therefore the consolidation quality has a significant effect on the mechanical properties. The exploration of the structure-property relationship is an essential step to understand the behaviour of this composite material.

After the lifecycle of the product, it has to be reprocessed. The main advantage of SRPC is the full reprocessability but no information is available in the literature concerning this topic.

Products are formed from the SRPCs mainly by thermoforming. The forming parameters have not been widely published because there are only two materials available commercially. The ductility and the forming parameters of the material are very important to manufacture a good quality product.

Based on the above mentioned facts, the main goals of the thesis are:

- To develop self-reinforced polypropylene composites exploiting the polymorphism of PP, processed by film-stacking method.

- To investigate the effect of processing temperature on the consolidation quality and the mechanical properties of the composite. It will be investigated by static and dynamic mechanical, peel and microscopic studies.
- To study the fracture and failure behaviour of the differently consolidated composites by microscopy and AE tests.
- To analyze the creep behaviour of the differently consolidated composites.
- To predict the long-term behaviour from short-term tests.
- To explore the reprocessability of SRPPCs and compare it to neat PP material.
- To determine the thermoformability of composites produced with different kinds of techniques.

3. MATERIALS, THEIR PROCESSING AND TESTING METHODS

A plain woven fabric (produced by Stradom S.A., Czestochowa, Poland) composed of highly stretched split PP tapes with a nominal weight of 180 g/m² was selected and used as the reinforcement. The reinforcing tape has a melting temperature of $T_m=172.4^\circ\text{C}$ (determined by DSC), and a tensile strength of 465 ± 32 MPa (measured on a single tape with a Zwick Z050 tensile machine).

Three kinds of PP were used as matrix materials: i) β -form of isotactic PP homopolymer Tipplen H388F (β -PP); ii) random PP copolymer Tipplen R351F (α -rPP), and iii) β -form of the latter (β -rPP). The non-nucleated PPs were provided by TVK Co. (Tiszaújváros, Hungary) and exhibited a melt flow index of 8 g/10 min (at 230°C and 2.16 kg load).

For the β -nucleation of PP 0.15 wt% of calcium salt of suberic acid (Ca-sub) was chosen as a selective β -nucleating agent due to its high selectivity.

For the β -nucleation of PP a masterbatch was produced first in a twin-screw extruder (Brabender, Duisburg, Germany). In the masterbatch 1.5 wt% of Ca-sub was incorporated. The extrusion temperature was 220°C and the screw revolution was 5 min^{-1} . After extrusion the materials were pelletized. From both PPs (H388F and R351F) neat and β -nucleated films with a thickness of 180 μm were extruded (Davo Viskosystem extruder, Troisdorf, West Germany) by in-situ mixing the neat pure PP with the masterbatch (in a ratio of 9:1), resulting finally in a β -form with 0.15 wt% Ca-sub content. The extrusion temperature was 230°C and the revolution was 60 min^{-1} (the preliminary studies showed that with increasing processing speed, β -content increased in the material, therefore the maximum possible screw revolution was selected). To promote the β -crystallization of PP, the rolls were heated close to 100°C because the preferred crystallization temperature range of the β -modification of PP is between 100 and 140°C . No drawing was used since molecular orientation does not support β -crystallization.

Composite sheets with a nominal thickness of 2.5 mm were produced using film-stacking method followed by hot pressing at seven different processing temperatures (at 5, 10, 15, 20, 25, 30 and 35°C above the related matrix melting temperature) and holding time of 90 s under a constant pressure of 7 MPa with a nominal reinforcement content of 50 wt%. The reinforcing layers were placed on each other in cross-ply arrangement therefore the resulting composite plates were orthotropic. The film-stacked packages were inserted between the preheated plates, held between them - without applying pressure - for 30 s, then pressed for

90 s at 7 MPa and then cooled down with a cooling rate of 7.5°C/min. The holding time at the processing temperature was kept short to prevent shrinkage and molecular relaxation of the fibres at high processing temperature.

The X-Ray scattering patterns of the matrices were recorded using a Philips PW 1710/PW type equipment with CuK α radiation at 40 kV and 35 mA and X Pert PRO MPD type equipment with CuK α radiation at 40 kV and 30 mA.

The crystallization and melting characteristics of the specimens were studied by DSC. The melting curves were recorded by a Pelkin Elmer DSC 7 apparatus. Samples having a weight of 3-5 mg were scanned at 10°C/min heating (v_h) and cooling (v_c) rates. In order to erase thermal and mechanical history, the samples were heated up to 220°C and held there for 5 min. Since the β -form of PP samples cooled below 100°C, recrystallised into the α -form during the partial melting of the β -phase, 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 as well.

The interlaminar (peel) strength was determined on rectangular specimens of 25.4x250 mm² using a Zwick Z020 universal testing machine according to standard ASTM D 3167-97 at a crosshead speed of 152 mm/min. Attention was paid to the peel-off of the last two reinforcing and matrix layers from the top of the composite sheets. To initiate peeling a small piece of thin aluminium foil (thickness of 50 μ m) was inserted in between the second woven fabric and the third matrix foils in the assembly prior to hot pressing. This way the related peel results can be compared accordingly.

The consolidation quality was inspected by reflection light microscopy (LM; Olympus BX51M) on polished cross sections of SRPPC sheets. Cross sections were cut from each composite and embedded in epoxy resin. After the preparation of the samples they were polished in a Struers polisher in four steps, using 320, 1000, 2400 and 4000 SiC papers and water as the lubricant.

Scanning electron microscopic pictures were taken of the reinforcement and fractured surfaces on a Jeol JSM-6380LA microscope. The samples were sputter coated with gold alloy. The morphology of the SRPPCs was studied on thin sections by polarized light microscopy (PLM) using a microscope of Leitz (Leica, Wild Leitz GmbH, Germany) with a λ -plate located diagonally between the polarizers. Thin sections of 8 μ m were cut from the composites with a microtome (Microm, Walldorf, Germany) at room temperature (RT).

The density of the samples was determined in absolute ethanol at 23°C according to MSZ EN ISO 1183-1. Prior to immersing the specimens, the edges of them were coated with wax in order to prevent the ethanol from diffusing into the samples. The test was performed at room temperature (23°C) and the average of five statistically relevant density data has been reported.

Static tensile tests were performed on rectangular specimens of 25x250 mm² (in case of composites) and injection moulded dumbbell specimens (in case of the reprocessing test) using a Zwick Z020 universal testing machine according to standard MSZ EN ISO 527 at a crosshead speed of 5 mm/min.

Static three point bending tests were performed on rectangular specimens of 60x15 mm² according to standard EN ISO 178 using a Zwick Z020 universal testing machine. The test speed was 2 mm/min. The span length was 48 mm.

Instrumented falling weight impact (IFWI) tests were performed on Fractovis 6785 (Ceast, Pianezza, Italy) using the following settings: maximal energy: 229.05 J; diameter of the dart: 20 mm; diameter of the support rig: 40 mm; weight of the dart: 23.62 kg and drop height: 1 m. Square shaped specimens of 70x70 mm² were used.

In order to obtain information about the failure mode during tensile tests, the acoustic emission (AE) technique (Sensophone AED-40 device with Physical Acoustics Corporation Micro30S sensors) was used in the frequency range of 100...600 kHz with logarithmic amplification. The threshold was set to 32 dB to filter ambient noises, and the reference voltage of the test device was 3 mV. The AE sensor was fixed on the surface in the middle of the specimen. To fix the sensor on the surface, a clip was used in each case (composite specimen, and reinforcement tape). To assist the registration of events, silicon gel was used between the specimen surface and the microphone. With the AE device amplitudes and cumulative events were registered.

Short-time flexural creep tests were performed using the three-point bending mode at different temperatures, ranging from -20 to 80°C, in a DMA Q800 apparatus (TA Instruments, New Castle, USA). In this temperature range, isothermal creep tests were run on the specimens with a stepwise temperature increment of 10°C. Prior to the creep measurement, each specimen was equilibrated for 5 min at each temperature and then the flexural creep behaviour was tested for 30 min under a constant load of 5 MPa. Test specimens of dimensions 60x15x2.5 mm³ (length x width x thickness) were used for creep tests.

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

4. THESES

I have prepared self-reinforced polypropylene (PP) based composites with 50 wt% nominal reinforcement content from commercially available base materials with the method of film-stacking and pressing. I have applied a woven fabric made from high stretched split PP tapes as the reinforcement, while I have prepared a β -modification of PP homopolymer (β -PP), alpha (α -rPP) and beta (β -rPP) modification of random PP copolymer, and this way the processing temperature range was ensured. The composites were produced in a matched mould at 7 MPa pressure using 90 s heat keeping time in a wide temperature range (5-35°C above the melting point of the matrix material), and this way different qualities were achieved in consolidation. Based on the above mentioned material and technology developments I have achieved the following results:

1. I have revealed that self-reinforced PP composites can be produced exploiting the polymorphism of PP in a sufficiently wide processing temperature range. I have proven that the consolidation of the composite improves significantly as the processing temperature increases, hence its tensile and flexural strength and modulus increase as well, meanwhile the energy absorption ability (perforation energy) decreases monotonously. I have shown that an optimal processing temperature exists 20-25°C above the melting temperature of the used matrix materials. In this limited temperature range the processed composite sheets consolidated in an excellent way, proven by the good interlaminar strength and the occurrence of a transcrystalline layer. These composite sheets have good energy absorption ability besides the maximal tensile and flexural properties. Above this temperature the properties of the composites deteriorate. This phenomenon can be explained with the relaxation of the reinforcement, and its partial melting at the highest temperature [1].
2. I have proven through acoustic emission investigations that there is a connection in wide processing temperature range between the consolidation quality of the self-reinforced PP composite and the run of acoustic signals. I have revealed that at low

processing temperatures, where poor consolidation takes place, the composite emits a large number of acoustic signals even in case of small loading (the cumulated number of events is more than 2000 until total failure). This phenomenon can be explained by the separation of the layers and the alignment of the reinforcing fabric. In case of improved consolidation, due to the strong fibre/matrix adhesion and the transcrystalline layer, the composite emits a low number of signals under loading (the cumulated number of events is less than 200) that only occur near the total failure. In this case the characteristic failure mode is fibre breakage [2].

3. I have shown that there is a relation between the failure of the self-reinforced composite and the amplitude of the emitted acoustic signals. I have proven with acoustic emission tests on fabrics and elementary tapes that the small amplitude signals (below 50 dB) are usually caused by the movement of reinforcing fibres, layer separation (fibre/matrix separation) and the fibre fibrillation, while high amplitude signals (above 65 dB) can be connected typically to fibre breakage [2].
4. I have proven with short time creep tests that the creep resistance of self-reinforced PP composites decreases with an increasing temperature. This phenomenon becomes significant above room temperature. Furthermore, I have shown that the consolidation quality of the composite influences its creep resistance to a great extent, as better consolidation increases the creep resistance of the composites. I have determined the theoretical minimum creep tendency of the single composites using the correlation method. In case of rPP based composites (both β -rPP and α -rPP) 0.8 GPa^{-1} and for β -PP 0.5 GPa^{-1} was obtained as the compliance. I have shown, furthermore, that with increasing processing temperature, the activation energies of the composites are monotonically increasing followed by the Arrhenius equation [3].
5. I have proven that the self-reinforced PP composite can be totally and easily reprocessed. The mechanical properties of PP are the same as that of the matrix raw material even after more cycles (5 cycles) of reprocessing at high temperatures (210°C). I have revealed that the random PP copolymer matrix composite with 50 wt% nominal reinforcing content (independent from its crystal modification) transformed to a one-phase system again, the melting temperature and the mechanical properties of which are between those of the homopolymer and the copolymer [4].

5. OWN WRITTEN PUBLICATIONS

- [1] Izer A., Bárány T., Varga J.: Development of woven fabric reinforced all-polypropylene composites with beta nucleated homo- and copolymer matrices. *Composites Science and Technology*, 69, 2185-2192 (2009). (IF₂₀₀₈=2,533)
- [2] Izer A., Stocchi A., Bárány T., Pettarin V., Bernal C., Czigány T.: Effect of the consolidation degree on the fracture and failure behavior of self-reinforced polypropylene composites as assessed by acoustic emission. *Polymer Engineering and Science*, accepted, in press, (2010). (IF₂₀₀₈=1,245)
- [3] Izer A., Bárány T.: Effect of consolidation on the flexural creep behaviour of all-polypropylene composite. *Express Polymer Letters*, 4, 210-216 (2010).
- [4] Bárány T., Izer A., Menyhárd A.: Reprocessability and melting behavior of self-reinforced composites based on PP homo and copolymers. *Journal of Thermal Analysis and Calorimetry*, accepted, in press, (2010). (IF₂₀₀₈=1,63)
- [5] Bárány T., Izer A., Karger-Kocsis J.: Impact resistance of all-polypropylene composites composed of alpha and beta modifications *Polymer Testing*, 28, 176-182 (2009). (IF₂₀₀₈=1,736)
- [6] Bárány T., Izer A., Czigány T.: High performance self-reinforced polypropylene composites. *Materials Science Forum*, 567-538, 121-128 (2007).
- [7] Izer A., Bárány T.: Hot consolidated all-PP composites from textile fabrics composed of isotactic PP filaments with different degrees of orientation. *Express Polymer Letters*, 1, 790-796 (2007).
- [8] Bárány T., Izer A., Czigány T.: On consolidation of self-reinforced polypropylene composites. *Plastics Rubber and Composites*, 35, 375-379 (2006). (IF₂₀₀₆=0,308)
- [9] Izer A., Kmetty Á., Bárány T.: Környezetbarát önerősítéses polimer kompozitok. *Műanyag és Gumi*, 45, 463-467 (2008).
- [10] Czigány T., Izer A., Tábi T.: Polimer kompozitok-áttekintés. *Műanyag és Gumi*, 44, 185-191 (2007).
- [11] Izer A., Bárány T.: Környezetbarát Polipropilén Kompozitok. *Gép*, 57, 8-11 (2006)
- [12] Bárány T., Izer A., Czigány T.: A konszolidáltság mértékének hatása az önerősítéses kompozitok mechanikai tulajdonságaira. *Anyagvizsgálók Lapja*, 4, 113-115 (2005).