

# IMPACT RESISTANCE OF ALL-POLYPROPYLENE COMPOSITES COMPOSED OF ALPHA AND BETA MODIFICATIONS

Tamás Bárány<sup>1</sup>, András Izer<sup>1</sup>, József Karger-Kocsis<sup>2</sup>

1 Department of Polymer Engineering, Budapest University of Technology and Economics,  
H-1111 Budapest, Műegyetem rkp. 3., Hungary

2 Institute for Composite Materials, Technical University of Kaiserslautern,  
D-67663 Kaiserslautern, Pf. 3049, Germany  
barany@pt.bme.hu

## ABSTRACT

In this paper the impact behaviour of self-reinforced polypropylene (PP) composites was studied. For matrix materials  $\alpha$  and  $\beta$  polymorphs of isotactic PP homopolymer and random copolymer (with ethylene), whereas for reinforcement a fabric – woven from highly stretched split PP yarns – were used. The composite sheets were produced by the film-stacking method and consolidated by hot-pressing at 5 and 15°C above the melting temperature ( $T_m$ ) of the related matrix. The composite sheets were subjected to static tensile, dynamic falling weight impact and impact tensile tests at room temperature. Moreover, dynamic mechanical thermal analysis (DMTA) was also performed on the related composites and their constituents. The results indicated that the  $\beta$  modification of the PP homopolymer is more straightforward than that of the PP copolymer. Stiffness and strength usually increased while the toughness (tensile impact strength, perforation impact energy) decreased with increasing temperature of consolidation. This was assigned to differences in the failure mode based on fractographic results.

## 1. INTRODUCTION

The development of environmental friendly engineering material has received top priority recently. Glass fiber (GF) reinforced polypropylene (PP) composites is one of the most widely used materials in the automotive industry due to its favourable properties. However, the presence of GF has become a major issue in the recycling of GF/PP composites. Considerable efforts have been devoted to find a more environmental friendly material than GF/PP. One of the possibilities is to use natural fibers (wood fiber, hemp, flax, sisal, etc.) as reinforcements. On the other hand, self-reinforced PP (SRPP) composites seem to be a viable alternative to GF/PP composites and their development is an extensively studied topic nowadays. For preparing SRPP composites different concepts (hot compaction [1], coextrusion [2], film-stacking [3, 4]) were tried. In these composites the excellent fiber/matrix adhesion is ensured without any coupling agent. Note that the best adhesion and the highest interfacial shear strength can usually be obtained between identical materials.

The basis of all above-mentioned techniques is to set a suitable processing window, which exploits the difference in the melting temperature ( $T_m$ ) of the reinforcement and the matrix (lower  $T_m$ ). This temperature difference can be widened by various manners, such as using fibres of different stretch ratio (less stretched ones become the matrix during hot compaction) or difference in the composition (coextruded films from random PP copolymer /becoming the matrix/ and PP homopolymer /remaining as reinforcement/ during consolidation). Note that the melting temperature of highly oriented PP fibre, tape is markedly higher than non- or less oriented versions [5].

All concepts and previous attempts to produce PP homocomposites overlook a very promising possibility, viz. the exploitation of the polymorphism of PP. Note that the  $\beta$ -form of isotactic PP homopolymer ( $\beta$ -PP) can be selectively produced (by adding

suitable nucleating agents [6]) and its melting temperature is up to 25°C lower than that of the usual  $\alpha$ -form ( $\alpha$ -PP). The peculiar characteristics of  $\beta$ -PP are well documented in the literature, especially in the works of Varga et al. (e.g. [6,7]).

The goal of this study is to investigate the impact behaviour of SRPP by using different PP foils as matrix materials and an  $\alpha$ -PP woven fabric as reinforcement. The fabric was woven from highly stretched split PP yarns. The composite plates have been produced by hot pressing using the film-stacking method whereby the temperature was fixed at either 5 or 15 °C above the melting of the related matrix ( $T_m$ ). Apart of the usual static tensile tests, dynamic mechanical thermal analysis, dynamic falling weight impact and tensile impact tests were performed on the plates.

## 2. MATERIALS AND TESTING

### 2.1 Materials

As matrix materials three kinds of PP were used: i)  $\beta$  polymorph of isotactic PP homopolymer (H388F); ii) random PP copolymer (R351F), and iii) its  $\beta$  polymorph. The non-nucleated PPs were provided by TVK Co., Tiszaújváros, Hungary and having a melt flow index of 8 g/10 min (at 230°C and 2.16 kg load). For the  $\beta$ -nucleation of the PP, first a masterbatch was produced in a Brabender extruder. In this masterbatch 1.5 wt% of calcium salt of suberic acid (Ca-sub) was introduced as selective  $\beta$ -nucleating agent. The extrusion temperature was 220°C and the screw revolution was 5 min<sup>-1</sup>. From both PPs neat and  $\beta$ -nucleated films with a thickness of 180  $\mu$ m were extruded (in a Viskosystem extruder) by in-situ mixing the neat PP with the masterbatch, resulting finally in a  $\beta$ -PP with 0.15 wt% Ca-sub content. The extrusion temperature was 230°C and the revolution was 60 min<sup>-1</sup>. To promote the  $\beta$ -crystallization of the PP, the rolls were heated close to 100°C, because the preferred crystallization temperature range of the  $\beta$ -modification of PP is between 100 and 140°C.

To characterise and compare the PP films wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) techniques were used. The DSC results are shown in Figure 1. The melting temperature values of the  $\beta$ -modification are clearly below that of the  $\alpha$ -phase, as expected.

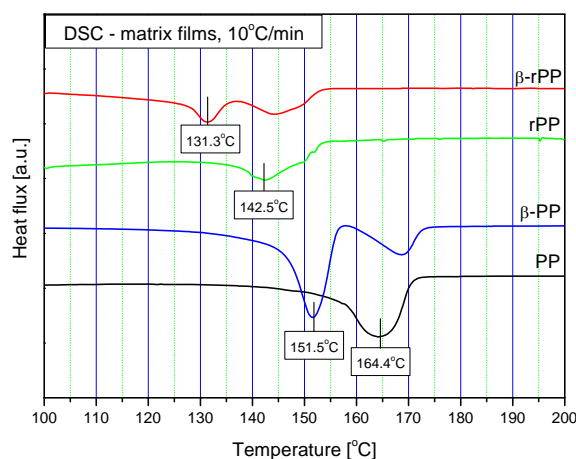


Figure 1: DSC curves of the different matrix materials

The WAXD results are displayed in Figure 2a and b. The crystalline form of the  $\alpha$ -PP is different from that of the  $\beta$ -PP, which is well reflected in the different diffraction peaks. The typical  $\alpha$  peaks ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ) appear at the scattering angles  $2\theta=14.2$ ; 17 and 18.8°, respectively, while the  $\beta$  peak ( $\beta_1$ ) can be found at 16.2°.

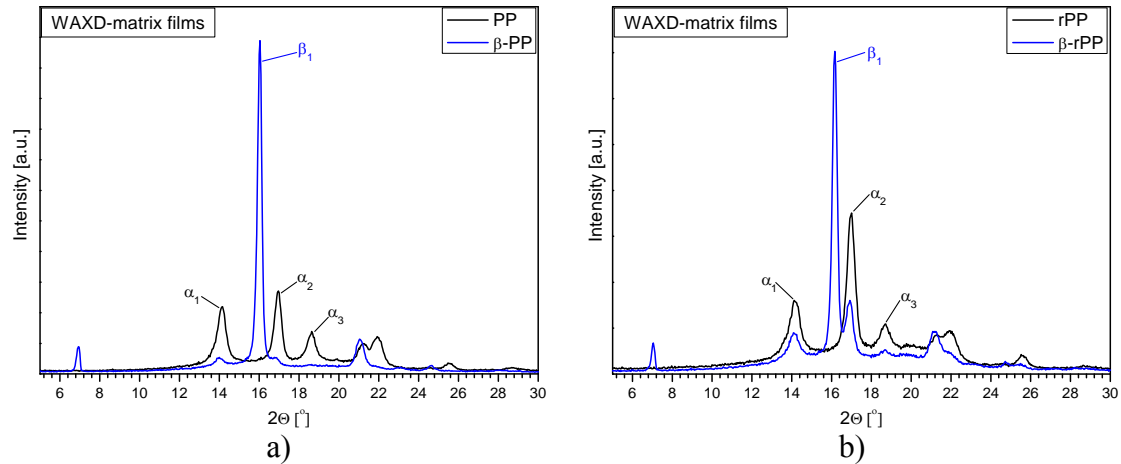


Figure 2: WAXD spectra of the PP and β-PP films (a); and the rPP and β-rPP films (b).

From the results, the β crystal content (“k” value) of the PP can be computed by the Turner and Jones equation (1) [8]:

$$k = \frac{H_{\beta_1}}{H_{\beta_1} + (H_{\alpha_1} + H_{\alpha_2} + H_{\alpha_3})} \quad (1)$$

where  $H_{\alpha_1}$ ,  $H_{\alpha_2}$ ,  $H_{\alpha_3}$  are the typical peaks of the α-crystal of the PP, and  $H_{\beta_1}$  is the typical peak of the β-crystal of the PP. The “k” values (max. 1.0) for β-PP and β-rPP were 0.898 and 0.715, respectively.

As reinforcement a woven fabric composed from highly stretched split PP yarns with a nominal weight of 180 g/m<sup>2</sup> was selected (Figure 3). It was a product of Stradom S.A. (Czestochowa, Poland). This reinforcement has a melting temperature of  $T_m=178^\circ\text{C}$  (measured by DSC), and tensile strength  $465\pm 32$  MPa (measured on a single tape).

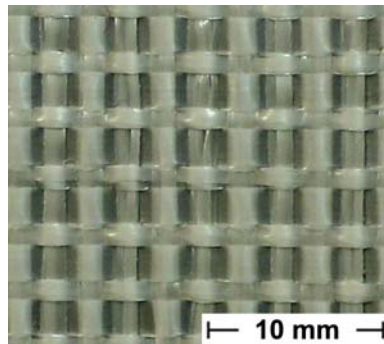


Figure 3: Woven fabric from highly stretched split PP yarns.

Composite plates with a thickness of ca. 1 mm were produced using film-stacking method by hot pressing at two different processing temperatures (at 5 and 15°C above the related matrix melting temperature) and holding time of 90 s under 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 are orthotropic. The film-stacked packages were inserted between preheated plates, hold between them - without applying pressure - for 30 s, pressed for 90 s at 7 MPa and then cooled down with a cooling rate of 20°C/min (as shown on

Figure 4). The holding time at processing temperature were kept short to prevent shrinkage and molecular relaxation of the fibres at the highest processing temperature.

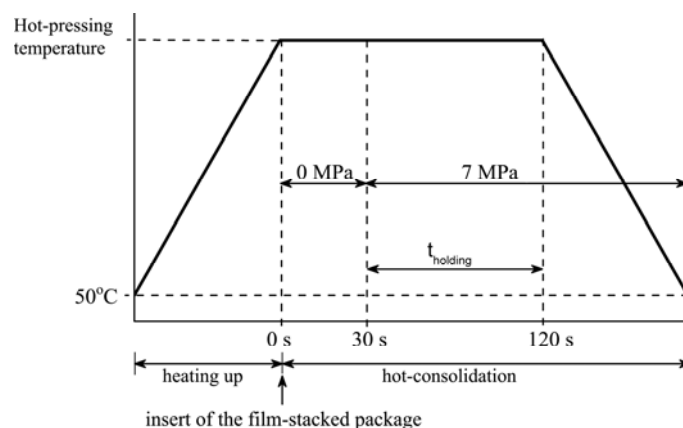


Figure 4: Process diagram of the hot pressing of SRPPCs.

## 2.2 Composite characterization

Static tensile tests were performed on dumbbell specimens using a Zwick Z020 universal testing machine with a crosshead speed of 5 mm/min.

Instrumented tensile impact tests were run on dumbbell specimens with an instrument type Resil Impactor Junior (Ceast, Pianezza, Italy) using the hammer of 15 J. The speed at impact was 3.7 m/s.

Instrumented falling weight impact (IFWI) tests were conducted in a Fractovis 6785 device (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: 13.62 kg and drop height: 1 m. Quadratic specimens of  $75 \times 75 \text{ mm}^2$  were subjected to IFWI tests.

All of the above mentioned tests were performed at room temperature.

Dynamic mechanical thermal analysis (DMTA) was done on rectangular specimens in tensile mode on an Eplexor Quaedimeter 25N (Gabo, Ahlden, Germany) at various frequencies (1, 10 and 100 Hz). The heating occurred stepwise, the temperature was increased by  $5^\circ\text{C}$  steps. The static and oscillating loads were set for 3 and  $\pm 1.5 \text{ N}$ , respectively, and the temperature range covered was  $-100$  to  $200^\circ\text{C}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 Static tensile test results

Figure 5a-c display the yield stress, tensile modulus and the elongation at break for the matrix materials and the related SRPPCs. One can see that both yield stress and tensile modulus increased and the elongation at break decreased with increasing consolidation temperature. The related values differ from those of the matrix materials significantly. Owing to the 50 wt% woven fabric reinforcement, the yield stress increased 4 times and the tensile modulus 2 times compared to the matrices. Note that the elongation at break of the composites decreased dramatically compared to the corresponding matrices.

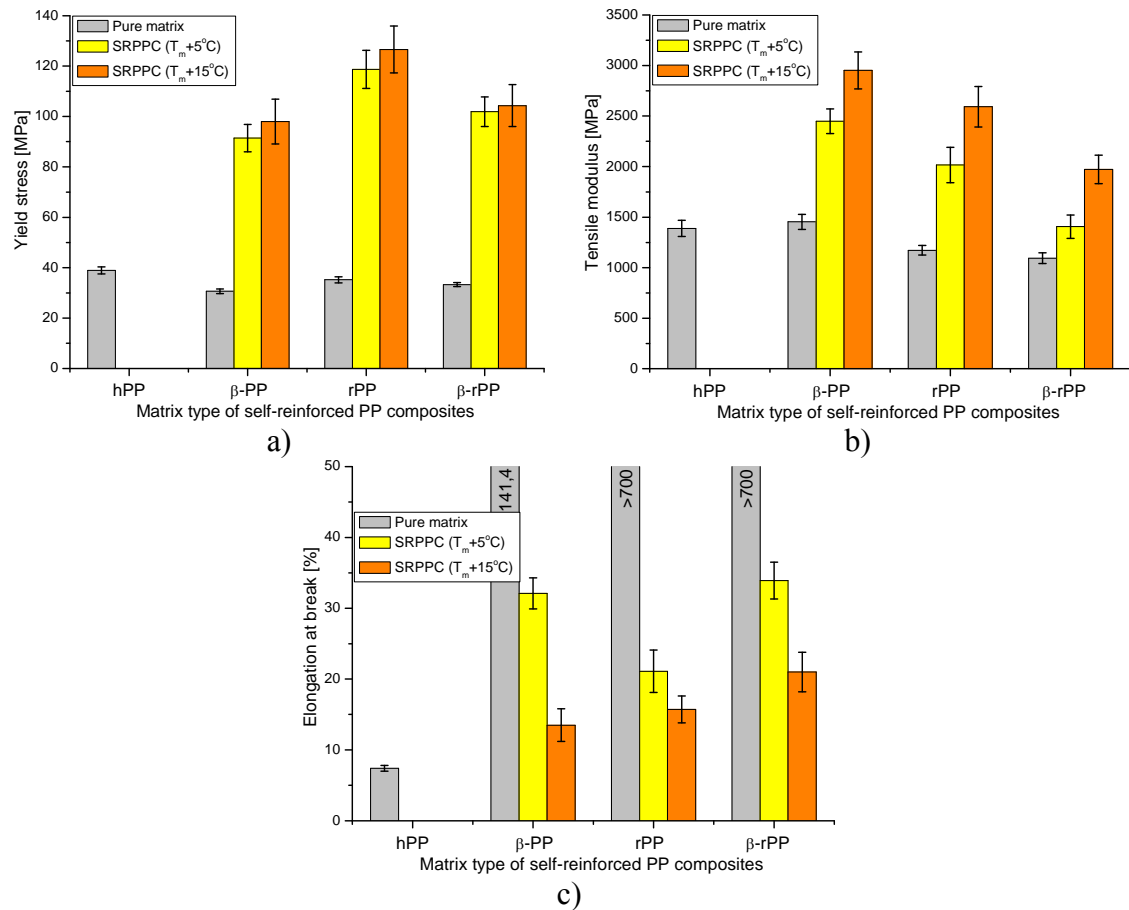


Figure 5: Tensile test results: yield stress (a); tensile modulus (b); and elongation at break (c).

### 3.2 Impact tensile test results

In Figure 6a the tensile impact strength can be seen for the matrices and different SRPPCs. One recognizes that the consolidation conditions strongly affect the tensile impact strength. Poorer consolidation, i.e. done at lower temperature, yields higher values. This is owing to delamination between the plies and fibre pullout events.

In the case of β-rPP based SRPPCs the consolidation conditions did not influence the tensile impact strength.

To collate the static and dynamic (impact) tensile test results in terms of toughness the specific static tensile energy (area under the tensile curve divided by the area of cross section) has been calculated – this is displayed in Figure 6b. An opposite trend to the dynamic behaviour can be stated for the static response as a function of consolidation quality. Recall that it assumed that impregnation at higher temperature results in a better wetting out of the reinforcement.

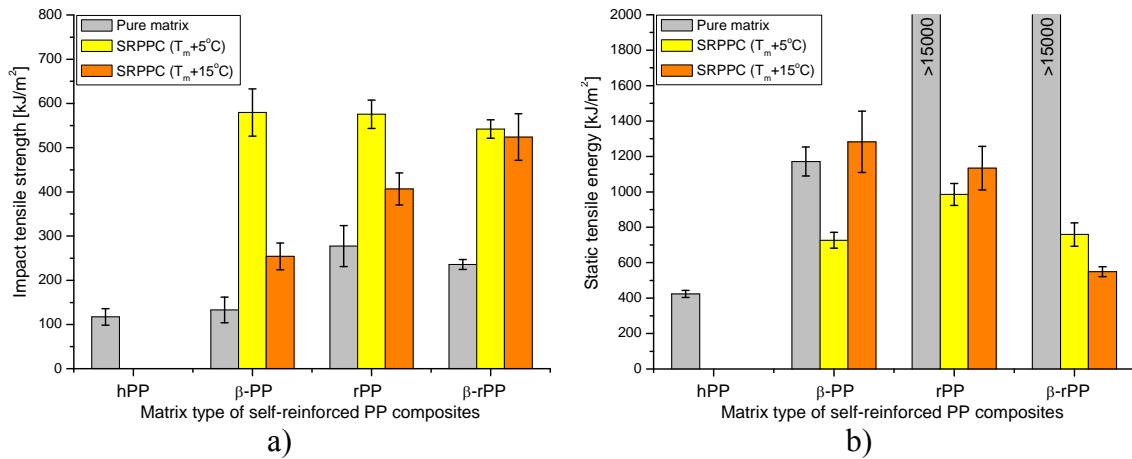


Figure 6: Impact tensile strength (a) and specific static tensile energy to break (b) for different SRPPCs.

### 3.3 Falling weight impact test results

The perforation energy values for the matrices and related SRPPCs are demonstrated in Figure 7. These results are in line with those from the tensile impact test as far as the consolidation conditions concern.

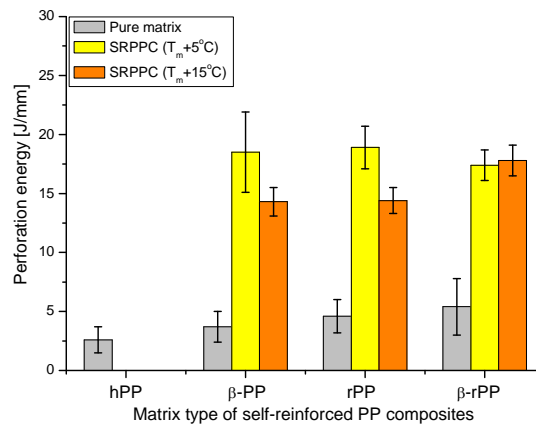


Figure 7: Thickness-normalized perforation energy values for the systems studied.

### 3.4 DMTA results

DMTA curves measured on β-PP matrix and its SRPPC sheets; and β-rPP matrix and its SRPPC sheets are given in Figure 8a and b, respectively. One can see that the storage modulus is lower for unreinforced β-nucleated matrix comparing to neat matrix and much higher for the reinforced composites in the whole temperature range. The stiffness (storage modulus) is always enhanced with increasing consolidation quality.

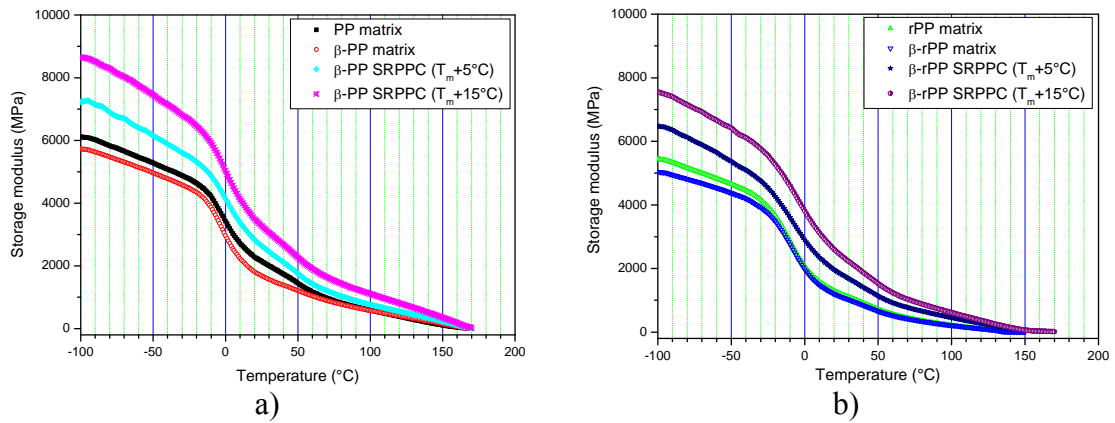


Figure 8: DMTA curves  $\beta$ -PP matrix and its SRPPCs (a);  $\beta$ -rPP matrix and its SRPPCs (b).

### 3.5 Failure behaviour

Figure 9 demonstrates the typical failure behaviour of specimens after static tensile (a) and tensile impact tests (b), manufactured at  $T_m+5^\circ\text{C}$  and  $T_m+15^\circ\text{C}$ , respectively. At low consolidation temperature the failure occurs typically by delamination and fiber pullout. At high consolidation temperatures the delamination was restricted and the specimens broke by the usual way. These results are in harmony with our previous studies [4,5,9,10].

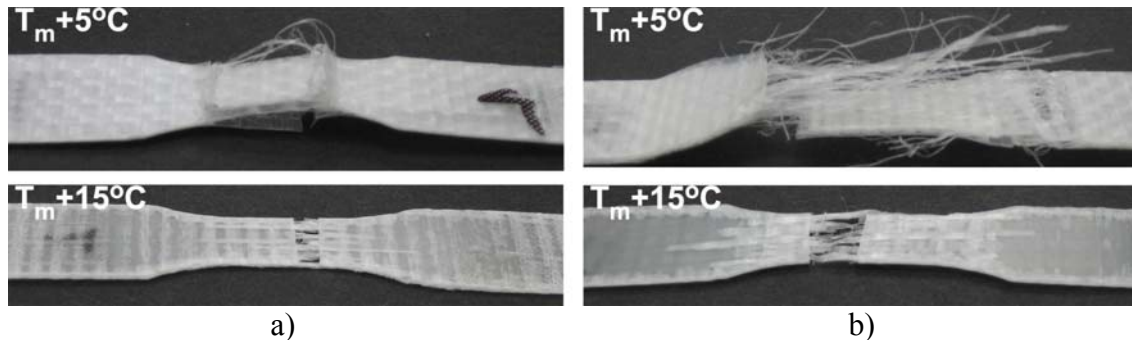


Figure 9: Typical failure behavior of dumbbell specimens manufactured at  $T_m+5^\circ\text{C}$  and  $T_m+15^\circ\text{C}$ . a) static tensile specimens; b) tensile impact specimens.

## 4. CONCLUSIONS

In this work the static mechanical and impact (perforation and tensile impact) performance of self-reinforced polypropylene (SRPP) composites were studied. The corresponding composites were produced by the film-stacking method using a woven PP fabric (woven from highly stretched split PP homopolymer yarns) as reinforcement. As matrix materials different polymorphs ( $\alpha$  and  $\beta$  polymorphs of both isotactic PP homo- and random PP copolymer) served which had the same melt flow index. Consolidation to SRPP composites occurred at temperatures lying 5 or 15  $^\circ\text{C}$  higher than the DSC melting peak of the related matrix. Consolidation at higher temperature was considered to deliver better composite quality. Based on this work, the following conclusions can be drawn:

- the effect of  $\beta$ -nucleation of the matrix giving material was markedly larger for the homo- than for the random PP copolymer,

- both static tensile and dynamic impact response were strongly affected by the consolidation temperature (and thus degree). Stiffness and strength values were mostly enhanced whereas the toughness reduced with increasing consolidation temperature. This adverse tendency was more prominent under dynamic than under static testing conditions.

## ACKNOWLEDGEMENTS

This work was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, the Hungarian Scientific Research Fund (OTKA F60505 and NI62729) and German Science Foundation (DFG Ka 1202/17). The authors are thankful to TVK Co. for providing the possibility for manufacturing the matrix films and to I. E. Sajó (Chemical Research Centre of the Hungarian Academy of Sciences) for his help in the WAXD measurements.

## REFERENCES

- 1- Ward, I.M. and Hine P.J., "The science and technology of hot compaction". *Polymer*, Vol. 45, pp. 1413-1427, 2004.
- 2- Peijs T, "Composites for recyclability". *Materials Today*, Vol. 4, pp. 30-35, 2003.
- 3- Houshyar S., Shanks R. A. and Hodzic A., "Influence of different woven geometry in poly(propylene) woven composites". *Macromolecular Materials and Engineering*, Vol. 290, pp. 45-52, 2005.
- 4- Bárány T., Karger-Kocsis J. and Czigány T., "Development and characterization of self-reinforced polypropylene composites. Carded mat reinforcement". *Polymers for Advanced Technologies*, Vol. 17, pp. 818-824, 2006.
- 5- Izer A. and Bárány T., "Hot consolidated all-PP composites from textile fabrics composed of isotactic PP filaments with different degrees of orientation". *Express Polymer Letters*, Vol. 1, pp. 790-796, 2007.
- 6- Varga J., "β-modification of isotactic polypropylene: preparation, structure, processing, properties, and application". *Journal of Macromolecular Science, Part B-Physics*, Vol. 41 pp. 1121-1171, 2002.
- 7- Varga J. and Ehrenstein G. W., "Beta-modification of isotactic polypropylene". In "Polypropylene: An A-Z Reference", Karger-Kocsis, J. (ed), Kluwer, Dordrecht, , pp. 51-59, 1999.
- 8- Turner J. A., Aizlewood J. M., Beckett D. R.: Crystalline forms of isotactic polypropylene, *Macromolecular Chemie* Vol. 75, pp. 134-158, 1964.
- 9- Bárány T., Izer A., Czigány T.: High performance self-reinforced polypropylene composites, *Materials Science Forum* Vol. 537-538, pp. 121-128, 2007.
- 10- Bárány T., Izer A., Czigány T.: On the consolidation of self-reinforced polypropylene composites, *Plastics, Rubber and Composites: Macromolecular Engineering* Vol. 35, pp. 375-379, 2006.