

Flame retarded self-reinforced polypropylene composites prepared by injection moulding

Dániel Vadas¹, Ákos Kmetty^{2,3}, Tamás Bárány^{2,3}, György Marosi^{1*}, Katalin Bocz¹

¹Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary

²Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

³MTA–BME Research Group for Composite Science and Technology, Műegyetem rkp. 3., H-1111 Budapest, Hungary

ABSTRACT

A method was elaborated to prepare flame retarded self-reinforced polypropylene composites by injection moulding. The effect of intumescent flame retardant (FR) loading was comprehensively investigated on the morphology, flammability and mechanical properties of the self-reinforced polypropylene composites and compared to non-reinforced counterparts of identical additive contents. Homogeneous distribution of both the reinforcing polypropylene fibres and the flame retardant additive was achieved endowing significantly improved strength and stiffness accompanied with increased fire resistance. At 10% FR content 37% reduction of peak of heat release rate, UL94 V-2 rating and LOI of 24.5 vol% were achieved without compromising the improved mechanical performance of the injection moulded self-reinforced composites, i.e. a 4-fold increase of tensile strength and a 7-fold increase of tensile modulus were reached compared to the non-reinforced counterpart. At higher loading (15% FR) the flame retardant properties improved further (LOI of 29.5 vol% was reached), however, due to the abrasive effect of the FR particles in the matrix, the structure of the reinforcing fibres tends to get damaged during the thermo-mechanical processing, and thus their reinforcing efficacy deteriorated. It is demonstrated that the combination of polymer fibre reinforcement with other fillers (such as flame retardants) is advantageous and feasible even by injection moulding, but the balance between the individual attributed properties need to be found.

Keywords: polymer composite, flame retardancy, injection moulding, self-reinforcement, mechanical property,

*Corresponding author: tel: +36 1-463-3654, e-mail: gmarosi@mail.bme.hu, address: Budafoki út 8, Budapest, 1111, Hungary

1 Introduction

Self-reinforced polymer composites (SRPCs) are composed of similar or identical polymeric materials for both reinforcement and matrix. This concept provides advantages in terms of interfacial properties, mechanical performance to weight ratio, recyclability and environmental impact [1] therefore SRPCs gain increasing interest in both academia and industries.

Nowadays, SRPCs are mainly produced by three processing methods; hot compaction, consolidation of coextruded tapes and film-stacking [2]. All of these methods yield in sheet-like (pre)products, these ways three-dimensional parts with complex geometry cannot be directly produced. Therefore, increasing attempts are being made to produce SRPCs by the more versatile injection moulding method. Polymer fibres with highly aligned molecular or supramolecular structure [3], generally created during spinning or drawing, can serve as suitable reinforcements in the structurally similar polymer matrix. One of the greatest challenges in using thermoplastic fibres to reinforce thermoplastic matrices is in their combination into a well-consolidated composite, which, normally achieved by thermal means, is complicated by the narrow window between the melting temperature of the matrix and that of the reinforcing fibres [4]. One possible way to disturb the regularity of the macromolecular chain and thus lower the crystalline melting temperature is copolymerization. Using a block or graft copolymer as matrix giving constituent fairly wide processing window can be ensured for SRPC preparation, wide enough even for injection moulding technology [5,6]. In the case of polypropylene, the increasing ethylene copolymer content is also positively correlated to the increase of the impact strength [7]. Sterzynski et al. used co-extruded composite pellets [8] and bicomponent fibres [9] as input materials for injection moulding of SRPCs, but to achieve homogeneous distribution of reinforcing fibres in the injection moulded products proved to be rather challenging, and due to undesired fibre aggregations the reinforcing efficacy remained moderate in both cases. Kmetty et al. proposed to use pre-impregnated pellets, prepared by film-stacking of high tenacity polymer fibres and copolymer matrix, serving as adequate starting material for injection moulding of SRPCs with homogeneous fibre distribution and improved mechanical properties [5,6]. Recently, researchers also drew attention to the advantages of using organic [10] and inorganic [11,12,13] fibres and fillers in SRPCs, but the feasibility of such hybrid composite preparation with the injection moulding technology was not yet studied.

SRPCs have found mainly applications in transportation and electronics fields, where fire hazard is an issue. Although the application of SRPCs, made entirely of highly flammable components, is accompanied with a high fire-risk, until recently no research were conducted towards their flame retardation. Our pioneering activity in the field of intumescent flame-retarded self-reinforced polypropylene composites (SR-PPCs) resulted in some relevant progress, furthermore, a completely new flame retardant mechanism was proposed [14,15]. It was found that in intumescent flame retarded SR-PPCs, when exposed to intense heat, the synergistic coincidence of expansion (foaming), induced by the intumescent flame retardant (IFR), and shrinking (relaxation) of the high tenacity reinforcing fibres results in a unique heat protecting layer of extraordinary fire extinguishing efficiency. This novel, physical interaction-based flame retardant synergism was successfully utilized in recycled SRPCs,

made entirely of secondary polyolefins [16], and also in biodegradable self-reinforced poly(lactic acid) composites [17]. It was evinced that the formation and efficiency of the special surface protecting layer is influenced by the structure of reinforcement (i.e. weave type), fibre alignment and degree of molecular orientation of the reinforcing fibres. Best flame retardant performance was found in SR-PPCs reinforced with unidirectional fibres. These composites, when prepared at optimum consolidation temperature, pass UL94 V-0 rating with additive content as little as 7.2 wt%, one third of the amount needed in non-reinforced polypropylene matrix [18].

In this work, we had dual purpose. On the one hand, our aim was to manufacture injection mouldable SR-PPCs in flame retarded form and to investigate the presence of synergism, evinced earlier both in primary and recycled film-stacked SR-PPCs. In contrast to the unidirectional or bidirectional plain-woven fabric reinforcement (used in multi-layered composite structures), the injection moulded composites comprise the reinforcing polymer fibres in short and randomly aligned form. This difference was expected to have significant influence on the cooperation of the expanding (intumescent flame retardant) and the shrinking (oriented fibres) domains. On the other hand, the investigation of the effect of ammonium-polyphosphate based flame retardant (FR) particles on the morphology and mechanical performance of the injection moulded SR-PPC was in the focus of our interest. Furthermore we expected that based on the example of FR loading, important conclusions could also be drawn regarding the feasibility of loading injection moulded SR-PPCs with other commonly used fillers, reinforcements and other solid particles.

2 Materials and methods

2.1 Materials

As matrix material, polypropylene-based thermoplastic elastomer (ePP) (Versify 4200, Dow Chemical Company) was selected. This matrix was characterised in our previous work [6]. As reinforcement, highly oriented polypropylene homopolymer (hPP) multifilament (Stradom S.A., Czestochowa, Poland) was used. This reinforcing hPP multifilament has a linear density of 7.2 g/den, melting temperature of 173.0°C (determined by DSC), single fibre diameter of $40.1 \pm 1.8 \mu\text{m}$, tensile strength of $581 \pm 30 \text{ MPa}$ and tensile modulus of $6432 \pm 490 \text{ MPa}$ (measured in single fibre tensile tests). Exolit AP766 (received from Clariant International AG, Muttenz, Switzerland), a combined ammonium polyphosphate and charring agent containing IFR additive, was used as flame retardant (FR) agent.

2.2 Composite preparation

The fibre reinforced composite sheets were manufactured according to a multi-step procedure. The fibre containing granules, suitable for injection moulding, were obtained by cutting the unidirectionally reinforced SR-PPCs prepared by film-stacking of flame retarded matrix foils and reinforcing polypropylene fibres. The details of preparation is as follows: First 0, 20 and 30 wt% FR additive (Exolit AP 766) was melt-compounded with the neat ePP matrix material from which 50 μm thick films were manufactured by Labtech LCR300 cast-film extrusion line (Labtech Engineering Co. Ltd. Samutprakarn, Thailand) (screw rotation

speed: 22 1/min; extruder temperature profile from feed zone to die: 205, 205, 215, 215 and 215°C, temperature of coat-hanger die: 235, 230 and 235°C; winding speed: 10 1/min). Additive-free and flame retarded consolidated SR-PPC sheets with 50 wt% nominal reinforcement content and unidirectional (UD) fibre direction were manufactured by filament winding followed by film-stacking method and compression moulding process. Actually, the processing window was 90°C. The filament-wound, film-stacked packages were inserted in between the preheated moulds to 140°C and held for 240 s without pressure, then compressed for 480 s under a pressure of 5.26 MPa and finally cooled to 45°C (under pressure). The thickness of the produced sheets was 1.6 mm. The consolidated plates were then cut into 5 (wide) x 5 (length) mm² sections (as pre-impregnated pellets) suitable for injection moulding. The length dimension of these cut pieces determined the length of the reinforcing fibres.

For comparison, additive-free and flame retarded ePP (Versify 4200) compounds with FR (Exolit AP766) contents of 0, 10 and 15 w% were produced by melt-compounding using a Labtech Scientific LTE-26-44 twin-screw extruder (Labtech Engineering Co. Ltd. Samutprakarn, Thailand; L/D: 44) (with temperature profile from feed zone to die of 200, 205, 210, 210, 210 and 215°C, and screw rotation speed of 70 1/min) to form non-reinforced elastomer sheets with identical FR contents as those of the equivalent SR-PPCs (with 50% reinforcement content and double portion of FR additive in the matrix).

Plaque specimens measuring 80 × 80 × 2 mm in dimensions and with flame retardant contents of 0, 10 and 15 wt% were injection moulded both from the non-reinforced and reinforced (50 wt% fibre containing) granulates with fan gate. The process parameters are listed in **Table 1**.

Table 1. Injection moulding parameters

2.3 Methods

The construction and consolidation quality of the SR-PPCs were examined by reflection *light microscopy* (Olympus BX51M, Olympus Co., Japan) on polished cross sections of the sheets cut perpendicular to the flow direction.

The *relative density*, meaning the ratio between the measured and the theoretical density, was determined for each type of samples. The density of the specimens (ρ_s) was obtained from weight measurements in air and water and calculated according to Equation 1, where m_a is the specimen's weight in air, m_e is the specimen's weight in ethanol and ρ_e is the density of ethanol at room temperature equal to 0.789 g/cm³.

$$\rho_s = \frac{m_a}{m_a - m_e} \rho_e \left[\frac{g}{cm^3} \right] \quad (\text{Eq. 1})$$

The theoretical densities were calculated by knowing the composition of the samples and the densities of the components. The density values of the used materials given by the producers are 0.876 g/cm³ for the ePP matrix material (Versify 4200), 0.910 g/cm³ for hPP multifilament, and 1.600 g/cm³ for IFR (Exolit AP 766).

Standard *UL94 flammability tests* (ASTM D 635 and ASTM D 3801) were also performed on the composite specimens. UL94 classification is used to determine dripping and flame spreading rates.

The flame retardant performance of the prepared samples was characterized by *limiting oxygen index* (LOI) measurements according to the ASTM D 2863 standard. The LOI value expresses the lowest oxygen to nitrogen ratio where specimen combustion is still self-supporting.

Mass loss type cone calorimeter tests were carried out by an instrument delivered by Fire Testing Technology Ltd. (East Grinstead, West Sussex, United Kingdom) using the ASTM E 906 standard method. Specimens (80 mm × 80 mm × 2 mm) were exposed to a constant heat flux of 50 kW/m² and ignited. Heat release values and mass reduction were continuously recorded during burning.

Dynamic mechanical analyses were performed using a Q800 dynamic mechanical analyser (DMA, TA Instruments Inc., New Castle, DE, USA) to determine the storage modulus and loss modulus as a function of temperature for the prepared PLA samples. Three point bending mode was applied with a span length of 50 mm. The width and length of the specimens were 10 mm × 60 mm (cut by water jet parallel to the flow direction), respectively. The scanning range of temperature was -100°C - 70°C, a heating rate of 5°C/min and a frequency of 1 Hz with a 0.08% deformation were selected.

Static tensile tests were performed on dumbbell-shaped (EN ISO 8256 Shape 3) specimens cut from injection moulded plaque specimens by water jet cutting parallel to the flow direction (**Fig. 1**). The tensile tests were carried out by a universal ZWICK Z020 testing machine (Zwick GmbH & Co. KG, Ulm, Germany) according to the standard EN ISO 527-4:1997 standard. The cross-head speed was set to 5 mm/min, and each test was performed at room temperature (24°C); at least 5 specimens were tested from each material.

Figure 1 Preparation of dumbbell specimens from the plaque specimens in the parallel to the flow direction

Instrumented falling weight impact (IFWI) tests were performed using a Ceast Fractovis 6785 instrument (Ceast S.p.A, Torino, Italy) on the following settings: maximal energy: 131.84 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 specimens with dimensions of 80 mm × 80 mm × 2 mm were subjected to IFWI tests at room temperature (25°C) and 25,5% relative humidity. From the IFWI tests the specific perforation energy (E_p [J/mm]) (Eq. 2) and the ductility factor (D_r [%]) (Eq. 3) were determined. The ductility factor was calculated as the ratio of the total impact energy (E_{max} [J]) to the energy absorbed until the maximum load (E_{Fmax} [J]). E_{Fmax} represents mainly the energy required to initiate fracture in the specimen and corresponds to the deformation at yield, while E_{max} indicates the total energy absorbed until ultimate deformation.

$$E_p = \frac{E_{max}}{h} \left[\frac{J}{mm} \right] \quad (\text{Eq. 2})$$

$$D_r = \frac{E_{max} - E_{Fmax}}{E_{max}} \cdot 100 \quad [\%] \quad (\text{Eq. 3})$$

Instrumented tensile impact tests were run on two-side notched specimens of $80 \times 10 \text{ mm} \times 2 \text{ mm}$ dimension (EN ISO 8256) with a Ceast Resil Impactor Junior (Ceast S.p.A, Torino, Italy) type instrument using a 15 J hammer. The speed at impact was 3.7 m/s.

Scanning electron microscopic (SEM) images were taken from the fracture surface of the SR-PPCs using a JEOL JSM-5500 LV type apparatus (JEOL Ltd., Akishima, Tokyo, Japan) using an accelerating voltage of 15 keV. The samples were coated with gold–palladium alloy before examination to prevent charge build-up on the surface.

3 Results and discussion

3.1 Morphology of the composites

In **Figure 2** homogeneous distribution of both reinforcing fibres and flame retardant additives is revealed by the optical microscopic photographs taken from the polished cross-sections (see **Fig. 1**) of the injection moulded SR-PPCs. There is no sign of fibre-matrix detachment or voids, indicating adequate consolidation quality of the composites. The skin-core formation, typical for injection moulded products is also observable; the fibres are aligned in the flow direction. In **Fig. 2c** the contours of the fibres of the 15% FR containing composite are less distinct as those of the additive-free (**Fig. 2a**) and 10% FR containing composites (**Fig. 2b**) which can be attributed to the increased fibre-matrix fusion or partial melting of the fibres, likely occurred as a result of firmer processing conditions generated by the abrasive effect of the FR additive being present at high concentration of 30 wt% in the matrix of the SR-PP_FR15 composite.

Figure 2 Optical microscopic images of the polished cross-sections (opposite side from the gate, perpendicular to the flow direction) of (a) SR-PP, (b) SR-PP_FR10 and (c) SR-PP_FR15

Density measurements confirmed that the fabricated composites are well consolidated; the measured density values were higher than 95% of the theoretical density in all cases (**Table 2**). With increasing FR content, however, the measured density values do not properly follow the expected increasing rate (the FR additive has higher density than the ePP). This tendency is the same for the non-reinforced and reinforced samples, therefore it was concluded that the difference between the measured and theoretical densities is not the consequence of the void fraction between the fibres [19] but more likely of the detachment of the polar FR particles from the apolar polymer matrix. The relative density of the SR-PPCs is practically identical with their non-reinforced counterparts indicating that in all the composites the fibres are properly impregnated by the matrix material.

Table 2 Relative density of the injection moulded specimens

3.2 Flammability characteristics

It was proposed earlier [18] that the type (organic, inorganic, char-forming or non-char forming polymer) and structure (degree of molecular orientation, fibre alignment, weave type) of reinforcement has particular effect on the effectiveness of an intumescent flame retardant system in SR-PPCs. In this work this phenomenon is further investigated using a new structure, i.e. in disordered, short fibre reinforced SR-PPCs.

The UL94 and LOI flammability test results of the two types of flame retarded injection moulded sheets are summarized in **Table 3**. The additive-free samples are inherently highly flammable, HB rating according to the UL94 standard and a LOI of 18 v/v% were determined for both type of samples. With FR addition the flammability properties could be significantly improved. At 15% FR loading, V-2 rating and noticeably increased LOI of 29.5 v/v% were reached. No significant difference could be evinced between the flammability behaviour of the non-reinforced and the self-reinforced samples of identical FR contents. Slightly better flame retardant performance was observed for the composites during vertical burning tests; some of the 15 wt% FR containing specimens showed self-extinguishing behaviour even after the second 10 s long ignition, which could be ascribed to the beneficial effect of the presence of highly oriented hPP fibres, in accordance with our earlier findings [14,15,18]. However, it has to be declared that the contribution of the short hPP fibres to the synergism with the IFR system is almost negligible compared to the winded hPP yarns or woven fabrics composed of highly stretched filaments.

Table 3 Comparison of the UL94 classifications and LOI values of injection moulded ePP sheets and SR-PPCs

The burning behaviour of the injection moulded SR-PPCs was compared to non-reinforced ePP sheets also using cone calorimeter tests. The obtained heat release rate (*HRR*) curves are presented in **Figure 3**. It can be seen that the *HRR* curves of the two types of samples are very similar. The increment of FR loading from 10 to 15% resulted more in time shift than in moderation of *HRR* values, about 35-40% reduction of peak of heat release rate (*pkHRR*) was reached compared to the additive-free references in both cases. Nevertheless, each composite outperformed its non-reinforced counterpart of same FR contents, however, the degrees of *pkHRR* reductions are not remarkable. Based on these results it was concluded that the incorporation of conventional FR additives in the matrix of injection moulded SR-PPCs has roughly the same effect on the flammability properties as in non-reinforced PP compounds. In contrast to continuous hPP fibres or woven fabrics [18], randomly aligned, short hPP fibres do not influence noticeably the foam forming process and the combustion behaviour of an intumescent flame retarded PP system.

Figure 3 Heat release rate curves of injection moulded non-reinforced and self-reinforced PP sheets

3.3 Mechanical properties

The storage modulus and $\tan\delta$ curves collected during DMA analyses performed on the non-reinforced and self-reinforced ePP sheets are plotted in **Figure 4**. In **Figure 4a** drastic fall of the storage modulus curves of the examined samples can be observed around -20°C which is due to the glass transition of the ePP matrix material. It can be seen that below the glass transition temperature of the ePP matrix the stiffness of the additive-free and the 10% FR containing composites exceeds significantly that of the non-reinforced samples indicating high reinforcement level of the embedded hPP fibres. In the case of the SR-PP_FR15 sample, however, the stiffening effect of the fibres does not prevail. Above the glass transition temperature of the amorphous ePP, the storage modulus of the non-reinforced samples holds close to zero. In this region, the storage moduli of all the composites preserve much higher values, which is due to the stiffening effect of the unmelted semicrystalline hPP fibre. By this means the temperature range of applicability of the flame retarded SR-PPCs is broadened compared to the non-reinforced ePP samples. The analysis of the $\tan\delta$ curves (**Figure 4b**) reveals identical glass transition temperature of -15°C for all the measured samples, but significant differences occur in the damping factor values depending on fibre content.

Figure 4 a) Storage modulus and b) $\tan \delta$ of the injection moulded flame retarded non-reinforced and self-reinforced PP samples

The mechanical performance of the injection moulded samples was characterized by standard tensile tests. Typical stress-strain curves are presented in **Figure 5**. The non-reinforced samples, after reaching the ultimate tensile strength, elongated non-uniformly with necking over the entire testing region (20 mm cross-head displacement). Apparently, the FR loading did not affect the character of the stress-strain curves of the non-reinforced ePP samples. In contrast, failure of the composites occurred due to significantly higher deforming stresses, and without preceding necking. At identical tensile stress, due to the presence of FR particles, the 10% FR containing composite (SR_FR10) elongated more than the additive-free self-reinforced composite (SR_PP). Rupture occurred around 30 MPa for both samples. At 15% FR loading, however, the SR-PPC (SR_FR15) barely exceeded 16 MPa tensile stress and fractured after relatively high deformation. It was found that during tensile tests the flame retarded composites elongated more than the additive-free SR-PPC because the presence of FR particles at the fibre-matrix interphase allowed the matrix to elongate more freely. Nevertheless, at 20% FR loading in the matrix (SR_FR10) the load bearing capacity of the SR-PPC did not change noticeably, but the presence of 30% FR particles in the matrix (SR_FR15) already caused significant deterioration of the tensile strength.

Figure 5 Comparison of the stress-strain curves of injection moulded flame retarded non-reinforced and self-reinforced PP samples

The results of the tensile tests are shown in **Figure 6a** and **b**. It can be seen that compared to the non-reinforced ePP, a 4-fold increase of the tensile strength and a 7-fold increase of the tensile modulus were achieved by preparing short-fibre reinforced SR-PPCs. The achieved noticeable improvement of the tensile properties is significantly better than achieved earlier by injection moulding technology using co-extruded composite pellets or bicomponent PP fibres as raw materials [8,9]. In our system the homopolymer fibres did not aggregate and could maintain their mechanical performance during processing and thus serve as adequate reinforcement in the composite. Furthermore, suitable adhesion could be formed between the hPP fibres and the ePP matrix even when 10% FR was added. The 15% FR containing composite, however, showed weaker mechanical performance, its tensile strength deteriorated by 50% and tensile modulus by 15%, respectively, compared to the SR-PPC of lower FR content, likely due to the structural damage of the reinforcing fibres occurred during the composite preparation and thermo-mechanical processing.

Figure 6 Comparison of the a) tensile strength and b) tensile modulus of injection moulded flame retarded non-reinforced and self-reinforced PP samples

As with increasing stiffness the impact resistance usually deteriorates, it is important to investigate this property of the SR-PPCs with increased modulus. The impact resistance of the injection moulded ePP and SR-PPC sheets was compared using instrumented falling weight impact tests. Based on the fractograms of **Figure 7** it can be seen that in the case of the non-reinforced samples plastic deformation dominates and failure of the specimens occurs under quasi-constant energy absorption, typically with disruption. In contrast, in the case of the composites the impact load increases linearly with time until fracture and the triangle-shape fractogram indicates rather rigid behaviour. After fracture initialization a slight plastic zone can also be observed, likely due to the disruption of the elastomer matrix. Failure of composites occurs typically within 8 ms compared to the 14 ms of the non-reinforced plates. The adverse consequences of the fibre damage of the 15% FR containing composite are also visible based on this test, failure of the SR-PP_FR15 composite occurs at significantly lower impact load than the other self-reinforced composites.

Figure 7 Comparison of the impact load-time curves of injection moulded flame retarded non-reinforced and self-reinforced PP samples

The calculated perforation energy and ductility index values are shown in **Figure 8a** and **b**, respectively. It can be seen that the perforation energy of the composites is about 50% of that of the non-reinforced samples, furthermore the 15% FR containing composite reached only 30% of the perforation energy of the ePP sample of identical FR content. The impact damping capability of the prepared flame retarded SR-PPCs still outperform that of a common polypropylene. As expected, high ductility indices are accompanied with the plastic deformation of the non-reinforced ePP samples, while decreased ductility factors are characteristic for the self-reinforced polymer composites with more rigid rupture.

Figure 8 Comparison of a) perforation energy and b) ductility factor of injection moulded flame retarded non-reinforced and self-reinforced PP samples

Common Charpy impact tests could not be performed on the ePP based samples because the elastomer-based specimens did not break during testing, therefore tensile impact test were performed to further characterize the impact resistance. It can be seen in **Figure 9** that the tensile impact strength shows decreasing tendency with increasing FR content for both types of injection moulded samples. It is proposed that the FR particles function as defect location in the matrix and thereby decrease the mechanical resistance. Considering the tensile impact strength results, the non-reinforced samples outperform their self-reinforced counterparts because during failure plastic deformation absorbs more energy than fibre pull-out or breakage (see also in **Figure 7**).

Figure 9 Comparison of the tensile impact strength (notched) of injection moulded flame retarded non-reinforced and self-reinforced PP samples

When considering all the examined mechanical characteristics of the prepared SR-PPCs it can be concluded that good balance between the strength, stiffness and impact resistance was reached as a result of combining high tenacity fibres with elastomer matrix. Up to 10% FR content the composites keep this advantageous mechanical performance, but at 15% FR loading loss of mechanical properties occurs. To further investigate the change in the structure of the composites as a function of increasing FR content, SEM micrographs were taken from the fracture surfaces. During SEM observation (**Figure 10**) prominent fibre-matrix adhesion was observed for all SR-PPCs, the hPP fibres are properly impregnated by the matrix material. It is also visible that the polar FR particles are well dispersed in the ePP matrix. Nevertheless, when exposed to tensile stress, the FR particles became easily detached from the apolar matrix and therefore as fault locations decreased the tensile strength of the flame retarded samples (see in **Figure 6**). Based on the SEM images it became also obvious that in the SR-PP_FR15 composite the structure of the reinforcing hPP fibres got damaged during processing likely due to the increased thermo-mechanical and abrasive stress caused by the FR particles being present at 30 wt% in the matrix. At lower FR loading (20 wt%) of the matrix (**Figure 10 b**), however, the hPP fibres seem to be intact. It is proposed that in the case of the SR-PP_FR15 composite, the high amount of FR particles cause significant changes in the shear forces and thermal conditions during injection moulding, which result in undesirable molecular relaxation, structural damage and partial melting of the reinforcing hPP fibres during processing and consequently in remarkable property loss of this composite.

Figure 10 SEM micrographs taken from the fracture surface of a) SR-PP, b) SR-PP_FR10 and c) SR-PP_FR15 samples

4 Conclusions

Flame retarded self-reinforced polypropylene composites were manufactured by injection moulding method for the first time. By this means, besides the conventional processing methods resulting in two-dimensional SRPC sheets, the production of three-dimensional products becomes also realizable. The elaborated multi-step composite preparation method allowed homogeneous dispersion of both hPP fibres and FR particles in the ePP matrix and thus to achieve simultaneous improvement in mechanical and flame retardant properties.

In the case of the short fibre reinforced injection moulded sheets, the synergistic effect, observed recently between longer oriented fibres and the intumescent flame retardant system, proved to be rather moderate. Based on these results it was concluded that the reinforcing fibre length, fibre alignment and the lay-up (structure) of intumescent flame retarded SRPCs are of key importance regarding their fire performance.

Nevertheless, it was found that the presence of up to 20% FR particles in the matrix material does not remarkably influence the mechanical performance of the injection moulded composites. At higher loading (30% FR in the matrix), however, the structure of the reinforcing PP fibres tends to get damaged during processing causing noticeable deterioration of the mechanical properties. Based on these results it can be concluded that unique hybrid composite systems can be manufactured by combining polymer fibre reinforcement with other fillers even with injection moulding method, however, by taking into consideration that the beneficial effect of increasing filler content is limited by filler-polymer incompatibility and the abrasive effect of the used fillers.

5 Acknowledgement

The research was financially supported by the Hungarian Scientific Research Fund (OTKA K112644 and PD121171). This work was supported by the National Research, Development and Innovation Fund in the frame of NVKP_16-1-2016-0012 and GINOP-2.2.1-15-2016-00015 projects. This research was realized in the frames of TÁMOP 4.2.4. A/1-11-1-2012-0001 „National Excellence Program – Elaborating and operating an inland student and researcher personal support system”. The project was subsidized by the European Union and co-financed by the European Social Fund. K. Bocz is thankful for the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

6 References

-
- [1] Poulíkidou S, Jerpdal L, Björklund A, Åkermo M. Environmental performance of self-reinforced composites in automotive applications - Case study on a heavy truck component. *Mater Design* 2016;103:321–329.
 - [2] Bárány T, Karger-Kocsis J, Czigány T. Development and characterization of self-reinforced poly(propylene) composites: carded mat reinforcement. *Polym Adv Technol* 2006;17:818–824.

-
- [3] Kida T, Hiejima Y, Nitta K-H. Molecular orientation behavior of isotactic polypropylene under uniaxial stretching by rheo-Raman spectroscopy. *Express Polym Lett* 2016;10:701–709.
- [4] Alcock B, Peijs T. Technology and development of self-reinforced polymer composites. *Adv Polym Sci* 2013;251:1-76.
- [5] Kmetty Á, Tábi T, Kovács JG, Bárány T. Development and characterisation of injection molded, all-polypropylene composites. *Express Polym Lett* 2013;7:134-45.
- [6] Kmetty Á, Bárány T, Karger-Kocsis J. Injection molded all-polypropylene composites composed of polypropylene fibre and polypropylene based thermoplastic elastomer. *Compos Sci Technol* 2012;73:72-80.
- [7] Aarnio-Winterhof M, Doshev P, Seppälä J, Gahleitner M. Structure-property relations of heterophasic ethylene-propylene copolymers based on a single-site catalyst. *Express Polym Lett* 2017;11:152–161.
- [8] Andrzejewski J, Szostak M, Barczewski M, Krasucki J, Sterzyński T. Fabrication of the self-reinforced composites using co-extrusion technique. *J Appl Polym Sci* 2014;131:41180.
- [9] Andrzejewski J, Szostak M, Krasucki J, Barczewski M, Sterzyński T. Development and characterization of the injection-molded polymer composites made from bicomponent fibers. *Polym Plast Technol Eng* 2015;54:33–46.
- [10] Andrzejewski J, Tutak N, Szostak M. Polypropylene composites obtained from self-reinforced hybrid fiber System. *J Appl Polym Sci* 2016;133:43283.
- [11] Swolfs Y, Crauwels L, Van Breda E, Gorbatikh L, Hine P, Ward I, Verpoest I. Tensile behaviour of intralayer hybrid composites of carbon fibre and self-reinforced polypropylene. *Compos A Appl Sci Manuf* 2014;59:78–84.
- [12] Swolfs Y, Meerten Y, Hine P, Ward I, Verpoest I, Gorbatikh L. Introducing ductility in hybrid carbon fibre/self-reinforced composites through control of the damage mechanisms. *Compos Struct* 2015;131:259–265.
- [13] Lucchetta MC, Morales Arias JP, Mollo M, Bernal CR. Self-reinforced composites based on commercial PP woven fabrics and a random PP copolymer modified with quartz. *Polym Adv Technol* 2016;27:1072–1081.
- [14] Bocz K, Bárány T, Toldy A, Bodzay B, Csontos I, Madi K, Marosi G. Self-extinguishing polypropylene with a mass fraction of 9% intumescent additive - a new physical way for enhancing the fire retardant efficiency. *Polym Degrad Stab* 2013;98:79–86.
- [15] Bocz K, Igricz T, Domonkos M, Bárány T, Marosi G. Self-extinguishing polypropylene with a mass fraction of 9% intumescent additive II – influence of highly oriented fibers. *Polym Degrad Stab* 2013;98:2445–51.

[16] Bocz K, Toldy A, Kmetty Á, Bárány T, Igricz T, Marosi G. Development of flame retarded self-reinforced composite from automotive shredder plastic waste. *Polym Degrad Stab* 2012;97:221–227.

[17] Bocz K, Domonkos M, Igricz T, Kmetty Á, Bárány T, Marosi G. Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance. *Compos Part A* 2015;70:27–34.

[18] Bocz K, Simon D, Bárány T, Marosi G. Key role of reinforcing structures in the flame retardant performance of self-reinforced polypropylene composites. *Polymers* 2016;8:289.

[19] Chen J, Yang W, Yu GP, Wang M, Ni HY, Shen KZ. Continuous extrusion and tensile strength of self-reinforced HDPE/UHMWPE sheet. *J Mater Process Technol* 2008;202:165–169.