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Fabrication of the Self-Reinforced Composites Using Co-Extrusion Technique

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ABSTRACT: The results of this work relate to the use of co-extrusion technology in the preparation of monocomposite pellets. The low-melting polypropylene copolymer was used as a matrix material. The high strength polypropylene fibers were used as a fibrous reinforcement. Research confirms the possibility to produce the pellets with fibrous structure. The prepared composite material in the form of pellets was processed and shaped using the injection molding technology. Obtained samples were subjected to mechanical testing in the static tensile test and dynamic mechanical analysis. Research complements microscopic observation of scanning electron microscopy. The measurement results confirm the reinforcing effect of the fibers. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41180.

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INTRODUCTION

The polymer composite belongs to the group of most popular manufactured materials, with still expanding application areas. In recent years there has been rapid development in the research areas of polymer nanocomposites,[1–3] biocomposites,[4] and the technologies of processing such a materials.[5,6] The biocomposites research found widespread industry applications, unfortunately the utility of the nanoscale fillers research results does not allow for the use of these technologies on an industrial scale.[7,8] Therefore, many laboratories still conducts research on polymer composites with conventional fillers and there are still a lot of support from research centers and manufacturers.

Innovation in the case of self-reinforcement composites as modern construction materials is the use of the oriented polymer fiber as the reinforcement for the matrix made from the same polymer.[9] The beneficial effect on the mechanical properties of composites goes hand in hand with good usability and low price of used materials. Another advantage of self-reinforcement products will be also the facilitated recycling and re-processing.[10–13]

The main objective of the research is to develop a methodology for the preparation of monocomposites by injection molding[14] and assess the impact of technological conditions of processing on the properties of products made from self-reinforced polymers.[15,16]

The most important problem that hinders the use of SRP composites (from self-reinforced polymer) is a "narrow" processing window, due to the small difference in melting temperature of the polymer matrix and reinforcement.[17,18] For the preparation of SRP composites, the commonly used materials are polypropylene[19–21] and polyethylene.[22–24] In the case of polypropylene, the problem of "narrow" processing window is eliminated by the use of low-melting copolymers of these polymers.[25,26] Thanks to the increased difference in melting temperature and the fiber matrix, it was possible to manufacture composites with less precise temperature control of the process. Finally, it created the possibility of using similar systems as potential materials suitable for injection molding, what is the essence of research described in this article.

To be more precise the aim of presented research is to determine the usefulness of two stage extrusion/injection molding technique. As the most popular plastics processing technologies the extrusion as the preparation technique and injection molding as the final shaping technology might be the basic processing procedures for self-reinforced composites. The traditional compression molding technique used so far as a main processing method should be replaced by more flexible processing methods. Compression molding methods limit the product shape, extend the processing time, and require the use of specialty tool/machine equipment. Most of the compression

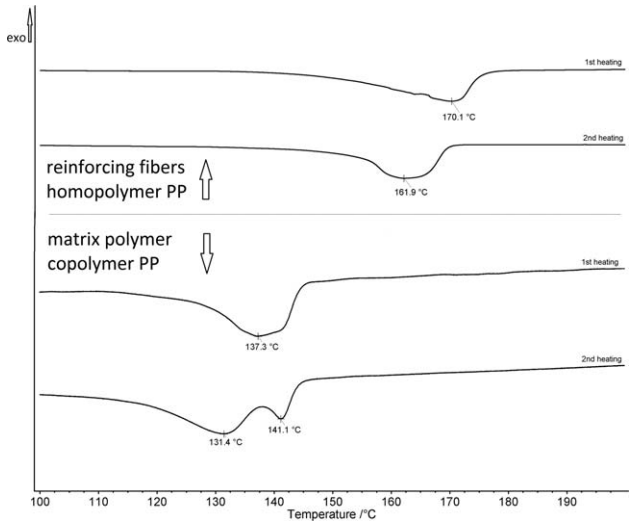

Figure 1. DSC thermogram of the reinforcing fibers and composite matrix.

molding drawbacks can be eliminated using the extrusion/injection molding techniques. The main difficulty concerning around the material properties and processing conditions selection are the subject of this study.

EXPERIMENTAL

Materials

The composite pellets were prepared using the polypropylene fibers and low-melting polypropylene copolymer as the input materials. The fiber material was oriented polypropylene homopolymer in a form of multifilament, the material was manufactured and supplied by STRADOM S.A. (Czestochowa, Poland), the melt flow index (MFI) of used polypropylene matrix was 42 g/10 min (230°C, 2.16 kg). Preliminary differential scanning calorimetry (DSC) tests showed the fibers melting point at about 170°C (Figure 1), the second heating showed the melting peak at 162°C, the difference between these two values is caused by strong fibers orientation. The matrix material was a random copolymer LUMICENE from TOTAL Petrochemicals, MFI = 60 g/min (230°C, 2.16 kg), the melting point of the matrix determined by DSC was 137°C (Figure 1). The

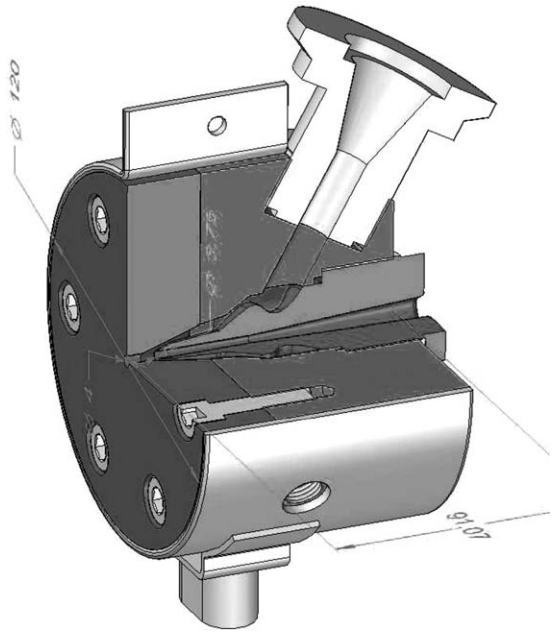

Figure 2. The co-extrusion die head used for srPP pellets preparation.

appearance of double peak during the second heating confirmed the copolymeric structure of the matrix polymer.

Sample Preparation

Co-Extrusion Process. The co-extrusion of polypropylene (PP) fibers was performed using the angular extrusion head (see Figure 2). Optimal co-extrusion parameters were set to achieve best filling of space between fibers and matrix and not to overheat and break fibers. The extrusion process and the co-extruded fibers of the type srPP/5% are observed in Figure 3. The co-extrusion trial tests were realized with a relatively low content of the fibers, hence the aim was to investigate the processing possibility of the line and particularly the selection of processing temperatures based on preliminary thermal tests. The low content of PP fibers allowed to avoid the problems usually observed by co-extrusion, such as breakage of the fibers, molten polymer flow instabilities, etc.

The next investigations were focused on production of the srPP/40% pellets with highest possible content of reinforcement

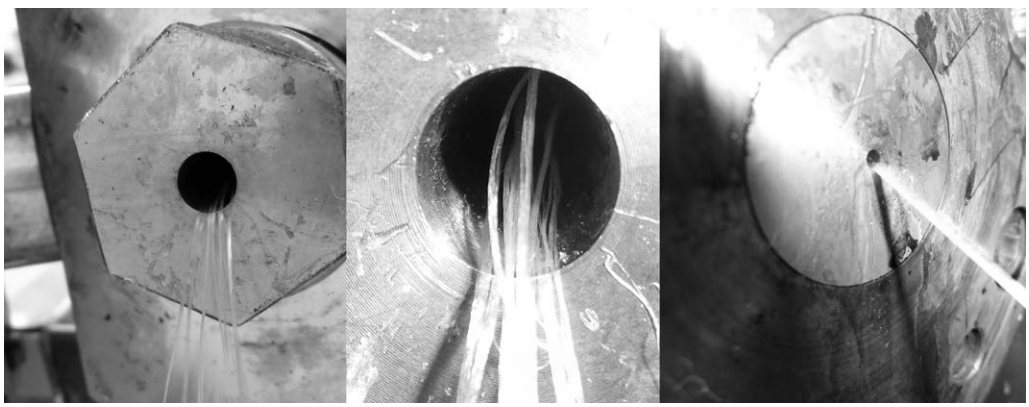

Figure 3. The inlet of the co-extrusion die with visible PP fibers (left, center) and the outlet of the die channel (right).

Table I. Coextrusion Process Parameters

Material	Die head (°C)	Zone 4 (°C)	Zone 3 (°C)	Zone 2 (°C)	Zone 1 (°C)	Screw speed (rpm)
srPP/5%[a]	150	155	155	150	145	15
srPP/20%	155	160	160	150	145	35
srPP/40%	155	160	160	150	145	35

[a] PP fibers content in weight.

fibers. Due to complexity of co-extrusion die arming with PP yarns, there was changed amount of fibers in the yarn. During preliminary tests there were 24 fibers in the yarn, one yarn has maximum 460 single fibers. The equipment and overall scheme of the co-extrusion process was the same as for previous preliminary test. The fibers content was calculated from the weight increase during the co-extrusion process and the average quantity of PP fibers has been estimated about 40% of weight. In order to make the co-extrusion process faster it has been decided to increase a screw speed, but because of the process stability problems resulting from higher amount of the reinforcement fibers there was also a need to decrease viscosity of matrix to ensure better filling of the space between fibers. So the processing temperature had to be increased. The shortening of the thermal exhibition time of the fibers in the die was also key to stabilize the process.

As in preliminary test the srPP extrudate was winded on the rotating barrel and then was cut using the pelletizing machine to small pieces. For the mechanical research, the obtained samples of pellets were injection molded. To check the influence of the fibers content on the mechanical properties, srPP/20% pellets with half of the maximal amount of fibers were also produced. These yarns containing together 230 PP fibers were produced with same processing conditions as the pellets with maximum of 460 fibers. The processing parameters of all co-extrusion cycles are detailed in Table I.

Injection Molding. The preliminary injection tests were performed for srPP/5% pellets with low reinforcement fibers content using a small piston injection molding machine and standard heating system. The barrel temperature was set to 155°C, and the mold temperature was 80°C.

The problem of fibers existence after injection molding process was solved, which can be easily seen in Figure 4. The other question of the fiber–matrix interface can be seen using the scanning electron microscopy (SEM) observations. The figures of the sample fracture presented below show the fibers inside the matrix and the holes remain after the pull-out effect. This could be very promising fact, because it means that polypropylene fibers properties are not reduced, from the mechanical point of view.

Characterization

In order to obtain full material characteristics, that is physical and mechanical parameters as well as morphology of the molded samples structure, four measurements procedures were applied for research purposes:

- SEM analysis;
- DSC analysis;
- Dynamic mechanical analysis (DMA);
- Static tensile test.

The SEM observations were performed in order to examine the morphology of the srPP samples particularly from the point of view of residence of reinforcement fibers as well as their distribution and size. Because the cross-section of the samples is observed, the specimens must be prepared so that to obtain a brittle fracture to be scanned. In order to attain that, the samples are placed in liquid nitrogen and next broken. The used equipment was Zeiss Ultra Plus Field Emission SEM, the device allows the observation of non-conductive samples, therefore the prepared fractures were uncoated, the acceleration voltage was 2 kV for each sample.

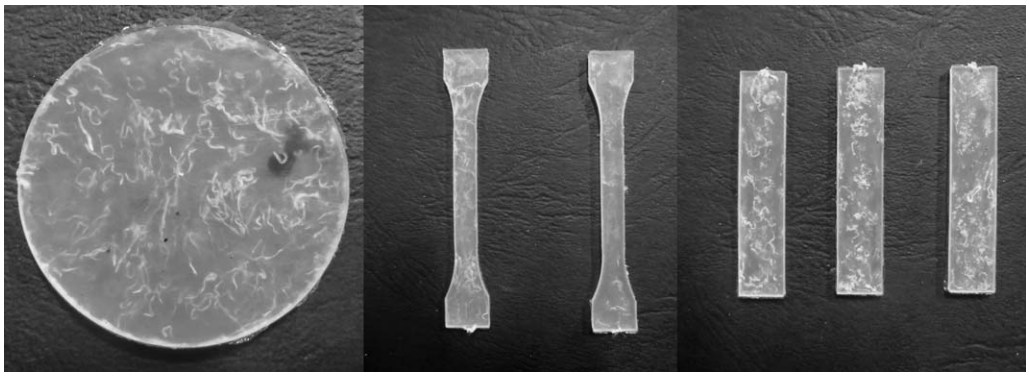

Figure 4. Injection molded samples, srPP/5%.

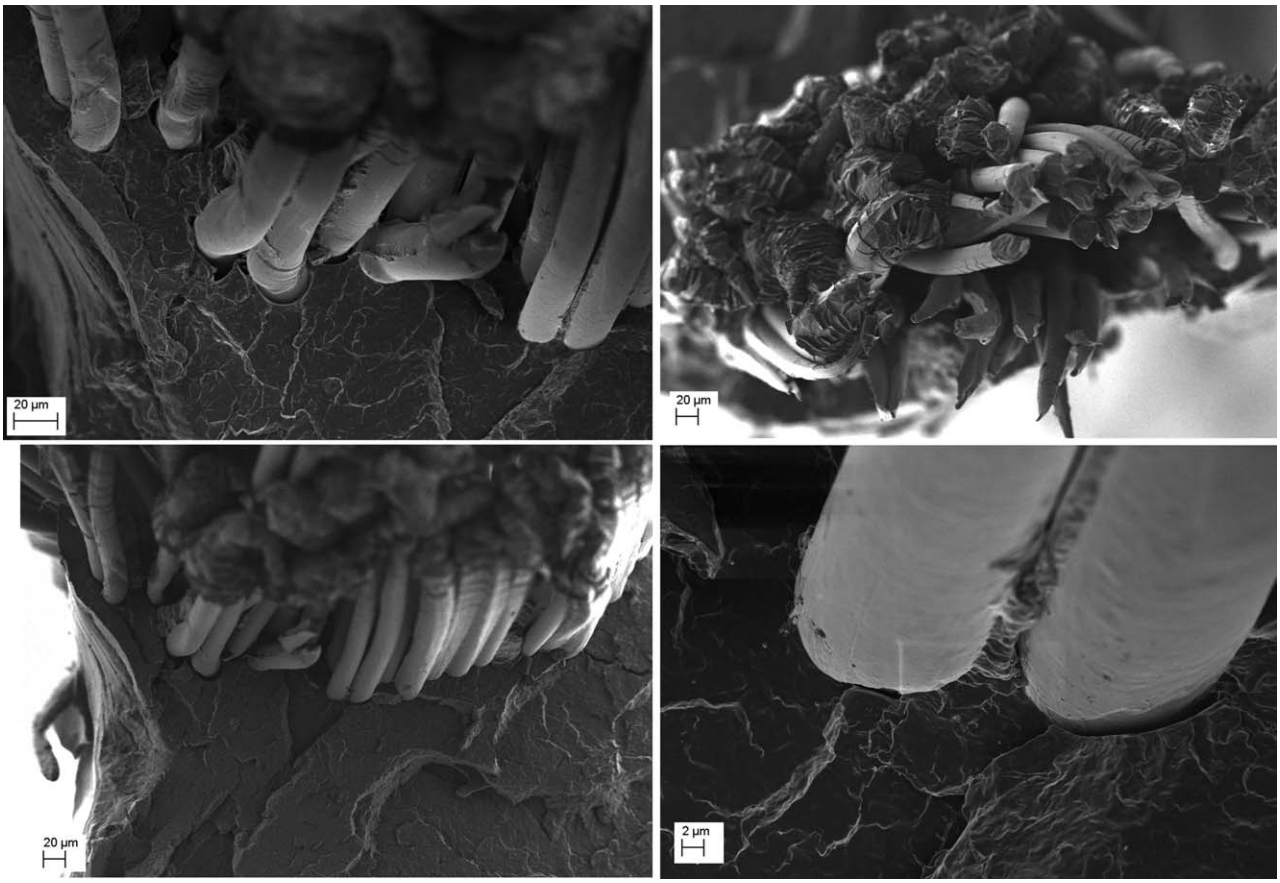

Figure 5. SEM images of the co-extruded pellets, srPP/5%.

DSC was used for examining srPP compounds to check their composition. The method can show possible polymer degradation by the lowering of the expected melting point. DSC investigations were performed by differential scanning calorimetry apparatus DSC Netzsch 204 F1 Phoenix. The measurements were carried out in the following conditions: heating and cooling rate 10°C/min, protection atmosphere N_2 with a flow rate of 20 mL/min, average sample weight was about 5 mg.

The DMA analysis was performed using the Anton Paar MCR 301 apparatus, the solid rectangular samples were mounted to the torsion system clamps. The measurement was carried out under following conditions: strain frequency = 1 Hz, strain amplitude = 0.01%, tests were performed from the −50°C up to 120°C, with the heating rate of 2 K/min.

The mechanical properties of tested specimens have been measured by means of a tensile testing machine Zwick Z02 according to method described by ISO 527. The tensile tests have been realized by the elongation rate of 10 mm/min. The presented results are the average of 10 measurements.

RESULTS AND DISCUSSION

srPP Pellets

The srPP pellets preparation process did not include the orientation of the obtained extrudate. The increase of the mechanical properties is the result of the initial parameters of oriented polypropylene fibers which are decreasing because of the relaxation process during the extrusion/injection molding cycle. The presented methodology is not the best solution in terms of possibilities to achieve maximum mechanical properties but this approach has been studied as the simplest method that does not require specialized instrumentation.

The SEM images of the developed srPP pellets are shown in Figure 5, where the interface between the fibers and PP matrix may be observed. The visible PP reinforcement fibers are surrounded by copolymer matrix, but also a local poor adhesion of matrix to the fibers may be observed.

The co-extruded PP pellets were examined also using DSC method. The DSC thermograms of the srPP/5% sample are shown in Figure 6, the srPP/40% in Figure 7. On the first DSC heating curve the peak of random copolymer at 138°C is visible; the second peak at 163°C is the melting point of the PP fibers. Second heating curve confirms the two components structure of the composite. The occurrence of the three peaks at the second heating of the sample is related to the structure of applied random copolymer. Comparing the melting thermograms of the samples containing 5% and 40% of fibers, it is clearly visible that the melting enthalpy of PP fibers increases, which can be regarded as the further confirmation of a significant increase of the reinforcing phase proportion.

A competitive method that can be used in the preparation of the self-reinforced composites on a large scale was proposed by Fakirov and his team. In a series of articles[12,27–31] they

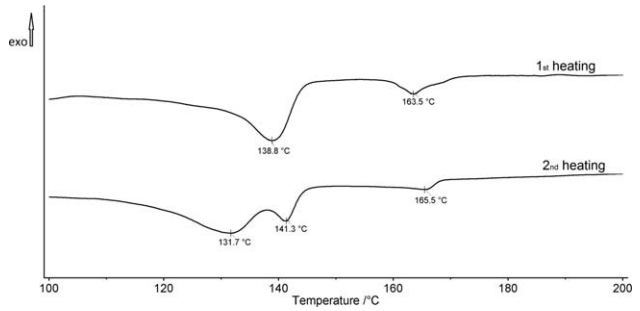

Figure 6. DSC thermogram of srPP/5% pellets.

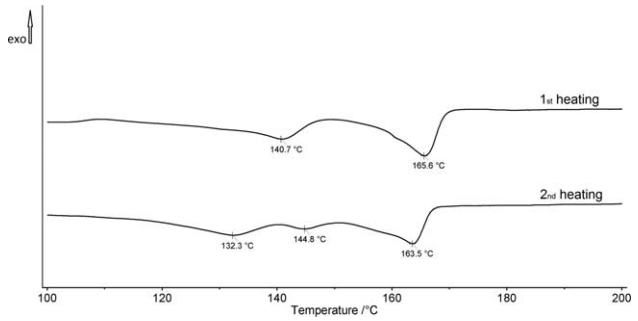

Figure 7. DSC thermogram of srPP/40% pellets.

presented the results of wide spectrum of research work. This technique involves the preparation of bicomponent polymer blend in the extrusion process, the second stage of process is drawing, the oriented structure of microfibrils is achieved using the rotating roller system. The extrudate prepared in this way can be collected on a spool or pelletized. The preparation process can be accomplished by compression or injection molding technique. This method allows a significant increase of the mechanical properties, however the presented materials selection did not meet the concept of self-reinforced materials. The research concerns the composition types: PP/PET, PE/PET, or PET/PA6 blends. The use of this method for preparing the self-reinforced composites should be the subject of further studies.

Injection Molded srPP Samples

The use of the composite granules in the standard injection molding process is the most desirable form of self-reinforced composites. The method presented in this work allows the production of granular composites. However the series of articles present a completely different approach to injection molding of the self-reinforced materials. The following works[14,32] can serve as an example. The first method is presented by Kmetty et al. in their work.[14] First solution presented by Kmetty et al. in their work is to prepare the composite material by fragmentation the compression molded sheets. The injection molding technique was used as a final shaping method. The second method described by Wang involves placing the reinforcing fabric in the interior of the mold, the matrix polymer was then injected to mold cavity. In both cases the reinforcing effect was confirmed; however, the material preparation was more time and energy consuming than solution presented in this work.

Figure 8 presents SEM micrograph comparison of neat PP, srPP/5%, and srPP/40% samples. Analyzing SEM images of the molded "dumbbell samples," the fracture of the srPP/5% sample shows the composite structure with visible PP fibers, despite their small amount. The SEM images show the two-component structure with very sharp boundary between fibers and polymer matrix. The breaking of the sample causes the brittle cracking of the copolymer matrix. The PP fibers were most often pulled

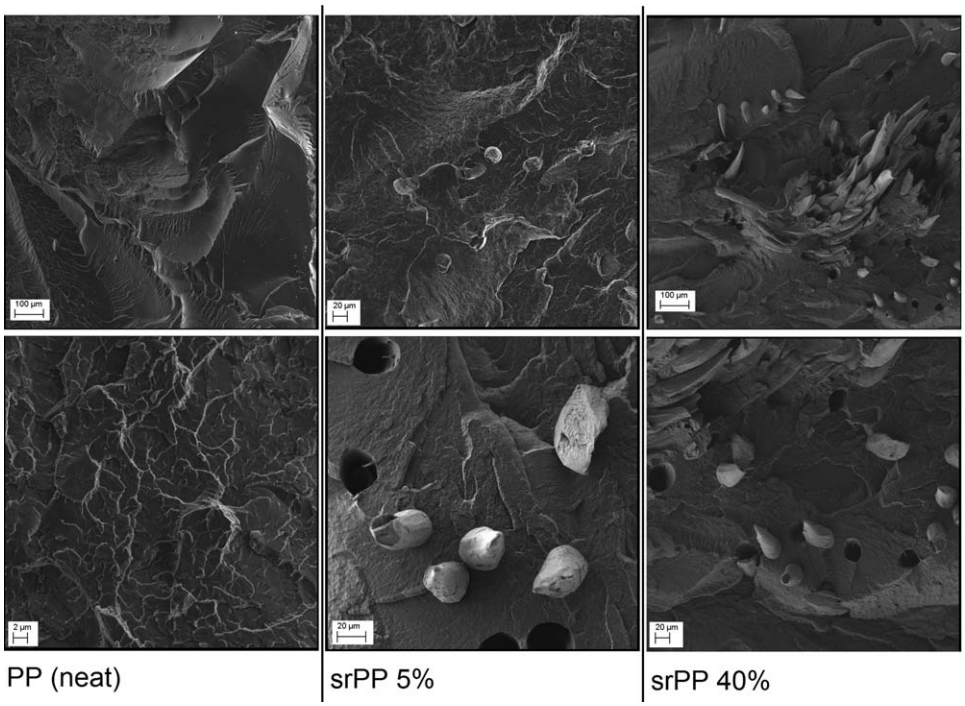

Figure 8. SEM images of injection molded samples, neat PP (left), srPP/5%(center), srPP/40%(right).

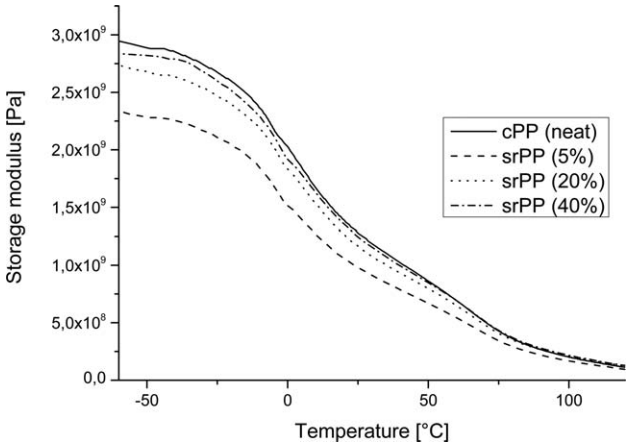

Figure 9. Storage modulus curves of the injection molded samples.

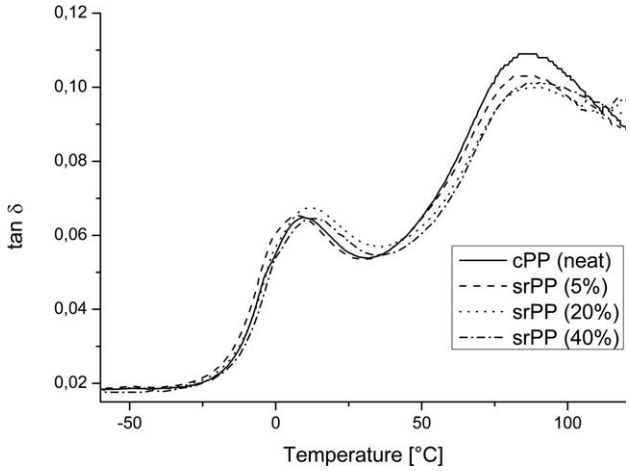

Figure 10. Tangent δ curves of the injection molded samples.

out from the matrix, the breakage was not formed at the surface of the main fracture of the matrix. The regular shape of the holes suggests the lack of joint penetration. PP fibers are not melted, even on the surface. For the srPP/40% samples can be seen additional tendency to clumping of fibers, which was not observed for samples with low fiber content. The observed fiber agglomeration process is certainly negative considering the mechanical properties of the composite it results in uneven distribution of fibers thus reducing the strengthening effect. Similar conclusions can be drawn from the other research works.[14,32] In most cases SEM images confirm the presence of clear boundary at the interface fiber/matrix, even for the structures where the significant fiber deformation can be observed.[32]

Thermo-mechanical analysis performed on the injection molded samples determine their storage modulus and tan delta values. The storage modulus curves shown in Figure 9 covers the range of temperature from −60°C to 120°C. The stiffness of the samples made from pure matrix material was surprisingly highest which may indicate a low reinforcement level. The lowest modulus values are noted for srPP/5% samples with low fiber content. The increase of the fiber content cause the significant rise of the modulus curve. Waveforms for samples srPP/20% and srPP/40% are almost similar to neat copolymer matrix. The analysis of the tan delta curves (Figure 10) reveals some variations in glass temperature of measured samples, however the changes are insignificant moreover the damping factor values are essentially similar for all samples.

The mechanical properties of the injection molded samples were measured by means of static tension test. The tests results should be concerned on the values of E modulus, yield stress, elongation at yield stress and at break and compared to the appropriate values of matrix material. As was described above there were prepared srPP samples with three different amount of fibers. First one with srPP/5%, second srPP/20%, and third srPP/40% with the maximum of fibers. The general view of "dumbbell" samples made by injection molding is shown in Figure 11 for srPP/5% samples and in Figure 12 for srPP/40% samples. Their mechanical properties were measured by means of static tension test. The mean values from tests results are presented in Table II.

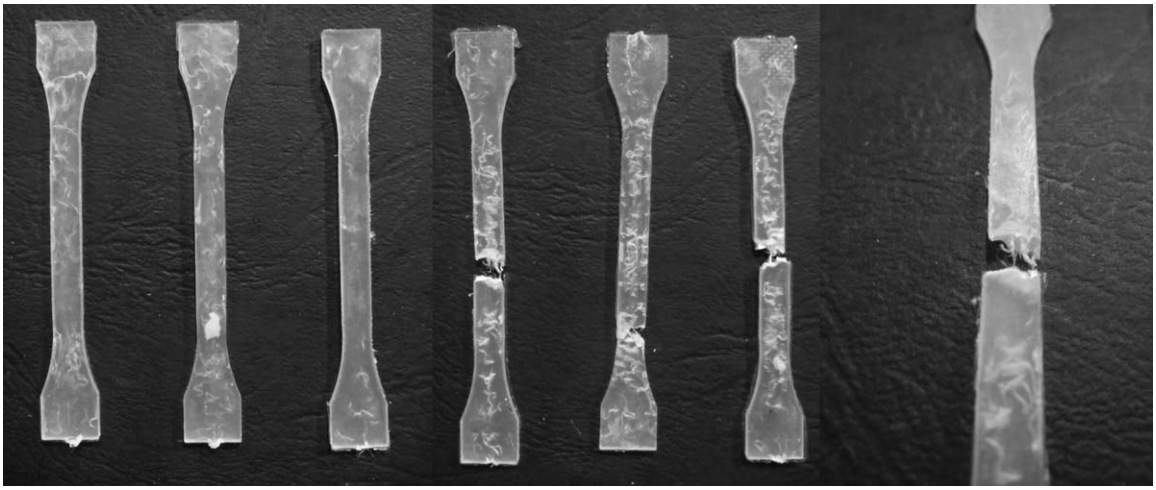

Figure 11. srPP/5% samples before (left) and after the tensile test (center), fracture view (right).

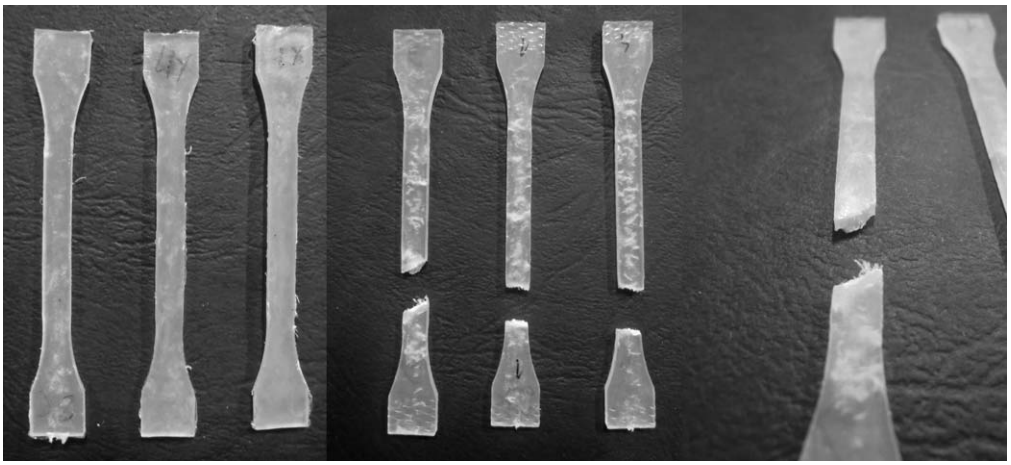

Figure 12. srPP/40% samples before (left) and after the tensile test (center), fracture view (right).

The mechanical properties of the preliminary srPP/5% samples were disappointing. The yield stress values were at the same level, but the *E* modulus value decreases. These poor material qualities confirm the negative impact of the small fibers content. In this case fibers with no interaction between them are acting like micro indentation.

The results obtained for the samples with higher fiber content are almost similar for samples srPP/20% and srPP/40%. The properties of these composites prove the effectiveness of the used technology. The increase of the yield stress refers not only to the preliminary srPP/5% samples. The comparison to neat matrix material shows the 11% increase of the maximum stress. Increasing yield stress goes hand in hand with fiber content. The increase also applies to the *E* module value. The difference reaches about 15%. The beneficial impact on the values of yield stress and *E* modulus is unfortunately associated with a decrease in elongation. Although the srPP/5% samples with low fiber content behave similar to pure matrix with extension of about 20%. But the increasing fibers content cause the drop to 8% for the srPP/40% samples.

The presented results of the injection molded srPP composites characterization confirm the reinforcing effect of the PP fibers. However the comparison of the mechanical properties to the standard self-reinforced composites show the relatively low growth of the properties for injection molded srPP samples. The probable reason for that is heterogeneous distribution of reinforcement fibres inside the sample after injection molding which is observed as a fibers aggregation. It can be caused by point shape die used during injection molding process and high shear rate during flow of the polymer. Such fibers aggregations can be considered as inside notches which reduce the strength parameters. Second issue which can determine insufficient changes in mechanical properties of samples are small differences between the melting temperature of polymeric matrix and fibers, which yields to loss of fibers properties during injection molding process. Nevertheless fibers are not melted and are still visible in the samples without drastic shape change.

The improvement of the mechanical properties was observed in the scientific studies representing a similar research methodology.[14,32] It is also discussed in review papers where the state of knowledge and future trends for self-reinforced composites are presented.[33,34] Regardless of the processing methodology for the materials shaped by injection molding technique the material strengthening does not reach high levels, in most cases the mechanical properties improvement (Young modulus, tensile strength) does not exceed 40%. Detailed analysis of the research work indicates that the characteristics assessed in the standard tension test do not allow for a proper evaluation of materials properties. The more useful results can be provided by dynamic tests represented by drop weight tests,[13,14,35] where the properties improvement of self-reinforced materials turns out to be more beneficial.

CONCLUSIONS

The copolymer matrix polymer and polypropylene reinforcement were used to produce pellets using co-extrusion process. Because during co-extrusion the material undergoes phase change and is subjected to high temperature and pressure,

Table II. Static Tensile Test Results for srPP Samples

Material	*E* modulus (MPa)	Yield stress (MPa)	Strain at yield point (%)	Strain at break (%)
PP[a]	1307 ± 22	27 ± 0.2	21 ± 0.5	450 ± 120
srPP/5%	896 ± 85	27 ± 1.4	20 ± 2.1	23 ± 3.3
srPP/20%	1470 ± 45	30 ± 0.9	9.2 ± 1.0	13.3 ± 3.0
srPP/40%	1517 ± 35	30 ± 0.7	7.9 ± 0.9	9.6 ± 1.6

[a] Pure PP matrix.

morphological and physical characterization were needed to assess the presence of fibers and the rheological properties of the compound. The DMA analysis performed before the mechanical tests showed a decrease in mechanical properties for all composite samples, however suggested that the increase of fiber content is correlated with increasing reinforcing effect. The results of tensile strength tests can be considered as satisfactory. When the content of fibers in the composite reach 40% the tensile strength is equal to 30 MPa (about 11% higher in comparison to neat matrix) while *E* modulus is about 1.5 GPa (about 15% higher to neat matrix). The composites with half quantity of reinforcing fibers yields have almost the same results.

The future work is related with the use of injection molding technique as the main processing technology for self-reinforced composites. In order to increase the range of processing temperatures the new group of materials will be used for the next research. The thermoplastic polyesters appear to be the most promising group of materials. Variety of polymers of this group is characterized by a very high melting temperature differences, which should finally eliminate the relaxation of fibers at high temperatures.

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