Mechanical properties of polypropylene copolymers composites filled with rapeseed straw

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Abstract*:* This study discusses the possibility of using polypropylene copolymer as matrix composite, because they can be processed at lower temperatures. Comparing the isotactic polypropylene (PP) with copolymer PP-*b*-PE, lower temperature allows avoiding the limitations related with the glass transition temperature of polypropylene. On the other hand, statistical copolymer (PP-*s*-PE) doesn't have such properties like block copolymer but its clarity and optical properties are better than PP polymer. Therefore, the aim of this paper was to determine the processing conditions and compare mechanical properties of polypropylene copolymer composites containing straw of oilseed rape with unfilled material as well as composites containing straw of oilseed rape with PP matrix. Two different copolymers of PP were used. Using extrusion and injection molding technique the composites with addition of 20 wt. % and 30 wt. % of lignocellulosic material were prepared. The following parameters were determined: Young's modulus at tensile, tensile strength, elongation at maximal strength, strength at break, elongation at break, strength at yield 0,2 %, Brinell hardness as well as Charpy impact strength. The performed investigations revealed that copolymer matrix has good mechanical properties and lower processing temperature in comparison to composites with polypropylene matrix, because of lower degradation of the rapeseed straw.

Keywords: polypropylene copolymers, polymer composites, rapeseed straw, mechanical properties.

Właściwości mechaniczne kompozytów kopolimerów polipropylenu napełnionych słomą rzepakową

Streszczenie: Poddano ocenie właściwości mechaniczne kompozytów na osnowie kopolimerów polipropylenu z dodatkiem napełniacza — rozdrobnionej słomy rzepakowej. Kompozyty w postaci granulatu otrzymywano metodą wytłaczania, a wypraski do badań mechanicznych — techniką wtryskiwania. Zawartość lignocelulozowego napełniacza w kompozytach wynosiła 20 lub 30 % mas. Określano parametry procesów wytłaczania i wtryskiwania kompozytów na osnowie kopolimerów: blokowego i statystycznego. Zastosowanie kopolimerów polipropylenu jako osnowy kompozytowej pozwala obniżyć temperaturę przetwarzania, co ma korzystny wpływ na właściwości wytwarzanych materiałów, dzięki ograniczeniu termicznej degradacji naturalnego napełniacza (słomy rzepakowej). Oceniano następujące właściwości mechaniczne: maksymalne naprężenie rozciągające, wydłużenie przy zerwaniu, wydłużenie przy maksymalnym naprężeniu, naprężenie na granicy plastyczności 0,2 %, moduł Younga, udarność metodą Charpy'ego i twardość metodą Brinella. Stwierdzono, że w przypadku niektórych zastosowań kompozytów, zamiana osnowy polipropylenowej na kopolimerową jest korzystna ze względu na jej odmienne właściwości, na przykład znacznie niższą temperaturę zeszklenia.

Słowa kluczowe: kopolimery polipropylenu, kompozyty polimerowe, słoma rzepakowa, właściwości mechaniczne.

There are a lot of articles discussing lignocellulosic materials as fillers in composites of thermoplastics. Polypropylene (PP) composites filled with crushed oilseed rape straw have favorable mechanical properties and increased sound absorption. In researches carried out so far no attempts have been made to investigate the lignocellulosic composites using PP copolymer as a matrix. The composites with natural lignocellulosic material like wood, sisal fibers, and ramie with thermoplastic homopolymers have been investigated and described in many papers [1—9].

Mechanical properties are very important source of practical applications of composites [10—14]. The study of the mechanical properties of polypropylene composites filled with rapeseed straw, infested by the fungal pathogen *Sclerotinia sclerotiorium* was devoted the work of D. Paukszta *et. al.* [15].

Polypropylene copolymers contain one or more different types of monomers in the polymer chain. In this study PP-PE copolymers are used. Random copolymer

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contains ethylene units inserted randomly along the polypropylene chain, disrupting the regular, repeating structure of isotactic polypropylene. The monomer content can be up to 7 % of ethylene. On the other hand, block copolymers can contain up to 25 % of ethylene. The added ethylene forms a dispersion of particles in the semicrystalline polypropylene matrix, providing elastomeric properties to the polymer [16].

Copolymers have some improved properties in comparison with PP polymers. Block copolymer (PP-*b*-PE) are more impact resistance than PP, even at the temperature below 0 °C. Products made by injection molding are much stiffer than using standard PP polymers. Due to addition of PE, block copolymers are more resistant to grinding. On the other hand, statistical copolymer (PP-*s*-PE) doesn't have such properties like block copolymer but its clarity and optical properties are better than those of PP polymer. Both copolymers, due to addition PE and additives, can be processed at lower temperature (190—200 °C). Most PP polymers are processed in the range of (220—230 °C) [17, 18]. Lignocellulosic materials during processing have tendency to degrade. Low processing temperature effects positively to mechanical properties of received composites [17, 18].

EXPERIMENTAL PART

Materials

The polymer matrices were Moplen RP384R (PP-*s*-PE) statistical copolymer of polypropylene (PP), polyethylene (PE), and Moplen EP300K block copolymer (PP-*b*-PE) in a form of granulate of Basell Orlen Polyolefins Ltd. Co. The lignocellulosic material was healthy oilseed rape straw from experimental field from Institute of Plant Genetics, Polish Academy of Sciences, Poznań, Poland.

Preparation of composites

The rapeseed straw was crushed into small pieces. Then using the pneumatic method, parenchyma was separated from scleroderma. At the last step of the preparation of the lignocellulosic material, wooden parts of rapeseed straw were ground and sieved into fraction 1—2 mm using a Retsch SM 100 mill (Retsch Germany).

Composite materials containing 20 wt. % of the rapeseed straw and 80 wt. % of copolymer EP300K, or 30 wt. % of the straw of oilseed rape and 70 wt. % of copolymer EP300K were prepared. The composites containing copolymer RP384R were prepared in the same way. Four composites were obtained by extrusion method using a Fairex single-screw extruder (Mc Nell Akron Repiquetn, France). The process was carried out at screw rotational speed 25 rpm at the following temperatures: chute zone 20 °C, zone I 140 °C, zone II 180 °C, zone III 190 °C, head temperature 195 °C. In order to obtain profiles intended for mechanical experiments, the obtained granules were subjected to injection molding using machine Engel ES 80/20 HLS (Engel, Austria GmbH) and applying parameters presented in Table 1.

T a b l e 1. Injection molding parameters of the studied polypropylene and composites

Processing parameters	Composite	Polypropylene
Injection pressure	70 MPa	70 MPa
Injection speed	60 mm/s	60 mm/s
Holding pressure	50 MPa	50 MPa
Holding pressure time	2 s	2 s
Cooling time	35 s	30 s
Injection time	1.38 s	1.38 s
Plasticization pressure	2 MPa	2 MPa
Screw rotational velocity	150 rpm	150 rpm
Mold temperature	22 °C	22 °C
Screw dosing lead	78 mm	78 mm
Injection temperature (°C) zoneI/zoneII/zoneIII/nozzle	160/170/180/195	180/200/215/220

Methods of testing

The mechanical properties were checked using Instron 4481 — testing machine on the samples, obtained by injection molding, of shape 150 mm long and 10 mm wide and 4 mm thick. The following mechanical properties were determined during the static tensile tests: Young's modulus, tensile strength, elongation at maximal strength, strength at break, elongation at break, strength at yield 0,2 % at constant speed of 10 mm/min. Additionally impact resistance (Charpy test) using Instron Wopert PW5 as well as Brinell hardness using Oberon KB150R (H132/30) were determined. The impact resistance was tested using small bars of 80 mm × 10 mm × 4 mm dimensions. The Brinell hardness test was done using cylinders, 20 mm in diameter and 4 mm thick. Mechanical properties and impact resistance tests were carried out for 10 randomly selected samples, while for hardness tests 20 randomly selected samples were used. Most mechanical properties were compared to unfilled polypropylene matrix.

RESULTS AND DISCUSSION

Figure 1 presents the results of mechanical properties tests, Fig. 2 shows impact resistance and Fig. 3 — the Brinell hardness.

It was observed that addition of the straw of oilseed rape caused a decrease in tensile strength in comparison with copolymer matrix for both polymers.

It is interesting that the drop of tensile strength from PP-PE to PP-PE 20 is higher for statistical copolymer than for block copolymer (Fig. 1a). In the case of previous

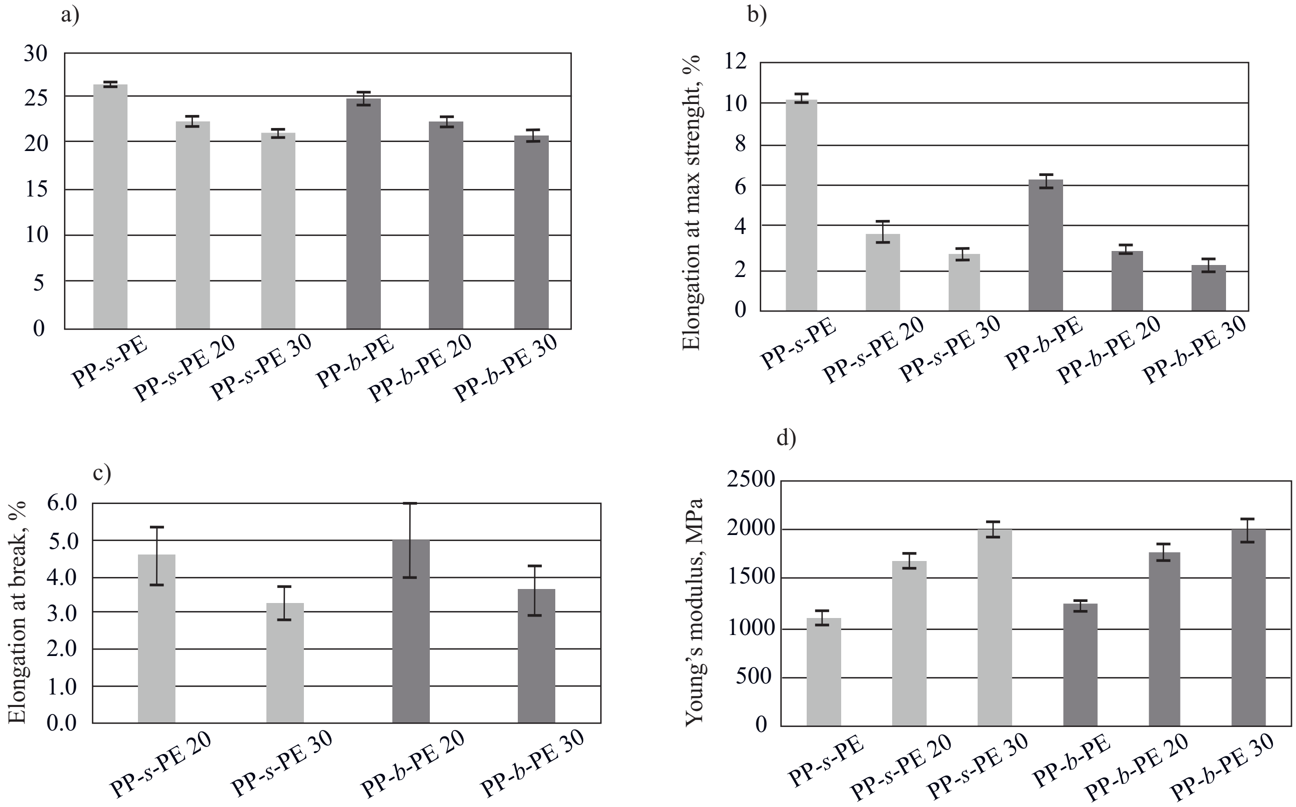

Fig. 1. Influence of the composite type on: a) the tensile strength PP-*s*-PE and PP-*b*-PE; b) elongation at maximal strength; c) elongation at break; d) the tensile Young's modulus

work, tensile strength for unfilled PP was higher for 15 %, and for filled PP with concentration of 30 wt. % of the straw of oilseed rape was also higher by about 10 % [15]. In addition, it is worth noting that for all the PP matrix composites [2, 15] the values of the tensile strength were similar and not less than 20 MPa.

Elongation at maximum strength of composite samples filled with lignocellulosic material are lower in compare to elongation value of thermoplastic polymer matrix (Fig. 1b). It should be noted that this parameter is affected by the type of matrix used. For composites containing 30 wt. % of copolymer rape straw elongation at maximum strength is slightly greater than 2 %, while for PP matrix composites is of the order of 4 % [15].

The characteristics of strength at break shows that addition of the straw of oilseed rape causes a decrease in strength at break. The highest value was observed for PP-*s*-PE 20 and the lowest for PP-*b*-PE 30. A similar trend in decrease of this parameter with the increase of the filler content of the lignocellulosic composites was observed with PP matrix. It is worth noting that the values of strength at break for PP-PEs are very close to the corresponding values for the polypropylene matrix composites. Statistical copolymer filled with lignocellulosic material has higher strength at break than block copolymer composites. The reason for these phenomena can be chemical structure of statistical copolymer. The polymer is more homogeneous than block copolymer which contains a segment of PE chain [15].

The elongation at break values of composite samples filled with 30 wt. % of the rapeseed straw are lower than observed for composite samples with 20 wt. % of filler [Fig. 1c]. The reason for such higher values for block copolymer is the structure of block copolymer. During testing the samples were stretched in several places. It was noticeable that the samples changed color in several places. The statistical copolymer was stretched only at one place without changing color. The elongation at break value for PP matrix filled with 30 wt. % of lignocellulosic material (5—7 %) was higher in comparison to copolymer composites with the same content of rapeseed straw and was of the order of 4 % [15].

Another important characteristic of composites is their Young's modulus. The obtained results have shown that addition of the oilseed rape straw increases Young's modulus (Fig. 1d). The more the lignocellulosic material, the higher is the Young's modulus. It is notable that both copolymer composites (statistical and block) have similar values of this parameter. Addition of 30 wt. % of lignocellulosic material gives 86 % higher Young's modulus, than for unfilled copolymer in both cases. Taking into account previous work for PP composites filled with the straw of oilseed rape the Young's modulus was about 1400 MPa [15]. In this paper the highest value of Young's modulus was 2000 MPa. Through the use of copolymer instead of isotactic PP this value is by 33 % higher. The reason for these phenomena is lowering the maximum temperature

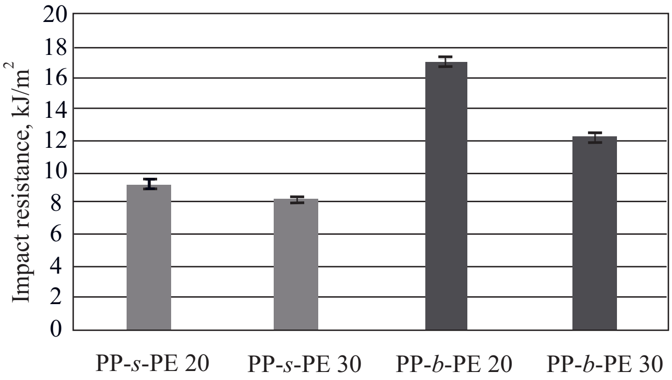

Fig. 2. Influence of the composite type on Charpy impact strength; explanation types are listed in Fig. 1

to 195 °C instead of 200 °C, which causes lower degradation of the rapeseed straw.

In all cases, the yield strength at 0.2 % had a comparable value, and there was observed a slight increase, within the limits of statistical error. It is worth noting that these values are very close to the strength at yield at 0.2 % for polypropylene composites filled with oilseed rape straw [15].

For all the investigated composites the impact resistance was decreasing with the oilseed rape straw content (see Fig. 2).

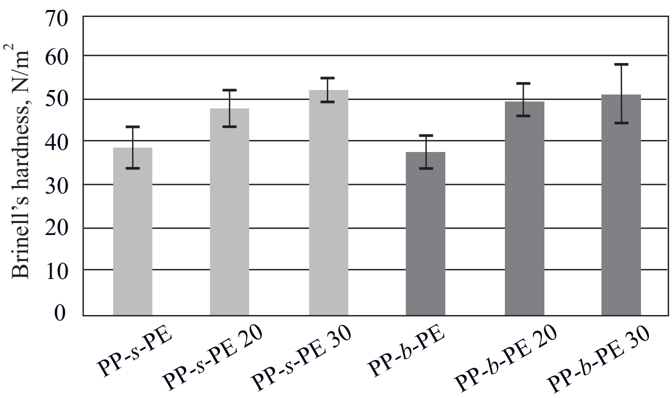

Fig. 3. Influence of the composite type on Brinell hardness; explanation types are listed in Fig. 1

The highest value was observed for the sample with block copolymer as a matrix with confirms higher impact resistance of PP-*b*-PE 20 and PP-*b*-PE 30 (Fig. 2). These values are of the same order as for the polypropylene matrix composites [2, 15].

In all the composites the hardness values were quite comparable and similar to that of the polypropylene matrix composites (Fig. 3).

The hardness was increasing with addition of lignocellulosic material [2]. There is no big difference between block and statistical copolymer composites. The presence of rapeseed straw in polypropylene composites increased Brinell hardness.

CONCLUSIONS

Based on the study we can draw the following conclusions:

— Replacement of polypropylene copolymer PP-*s*-PE or PP-*b*-PE can lower the temperature of receiving and processing of the composites obtained.

— The value of tensile strength for composite filled with the rapeseed and polypropylene (pure or copolymers) as a matrix shows no significant differences, the value of this parameter is for all composites slightly higher than 20 MPa.

— The values of the strength at break of the material with PP-*s*-PE as a matrix are almost identical to those of the composites of homo PP, they are also much higher than for material with PP-*b*-PE as a matrix.

— The use of a copolymer matrix causes a decrease in the value of elongation at break compared with a polypropylene matrix composite.

— Young's modulus for the composite with the matrix copolymer is in the range of 2000 MPa and is much higher than for the polypropylene matrix composites.

— Impact resistance values for the composite with PP-*b*-PE matrix are comparable to the values for polypropylene composites, but impact resistance of PP-*s*-PE composites is much lower.

— The hardness of the composites with a matrix and a polypropylene copolymer are comparable.

As can be seen from the studies described in this work, changing the polypropylene to copolymer with PP-*s*-PE or PP-*b*-PE matrix modifies certain properties of composites. The biggest changes are observed in parameters such as elongation at break and Young's modulus, but that does not mean worse performance in the copolymer matrix composites. On the contrary, since the wider applicability of the composites at low temperatures can be obtained with copolymers of PP-*b*-PE.

It appears that similar properties will be characterized by composites filled with other lignocellulosic materials, but this should be confirmed by subsequent studies.

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