PROCESSING PROPERTIES OF MODIFIED RECYCLATED POLYAMIDE-POLYETHYLENE COMPOSITES

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S u m m a r y

New composite materials based on recycled polyamide-polyethylene materials (PAPE) and fillers of PAEK (RC) wastes with particle size up to 0,063 mm are created and manufactured. The processing properties of composites were defined according to results of studies of filling of moulds in the form of a round or square spiral and a multi-stage injection moulding cavities in dependence of processing parameters (injection pressure, injection temperature, mould temperature) and amount of PAEK (polyaryletherketone) filer in composite material. The filling stage of mould was studied on the basis of the moulding length in the spiral form (round, square). It was obtained, that increasing injection pressure and injection temperature results in increasing filling stage of injection moulding cavity. High-filled composites (40-50% – wt. RC) may be used for manufacturing of thick-walled products, and composites whit filler content up to 30% – wt. for thin-walled products.

Keywords: recycling, waste, polyamide-polyethylene foil, carbon fibre reinforced polyaryletherketone composite, injection, spiral.

Właściwości przetwórczych modyfikowanych recyklatowych kompozytów poliamidowo-polietylenowych

S t r e s z c z e n i e

Wytworzono nowe materiały kompozytowe z recyklatów poliamidowo-polietylenowych (PAPE) oraz napełniaczy odpadowych PAEK (RC) o rozmiarach cząstek do 0,063 mm. Określono właściwości przetwórcze kompozytów przy użyciu form z gniazdem spiralnym okrągłym, kwadratowym i gniazdem wielostopniowym w zależności od parametrów przetwarzania (ciśnienia i temperatury wtrysku, temperatury formy) oraz zawartości napełniacza PAEK w kompozycie. Wypełnienie gniazda spiralnego określono na podstawie długości wypraski spiralnej. Stwierdzono, że wzrost ciśnienia oraz temperatury wtrysku powoduje zwiększenie wypełnienia gniazda formującego. Wysokonapełnione kompozyty (40-50% RC) mogą być stosowane na wyroby grubościenne, natomiast kompozyty o zawartości napełniacza do 30% na wyroby cienkościenne.

Słowa kluczowe: recykling, odpady, folie poliamidowo-polietylenowe, kompozyty z włóknem węglowym i napełniaczem PAEK, wtrysk, spirala

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Introduction

The injection molding is a basic method of processing in the large-lot production of products made of thermoplastic plastics. Products of different sizes and of complicated shapes and determined properties are manufactured by this method. For manufacture of products of appropriate qualities processing properties of used materials, processing parameters and the design of forming tools are decisive. One of the essential processing properties of plastics in their plastic flow state is the viscosity η, which depends on the shear rate γ and the shear stress τ [1, 2]. The viscosity characterizes every plastic material. The studies of viscosity (the rheological study) of plastics with the aid of various research methods are described in special bibliography [3, 4]. Most studies are carried out within a shear rate of 10^{-2} to 10^{4} s^{-1} therefore are equivalent to processing of materials by different technologies (mixing, homogenization, extrusion, injection molding). Most interesting are the changes in the plastic material viscosity, taking place within a shear rate in the range of up to $6x10^{2}s^{-1}$ (processing by extrusion), where a great dependence of the viscosity on the plastifying temperature and the shear rate can be determined. For low and medium shear rates the viscosity of polymers change only insignificantly - this is being conditioned by the orientation of polymer particles (position in relation to the flow direction) [2, 5]. Therefore, to evaluate the material viscosity, the information of changes for shear rates up to 10^{3} s^{-1}. As it is known the material viscosity is affected by its composition and in case fillers are used their size, shape and the capacity to deform and degrade etc. [5, 6].

For industrial practice processing properties of materials are determined basing on the melt flow rate and melt volume rate (MFR, MVR) and the filling percentage of a forming mould cavity of a spiral shape or of a multi-stage mould cavity [5, 7, 8]. The melt flow rate allows determining the material properties under constant conditions, i.e. at a stabilized temperature, and stable shear rate and shear stress. By examination at a number of points one can determine for a given material the viscosity curve and the flow curve. These measurements are carried out within a range of small shear rates and can serve for an initial evaluation, and comparison of materials, provided they have been conducted at identical conditions.

More information on processing properties of materials is gained basing on the determination of the extent to which moulds with spiral channels or multi-stage moulds are filled. Forming mould cavities can have round spiral channels (Archimedes spiral) or square spiral channels [5, 9, 10]. Open or closed channels are used. The most common length of a channel is up to 1.5 m and the channel cross-section 5-35 mm^{2} [11]. These studies reflect the real conditions of injection of materials into the mould cavity.

The main difficulty when comparing test results at various research centers is the use of moulds with cavities for which the size of spiral channels differs.

Therefore, test results are strictly dependent on an adopted method of studies and moulds used for these studies.

During the injection process a material in viscoelastic state flows from a plastifying system of an injection molding machine via runner in a mould into mould cavity. Depending on the cavity shape and its size, when the space between the punch and the die fills up, a material can flow freely or be in its flow impeded (the flow in a perpendicular plane or in any other plane in relation to the flow direction, changing product cross-sections).

The available scientific literature on processing properties of plastics most usually presents test results for the melt flow rate, however, information on the degree of filling up forming mould cavities lacks. Moreover, these studies are concerned with primary (virgin) materials and only to limited extent with recyclate plastics. With a growing amount of recyclate used for manufacturing of technical products the knowledge of their processing properties is necessary.

The determination of recyclate composite manufacturing properties according to the filling degree of a mould cavity with spiral channels and multi-stage moulds at varying processing parameters is the subject of this paper. Recyclate composites made of multi-layer PAPE foil as the matrix and post-production PAEK laminate containing carbon fiber were subject to testing. So far such composites were not manufactured. According to possibility of use of these materials for technical products the performed studies allow optimizing the processing conditions. The presented study complements our knowledge on multi-component recyclate composite processing properties.

Materials

The tested materials were recyclate composites consisting of:

- Polymer matrix – a multi-layer polyamide-polyethylene foil type PAPE. The recyclate was obtained from production wastes of a 5-layer barrier foil with components: polyamide (30% – wt.), polyethylene (67% – wt.) and adhesive/barrier layer of EVA/EVAL (30% – wt.). The material was characterized with following parameters: density 0.976 g/cm^3 and melt flow rate (MFR) of 3.396 g/10 min (493 K, 31,36 N).
- Filler – milled post-production waste of PAEK (polyaryletherketone) composite (laminate) containing 60% of carbon fibers. The waste in form of chips from mechanical processing was ground to 0.063 mm particles. The material was designated with the RC symbol and its density was determined at 1,47 g/cm^3. The composite from PAEK due to its properties is used in the medical industry for manufacture of parts of surgical instruments.

The PAPE/RC composites were made from these materials and contained 10, 20, 30, 40 and 50% – wt. of the RC filler. For first testing composites made in a Brabender mixer (mixer chamber temperature: 493 K, mixing time

60-120 sec. depending on the required filler concentration in the composite) were used, where for further testing composites made with a twin-screw extruder operated in a cold granulation line were used. The processing properties were determined experimentally for every kind of material (from 453 to 493 K). The obtained regranulated product was processed with a BOY 15 injection-moulding machine.

Methods

The processing properties studies were carried out with special moulds of a round open spiral channels (Fig. 1), a square spiral channel mould (Fig. 2) and with a multi-stage mould (Fig. 3) [5]. The applied moulds were provided with a cooling system to keep the temperature constant. For testing manufactured regranulates were used. The processing was carried out with a screw injection moulder BOY 15. To determine the filling degree of a spiral cavity mould (Fig. 1 and 2) initial testing was performed to determine the plastic amount needed to ensure the maximum length of a moulding at following processing parameters: injection pressure 125 MPa, processing temperature 503 K (temperature of individual heating zones: 503, 493, 453 K) and the mould temperature: 298 K. During background tests (screen test) the injection pressure, the processing temperature and the mould temperature was modified with a specified amount of plastic kept unchanged. The mould filling degree was determined basing on the moulding length. To determine the mould filling degree for a mould with a multi-stage cavity (Fig. 3) processing properties ensuring a complete filling of a cavity at the injection pressure of 100 MPa and

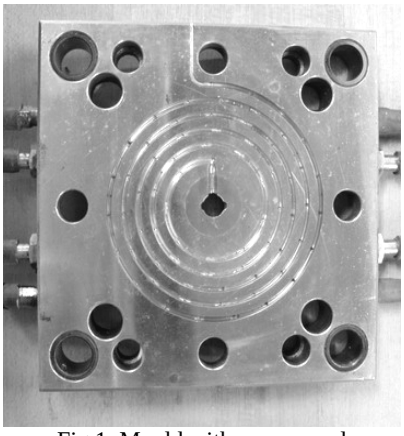

Fig.1. Mould with open round spiral channels

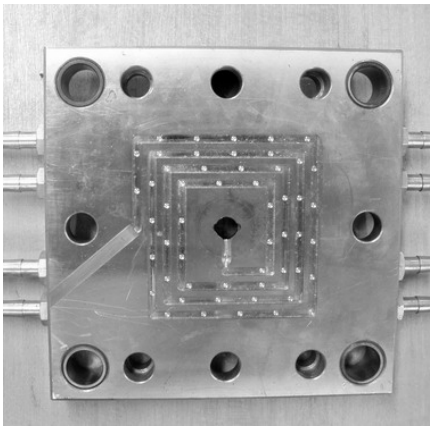

Fig. 2. Mould with open square spiral channels

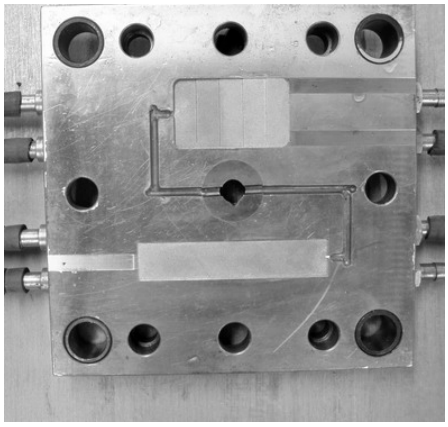

Fig.3. Mould with multi-stage cavity

the injection temperature of 503 K were first determined. For screen test the processing parameters and the mould temperature was changed, however, the specified plastic amount was kept unchanged. The mould filling degree for a multi-cavity mould was determined for each moulding thickness. The adopted tests methodology is presented in author's publications [5, 9, 10].

Results

Processing properties of modified recyclate composites were studied on the basis of the moulding length in the form of a round or square spiral moulding and a multi-stage moulding. The influence of the injection pressure and the composite processing temperature for composites of varying filler content on the length of obtained moulding was determined. The tests were conducted at two temperatures of a mould i.e. 298 and 318 K.

The dependence of the round spiral moulding length on the RC filler content for the PAPE/RC composite is shown in Fig. 4. The greater the RC filler content the shorter is the obtained moulding. For all examined composites with increasing injection pressure the moulding length increases.

The largest increase in the moulding length was found out for composites containing up to 30% – wt. of filler. With the injection pressure growing from 100 to 125 MPa the length of a spiral moulding made of composites containing up to 30% – wt. of a filler was up by some 46%, while for composites containing 40 and 50% – wt. of a filler this length grew up by some 26%.

Similar changes in the moulding length depending on the filler contents and the injection pressure were found out for mouldings of a square spiral shape. Fig. 5 presents a comparison of the length L of mouldings from a round and square spiral mould cavity depending on the injection pressure of 100 or

125 MPa and at a processing temperature of 493 K. As can be seen the greater the content of filler the shorter is a spiral moulding.

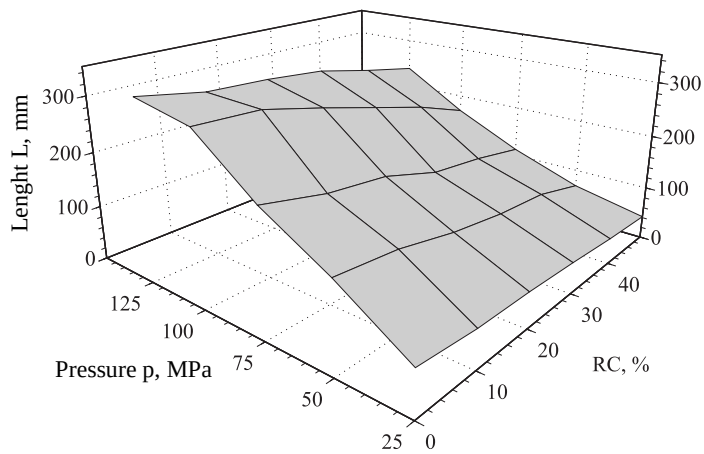

Fig. 4. Changes in the length of a spiral moulding of the PAPE/RC composite depending on the RC-content and the injection pressure (RC – particles size up to 0.063 mm, T – 493 K)

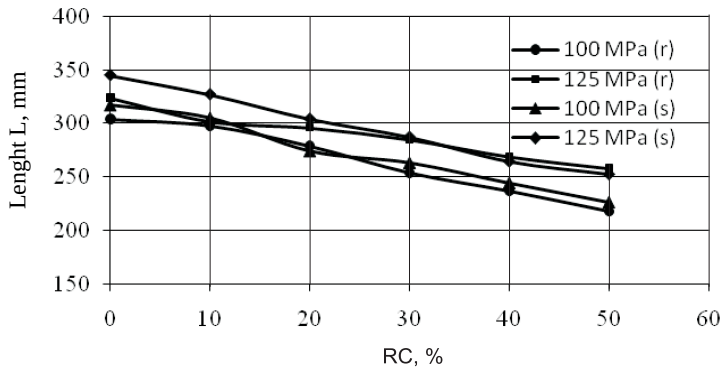

Fig. 5. Comparison: the length of a round spiral moulding (r) and the length of a square spiral moulding (s) of the PAPE/RC composite as a function of the RC-content in composite (p – 100, 125 MPa, injection temperature 493 K, size of RC-particles up to 0.063 mm)

We can notice that for individual filler concentrations at identical processing conditions moulding lengths are similar. This proves mould cavities can be filled with a composite both at a free flow (a mould with a spiral, open cavity) and with the flow being restricted (a mould with a closed square spiral cavity). The dependence of the round spiral moulding length at the injection pressure 125 MPa on the processing temperature and on the RC-filler content is shown in Fig. 6.

With increasing material plastifying temperature the moulding length increases for all composites under study. This results from the changing rheological properties of a material. The composite viscosity falls and due to this the mould cavity filling is more complete.

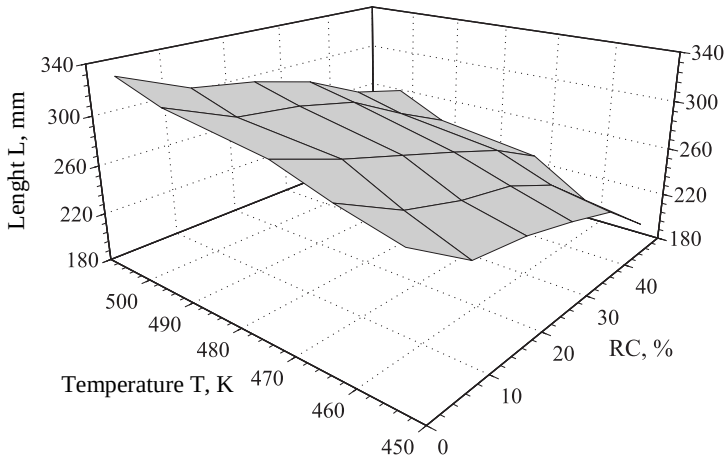

Fig. 6. Changes in the length of a spiral moulding of the PAPE/RC composite depending on the RC-content and the injection temperature (RC- particles size up to 0.063 mm)

This accords with results for similar high-filled composites with non-organic fillers. For high-filled composites (filler content 40-50% – wt.) a rise in the processing temperature between 493-513 K causes the filling of a mould cavity to grow by 15-22%.

A study of filling of moulds with a multi-stage cavity (grading by 0.5 mm from 0.5 up to 2.5 mm) was carried out at injection pressures of 25-125 MPa, at processing temperatures of 463 up to 513 K and the mould temperature of 298 and 318 K. A 100% filling of the mould multi-stage cavity for composites containing up to 30% – wt. of filler was achieved at injection pressures 100-125 MPa and injection temperatures within a range 483-513 K. At the injection pressure of 25 MPa and the plastifying temperature of 463-513 K an up to 70% – wt. filling of a 2,5 mm deep cavity was achieved. Further increase of the injection pressure up to 75 MPa allowed filling an up to 1.0 mm deep mould cavity. With growing filler content the mould cavity filling was decreasing. Fig. 7 shows the filling of a mould cavity with a composite containing 40% – wt. of filler at the injection pressure 100 MPa and the injection temperature of 503 K. As we can see a 0.5 mm deep part of the moulding is filled up to ca. 70%.

Fig. 7. Multi-stage moulding, mould cavity filling degree – 70%
(RC-filler content – 40%, injection pressure – 100 MPa, T – 503K,
filler particle size up to 0.063 mm)

An additional investigation of the melt flow rate (MFR) was carried out for composites containing up to 50% – wt. of the RC-filer. The results are presented in Fig. 8.

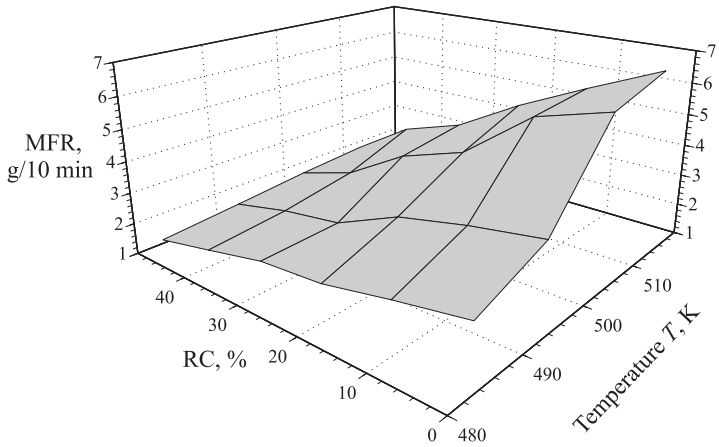

Fig. 8. MFR flow speed coefficient for the PAPE/RC
composite containing up to 50% – wt. of a filler

As we can see with a growing content of fillers the MFR drops. When the material plastifying temperature rises up to 493 K the MFR for every examined material in compare to MFR results obtained for these materials at 473 K increases.

Conclusions

Based on analysis carried out, the following conclusions can be drawn:

- Modification of the polyamide-polyethylene (PAPE) composite using PAEK composite waste filler a new material for injection processing can be obtained.
- Composite processing properties depend greatly on the RC-filler content.
- With growing filler content in a composite the mould filling degree falls (the moulding length decreases).
- Composite containing up to 30% – wt. of the RC-filler can be used for manufacture of thin-walled products (up to 0.5 mm).
- Composites containing above 30% – wt. of filler can be used for manufacture of thick-walled products (1.5-2.5 mm).
- For injection pressures 100 and 125 MPa the difference in the spiral length from round and square spiral mould cavities are similar.
- Mouldings containing 40 and 50% – wt. of filler at the injection pressure 100 and 125 MPa characterize a very high surface smoothness and low shrinkage.
- The best processing parameters for composites containing up to 30% – wt. of a filler are as follows: injection pressure 100 MPa, processing temperature up to 493 K, and for composites containing 40 and 50% – wt. of a filler: injection pressure: 125 MPa, processing temperature: 503-513 K.

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