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ORIGINAL ARTICLE

# Application of waste bulk moulded composite (BMC) as a filler for isotactic polypropylene composites

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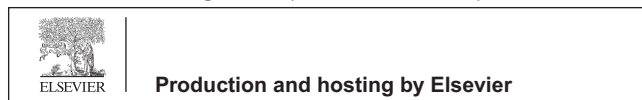
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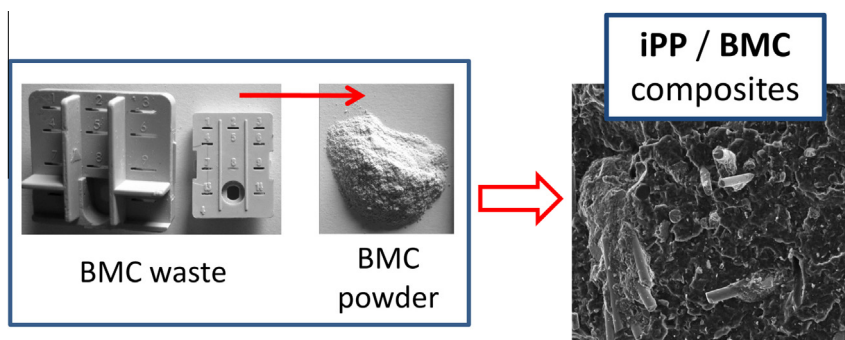


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A B S T R A C T

The aim of this study was to produce isotactic polypropylene based composites filled with waste thermosetting bulk moulded composite (BMC). The influence of BMC waste addition (5, 10,

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20 wt%) on composites structure and properties was investigated. Moreover, additional studies of chemical treatment of the filler were prepared. Modification of BMC waste by calcium stearate (CaSt) powder allows to assess the possibility of the production of composites with better dispersion of the filler and more uniform properties. The mechanical, processing, and thermal properties, as well as structural investigations were examined by means of static tensile test, Dynstat impact strength test, differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS), melt flow index (MFI) and scanning electron microscopy (SEM). Developed composites with different amounts of non-reactive filler exhibited satisfactory thermal and mechanical properties. Moreover, application of the low cost modifier (CaSt) allows to obtain composites with better dispersion of the filler and improved processability.

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## Introduction

Reinforced thermoset composites containing inorganic fibres defined as bulk moulding composites (BMC) and sheet moulding composites (SMC) are still applied in automotive and civil engineering industries. The production of these materials in the year 2014 in Europe reached approximately 264 kt [1]. The growing use of fibre reinforced composites (FRP) in industry results in high amount of FRP wastes. Hence, discovering an appropriate area of application for these types of waste material is currently of utmost importance task for scientists [2–7]. There has been an alarming rise in the amount of FRP waste, and in 2015 only the 304 kt FRP waste will be produced [8].

BMC and SMC materials usually contain polyester resins with short glass fibres (10–25% by volume), colourants, inhibitors, and high amount of fillers, such as calcium carbonate or fire retardant alumina trihydrate [9,10]. The filler introduction to the matrix should provide the product with sufficient mechanical strength, psychical properties and quality. Fillers such as clay, talc, carbon black, marble dust, glass, wood flour and metals are added to polymers at range from 10 to 50 wt% [10]. The introduction of glass fibres into composites leads to good mechanical properties, while inorganic fillers reduce the product final price [11,12].

Plastics recycling process involves recovering scrap or waste polymers and reprocessing the material into useful applications [10]. Popular thermoset materials recycling method is their cutting into smaller pieces and grinding to produce very fine powder. As a result of this process, fibrous fraction, with the large particle of the reinforcement fibres, and the polymeric matrix fine powder fraction are recovered [13,14]. Other method is chemical recycling BMCs and SMCs; however, often a large amount of chemical waste is produced in the process [15–17]. Therefore, fine powders of these thermosetting polymers can replace calcium carbonate filler in new SMC or BMC [9].

Nevertheless, the introduction of high content of recyclate into polymers may result in processing problems and significant lowering at the mechanical properties [18–21]. Many from the FRP recyclates could be applied in the construction industry for the non-critical materials, such as partitions, insulation products, fibreboard, pipes, aggregates, cements, asphalts and concretes where shredded waste materials provide required bulk and lower price of product [2]. Moreover, the addition of the thermoset glass fibre recyclates to neat polymers brings environmental benefits of reducing waste amount. Isotactic polypropylene is a popular polymer with good processability, frequently used as matrix for composites. To conclude, the aim of this study was to determine the possibility of bulk moulding compound waste usage as a non-reactive, low cost filler for isotactic polypropylene.

## Experimental

### Materials and sample preparation

The commercial injection moulding grade isotactic polypropylene (iPP) Moplen HP500N, with a melt flow rate (MFR) of 12 g/10 min (230 °C, 2.16 kg) from the Basell Orlen Polyolefins (Poland) was used in our experiments. The selected polymeric matrix was characterized by a low modification level.

The bulk moulding compound (BMC) waste was first disintegrated in a low-speed mill cutter Shini SC-1411 and then milled in high-speed mill Retsch ZM200 ($n$ = 6000 rpm). The obtained waste BMC powder was used as filler. Application of the two step milling allows to obtain non-degraded hybrid filler that consists of polyester resin coated calcium carbonate powder and agglomerated as well as separated glass fibres. Characterization of particle size was realized by means of scanning electron microscopy (SEM) (Fig. 1a). Particle size distribution was also evaluated by using laser particle sizer Fritsch ANALYSETTE 22 apparatus operated in the range of 0.08–2000 μm. In Fig. 1b particle size distribution function ($Q3(x)$) and its derivative ($dQ3(x)$) as a function of particle size ($x$) were presented. The arithmetic mean of hybrid filler fraction after milling was equal to 10.53 μm. Comprehensive characteristics of the filler including FT-IR analysis was presented in our previous work [22]. Calcium stearate (CaSt) was used as compatibilizer for modification of BMC powder (cBMC).

Before mixing in a molten state, iPP pellets were milled into powder in a Tria high-speed grinder. iPP and BMC/cBMC powders were then premixed using a high speed rotary mixer Retsch GM200 ($t$ = 3 min, $n$ = 3000 rpm) with different amounts of filler (5; 10 and 20 wt%). After physical premixing, the blends were dried in a vacuum at 80 °C for 3 h. Next, all blends were mixed in a molten state using a ZAMAK twin screw extruder that operated at 190 °C and 120 rpm, and pelletized after cooling in a water bath. The screws were configured to process polyolefins with inorganic fillers [23]. The normalized specimens for tensile and impact strength test were prepared with a Engel HS 80/20 HLS injection moulding machine operated at 200 °C.
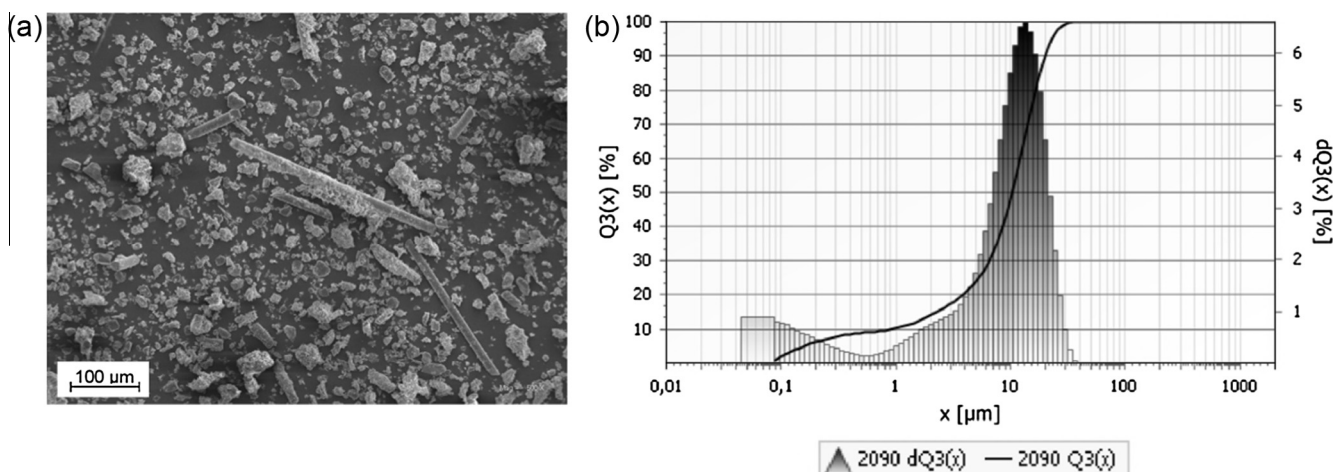
**Fig. 1** SEM microphotograph of milled BMC powder (magnitude 500×) (a), particle size distribution (b).

*Measurements*

Mechanic properties of pure iPP and iPP composites were realized in static tension test according to European standard PN-EN ISO-527 by means of Zwick Roell Z020 TH ALLround Line universal testing machine with 20 kN nominal force. Tests were realized with 50 mm/min crosshead speed.

The impact strengths of the unnotched samples with $10 \times 4 \times 15$ mm dimensions were measured by the Dynstat method (DIN 53435). Hardness evaluation was carried out with the use of Sauter HBD 100-0 Shore D durometer.

Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 204 F1 Phoenix® with aluminium crucibles and approximately 5 mg samples under a nitrogen flow. All of the samples were heated to 230 °C and held in a molten state for 5 min, followed by cooling to 30 °C at $\varphi = 10$ °C/min cooling rate. This procedure was conducted twice to evaluate the DSC curves from the second melting procedure and gain broad information about iPP matrix and iPP-BMC/cBMC composites thermal properties. The crystallinity degree was calculated from DSC thermograms recorded during the second heating. The crystallinity degree ($X_c$) was evaluated on the basis of the melting heat ($\Delta H_m$) during crystallization at a cooling rate of $R = 10$ °C/min. The crystallinity degree of pure iPP and iPP-BMC/cBMC composites was calculated using the following equation:

$$X_c = [(\Delta H_m/(1 - \phi) \cdot \Delta Ho)] \cdot 100\% \tag{1}$$

where $\Delta Ho$ is the melting heat of entirely crystallized iPP and its value is equal to 207.1 J/g, and $\phi$ is amount of filler [24]. Moreover, crystallization temperature ($T_c$) recorded during first cooling and melting temperature ($T_m$) determined during second heating were analysed.

Wide-angle X-ray diffraction (WAXS) measurements were carried out by using a Seifert URD 6 apparatus. A monochromatic X-ray radiation with a wavelength of $\lambda = 1.5406$ Å (Cu Kα) was used. Identification was based on a reflected X-ray peak intensity analysis at a defined $2\theta$ angle.

Melt flow index of isotactic polypropylene and composites was carried out by means of Dynisco LMI 4004 plastometer according to ISO 1133. The measurements were conducted at temperature of 230 °C under 2.16 kg load.
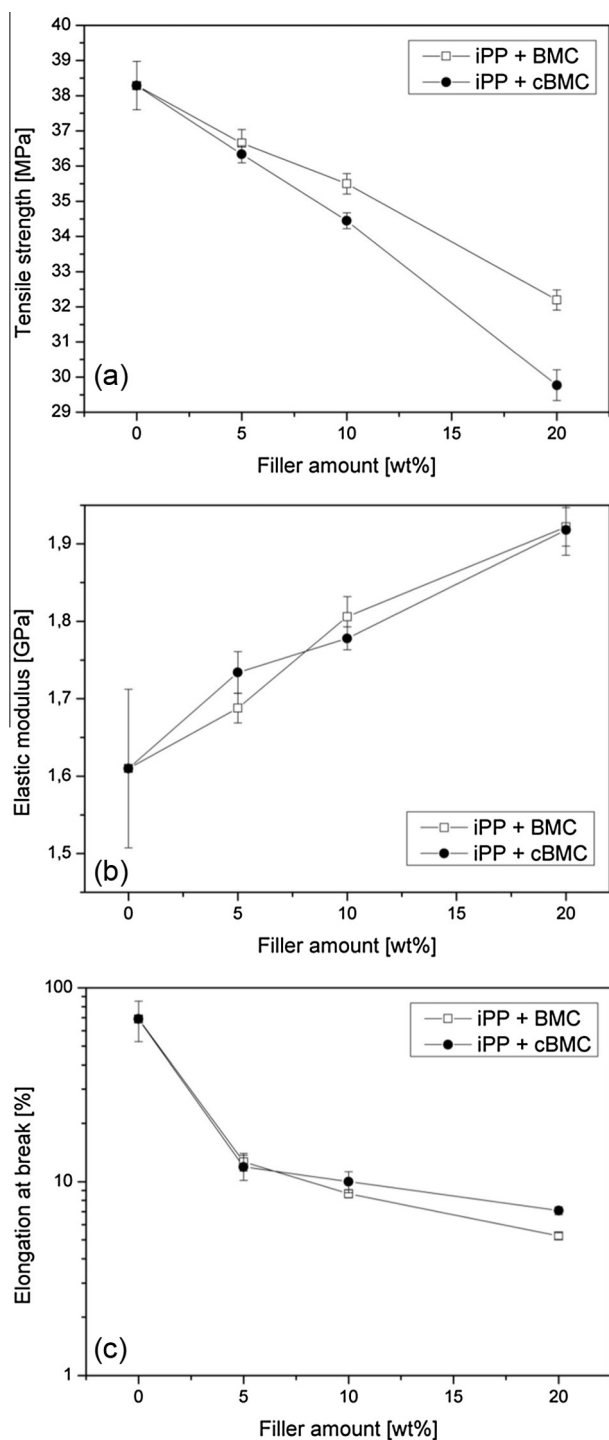
In order to assess the structure of composites, the scanning electron microscope (SEM), model Vega 5135MM, produced by the Tescan (Czech Republic) was used. The structures of iPP-BMC/cBMC composites were investigated by a Back Scattered Electron signal (BSE) and a Secondary Electron signal (SE) with an accelerating voltage of 12 kV. All photographed samples were broken after being cooled below the iPP glass transition temperature.

**Results and discussion**

*Mechanical properties*

The influence of BMC and cBMC addition, as a function of filler amount, on tensile strength, elastic modulus and elongation at break of iPP based composites, measured during static tensile test was, presented in Fig. 2a–c. In Fig. 2a, strong influence of CaSt coating on tensile strength of iPP-cBMC composites was observed. The increasing content of filler caused consistent drop of yield strength. In case of composites filled with modified filler (cBMC), tensile strength values were lower in comparison with those containing untreated filler (BMC). This effect may be attributed to plasticizing effect of calcium stearate (CaSt) whose presence is an effect of reaction between stearic acid and calcium carbonate which is a content of BMC waste. Young modulus of prepared composites is similar for both material series and no significant influence of CaSt presence was observed (Fig. 2b). The increasing content of filler caused gradual elastic modulus growth. In case of elongation at break (Fig. 2c), slight difference may be observed for both types of composites. Samples containing cBMC filler attributed slightly higher elongation values, and as described above, this effect may be assigned to compatibilizing effect of CaSt and better dispersion of filler in polypropylene matrix.

The results of Dynstat impact strength test are presented in Table 1. The addition of BMC and cBMC powder resulted in significant decrease of the impact strength in comparison with

**Fig. 2** Comparison of tensile strength (a), elastic modulus (b) and elongation at break (c) of iPP-BMC/cBMC composites as a function of filler amount.

**Table 1** Dynstat impact strength.

| Filler amount | Dynstat impact strength | |
|---|---|---|
| | BMC | cBMC |
| [wt%] | [kJ/m$^2$] | |
| 0 | 40.58 ± 4.89 | |
| 5 | 11.75 ± 2.33 | 14.14 ± 2.21 |
| 10 | 11.08 ± 2.44 | 11.83 ± 6.4 |
| 20 | 6.81 ± 1.26 | 9.24 ± 1.04 |

**Table 2** Shore D hardness.

| Filler amount | Shore D hardness | |
|---|---|---|
| | BMC | cBMC |
| [wt%] | [°] | |
| 0 | 76.11 ± 0.78 | |
| 5 | 80.75 ± 0.93 | 79.93 ± 0.98 |
| 10 | 80.31 ± 1.13 | 80.5 ± 1.07 |
| 20 | 80.28 ± 0.71 | 79.22 ± 1.28 |

strength denoted for cBMC filled composites could be the effect of CaSt presence and better dispersion of filler in polymer matrix. No significant influence of BMC incorporation on the hardness of the iPP based composites was observed. The addition of both unmodified and modified fillers increased 4° of Shore D hardness (Table 2).

*Differential scanning calorimetry*

Influence of unmodified and modified filler addition on thermal properties of isotactic polypropylene based composites was determined by means of calorimetric investigations. The changes of crystallization and melting temperature, as well as enthalpy of fusion as a function of filler amount are presented in Table 3. It may be clearly seen that the addition of BMC and cBMC as fillers to iPP led to the increase of crystallinity level and therefore it can be stated that recycled thermoset powder has nucleation ability. Moreover, differences in values of melting heat fusion and crystallinity level between iPP-BMC and iPP-cBMC were observed. Modification of calcium carbonate or fillers containing calcium carbonate resulted in the decrease of filler free surface which led to lowering of the filler nucleation ability [25,26]. The presence of CaSt, for iPP-cBMC composites, first increased $\Delta H_m$ and $X_c$ values in comparison with pure iPP samples. However, the increasing amount of the filler was connected with higher amount of CaSt which decreased composite melting enthalpy. It should be also mentioned that incorporation of both fillers into a polypropylene matrix resulted in slight increase of crystallization temperature. Melting temperature did not change with BMC and cBMC addition. To sum up, thermal properties of iPP-BMC/cBMC indicated that application of CaSt used as a compatible agent, increased processability of composites. This phenomenon could correlate with slight increase of crystallization temperature which may reduce cooling time during melt processing in case of injection moulding of the thermoplastic

pure iPP reference sample. The brittleness of composite materials increased with the increase of BMC content in polypropylene matrix. This effect is caused by the lack of interactions between polymer and filler. Slightly higher values of impact

**Table 3** DSC melting and crystallization parameters of pure iPP and iPP composites.

| Filler amount | BMC | | | | cBMC | | | |
|---|---|---|---|---|---|---|---|---|
| [wt%] | $T_m$ [°C] | $\Delta H_m$ [J/g] | $X_c$ [%] | $T_c$ [°C] | $T_m$ [°C] | $\Delta H_m$ [J/g] | $X_c$ [%] | $T_c$ [°C] |
| 0 (iPP) | 163.4 | 91.07 | 44 | 116.3 | 163.4 | 94.71 | 45.7 | 116.3 |
| 5 | 164.1 | 115.5 | 58.7 | 121.4 | 163.5 | 110.1 | 56 | 121.6 |
| 10 | 163.4 | 102.6 | 55 | 121.9 | 164.1 | 107.5 | 57.7 | 121 |
| 20 | 163.1 | 104.4 | 63 | 122 | 162 | 85.38 | 51.5 | 121 |
| 40 | 160.2 | 72.34 | 58.2 | 121.8 | 161.6 | 68.34 | 55 | 119.5 |

$\Delta H_m^{100\%} = 207.1$ [J/g].
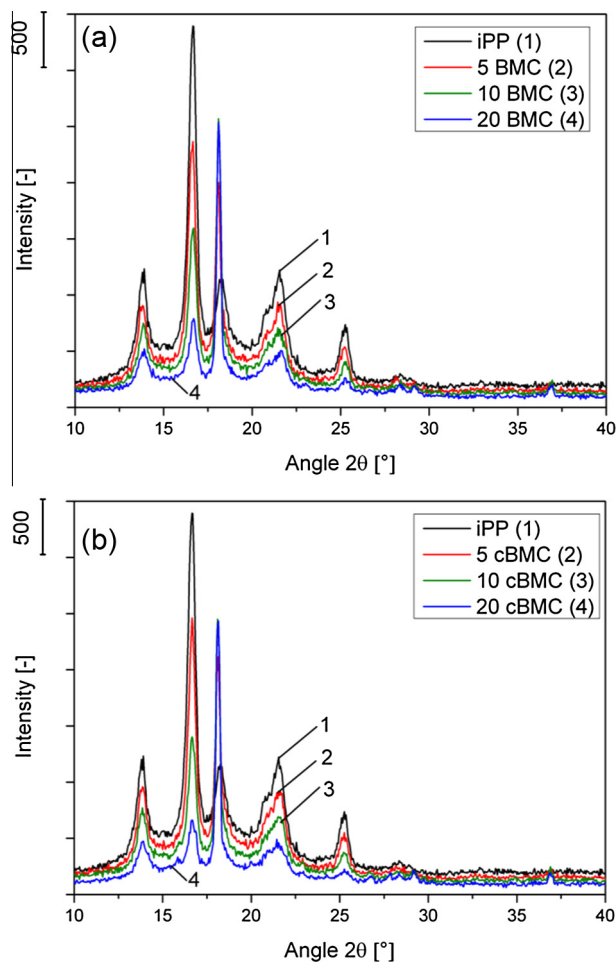


**Fig. 3** WAXS diffractograms of pure iPP and iPP-BMC/cBMC composites.

materials. Moreover, reduction of melting enthalpy of iPP-cBMC composites in comparison with iPP-BMC allows to reduce the energy which is needed to melt the materials during forming.

### Wide angle X-ray scattering (WAXS)

Fig. 3 shows WAXS diffractograms of iPP-BMC (Fig. 3a) and cBMC (Fig. 3b) composites presented as a function of filler amount, registered at a room temperature. In all considered samples monoclinic α-crystalline formation occurred and no evidence of the hexagonal β-crystalline form was observed. The characteristic reflections at angles of $2\theta$ (14.1, 16.9, 18.5, 21.2 and 22.0), corresponding to the crystalline planes (110), (040), (111) and (130) respectively, were clearly visible. No additional reflections at 16.2 (300) and 19.8 (117) corresponding to β or γ iPP crystalline forms were observed [27–29]. Therefore, it can be stated, in accordance with previously presented DSC data, that addition of BMC and cBMC led only to insignificant changes of crystallization behaviour and did not influence polymorphism of isotactic polypropylene matrix. The lowered intensities of diffractogram peaks, recorded for the samples containing higher filler amounts, presented in Fig. 3 are the result of decreasing content of polymeric material in composite structure. Moreover, it should be mentioned that higher crystallinity corresponds to higher diffractogram peak intensities of iPP-BMC composites (Fig. 3a) in comparison with iPP-cBMC composites (Fig. 3b). The mentioned difference in crystallinity level of the composites containing BMC and cBMC was caused by the reduction of the filler free surface as a result of the calcium stearate incorporation which led to decrease nucleation ability of modified filler.

### Scanning electron microscopy

The SEM micrographs of the iPP-BMC/cBMC composites with different amounts of thermosetting waste filler are presented in Fig. 4. Irregular inclusions visible in photographs correspond to calcium carbonate and polyester milled waste. Moreover, glass fibres which are often used as a reinforcement of BMC composites can be also observed. The orientation and length of the fibres were random and oscillated between 70 and 120 μm. What should be noticed is that after two step milling of BMC waste, it still may act as a reinforcement because of partially fiber-like structure of thermoset waste. In case of 20 wt% of cBMC (Fig. 4f), the CaSt was observed clearly as a layer of BMC containing calcium carbonate, polyester waste and glass fibres. For iPP-cBMC composites (Fig. 4a–c), the homogeneity of the filler in polymer matrix was better than for iPP-BMC composites (Fig. 4d–f).

### Melt flow behaviour

As distinct from results presented by Mencel et al., incorporation of BMC into iPP matrix resulted in the growth of melt
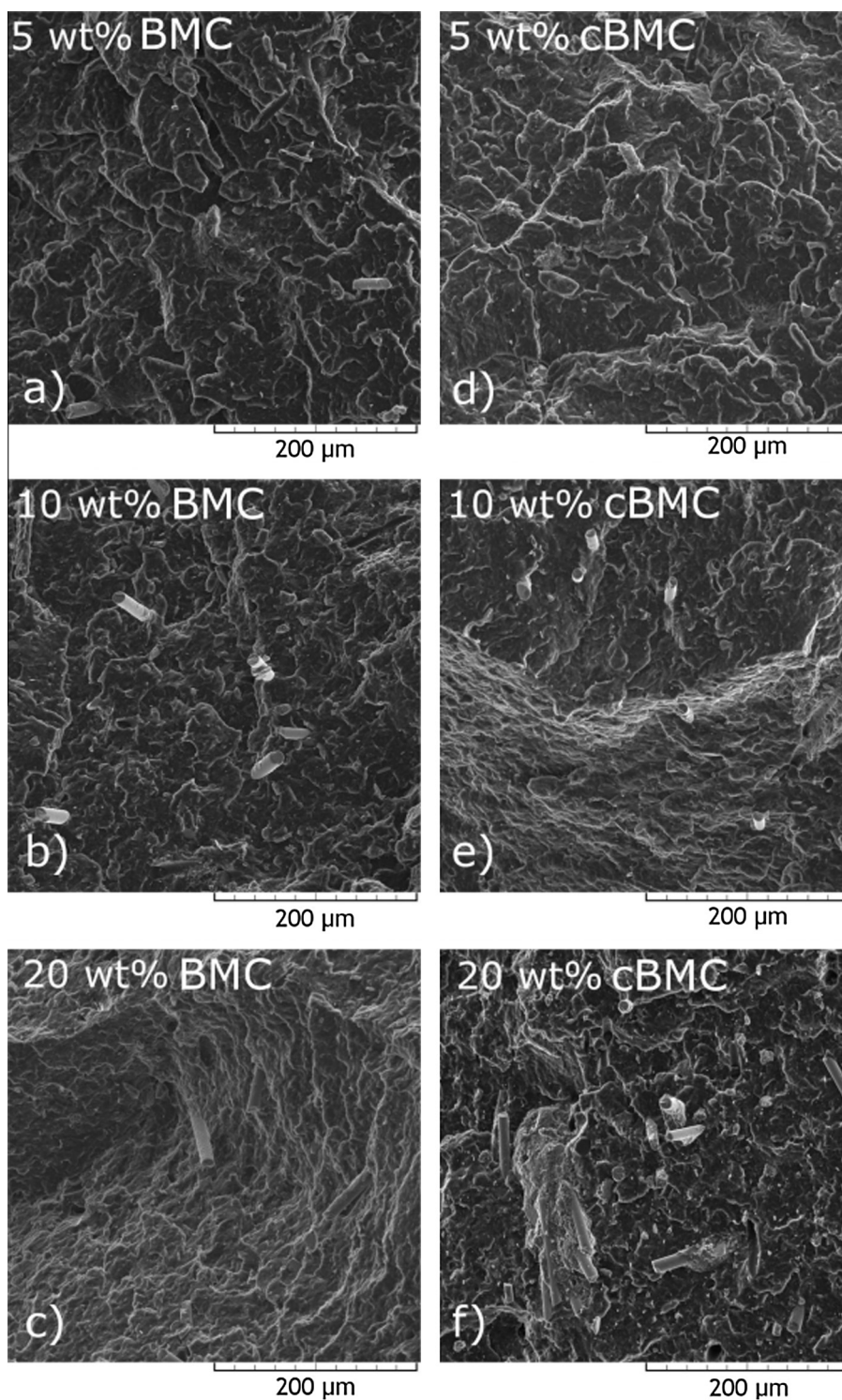
**Fig. 4**    SEM microphotographs of iPP-BMC (a–c) and iPP-cBMC (d–f) composites containing various amounts of the filler.

flow index (Table 4) [30]. The values of MFI composites increased with the increase of BMC content in polymer matrix. This effect may be interpreted as a result of partial decomposition of the organic part (polyester thermoset) of the filler. The low molecular weight parts of degraded polyester act as slipping agent which increases melt flow index of iPP-BMC/cBMC composites. Moreover, strong influence of compatible agent (CaSt) on MFI values was observed. Additionally MFI value for iPP-cBMC composites was higher than iPP-BMC composites.

**Table 4** Melt flow index of pure iPP and iPP-BMC/cBMC composites.

| Filler amount | BMC | cBMC |
|---|---|---|
| [wt%] | [g/10 min, 230 °C 2.16 kg] | |
| 0 (iPP) | 13.65 ± 0.35 | |
| 5 | 12.63 ± 1.22 | 13.76 ± 0.83 |
| 10 | 15.4 ± 1.06 | 16.56 ± 0.73 |
| 20 | 31.2 ± 1.08 | 34.67 ± 1.22 |

## Conclusions

The application of BMC waste used as a filler for isotactic polypropylene was successful. Prepared composites with different amounts of non-reactive filler exhibited satisfactory thermal and mechanical properties. Even if mechanical properties of composites containing more than 10 wt% of BMC filler were lower in comparison with pure isotactic polypropylene, decrease of the tensile and impact strength would not exclude presented composites as a material for low demanding parts and applications. Therefore, obtained composites can be used as low cost materials. Moreover, in this study the influence of compatible agent (calcium stearate) on thermal and mechanical behaviour was investigated. As a result, it was proved that incorporation of low cost additive may cause better dispersion and processability of iPP-cBMC composites.

## Conflict of Interest

*The authors have declared no conflict of interest.*

## Compliance with Ethics Requirements

*This article does not contain any studies with human or animal subjects.*

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