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Water-Assisted Production of Polypropylene/Boehmite Composites

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Abstract

In this study polypropylene (PP) matrix-based boehmite alumina (BA) reinforced composites were prepared batchwise in an internal mixer. BA particles up to 10 wt.% were incorporated by 1. traditional melt mixing and 2. in a novel, Water-Assisted (WA) way, called fast evaporation mixing, during which BA was dispersed in PP with the use of an aqueous carrier medium. The WA way with pure water as medium proved to be ineffective because of the presence of the Leidenfrost effect. Therefore, an additional agent, carboxymethyl cellulose (CMC) was used to increase the boiling temperature of the water. Mechanical, morphological and thermal properties of the composites were determined. Scanning electron microscopy images revealed a partially dispersed structure of BA within the PP matrix in all cases, where aggregates and dispersed particles were identified as well. The size of the agglomerates observed was the smallest when BA was incorporated by being dispersed in water/CMC firstly. The mechanical tests results indicated that the reinforcing effect of BA was also most prominent in this case. However, CMC had an opposite effect on PP, than BA thus reducing the overall enhancement in mechanical properties. Differential scanning calorimetry showed an increase in the crystallinity ratio of PP with increasing BA content, which indicates a nucleating effect of BA.

Keywords

polypropylene, boehmite alumina, nanocomposite, Water-Assisted production, structure-property relations

1 Introduction

Polypropylene (PP) is one of the most widely used plastic materials in the packaging and textile industries. In the past few decades, numerous researchers dealt with the topic of modifying PP through various ways to increase its range of applications [1]. A widely used method to improve the mechanical properties of PP is to incorporate natural and synthetic fillers into the polymer matrix. Fillers traditionally used for this purpose are glass, carbon, cellulose, cotton, sisal, basalt, and aramid fibers [2, 3]. In the last decades there has been an emerging trend of using nanosized reinforcements since they enhance the polymer matrix at a relatively low amount of filler loading [4, 5].

When fabricating polymer composites with micro- and nanoscale particulates, the main issues are to decompose the agglomerates (bundles of multiple particles) and to disperse the particles homogenously within the polymer matrix. Depending on the level of the disintegration of the agglomerates the literature distinguishes the intercalated, the flocculated and the exfoliated structure of the dispersed phase. Both the degree of dispersion and the structure of the dispersed phase influences the properties of the resulting composites greatly [6]. Nanocomposites can be produced in various ways, including the in situ polymerization, the solution-assisted and the traditional melt mixing methods. Each has its advantages and disadvantages discussed in the literature in details [4]. Some researchers reported other methods as well [7–9].

A relatively new technique is the so-called Water-Assisted melt mixing (WA), during which the nanoscale additives are introduced into the polymer matrix in their aqueous slurry. WA-based techniques have numerous benefits, including:

1. reduced health risks,
2. improved dispersion of nanoparticles and

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3. no need for expensive surface modification of the fillers.

In order to be used with this technique, nanofillers have to be swellable or dispersible in water. The improved filler dispersion is also supported by the "blow-up" phenomenon occurring when the pressurized aqueous liquid evaporates. The production of nanocomposites can be performed continuously or batchwise as well. It should be noted that such compounding is only possible, if the polymer matrix is resistant to hygrothermal decomposition [10].

Gao and Guo [11] proposed a novel WA processing method for layered silicate reinforced flourelastomer-based composites, which they called "fast evaporation mixing". During this, the polymer is first melted in an internal mixer and then the aqueous slurry of the nanoparticles is added to the matrix drop by drop. As the processing temperature (150 °C) significantly exceeds the boiling point of water, it almost instantly evaporates leaving only the dispersed layered silicate platelets behind.

Boehmite alumina (BA), whose chemical composition is AlO(OH), is a very promising synthetic nanofiller. The property enhancing potential of micro- and nanosized BA particles with and without surfactants has already been checked in various polymer matrices [12]. It is also dispersible in water, and several researchers have prepared BA reinforced composites via a WA technique. Research in this field, however, has been mostly restricted to continuous techniques (e.g. extrusion) that requires a costly high pressure pump and additional equipment [13]. In the meanwhile no previous study has investigated the batchwise WA preparation of BA reinforced composites.

This current study investigated the possibility of preparing PP/BA nanocomposites with the fast evaporation mixing method. As the processing temperature of PP greatly exceeded the boiling temperature of the water used as a carrier medium, major issues emerged. As a solution, a new component, carboxymethyl cellulose (CMC) was introduced into the slurry. The paper focuses on the assessment of the structural, mechanical and thermal properties of the nanocomposites prepared.

2 Experimental

2.1 Materials

A PP of medium molecular weight, PP H 543 F, was used as matrix (MFR = 4 g/10 min at 230 °C and 2.16 kg). It was supplied by MOL Petrolkémiai Zrt, (Tiszaújváros, Hungary).

Disperal® 40 grade of Sasol GmbH (Hamburg, Germany) was used as BA reinforcement. Disperal® 40 has an Al_2O_3 content of 80 m%, an average particle size of 35 μm, and a surface area of 100 m^2/g.

Carboxymethyl cellulose, Masstex Pure CMC, an agent used to increase the boiling point of water (explained later) was obtained from Fractal Colors Ltd. (Csömör, Hungary).

2.2 Preparation of composites

Firstly, the PP pellets were masticated in a counterrotating internal batch mixer PL2000 Plasti-Corder (Brabender GmbH., Duisburg, Germany). Then an aqueous slurry of water and BA (and CMC) was introduced, according to the fast evaporation compounding method described by Gao and Guo [11]. Mixing occurred for 5 minutes at a temperature of 180 °C and 60 rpm.

Sheets of 2 mm thickness were compression molded with a Teach-Line Platen Press 200E hot press machine (Dr. Collin GmbH., Munich, Germany). Sheeting was carried out at 200 °C for 3 mins, the pressure was set to 25 bar.

Prismatic specimens (width = 10 mm, length = 100 mm) were cut out of the compression molded sheets with a Mutronic Diadisk cutter (Mutronic GmbH, Rieden, Germany).

2.3 Characterization and testing

Tensile tests were performed on a universal testing machine (Zwick Z005, Ulm, Germany) at a crosshead speed of 25 mm/min at room temperature. A clamping distance of 50 mm was applied. The average values of mechanical properties were calculated from five parallel measurements.

Charpy tests were performed using a Ceast Resil Impactor Junior impact test machine with a 2 J hammer at room temperature on notched specimens. The notch length to width ratio of the Charpy specimens was a constant, viz. 0.5. The given test results represent average values derived from five tests per sample.

The dispersion of BA in the PP matrix was investigated using a scanning electron microscope (SEM; JEOL JSM 6380LA, Tokyo, Japan). Fracture surfaces of the Charpy impact test specimens were coated with a gold/palladium alloy prior to their SEM examination.

The Differential Scanning Calorimetric (DSC) curves were recorded with a DSC Q2000 type calorimeter (TA Instruments, New Jersey, USA). The scanning process consisted of three steps. First, the PP/BA composites were heated up to 200 °C and maintained on this temperature for 3 mins to have their thermal history erased. Then the samples were cooled from 200 °C to 0 °C at a rate of 10 °C/min, and then heated from 0 to 200 °C at 10 °C/min. Tests were performed under nitrogen purge with a flow rate of 50 ml/min. The transition temperatures were taken as the maximum or minimum of peaks in the calorimetric curves. The crystallinity ratio (X_c) was calculated upon the second heating according to Eq. (1):

$$X_c(\%) = \frac{\Delta H_{m\text{PP}}}{\Delta H_{m\text{PP}}^{\infty} \times \omega_{\text{PP}}}, \qquad (1)$$

where $\Delta H_{m\text{PP}}$ is the apparent melting enthalpy of PP, $\Delta H_{m\text{PP}}^{\infty}$ is the extrapolated value of enthalpy corresponding to the melting of a 100 % crystalline sample (taken as $H_{m\text{PP}}^{\infty}$ = 207 J/g) [14], and ω_{PP} indicates the weight fraction of PP in the corresponding sample.

The effect of BA content was studied by twosample *t* tests. A *p*-value of < 0.05 was considered significant.

3 Results and discussion

Throughout the research ten samples were prepared in three consecutive steps. Table 1 contains the compositions of the different samples.

The amount of water used as carrier medium was determined empirically: the lowest amount was used in which the BA particles could still be dispersed homogenously. This weight ratio of BA and water was 1:3. Water in itself proved to be an inadequate medium as its boiling temperature is much lower than the processing temperature of PP. Therefore, when it was added to the PP drop by drop, the aqueous dispersion of BA could not enter the molten polymer. Instead, because the Leidenfrost effect, the droplets only hovered on its surface until all the water evaporated, leaving only the dry BA behind. (The Leidenfrost effect is a phenomenon that occurs when a liquid gets close to a surface which has a temperature much higher than the boiling point of the liquid. Due to this a thin layer of vapor is generated that creates a repulsive force between the hot surface and the liquid.) To overcome this issue a third component, carboxymethyl cellulose was introduced in order to increase the boiling point of the aqueous slurry. According to the literature [15, 16] this water-soluble polymer can also improve the properties of PP. The concentration of CMC was set to the lowest at which the Leidenfrost effect was no longer experienced. Therefore, this weight ratio of water/CMC was 40:1.

Table 1 Composition of the neat and the modified PP samples

Prep. step	Sample	Water [wt.%]	CMC [wt.%]	BA [wt.%]
1	PP	-	-	-
	PP_W(5)	15	-	-
	PP_CMC(5)	15	0.375	-
2	PP_5BA	-	-	5
	PP_W_5BA	15	-	5
	PP_CMC_5BA	15	0.375	5
3	PP_CMC_(2.5)	7.5	0.1875	-
	PP_CMC_2.5BA	7.5	0.1875	2.5
	PP_CMC_(10)	30	0.75	-
	PP_CMC_10BA	30	0.75	10

Note: The samples with a value in parenthesis within their designations contain the required water and CMC for the incorporation of that specific amount of BA, however without the BA being actually introduced.

On the first set of samples the effect of the amount of carrier media necessary to incorporate 5 wt.% BA was determined. In the second step, it was examined how the different methods influence the dispersion of BA within the PP matrix. Thirdly the amount of BA was varied between 2.5 and 10 wt.%.

3.1 The effects of the carrier medium on the properties of the polypropylene

Stiffness, strength, deformability and toughness of the samples was determined to characterize their mechanical behavior. Fig. 1 shows the modulus, tensile strength (Fig. 1 (a)), elongation at yield point and impact strength (Fig. 1 (b)) measured on the PP, PP_W(5) and PP_CMC(5) samples. The results indicate that the presence of water had no effect on the mechanical properties of PP. There are two possible explanations for this:

1. the water did not enter the polymer melt as a consequence of the Leidenfrost effect and
2. even if some of it did, PP is not sensitive to hygrothermal degradation.

At the same time, CMC slightly increased impact strength (5.2 kJ/m^2 → 6.3 kJ/m^2) and elongation at yield point (10.6 % → 13.5 %), at the cost of stiffness (1225 MPa → 1026 MPa). It is suggested that the PP/CMC interface is not strong enough to ensure an effective load transfer, although this weaker interaction allows higher energy dissipation during dynamic loading.

3.2 The effects of the carrier medium on the dispersion of BA inside the polypropylene

The relative changes in the mechanical properties of the second set of samples (PP_5BA, PP_W_5BA and PP_CMC_5BA) are displayed in Fig. 2. The relative values are correlated with samples of same composition but

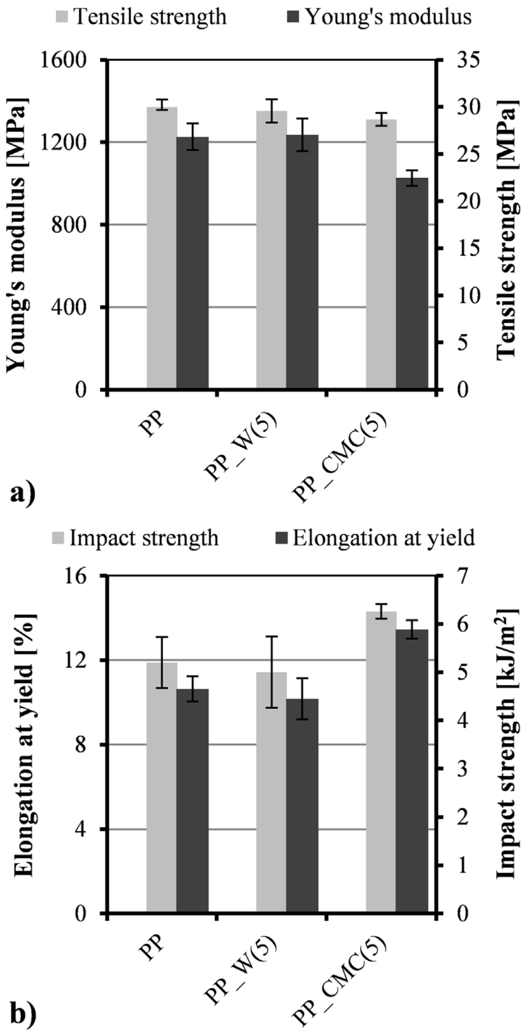

Fig. 1 a) The Young's modulus, tensile strength, b) elongation at yield point and impact strength of the PP, PP_W(5) and PP_CMC(5) samples

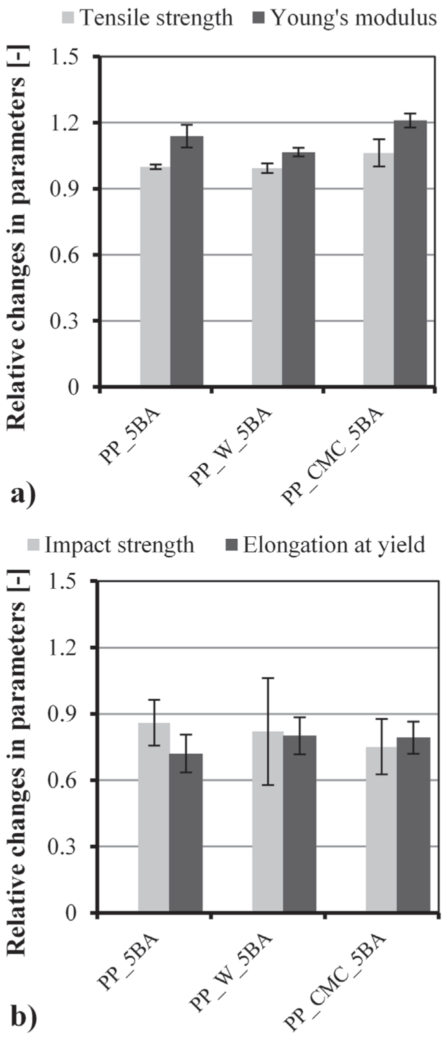

Fig. 2 a) Relative changes in the Young's modulus, tensile strength, b) elongation at yield point and impact strength of samples PP_5BA, PP_W_5BA and PP_CMC_5BA
(Note: the relative values are correlated with samples of same composition but without BA)

without BA (PP, PP_W(5) and PP_CMC(5)), to demonstrate how the different carrier media influence the reinforcing effect of boehmite particles. Mechanical properties are given in form of Young's modulus, tensile strength (Fig. 2 (a)), elongation at yield point and impact strength (Fig. 2 (b)). The figures clearly show that the properties measured strongly depend on the utilized carrier medium. Using an aqueous dispersion without CMC results in similar tensile strength as dry incorporation. In both cases BA was not able to provide any reinforcement to the matrix. At the same time, a relative increase of 6 % in tensile strength was observed when BA was incorporated with the aid of CMC/water. Young's modulus exhibited an increase in the case of both methods. The most significant increase was observed for PP_CMC_5BA (21 %) followed by PP_5BA (14 %) and PP_W_5BA (7 %). According to Fig. 2 (b), the changes in elongation at yield point and impact strength are approximately the same (a decrease of ~25 %) and are within the deviation range for all methods.

SEM observations were conducted on the composites in order to determine the dispersion achieved when incorporating BA particles using different methods. Fig. 3. and Fig. 4. show the fracture surfaces of samples PP_5BA, PP_W_5BA and PP_CMC_5BA at a lower (100×) and a higher (5000×) magnification, respectively.

In all three cases, BA shows a partially dispersed structure within the PP matrix, where aggregates and dispersed particles can also be observed. In the samples where BA was added in its dry form (Fig. 3 (a)), the size

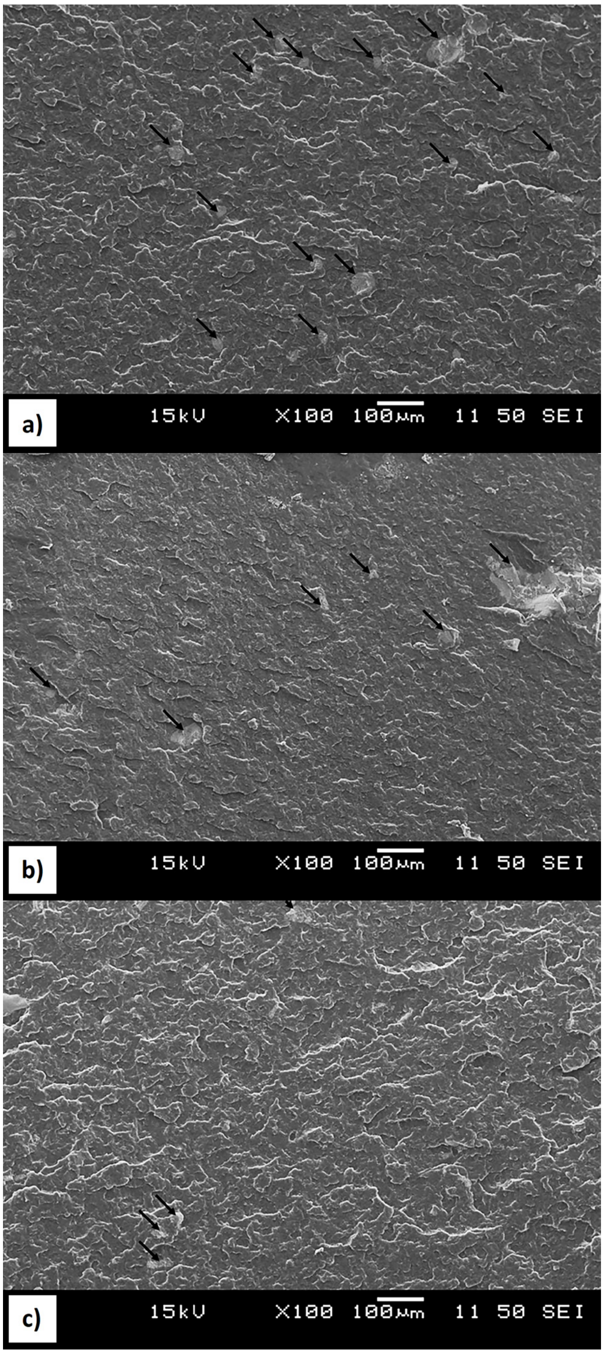

Fig. 3 a) SEM images of the samples PP_5BA, b) PP_W_5BA and c) PP_CMC_5BA at a magnification of 100×

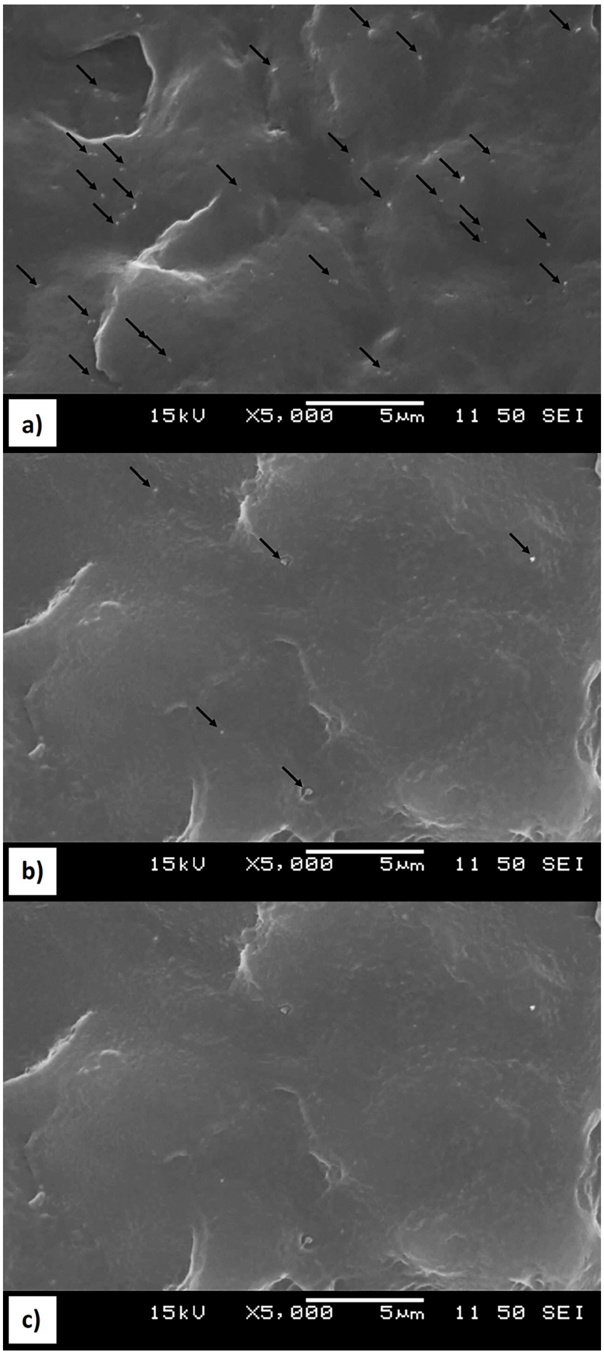

Fig. 4 a) SEM images of the samples PP_5BA, b) PP_W_5BA and c) PP_CMC_5BA at a magnification of 5000×

of the particles is in the range of 20–80 µm. A considerable increase in size (50–300 µm) can be observed when BA is incorporated in its aqueous dispersion (Fig. 3 (b)). It is suggested that as a result of the Leidenfrost effect, the particles situated in the same droplet form a single aggregate. Apparently, these agglomerates cannot be decomposed by the shear forces of mixing. By contrast, the use of a water/CMC-based carrier resulted in far smaller particle sizes compared to the two other methods investigated. In this respect, this latter technique proved to be the most promising. This is in good agreement with the mechanical tests results.

According to Fig. 4 (a), in sample PP_5BA, a high number of BA particles dispersed at nanometric level can be seen. In contrast, PP_5BA_W (Fig. 4 (b)) contains far fewer of these. This fact confirms the theory that the BA particles in the same droplet form a single aggregate and do not decompose. In sample PP_CMC_5BA (Fig. 4 (c)), the aggregates of similar size (0.2–5 μm) can be seen that were also identified in Fig. 3 (c). Recall, that this is the same size range that CMC domains exhibited in sample PP_CMC. Therefore, it is likely that BA particles are mostly located within the CMC in this case.

3.3 The effects of the amount of BA on the properties of polypropylene

Fig. 5 shows the relative changes in the mechanical properties of the samples with different BA contents (PP_CMC_2.5BA, PP_CMC_5BA and PP_CMC_10BA). The relative values are correlated with samples of same composition but without BA (PP_CMC(2.5), PP_CMC(5) and PP_CMC(10)).

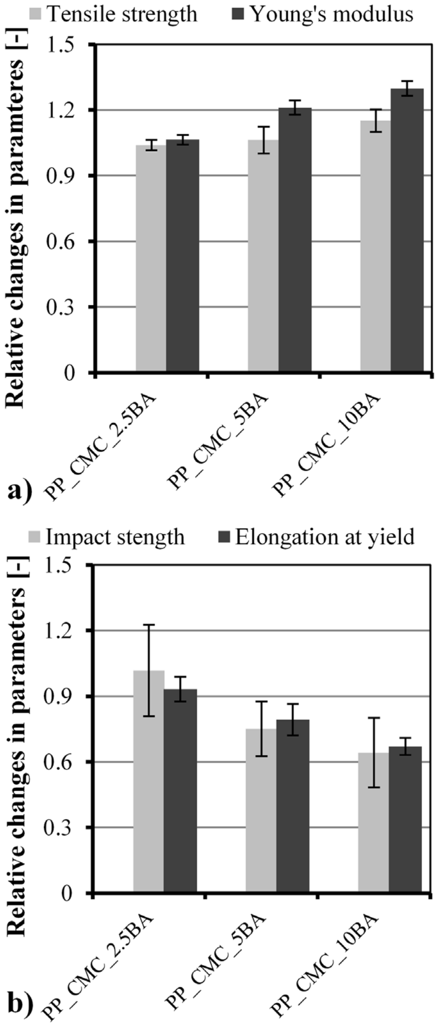

Fig. 5 a) Relative changes in the mechanical properties of the samples PP_CMC_2.5BA, PP_CMC_5BA and PP_CMC_10BA in form of Young's modulus, tensile strength, b) elongation at yield point and impact strength (Note: the relative values are correlated with samples of same composition but without BA)

Fig. 5 (a) indicates that the incorporation of boehmite enhances both strength and stiffness. The addition of 2.5, 5 and 10 wt.% BA causes a 4, 6 and 15 % increase in tensile strength, respectively. The increase of Young's modulus with increasing BA content was even more remarkable, peaking at 30 %. Elongation at yield, however, dropped by 34 % when 10 wt.% BA was incorporated. With a boehmite content higher than 2.5 wt.%, impact strength also showed a moderate decrease.

Fig. 6 displays the absolute values of the mechanical properties as a function of boehmite content. It should be noted, that the more BA also means more CMC. In this aspect, the reinforcing effect of BA is not that prominent, as the two additives (BA and CMC) have an opposite effect on the mechanical properties of PP. As a result, the tensile strength of all samples was within the deviation range in all cases. A slight increase in Young's modulus can be observed when BA content is 10 wt.% (1225 MPa → 1285 MPa), however, according to the two-sample *t* test this increment cannot be considered significant. In turn, both the

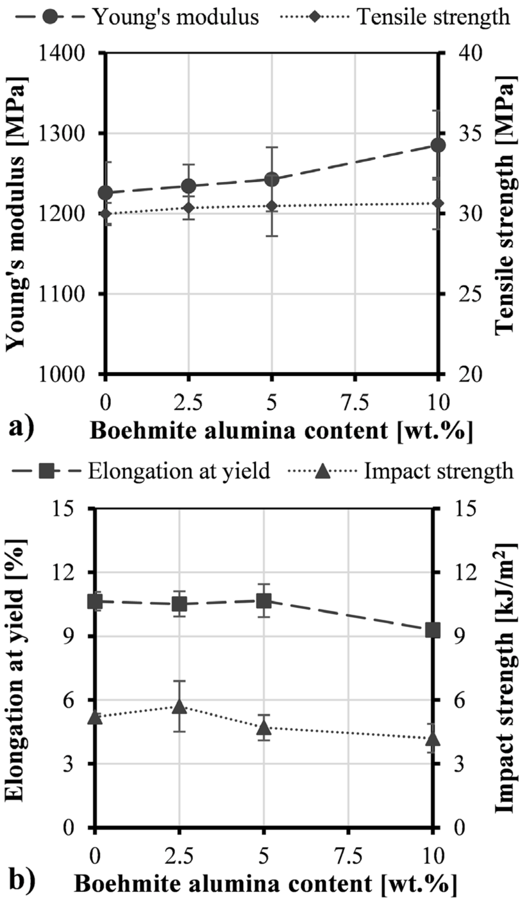

Fig. 6 The effect of BA content on the mechanical properties of PP–based composites prepared in a water/CMC assisted way

Table 2 DSC analysis data determined for PP and its BA reinforced nanocomposites

Sample	Melting temp., T_m [°C]	Cryst. temp., T_c [°C]	Cryst. ratio, X_c [%]
PP	163.7	123.0	43.4
PP_CMC(5)	163.8	122.9	43.2
PP_CMC_2.5BA	163.0	123.8	44.8
PP_CMC_5BA	162.9	124.2	45.2
PP_CMC_10BA	164.4	124.9	46.8

Note: X_c and T_m values were determined upon the second heating procedure

impact strength (5.2 kJ/m^2 → 4.2 kJ/m2) and the elongation at yield (10.6 % → 9.3 %) decreased only marginally (but significantly).

Table 2 summarizes the results obtained from DSC measurements. According to the data, the presence of CMC (PP ⇔ PP_CMC(5)) had no effect on the melting temperature (T_m) and the crystallization temperature (T_c) of PP. BA also did not affect T_m, although T_c slightly shifted to higher (123.0 °C → 123.8 °C → 124.2 °C → 124.9 °C) temperatures in the samples containing 0, 2.5, 5 and 10 wt.% BA, respectively. This is likely due to the nucleating effect of the particles. Besides, a slow but steady increase in the crystallinity ratio can be observed as well as a function of BA content (43.4 % → 44.8 % → 45.2 % → 46.8 %).

4 Conclusions

The present study was aimed to determine the effect of BA incorporated into a PP matrix with various techniques. It has been presented that the fast evaporation mixing method is not functional when the processing temperature is much higher (in this case 180 °C) than the boiling point of water (100 °C). The problem caused by the occurring Leidenfrost effect was overcome with the use of an additional component, CMC, which stabilized the procedure by increasing the boiling temperature of the aqueous dispersion. The SEM images showed that PP/BA composites had a partially dispersed structure, with both aggregates and dispersed particles being present, if the additive was incorporated as dry powder. Using water as a carrier media led to intensive aggregation, which can be explained with the Leidenfrost effect. At the same time, the water/CMC medium facilitated the decomposition of BA aggregates, leading to a markedly better dispersion of the particles within the polymer matrix. The mechanical tests results showed that the presence of CMC:

- increased reinforcing efficiency,
- but had an opposite effect on the mechanical properties compared to BA.

Therefore, the improvement in strength and stiffness was limited. However, elongation and toughness, which should have dropped prominently otherwise, exhibited only a marginal decrease. The DSC results showed that BA acted as a nucleating agent by increasing both the crystallization temperature and crystallinity ratio of PP

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