Injection molding of ceramic filled polypropylene: The effect of thermal conductivity and cooling rate on crystallinity

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Abstract

Three different nano- and micro-sized ceramic powders (boron-nitride (BN), talc and titanium-dioxide (TiO_2)) in 30 vol% have been compounded with a polypropylene (PP) matrix. Scanning electron microscopy (SEM) shows that the particles are dispersed smoothly in the matrix and larger aggregates can not be discovered. The cooling gradients and the cooling rate in the injection-molded samples were estimated with numerical simulations and finite element analysis software. It was proved with differential scanning calorimetry (DSC) measurements that the cooling rate has significant influence on the crystallinity of the compounds. At a low cooling rate BN works as a nucleating agent so the crystallinity of the compound is higher than that of unfilled PP. On the other hand, at a high cooling rate, the crystallinity of the compound is lower than that of unfilled PP because of its higher thermal conductivity. The higher the thermal conductivity is, the higher the real cooling rate in the material, which influences the crystallization kinetics significantly.

Keywords: thermally conductive polymers, DSC measurement, explicit difference method, cooling rate, thermal conductivity, crystallinity

1. Introduction

In the last decade, composite materials with a thermoplastic polymer matrix get more and more attention in research and industrial applications. With the application of composite systems, not only the mechanical properties, but also the thermal properties of polymeric matrices can be improved. One of the important thermal parameters of polymers is thermal conductivity, which can be enhanced by micro- and nano-sized fillers or reinforcements [1-3]. If the dielectric behavior of the composite is an important requirement, thermally conductive but electrically non-conductive particles should be applied. Ceramic fillers, such as boron nitride, aluminum oxide, aluminum nitride, silica, talc and many others can be used in such cases [1, 2, 4].

These kinds of polymer composites are utilized mainly in electronics, where it is important to both increase the power and decrease the size of the components at the same time. In some instruments, such as LED lamps or integrated memory chips, fast and efficient heat dissipation is a key issue, because the generated heat can raise the temperature of the device over its thermal stability limit. Over the critical temperature lifespan decreases significantly or the instrument may be damaged [4].

Many publications investigated the influence of the filler fraction on thermal conductivity and mechanical properties, but few of them examined crystallinity, thermal parameters, cooling behavior and their relationship. One of the most important physical parameters of semi-crystalline polymers is their degree of crystallinity, as it determines their mechanical properties. Thus the modulus of elasticity, yield stress and impact resistance increase gradually with crystallinity [5-7]. During injection molding crystallinity and crystalline morphology are critical parameters, because they are strongly influenced by processing conditions, including molding temperature, cooling rate, holding time and temperature [8]. Among others, there is a correlation between cooling rate and crystallinity. The degree of crystallinity is proportional to the cooling rate, and it can be determined by DSC measurements [8, 9]. Furthermore, the fillers added to increase thermal conductivity can work as an effective nucleating agent. Thus they can increase the number of crystal nuclei. [10].

Although widespread and comprehensive research has been conducted on nucleating agents, so far the adverse effect of the increased cooling rate of the conductive polymers on the nucleating efficiency of the fillers in the molding process has not been investigated. In this study we examine the effects of different ceramic fillers on the cooling rate and thermal properties of polypropylene-based compounds. Our work shows that the thermal conductivity of the fillers has great influence on the cooling rate and crystallinity of the compounds. The measured parameters and relationships can be used to improve simulation software to make the calculations and the results more reliable and precise, making the results closer to reality.

2. The experiments

2.1 Materials

H145 F homo-polypropylene was purchased from Tiszai Vegyi Kombinát Nyrt. (Hungary). The polypropylene matrix was compounded with different thermally conductive fillers, such as hexagonal boron-nitride (BN), talc and titanium-dioxide (TiO_2). Plate-like hexagonal boron-nitride grade A 01 powder was obtained from H.C.Starck GmbH (Germany). The density and the thermal conductivity of the BN powder are 2.2 g/cm^3 and 60-65 W/mK respectively [11]. Plate-like talc powder was supplied by Novia Kft. (Hungary). Its thermal conductivity coefficient is about 2-10 W/mK [12] and its density is 2.7 g/cm^3. The titanium dioxide (TiO_2) was also obtained from Novia Kft. (Hungary). According to literature, the thermal conductivity of the TiO_2 bulk is 5-7 W/mK [13].

2.2 The preparation of the samples

In this study the surface of the fillers was not treated. The compounds were prepared with 30 vol% filler content with a LabTech Scientific extruder and granulated with a LabTech pelletizer. The 80x80x2 mm sized samples were injection molded with an Arburg Allrounder 370S 700-290 injection molding machine (Table 1).

2.3 Measurement and calculation methods

The thermal conductivity of the samples was measured with the hot plate method [14]. A 10°C temperature difference was generated between the hot and the cold side and the result was calculated at 55°C. The results were calculated with Fourier’s law (Eq. (1)) [15, 16].

$$q(x,t) = -\lambda \cdot \nabla T(x,t) \quad (1)$$

A DSC Q2000 (TA Instruments) differential scanning calorimeter was used to analyze the specific heat, the crystallization temperature and the crystallinity of the samples. 3-5 mg samples were cut off from the centre of the injection molded plates and placed into pans. The measurements consist of three phases: heating to 225°C from 25°C, cooling back to 25°C and heating to 225°C again. The first heating is used to measure the effect of the injection molding process, as in the next two phases crystals are created and melted during a controlled process (a heating and cooling rate of 10°C/min). The degree of crystallinity (X) was determined from the exothermic and the endothermic peaks with Eq. (2), which takes into account the filler fraction of the compound [8, 17].

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1-\varphi)}. \quad (2)$$

where ΔH_m is the enthalpy at melting point, ΔH_{cc} is the enthalpy of cold crystallization, ΔH_f is the enthalpy of the fully crystalline polymer and φ is the mass fraction of the filler. According to the literature, the theoretical value of ΔH_f of polypropylene is 165 J/g [18].

The temperature distribution in the specimen can be described with the heat diffusion equation (Eq. (3)) [19]. This differential equation was solved numerically by a using finite difference equation (explicit difference method) (Eq. (4)). This numerical method describes the cooling process in the substance using a one-dimension model without an inner heat source [15].

$$\frac{1}{\alpha} \cdot \frac{\partial T}{\partial t} = \nabla^2 T + \frac{\dot{q}}{\lambda}. \quad (3)$$

$$\frac{T(x,t+\Delta t) - T(x,t)}{\Delta t} = \alpha \cdot \frac{T(x+\Delta x,t) + T(x-\Delta x,t) - 2T(x,t)}{\Delta x^2}. \quad (4)$$

where T is the temperature, x and t indicate the place and time, Δx and Δt are the distance and time step in the calculation, and α is the thermal diffusivity. Thermal diffusivity was calculated as the proportion of the thermal conductivity and the product of the density and the specific heat capacity (Eq. (5)). Using temperature-dependent values in the equations, more accurate results can be achieved.

$$\alpha(T) = \frac{\lambda(T)}{\rho \cdot c_p(T)}, \quad (5)$$

where ρ is the density, c_p is the specific heat and λ is the thermal conductivity.

In an actual process the polymer shrinks and warps during cooling. Therefore, thermal contact resistance (R_s) varies during the cycle. Several studies have examined the thermal contact resistance between the polymer and the metal surface, in which the mean value of resistance is $5 \cdot 10^{-4}$ m^2K/W [20, 21]. Contact resistance induces a temperature difference between the polymer (T_{ps}) and the mold surface (T_{ms}). Eq. (6) gives the temperature field which is the input data of the explicit difference method.

$$T_{ps}(t) = R_s \cdot q(t) + T_{ms}. \quad (6)$$

The heat flux (q) was calculated from the temperature drop (ΔT) in the substance between two discrete points (Δx) (Eq. (7)), according to Fourier's law. This heat also flows through the air gap between the surface of the mold and the polymer.

$$q(t) = \lambda \cdot \frac{\Delta T}{\Delta x} . \quad (7)$$

The cooling rate of the sample was calculated from the temperature field, which was obtained from the explicit difference method. The derivation of the time-temperature curves at discrete distances from the surface gives the cooling rate (v_{cool}) as a function of the time and distance (Eq. (8)).

$$v_{cool}(x,t) = \frac{\partial T(x,t)}{\partial t} . \quad (8)$$

The cooling time required to reach the ejection temperature was determined with three different methods: simulation; the explicit difference method and an empirical formula (Eq. (9)) [22]. The simulations were performed with the MoldFlow injection molding simulation software.

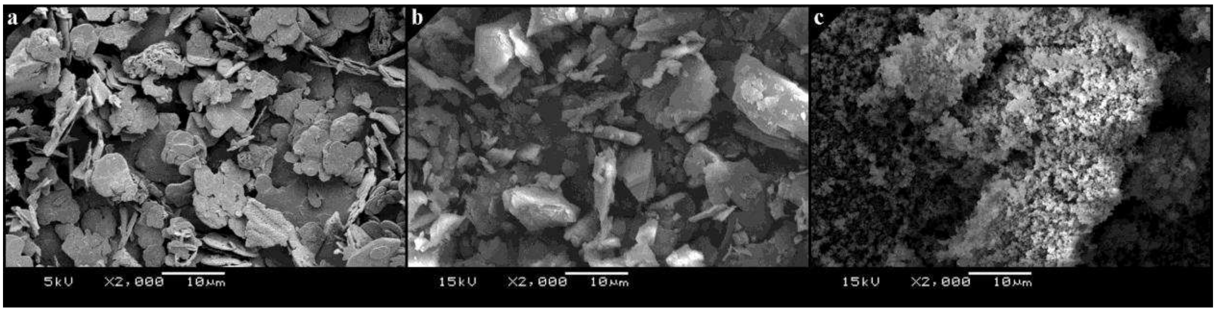
$$t_{cool} = \frac{s^2}{\pi \cdot \alpha} \cdot \ln\left(\frac{4}{\pi} \cdot \frac{T_{me} - T_{mo}}{T_e - T_{mo}} \right) . \quad (9)$$

where s is the thickness of the sample, T_{me} is the melt temperature, T_{mo} is the mold temperature and T_e is the ejection temperature.

3. Results and discussion

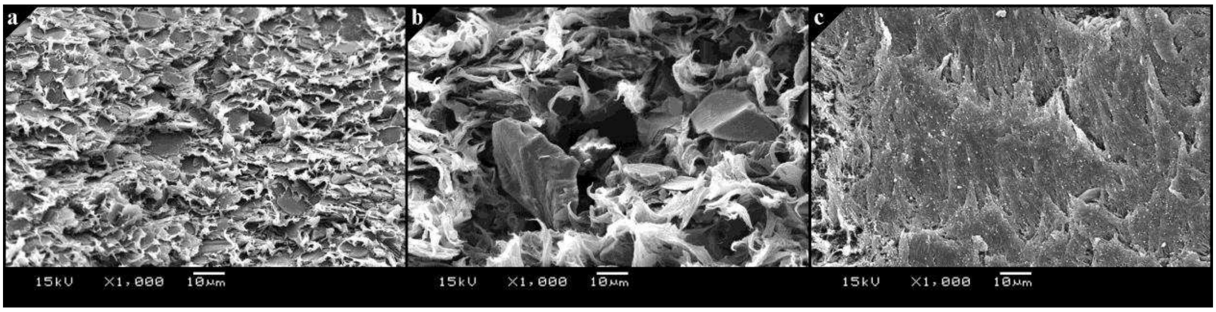
3.1 SEM analysis of the fillers and compounds

The SEM analysis of the fillers shows that boron nitride and talc have a plate-like shape. The average size of BN particles is under 10 μm but particles in the nanometer range can also be found but in the aggregates. The thickness of the plates is also in the nanometer range. Talc has a higher average particle size, between 5 and 50 μm, while the thickness of the particles is also in the micrometer range, although the individual plates are thinner than one micrometer. In spite of the bigger size of talc particles, the final material could contain much smaller particles, as talc is a very soft material, and thus high shear during the molding process can break them. The titanium dioxide particles are spherical and their size is about 100 to 300 nm according to SEM analysis (Fig. 1).



1. Figure SEM pictures of the powders (a – boron nitride; b – talc; c – titanium dioxide)

The SEM pictures of the fracture surfaces (Fig. 2) show that the fillers were smoothly dispersed in the matrix material. Although filler content was quite high (30 vol%), larger aggregates could not be found.



2. Figure SEM pictures of the fracture surface of the compounds (a – PP + 30 vol% BN; b – PP + 30 vol% talc; c – PP + 30 vol% TiO2)

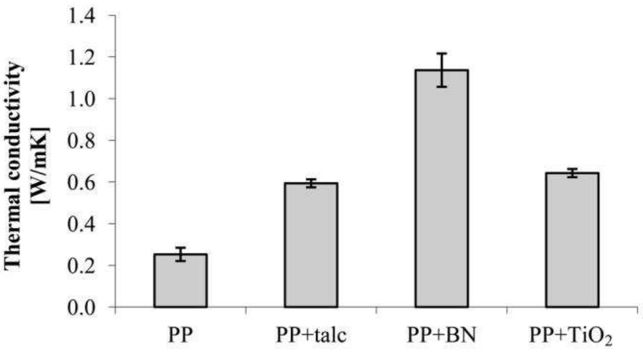
The particles can form a conductive network in the compound and this way improve thermal conductivity more efficiently. The compound is densely packed, interparticle distance is smaller, and thus the particles can come into contact with each other.

3.2 Specific heat

The three stages of the specific heat measurement (heat-cool-heat) are plotted in Table 2. Only unfilled PP shows a significant difference between the first and the second heating, which is about 500 J/kgK. In the case of the filled materials there is no considerable difference between the two measurements. In the neat PP the first heating phase refers to the injection molding process, and the second heating to the controlled cooling caused behaviors. In the filled PP this effect is not significant, because there are no changes in the fillers at this low temperature range, therefore the high filler content leads the process. On the other hand, there are significant differences between the values measured in the heating and the cooling phase. The specific heat measured during the cooling phase has to be used for calculations, as Eq. (4) describes a cooling process.

3.3 Thermal Conductivity

Fig. 3 presents the through-plane thermal conductivity values of the injection molded plates.

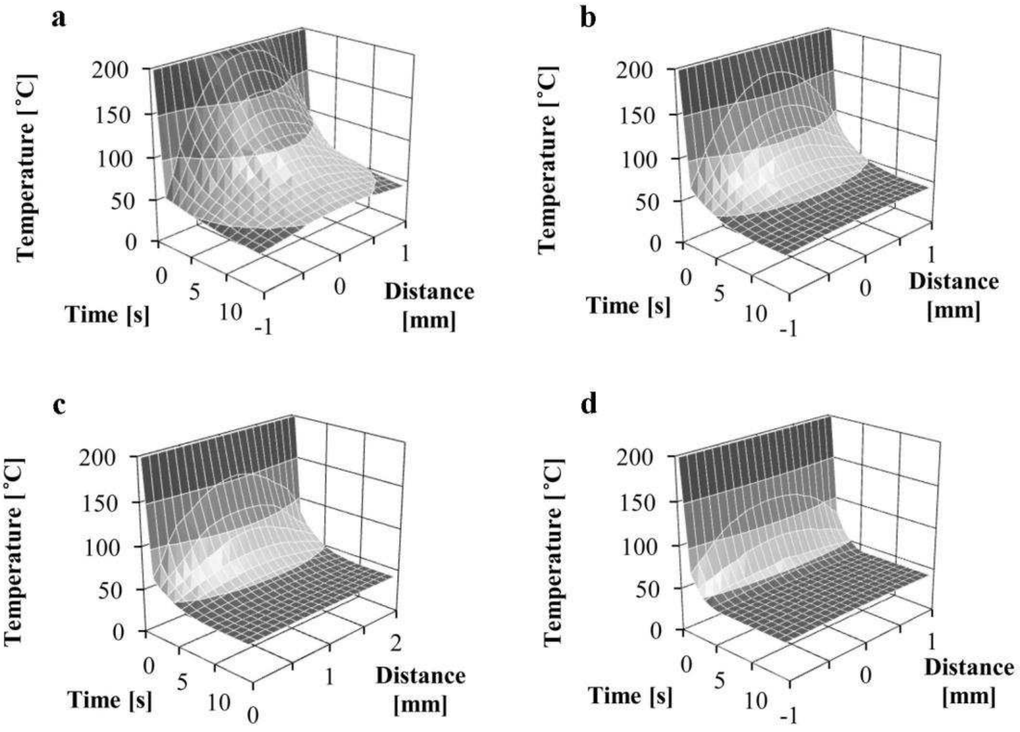


3. Figure Thermal conductivity of PP and its compounds with 30 vol% talc, BN and TiO$_2$

All the three fillers increase the thermal conductivity of the composite material. Talc and titanium-dioxide have only a minor effect; the coefficient increased from 0.25 W/mK to 0.59 and 0.64 W/mK respectively. When boron-nitride was used, thermal conductivity increased to 1.14 W/mK. The increased thermal conductivity leads to faster cooling of the injection molded samples, which in turn shortens cooling time and cycle time.

3.4 Cooling rate

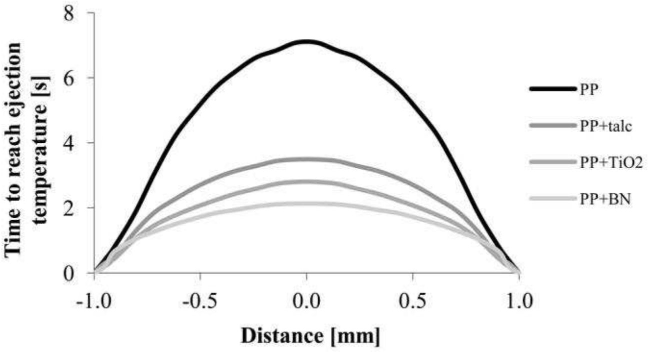
The cooling gradients were determined as a function of the time and positions across the thickness using the explicit difference method. In accordance with the injection molding tests, a melt temperature of 200°C and a mold temperature of 40°C were used in the calculations. The specific heat and as a result the calculated heat diffusivity varied as a function of the temperature. The temperature was uniform through the whole specimen at the initial calculation step, then it started to cool down to 40°C. The cooling gradients (Fig. 4) show that unfilled PP has the lowest cooling rate. When 30 vol% of filler is used, cooling time can be shortened significantly.



4. Figure Cooling gradients of the samples (a, PP; b, PP + 30 vol% talc; c, PP + 30 vol% TiO2; d, PP + 30 vol% BN)

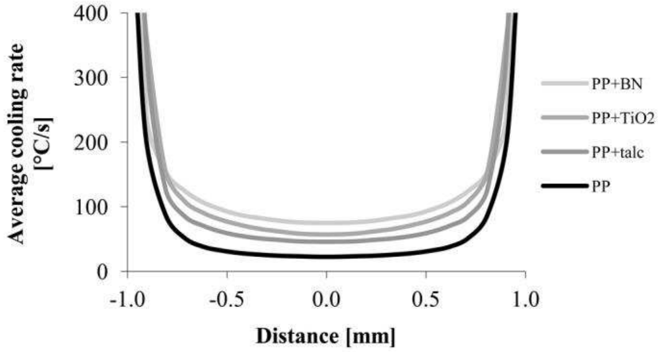
The maximum ejection temperature of polypropylene is about 100-110°C. It means that if the temperature is lowered below this value, the polymeric parts are rigid enough to be removed from the mold without any damage [23]. With 30 vol% of TiO_2 the cooling time to reach ejection temperature decreased by 35%, with talc it decreased by 50% and in the case of BN by more than 70%.

The time to reach ejection temperature in the cross section is shown in Fig. 5. From the cooling gradients the cooling rates can be calculated.



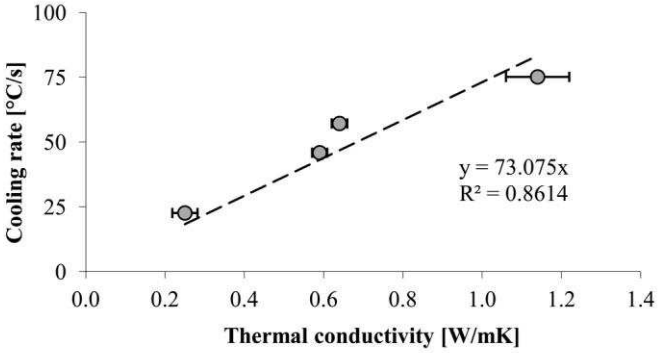
5. Figure The time to reach ejection temperature in the cross section

Fig. 6 shows the average cooling rate of the material between the injection temperature (200°C) and the ejection temperature (100°C) as a function of position across the thickness.



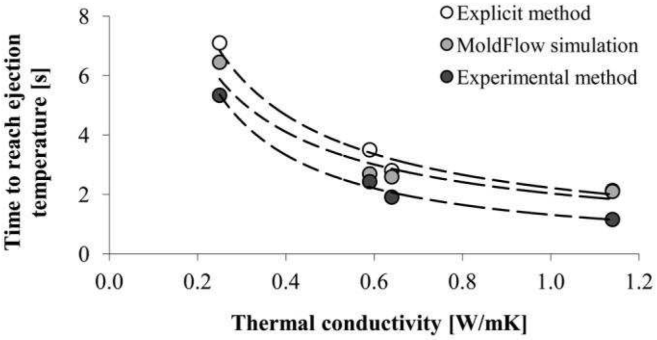
6. Figure The average cooling rate between the injection and ejection temperatures

On the surface a very high cooling rate can be observed, but it decreases rapidly towards the center. In the middle of the PP sample the average cooling rate is 22.6°C/s. With 30 vol% of talc the cooling rate is 45.8°C/s, with TiO_2 it is 57.1°C/s and with BN it increases to 75°C/s. These significant differences in the cooling rates can be explained by the differences in thermal conductivity (F). Moreover, there is a strong linear correlation between the cooling rate and thermal conductivity (Fig. 7.).



7. Figure Relationship between the cooling rate and the thermal conductivity of the compounds

The explicit difference method was compared to other cooling time calculation methods (empirical calculation and MoldFlow simulation). The explicit difference method shows good agreement with the Mold Flow simulation, especially in higher thermal conductivity ranges (Fig 8.).

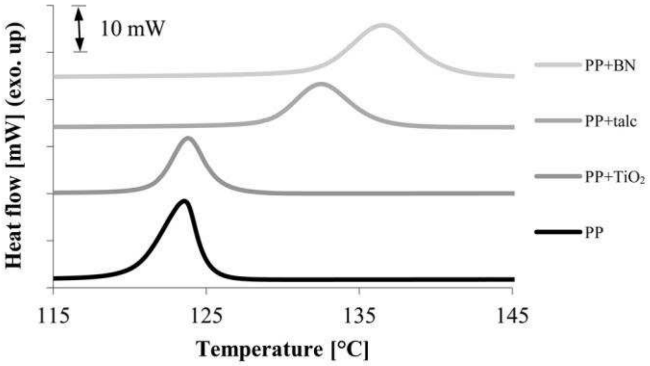


8. Figure Time to reach ejection temperature in the compounds

The empirical method gives a lower estimation of the real processes, because this equation uses an average thermal diffusivity value and approximates the gradient with a logarithmical curve.

3.5 Thermal characterization

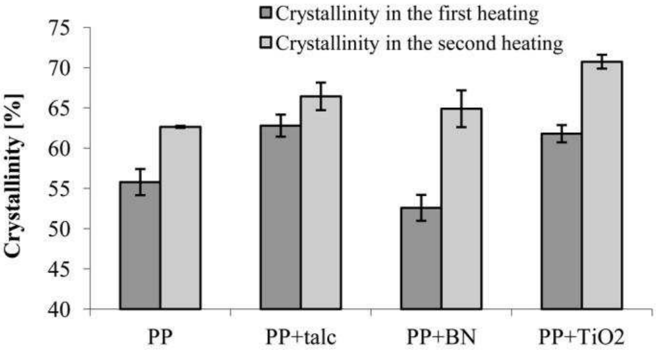
The thermal characterization of the compounds was performed with DSC apparatus. During the measurement the crystallization peaks of the compounds were observed. According to Fig. 9 and Table 3, there is a remarkable shift in the crystallization peaks. The biggest difference is about 13°C using 30 vol% of BN. It means that the crystals can be created at a higher temperature, and the polymer material has a longer time for crystallization.



9. Figure Shift of the crystallization peak as a function of the different fillers

In the DSC measurements, the thermal history of the materials was erased during the first heating, then the crystals were created and melted under controlled circumstances with a slow cooling and heating rate. This method is widely used when a small amount of fillers is added to the polymer matrix. This way the effect of the fillers on crystallinity can be compared. On the other hand, in a real process, such as injection molding, the cooling rate is more than 15°C/s, thus the polymers have less time for crystallization. The higher the cooling rate is, the lower crystallinity will be. Process-induced crystallinity can be obtained from the first heating scan of DSC measurements.

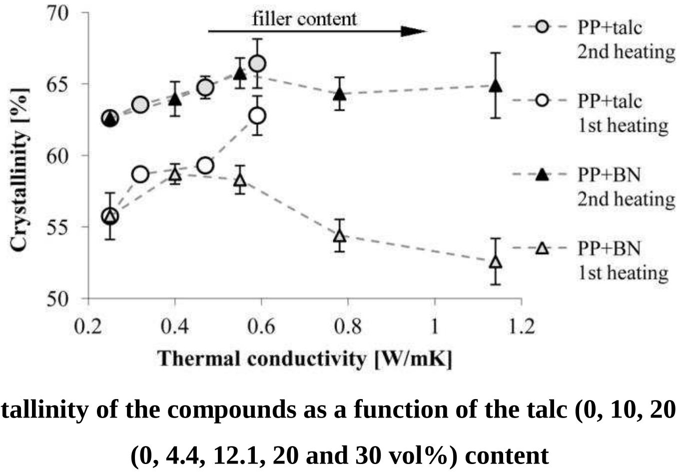
The results of the crystallinity measurements are shown in Fig. 10.



10. Figure Crystallinity of the compounds in the first and second heating phase

It can be seen that the degree of crystallinity increased with the adding of fillers when the heating and cooling rate was 10°C/min (the second heating and the first cooling). Of the three filler types, the best nucleating agent is titanium dioxide. It increased the crystallinity of PP from 63% to 71%. BN or talc only increased it to 65-66%. Injection molding-induced crystallinity was determined from the first heating phase. It is noticeable that crystallinity is 5-15% lower than after recrystallization. With 30 vol% boron-nitride crystallinity is only 64.2%, which is lower than in the case of unfilled polypropylene (68.1%). This drop can be explained by higher thermal conductivity. While the unfilled polypropylene cooled slowly in the mold after injection, the 30 vol% boron-nitride filler increased thermal conductivity and also the cooling rate. Thanks to the higher cooling rate, lower crystallinity can be obtained. It means that the nucleating effect of the boron-nitride was not enough to compensate for the effect of thermal conductivity.

The crystallinity of talc and BN filled compounds were investigated as a function of the filler content (Fig. 11).



11. Figure Effect Crystallinity of the compounds as a function of the talc (0, 10, 20 and 30 vol%) and BN (0, 4.4, 12.1, 20 and 30 vol%) content

Up to 30 vol% talc (λ=0.58 W/mK) crystallinity increased monotonously, which shows a good nucleating agent behavior. On the other hand, adding boron nitride to the PP matrix, first crystallinity increases and above a threshold it decreases. This limit value is 10 vol%, where the thermal conductivity of the compound is 0.55 W/mK. Above 10 vol% BN fraction, the high thermal conductivity results in faster cooling during injection molding, thus crystallinity decreases.

4. Conclusion

This study focused on the molding process-induced thermal properties of filled polypropylene. Compounds filled with 30 vol% ceramic powder (talc, titanium-dioxide, boron-nitride) were produced with extrusion and 2 mm thick samples were made with injection molding. The thermal conductivity of the polypropylene was determined as 0.25 W/mK, while the thermal conductivities of compounds filled with talc, TiO_2 and BN were 0.59, 0.64 and 1.14 W/mK respectively. To characterize the cooling phase under injection molding circumstances, the cooling gradients and the cooling rates were determined with the explicit difference method. The input data were the thermal conductivity, the density and the specific heat curve of the materials. The results show that thermal conductivity has a great influence on the cooling rate. The higher the thermal conductivity is, the higher the cooling rate is. On the other hand, the cooling rate influences the crystallinity of the polymers. Thus after injection molding, highly filled polymer compounds with a high thermal conductivity have lower crystallinity than the unfilled polymer, in spite of the fact that the filler is an efficient nucleating agent.

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