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Effect of *N*,*N'*-Dicyclohexyl Terephthalic Dihydrazide on the Crystallization and Properties of Isotactic Polypropylene

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Abstract

Application of nucleating agents is a common way to manipulate the structure and properties of crystalline polymers. Our goal was to synthesize *N*,*N'*-dicyclohexyl terephthalic dihydrazide (DCTDH) and study it from the viewpoint of applicability as a nucleating agent for isotactic polypropylene (iPP). We used differential scanning calorimetry to investigate the efficiency of DCTDH in samples containing the nucleating agent in a wide concentration range. We used polarized light microscopy to study the crystalline morphology developed in the presence of this nucleating agent. To characterize the mechanical properties of the nucleated samples, we performed tensile and impact tests on injection molded specimens. DCTDH proved to be a non-soluble α-nucleating agent in iPP, with a saturation concentration around 300 ppm. The nucleating agent has a significant effect on the crystalline structure of iPP, microspherulitic structure forms in its presence. Owing to the different structure, a considerable change in the mechanical properties is observable: with increasing nucleating agent content the tensile modulus increases, while impact resistance has a maximum value around 300 ppm nucleating agent content.

Keywords

semicrystalline polymers, crystalline structure, nucleation, hydrazides

1 Introduction

Isotactic polypropylene (iPP) is a commodity polymer used in large amounts by industry [1]. It is a semicrystalline polymer, with different polymorphic modifications [2–9], among which only the α- and the β-polymorphs have industrial importance. The thermodinamically stable modification is α-iPP, therefore this modification forms under conventional industrial conditions [10]. The formation of β-iPP requires special thermal conditions and the presence of special additives (β-nucleating agents) [8]. As the properties important from the viewpoint of application (such as mechanical and optical properties) depend mostly on the crystalline structure, manipulating the structure is an appropriate way to achieve the required properties. To attain this goal, the application of special additives, called nucleating agents, is the most versatile method used in industry. During the last few decades several types of materials proved to possess nucleating effect in iPP. The nucleating agents can be classified from more viewpoints like selectivity or dispersability for example. In this short summary we focus on those non-soluble nucleating agents, that are selective for the α-modification of iPP. Although several chemically different compounds belong to this family of nucleating agents, the one thing they have in common, that during the polymer processing all of them are present as solid, heterogeneous surfaces, they are not soluble in the polymer melt at all. One of the most frequently used nucleating agents is talc, an inorganic layered silicate with anisotropic needle-like or lamellar crystals [11–13]. Talc is used mainly as filler in composite materials, however, it also possesses nucleating effect over 1000 ppm concentration [14]. Other non-soluble nucleating agents commonly used in the industrial practice are sodium-benzoate, NA-11 and NA-21E. These latter two are organic phosphate derivatives [15–17]. The efficiency of a nucleating agent is generally characterized by the crystallization peak temperature (T_{cp}) measured on samples nucleated with different amounts of the nucleating agent. In the case of the non-soluble nucleating agents T_{cp} changes according to a characteristic curve as a function of the nucleating agent content. At low concentrations T_{cp}

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increases rapidly, then reaches a saturation level at a temperature and concentration depending on the efficiency of the nucleating agent. The presence of the nucleating agent has a complex effect on the developing supermolecular structure. Owing to the elevated T_{cp} the thickness of the lamellae is larger, and the increased number of nucleation sites leads to the reduction of spherulite size. The crystalline structure formed is called "microspherulitic structure", as the size of the spherulites is in the micrometer range. These changes in the structure lead to changes in the properties. In the presence of a nucleating agent the ratio of the crystalline phase increases, and, because of the elevated crystallization temperature, the thickness of the lamellae increases, as well. Both of these changes result in a higher tensile modulus, which can be predicted with an empirical correlation proposed by Pukánszky et al. [18] or by other empirical models developed later [19–21].

The nucleating effect of hydrazides had been investigated by some researchers, however, in their works the additives were introduced mainly in poly(lactid acid) (PLA) [22–26]. Zhang and Mao [27] and Mao et al. [28] used iPP in their works and introduced different hydrazide compounds in it. They concluded that the investigated compounds were α-nucleating agents, and according to the DSC measurements some of them had remarkable nucleating effect. Although these works supply valuable information, they are restricted to the thermal properties and the nucleating efficiency of hydrazides in iPP, and the thorough investigation of the effect on the properties important from the viewpoint of application are missing in these papers.

Our goal was to synthesize *N*,*N*′-dicyclohexyl terephthalic dihydrazide (DCTDH), and investigate its applicability as a nucleating agent in iPP. We used differential scanning calorimetry (DSC) to determine the nucleating efficiency of DCTDH, and investigated the supermolecular structure developing in its presence using polarized light microscopy (PLM). To thoroughly characterize how DCTDH modifies the mechanical properties of the polymer, we performed tensile and impact tests.

2 Materials and methods

2.1 Materials

In the study we used a commercial homopolymer grade isotactic polypropylene, TIPPLEN H 649 FH homopolymer (MFR = 2.5 g/10 min at 230 °C, 2.16 kg), supplied by MOL Petrochemicals Hungary. The polymer was in the form of stabilized granules, and we used the material as received. We have selected this commercial grade, because it does not contain any additive having nucleating effect. It contains only basic stabilization and an acid scavenger, but its exact composition is not known by us. We have used this material routinely in our recent previous works. Accordingly, the present results are comparable with the previous ones [29]. We synthesized the investigated compound in the reaction of terephthalic dihydrazide and cyclohexanecarbonyl chloride (for the reaction scheme and structure, see Scheme 1).

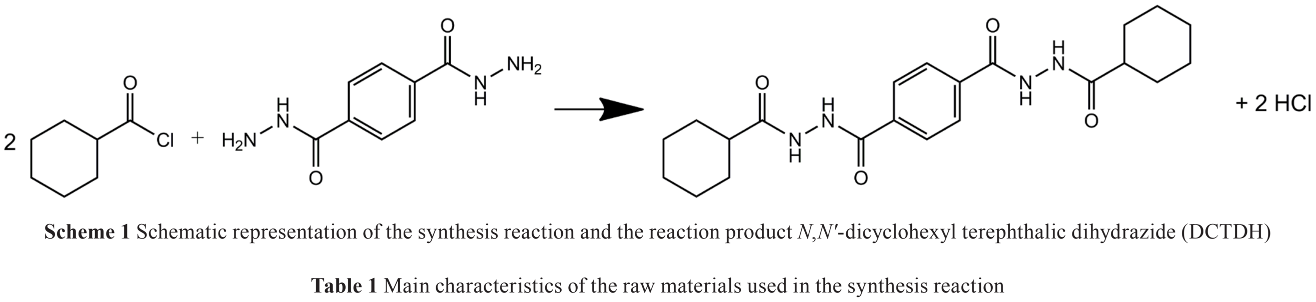
We list the types and the main characteristics of the raw materials used in the reactions in Table 1.

The raw materials were purchased from the suppliers listed in Table 1, and we used them without any further purification.

2.2 Methods

2.2.1 Synthesis of the nucleating agent

In the reaction we used *N*,*N*-dimethylformamide (DMF) as a solvent, and pyridine as an acid scavenger. The reactor was a four-neck round-bottom flask, equipped with a reflux



Scheme 1 Schematic representation of the synthesis reaction and the reaction product *N*,*N*′-dicyclohexyl terephthalic dihydrazide (DCTDH)

Table 1 Main characteristics of the raw materials used in the synthesis reaction

Material	Molecular weight (g/mol)	Role	Supplier (purity)
Terephthalic dihydrazide	194.19	Reagent	Alfa Aesar (95%)
Cyclohexane-carbonyl chloride	146.62	Reagent	Alfa Aesar (> 97.0%)
N,*N*-dimethylformamide	73.10	Solvent	Molar Chemicals (> 99.5%)
Pyridine	79.10	Acid scavenger	Molar Chemicals (puriss.)

condenser. The reaction suspension was stirred during the whole process under an inert argon atmosphere. As a first step, we dispersed 13.7 g (0.07 mol) terephthalic dihydrazide in 100 ml DMF, and we poured the suspension in the reactor. Then we measured 15.01 ml (0.19 mol) pyridine in the reactor, using an automatic pipette. Subsequently, we cooled down the reactor to 0 °C, using an ice bath, and from that point we monitored the temperature until the end of the reaction. To avoid the formation of monosubstituted reaction products, we applied the dichloride reagent in a surplus amount: we mixed 0.17 mol dichloride component (22.7 ml cyclohexanecarbonyl chloride) with another 100 ml DMF, and we added the mixture drop by drop, using a dropping funnel, in order to avoid sudden temperature increase caused by the exothermic reaction. Furthermore, we monitored the temperature during this process, and kept it under 5 °C (if the temperature reached this value, we stopped adding the reagent for a short time). After adding the whole amount of the reagent, we exchanged the ice bath to an oil bath, and heated the reactor to a temperature between 75 and 80 °C. We kept the temperature of the reaction suspension in this range for 5 hours. By the end of the 5 hours, the originally light yellow suspension became white. Then, we filtered the product using a glass funnel filter with sintered glass disc, and washed it with cold distilled water and cold methanol, to remove residual non-reacted reagents. Finally, we dried the product at 110 °C, until constant weight (for around a day).

2.2.2 Characterization of the nucleating agent

We used proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy to check if the reaction and the subsequent washing steps were successful, in other words, if we got the desired product in sufficient purity. For the measurement we prepared the sample by dissolving 15–20 mg of the powder in 1 ml anhydrous deuterated dimethyl sulfoxide (DMSO-d_6). We recorded the spectra with a Bruker Avance 300 NMR Spectrometer.

We determined the melting point and the decomposition temperature of the synthesis product, because these are the most important thermal properties from the viewpoint of application as a nucleating agent. In these measurements we applied simultaneous thermal analysis, using a PerkinElmer STA 6000 equipment. We placed approximately 7–10 mg of the powder in an alumina crucible, and we heated it up from 30 °C to 900 °C at a heating rate of 10 °C/min under a N_2 atmosphere. We registered both the heat flow and the mass curves, then evaluated them using Pyris software.

2.2.3 Preparation of iPP samples nucleated with DCTDH

After checking the abovementioned characteristics, we introduced the compound in the polymer in a wide concentration range: we prepared samples containing 10, 50, 100, 300, 500, 1000 and 2000 ppm of the additive. We carried out the procedure with extrusion technique, using a Brabender DSK 42/7 twin-screw extruder, driven by a Brabender Plasti-Corder PLE 3000 driving unit. The temperature profile was 210−220−230−230 °C from the hopper to the die, and the rotating speed was 50 rpm. For comparison, we extruded once also the neat polymer, thus preparing a reference sample.

2.2.4 Nucleating efficiency

To investigate the nucleating efficiency of the synthesized compound, and also to determine the crystallization and melting properties of the nucleated samples, we applied differential scanning calorimetry (DSC). For these measurements we used a Perkin Elmer DSC 7 calorimeter, and applied a thermal program proposed by Varga [30]. Although this thermal program was developed to β-nucleated samples, we used it because we could not foresee the nucleating effect. We prepared 3–5 mg pieces of the nucleated polymer samples. First, the samples were heated up to 220 °C, and were held at this temperature for 5 minutes to erase their thermal and mechanical prehistory. In the next step, the samples were cooled down to 30 °C, and were held at this temperature for 1 minute, to let the crystallization process taking place completely. Then the samples were heated up to 220 °C again, and were held at this temperature for 3 minutes. In the second cooling run the samples were cooled down only to 100 °C, which is the $T(\alpha\beta)$ critical temperature (limited recooling step). The samples were held at this temperature for 1 minute, then they were heated up to 220 °C again. If the samples contain β-iPP apart from the α-modification, the data recorded in the last heating run are necessary for the determination of their polymorphic composition. The value of the heating and the cooling rates was 10 °C/min in every step.

2.2.5 Supermolecular structure

To study the supermolecular structure developing in the nucleated samples we used polarized light microscopy (PLM) technique. We placed small (3–5 mg) pieces of the non-nucleated sample and the sample containing 500 ppm DCTDH to a glass slide, roughly 0.5 cm far from each other. Then we covered the samples with another glass slide, and used a heated furnace with accurate temperature regulation to prepare a thin film. First, we started to heat the polymer pieces to 220 °C, and when the temperature reached 190 °C we pressed the sample gently by hand to make the thin film. After that we placed a weight on the top of the sample cover to keep the thickness as small as possible. At 220 °C we turned the heating off, and let the sample to slowly cool down. Subsequently, we removed one of the glass slides, and we put a cover glass on the polymer film.

In the next step we inserted the glass slide with the polymer film into a Mettler FP82HT hot stage and we applied the following thermal program, to investigate the isothermal crystallization process. We held the sample at 220 °C for 3 minutes to erase its thermal and mechanical prehistory. Then we cooled the sample down as rapidly as possible (quenching) to the crystallization temperature (140 °C), and held the sample at this temperature until the crystallization completed. We studied the sample during the crystallization process, using a Zeiss Axioskop optical microscope in which a λ-plate was located diagonally between the crossed polarizers. The microscope was equipped with a Leica DFC 320 digital camera, thus we took micrographs in the different stages of the crystallization process.

2.2.6 Sample preparation for mechanical testing

For the mechanical testing we prepared injection molded ISO 527 tensile bars using a Demag IntElect 50/330-100 machine. The temperature profile was 205–210–220–230 °C and the temperature of the mold was 40 °C. The holding pressure and time were 500 bar and 20 s, respectively. Before testing mechanical properties of the specimens, at least 1 week passed to be sure that secondary crystallization completed.

2.2.7 Testing of mechanical properties

To carry out tensile tests we used an Instron 5566 apparatus with a gauge length of 115 mm. In the first step of the measurement, up to 0.02% elongation the cross-head speed was 0.5 mm/min. We used the data recorded in this elongation range to determine the tensile modulus of the samples. In the next step of the measurement the cross-head speed was 50 mm/min, and the deformation lasted until the sample broke. To test the impact resistance of our samples we performed notched Charpy impact tests, according to ISO 179 standard, using a Ceast Resil 5.5 type machine equipped with a 1 J hammer. In the measurements we used injection molded specimens, with a 2 mm notch depth. All the mechanical testing measurements were performed at 23 °C and 50% relative humidity.

3 Results and discussion

3.1 Chemical structure of the synthesis product

We performed a ^{1}H-NMR spectroscopy measurement to prove that in the reaction the expected product had been formed. In Fig. 1 we present the recorded spectrum, together with the structure of the molecule. The chemically equivalent hydrogen atoms are marked with the same letters, from *a* to *g*. The chemical shift of a hydrogen atom attached to a benzene ring is generally located between 6.5–8 ppm. In our spectrum a singlet peak with a chemical shift of 7.95 ppm appears, which corresponds to the hydrogen atoms marked with the letter *a*. Another two singlet peaks, with smaller intensities are present around 10 ppm. In the range of 10–12 ppm hydrogen atoms attached to highly electronegative atoms show peaks, thus we can conclude that these two peaks correspond to the hydrogen atoms attached to the nitrogen atoms (marked with the letters *b* and *c*). A triplet is located around 2.26 ppm, which corresponds to the hydrogen atoms marked with the letter *d*, as hydrogen atoms attached to a carbon atom in a carbonyl group are generally located in the chemical shift range of 2–2.5 ppm. The peaks of the other hydrogen atoms (marked with the letters *e*, *f* and *g*) are located in the range of 1–2 ppm. This chemical shift range corresponds to the hydrogens attached to carbon atoms far from electronegative atoms. Because of the spin-spin splitting caused by the neighboring hydrogen atoms these multiplet peaks are difficult to distinguish from each other. Considering the number and the location of the peaks we can state that in reaction the expected product formed in high purity. In Table 2 we show the integrals of the peaks, as well.

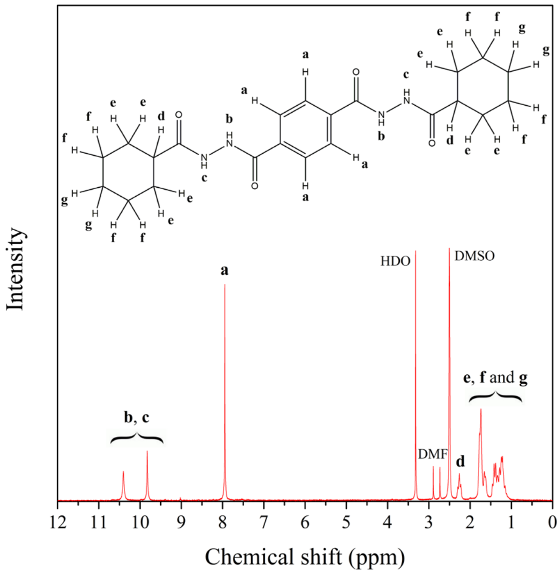


Fig. 1 ^{1}H-NMR spectrum of the synthesis product

Table 2 Chemical shift and integral values of the hydrogen atoms of the molecule

Letter of H atom	Chemical shift (ppm)	Integral
a	7.95	2.02
b and *c*	9.83	0.96
	10.41	0.91
d	2.26	0.99
e, *f* and *g*	1-2	10.11

3.2 Thermal properties of the synthesis product

A nucleating agent has to fulfill many criteria, among which we have to highlight three. The nucleating agent has to have a higher melting point than the polymer, so that it can be present as a heterogeneous surface when the crystallization of the polymer starts. The nucleating agent also has to be inert and chemically stable [16]. We determined the melting point and the decomposition temperature of the nucleating agent using simultaneous thermal analysis (STA). In Fig. 2 we present the heat flow (black line) and the mass (red line) as functions of the temperature. In the heat flow curve an endothermic peak appears around 343 °C, which can be identified as the melting point (T_{mp}) of the material. This value is approximately 180 °C higher than the melting point of the polymer, thus the requirement concerning the melting point of the additive is fulfilled. The decomposition temperature can be determined from the curve representing the mass loss. To characterize the decomposition of the material, we chose the temperature belonging to the 5% mass loss ($T_{5\%}$), which is the value generally used in thermoanalytics to characterize the decomposition of a material. The value of $T_{5\%}$ is 327 °C, which is much higher than 230 °C, the highest processing temperature. We can conclude that the material satisfied the abovementioned criteria, thus it was worth to investigate from the viewpoint of nucleating efficiency.

3.3 Nucleating efficiency

The efficiency of a nucleating agent is generally characterized by the peak temperature of crystallization (T_{cp}) measured on the samples nucleated with the nucleating agent in question. The T_{cp} values, together with the heat of crystallization values (ΔH_c) are present in Fig. 3. Both the T_{cp} and the ΔH_c values increase rapidly in the smaller concentrations and reach a plateau at a nucleating agent content around 300 ppm. This trend is characteristic for the conventional non-soluble nucleating agents. In the effective nucleating agent content range (above 300 ppm) the T_{cp} values are increased by almost 10 °C, which is nearly similar to the efficiency of the commercial nucleating agents [16, 31]. We should note here, however, that the nucleating efficiency can depend slightly on the molecular structure of the polymer in which it is used [32]. The increase of the ΔH_c values means that the crystallinity of the polymer increases in the presence of DCTDH. We can conclude that DCTDH is a conventional non-soluble nucleating agent in iPP with a good nucleating efficiency.

The melting curves registered during the second heating run of the samples nucleated with DCTDH are shown in Fig. 4. The melting peaks around 165 °C belong to the melting of the α-modification of iPP. The absence of another peak around 155 °C proves that the investigated compound is selective for the α-modification, in other words, DCTDH is an α-nucleator. A slight increase in the T_{mp} values is observable, respective to the T_{mp} value of the non-nucleated

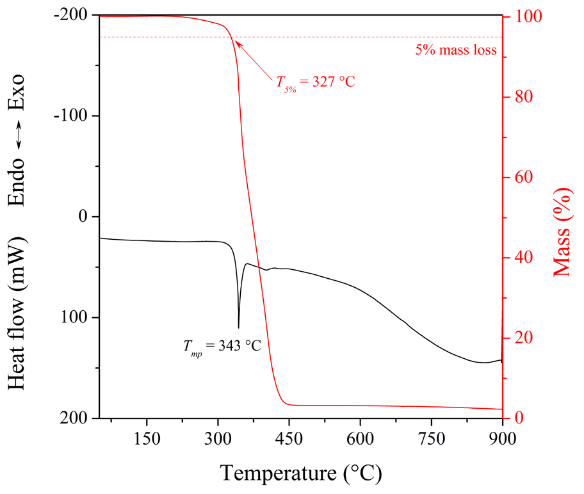


Fig. 2 Heat flow (black line) and mass (red line) as functions of the temperature in the case of the synthesis product

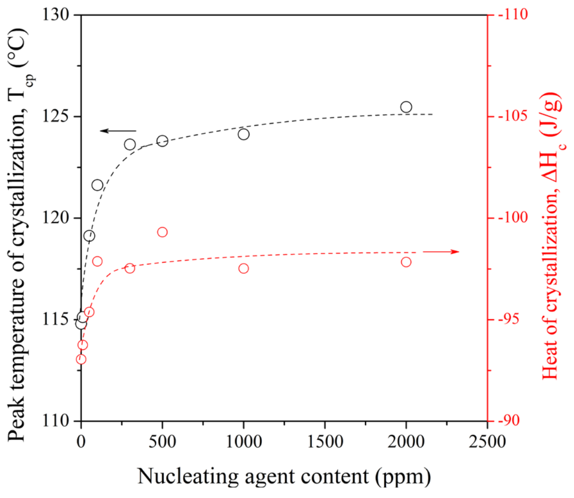


Fig. 3 Peak temperature of crystallization (black circles) and heat of crystallization (red circles) of samples nucleated with DCTDH

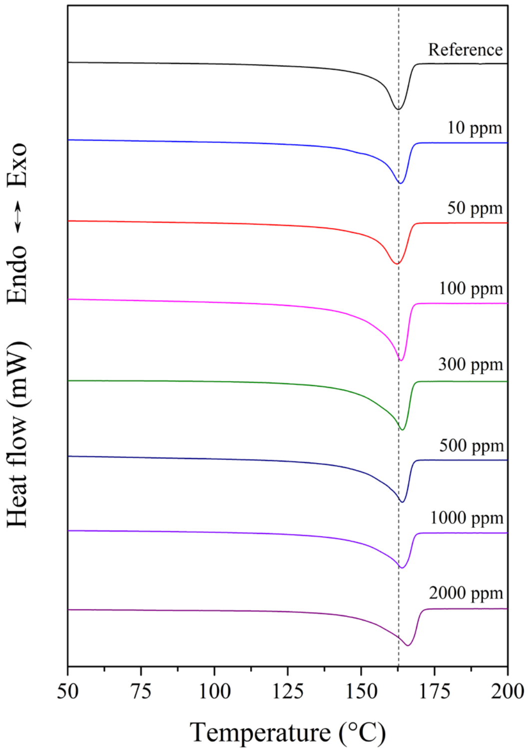


Fig. 4 Melting curves of the samples nucleated with DCTDH. The dashed line helps to see the increase of the T_{mp} values respective to the non-nucleated reference sample

reference sample. In the presence of the nucleating agent, as a result of the elevated crystallization temperature, a more perfect lamellar structure develops. With the increasing thickness of the lamellae T_{mp} values increase, as well.

3.4 Crystalline structure of the nucleated samples

The effect of DCTDH on the crystalline structure of iPP is presented in Fig. 5, on the example of the sample containing 500 ppm DCTDH. Only the left part of the sample is nucleated, the right part of the sample is neat polymer. The crystallization temperature (T_c) was 140 °C, the pictures were taken at different stages of the crystallization process. The micrograph presented in Fig. 5 (a) was taken at the beginning of the process (t_c = 0 min), when the sample was completely in molten state. In Fig. 5 (b) it is visible, that the nucleated part of the sample started to crystallize only after 1 minutes. After 30 minutes (Fig. 5 (c)) the nucleated part of the sample was completely crystallized, while only a few spherulites appeared on the non-nucleated part. At the boundary of the nucleated and the neat polymer a transcrystalline layer developed. After 90 minutes (Fig. 5 (d)) the non-nucleated part of the sample was still not completely crystallized, fewer but much larger spherulites developed in that area. The boundary

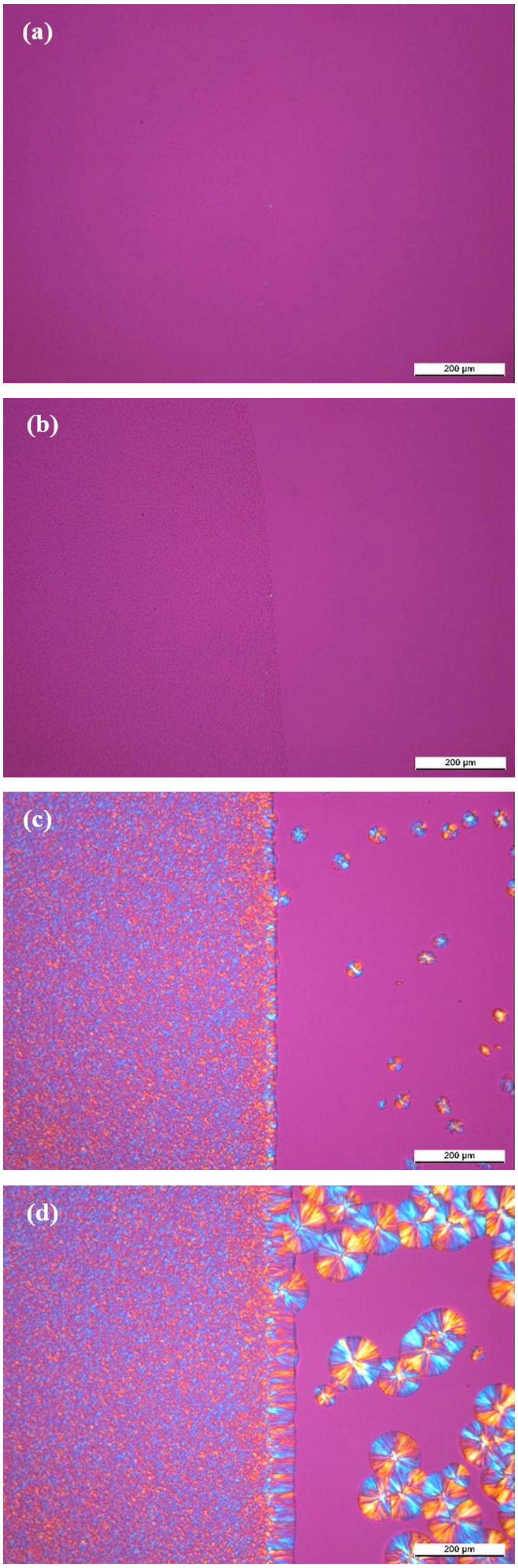


Fig. 5 PLM micrographs taken during the isothermal cyrstallization of iPP at 140 °C for (a) 0 min, (b) 1 min, (c) 30 min and (d) 90 min. The left part of the sample is nucleated with 500 ppm DCTDH, the right part of the sample is non-nucleated

of the two parts of the sample remained constant and stable during the whole process of the crystallization. This corroborates our conclusion made after the calorimetric measurements, that DCTDH is not (or only in a negligible extent) soluble in the polymer melt. In the left part of the sample the nucleus density was larger, thus a lot more, but smaller sized spherulites developed, than in the neat polymer. The structure developed in the nucleated part of the sample is called "microspherulitic structure", as the size of the spherulites is in the micrometer range, and the size distribution of the spherulites is more homogeneous, than in the non-nucleated polymer.

3.5 Mechanical properties

The change in the crystalline structure caused by the presence of a nucleating agent leads to changes in the properties important from the viewpoint of application. To characterize the mechanical properties of the samples nucleated with DCTDH, we performed standard tensile and impact resistance tests on them. We show the tensile modulus as a function of the DCTDH content in Fig. 6. In the range of smaller concentrations there is no considerable effect of the nucleating agent, however, in the effective concentration range (above 300 ppm) the stiffness of the polymer increses. As we mentioned in the *Introduction* part, according to the literature [18], with increasing T_{cp} the tensile modulus increases, thus this change of the stiffness corresponds to our expectations considering the results of the DSC measurements.

Other main characteristics of a polymer are the stress and the tensile strain measured at the yield point. These properties are present in Fig. 7 as functions of the DCTDH content. With increasing concentration, the yield stress increases, accordingly, the strain decreases. We can conclude that the investigated compound can enhance both the tensile modulus and the yield stress of the polymer, thus this nucleating agent affect the properties similarly to the previous conventional non-soluble nucleating agents, however, we have to note that the saturation point is at lower concentration. Accordingly, less nucleating agent is necessary to obtain the same advantageous mechanical properties, which might be the main advantage of this additive. This is more visible in Fig. 8, where the yield stress is presented as a function of the tensile modulus. As the black arrow shows, with increasing DCTDH contents the datapoints move towards the higher tensile modulus and yield stress region of the diagram.

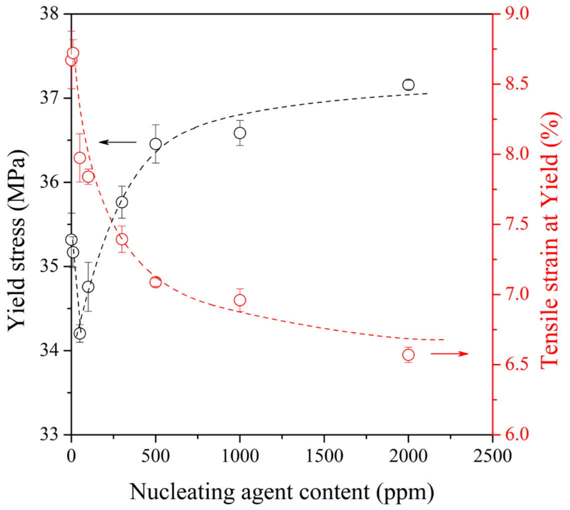


Fig. 7 Yield stress and tensile strain at yield as functions of DCTDH content

Beside the tensile properties, impact resistance is also an important feature of the nucleated polymers. Fig. 9 shows the dependence of the impact resistance on the DCTDH content. The impact resistance does not change considerably, and all values are almost within the scattering of the data. However, a slight increase can be seen below the saturation

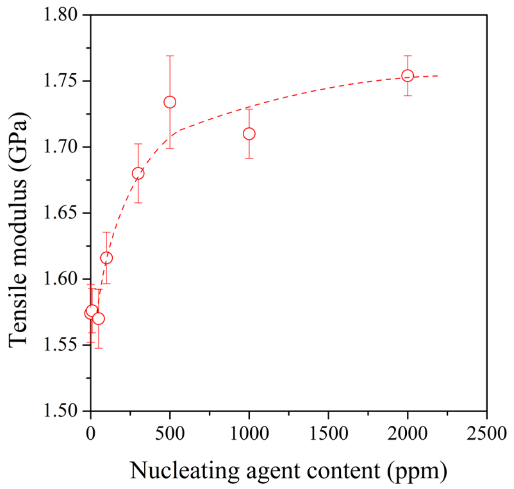


Fig. 6 Tensile modulus as a function of DCTDH content

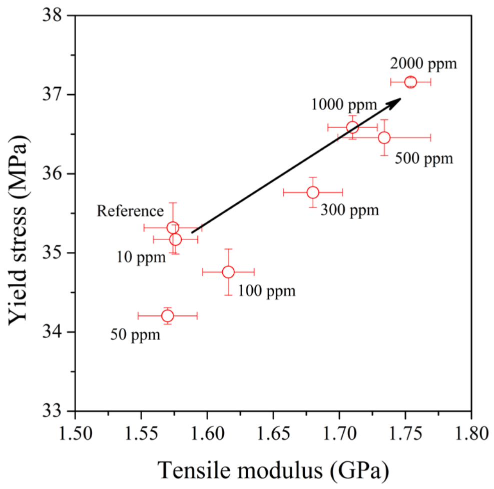


Fig. 8 Yield stress as a function of tensile modulus

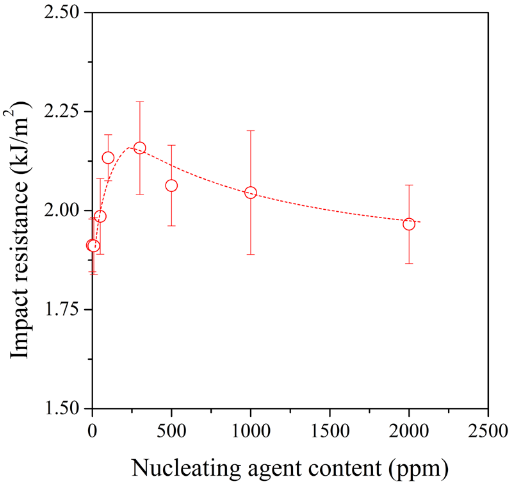


Fig. 9 Impact resistance as a function of DCTDH content

concentration because the microspherulitic structure is more homogeneous and contains less defects, which could be the initial point of crack propagation. Consequently, the impact resistance increases a little at low concentrations. However, the samples become stiffer and the yield strength increases above 300 ppm of nucleating agent content, which is accompanied by slight decrease of impact resistance. This corresponds to our expectations, as the same tendency is observable in the case of a polymer nucleated with non-soluble nucleating agents [31]. Considering all the mechanical properties, we can conclude that 300 ppm is the optimal value of the DCTDH content, as the stiffness, the yield stress and the impact resistance are increased simultaneously around this DCTDH content.

4 Conclusion

The purpose of this work was to synthesize *N,N'*-dicyclohexyl terephthalic dihydrazide (DCTDH), and investigate it from the viewpoint of applicability as a nucleating agent in isotactic polypropylene (iPP). The synthesis product was thermally stable at the temperature of polymer processing, and had a higher melting point than the polymer, thus it meets the requirements for nucleating agents because it is capable to form heterogeneous surfaces in the polymer melt. According to the calorimetric measurements, DCTDH is a conventional, non-soluble α-nucleating agent of iPP and it is effective even in 300 ppm concentration. Its efficiency is reasonably good since it shifts the peak temperature of crystallization by 10 °C compared to the non-nucleated sample. These findings are corroborated also by the microscopic studies. In the presence of the nucleating agent the crystallization of the polymer takes much less time, and owing to the higher nucleus density, a lot more, but smaller spherulites develop and a microcrystalline structure is formed in its presence. Tensile modulus also increases and the impact resistance changes slightly in the nucleated samples, as well. As a summary, we can state that the investigated novel nucleating agent is efficient in iPP and has similar effect compared to the already existing nucleating agents with high efficiency, but DCTDH possesses the high efficiency even at 300 ppm nucleating agent content. This concentration is much smaller than the necessary concentration of the conventional non-soluble nucleating agents.

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