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Novel nucleating agents for polypropylene and modifier of its physical-mechanical properties

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ABSTRACT

In this paper, we demonstrate that dicalcium salt of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) can be used as a component of nucleating agents for isotactic polypropylene (iPP) - one of the most widely used commercial polymers. Based on dicalcium HEDP salt novel nucleators show high efficiency in the nucleation of iPP α -crystals. At a concentration of 0.25 wt% the nucleators demonstrate an increase in crystallinity (+ 1.5 % in composition with calcium stearate and + 4% - with zinc stearate). When the dicalcium HEDP salt based nucleator is added to the iPP, the flexural modulus increases by 8–12 %. Assumptions are suggested about the mechanism of action of the new nucleator, based on its core-shell structure. The main component of the nucleating agent, the dicalcium HEDP salt, is synthesized by the one-step reaction in a non-toxic aqueous medium with commercially available reagents. The synthetic protocol gives a finely friable product that does not require further grinding. The synthesis is cheap and environmentally friendly since only deionized water is used as a solvent.

1. Introduction

Isotactic polypropylene (iPP) is one of the most common commercially available polymers due to its relatively high strength and low cost. The method of modifying base polymers to increase strength and give special properties to products is the introduction of various types of organic or inorganic fillers [1–4]. The combination of moderately slow crystal growth at large undercooling together with the practical absence of sporadic nucleation makes iPP an ideal material for controlled nucleation [5].

Historically, polymers have a long time been divided into semi-crystalline and amorphous [6]. After crystallinity was determined as an essential factor in the thermomechanical behavior of such important bulk polymers as polyethylene, polypropylene, and most polyamides, interest arose in crystallization control methods both in industry and research. The crystallinity of the iPP is crucial for achieving the final physical and mechanical properties [7–10]. The degree of crystallinity of iPP can be increased as a result of: (a) inducing shear (melt orientation in the stream during casting) [11,12], (b) applying cooling temperature

gradient [1], (c) recrystallization of the melt of iPP chains (self-nucleation of polymer chains) [13], or administration of specific nucleating agents [14–16].

Three crystallographic modifications are known in which iPP can crystallize: α , β , and γ [17–19]. The α - and β -phases are probably the most common and technologically interesting crystalline forms of iPP [20]. For iPP homopolymers, the α -phase is more thermodynamically stable and has a monoclinic crystal structure [2]. In contrast, the β -phase is usually obtained almost only by specific nucleation [10,21–23]. For this reason, a seed addition is required to obtain any significant amount of the β -form, while many β -nucleators also contribute to the formation of the α -phase [2,17,24].

Both organic compounds (polycyclic aromatic hydrocarbons, organic acids/salts, and amides [25], benzoic acid salts [26], hydrazide compounds [27], various organic pigments) and inorganic compounds (salts, oxides, e.g., CaCO_3 [28,29], talc [30], and Al_2O_3) were used as nucleators for iPP [31]. The disadvantage of organic nucleators is that the technology of their producing is not environmentally friendly green, which usually include several stages of organic synthesis using specialty

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compounds, as well as flammable and toxic solvents, mineral acids. In this case, one stage of the synthesis can take up to three days, and the resulting product requires cleaning, vacuum drying, following grinding, and permanent hygroscopicity control to prevent slumping.

Abundant and cheap inorganic fillers (talc, wollastonite, silica, mica, kaolin, diatomite, and calcium carbonate) are still the most industrially used inorganic fillers for polypropylene [32]. In addition to a general improvement in mechanical properties and fire resistance, reducing warpage and shrinkage, they induce the formation of a crystalline structure in PP, which leads to the desired improvement in mechanical properties. However, inorganic nucleators usually exert an effect at high concentrations (up to 30 wt%) [28], which makes a detrimental contribution to the plasticity of the polymer (the transition from plastic to brittle fracture) and assumes color to polypropylene, as a result of which it is impossible to obtain a transparent colorless plastic.

As noted above, among β -nucleators for PP, a number of salts of dicarboxylic acids (pimelic, suberic etc.) were previously used [33]. However, there is controversial information about the ability of the calcium salts of these acids to act as β -nucleators [34–36]. Meanwhile, β -crystallization of PP is also promoted by calcium salts of malonic acid [37], phthalic, terephthalic, pyromellitic acids [38,39] and pimelic acid [40,41].

Among the metal dicarboxylic acid salts the most industrially used and effective iPP α nucleators are the Milliken Chemical products: Hyperform^(TM) HPN-20E [42–44] (cis-1,2-cyclohexanedicarboxylic acid calcium salt), and Hyperform^(TM) HPN-68L [45,46] (bicyclo[2.2.1]heptane-2,3-dicarboxylic acid disodium salt). In iPP, these nucleating agents exhibit a very strong and specific crystalline orientation, which leads to useful physical properties [46], low and balanced shrinkage, and excellent impact resistance. The Hyperform^(TM) HPN-20E nucleating additive was chosen as the reference in our work.

The use of metal salts with noncarboxylic acids as nucleators for PP is practically unknown except sodium 2,2'-methylene-bis-(4,6-di-tert-butylphenyl) phosphate (Adekastab NA-11^(TM) by Asahi Denka Kogyo KK, Japan) and hydroxy aluminium bis(2,4,8,10-tetra-trans-butyl-6-hydroxy-12H-dibenzo[d,g][1.3.2]dioxaphosphocin-6-oxide; main component (Adekastab NA-21^(TM) by Asahi Denka Kogyo KK, Japan). The α -phase nucleating agent mainly affects crystallization at high rates of cooling and minimize crystallization halftime. Only minor increase of the crystallization temperature by few degrees is observed in presence of α -nucleating agent [47].

Earlier we investigated compounds of a number of metals with 1-hydroxyethane-1,1-diphosphonic acid (HEDP, C₂H₈O₇P₂) [48,49]. The low solubility of many metal/HEDP compounds is well-known, as well as the ability of calcium ions to form nanoscale polynuclear complexes [50–56]. With this in mind, we carried out a series of syntheses of calcium HEDP compound using various initial reagents and reaction conditions. In this work, we describe the synthesis of dicalcium HEDP salt by the reaction of HEDP with calcium carbonate and its use as an additive, affecting nucleation of iPP and its properties.

It is noteworthy that in almost all nucleation studies the samples of commercial PP that contain certain additives (antioxidants, nucleators, clarifying agents, etc.) are used. In the work, we also used polypropylene powder from the reactor as a polymer matrix to evaluate the "pure" effect of all additives, including nucleators and to calculate the efficiency of nucleating agents, and these results are given in the supplementary information.

2. Experimental part

2.1. Materials

All the experiments used isotactic polypropylene homopolymer (iPP) (1262R brand) manufactured by PJSC "Nizhnekamskneftekhim" (Russia). The iPP used is a base polymer from the reactor, without additives with a melt flow of 18 g/10 min (230 °C, 2.16 kg). 1-

Hydroxyethane-1,1-diphosphonic acid (HEDP) and calcium carbonate (CaCO₃) were supplied by "TatKhimProduct" LLC (Russia). Commercial α -nucleating agent Hyperform HPN-20E manufactured by the Milliken Chemical was used in some experiments. All iPP samples contain an antioxidant system Irganox B 225 (BASF). Calcium stearate ([CH₃(CH₂)₁₆COO]₂Ca) and zinc stearate ([CH₃(CH₂)₁₆COO]₂Zn) were purchased from Sigma-Aldrich. The chemicals were used without further purification. All other reagents and solvents were purchased from commercial suppliers and used as received.

2.2. Synthesis and characterization of dicalcium HEDP salt

HEDP (H₄L) forms with calcium two stoichiometric insoluble salts: CaH₂L and Ca₂L, the last being much less soluble [54,55]. In preliminary experiments we tried several calcium sources (hydroxide, chloride, carbonate) and revealed that the best result for further using the product in experiments with iPP was achieved with calcium carbonate. In order to synthesize the dicalcium salt Ca₂L 10.7685 g (0.0523 mol) HEDP were dissolved in 50 cm³ of distilled water and 9.5883 g (0.0958 mol) of calcium carbonate were placed in another beaker with 50 cm³ of distilled water and thoroughly stirred to obtain a suspension. Thus, the slight excess of HEDP relatively to 2:1 stoichiometry of dicalcium salt was taken to full transformation of calcium carbonate. According to Deluchat et al. [57] dicalcium HEDP salt exists in pH range 6–9. Regarding this, an HEDP solution was added to calcium carbonate suspension to avoid potential formation of traces of monocalcium salt, at pH range 5–7 [57]. The HEDP solution was added quickly to prepared calcium carbonate suspension under constant stirring. After all the HEDP solution was added, the supernatant had pH close to neutral, thus all the acid was out. The precipitate was separated and washed several times with distilled water using Buchner funnel vacuum filtration in order to get rid of traces of HEDP monocalcium salt. After drying under air product mass was 18.3903 g. Synthesized sample after drying in the air is a fine-dispersed and friable powder, thus it can be used for further processing without prior grinding.

The sample was characterized by various methods to identify the resulting substance and to analyze the synthesis reproducibility. The thermogravimetric analysis (TGA) of the sample was carried out by a NETZSCH TG 209 F1 under a nitrogen flow rate of 60 ml/min from 25 °C to 350 °C with a heating rate of 10 °C/min. The FT-IR spectra of these salts were recorded in the range 4000–400 cm⁻¹ using Perkin Elmer FT-IR Frontier spectrophotometer with the KBr pellet technique. The diffraction spectra of the samples were recorded on a D2 Phaser diffractometer (Bruker Axs GmbH) with a standard Bragg-Brentano [θ - θ] geometry for reflection and a goniometer radius of 141.4 mm. The morphology of the sample was studied using the high-resolution scanning electron microscope Zeiss Ultra-Plus FEG-SEM. To determine the hygroscopicity, the samples were previously dried in a drying chamber at 130 °C for 2 h. After drying, the samples were weighed and placed in a desiccator in the lower part of which distilled water was poured. The desiccator was placed in the climatic chamber Hyde Science and Technology LG-XD110 G at 25 °C. The test was carried out for 192 h; the increase of the mass of samples was recorded every 24 h.

2.3. Preparation of nucleators

To reduce the hygroscopicity the HEDP dicalcium salt was mixed with calcium or zinc stearates in a ratio of 70 wt% Ca₂L salt to 30 wt% stearate. The stearates also exhibit properties of acid scavengers present within polypropylene formulations and protectors, stabilizing additives from catalyst residue attack. The components were mixed using planetary ball mill Retsch PM100 in stainless steel grinding jar with a volume of 125 ml with 3 stainless steel balls of 10 mm diameter. The grinding jar was filled with 1/3 vol components for better mixing. Mixing was performed at 100 rpm for 10 min; the slow rotation was chosen to ensure mixing without grinding the particles. Nucleator samples were specified

as: NA-C (blend of dicalcium HEDP salt with calcium stearate), and NA-Z (blend of dicalcium HEDP salt with zinc stearate).

2.4. Polypropylene samples preparation

Polypropylene and nucleating agent were compounded in LabTech Engineering Scientific LTE 16–40 co-rotating twin-screw extruder with a high shear screw (diameter 16 mm, L:D - 40:1) configuration for better mixing. The screws contain 4 kneading blocks with a 30° and 60° stagger angle. The processing temperature profile (feed zone 190 °C, and from mixing zone to die zone 200 °C) was selected such as to ensure proper melt viscosity for the mixing while at the same time minimizing degradation of both the polymer and fillers. Before melt processing, all the components were dried at 80 °C for 1 h. During extrusion processing, a feed rate was maintained 70 rpm, melt-pressure 30–35 bar, degassing of volatile substances with a vacuum pressure of 0.6 bar. The extruded strands were cooled stretching through a water bath, followed by vacuum drying. Then the strands were granulated, the size of the granules was 2.75 mm, the feed rate of the strand into the granulator was 6–7 m/min. To prevent thermo-oxidative degradation, the antioxidant Irganox B 225 was administrated into the melt. All formulations of filled polypropylene are given in Table 1.

2.5. Characterization of polypropylene modified by nucleating agents

Polypropylene nucleation experiments were performed using differential scanning calorimetry, using NETZSCH DSC 214 Polyma instrument. The samples of 7.0 ± 0.5 mg weight were cut from the granules and placed in aluminum crucibles (25 μ l) with lids. The crystallization behavior of the polymers was characterized by a heating-cooling-heating thermal ramp. The samples were heated from 25 to 230 °C, annealed in the melt for 3 min, cooled down to 50 °C again, and finally melted by bringing them to 230 °C. All heating and cooling ramps were performed at a rate of 10 °C/min and a nitrogen flow rate of 60 ml/min. The degree of crystallinity was calculated from the melting enthalpy using the formula (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} * 100\% \quad (1)$$

where ΔH_m is the measured heat of melting, while ΔH_m^0 is the heat of melting of fully crystalline polypropylene ($\Delta H_m^0 = 209$ J/g). [58,59]

Wide-angle X-ray diffraction experiment was conducted with a Bruker D2 Phaser with standard Bragg-Brentano (θ - θ) reflection geometry and a goniometer radius of 141.4 mm. Polypropylene samples for WAXD recording 1 mm thick and 25 mm in diameter were prepared by hot pressing between steel plates at a temperature of 200 °C, after which the samples were cooled at a rate of 10 K / min, the temperature and cooling rate were set by a Peltier element.

The samples preparation for mechanical tests was performed by injection molding press Ray-Ran TSMP. The polymer was melted in an injection cylinder at a 200 °C for 5 min, and then injected into the standard mold at 60 °C. Determination of flexural properties of polypropylene samples was carried out with universal testing machine Instron 5882, according to the ISO 178 standard method with a test speed of 2 mm/min. Five specimens of each composite were tested to obtain

Table 1
Formulations of polypropylene modified by nucleating agents.

Samples	Nucleating agent type	Content (wt%)	
		Nucleating agent	Antioxidant
PP-1	–	–	0.30
PP-2	Hyperform HPN-20E	0.25	0.30
PP-3	NA-C (Ca_2 HEDP/ Ca Stearate)	0.25	0.30
PP-4	NA-Z (Ca_2 HEDP/ Zn Stearate)	0.25	0.30

the standard deviation.

Determination of Izod impact strength was measured with the pendulum impact tester TSKM-50 from the "Test Systems" (Russia), according to the ISO 180 standard method. The hammer strike energy was 7.5 J. Five samples were measured for each loading, and the average values were presented. Samples with V-notches of type b were used for the test.

3. Results and discussions

3.1. Characterization of dicalcium HEDP salt

Fig. 1 shows TG and DSC data for the dicalcium HEDP salt. The DSC signal does not deviate from the baseline at 140–150 °C, so we assume the sample loses all the water mass upon heating up to these temperatures. At the re-heating of the sample, no heat effect is observed. Mass loss in the TG plot (Fig. 1a) due to heating up to 130 and 150 °C from the starting temperature is 29.42 and 30.62 % respectively. The peak observed on the DSC curve (Fig. 1b) was attributed to water release. Temperatures of start, peak, and end of the process are 83.5, 106.8, and 117.7 °C respectively.

Suggesting that the dicalcium HEDP salt forms according to the process (2), the number of water molecules in the product sample (x) can be calculated by Eq. (3):

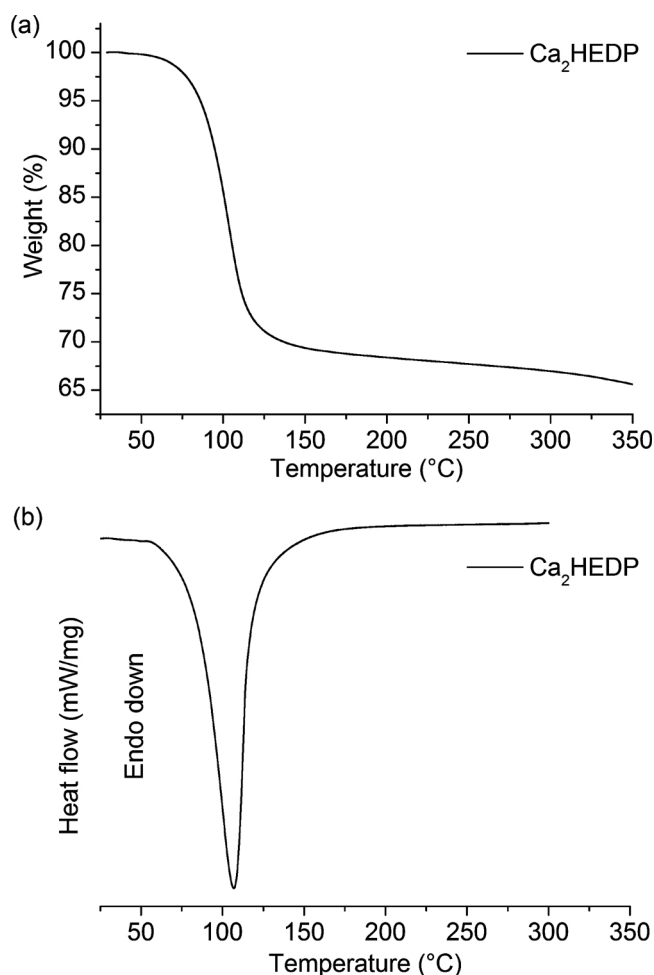
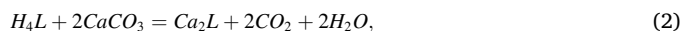


Fig. 1. The mass loss (a) and DSC (b) curves of the temperature for dicalcium HEDP salt.

$$\frac{x \cdot M(H_2O)}{M(Ca_2HEDP) + x \cdot M(H_2O)} \cdot 100\% = \omega, \% \quad (3)$$

where $M(Ca_2HEDP) = 268.13$ g/mole, $M(H_2O) = 18.02$ g/mole – molar masses, ω – mass loss in %. The calculated number of water molecules is 6.6 for 30.62 % mass loss and heating up to 150 °C, thus synthesized product can be presented as $Ca_2HEDP \cdot 6.6H_2O$ with 91 % product yield. However, based on experimental data, it does not seem possible to determine if it was crystallization water.

Since the polypropylene is filled at processing temperature up to 230 °C, nucleating agent should be thermally stable up to processing temperatures. Thus, the water must be eliminated from the nucleating agent. Based on TG and DSC data (Fig. 1), temperature of 130 °C was chosen for thermal treatment of the nucleating agent before administration into iPP.

The synthesized compound has low hygroscopicity – exposure of the sample to saturated aqueous vapor at 25 °C for 72 h resulted in a 10 % mass increase. Further exposure kept mass increase almost constant: at total exposure for 190 h, only 11 % mass increase was observed. The sample is still crumbly after aqueous vapor absorbance. Its particles greatly stick to polypropylene granules, which must result in more even distribution of the additive in the polymeric bulk.

Fig. 2 shows the FT-IR spectra of the obtained dicalcium HEDP salt and the reagents.

A significant difference of the salt FT-IR spectrum relative to the spectra of the reagents is observed, especially in the 900–1100 cm^{-1} region, where stretching and deformation P–O(H) or POH– vibrations in HEDP molecule appear [60]. They are dramatically changed when the HEDP protons are substituted by calcium ions. Basing on striking changes of (I) intensive peak 1440 cm^{-1} and two peaks at 871 and 712 cm^{-1} , corresponding to asymmetric C–O stretching vibrations and to the O–CO– bending (in-plane deformation) in calcium carbonate [61]; (II) wide HEDP absorbance peak in ≈ 2200 –3000 cm^{-1} region, one may propose full conversion of initial reactants.

However, further XRD investigation (Fig. 3) of the synthesized

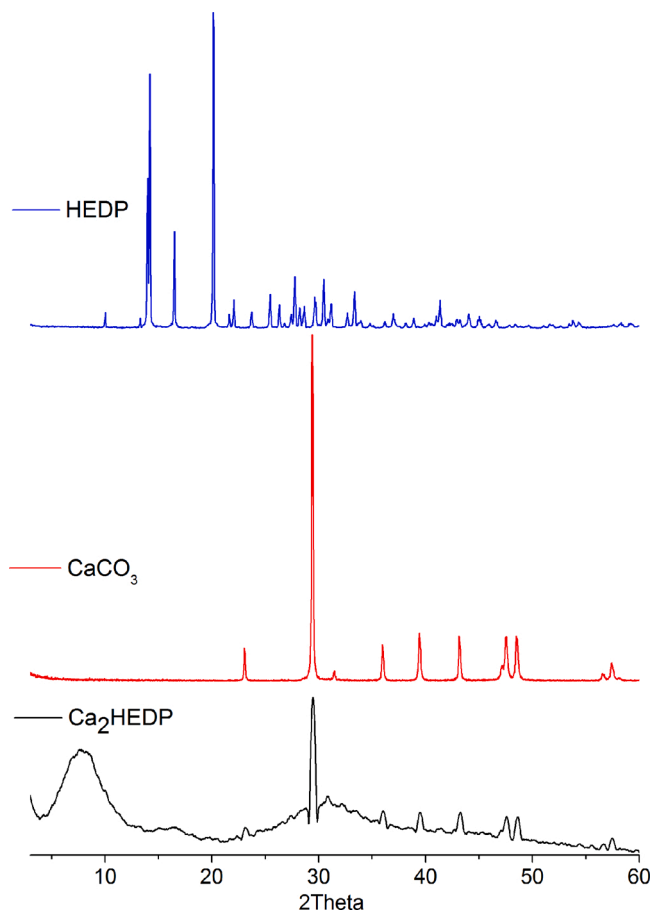


Fig. 3. XRD spectra of HEDP, calcium carbonate, and dicalcium HEDP salt.

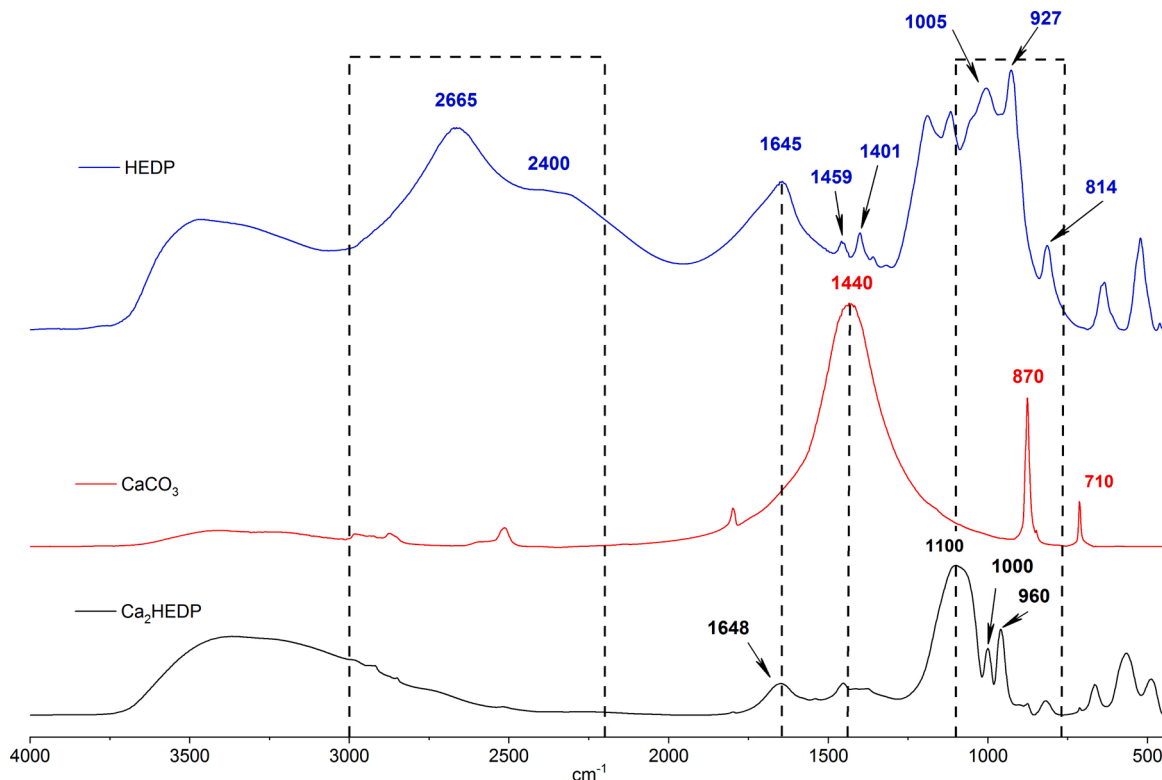


Fig. 2. FT-IR spectra of HEDP, calcium carbonate, and dicalcium HEDP salt.

dicalcium HEDP salt and initial reagents cast a doubt the 100 % reaction progress.

According to the XRD spectrum the calcium carbonate used in the synthesis is in the form of calcite. In the Ca_2HEDP spectrum a wide signal corresponding to the amorphous phase and bands characteristic for calcite are observed and there are no signals corresponding to HEDP. In order to comply the IR and XRD data, we hypothesized that in this case the core-shell particles are formed. During the reaction (2) the dicalcium HEDP salt is formed on the surface of the calcite particles as amorphous phase, and prevents the complete dissolution of calcium carbonate particles, which are saved as the calcite cores. Thus, the addition of diluted HCl leads to a very weak gas evolution from behind the protective layer of dicalcium HEDP salt on the surface of CaCO_3 . Calcium carbonate core inside the particle cannot be detected using FT-IR due to the low penetration power of infrared radiation through the Ca_2HEDP salt amorphous shell.

The nano- CaCO_3 with the shell of pimelic acid is known to use as a β -nucleating agent for iPP [62]. Also is known the invention where the β -nucleating agent comprises a particulate natural mineral solid support comprising a compound of a IUPAC Group 2 metal, and on the surface of the particulate mineral solid support a salt of a dicarboxylic acid, wherein the dicarboxylic acid has from 7 to 10 carbon atoms, and a dispersing agent [63].

More thorough information on particle size and chemical composition was obtained with HR SEM data. Fig. 4a-b present crystal cross-section: Fig. 4a shows a scan made with InLens secondary electrons detector, while Fig. 4b shows a scan made with a backscattered electron detector (ESB). Brightness is higher for heavier atoms, so the brighter phase corresponds to phosphorus-containing compounds. One can see in Fig. 4c-d that the certain particle consists of thin phosphorous-based phase and internal phase of, apparently, calcium carbonate.

Taking into account the synthesis conditions – the fast addition of HEDP to calcium carbonate suspension – this approves our hypothesis that the reaction is stopped on the surface of the calcite as a result of formation of a layer of dicalcium HEDP salt preventing the complete dissolution of calcite particle. In some cases, calcite particles in the

analyzed sample were free of such surface layer, e.g. if they were aggregated at the start of the reaction and disaggregated during further processing. The surface borders of such “naked” particles are sometimes visible on the cross-section (Fig. 4c, d; signal SE2 – detector outside of the lens and registering secondary electrons, signal InLens - detector inside of the lens and registering secondary electrons, signal ESB – detector, registering backscattering electrons).

3.2. Non-isothermal crystallization of polypropylene

Fig. 5 shows diagrams of non-isothermal crystallization of neat and nucleator-added iPP. Related non-isothermal crystallization parameters, including crystallization peak temperature (T_c), the temperature crystallization onset (T_{oc}), melting enthalpy (ΔH_m), and degree of crystallinity (X_c) are provided in Table 2.

The temperatures of start, peak, and end of the melting process do not change significantly after nucleator addition. DSC melting curves has a peak corresponding to the melting of α -crystallites [64]. Nucleators injected to polypropylene shift crystallization to the higher temperatures regime (Table 2). All the nucleators reported here shift crystallization to the higher temperatures. Dicalcium HEDP salt is inferior to Hyperform HPN-20E in the efficiency of shifting the polypropylene crystallization temperature towards higher values. Nevertheless, it demonstrates larger enhance of crystallinity degree: +1.5 % (NA-C) and +3.9 % (NA-Z), Hyperform +3.5 %.

However, in view of HEDP large-scale commercial production, one can approve the competitiveness of HEDP-based nucleators and Hyperform HPN-20E taking into account the price/quality ratio.

Fig. 6 shows the diffraction diagrams obtained during the experiment, in which the characteristic intensities of the (110), (040) and (130) reflections of α -phase, respectively, and their corresponding diffraction angles are $2\theta = 14.1^\circ, 16.9^\circ, 18.7^\circ$, respectively [65]. In samples PP-2 and PP-4, the intensity of peak 040 is significantly increased, which is a consequence of the formation of α -crystals. The presence of β -crystals (peak 300 at $2\theta = 16.0$) was not detected in the studied samples.

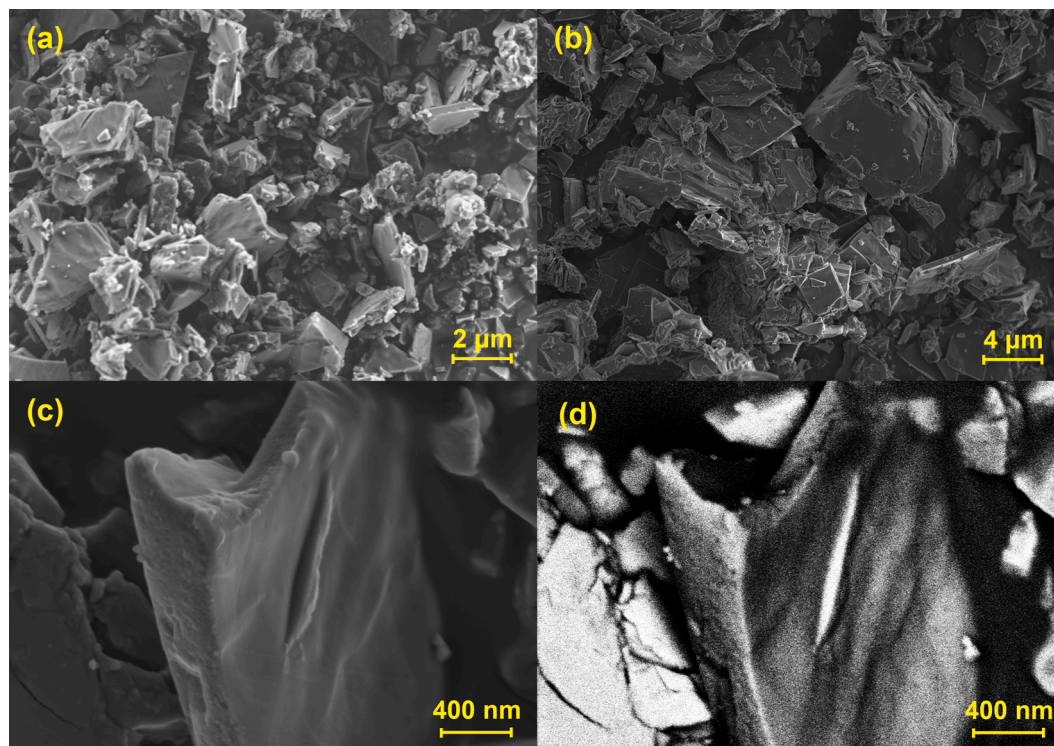


Fig. 4. SEM micrographs of dicalcium HEDP salt (a) 15 K X Signal SE2, (b) 7 K X Signal A InLens, (c) 94 K X Signal A InLens, (d) 94 K X Signal A ESB.

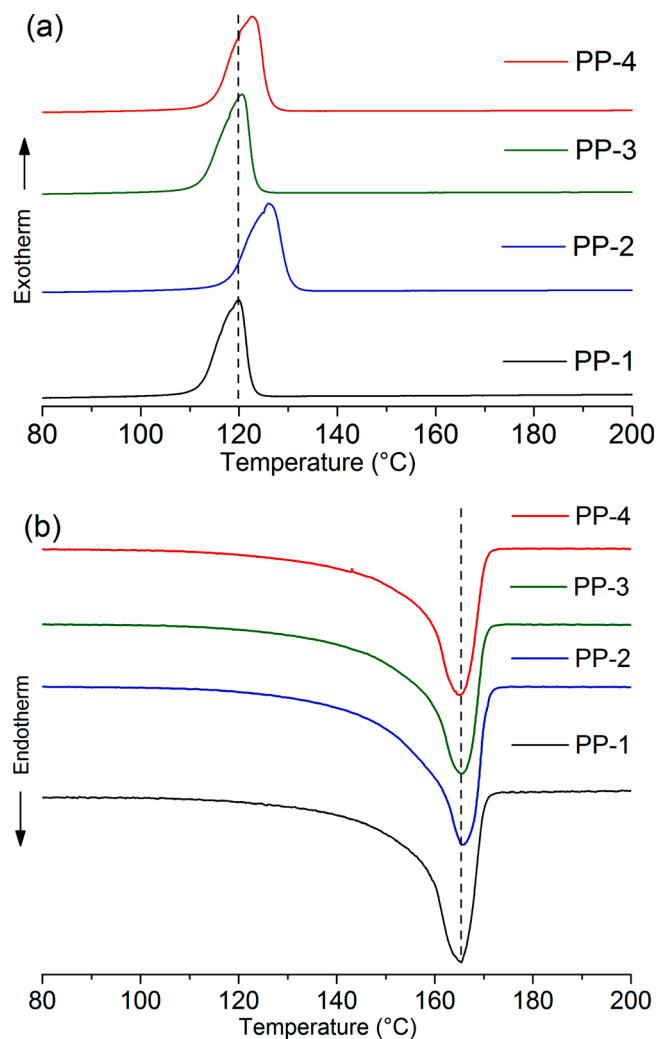


Fig. 5. The melting and crystallization curves of the DSC for iPP modified by nucleating agents: (a) crystallization curves and (b) melting curves.

Table 2
Non-isothermal crystallization parameters of iPP.

Samples	T_{oc} , °C	T_c , °C	ΔH , J/g	X_c , %
PP-1	123	120	93	45
PP-2	130	126	100	48
PP-3	120	121	96	46
PP-4	126	123	101	49

T_{oc} – the temperature crystallization onset, T_c – crystallization peak temperature, ΔH – melting enthalpy, X_c – degree of crystallinity.

3.3. Mechanical tests of polypropylene

The main goal of using nucleating agents is an improvement of mechanical characteristics of the polymer, as well as related properties like creep resistance or heat deflection temperature. A rather important contribution to the mechanical performance of polyolefins is the correlation of modulus to not only the overall crystallinity but also the lamellar thickness in the system [66,67]. Increase of polypropylene stiffness is also possible by addition of any filler – but with normally negative consequences on impact strength, transparency and surface structure. Specific nucleation agent, in contrast to that, can even improve the stiffness/impact balance and even the stiffness/optics balance [2]. Fig. 7 presents results of mechanical tests of iPP modified by nucleating agents.

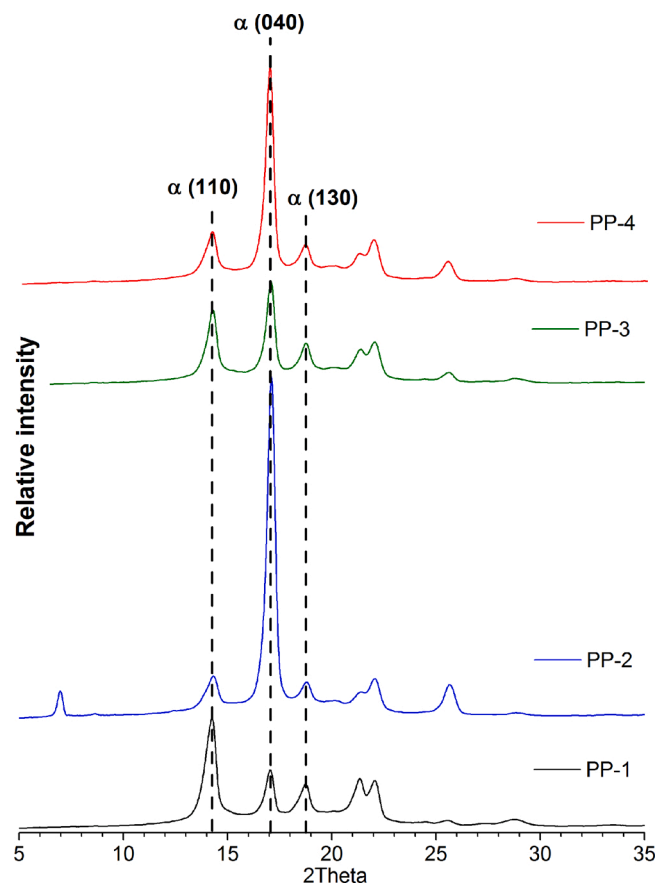


Fig. 6. X-ray diffraction diagrams of pure iPP (PP-0) and modified by nucleating agents: HPN-20E (PP-2), NA-C (PP-3), NA-Z (PP-4).

It is evident from Table 3 that introduction of commercial nucleator at iPP leads increase elastic modulus to 14 % (sample PP-2), whereas dicalcium HEDP salt yields 8% increase for composition with calcium stearate (sample PP-3), and 12 % increase – with zinc stearate (sample PP-4).

The effect of nucleating additives on elastic modulus correlates with an increase in the degree of crystallinity for all compositions. Impact strength changes with X_c insignificantly, which is attributed to the formation of α - and miss β -phase crystals due to addition of new nucleators.

Basing on the abovementioned results some ideas concerning the mechanism of action of the new nucleators can be proposed. Calcium carbonate, taking into account the possibility of obtaining its nanoscale forms, is one of the most common additives to the polymers [68]. Polymer composites containing nanoscale particles are very difficult to fabricate using classical processing techniques common to conventional plastics, due to the strong tendency of nanoparticles to agglomerate, which is difficult to overcome due to limited shear during mixing. The key issue in destroying agglomerates of calcite nanoparticles is the surface modification of these particles. In this regard, the surface of CaCO_3 particles was modified, for example, by the addition of stearic or oleic acids, or by various compatibilizing agents. [28,29,69,70]. Moreover, this procedure, which requires the use of organic solvents, is an additional step in the preparation of the modified CaCO_3 commercial product before introduction into the polymer.

In our work, we obtained the product of the interaction of calcite with HEDP, which, according to the XRD and SEM data, is actually a core-shell fine particle. In this case, the core is unreacted nanosized calcite, and the shell is formed by the amorphous phase of dicalcium HEDP salt. As a result, such particles turned out to be well protected

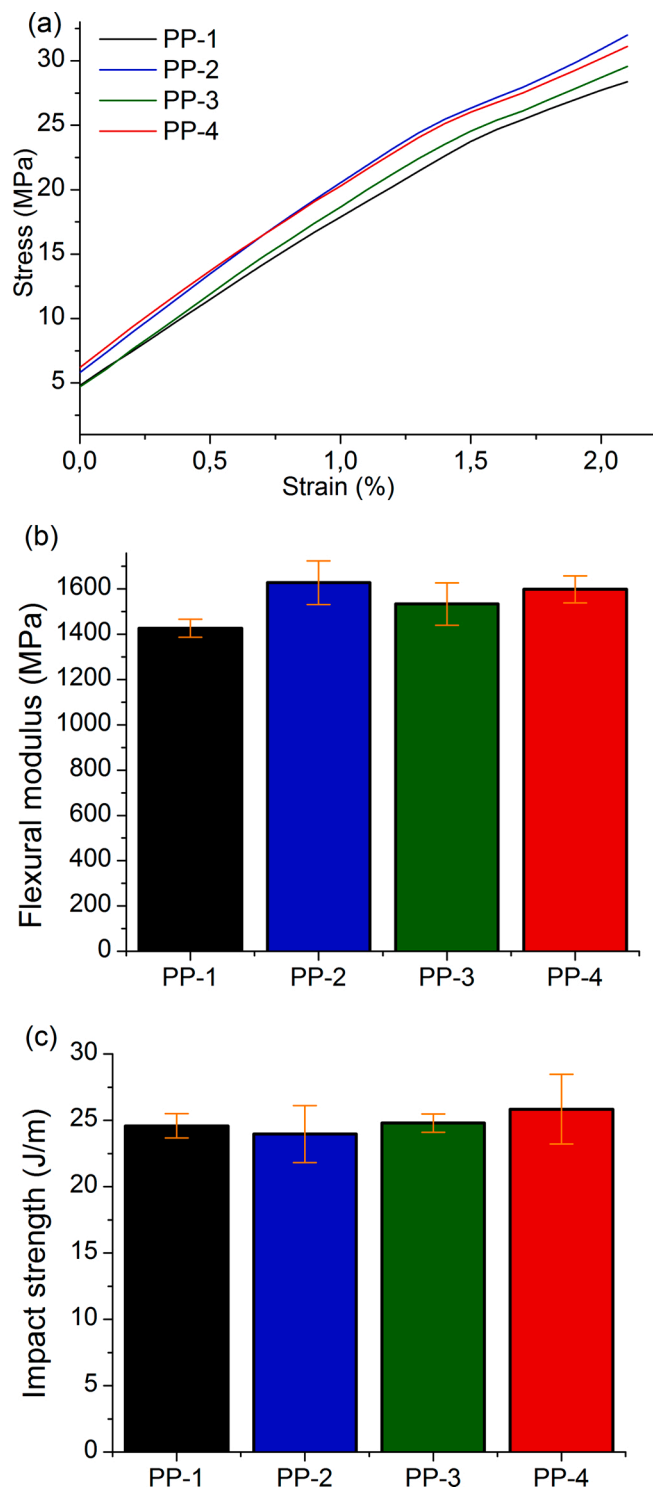


Fig. 7. Mechanical properties of iPP modified by nucleating agents: (a) Stress-strain curves of flexural tests (average for six samples of each iPP composition) and (b) Flexural modulus diagram and (c) Impact strength diagrams.

Table 3
Mechanical properties of iPP.

Samples	Flexural modulus, MPa	Strength, MPa	Impact strength, J/m
PP-1	1427 (± 40)	32.2 (± 0.9)	24.6 (± 0.9)
PP-2	1628 (± 97)	32.2 (± 0.9)	24.0 (± 2.2)
PP-3	1534 (± 94)	29.3 (± 1.2)	24.79 (± 0.7)
PP-4	1598 (± 59)	30.2 (± 0.9)	25.83 (± 2.6)

from aggregation. When the melt is cooled, they act as crystallization centers, leading to the observed effects in crystallization temperatures and crystallinity. Thus, the obtained products of the reaction between calcite and HEDP can be proposed as the basis for nucleators and modifiers of the mechanical properties of polypropylene.

4. Conclusions

Novel nucleating agents developed on the basis of the reaction between calcite and HEDP with addition of calcium stearate (NA-C) or zinc stearate (NA-Z) as an auxiliary component show good α -crystalline nucleation effect for isotactic polypropylene. Dicalcium HEDP salt is inferior to Hyperform HPN-20E in the efficiency of shifting the polypropylene crystallization temperature towards higher values. However, 0.25 wt% dicalcium HEDP salt based nucleators demonstrate larger enhance of crystallinity degree: +1.5 % (NA-C) and +4% (NA-Z).

Basing on the results of FT-IR and XRD spectroscopy, it was concluded that the reaction between HEDP and calcite was incomplete during the preparation of the dicalcium salt. Presumably the particles of the product consist of a nanocrystal calcite core and a shell of amorphous phase of dicalcium HEDP salt, which prevents the formation of large particles and agglomerates during synthesis and further processing. Formation of core-shell particles of the studied nucleator is an important aspect for obtaining stable nucleation results. The main component of nucleating additive - dicalcium HEDP salt - can be synthesized by the one-step reaction in a non-toxic medium using low cost commercial reactants. After water elimination, the sample is stable at polypropylene processing temperatures. Synthetic protocol yields fine-dispersed product, not requiring further grinding. The synthesis is environmentally friendly "green" since only deionized water is used as a solvent. Dicalcium HEDP salt is mixable with auxiliary components. An obtained nucleator greatly sticks to polypropylene granules, which results in more even distribution of additive inside the polymeric matrix.

It should be noted, that according to preliminary results, dicalcium HEDP salt itself can also enhance polypropylene stability at oxidative thermal destructive conditions. Therefore, if using the developed nucleators, the thermostabilizing additives may be excluded, or used at lower concentrations.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.mtcomm.2020.10.1783>.

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