Organogelators with dual β - and α -nucleating ability in isotactic polypropylene

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Abstract

Nucleation efficiency and the special supermolecular structure formed in the presence of novel nucleating agents, N,N'-dicyclohexylsuberoylamide and N,N'-dicyclohexylsebacoylamide are presented in this work. The nucleation effect is studied in isotactic polypropylene (iPP). The melting and crystallization processes as well as the polymorphic composition are studied using calorimetric and thermo-optical techniques, while the solubility of the nucleating agents is studied by rheology. The properties of the iPP products nucleated by the novel compounds are characterized by conventional tensile and impact tests and the optical properties are measured by standardized haze measurements. The results indicated clearly that the studied nucleating agents are partially soluble in the iPP melt and possess dual nucleating ability. The formation of β -phase is evidenced by the calorimetric and thermo-optical measurements. The morphology of the nucleated samples shows similarity to iPP nucleated by well-known soluble “organogelators”; however, the nucleating agents introduced in this work are the first “organogelators” with β -nucleating efficiency.

Keywords Nucleating agent · Supermolecular structure · Morphology · Solubility

Introduction

Isotactic polypropylene (iPP) is a commodity polymer with very advantageous price/performance ratio, thus this polymer is used in very large amount in various application fields [1]. iPP is a semi-crystalline material consequently its properties are determined predominantly by its crystalline structure. Accordingly, the structure and proportionally the properties of iPP can be varied within a wide range. Nucleating agents with different efficiency are used for this purpose in the industrial practice nowadays [2].

Nucleating agents are additives which form heterogeneous surfaces in the polymer melt. On these surfaces the nucleation is thermodynamically preferred [3]. The efficiency of the nucleating agents can be explained by the “matching lattice theory” introduced by Alcazar et al. [4]. iPP is a polymorphic polymer and it has four different modifications

like the α -form, which develops under traditional processing conditions. Most of the nucleating agents induce the formation of this modification [2]. The β -modification, which has larger impact resistance, can be prepared using β -nucleating agents or by special temperature gradient method [5]. The γ - and the ϵ -modifications do not have specific nucleating agents, but may form during special processing conditions, or as a result of polymer structure [6–8] and they can influence the properties of the products [9, 10].

Nucleating agents can be classified into two large groups. The first group is the conventional heterogeneous nucleators, which are small particles, that should be distributed in the polymer melt as homogeneously as possible. The final supermolecular structure and the nucleus density depend on the number of the distributed particles, and the better is their distribution the larger is the nucleus density. This structure is usually designated as “microspherulitic” structure in the literature and if the nucleus density is larger than a critical limit [11, 12] the optical properties are usually enhanced also proportionally. The second large class are soluble nucleating agents, which dissolve in the polymer melt partially. These nucleating agents need to recrystallize during cooling in order to form heterogeneous surfaces, that are essential to the crystallization process. Consequently, the homogeneity

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of these nucleating agents is usually better compared to the nucleating agents in the first group, because the dissolved additive is always homogeneous. The final morphology developing during the crystallization process in the presence of a soluble nucleating agent, however, depends on the recrystallization process and on the subsequent crystallization of the polymer. Accordingly, these nucleating agents can be effective only if their recrystallization temperature is higher than the crystallization temperature range of iPP. The recrystallization of the soluble nucleating agents depends on several parameters, like concentration, cooling rate [13] and on shearing conditions as well [14].

Sorbitol based nucleating agents are partially soluble α -nucleating agents [15–19] and a characteristic fibrillar structure develops in their presence during recrystallization of the nucleating agent [20, 21]. The presence of this fibrillar network had been proved by rheological measurements as well because the flow properties change after the formation of the sorbitol network (organogelating effect) [9, 21]. The lateral surfaces of the fibrils are effective nucleating surfaces [20], but the crossing points are even more efficient [13]. This leads to the formation of a unique non-spherulitic, so called microcrystalline structure [12], which results in relatively good mechanical and excellent optical properties [22]. The formation of this fibrillar structure is accompanied by the development of large number of nucleation centers and consequently the nucleation density is very large in these polymers, which leads to the aforementioned good optical properties [11, 12, 23].

Other soluble nucleating agents are soluble β -nucleating agents having dual nucleating ability, for example N,N'-dicyclohexyl-terephthalamide [24, 25]. Accordingly, it induces the formation of the α - and the β -modifications as well. The crystallization process in the presence of this non-selective and partially soluble nucleating agent is very complex, because the recrystallization of the nucleating agent as well as the formation and growth rates of the α - and β -modifications depend on the temperature and all these parameters influence the final morphology. Consequently, various supermolecular structures with different final properties can develop in samples nucleated by such nucleating agents [24, 26].

Recently, the development of nucleating agents is turned to the direction of partially soluble nucleators because of their better homogeneity and clarifying effect. Accordingly, several novel compounds were synthesized, which are partially soluble in iPP and have good efficiency, like N,N'-dicyclohexyldicarboxamides [27–29], different hydrazide derivatives [30] and others [31, 32]. These nucleating agents may be good alternatives to the existing ones in future.

The present work aims the detailed characterization of the interesting supermolecular structure formed in the presence of the recently synthesized nucleating agents

N,N'-dicyclohexylsuberoylamide (DCHSubA) and N,N'-dicyclohexylsebacoylamide (DCHSeA). The efficiency as well as the supermolecular structure are studied in iPP homopolymer, heterophasic and random copolymer grades in order to provide complete picture about the effect of these additives in all possible iPP based polymers. Moreover, solubility and the recrystallization of the nucleating agents are investigated in the work using rheological measurements in order to prove clearly the dissolution and the recrystallization of these nucleating agents.

Experimental

Commercial iPP homopolymer TIPPLEN H 649 FH (MFR = 2.5 g 10 min⁻¹ at 230 °C, 2.16 kg), random copolymer R 605 (MFR = 3.0 g min⁻¹ at 230 °C, 2.16 kg) and heterophasic copolymer K 693 (MFR = 2.0 g min⁻¹ at 230 °C, 2.16 kg) were used as polymers in this work. The homopolymer selected here is the same as the one used in our previous study for good comparability of the results [27]. All polymer grades were supplied by MOL Petrochemicals Hungary. The homopolymer and heterophasic copolymer were commercial grades, but the random copolymer was in the form of reactor grade powders, because most of the random copolymers contain stronger or weaker nucleating agents as additives. Consequently, these commercial random copolymer grades are not usable for testing a nucleating agent. In order to avoid any nucleating additive only 400 ppm DHT-4A (acid scavenger), 1000 ppm Irgafos 168 (secondary antioxidant) and 500 ppm Irganox 1010 (primary antioxidant) were added to the random copolymer powder and this sample was homogenized in our laboratory. We may note that the homopolymer and the heterophasic copolymer contain almost the same additive package.

The nucleating agents were synthesized in our laboratory through the reaction of carbonyl dichlorides and cyclohexylamine using a four-neck glass flask under continuous and vigorous stirring. All detailed information regarding to the synthesis of the nucleating agents can be found in our previous publications [26, 27]. All chemicals (analytical grade) were purchased from TCI or Sigma-Aldrich and were used without any further purification. Diethyl ether was used as solvent and triethylamine was used as the acid scavenger. The reactor was tempered between 0 and 10 °C. The entire process was carried out under an inert argon atmosphere.

The obtained nucleating agents were added in wide concentration range (0–5000 ppm) to the different polymer matrices and homogenized in a twin-screw compounder (Brabender DSK 42/7) driven by a Brabender Plasti-Corder PLE 3000 apparatus. The rotating speed was set to 50 rpm, and the temperatures of the zones were adjusted to 210–220–230–230 °C, respectively. The extruded material

was pelletized and used in pellet form for the subsequent studies.

Calorimetry was used to study the crystallization and melting properties as well as the polymorphic composition of the nucleated samples. PerkinElmer Diamond DSC a power compensated calorimeter, calibrated using high purity indium and zinc, was used for all measurements. Samples of 3–5 mg were heated up to 220 °C and held there for 5 min to erase the thermal and mechanical prehistory. The samples were cooled down to 25 °C, kept at this temperature for 1 min, and then heated up to 220 °C. Subsequently, the samples were cooled to 100 °C and reheated again to 220 °C. This limited recooling step is necessary to eliminate the “melting memory effect” of the β -iPP [33], because the earlier measurements proved that the nucleating agents studied in this work have moderate β -nucleating efficiency [27]. The applied heating (V_h) and cooling rates (V_c) were 10 °C min⁻¹. The ratio between the α - and β -modifications were calculated from the separated melting curves registered after the recooling step.

Thermo-optical microscopy (TOM) was used to follow the crystallization process during cooling of the samples. To prepare thin polymer films for this measurement, the following procedure was done on the samples. A small piece (3–5 mg) of the nucleated sample was placed on a glass slide and was covered with another glass slide. A heated furnace with accurate temperature regulation was used to prepare the thin film. First, the sample was heated, and when the temperature reached 190 °C, the sample was pressed gently by hand to make the thin film (around 30 μ m). After that a mass was placed on the top of the sample cover to keep the thickness as small as possible. At 220 °C the heating was turned off, and the sample was let slowly cool down. Subsequently, one of the glass slides was removed, and a cover glass was placed on the polymer film.

Zeiss Axioskop equipped by a Leica DFC 320 type digital camera was used for the optical studies. The micrographs were recorded using a Leica IM 50 software. The microscope was used in polarized mode, and it was equipped by a first order λ -plate, which is necessary for the investigation of the spherulitic structure. The mechanical and thermal prehistory of the microscopic samples was erased at 220 °C for 5 min similarly to the calorimetric measurements. Subsequently, the samples were cooled down as fast as possible (quenched) to the crystallization temperature (T_c).

ISO 527 tensile bars were prepared using injection molding technique from the nucleated samples. For this a Demag IntElect 50/330–100 machine was used, and the temperature profile was set to 205–210–220–230 °C, with 40 °C mold temperature. The holding pressure was 500 bar, and the molding time was 20 s. For the measurement of haze plate shaped samples with 1 mm thickness were also prepared by injection molding. The temperature profile and the

mold temperature were the same as in the case of tensile bars. The holding pressure and time were 660 bar and 10 s, respectively. To ensure that the secondary crystallization completed, at least one week passed before testing mechanical and optical properties of the specimens.

To carry out tensile tests, an Instron 5566 apparatus with a gauge length of 115 mm was used. Up to 0.02% elongation the crosshead speed was 0.5 mm min⁻¹, and above this deformation value the crosshead speed was 50 mm min⁻¹, and the measurement lasted until the sample broke. Tensile modulus was determined from the data recorded in the first elongation range (up to 0.02%). Impact tests were performed using a Ceast Resil 5.5 type machine equipped with a 1 J hammer. Both tensile and impact tests were performed at 23 °C and 50% relative humidity.

Measurement of haze were performed on the injection molded plates using a Hunterlab ColorQuest XE machine following standard ASTM D-1003-95.

To compare the crystalline structure developed in the thin films to the structure developed in the injection molded tensile bars, SEM investigations were performed on the surface of samples previously subjected to impact tests. Before the SEM investigation the surface of the samples was etched applying a method described in the literature [34] in order to dissolve the amorphous part and to make the crystalline structure more clearly observable. The samples were sputtered using gold in a standard sputtering apparatus. SEM micrographs were taken using a JEOL JSM 6380LA type equipment with an electron acceleration voltage of 10 kV.

The organogelating effect of the nucleating agents in the polymer melt was investigated by rheology, using an Anton-Paar Physica MCR301 modular compact rheometer with plate-plate geometry. The angular frequency was 0.5 rad s⁻¹, and the amplitude was 0.5%. In the measurements, the storage modulus was recorded as a function of the temperature. In the measurements the samples were cooled from 240 °C to 110 °C, with a cooling rate of 5 °C min⁻¹.

Results and discussion

Melting and crystallization behavior

The efficiency of the nucleating agents was characterized using calorimetry, using the shift of the crystallization peak temperature (T_{cp}). The crystallization curves recorded in the presence of DCHSeA and DCHSubA in iPP homopolymer are plotted in Fig. 1a and b, respectively. It is clearly visible that both nucleating agents have nucleating efficiency, but this effect appear only at larger concentration ranges. At smaller concentration ranges (below 2000 ppm) the T_{cp} decreases compared to the non-nucleated polymers. This negative effect can be

Fig. 1 Calorimetric crystallization curves recorded in iPP homopolymer nucleated by **a** DCHSeA and **b** DCHSubA

explained by the dissolution of the nucleating agent in the polymer melt. At low concentration the nucleating agent cannot recrystallize before the crystallization of the polymer starts. During the crystallization of the polymer the volume of the melt decreases, consequently the apparent concentration of the dissolved nucleating agent increases continuously because the polymer molecules exclude the dissolved nucleating agent molecules during incorporation in the crystalline phase. This process hinders the mobility of the polymer molecules and the crystallization process as well. Accordingly, T_{cp} shifts slightly to lower temperatures. At a critical point the concentration of the dissolved additive reaches its saturation point, the recrystallization of the nucleating agent starts, and the concentration of the dissolved nucleating agent will be always at the saturation point until the entire volume crystallizes. We may note that the saturation point depends on the temperature thus it decreases monotonously, and the recrystallization of the nucleating agent accelerates. This negative effect was observed by other researchers as well, thus the present results are in good agreement with the effect of other soluble nucleating agents [17, 27]. T_{cp} , however, increases above 2000 ppm nucleating agent content, because in this concentration range the saturation point is higher compared to the crystallization onset temperature of the polymer matrix. In this range the nucleating agent appear to be effective, as the other soluble or non-soluble nucleating agents. Very similar trends were observed in the random and heterophasic copolymers as well; thus, the T_{cp} values are presented in Fig. 2.

It is clearly visible that the nucleating agents are effective in all polymer matrices; however, we have to note that the efficiency is slightly dissimilar in the different polymers, because it is known that the molecular structure of the polymer influences the efficiency of the nucleating agent [22, 35]. It seems that the nucleating agents in the study do not match well to the selected homopolymer. The effect of solubility is also well discernible, since all T_{cp} curves have sigmoid shape, but effect of solubility is smaller in random copolymer. The results prove that 2000 ppm is the critical concentration, thus at least 2000 ppm of these nucleating agents is necessary to reach the efficient region and this critical concentration is very similar in all the selected polymer grades. Interestingly, the hindering effect of the nucleating agents is not pronounced in heterophasic and random copolymers. We may speculate on this observation, and it can be stated that homopolymer crystallizes at the fastest rate, thus the hindering effect should be the most pronounced in this polymer type.

The melting process of the homopolymer samples recorded during heating after the limited recooling step is presented in Fig. 3a and b, respectively.

The melting curves presented prove clearly that the nucleating agents have dual nucleating ability, so they induce the formation of the α - and the β -modifications at the same time [24, 25, 36]. In such a case, the polymorphic composition depends on the polymer structure, selectivity of the nucleating agent and on the thermal conditions like temperature range and cooling rate. As it can be seen the melting peaks shift to the higher temperatures with increasing nucleating

Fig. 2 Peak temperature of crystallization as a function of **a** DCHSeA and **b** DCHSubA nucleating agent content in different polymer matrices

Fig. 3 The melting curves recorded after limited recooling step in homopolymer samples in the presence of **a** DCHSeA and **b** DCHSubA

agent content, as a consequence of the efficient nucleating effect. It is also discernible that the β -modification appears above 1000 ppm nucleating agent content in the case of DCHSeA and DCHSubA as well, which is very close to that concentration where the efficiency also starts to increase. This proves clearly that the nucleating agent can dissolve in the iPP melt and it can recrystallize at a temperature higher than the crystallization temperature range of the polymer only above this content. The polymorphic composition can be estimated from the partial area of the melting curves, because the $\beta\alpha$ -recrystallization, which is also known as “melting memory effect” does not occur if the samples were not cooled below 100 °C ($T(\alpha\beta)$ [33, 37–39]). The partial areas can be estimated using vertical lines or peak fitting methods. We used the original “vertical line” method

proposed by Varga et al. [40], since we have used this methodology in our previous publications also, but we have to highlight that this method is less accurate in the case of low β -content. However, it can be used for reliable monitoring of polymorphic composition even at small β -content according to our earlier experiences [41, 42]. We have to note that the polymorphic composition is different in the presence of the two nucleating agents and the melting curves hint that the β -content is larger in the presence of DCHSubA. In addition, a perfection process of the β -form is also observed in the presence of DCHSubA, which means that the larger β -content is accompanied by less structural stability. Accordingly, complex melting peaks are seen in Fig. 3b, because the perfection of the β -modification as well as the melting of the α -form is observable on the melting curves. The β -content

of the samples is presented in Fig. 4, and it is larger in the presence of DCHSubA.

β -content has a maximum, which is in good agreement with the earlier results obtained in the presence of β -nucleating agents with dual nucleating ability [25, 26]. The maximum in the β -content is originated from the dual nucleating ability. The surface of the nucleating agent promotes the formation of both modifications and the smaller the amount of the nucleating agent is the smaller the number of the crystallization centers is. Since the β -modification grows faster between 100 and 140 °C [38, 39, 43], the α -modification formed on the surface of the relative small amount of active nucleating surfaces is occluded in the early stage of the crystallization and the bulk of the polymer crystallizes throughout the growth of the β -crystalline front. If the crystallization takes place within 100 and 140 °C, the faster growth rate of the β -form prevents the β -to- α transition during crystallization and the β -content will be larger [44, 45]. However, with the increase in the nucleating agent content, the number of α -crystallization centers also increases proportionally and consequently, the β -content decreases in the final polymorphic composition. The only exception, where the estimated β -content shows a different trend is the heterophasic copolymer nucleated with DCHSubA. In these samples the polypropylene sequences are less regular compared to the homopolymer, thus a pronounced perfection process superposes onto the melting peak of the β -form. Consequently, two peaks appear, and their relative apparent area is large. Above 2200 ppm of DCHSubA the perfection process is suppressed due to the large nucleating agent content and the relative area of the β -melting peak decreases. Unfortunately, the formation of β -modification in random copolymers was not observed, because this polymer grade has the lowest chain regularity, and the selectivity of the nucleating agent is not shifted to the β -form enough to form considerable amount of β -modification during the crystallization process. We may note that the distribution of C2

units in random copolymers influences the polymorphic composition and occasionally it can suppress the formation of β -modification [46–49]. In addition most random copolymer samples crystallize below 100 °C, which is the lower temperature limit of the formation of β -form [39]. Accordingly, even if both modifications are formed on the surface of the nucleating agent fibrils, the α -modification grows faster below 100 °C and thus the α -form immediately occludes the β -secondary nuclei. This phenomenon was discussed at different temperatures by Lojímans et al. [44, 50].

The melting curves recorded during heating from room temperatures, however, demonstrate clearly the “melting memory” effect of the β -modification [33, 51] (Fig. 5). The process is presented in the case of homopolymers, but very similar curves were recorded in all cases, where β -form was present in the samples. It is clearly visible that the small β -content is accompanied by limited $\beta\alpha$ -recrystallization thus the melting memory effect is less visible in the presence of DCHSeA. However, pronounced recrystallization can be observed in the presence of DCHSubA if the nucleating agent content is larger than 1800 ppm. The most complex melting curve can be seen in the case of 1800 ppm of DCHSubA, because this concentration is the lowest efficient concentration and the β -content is relatively large, but the structural stability of the β -form is small. Several overlapping processes can be seen on this curve, which is presented in detail in Fig. 6. The β -form starts to melt around 100 °C, due to its lower melting point and the less perfect β -lamellas melt at the lowest temperature; however, a structural perfection process within the β -phase starts simultaneously due to the low level of stability of the β -phase present originally in the sample ($\beta\beta'$ -perfection process marked by dotted arrow). Meanwhile, limited amount of melt is generated also and the molten iPP at this temperature is in strongly supercooled state. Consequently, a crystallization process starts at the surface of the α -modification, which is also present in the sample, which is called $\beta\alpha$ -recrystallization process (marked

Fig. 4 The estimated β -content in the presence of **a** DCHSeA and **b** DCHSubA as a function of the nucleating agent content

Fig. 5 Melting curves of homopolymer nucleated with **a** DCHSeA and **b** DCHSubA recorded during heating from 50 °C

Fig. 6 Melting curve of iPP homopolymer nucleated by 1800 ppm DCHSubA recorded during heating from room temperature

by dashed arrow). Subsequently, α -phase with different levels of perfection is present in the sample, α_1 has lower, and α_2 higher level of perfection and, consequently, the latter has higher melting point. α_1 is the α -modification, which is formed originally during the crystallization process in the presence of the non-selective nucleating agent with dual nucleating ability. However, α_2 is the α -form developed as a result of the $\beta\alpha$ -recrystallization process, which takes place above 140 °C. This α_2 phase accordingly, forms at higher temperature compared to the α_1 phase, thus the melting point of α_2 phase will be proportionally slightly higher and a mild shoulder appears on the melting curve. As a result of these

complex processes the melting peak of the α -modification is broader since it represents the melting processes of at least two α -phases.

Organogelating effect

The organogelators are known as nucleating agents in the literature, which modify the viscosity of the polymer melt during cooling. The mechanism is mostly the formation of fine fibrils in the melt, which build up a network structure. Once the density of the network points reaches a critical limit the viscosity of the melt increases step-wisely although the crystallization process has not started yet [9, 20, 21]. However, no similar results have been published in the case of β -nucleating agents up to now, according to the best of our knowledge. The change in viscosity in the different polymer matrices at the largest 5000 ppm nucleating agent content is presented in Fig. 7.

The results prove clearly, that the solubility and organogelating effect is different in the different polymer matrices, which is in good agreement with several earlier studies, stating that the effect of the nucleating agent depends on the molecular structure of the polymer as well. The most pronounced gelation effect appears in the random copolymer, probably due to the smallest solubility of the nucleating agents. If we compare the data presented in Fig. 2, T_{cp} starts to increase at the smallest nucleating agent concentration in random copolymer, which also proves that a larger amount of nucleating agent recrystallizes in the random copolymer compared to the heterophasic and homopolymers at the same nucleating agent content, respectively. Accordingly,

Fig. 7 The storage modulus recorded during cooling the melt in the presence of 5000 ppm **a** DCHSeA and **b** DCHSubA

the formation of active nucleating surfaces starts earlier in random copolymer, and the fibrillar network, which results in the organogelating effect, is formed also earlier. In addition, the intensity of the step in the storage modulus curves also demonstrates that the largest organogelating effect can be observed in the random copolymer. The concentration dependency of the gelation effect is demonstrated in Fig. 8 in the case of random copolymer matrix. The results indicate clearly that the gelation temperature increases with increase in nucleating agent content. In other words, the larger the nucleating agent content is the earlier the gelation starts, because larger amount of recrystallized nucleating agent can be found in the sample. With decreasing nucleating agent content, the gelation temperature shifts to the lower temperature range and the crystallization of the polymer starts before the efficient gelation. In these cases, the step in storage modulus cannot be measured by rheology anymore, because storage modulus starts to increase steeply due to the formation of the crystalline phase. As a summary, it can be said that the gelation effect can appear if the concentration of the nucleating agent and the thermal conditions are

appropriate. In addition, the polymer grade has also an influence on this process as well, because the results indicate clearly that the solubility of the nucleating agents studied is varied in the different polymer matrices.

Supermolecular structure

The supermolecular structure that develops in the presence of DCHSeA and DCHSubA is demonstrated in Figs. 9 and 10, in the case of homopolymer matrix. The crystallization has been carried out at 130 °C and the nucleating agent content was 2500 ppm in both cases. The images represent an interesting process. In the presence of DCHSeA the matrix starts to crystallize at the early stage of crystallization (Fig. 9a) and conventional spherulitic crystallization can be observed. However, the concentration of the dissolved nucleating agent increases because the volume of the melt decreases proportionally to the conversion of crystallization. At a certain point of conversion, the recrystallization of the nucleating agent starts and a different non-spherulitic morphology appears on the images, which formed on the

Fig. 8 The storage modulus of the random copolymer matrix in the presence of different amount of **a** DCHSeA and **b** DCHSubA

Fig. 9 Crystallization process in the presence of 2500 ppm DCHSeA in homopolymer matrix at 130 °C: **a** $t = 5$ min; **b** $t = 6.5$ min; **c** $t = 9.5$ min; **d** $t = 14$ min

surface of the recrystallized nucleating agent (Fig. 9b–d). We selected this process to demonstrate the complex morphology around the saturation limit, where the recrystallization temperature is close to the crystallization temperature of the polymer.

In the presence of DCHSubA the gelation effect appears around 160 °C in the homopolymer and heterophasic copolymer matrices (see in Fig. 7b), thus the crystallization on the surface of the recrystallized nucleating agent can be visualized better. The crystallization process is demonstrated at 135 °C in the presence of 2500 ppm DCHSubA in Fig. 10. At this temperature the formation of the individual spherulites is suppressed, so the non-spherulitic structure is more visible. Although, the structure of the recrystallized nucleating agent cannot be seen in the microscopic images the development of the crystalline phase can be followed on its surface. The structure formed hints that the recrystallization of the nucleating agent resulted in a fibrillar structure, and a special “dendritic structure” develops on the surface of the recrystallized fibrils, which differs considerably from the conventional microcrystalline structure (Fig. 10b–d). It

is interesting that this superstructure as well as the centers of the dendritic structures are clearly visible at the end of the process. We have to note that the structure presented in these images is significantly different from the well-known “microspherulitic” and “microcrystalline” structures which are formed usually in the presence of efficient nucleating agents and which has usually good optical properties [12, 22, 52–54].

The structure formed in heterophasic and random copolymers is presented in Figs. 11 and 12. Since the process is similar to crystallization in homopolymer, only the early stage and the final supermolecular structure is presented on the images. The crystallization process in heterophasic copolymer is presented in Fig. 11 at 130 °C. The process is very similar compared to the crystallization process presented in Fig. 10. Dendritic structure is observed both in the presence of DCHSeA and in the presence of DCHSubA as well, but we have to highlight that the crystallization centers are denser in the presence of DCHSubA, indicating its slightly larger efficiency. The dendritic structure is clearly visible and the crystallization centers can be seen even at the

Fig. 10 Crystallization process in the presence of 2500 ppm DCHSubA in homopolymer matrix at 135 °C: **a** $t=5$ min; **b** $t=15$ min; **c** $t=31$ min; **d** $t=60$ min

end of the crystallization process in the heterophasic copolymer as well. In addition, the polymorphic composition is also observable in Fig. 11d. The small lighter crystals with strong birefringence refer to the β -modification, which is in good agreement with the DSC results, since heterophasic copolymer nucleated by DCHSubA contain a larger relative amount of β -phase. These β -crystals develop simultaneously to the α -form, but they have faster growth rate and occlude the slower α -modification. This process had been reported in detail in our earlier studies [24, 25].

The same tendency can be observed in random copolymer as well, which is presented in Fig. 12, because DCHSubA has larger efficiency in random copolymer as well. The crystallization in the case of random copolymer had to be recorded at a lower temperature at 125 °C, since the crystallization temperature range of the random copolymer is lower than that of the other two matrices. Although, the formation of the fibrillar structure of the nucleating agents is not visible in optical microscopy, it can be visualized in random copolymer because of its slower growth rate. At relatively high temperature the polymer crystals grow slowly, and the initial

stage can be captured. In order to demonstrate the initial structure of the dendrite the images were taken without the λ -plate because the contrast is better in the case of grayscale images. The thin fibrils are clearly observable in Fig. 12a and c, which are the incubation stages of the dendrites represented in the previous images. The well-developed dendrites are similar to the ones presented already in Fig. 11. We have to note here that the formation of β -form was not observed in random copolymer, supporting the calorimetric results that the selectivity of the nucleating agents is not large enough to induce the formation of remarkable amount of β -iPP even if the temperature is within the favorable range of β -form.

As it is demonstrated in Fig. 11d, considerable amount of β -modification forms in the presence of DCHSubA in heterophasic copolymer. The polymorphic composition cannot be seen clearly on the figures presented above (Figs. 9–12), because the size of the supermolecular units is small. To demonstrate the polymorphic structure, the samples were heated above the melting point of the β -form (156 °C), thus the β -modification can be selectively melted, without melting the α -iPP. The structure after the separate melting of

Fig. 11 Supermolecular structure of heterophasic copolymer crystallized at 130 °C in the presence of 2500 ppm DCHSeA **a** $t = 30$ s; **b** $t = 2$ min or DCHSubA **c** $t = 30$ s; **d** $t = 2$ min

β -iPP is presented in Fig. 13a. The structure indicates clearly that the birefringence of the sample decreased remarkably, and the small bright crystals disappeared as well. Accordingly, large part of the sample melts during the heating from the crystallization temperature ($T_c = 135$ °C) to 157 °C, which proves that remarkable part of the sample was crystallized in β -modification, which is in good agreement with the DSC studies. The residual α -dendrites are similar to the structure formed in random copolymer. The centers of the dendrites are clearly discernable in Fig. 13a as well.

In order to demonstrate the presence of the fibrillar network of the recrystallized nucleating agent, the same sample (heterophasic copolymer nucleated by 2500 ppm DCHSubA) was heated up to 167 °C after the separate melting of β -phase. At this temperature all crystals were melted. Subsequently, the sample was cooled back to 155 °C and held there for a couple of hours. At this temperature the crystallization of the polymer is extremely slow, therefore no individual spherulites or self-nuclei are formed. However, the secondary crystallization is running, although at a very slow rate, thus a crystalline front grows on the

surface of the nucleating agent, which becomes visible after a couple of hours and visualizes the fibrillar structure of the nucleating agent (see in Fig. 13b).

The structure of the fibrillar network of the nucleating agent and the supermolecular structure formed on its surface could be demonstrated by the images taken by optical microscope in quiescent melt. These measurements helped to understand the rules of formation of the supermolecular structure in the presence of the investigated nucleating agents. However, the structure of the polymer after real processing step is significantly different compared to the previous examples. Consequently, fracture surfaces of the tensile bars were etched and investigated using SEM technique in order to present the structure of this interesting “dendritic” structure at larger magnifications. The homopolymer sample was used for presentation, which was processed by injection molding according to the protocol given in the experimental section. The presented sample contained 2500 ppm DCHSubA as a nucleating agent. The SEM images are included in Fig. 14.

Fig. 12 Supermolecular structure of random copolymer crystallized at 125 °C in the presence of 2500 ppm DCHSeA **a** $t = 3$ min; **b** $t = 60$ min or DCHSubA **c** $t = 3$ min; **d** $t = 60$ min

Fig. 13 Supermolecular structure in heterophasic copolymer nucleated by 2500 ppm DCHSubA **a** after separate melting of β -phase at 157 °C and **b** after complete melting at 167 °C and crystallized at 155 °C for 120 min

The structure is not spherulitic, as it can be also seen in the optical microscope (Fig. 10b-d). Although the SEM technique cannot visualize the crystallization process, the

final structure of the sample is well discernible. It is clearly visible that the dendritic branches are located at every direction in the sample in very large density, so the presented

Fig. 14 The fine supermolecular structure of the homopolymer sample nucleated by 2500 ppm DCHSubA at **a** $\times 2000$, **b** $\times 5000$, **c** $\times 10,000$ and **d** $\times 50,000$ magnifications

morphology is quite homogeneous. As it can be seen the main difference is that the formation of large dendrites cannot be observed, due to the intense shearing conditions during processing. The small lamella-like formations in Fig. 14b and c can be related to those fibrillar structures, which were in the plane of fracture and could be etched efficiently. These formations are present in the entire sample in large density. An individual branch of the dendrite is presented in Fig. 14d. The structure is very similar to the conventional lamellar branches, however, the sizes of the branches are different. It is known that iPP forms lamellas in the thickness range of 10–50 nm [55]; however, in our sample the branches are in the range of 50–100 nm. Accordingly, we may suppose that a monolayer of lamella forms on the surface of the recrystallized fibrils and we see only these formations. The thickness should be in this case in the range of two times the lamellar thickness plus the thickness of the fibril, that we cannot see unfortunately. If we suppose that the thickness of the fibril is also in the range of few nanometers (5–50 nm), which is confirmed by the fact that we cannot see them in the optical microscope, the final thickness of the branches should

fall within the 100 nm range. Accordingly, we may suppose that the final structure is built up by nucleating agent fibrils covered by thin polymer crystals (lamellas), which structure is interesting and was not frequently obtained or investigated in the literature. Therefore the basic properties of this supermolecular structure (mechanical and optical properties) were investigated and discussed in the following chapters.

Mechanical properties

The mechanical properties of the nucleated samples are presented because these additives are usually used to enhance mechanical stiffness and/or reduce the haze of the materials. Accordingly, we are summarizing the mechanical properties of the nucleated samples in Fig. 15 in the presence of DCHSeA and DCHSubA, respectively. It can be seen that the nucleating agent improves both of the tensile modulus and the stress at yield values. This is in good agreement with the effect of the efficient nucleating agents in crystalline polymers [13], because the crystallinity and lamellar thickness are increased in the presence of a nucleating agent.

Fig. 15 The basic mechanical properties in the presence of **a** DCHSeA and **b** DCHSubA

Although the random and the heterophasic copolymers have different mechanical properties because of their different molecular structure, the tendencies presented in Fig. 15 are clear. We have to note here that β -modification has smaller tensile modulus compared to the α -form, but the selectivity of the nucleating agent studied in this work is not large enough to form predominantly β -iPP, thus the improvement of the modulus of the α -modification, which is present in all samples will determine the stiffness.

The effect of the nucleating agents on impact resistance is presented in Fig. 16. The results indicate that the impact resistance also increases due to efficient nucleation. First, we have to note that the impact resistance of the heterophasic copolymer is significantly larger compared to the other two types, because this grade has a heterogeneous phase structure, and the presence of the elastomer phase is accompanied by the large increase in impact resistance. It is obvious that if considerable amount of β -form develops in the sample the impact resistance will be also larger,

because the β -modification of iPP has significantly larger impact resistance than the conventional α -form [5]. The most pronounced increase in impact resistance can be seen in the presence of DCHSubA in heterophasic copolymer, because this sample contains the largest amount of β -iPP. This observation is in good agreement with the results presented in Fig. 4. It is also important to highlight, that the impact resistance of the random copolymer as well as that of the homopolymer also increases slightly. Although β -modification forms in the homopolymer samples, its amount and consequently its effect is much smaller. In addition, the impact resistance increases in the random copolymers as well, in which β -modification does not form. In this case the improvement of impact resistance can be explained by the nucleating effect of DCHSeA and DCHSubA. Our earlier works indicated that some soluble nucleating agents result in a special effect in random copolymers because the phase structure changes in their presence [56]. This special phase separation can also lead to the slight increase in impact resistance.

Fig. 16 Impact resistance in the presence of **a** DCHSeA and **b** DCHSubA

Fig. 17 The haze values in the presence of **a** DCHSeA and **b** DCHSubA

Optical characterization of the nucleated samples

The optical properties were also investigated, because most of the organogelators are used as clarifiers, in other words the optical properties of the products are improved a lot in their presence. Accordingly, we have investigated the standard haze values (ASTM1003-95) of the samples nucleated using the studied nucleating agent (Fig. 17). It is clear that the heterogeneous phase structure in heterophasic copolymers results in large haze around 100% and this value does not change due to efficient nucleation because the optical properties of the heterophasic copolymer are determined by the phase structure of the polymer. The homopolymer and the random copolymer have significantly smaller haze, but the larger the nucleating agent content is the larger the haze value will be as well. The improvement of haze is originated from the appearance of β -modification, since it has more pronounced birefringence compared to the α -form, which is accompanied by the significant improvement in haze values [57]. In addition, the formation of the special dendritic structure, may also scatter the light and contribute to the improvement of haze of the sample. As it was revealed by SEM measurements the size of the fibrillar associates is larger than 1–5 microns even in injection molded samples, thus these formations have pronounced light scattering effect leading to improved haze in the presence of the studied nucleating agents. In the case of random copolymers this special supermolecular structure results in the slight enhancement in haze despite of the general trend that haze usually decreases in nucleated sample. Haze is constant below the critical concentration of the nucleating agent and starts to increase in all polymers in the case of efficient nucleation. Accordingly, we have to state that the studied nucleating agents are organogelators, but they do not act as clarifiers as the sorbitol derivatives.

Conclusions

The present work introduces the effect of two nucleating agents (N,N'-dicyclohexylsuberoylamide and N,N'-dicyclohexylsebacoylamide) in polypropylene. Calorimetric measurements indicated that the nucleating agents are efficient in iPP homopolymer, heterophasic and random copolymers as well, because a remarkable shift in the peak temperature of crystallization was observed in all iPP matrices. In addition, the calorimetric studies revealed that both nucleating agents are soluble in the polypropylene melt, because their efficiency appears only above 2000 ppm of concentration and such threshold concentration is characteristic for soluble nucleating agents. Furthermore, the solubility of the nucleating agents was proved using rheological measurements, because a pronounced step in storage modulus appeared above the crystallization of the polymer matrix. This stepwise increase in storage modulus is usually associated to the network formation of the recrystallized nucleating agent fibrils in the polymer melt. The calorimetric results also revealed that polymorphic structure consisting of mixed β - and α -modifications of iPP forms during crystallization, which indicates clearly that both nucleating agents induce the formation of the β - and the α -forms, thus they have dual nucleating ability, however, we have to note that the amount of β -form is usually formed as minor crystalline phase. Accordingly, it can be stated that the selectivity to the β -form is low for both nucleating agents. The microscopic study of the supermolecular structure formed in the presence of the two nucleating agents proved clearly also that a fibrillar structure forms during the recrystallization of the nucleating agents from the polymer melt and the polymer starts to crystallize on the surface of these fibrils. All these results show similarity to the effect of sorbitol derivatives, thus N,N'-dicyclohexylsuberoylamide and N,N'-dicyclohexylsebacoylamide can be called as organogelators

with dual β -nucleating ability. Accordingly, the final morphology of the samples nucleated with these nucleating agents is complex. From one hand side, the α -form acts as a conventional crystalline phase and the lamella thickness as well as the crystallinity increase because of efficient nucleation. Since the major phase is the α -form, the stiffness and strength are determined by this phase. However, in the samples, in which β -modification forms, the presence of minor β -phase leads to improved impact resistance. The supermolecular structure of the samples shows a dendritic structure, which is built on the surface of the fibril network developed during the recrystallization of the nucleating agent from the polymer melt. This dendritic structure, however, scatters the visible light, thus the haze of the nucleated samples is large; moreover, haze increases significantly above the critical 2000 ppm of nucleating agent content. In summary these nucleating agents act as organogelators, that result in improved mechanical properties, namely larger stiffness, strength and impact resistance. The optical properties are disadvantageous, so no clarifying effect was observed.

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