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Isotactic polypropylene modified with sorbitol-based derivative and siloxane-silsesquioxane resin

Monika Dobrzyńska-Mizera [a,*], Michał Dutkiewicz [b], Tomasz Sterzyński [a], Maria Laura Di Lorenzo [c]

[a] Poznan University of Technology, Institute of Materials Technology, Polymer Division, Piotrowo, 3, Poznan 61-0138, Poland
[b] Centre for Advanced Technologies, Adam Mickiewicz University, Umultowska, 89 C, Poznan 61-614, Poland
[c] Consiglio Nazionale Delle Ricerche, Istituto per i Polimeri, Compositi e Biomateriali, c/o Comprensorio Olivetti, via Campi Flegrei, 34, Pozzuoli, NA 80078, Italy

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ABSTRACT

This study details new polypropylene-based materials containing a siloxane-silsesquioxane resin and a sorbitol derivative. Molecular adducts originating from the synergistic interactions of siloxane-silsesquioxane resin (SiOPh) containing phenyl functionalities and 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol, Millad 3988 (DMDBS), strongly influence crystallization of isotactic polypropylene (iPP) as well as its morphology, transparency and mechanical properties. DMDBS is a commonly used clarifying agent for a variety of iPP grades. However, its disadvantage is that when added into iPP during extrusion, it allows only low draw ratios, because it increases crystallization temperature of iPP. Addition of SiOPh allows for control of the nucleation efficiency of the sorbitol derivative and adjust crystallization rate of iPP, to attain transparent formulations suitable for extrusion processes. iPP-based compounds were produced by co-rotating twin screw extrusion and further analyzed by differential scanning calorimetry, wide-angle X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. Moreover, rheological, haze and static tensile measurements were conducted to determine the influence of composition on material properties. It was found that the best combination of properties is achieved when 1 wt% of SiOPh and 0.25 wt% DMDBS are added to iPP. This formulation can significantly change the crystallization behavior of iPP to be tailored for production of highly oriented and transparent products.

1. Introduction

Isotactic polypropylene (iPP) is one of the most widely used thermoplastic polymers due to its good mechanical properties, low cost and ease of processing [1–3]. Moreover, polypropylene can develop various crystal forms called α-, β-, γ-, and ε-structures, as well as a conformationally disordered mesophase [4–12]. β-crystal modification of polypropylene is industrially significant as it reveals good thermomechanical properties and impact resistance [5,12]. However, the α-structure is technically important since it ensures to iPP better transparency as well as higher modulus and tensile strength, compared to the other crystal modifications [13,14]. Possible ways to obtain the desired structure include differentiation of crystallization conditions and/or introduction of nucleating agents into the polymeric matrix.

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* Corresponding author.
E-mail address: monika.dobrzynska-mizera@put.poznan.pl (M. Dobrzyńska-Mizera).

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Sorbitol derivatives are extensively used clarifiers to obtain transparent products due to their high efficiency [15]. Although the cost of sorbitol derivatives are relatively high, their effect on polypropylene transparency is unique, not attainable by other cheaper nucleating agents actually available. Moreover, the addition of sorbitol derivatives results in accelerated crystallization of polypropylene which is crucial from an application point of view [16]. This is an advantage during injection molding, as faster crystallization allows for shorter cycle time and reduced production cost. Conversely, it is detrimental in case of extrusion, because high crystallization rates limit production of oriented goods, such as films and fibers, since these products must be shaped exclusively prior to crystallization, i.e. before formation of oriented chain segments [17]. Hence, if crystallization occurs at too high temperature, only limited stretching can be applied during extrusion.

For this reason, large research efforts are devoted to sorbitol modifiers capable of controlling the crystallization process of nucleated polypropylene. It was proved that the addition of silsesquioxanes (POSS), a cage-like organosilicon compounds functionalized with phenyl side groups, to polypropylene matrix nucleated with a sorbitol derivative allowed polypropylene to be stretched to higher draw ratios during extrusion [18–20]. Silanol silsesquioxane and the sorbitol derivative, namely di (benzylidene)sorbitol, are capable of forming several complex molecular adducts, thanks to noncovalent hydrogen bonding [21]. Such a formation prevents fibrillation of the sorbitol derivative upon cooling and in turn allows to tailor crystallization of iPP. Unfortunately, the very high cost of commercial POSS has limited its use so far, and there is still a need to seek for lower cost modifiers.

As an effort to find lower cost modifiers able to control crystallization of polypropylene containing sorbitol derivatives, a number of novel siloxane-silsesquioxane resins (SiOPh) were synthesized in our laboratory. These molecules can be easily functionalized and can potentially replace silsesquioxanes thanks to their low cost synthesis procedure [22]. The siloxane-silsesquioxane resin contains silanol groups which are expected to interact with the functional groups of sorbitol [18] and/or polyolefins [23]. Thus, the addition of SiOPh into iPP/DMDBS may allow to lower crystallization temperature compared to iPP/DMDBS only, while preserving the clarifying effect gained upon the addition of the sorbitol derivative. This in turn will provide iPP-based products with enhanced transparency and anisotropic mechanical properties. According to our knowledge, the iPP/DMDBS/SiOPh compositions have not been presented in the literature before.

The influence of a brand new siloxane-silsesquioxane resin with phenyl groups, on properties of iPP containing a commercial sorbitol derivative, namely 1,2,3-tridesoxy-4,6:5,7-bis-O-[(4-propylphenyl)methylene]nonitol sorbitol (NX8000), has been discussed in previous articles [24,25]. Since both modifiers contain free hydroxyl groups, able to create mutual molecular adducts, they are expected to suppress fibrillation of percolated network of sorbitol derivative upon cooling of polypropylene [21]. This allows for tailoring the crystallization process of polypropylene matrix and enables production of transparent, highly oriented films or fibers. However, the addition of SiOPh did not affect nucleation efficiency of NX8000, indicating negligible interplay between modifiers, therefore a different commercial sorbitol derivative, namely 1, 3:2,4-bis(3,4-dimethylbenzylidene)sorbitol, Millad 3988 (DMDBS), was tested in combination with SiOPh. Compared to NX8000, DMDSB has varied functionalization of the hydroxyl rings, which may affect interaction with SiOPh.

The influence of both additives on the crystallization under static and shearing conditions as well as morphology, mechanical and optical properties of iPP were investigated. The goal is to develop an iPP-based formulation with optimized optical and mechanical properties as well as production costs, with tailored crystallization rate.

2. Experimental

2.1. Materials

A commercial iPP, Midilena III PPF401, with MFR = 3 g/10 min (230 °C, 2.16 kg) from Rompetrol Petrochemicals S.R.L. (Romania) was used. The selected iPP grade is characterized by a low modification level, i.e. there are no plasticizers, colored masterbatches or nucleating agents added.

The sorbitol derivative added to iPP, 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol, Millad 3988 (DMDBS), was kindly provided by Milliken Chemical Company (Belgium, USA). Previous investigations revealed that 0.25 wt% is the sufficient amount of sorbitol able to promote α-crystal nucleation in isotactic polypropylene [26]. Siloxane-silsesquioxane resin modified with phenyl groups of general formula [PhSiO1.5]n, abbreviated SiOPh, which acts as a modifier for the nucleating agent, was synthesized in our laboratory. The synthesis route of spherical particles, with an average size of 1 μm, was detailed in the previous manuscript [24]. The thermal stability of siloxane-silsesquioxane resin was determined using thermogravimetry (TGA), which proved that the component does not undergo thermal degradation at the used processing temperatures of iPP. The chemical formulas of DMDBS and SiOPh are presented in Fig. 1.

2.2. Sample preparation

Polypropylene pellets were milled into powder in a Tria high-speed grinder. Polymer was mixed with the sorbitol derivative and SiOPh in the rotary mixer Retsch GM 200 for 3 min at a rotation speed of 3000 rpm. Homogenization of the premixed compositions with different SiOPh contents (0.1–1.5 wt%) and a fixed sorbitol concentration of 0.25 wt% was ensured by molten state extrusion with a Zamak corotating twin screw extruder operated at 190 °C and 70 rpm. The

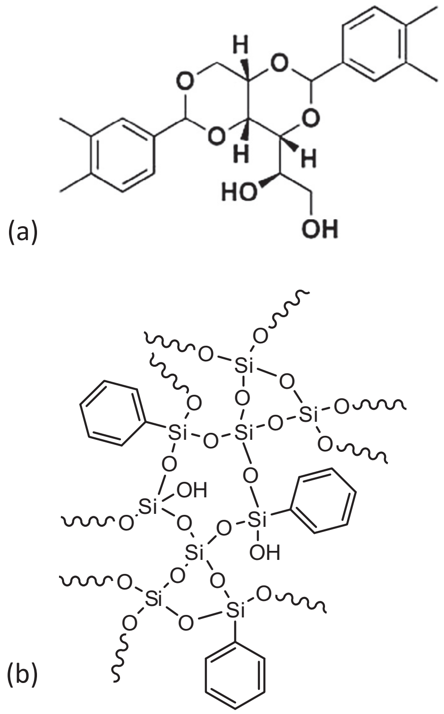

Fig. 1. Chemical structures of (a) DMDBS and (b) SiOPh.

Table 1
Designations and mass concentrations of samples.

Designation	Mass concentration (%)		
	iPP	DMDBS	SiOPh
iPP	100	0	0
iPP + DMDBS	99.75	0.25	0
iPP + DM + 0.1SiOPh	99.65	0.25	0.1
iPP + DM + 0.5SiOPh	99.25	0.25	0.5
iPP + DM + 1SiOPh	98.75	0.25	1.0
iPP + DM + 1.5SiOPh	98.25	0.25	1.5

extruded rod was pelletized in a water bath. iPP/DMDBS/SiOPh composites at various compositions were prepared, as summarized in Table 1.

The composites were compression-molded with a Collin Hydraulic Laboratory Forming Press P 200 E at a temperature of 200 °C for 3 min, without any pressure applied, to allow for complete melting. After this period, a pressure of about 10 MPa was applied for 3 min, then the samples were cooled to room temperature in less than 3 min by means of cold water circulating in the plates of the press. iPP-based sheets with a thickness of 150 μm and 1.2 mm were obtained. The thin films were used for the study of crystallization rate, to limit the effect of thermal gradients within the sample during the phase transition, whereas the thick films were used for the investigation of mechanical properties of the materials, to comply with ISO standards.

2.3. Methodology

Scanning Electron Microscopy (SEM). Morphological analysis of cryogenically fractured iPP/DMDBS/SiOPh composites was performed using a FEI Quanta 200 FEG environmental scanning electron microscope (ESEM) (Eindhoven, The Netherlands) in low vacuum mode, using a Large Field Detector (LFD) and an accelerating voltage of 10–20 kV. Before analysis, the samples were sputtered-coated with Au-Pd alloy using Baltech Med 020 Sputter Coater System, then mounted on aluminum stubs.

Differential Scanning Calorimetry (DSC). The thermal properties of iPP and its composites were investigated using a Mettler DSC 822 calorimeter, Mettler-Toledo, Inc., equipped with a liquid-nitrogen accessory for fast cooling. The calorimeter was calibrated in temperature and energy using indium. Dry nitrogen was used as purge gas at a rate of 30 ml/min.

In order to set the structure for the analysis of crystallization kinetics, each sample was heated from 25 to 200 °C at a rate of 20 °C min^{-1}, melted at 200 °C for 10 min to erase previous thermal history, quickly cooled to 160° at 20 °C min^{-1} to limit as much as possible the exposure to high temperatures, then cooled at various rates, ranging from 0.5 to 4 °C/min.

Crystallization is an exothermic process, and the heat evolved during the phase transition may cause some thermal gradients within the sample. As a consequence, transitions can occur at temperatures that do not correspond to those detected by the instrumentation [27,28]. The thicker the sample, the more critical this problem. In minimize this issues, sample mass was limited to 3.0 ± 0.2 mg, and cooling rates did not exceed 4 °C min^{-1}.

Oscillatory Rheological Measurements. The MCR Anton Paar rheometer with a plate diameter of 25 mm operating in the plate-plate configuration under oscillatory shear mode with a frequency $\omega = 10\ \text{rad s}^{-1}$ and a strain of 1% was used in the rheological investigations. In each experiment the sample was melted at 220 °C and held at for 10 min to erase memories of previous processing, as well as to reduce the internal stress associated to sample preparation. Afterward, the sample was cooled to the final temperature of 100 °C at a constant cooling rate of 4 °C min^{-1}. Crystallization was monitored using the oscillatory shear mode [29].

Fourier Transform Infrared Spectroscopy (FTIR). The IR spectra were collected with a Bruker Vertex 70 FTIR spectrometer in absorption mode using 64 scans. The spectra resolution was 1 cm^{-1}. Sample specimens were prepared by mixing SiOPh and DMDBS with milled potassium bromide (KBr). This powder was then compressed under vacuum into thin pellets using a pressure of 20 MPa. Four different mixtures were examined by FTIR. The first and second samples were prepared at ambient temperature using pure SiOPh and DMDBS, respectively. The other specimens were mixtures of SiOPh and DMDBS with a ratio of 1: 1. For the tests, one sample was kept at ambient temperature and the second was heated to 190 °C. All of the spectra were submitted to a weather correction, including the correction for CO_2 [30–32].

Wide-Angle X-ray Diffraction (WAXD). WAXD measurements were performed on a Philips Analytical X-ray, model PW 1830 diffractometer with Cu Kα radiation. The scanned 2θ range was from 2 to 45° with a scanning rate of 0.02° and time per step of 1 s. The samples used for WAXD analysis were in a form of compression molded sheets of 1.2 mm thickness. Characteristic peaks were assigned according to the literature [7].

Haze. The optical behavior of the polymers was characterized by haze measurements carried out on the 150 μm compression molded films according to the PN-84/C-89100 standard [33] using a Haze Meter HM-150 produced by Murakami Color Research Laboratory (Japan).

Static Tensile Tests. Mechanical properties of iPP-based compression-molded sample bars were evaluated as per ISO 52732 using Instron tensile tester, model 4505. Measurements of elastic modulus were conducted at a crosshead speed of 1 mm min^{-1}, to ensure deformation rate close to 1% of measuring section length per minute [34]. Elongation at break was estimated at a speed of 50 mm min^{-1} for a reasonable duration of the experiments [35,36].

3. Results and discussion

Scanning electron microscopy was used to investigate phase structure and morphology of iPP-based composites modified with the sorbitol derivative and siloxane-silsesquioxane resin. The results are presented in Fig. 2. Fig. 2a illustrates the cryogenically fractured surface of a compression molded iPP sheet, which appears quite smooth as expected. Polypropylene nucleated with DMDBS reveals denser network of lines visible on sample surface (Fig. 2b). Morphology seems to be homogeneous as the nucleating agent well dissolves in iPP while processing [16]. However, small spherulite size and minute amount of DMDBS added do not allow to distinguish particular components in the fractured sample presented in SEM micrograph. Fig. 2-c illustrates morphology of the composite containing both modifiers and it significantly differs from the fractured surfaces shown in Fig. 2a and b. Single particles that adhere to the iPP surface are visible, which can be probably ascribed to SiOPh. Their average diameter is about 1 μm which well compares with the average size of the synthesized material. This indicates that negligible agglomeration of the fillers occurred upon melt processing. The modifier is nicely distributed and attached to the studied surface, which reveals good distribution of the filler within the sample.

Calorimetric studies were realized by differential scanning calorimetry measurements at four different cooling rates, to obtain in-depth information on the crystallization behavior of iPP composites. The raw DSC curves for the cooling rate of

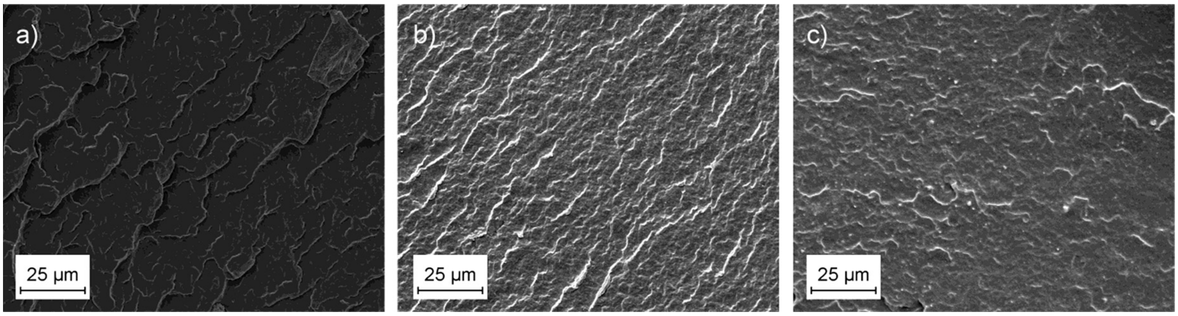

Fig. 2. SEM micrographs for iPP (a), iPP + DMDBS (b), iPP + DM + 1.5SiOPh (c).

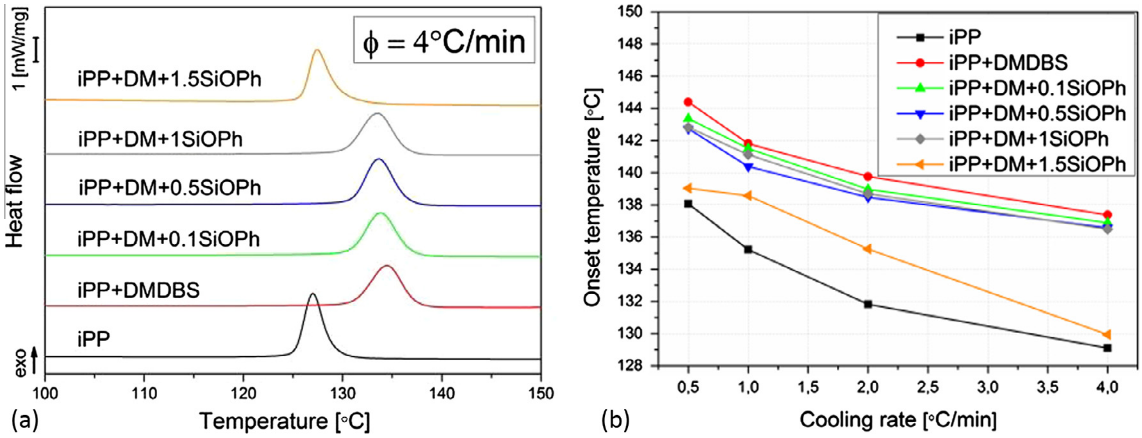

Fig. 3. DSC crystallization curves and the onset temperature versus cooling rates.

4 °C/min are presented in Fig. 3a. Neat iPP starts its crystallization at 129 °C, when cooled at 4 °C/min. Upon the addition of sorbitol derivative the onset of crystallization is shifted by 8 °C towards higher temperatures, i.e. to 138 °C. This proves that the sorbitol derivative enhances nucleation of iPP spherulites, which occurs at higher temperatures, as expected [16]. Addition of the siloxane-silsesquioxane resin slightly reduces the crystallization temperature of iPP, compared to the formulation containing iPP and DMDBS only. A significant decrease of the crystallization range occurs in the presence of 1.5 wt% of SiOPh, as seen in Fig. 3a. The influence of SiOPh/DMDBS composition on nucleation efficiency of DMDBS is quantified in Fig. 3b, which presents the DSC onset temperature of crystallization as a function of the cooling rate. The onset point was taken as the intersection of the baseline before the transition and the inflectional tangent and the peak temperature as the maximum of the exotherm [37]. As seen in Fig. 3b, the onset of the phase transition shifts towards higher temperatures with decreasing cooling rate, as typical for polymer crystallization: lower ϕ ensures more time to overcome the energy barriers for nucleation [27]. More importantly, at parity of cooling rate, compared to iPP containing DMDBS only, increasing amounts of SiOPh induce crystallization to start at progressively lower temperatures, indicating that the presence of the siloxane-silsesquioxane resin significantly affects nucleating efficiency of the sorbitol derivative.

DMDBS dissolves in molten iPP and thereby, distributes homogenously during processing through the whole volume of polymeric matrix. As proposed in Ref. [26,38,39], intermolecular hydrogen bonding and π_π interactions between the adjacent phenyl rings are established upon cooling, and sorbitol crystallizes with development of a percolated fibrillar network that facilitates growth of polypropylene spherulites [16]. As mentioned above, the increased crystallization temperature of the iPP/DMDBS composite proves that 0.25 wt% is a sufficient amount to allow precipitation of sorbitol upon cooling. Progressive addition of SiOPh causes a corresponding delay in crystallization, quantified in Fig. 3. Both DMDBS and SiOPh, whose structures are depicted in Fig. 1, have functional groups that may in principle interact upon melt mixing [18]. Moreover, it was proved [21] that the fibrils of sorbitol derivative have higher affinity to molecules modified with silanol groups. This indicates that some kind of interaction between DMDBS and SiOPh is established, however the modified sorbitol maintains its efficiency as nucleating agent for isotactic polypropylene, at least for the analyzed composition range, i.e. below 1.5 wt% of SiOPh.

Table 2 summarizes the main parameters obtained during non-isothermal crystallization of iPP composites. The onset temperature are pictured in Fig. 3b, hence are not repeated in Table 2, which only shows the peak temperatures (T_p) and crystallinity degree (X_c). The latter was calculated from the data obtained from the DSC plots, gained during cooling at different rates, according to the following Eq. (1):

$$X_C = \frac{\Delta H_M}{(1-\phi)\Delta H_0} \times 100\% \tag{1}$$

Table 2
Peak of crystallization temperature and crystallinity degrees for all samples solidified at various cooling rates.

	4 °C/min		2 °C/min		1 °C/min		0.5 °C/min	
	T_{peak}(°C)	X_c (%)	T_{peak}(°C)	X_c (%)	T_{peak}(°C)	X_c (%)	T_{peak}(°C)	X_c (%)
iPP	127.0	51	129.5	48	132.5	48	135.5	53
iPP + DMDBS	134.5	50	137.0	50	139.0	50	141.0	51
iPP + DM + 0.1SiOPh	134.0	52	136.5	49	139.0	49	141.0	51
iPP + DM + 0.5SiOPh	133.5	52	135.5	47	138.0	47	141.0	47
iPP + DM + 1SiOPh	133.5	52	135.5	49	136.0	49	139.0	51
iPP + DM + 1.5SiOPh	127.5	47	131.5	50	134.0	50	136.0	48

where ΔH_M is the experimental heat of fusion, ΔH_0 is the enthalpy of fusion of the fully crystalline polymer, equal to 207.1 J g^{-1} [40], and ϕ is the weight fraction of the modifiers. As reported in Table 2, the crystal fraction developed upon cooling at rates up to 4 °C min^{-1} is $X_c = 50 \pm 3\%$, independently of composite composition. This indicates that the addition of DMDBS only, or coupled with up to 1.5 wt% of SiOPh, does not affect final crystalline content of polypropylene, under the chosen experimental conditions. It influences only crystallization efficiency of iPP, as the onset and peak points are shifted to higher temperatures due to enhanced nucleation of iPP spherulites.

Differential scanning calorimetry data provided information on crystallization upon quiescent cooling from the melt. Further information were gained by oscillatory rheological measurements conducted during cooling, to evaluate the effect on viscosity changes under shearing conditions. Fig. 4 shows the values of complex viscosity as a function of temperature for samples containing different amounts of SiOPh and a fixed content of sorbitol derivative of 0.25 wt% (see Table 1).

The differences between nucleated and non-nucleated iPP are significant in terms of the crystallization behavior. The onset of crystallization in unfilled polypropylene is induced from a sudden and abrupt increase in complex viscosity at 130 °C. In case of the nucleated sample, the onset of dynamic viscosity appears earlier during cooling, prior to crystallization of iPP, and increases due to the fibrillar network formation of DMDBS [40,41]. In contrast, an increasing SiOPh content leads to a decrease in the viscosity growth that was caused by DMDBS nucleation effect. In case of the addition of 1.5 wt% of SiOPh, an overall suppression of primary DMDBS activity is observed. Looking at the sample containing 1 wt% of SiOPh, a different crystallization behavior is observed. Despite the fact that the interaction between SiOPh and DMDBS leads to the removal of an early onset viscosity increase, the nucleation efficiency was only slightly reduced as also proved by DSC measurements.

As evidenced by DSC, upon cooling at 4 °C/min the polypropylene sample that contains 1 wt% of SiOPh starts to crystallize at 137 °C, which coincides with rheology results. It is worth noting that DSC analysis reveals crystallization of iPP under static conditions. Conversely, rheological measurements determine complex viscosity of formulation under shear, which significantly increases upon crystallization of sorbitol fibrillar network (Fig. 4). This allows to more efficiently simulate processing conditions and possibly predict the influence of siloxane-silsesquioxane resin on formation of sorbitol network upon processing. Addition of SiOPh significantly influences establishment of sorbitol fibrillar network, which is expected to grow upon cooling. The addition of 1 wt% of SiOPh moved formation of fibrillar network towards lower crystallization temperature by over 15 °C. This feature is crucial especially for production of oriented goods, such as films and fibers. During extrusion process, the molten polymer is initially shaped in a die, then it is further stretched in order to enhance its anisotropic mechanical properties. The latter can be attained exclusively before occurrence of crystallization. Introduction of SiOPh shifts the onset of crystallization towards lower temperatures, thus extending the time available for stretching. This phenomenon allows to apply higher draw ratios and in turn improve anisotropic mechanical properties of oriented products.

Studies of crystallization of iPP modified with both the sorbitol derivative and siloxane-silsesquioxane resin by DSC and oscillatory rheology indicate possible interactions between the fillers. Moreover, literature data indicate that even small amount of silsesquiaxane functionalized with phenyl groups may interfere in formation of DMDBS fibrillar network upon iPP cooling from a molten state [18,21]. Since siloxane-silsesquioxane resin used in the study contains such functional groups, possible interactions between DMDBS and SiOPh need to be studied. Such interactions may lead to suppression of fibrillar network formation which is supposed to be maintained by the formation of hydrogen bonds between —OH groups included in the sorbitol derivative. Possible interaction between functional groups of the two fillers was investigated by FTIR [21].

The FTIR spectra of neat DMDBS and SiOPh are presented in Fig. 5a. In DMDBS, a broad O—H stretching peak is observed at wavenumbers of 3189 and 3139 cm^{-1}, and peaks at a wavenumber of 2900 cm^{-1} are associated with CH_2 and CH_3 groups. A separate peak at 1247 cm^{-1} is assigned to C—O stretching group. The FTIR spectrum of pure SiOPh shows broad bands at 3613 and 3130 cm^{-1}, which are attributed to the presence of silanol groups (respectively free —OH and hydrogen bonded ones). Moreover, aromatic C—H stretching is detected at a wavenumber of 3021 cm^{-1}. The presence of phenyl groups is

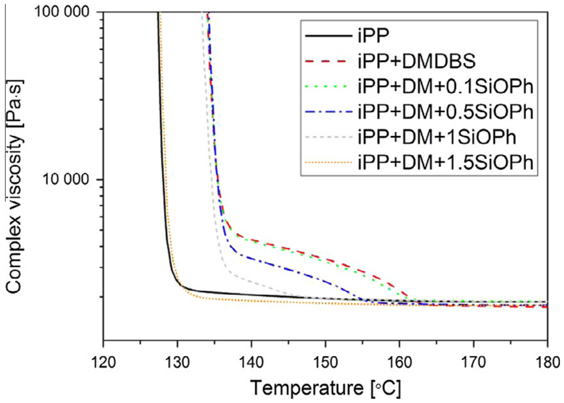

Fig. 4. Complex viscosity curves vs. temperature obtained during cooling of nucleated iPP modified with different amount of SiOPh (ϕ = 4 °C min^{-1}).

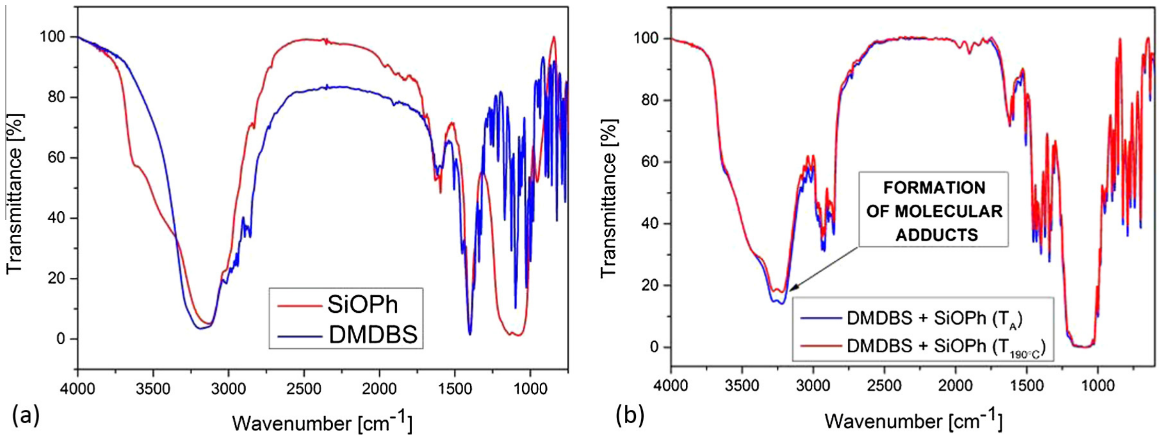

Fig. 5. FTIR spectra of (a) neat siloxane-silsesquioxane resin and sorbitol derivative and (b) DMDBS and SiOPh mixtures at ambient and processing temperatures.

confirmed by the stretching vibrations of C═C at 1597 and 1400 cm^{-1}. A high intensity band, with two maxima at 1135 and 1080 cm^{-1}, results from stretching vibrations of Si—O—Si bands and is characteristic for silicon materials [42]. The band at 954 cm^{-1} characteristic for Si—OH groups is also observed in the spectrum.

SiOPh–DMDBS mixtures were examined to infer possible hydrogen bonding between the two modifiers used in the study. The two powdered fillers were mixed at room temperature, where no interaction between functional groups are expected [21], as well at the processing temperature (190 °C). The FTIR spectra of the two mixtures are compared in Fig. 5b. The O—H stretching peak of Si—OH group in siloxane-silsesquioxane resin is found at 3130 cm^{-1} while the one originating from C—OH stretching group in DMDBS is at 3189 cm^{-1}. The height of O—H stretching was controlled as its lower intensity would indicate an interaction between DMDBS and siloxane-silsesquioxane resin. Fig. 5b proves that O—H stretching peak of the heated sample lowers its intensity showing occurrence of possible interaction. For this reason, areas under O—H stretching peaks for both mixtures, at ambient temperature and heated to processing temperature, were used for calculations according to Eq. (2) [42–44]:

$$\mathrm{DH_{FTIR}} = 100 - \left(\frac{(\text{absorbance O—H})_{\text{heated}}}{(\text{absorbance O—H})_{\text{ambienttemperature}}} \cdot 100\% \right) \tag{2}$$

where absorbance O—H is the area of the signal of O—H groups. A comparison of the peak areas allows for assessing a change in number of available O—H groups. Substituting peak areas to the equation (2) revealed that the heated sample possesses about 4% less available O—H groups in comparison to the mixture at ambient temperature. This indicates considerable weakening of the hydrogen bonds between the DMDBS particles and consequently overlap of the interactions between the DMDBS and SiOPh molecules. In other words, interactions between the DMDBS and SiOPh molecules possibly occur via hydrogen bonding [21], which may lead to an interference in DMDBS fibrillation, and in turn vary its nucleation efficiency.

Wide-angle X-ray diffraction (WAXD) analyses were performed to determine a possible effect of the additives on phase transitions in isotactic polypropylene. WAXD spectra of three representative samples of pure iPP, iPP nucleated with DMDBS and iPP containing both DMDBS and 1.5 wt% of SiOPh are presented in Fig. 6. Distinct and sharp reflections are observed for all samples at $2\theta = 14.1°$, 16.9°, 18.5°, 21.2° and 21.8°, corresponding to (1 1 0), (0 4 0), (1 3 0), (1 1 1) and (0 4 1) respectively, which are characteristic for α phase [7]. Moreover, it is proved that β and γ phases do not appear in the samples as no additional peaks at 16.2 and 19.8 were noticed [7]. The crystal fraction measured by WAXD is also unaffected by addition of sorbitol and silicate, in agreement with the DSC results detailed above. Hence, the additives do not modify crystal structure of isotactic polypropylene, at least for the analyzed compositions and thermal history.

The sizable effects of the fillers on crystallization of iPP, detailed above, are expected to influence also optical and mechanical properties. In isotactic polypropylene, similarly to other semicrystalline polymers, light scattered on the larger structural units makes the products opaque [45]. Often the size of the crystalline units is large enough to interfere with visible light and this interference results in considerable haze. Haze is associated with a loss of contrast due to light scattering at large angles, and is defined as the total flux of light scattered within the angular range between 2.5° and 90° and normalized to the total transmitted flux [46].

The influence of sorbitol derivative and siloxane-silsesquioxane resin on haze of polypropylene films is presented in Fig. 7. The addition of nucleating agent results in a significant decrease in haze values, which means that the nucleated sample is more transparent in comparison with pure iPP. Gradual addition of SiOPh only slightly reduces transparency of polymeric matrix, as seen in Fig. 7. These data parallel the variation in crystallization of iPP upon addition of the two modifiers, where

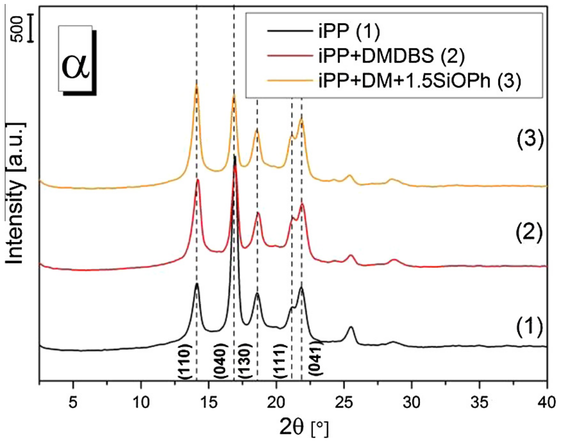

Fig. 6. WAXD patterns of pure and modified polypropylene.

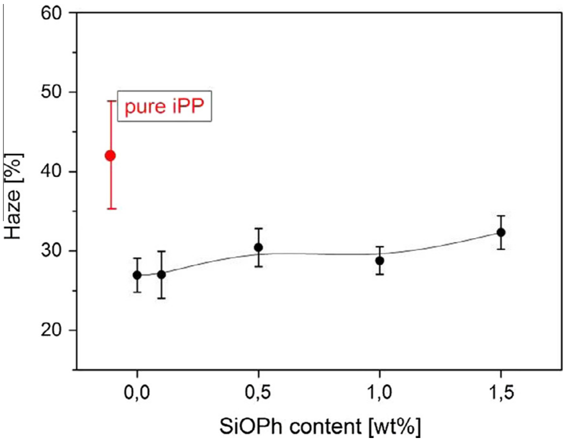

Fig. 7. Dependence of haze on SiOPh concentration in iPP/DMDBS composites for compression-molded sheets with thickness of 150 μm.

precipitated sorbitol serves as substrate for the growth of iPP spherulites, whose number is enhanced and their size is reduced in the formulations containing DMDBS and SiOPh. The size of the spherulites depends on composition. Addition of SiOPh resin to the composite that contains also DMDBS alters fibrillation of percolated network of sorbitol, which smoothens its nucleating efficiency. Lowering spherulite size improves transparency of the material, with only slightly worsened optical properties in the formulations containing both fillers, however they still remain transparent enough to ensure their applicability as e.g. packaging products.

Mechanical properties of the iPP/DMDBS/SiOPh composites were determined using static tensile tests. Main results are summarized in Fig. 8. A qualitative change in the stress-strain behavior was noted for all the compositions, since the samples that contain either DMDBS only or both modifiers do not undergo yielding. The composition dependence of elastic modulus (E), reported in Fig. 8a, reveals an increase in E for the nucleated sample in comparison to the pure one, from 1.25 to 1.45 GPa, and further decrease to a value of 1.3 GPa for the sample containing the highest amount of SiOPh modifiers. On the contrary, the addition of sorbitol derivative results in a decrease in the elongation at break (ε_r) value, from $\varepsilon_r = 600\%$ for pure polypropylene, down to $\varepsilon_r = 150\%$ for the nucleated sample. However, the addition of siloxane-silsesquioxane resin results in a gradual increase of ε_r up to 250%. Decreased ductility of polypropylene nucleated with sorbitol derivatives has been reported also by other authors [47–49].

As detailed in the literature [50] there are two mechanisms of crack propagation in α polypropylene during a uniaxial tensile test: crazes appear at the center of spherulite, grow parallel to a radial direction and eventually reorient their propagation direction perpendicularly to the tensile axis. Alternatively, in some cases the flaws are initialized at the spherulite boundary. Both mechanisms lead to the formation of major cracks affecting mechanical behavior of the samples. Introduction of DMDBS into iPP results in creation of bigger amount of smaller spherulites and drastically increases the total length of spherulite boundaries. All the above promote crack propagation in nucleated samples, hence they reveal more brittle

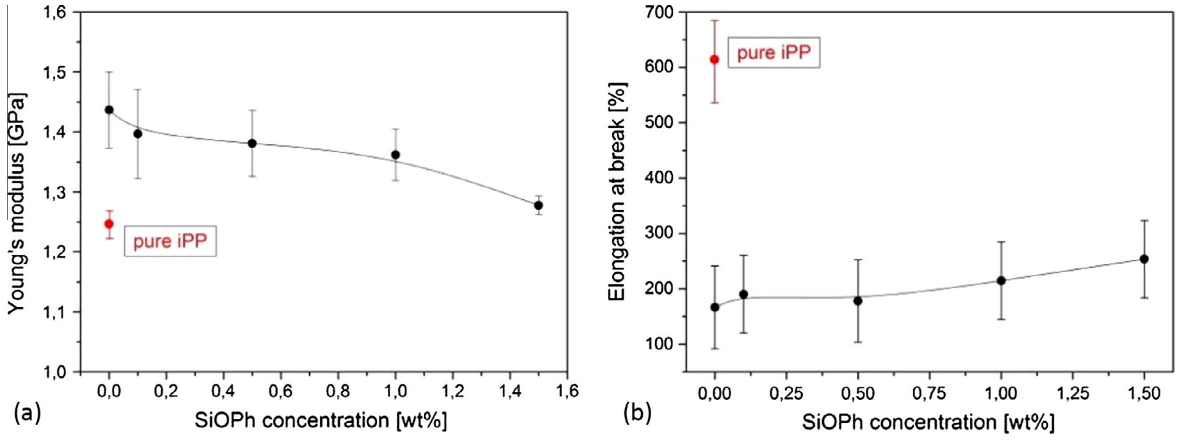

Fig. 8. Mechanical properties of pure, nucleated and modified polypropylene matrix; (a) Young's modulus and (b) elongation at break (the lines were drawn to guide the eye).

character. The addition of siloxane-silsesquioxane resin causes suppression of fibrillar network of sorbitol formation hence the spherulites are slightly bigger with the composition. This in turn is reflected in slightly improved plastic properties (higher ε_r).

4. Conclusions

This study details how a combination of the sorbitol derivative and functionalized siloxane-silsesquioxane resin influences properties of iPP-based composites. Addition of the sorbitol derivative to iPP results in increased crystallization temperature, due to enhanced nucleation density. Incorporation of SiOPh into polypropylene already modified with the sorbitol significantly affects formation of sorbitol fibrillar network, due to synergistic interaction between active functional groups of both modifiers. Furthermore, transparency is improved on the addition of sorbitol and not further affected by incorporation of SiOPh. The modified samples are also stiffer, with a decreased elongation at break and increased Young's modulus upon addition of sorbitol-based modifier. All the above is attributed to interaction between —OH groups present in both modifiers. Hence, combining isotactic polypropylene with sorbitol-based derivative and siloxane-silsesquioxane resin allows to obtain iPP with enhanced anisotropic mechanical and optical properties. Therefore, a new iPP-based formulation containing the sorbitol derivative and siloxane-silsesquioxane resin, suitable for extrusion processes, has been developed. The synthesis of newly proposed SiOPh is substantially easier and cheaper, in comparison to previously studied POSS molecules, ensuring its possible replacement.

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