

# Nucleation ability of advanced functional silica/lignin hybrid fillers in polypropylene composites

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**Abstract** Novel advanced functional silica/lignin hybrid fillers were synthesized for the purpose of their application in composites with polypropylene. The use of lignin for the production of hybrid fillers is justified due to the advantages such as reduction in cost of products, improvement in biodegradability as well as antioxidant and antimicrobial properties. The study encompasses an analysis of the dispersive and morphological properties of the hybrid fillers, and investigations of phase transitions and the supermolecular structure of the composites by means of differential scanning calorimetry, polarized light microscopy, and X-ray diffractometry. The nucleation activity of the hybrid fillers was found to be strongly correlated with the chemical composition of the fillers, and their dispersive properties and porous structure characteristics. Furthermore, the particle size and area surface of the hybrid fillers play an important role in the development of polymorphic varieties of the polypropylene matrix. The study also discusses the mechanism of the formation of the  $\beta$ -PP variety and the transcrystalline structure in the context of the nucleation ability of the hybrid fillers. The investigations are very significant because they address the impact of the actual physicochemical parameters of the hybrid fillers on the nucleation ability and structure of composite materials.

**Keywords** Polypropylene · Silica/lignin hybrid filler · Lignin · Composites · Nucleation · Structure

## Introduction

In recent years, much attention has been focused on polymer composites based on inorganic filler (including silica) [1–3] and lignin [4–8].

Silica is well known and described as inorganic compound, which has high chemical resistance, hardness, and porosity. The incorporation of silica into polypropylene matrix is an attractive way to significant improvements in the properties of the composites, e.g., mechanical strength and elastic modulus, thermal stability, chemical resistance, heat and flame resistance, and reduction in gas permeability [9–13]. These properties led to the application of silica/polypropylene composites in various industrial fields, e.g., packaging, automotive, medical, and textile industries [14–16].

Lignin is a natural amorphous polymer, which together with cellulose and hemicelluloses is one of the main constituents of wood. Lignin ranks as the second most abundant biopolymer after cellulose on the earth [17], although up to now the majority of them is used as fuel and only 2 % is utilized in other way [18, 19]. It is a waste product during paper production when the “kraft” pulping process separates it out from wood cellulose fibers. Therefore, lignin could be used as a filler to reduce the cost of products and improve biodegradability. For many years, lignin has been investigated as antioxidant [20–22] and as compatibilizer [20, 23] because of a large number of polar functional groups. Moreover, lignin presents a good capacity to adsorb hazardous metal ions [24, 25] and is a source to prepare precursors for carbon-based materials, such as

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activated carbon or carbon fibers [26] and may be used as a starting material for hydrogel applications [27, 28].

The literature contains numerous examples of the use of lignin as a filler of polymer matrix, e.g., polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate), and poly(ethylene oxide) where lignin can act as a stabilizer against UV degradation or thermo-oxidation [23, 29]. It is worth stressed that much less information is concerning the use of lignin as reinforcement in commodity polymer such PP and PE [30]. In these systems, the mechanical properties are generally lowered as compared to the neat polymer, because of poor stress transfer between phases [5, 6, 31–33]. Moreover, lignin is difficult to process since it cannot be heated to temperature greater than 170 °C at which degradation takes place and mechanical properties are dramatically reduced [5]. To overcome these limitations and enhance their potential, different strategies have been realized, e.g., compatibilization of lignin/polymer composites [34, 35], production of lignin graft copolymers [36, 37], and using the lignin as a monomer for polymerization reactions [38].

Recently, much attention has been paid to the possibility of preparation functional fillers of silica combined with natural polymers, including lignin [39, 40]. Silica with its good mechanical and thermal resistance can form interesting combination with cheap and environmentally friendly lignin. New hybrid materials may be used as functional biosorbents [41, 42] and also as polymer fillers [43]. The high interest for these materials is the effective surface of the nanosized filler making it possible to tailor and handle the properties of the material with very small proportions of the filler. The present work is the continuation of our earlier studies [43] on novel functional silica/lignin hybrid material as a potential bio-based polypropylene filler. In a preliminary study, we showed that the incorporation of silica/lignin hybrid filler influences on elongation at break and impact strength. Moreover, concentration of silica/lignin filler in polymer matrix is the most important factor determining their mechanical properties.

Another problem in the area of innovative composite materials is the influence of functional hybrid filler on the supermolecular structure and morphology of the polymer matrix. The interfaces between the filler and the matrix in composite materials are widely regarded as the most important factor determining their mechanical properties [44]. It is well known that lignocellulosic materials may act as heterogeneous nucleating agents and nucleate crystallization along the interface with sufficiently high density of nuclei [45]. The nucleation ability of filler and transcrystalline structure in composite system has profound effect on the ultimate properties of the polymer matrix and hence on the composite. The interphase surface is responsible for transfer of stress appearing in the system. Weak interphase

interactions are responsible for the appearance of cracks and delamination of the composites, leading to considerable deterioration of mechanical strength. In view of the above, the presence of transcrystalline structures can be vital for getting composites of desired properties [46]. Additionally, knowledge of the phenomena taking place at the interphase boundary polymer/filler permits optimization of the processing leading to products of target properties.

Moreover, the effect of filler-related characteristics, such as particle size, dispersion, surface area, porous structure, particle loading, particle shape, and geometry, requires extra attention during their mechanical property evaluation. The smaller particles may have a higher surface area than that of larger particles, and therefore induce excellent bonding between filler and matrix [47].

Unfortunately, there is very limited number of works that were involved in determining the nucleation ability of functional filler in polymer matrix. This indicates that the relation between nucleation ability of filler and the dispersive and morphological properties of the hybrid still remains unclear, and further investigation is still required.

Therefore, the purpose of this study was to evaluate the effect of physicochemical parameters of silica/lignin hybrid material on their nucleation ability and formation of transcrystalline structure in polypropylene matrix. There are considerable numbers of literature associated with the silica/polypropylene and lignin/polypropylene composites; however, silica/lignin hybrid filler/polypropylene composites have not been comprehensively studied.

## Experimental

### Materials

Isotactic polypropylene Moplen HP500N grade was supplied by Basell Orlen Polyolefins (Poland) with a melt flow rate  $MFR_{230/2.16}$  of 12 g/10 min, isotacticity—95 %,  $T_m = 163$ – $164$  °C. This commercially available polypropylene does not contain any antiblocking or clarifying agents.

Commercial Syloid 244 was acquired from W.R. Grace & Co. (USA), and kraft lignin was obtained from Sigma-Aldrich (Germany).

### Preparation of silica/lignin hybrid fillers

Amorphous silica type Syloid 244 was combined with kraft lignin using a mechanical method. The composition of silica to lignin in hybrid fillers was as follows: 1:1, 2:1, 5:1, and 20:1.

To combine the  $SiO_2$  and lignin, a mechanical process was used whereby the initial powders were ground and

simultaneously mixed using a grinder mortar RM 100 (Retsch GmbH & Co., Germany). To obtain a suitably homogeneous final material, grinding was conducted for 2 h. To prevent possible overheating of the material due to continuous grinding, every 30 min the mill automatically switched off for 2 min, after which it began operating again. Immediately after grinding, the silica/lignin hybrid fillers were sifted using a sieve with a mesh diameter of 40  $\mu\text{m}$ . The fillers obtained in this way then underwent further analysis and functional testing.

### Physicochemical evaluation of silica/lignin hybrid fillers

Particle size distributions were determined using a Zeta-sizer Nano ZS (Malvern Instruments Ltd., UK) enabling measurement of particle diameters in the range 0.6–6000 nm (noninvasive backscattering technique, NIBS). The measurement involves passing through the material a red laser beam of wavelength 663 nm. During measurement, the intensity of fluctuations of scattered light is identified, these representing the illuminated particles of the sample. The particles within the fluid exhibit Brownian motion, which makes the measurement possible.

The dispersive properties of the products were also characterized with the use of an Mastersizer 2000 apparatus (0.2–2000  $\mu\text{m}$ ), also from Malvern Instruments Ltd. (UK), employing the method of laser diffraction. This method assumes that the particles are spheres and are arranged randomly in the suspension, that there is no interaction between them, and that there is no shielding of smaller particles by larger ones.

The surface morphology and microstructure of hybrid filler products were examined on the basis of the SEM images recorded from an EVO40 scanning electron microscope (Zeiss, Germany). Before testing, the samples were coated with Au for a time of 5 s using a Balzers PV205P coater.

In order to characterize the parameters of the porous structure of the obtained fillers, surface area, pore volume, and average pore size were determined using an ASAP 2020 instrument from Micromeritics Instrument Co. (USA). The surface area was determined by the multipoint BET (Brunauer–Emmett–Teller) method using data for adsorption under relative pressure ( $p/p_0$ ). The BJH (Barrett–Joyner–Halenda) algorithm was applied to determine the pore volume and average pore size.

### Preparation of polypropylene/silica/lignin composites

Polypropylene pellets were mixed with selected hybrid fillers and pristine lignin using tumbler agitator. Time and

mixing speed were set, respectively, as 10 min and 40 rpm. Then, mixed dry components containing 5 % by mass of  $\text{SiO}_2$ /lignin filler were dried in an oven dryer at 80  $^\circ\text{C}$  for 12 h. Dried components were melt-blended in a corotating twin screw extruder. For this purpose, 16 mm of screw diameter and 40 L/D ratio (Zamak 16/40 EHD, Poland) extruder were used. The plasticizing unit was equipped with three kneading disc blocks and mixing elements (the screw configuration is described with details in our work [43]). The process was performed in the 160–200  $^\circ\text{C}$  barrel temperature, and the rotation speed of the screws was set as 150 rpm. The extruded pellets were injection molded into dumbbell-shaped specimens using an ENGEL 80/25 HLS injection molding machine, at the mold temperature of 30  $^\circ\text{C}$ . The injection speed was set as 80 mm/s. After moulding, the specimens for the structure investigation were immediately sealed in a polyethylene bag and placed in a vacuum desiccator for a minimum of 24 h prior to structural testing.

## Characterization of composite materials

### Thermogravimetric analysis

Thermogravimetric analysis of examined samples was performed using a Jupiter STA449 F3 (Netzsch, Germany). Samples weighing approximately 10 mg were placed in an  $\text{Al}_2\text{O}_3$  crucible and heated at a rate of 10  $^\circ\text{C min}^{-1}$  from 30 to 1000  $^\circ\text{C}$  in a nitrogen atmosphere, at a flow rate of 40  $\text{cm}^3 \text{min}^{-1}$ .

### Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were taken on Netzsch DSC 200 (Germany). The samples (each ca. 10 mg) were heated to 200  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C/min}$  under an argon atmosphere and maintained at this temperature for 5 min in order to eliminate the thermal history of the material. In the second step, the samples were cooled from 200 to 40  $^\circ\text{C}$  at a cooling rate of 5  $^\circ\text{C min}^{-1}$ . This procedure was repeated two times, and second segment was supplied to calculation part. The crystallization temperatures ( $T_{\text{cp}}$ ) of composites were obtained from the maximum of the exothermic peaks. The parameters of crystallization of the polypropylene matrix in the presence hybrid filler like the half-time of the crystallization and the crystal conversion were determined. Based on the determined values for the enthalpy of crystallization ( $H$ ), the extent of crystallization (crystal conversion),  $\alpha$ , was calculated:

$$\alpha = \frac{\int_0^t (dH/dt) \cdot dt}{\int_0^\infty (dH/dt) \cdot dt} \quad (1)$$

From the curves of  $\alpha$  against time ( $t$ ), the half-time of crystallization ( $t_{0.5}$ ) was determined as time when crystal conversion was 50 %.

### Polarizing optical microscopy (POM)

Crystallization of polypropylene in the presence of hybrid filler was carried out using a hot-stage optical (Linkam TP93, Japan) and a polarizing optical microscope Labophot-2 (Nikon, Japan) equipped with a Panasonic CCD camera (KR222, Japan). The samples were prepared manually between microscopy slides on a hot plate. All the composite samples were first heated to 200 °C and kept at this temperature for 5 min to erase the previous thermal effect. Finally, the samples were cooled at 40 °C min<sup>-1</sup> to 136 °C, at which isothermal crystallization of the PP was allowed. Dry nitrogen was introduced to eliminate any possible degradation during measurement.

### Wide-angle X-ray scattering (WAXS) measurements

The structure of composite materials was analyzed by means of wide-angle X-ray scattering (WAXS). The diffraction pattern was recorded between 5° and 30° ( $2\theta$ -angle range) in the step of 0.04°/3 s. The wavelength of the Cu K $\alpha$  radiation source was 1.5418 Å, and the spectra were obtained at 30 mA with an accelerating voltage of 40 kV.

The deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [48], improved and programmed by Rabiej [49]. After separation of X-ray diffraction lines, the contents of  $\beta$ -phase ( $k$ ) were calculated by using the Turner-Jones formula [50]. The changes in the supermolecular structure of PP were analyzed as a function of the type of hybrid filler.

## Results and discussion

### Physicochemical and structural properties of silica/lignin fillers

The silica/lignin hybrid fillers were analyzed to determine its dispersive and morphological properties. Table 1 presents particle size distributions for all filler types.

It can be noted that silica has particles with sizes in the range of 39–68 and 1720–2670 nm, and lignin—in the range of 1990–2670 and 3580–5560 nm. The investigations revealed a very interesting correlation for the SiO<sub>2</sub>/lignin hybrid fillers. An increase in the content of silica in the hybrid filler is responsible for a decrease in particle size. For the SiO<sub>2</sub>/lignin fillers at a ratio of 20:1, the particle size is the smallest and amounts to 51–91 and

1480–4800 nm. For the SiO<sub>2</sub>/lignin (1:1) systems, the size of the particles exceeds 100 nm. Based on the data obtained from the Mastersizer 2000 analyzer (see Table 1), it was concluded that 10 % of the volume of such fillers as silica and lignin contains particles that are under 2.1 and 4.9  $\mu\text{m}$  in size, respectively; 50 % of the sample volume contains particles smaller than 7.3 and 12.3  $\mu\text{m}$ , respectively; and 90 % of the sample contains particles under 18.3 and 38.4  $\mu\text{m}$  in size. Hybrid fillers demonstrate that an increase in the silica content has an effect on decreasing particle sizes for a given fraction.

The basic porous structure parameters were also determined, including the BET surface area, average pores diameter, as well as total volume of pores (see Table 2).

The BET surface area of silica is 262 m<sup>2</sup> g<sup>-1</sup>, and the total pore volume ( $V_p$ ) and pore size ( $S_p$ ) are 0.12 cm<sup>3</sup> g<sup>-1</sup> and 3.8 nm, respectively. For lignin,  $A_{\text{BET}}$ ,  $V_p$ , and  $S_p$  achieve the values of 1 m<sup>2</sup> g<sup>-1</sup>, 0.01 cm<sup>3</sup> g<sup>-1</sup>, and 12.1 nm, respectively. The porous structure parameters determined for the hybrid fillers reveal an interesting correlation. An increased content of silica in the SiO<sub>2</sub>/lignin hybrid filler contributes to increased  $A_{\text{BET}}$  and  $V_p$  values, and a decreased average pore diameter ( $S_p$ ). The results show that the chemical composition of hybrid systems is a factor determining the activity level of the obtained fillers.

Figure 1 presents SEM images of silica, lignin, and hybrid fillers. As the SEM microphotograph shows, silica can have diverse morphological and microstructural properties (see Fig. 1e). However, the presence of single primary particles of nanometric size, which tend to create aggregates (<1  $\mu\text{m}$ ), as well as agglomerates (>1  $\mu\text{m}$ ), can be noticed. SEM image of the second precursor is given in Fig. 1f. Lignin has particles in micrometric range, which is confirmed in the results obtained on the apparatus Zetasizer Nano ZS and Mastersizer 2000. The morphological properties of hybrid materials made of unmodified silica and kraft lignin are comparable (see Fig. 1a–d). The samples of hybrids contain primary particles and larger agglomerate structures. With increasing content of lignin, the amount of agglomerates increases.

### Thermal stability

In Fig. 2, thermogravimetric curves for unfilled polypropylene, PP filled with both lignin and silica as well as composites based on silica/lignin hybrid fillers are presented. In general, thermal stability of PP and all composites decreased with increasing temperature. The results show that pure polypropylene is thermally stable to a temperature of approximately 400 °C, which is then followed by its decomposition. This degradation behavior is consistent with the literature data [51]. Addition of lignin

**Table 1** Dispersive properties (particle size distribution range from Zetasizer Nano ZS and average particle diameter from Mastersizer 2000) for individual additives (silica and lignin) and SiO<sub>2</sub>/lignin hybrid fillers

Sample	Dispersive properties			
	Particle size distribution range from Zetasizer Nano ZS/nm	Particle diameter from Mastersizer 2000/ $\mu\text{m}$		
		$d(0.1)$	$d(0.5)$	$d(0.9)$
Silica	39–68; 1720–2670	2.1	7.3	18.3
Lignin	1990–2670; 3580–5560	4.9	12.3	38.4
Silica + lignin (20:1)	51–91; 1480–4800	2.5	8	19.1
Silica + lignin (5:1)	79–122; 1720–5560	2.7	8.8	19.5
Silica + lignin (2:1)	68–220; 1990–4800	2.7	9	19.9
Silica + lignin (1:1)	106–295; 1990–5560	2.8	9.1	19.9

**Table 2** Parameters of porous structure (BET surface area, total volume of pores, and average size of pores) for silica, lignin, and SiO<sub>2</sub>/lignin hybrid fillers

Sample	Porous structure properties		
	Surface area $A_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	Total volume of pores $V_p/\text{cm}^3 \text{ g}^{-1}$	Average size of pores $S_p/\text{nm}$
Silica	262	0.12	3.8
Lignin	1	0.01	12.1
Silica + lignin (20:1)	206	0.11	4.0
Silica + lignin (5:1)	174	0.10	4.8
Silica + lignin (2:1)	158	0.08	5.4
Silica + lignin (1:1)	137	0.06	7.9

to a polypropylene does not increase the thermal stability of the composite, which is associated with the decomposition of biopolymer at temperature of about 250–300 °C. Also, Thakur [52] showed that the presence of cellulose fibers affects the degradation process of polymer composites. Higher thermal stability was achieved for the system filled with silica (total loss of mass is 90.2 %). This is associated with a significant stability of the inorganic filler. In turn, as expected, the tested composites with the addition of SiO<sub>2</sub>/lignin hybrid fillers have intermediate values of thermal stability fitting between composites filled with pure lignin and silica. The increase in thermal stability of the composites was observed for increasing mass content of silica in hybrid filler. Total mass loss for systems PP + SiO<sub>2</sub>/lignin (20:1), PP + SiO<sub>2</sub>/lignin (5:1), PP + SiO<sub>2</sub>/lignin (2:1), and PP + SiO<sub>2</sub>/lignin (1:1) are: 91.3, 92.5, 93.4, and 95.9 %, respectively.

### Differential scanning calorimetry

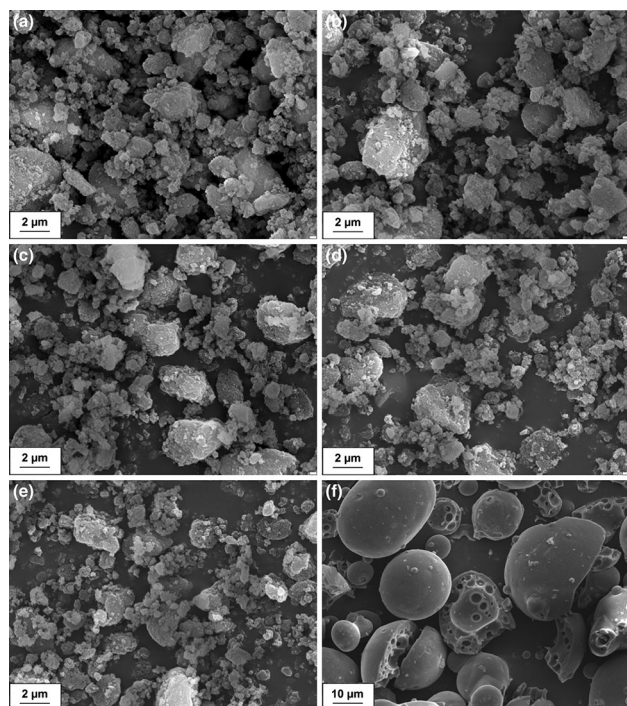
DSC measurements can be used to investigate the crystallization of polypropylene in composite systems. Figure 3 shows a typical exothermic behavior (manifested by a

single well-defined exothermic peak) of polypropylene and polypropylene containing silica, lignin, and SiO<sub>2</sub>/lignin hybrid fillers.

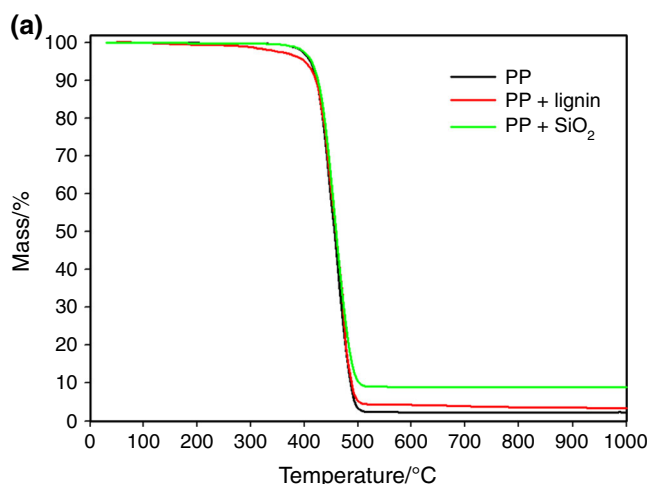
The peaks at 113.3–125.6 °C are attributed to the crystallization of PP. For the pure polymer, an exothermic peak occurs at 113.3 °C. For the composites, these exothermic peaks shift in all cases to a higher temperature. The application of conventional fillers, i.e., SiO<sub>2</sub> and lignin, resulted in an observed increase in the crystallization temperature by 5 and 2 °C, respectively. The composites with a hybrid filler are characterized by a markedly higher increase in  $T_c$ ; however, the crystallization temperature depends on the content of both filler components. A strong rise in the crystallization temperature by 13 °C was found for the PP + SiO<sub>2</sub>/lignin (20:1) composites in comparison with pure PP.

The higher crystallization temperature values of the composites indicate that crystallization is enhanced in the presence of a hybrid filler with a high content of SiO<sub>2</sub> in the SiO<sub>2</sub>/lignin systems. It is clear from Fig. 3 that the addition of lignin to PP only had a marginal effect on the crystallization temperature. It is worth noting that results of the studies have revealed a very good correlation between the

crystallization temperature of polypropylene and dispersive and porous structure properties of silica/lignin hybrid fillers. It is interesting that the highest value of crystallization temperature indicating a high ability of heterogeneous nucleation is especially visible in systems with hybrid fillers, which exhibit the smallest of particle size (Table 1) as well as highest surface area and volume of pores (Table 2).



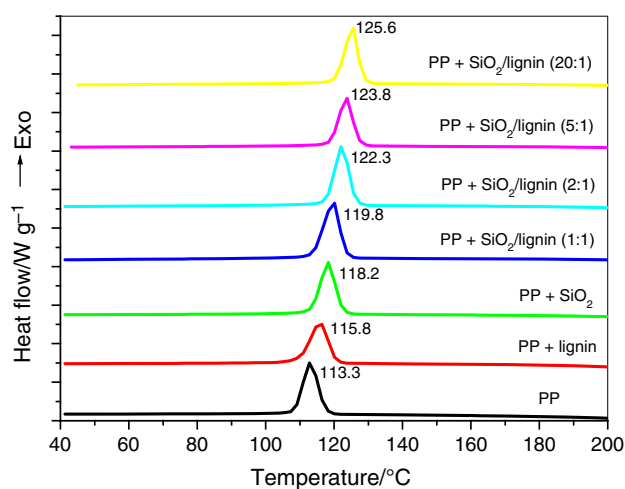
**Fig. 1** SEM micrographs of silica, lignin, and hybrid fillers: **a** SiO<sub>2</sub>/lignin (1:1), **b** SiO<sub>2</sub>/lignin (2:1), **c** SiO<sub>2</sub>/lignin (5:1), **d** SiO<sub>2</sub>/lignin (20:1), **e** SiO<sub>2</sub>, and **f** lignin



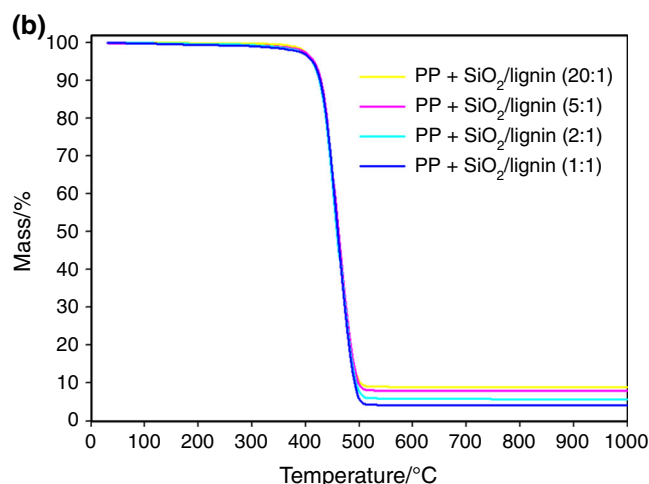
On the other hand, an increase in particle size and  $S_p$  as well as reduction in  $A_{BET}$  and  $V_p$  of the hybrid filler results in significant decrease in the crystallization temperature which equals 119.8 °C for the PP + SiO<sub>2</sub>/lignin (1:1) system. Summary of the results shows that the dispersive and porous structure properties of hybrid systems are factors determining the nucleating ability of the obtained fillers.

Moreover, in the case of pure PP and the composite materials, one melting endotherm is observed with a maximum situated between 164 and 167 °C (Table 3).

The evolution of the crystallization process from the melt state to the crystal state was followed by means of



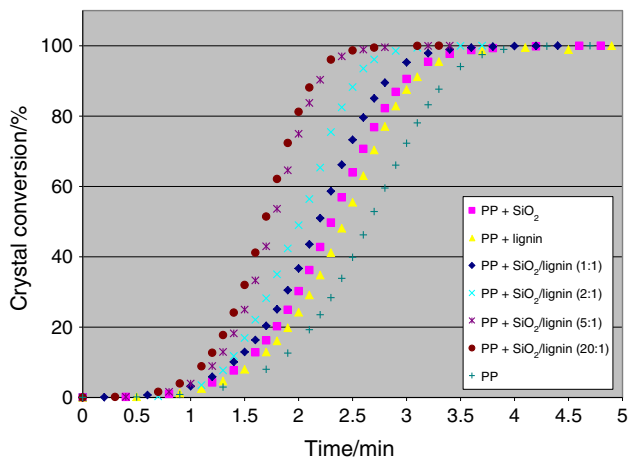
**Fig. 3** Crystallization exotherms of pure PP and PP with various fillers containing the same amount of filler equal to 5 % (cooling rate equal to 5 °C min<sup>-1</sup>)



**Fig. 2** Thermogravimetric curves of **a** pure PP, PP + SiO<sub>2</sub> and PP + lignin composites, and **b** PP + SiO<sub>2</sub>/lignin composites with different contents of inorganic-organic hybrid filler

**Table 3** Thermal parameters measured from DSC curves for pure PP and composites materials with various fillers

Samples	Crystallization temperature/°C	Melting temperature/°C	Half-time of crystallization/min
PP + SiO <sub>2</sub>	118.2	164.6	2.3
PP + lignin	115.8	164.8	2.42
PP + SiO <sub>2</sub> /lignin (1:1)	119.8	165.3	2.2
PP + SiO <sub>2</sub> /lignin (2:1)	122.3	165.8	2.0
PP + SiO <sub>2</sub> /lignin (5:1)	123.8	166.8	1.75
PP + SiO <sub>2</sub> /lignin (20:1)	125.6	167.6	1.68
PP	113.3	164.2	2.66

**Fig. 4** Crystal conversion versus time for unfilled PP and PP in the presence of different fillers

variation in conversion. This is detailed in Fig. 4 for polypropylene and the composites.

It is seen that the crystallization of PP is strongly influenced by the presence of a filler. All the composites show an increase in the crystal conversion of polypropylene as compared with the pure polymer, which is attributed to the nucleant effect of the fillers on PP crystallization. However, the composites containing lignin and SiO<sub>2</sub> are characterized by crystal conversion that are similar to the pure polypropylene. The highest crystal conversion was found for polypropylene composites with the hybrid fillers. It is quite evident from these curves that an increase in the amount of SiO<sub>2</sub> in the hybrid fillers caused a very significant increase in the crystal conversion, which proves good nucleation properties.

Similar relationships can be found in the case of the determined values of crystallization half-times ( $t_{0.5}$ ) presented in Table 3. The  $t_{0.5}$  is defined as the time necessary to reach a degree of crystalline transformation of 50%. The crystallization half-time of the composites with lignin and SiO<sub>2</sub> is 2.42 and 2.30 min, respectively, while for pure polypropylene it is 2.66. Calorimetric studies showed a

high variation in the determined half-times for the composites containing hybrid fillers. For the SiO<sub>2</sub>/lignin (1:1) composites, the half-time is 2.2 min and is comparable to that noted for the silica-filled composites. An increase in the content of SiO<sub>2</sub> in the hybrid filler leads to a considerable decrease in the crystallization half-times. The shortest values of the parameter ( $t_{0.5} = 1.68$  min) were observed for the composite with SiO<sub>2</sub>/lignin (20:1). The values obtained for the half-times are consistent with the determined values of crystallization temperatures. The combination of polypropylene with conventional fillers such as lignin or SiO<sub>2</sub> causes a slight increase in  $T_c$  and a slight reduction in  $t_{0.5}$  compared to pure polypropylene, which suggests that the fillers have a small nucleating effect. For the composites containing the hybrid fillers, considerable changes were observed in the process of nucleation and crystallization of the polymer matrix. However, it needs to be emphasized that the nucleation activity is a function of the hybrid filler composition: the higher the silica content in the SiO<sub>2</sub>/lignin hybrid material, the greater the nucleation ability manifesting itself as a considerable reduction in the half-times and as an increase in the crystal conversion and crystallization temperatures.

The results obtained in the present study demonstrate that a hybrid filler with a higher silica content induces a reduction in the nucleating agents size needed for crystal growth because the formation of an interface between the polymer crystal and the filler can be less difficult than the formation of a corresponding free polymer surface. Therefore, a question arises as to why an increase in the content of silica in the composition of the SiO<sub>2</sub>/lignin hybrid filler has a considerable impact on improving the nucleation ability of this filler type. At present, there are no literature reports on studies of PP composites with the SiO<sub>2</sub>/lignin hybrid fillers; however, the results obtained can be correlated with studies investigating the crystallization behavior of conventional fillers like PP/SiO<sub>2</sub>. Huang et al. [53] observed that an increase in crystalline peak temperature and the degree of crystallinity of PP were due to the

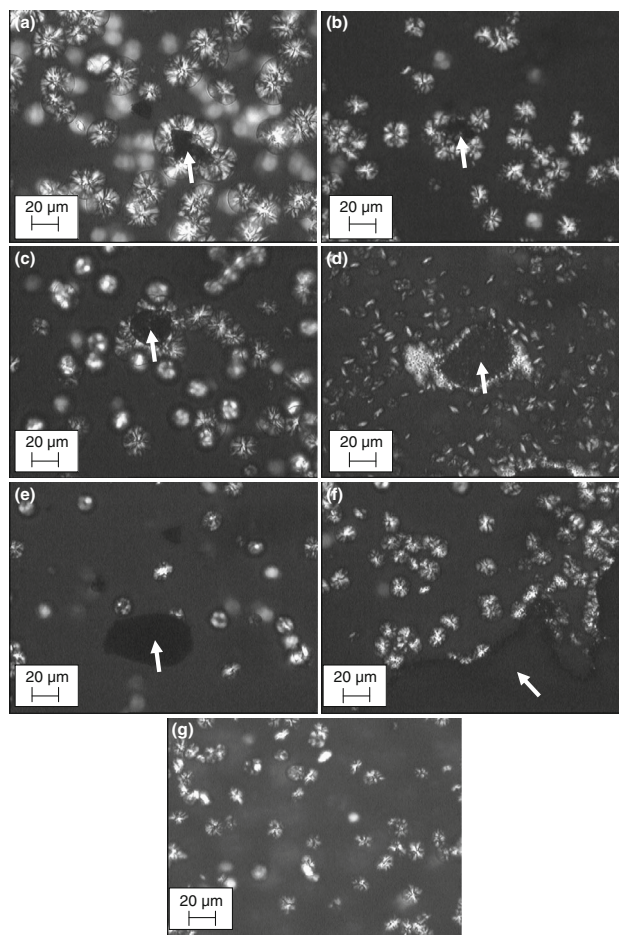
increasing content of  $\text{SiO}_2$ . Similar results were recorded by Papageorgiou et al. [54], who noted that the crystallization half-time was decreased along with an increase in the content of silica in the polypropylene matrix. The effect of the amount of  $\text{SiO}_2$  on the nucleation ability is presented in the study by Jain et al. [54] which showed the nucleation effect to increase in line with the increasing silica content, indicating that  $\text{SiO}_2$  was acting effectively as a nucleation agent in the PP matrix. The authors also conclude that silica, being a heterogeneous nucleating agent, accelerates the primary stage, resulting in more perfect crystals. On the basis of Jain et al.'s calculations [55], the crystallization activation energy decreases with the increasing silica content in the PP/silica composites, accelerating the crystallization process. The above publications confirm that the presence of silica particles may reduce the work necessary to form a new surface, leading to a faster crystallization rate.

As explained earlier, the reason for the apparent increase in the nucleation efficiency of hybrid fillers is not clear at this moment and needs to be resolved using other experimental techniques. Another aspect that must be considered is the analysis of interface structures in the polymer/filler composites. The next section is devoted to the microscopy-based investigation of heterogeneous nucleation.

### Microscopic analysis

Figure 5 illustrates the process of polypropylene crystallization in samples containing different types of fillers, taking place at 136 °C. The morphology of the PP matrix varies significantly with the type of filler surface.

The microscopic images of all investigated composite systems present the crystallization of polypropylene in the form of distinctive spherulites emerging in the bulk polymer. Additionally, when the PP melt is allowed to cool in contact with the filler which is a source of nucleating centers, the proximity of these sites on the surface inhibits the lateral growth of the resultant spherulites. Consequently, crystallization also develops in the direction normal to the filler surface. This supermolecular structure is identified as the transcrystalline layer. It must be stressed, though, that the efficiency of transcrystalline layer formation depends on filler type. It can be noted that the  $\text{SiO}_2$ /lignin hybrid fillers (Fig. 5a–d) have a considerably higher ability to induce transcrystalline layers compared to lignin and  $\text{SiO}_2$  (Fig. 5e–f). The composites containing a hybrid filler reveal a markedly higher nucleation density and width of the TCL layer. In these systems, hybrid fillers act as nucleating agents for PP, as nucleation occurs preferentially around the fillers. In the composites with lignin or silica, nucleation sites develop only on some fragments of the filler surface.



**Fig. 5** Optical micrographs of polypropylene melt crystallizing at 136 °C in the presence of **a**  $\text{SiO}_2$ /lignin (20:1), **b**  $\text{SiO}_2$ /lignin (5:1), **c**  $\text{SiO}_2$ /lignin (2:1), **d**  $\text{SiO}_2$ /lignin (1:1), **e** lignin, **f**  $\text{SiO}_2$ , and **g** PP (arrows indicate the filler particles)

It is interesting that the appearance of transcrystallinity indicating a high capability of heterogeneous nucleation is especially visible in systems with hybrid fillers with the highest silica contents in  $\text{SiO}_2$ /lignin (Table 4). Such composites exhibit the highest crystal rate of TCL, which for the PP +  $\text{SiO}_2$ /lignin (20:1) system amounts to 9.1  $\mu\text{m}/\text{min}$ . A reduction in the silica content in the hybrid filler results in significant decrease in the crystal rate of TCL which equals 2.7  $\mu\text{m}/\text{min}$  for the PP +  $\text{SiO}_2$ /lignin (1:1) system. The composites with a hybrid filler having the lowest  $\text{SiO}_2$  content display a comparable nucleation activity to the PP/ $\text{SiO}_2$  and PP/lignin systems. Similar correlations can be observed for the induction time (Table 4).

Lignin-based or silica-filled composites are characterized by induction times that are comparable to the polypropylene matrix (ca. 50–60 s). However, incorporating a hybrid filler with an increasing silica content leads to a decrease in the induction time (to ca. 20 s).

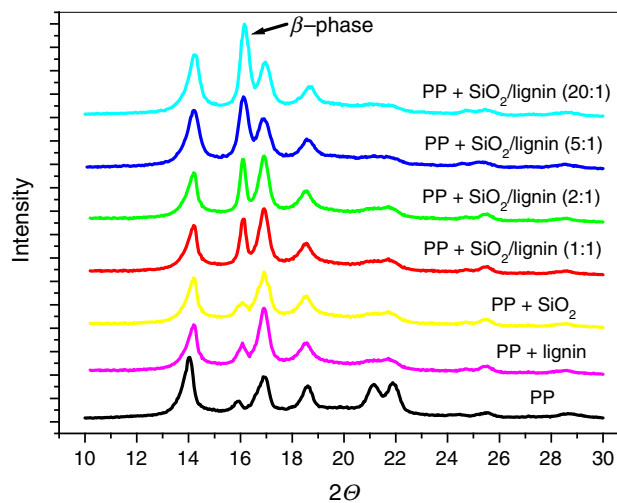


**Table 4** Crystal rate, induction time, amount of  $\beta$ -PP, and crystallinity index of PP in composite materials and polypropylene matrix

Samples	Crystal rate of TCL/ $\mu\text{m min}^{-1}$	Induction time/s	Amount of $\beta$ -PP/%	Crystallinity index/%
PP + SiO <sub>2</sub>	2.5	50	13	54
PP + lignin	1.8	60	10	54
PP + SiO <sub>2</sub> /lignin (1:1)	2.7	40	27	57
PP + SiO <sub>2</sub> /lignin (2:1)	5.5	40	31	58
PP + SiO <sub>2</sub> /lignin (5:1)	7.3	30	35	60
PP + SiO <sub>2</sub> /lignin (20:1)	9.1	20	40	63
PP	–	50	8	52

The obtained results conform with those achieved using the DSC method. There are, as yet, no literature reports on studies investigating by polarized light microscopy the process of crystallization of semicrystalline polymers with the silica/lignin hybrid fillers. A literature review only identified studies of the effect of SiO<sub>2</sub> on the crystallization of PP. A study by Palza et al. [56] found that the addition of a low amount of silica particles raised the spherulite growth rate. Nucleation was faster in the presence of these particles, as the work needed to create a new crystal surface was reduced, thus increasing the crystallization processes. The opposite effect was reported in the study [57]. Nitta et al. found that the linear growth rates of spherulites in the PP composites filled with silica particles were reduced as the content of the silica particles increased. The authors claim that the reduction in growth rates may result from the spatial constraints on crystallizing units introduced by confining them to the restricted space between the particles.

In the present study, the most pronounced nucleating effect was noted for the composite systems containing fillers with an increasing content of silica in the SiO<sub>2</sub>/lignin hybrid filler. The kinetics of PP crystallization in the presence of fillers can be analyzed according to the classical crystallization theory based on the transport process from the melt to the crystal surface and the secondary nucleation process on the spherulite front surface [58]. As a consequence, an increase in the growth rate (for hybrid fillers) is attributed to an increase in mobility or a marked decrease in the activation energy of the precursor units restricted or confined by the particles. The presence of particles in the polymer melt can decrease both the work required to create a new surface and the nucleus size for the crystals. Therefore, heterogeneous nucleation reduces the free energy opposing the primary nucleation by means of a foreign preexisting surface [59]. As a consequence, fillers with a high specific area exhibit a higher degree of heterogeneous nucleation. The present study proves that the hybrid fillers with a higher content of SiO<sub>2</sub> have smaller particle sizes and higher  $A_{\text{BET}}$  values. The study by Palza [56] also demonstrates that the fillers which are smaller in

**Fig. 6** X-ray diffraction patterns of pure polypropylene and composites with various fillers

size are able to radically increase the nucleation density and the spherulite growth rate of the polymer matrix, whereas larger particles do not affect the spherulite dynamics. The authors argue that the increases can be attributed to the presence of an external surface (from the filler) facilitating the formation of polymer crystals from the melt.

### X-ray diffraction analysis

The supermolecular structure of the composite materials was analyzed as a function of filler type. The X-ray diffraction patterns show the crystallization of iPP in the presence of different fillers (Fig. 6).

The diffractograms obtained in the study reveal the presence of the maximum at the diffraction angle of 16.2°, produced by the  $\beta$ -PP variety. It has been established that the development of polymorphs of the polypropylene matrix due to melt-shearing depends strongly on the type of filler. In the case of composites containing silica or lignin, the content of the  $\beta$  variety is approximately 10–13 % and is thus slightly higher than in the unfilled matrix for which

the recorded content of the polymorphic variety was 8 % (see Table 4).

A particularly interesting observation was related to a considerable amount of the hexagonal variety of PP which was found in the presence of the SiO<sub>2</sub>/lignin hybrid fillers. In these systems, the content of  $\beta$ -PP ranges from 27 to 40 %. Furthermore, the content of silica in the SiO<sub>2</sub>/lignin hybrid filler is responsible for generating a greater amount of the  $\beta$ -PP variety.

The crystallinity of different composite materials was also calculated, and the results are shown in Table 4. As it can be seen, the pure polypropylene has the crystallinity index of 52 %. Moreover, composites with lignin or silica fillers are characterized by values of the crystallinity almost identical with the systems which unmodified systems. The observation is very interesting and implies that one-component fillers do not induce changes in crystallinity. It is perfectly visible that crystallinity of polypropylene is strongly influenced by the presence of hybrid fillers. It can be found that the crystallinity index of PP essentially increases when two-component filler is applied. It is worth noting that an increasing content of silica in the silica/lignin hybrid filler contributes to the achievement of high values of crystallinity index. Our data reveal that for the crystallization of PP in contact with hybrid filler [SiO<sub>2</sub>/lignin (20:1)], the crystallinity index is the highest (63 %).

The outcomes of the experiments performed in the present study correspond to the results reported by Varga and Karger-Kocsis [59]. According to these authors, the shearing of fibers yields  $\alpha$ -row nuclei, and the surfaces of these  $\alpha$ -row nuclei may induce the formation of the  $\beta$ -form of PP. Also, Somani et al. [60, 61] found that the formation of oriented  $\alpha$ -crystals occurred immediately after the application of the shear field, following which the growth of primarily unoriented  $\beta$ -crystals was observed. The authors showed that  $\beta$ -crystals grew only after the formation of oriented  $\alpha$ -crystals in the sheared iPP melt.

The differences in particle size and porous structure of the hybrid fillers can explain the mechanism of  $\alpha$ -row nuclei formation on the surface of fillers in the composite materials. We conclude that it is very probable that the molten PP located in the filler (which is referred to in [62] as “the inside polymer”) can be shifted together with the hybrid filler. In this situation, the shear forces between the hybrid filler and “the inside polymer” are not present due to the same velocity, and as a consequence, the creation of the  $\alpha$ -phase (termed “ $\alpha$ -row nuclei” by Varga and Kocsis) is only observed at the surface. The efficiency of the  $\alpha$ -row structure formation may depend on the specific surface area and the filler particle size. The increase in the surface area and pore volume is attributed to the crystallization of the  $\alpha$ -form crystal. In the composites analyzed here, the particle size and the surface area of the hybrid filler are considerably

diversified (due to the different contents of the SiO<sub>2</sub> and lignin components in the hybrid filler), which can lead to changes in the nucleation activity of the  $\alpha$ -row nuclei and, consequently, influence the formation of the hexagonal phase. The experiments performed in the present study confirmed that the highest content of the hexagonal form of PP was found in the composites with fillers having the highest silica content (smaller particle size and highest surface area as well as pore volume). In another scenario, if a composite contains a filler with the lowest content of silica, the nucleation of oriented  $\alpha$ -row crystallites is decreased by the higher particle size and smaller surface area of the hybrid filler. Such dispersive and porous structure properties definitely affect the nucleation activity of the hybrid surface. The above considerations may also be reflected in the results of studies based on polarized light microscopy. The emergence of  $\alpha$ -row crystallites is also a characteristic finding during the formation of transcrystalline structures in the composite systems. Based on microscopic studies, the most pronounced TCL structure-forming ability was found in systems containing a hybrid filler with the highest silica level.

Another explanation for the variation in the content of polymorphic varieties in the composite systems is the kinetic aspect associated with the process of polypropylene crystallization. In establishing the role of the hybrid filler, relaxation should play an important role during crystallization. Huo et al. [63] reported that under certain conditions of the crystallization process, it is impossible to eliminate the shear-induced orientation and fully stretch the PP chains before the commencement of PP crystallization. As the results of the present study show, the contribution of the  $\beta$ -phase was greater along with the higher nucleation activity of the hybrid filler. The composites having a filler with the highest silica content [PP + SiO<sub>2</sub>/lignin (20:1)] were associated with the highest formation rate of transcrystalline structures, crystallization temperature and crystal conversion, and the shortest half-time values. A possible explanation is that at a higher rate of the crystallization process, the  $\beta \rightarrow \alpha$  phase transition is inhibited. Consequently, an increased content of the  $\beta$ -PP variety is observed.

Similar results with regard to the identification of a correlation between the determined parameters of the PP crystallization process and the development of its polymorphic varieties were recorded in our previous studies and were also confirmed for other fillers [61].

## Conclusions

Differences in the dispersive and porous structure properties of the novel hybrid fillers are a more attractive explanation for the observed differences in the nucleation ability. The findings made in the study can be shortly summarized as follows.

The determined parameters of the crystallization process for polypropylene systems combined with lignin or silica—such as the crystallization half-time, crystal conversion, crystallization temperature, and formation rate of transcrystalline structures—indicate that the fillers have a low surface activity compared to the unfilled matrix. The application of the SiO<sub>2</sub>/lignin hybrid fillers modifies the nucleation ability of the PP matrix; however, the nucleation activity is closely correlated with the hybrid filler composition. An increasing content of silica in the silica/lignin hybrid filler contributes to the achievement of very high nucleation activity. Investigations of the dispersive and porous structure properties of the novel materials showed the hybrid fillers with an increasing content of silica in the composition to be characterized by smaller particles, a larger specific surface area  $A_{\text{BET}}$  and pore volume, and a smaller pore surface. The study found a correlation between the dispersive and porous structure properties of the hybrid fillers and their nucleation ability. Moreover, the increase in thermal stability of the composites was observed for increasing mass content of silica in hybrid filler.

The applied hybrid fillers also differ in their ability to induce the formation of the hexagonal polymorphic variety of polypropylene under processing conditions. The SiO<sub>2</sub>/lignin hybrid fillers with a high content of silica in the composition display a high level of activity in terms of  $\beta$ -PP form generation. The study outlines a possible mechanism underlying the development of this polymorphic variety, including the formation of the so-called  $\alpha$ -row nuclei (previously described in the literature). It has been shown that the efficiency of formation of  $\alpha$ -row nuclei may be a function of the dispersive and porous structure of hybrid fillers. Moreover, the development of the supermolecular structure of the polymer matrix depends on the nucleation and crystallization processes which determine the progression of the  $\beta \rightarrow \alpha$  phase transition and, in effect, the amount of polymorphic varieties of polypropylene.

Understanding the dependence of the nucleation ability of the advanced functional silica/lignin hybrid fillers on the formation of the supermolecular structure is an important step toward designing optimal thermal processing protocols for these thermoplastic composites.

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