Silver nanoparticles in isotactic polypropylene (iPP)*) Part I. Silver nanoparticles as metallic nucleating agents for β-iPP polymorph

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Abstract: Isotactic polypropylene (iPP) nanocomposites containing 0.1, 0.2, 0.4 and 0.6 wt % of silver nanoparticles (nAg) were prepared by melt compounding in a one-screw extruder. Selected samples were isothermally recrystallized at different temperatures 50, 75, 100, 125, 130 and 135 °C, and under non-isothermal conditions. The size of the silver particles dispersed in the iPP matrix were estimated by ultraviolet/visible spectroscopy (UV-VIS). The effects of nAg additions on the structure of the iPP were studied by wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) techniques. The results clearly indicate that the addition of nAg induces the formation of the β-iPP polymorph. It is shown that the relative amount of the β form in the recrystallized nanocomposites depends on both the concentration of silver nanoparticles and thermal conditions of recrystallization.

Keywords: isotactic polypropylene, silver nanoparticles, polymorphism.

Nanocząstki srebra w izotaktycznym polipropylenie (iPP). Cz. I. Nanocząstki srebra jako metaliczne nukleanty formy β-iPP

Streszczenie: Nanokompozyty zawierające 0,1, 0,2, 0,4 oraz 0,6 % mas. nanocząstek srebra (nAg) w matrycy izotaktycznego polipropylenu (iPP) otrzymano w procesie wytłaczania za pomocą wytłaczarki jednoślimakowej. Próbki poddano rekrystalizacji w warunkach izotermicznych, w temp. 50, 75, 100, 125, 130 i 135 °C oraz rekrystalizacji nieizotermicznej. Wymiary cząstek srebra rozproszonych w matrycy iPP określano metodą spektrometrii UV/VIS. Wpływ nanocząstek srebra na formowanie struktury nadcząsteczkowej izotaktycznego polipropylenu oceniano techniką szerokokątowej dyfrakcji promieni rentgenowskich (WAXS) oraz różnicowej kalorymetrii skaningowej (DSC). Badania wykazały, że dodane cząstki Ag przyczyniają się do powstawania formy β w matrycy iPP. Względna zawartość tej polimorficznej odmiany w matrycy iPP zależy od stężenia nanocząstek srebra w rekrystalizowanym nanokompozycie oraz warunków termicznych procesu rekrystalizacji.

Słowa kluczowe: izotaktyczny polipropylen, nanocząstki srebra, polimorfizm.

Isotactic polypropylene (iPP) occurs in several polymorphic forms: α-monoclinic, β-hexagonal and γ-triclinic, from which the β form has recently been the subject of particular interest in many laboratories [1—6]. This interest stems from the specific physical and chemical properties of this form, different from that of the α form commonly occurring in the final product. The presence of the β form causes deterioration of the elastic modulus and strength at break, but has a positive effect on the elongation at break and the plasticity of the material [7, 8]. These changes in the properties of isotactic polypropylene are very attractive for many applications, e.g. in the packaging industry [9, 10].

The β form can be obtained by adding specific compounds of low molecular mass, known as nucleating agents, to molten polypropylene [5, 11—16]. The best known and most effective compounds of this type are pigment Red E3B [17], as well as calcium salts of pimelic and suberic acids [18]. There are also other methods of obtaining the β forms that may require employment of specific thermal conditions [6, 19, 20] or an appropriate processing method [21—26]. Varga, Nakamura and Lotz, in their studies on the β form of iPP, have proved that, beyond a certain temperature (135—140 °C), the α form is thermody-

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namically favored [6, 19, 27]. In previous publications, we have shown that the content of the α phase increases [28] as a result of β form transformation into the α form [29] above 147 °C.

Recently, it has been reported that silver nanoparticles (nAg) can induce the formation of the β form of isotactic polypropylene [30, 31]. The samples analyzed by Chae and Kim were obtained by dynamic crystallization in reometry at 130 and 140 °C and at the angular frequency 1 or 5 rad · s^{-1} [30]. As a result of such a dynamic crystallization, the β form of iPP appeared in samples containing 5 % nAg and at only 130 °C. Tjong and Bao have analyzed the samples obtained by injection at a mold temperature of 40 °C, therefore the crystallization proceeded quasi-isothermally and with the involvement of shear forces. As a result of such an experiment, the samples contained ca. 20 % of β form irrespective of the amount of added nanoparticles [31]. In the above cited works, the formation of the beta polymorph was a result of a simultaneous effect of silver nanoparticles and shear forces. Therefore, a direct role of silver in the formation of beta polymorph of isotactic polypropylene remains an open question. To clarify this point, we decided to study samples recrystallized without external forces. The procedure of hot stage recrystallization would allow elimination of the processing influence and permit an estimation of the role of silver nanoparticles in the formation of the β-iPP form. The study reported in this paper is the first step to explain the phenomenon of silver nanoparticles inducing the appearance of the β form in isotactic polypropylene matrices.

EXPERIMENTAL PART

Materials

Isotactic polypropylene MOPLEN HP 500J with a melt flow index $MFI_{(230\ °C/2.16\ kg)}$ = 3.2 g/10 min was obtained commercially from Basell Orlen Polyolefins. Silver nanoparticles of particle size less than 100 nm in powder form were supplied from the Sigma-Aldrich Corporation.

Preparation of polypropylene/silver nanocomposites

Polypropylene granules containing silver nanoparticles in the amount of 0.1, 0.2, 0.4 or 0.6 wt % were obtained by double extrusion in a single screw extruder (HAAKE PolyDrive) with the following temperatures in the particular sections: 140 °C, 190 °C, 210 °C, 210 °C and a screw speed of 20 rpm. Extrusion was preceded by mechanical mixing of components.

Recrystallization of samples

The obtained nanocomposite granules were recrystallized on the Boetius hot stage between microscope slides under isothermal and non-isothermal conditions. The temperature program used during recrystallization is shown in Fig. 1.

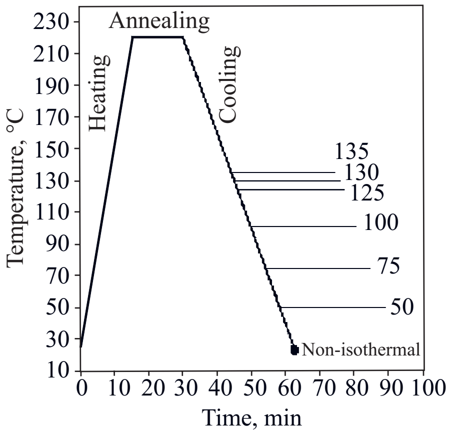

Fig. 1. Temperature program used in the recrystallization of nanocomposites of polypropylene with silver nanoparticles

Methods of testing

UV/VIS spectrophotometry

The nanocomposite granulates were converted into thin films. After that, UV/VIS spectra were obtained on a V-630 spectrometer (Jasco) in the transmission mode to confirm the presence of silver nanoparticles in the iPP bulk [32, 33]. The spectra were analyzed in the range 300—500 nm.

Wide angle X-ray scattering

The structures of recrystallized samples were analyzed by means of wide angle X-ray scattering (WAXS) using a TUR M-62 apparatus with a horizontal goniometer HZG-4. The whole measurement system was modernized and equipped with computer control. The X-ray diffraction pattern was recorded using CuKα radiation at 30 kV and 25 mA anode excitation for the range of 2θ = 10—30° at a step of 0.04°/3s. Deconvolution of the WAXS curves to single peaks was performed by a hybrid system using a combination of Gauss and Cauchy functions [34], improved and programmed by Rabiej [35]. After separation of X-ray diffraction lines, the content of the β form (parameter k) was calculated by using the well known Turner–Jones formula [36]:

$$k = \frac{I_{\beta 1}}{I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}} \cdot 100\ \% \qquad (1)$$

where: $I_{\alpha 1}$, $I_{\alpha 2}$, $I_{\alpha 3}$ — the intensities of three typical peaks of α form assigned to the (110), (040) and (130) planes of the α cell, respectively, $I_{\beta 1}$ — the intensity of the strongest diffraction peak of the β form assigned to the (300) plane.

Differential scanning calorimetry

DSC studies were carried out using a differential scanning calorimeter, DSC 200 (Netzsch). The samples crystallized under non-isothermal conditions were placed in calorimetric pans. The reference was an empty pan, measurements were made in argon atmosphere at a heating rate of 10 K/min and then at a cooling rate of 5 K/min. Cooling was preceded by annealing at 220 °C for 15 min.

RESULTS AND DISCUSSION

Spectrophotometry UV/VIS

The absorption bands of silver plasmon resonance appeared in the range from 390 to 410 nm in all UV/VIS spectra of the composites (Fig. 2). The spectra confirmed the silver particles size as below 100 nm [32, 33].

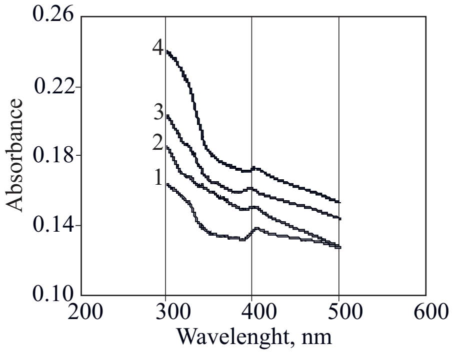

Fig. 2. UV/VIS spectra for isotactic polypropylene composites containing silver nanoparticles: 1 — 0.1 wt % nAg, 2 — 0.2 wt % nAg, 3 — 0.4 wt % nAg, 4 — 0.6 wt % nAg

Wide angle X-ray scattering

Figure 3 shows the diffraction pattern of isotactic polypropylene without silver (a) and of nanocomposite containing 0.4 wt % silver nanoparticles, as an example (b).

In the WAXS pattern of iPP without silver nanoparticles (Fig. 3 a), only five characteristic peaks of α form iPP were detected at 2θ = 14.1°, 16.9°, 18.5°, 21.2° and 21.8° of (110), (040), (130), (111) and (041) planes, respectively. However, all the X-ray diffraction patterns of iPP/nAg composites exhibited another distinct diffraction peak at 2θ = 16.1°, which is assigned to the (300) crystal plane of β form (Fig. 3 b). Furthermore, the intensity of the diffraction peak at 21.2° was higher than that of the peak at 21.8°.

Table 1. Content of β-iPP (*k*) in obtained composites after iso- and non-isothermal crystallization

nAg content wt %	Parameter *k*, %						
	Temperature of isothermal crystallization, °C						non-isothermal
	50	75	100	125	130	135	
0.1	10.0	12.6	17.2	40.6	46.6	43.9	29.5
0.2	16.8	31.2	28.5	64.7	63.9	48.7	28.8
0.4	22.7	27.0	46.1	68.8	64.3	49.7	33.4
0.6	22.5	30.0	39.8	70.4	70.6	51.0	67.1

Analysis of Fig. 4 and the data collected in Table 1, has shown that the formation of β form depends on the amount of silver nanoparticles, as well as temperature of crystallization.

The smallest amount of β-iPP was noted in the samples containing 0.1 wt % nAg and after crystallization at relatively low temperatures (50 and 75 °C). In the samples with all other contents of nAg, after crystallisation at 50 °C, the contribution of β-iPP form was close to 20 %, which is in agreement with the results of Tjong and Bao [31]. However, we should remember that shear forces related to the process of injection could play a certain role in the crystallization reported by Tjong and Bao. This fact confirms that the shear forces have a significant influence

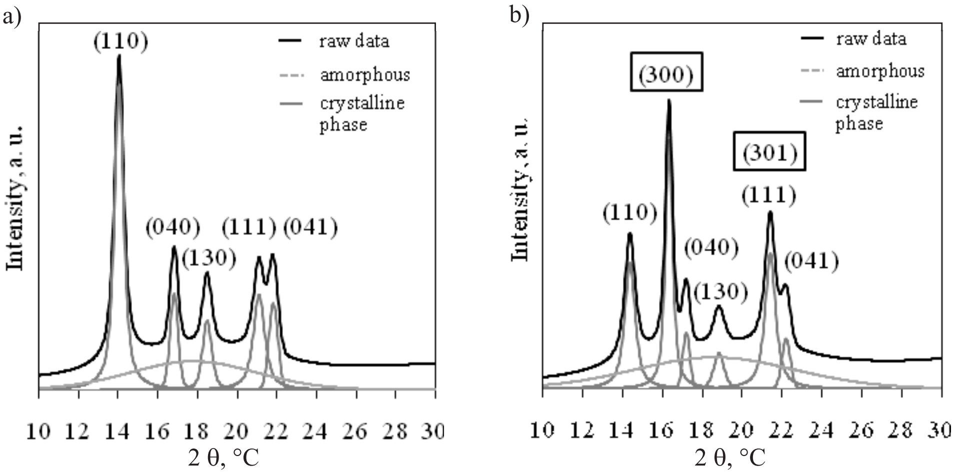

Fig. 3. WAXS patterns of isotactic polypropylene with separation of maxima: a) isotactic polypropylene without silver nanoparticles, b) composite containing 0.4 wt % nAg

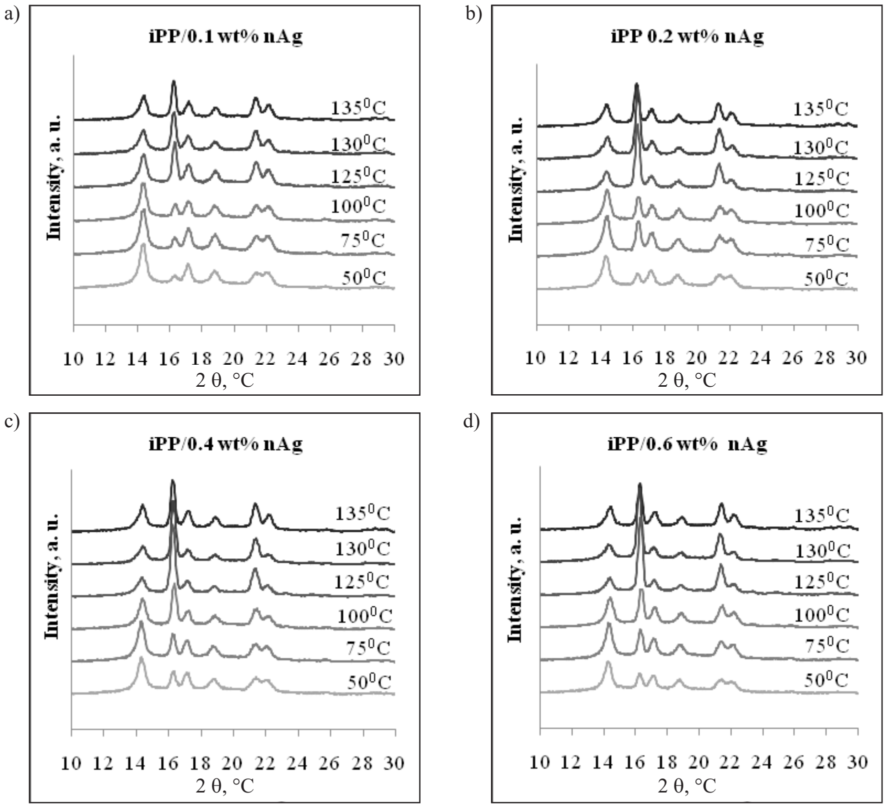

Fig. 4. WAXS patterns of iPP/nAg nanocomposites obtained in isothermal conditions containing: a) 0.1 wt % nAg, b) 0.2 wt % nAg, c) 0.4 wt % nAg, d) 0.6 wt % nAg

on the quantity of β form, especially when the filler content is low.

The highest amount of β form was observed in samples containing 0.6 wt % nAg after crystallization at 125 °C and 130 °C, or in samples obtained under non-isothermal conditions. These results correspond with literature data indicating that temperatures between 100 °C and 141 °C are the most favorable for the formation of the β form [6].

Contrary to Tjong and Bao's observations, our results clearly show that the number of active sites on the surfaces of nanoparticles distributed in the molten polymer has a significant influence on the arrangement of chains in the iPP matrix.

Differential scanning calorimetry

Fig. 5a shows the melting curves recorded for the composites and unfilled polypropylene in non-isothermal conditions. The spectra of the composites show an extra peak at about 151 °C in comparison to the spectrum of unfilled iPP (Table 2), which confirms the presence of β form iPP in the nanocomposites [19, 31, 37, 38].

For all composites obtained under non-isothermal conditions, a small increase in the crystallization temperature was observed compared to pure polypropylene (Fig. 5 b and Table 2).

Such an observation was also made by Chae, Kim [30] and Tjong, Bao [31].

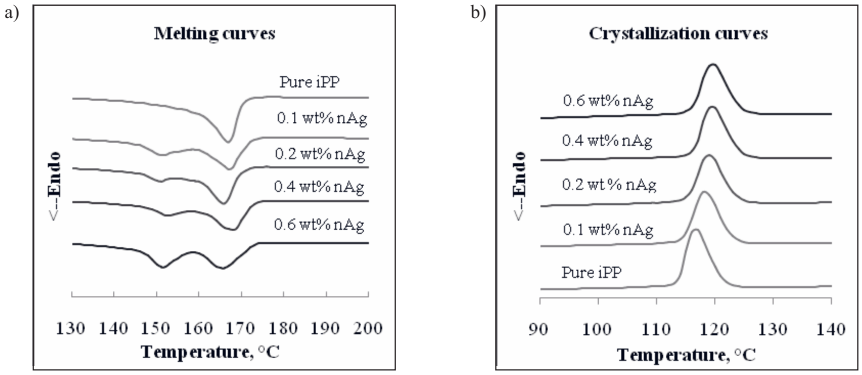

Fig. 5. Melting (a) and crystallization (b) curves of the pure iPP and composites obtained in non-isothermal conditions

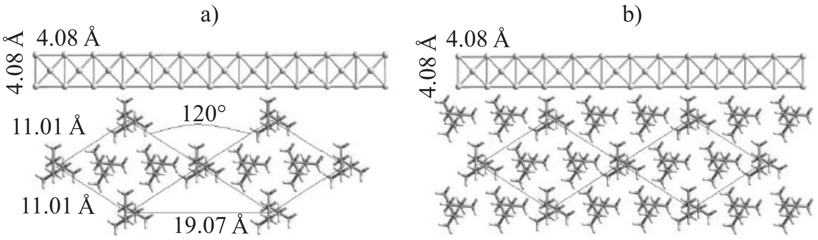

Fig. 6. Dimensional lattice matching between Ag surface and β form iPP: a) conformation of iPP chains at the layer adjacent to the Ag surface, b) growing β form iPP matrix

Table 2. Melting point of the α (T_m^{α}) and β (T_m^{β}) forms, and crystallization temperature (T_c) of iPP nanocomposites obtained under non-isothermal conditions

Sample	T_m^{β}, °C	T_m^{α}, °C	T_c, °C
iPP		167	117
iPP+0.1 wt % nAg	151	167	118
iPP+0.2 wt % nAg	151	167	119
iPP+0.4 wt % nAg	152	168	120
iPP+0.6 wt % nAg	151	166	120

Mechanism of the β-iPP nucleation

Taking into account the above observations, we can consider two reasons for the formation of the beta form. The first is epitaxial growth of iPP on the surface of Ag, while the second is the difference in specific heat of Ag and iPP.

The mechanism of formation of β form isotactic polypropylene on the surface of nucleating agents has been analyzed several times [6, 39—44]. The epitaxial theory has been proposed by several researchers as a result of matching the nucleating agents lattice and the crystal lattice of the α and β form isotactic polypropylene [40, 45]. Lotz and coworkers have proposed a "dimensional lattice matching theory" on the basis of analysis of structural relationships between nucleating agents and the β form [42].

According to the proposition of Kawai and coworkers, epitaxy occurs when the relative difference between the lattice parameters of the substrate (nucleating agent) and the macromolecule is less than 15 % [45]. This difference, called the misfit factor (f_{m}), can be calculated according to the following equation:

$$f_m = \frac{\mathrm{PB} - \mathrm{PA}}{\mathrm{PA}} \cdot 100\ \% \qquad (2)$$

where PA and PB are the appropriate period lengths of the substrate and polymer, respectively.

However, if we compare the distance between neighboring Ag atoms (parameter *a* = 4.0853 Å) [46] and H atoms from methyl groups of iPP, we can find that the misfit factor f_{m} (eq. 2) very much exceeds 15 %. The above results indicate that the interactions between protons and silver particles may not take place with any neighboring Ag atoms but with atoms located at distances that are multiple of the *a* parameter (Fig. 6 a).

The distance between protons of methyl groups from adjacent chains in the unit cells of β form iPP is about 19.07 Å [47—49]. However, the distances between neighboring Ag which is parameter *a* multiplied by 5 is 20.43 (5×4.0853 Å). The ratio f_{m} calculated on the basis of these values gives 6.6 %. This implies that one of three polypropylene chains undergoes weak adsorption on the surface of silver (Fig. 6a), which imposes the appropriate arrangement of the first layer iPP crystal lattice adjacent to the silver surface. This arrangement of polypropylene chains favors the formation of the β form (Fig. 6 b). A possibility of interaction of Ag and H has been shown by Baetzold [50] and Akbulut [51], who on the basis of quantum mechanical computation have demonstrated that weak electrostatic interactions between the metal surface and hydrogen of hydrocarbons can exist. These interactions have a dipole-dipole nature and depend on the electron configuration of the metal. Therefore, it is possible that iPP chains have been adsorbed on the surface of silver particles as a result of interactions of protons from CH_3 groups with electrons on the metal surface.

Considering the role of Ag in formation of β iPP, we also should take into account the difference in specific heat of silver [Ag (0.235 J/g·K) and iPP (2 J/g·K)], the former is around 10-times lower than the latter. This suggests that during crystallization as an exothermic process, the heat from the solidifying iPP matrix has been quickly absorbed by silver particles and, in consequence, the temperature in the polymer around Ag decreased. Such a thermal condition favors crystallization and the appropriate arrangement of iPP chains at the layer adjacent to the silver surface. The role of nAg in the distribution of heat in the polypropylene matrix has been also suggested by Chae and Kim, who on basis of an investigation of TGA (Thermogravimetric analysis) noted: "that the nanoparticles in polymer matrix play a role in retarding heat penetration" [30].

Verification of the above hypotheses is the subject of our next study, described in part II, including molecular modeling by using computational procedures.

CONCLUSIONS

In this study, the nucleating ability of silver nanoparticles toward iPP and their influence on the content of the β form and the crystallization behavior of iPP under isothermal and non-isothermal conditions of the crystallization process was investigated. The experimental results indicate that silver nanoparticles are a temperature-dependent, selective nucleating agent in iPP crystallization. The content of β-iPP is strongly related to the amount of silver nanoparticles added and the temperature conditions of crystallization.

The mechanism of formation the β form may be related to the epitaxial growth of iPP on the surface of Ag or to the differences between specific heat of iPP and nAg. We do not exclude that both of these factors contribute to the process and complement each other.

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