Available online at www.sciencedirect.com

ScienceDirect

Polymer 47 (2006) 6457–6463

polymer

www.elsevier.com/locate/polymer

The effect of the addition of silica particles on linear spherulite growth rate of isotactic polypropylene and its explanation by lamellar cluster model

Koh-hei Nitta [a],*, Kazuo Asuka [b], Boping Liu [b], Minoru Terano [b]

[a] *Department of Chemical Engineering, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan*
[b] *School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Ishikawa 923-1292, Japan*

Received 24 March 2006; accepted 19 June 2006
Available online 18 July 2006

Abstract

The effect of the addition of silica particles on spherulite growth rates of isotactic polypropylene has been investigated using an optical microscope. The spherulite growth rate remained constant with time and the growth rates decreased with increasing the silica content. The addition of silica particles generally causes a reduction of the average distance between adjacent silica particles and the linear growth rates become zero when the inter-particle distance reached to the end-to-end distance of the matrix chains. The reduction in the linear growth rate can be explained by assuming the lamellar clustering process that the precursor or solidified units with the single chain space, which spontaneously are built up from the melt, act as the crystallizing units and the diffusive mobility of the units was restricted by spatial confinement between adjacent silica particles.

Keywords: Isotactic polypropylene; Nanocomposite; Spherulite growth rate

1. Introduction

Much attention has been paid to polymer/inorganic filler nanocomposites in the development of novel engineering materials because of their considerable improvements of strength and modulus, gas barrier resistance, and optical transparency [1]. In particular isotactic polypropylene (iPP) based nanocomposites are of great interest for various industries since iPP has been extensively used in a variety of products such as automotive parts, furniture and containers [2–10].

As well known, iPP crystallized from melt shows spherulitic structure in which crystalline lamellae composed of folded chains radiate from a fixed point and the amorphous phase resides in the interlamellar regions. In the previous works [11,12], we have proposed a new solidification process in crystallizable polymers such as polyethylene (PE) and iPP in which the lamellar clustering takes place in the crystallization process under higher supercoolings. Clustering of lamellae will be a two-step process: the first step is the exclusion process of chain ends from the single chain space being accompanied by the cooperative alignment of stiffened segments and this leads to the precursor units including several intertwined chains, and it is followed by the two-dimensional developments of the quasi-solidified units into the final lamellar cluster. Considering the fact that a molecule has a dimension in the melt greater than the distance between the adjoining crystallites (ranged from 10 to 20 nm), the segregation of chain ends causes the tie molecules, which run from one lamella to a neighboring one in crystallized solids, to bind several stacked lamellae. This solidification process leads to the lamellar clusters with thickness being comparable with the end-to-end chain distance.

Spherulite morphology is a macroscopic superstructure, the size of which is usually in the order of 1–10 μm, leading to opaqueness and turbidity of the materials. As a result, the reduction of the spherulite size significantly improves the

---

* Corresponding author. Tel.: +81 76 234 4818; fax: +81 76 264 6220.
E-mail address: nitta@t.kanazawa-u.ac.jp (K.-h. Nitta).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.06.054

transparency in the materials. In our preceding paper [13], spherical silica particles can be highly dispersed into iPP matrix using a two-roll mixer and we also observed the disappearance in turbidity of iPP composite sheets filled with nanoscopic silica spheres.

The purpose of this study is to investigate the effects of the addition of spherical silica particles on the spherulite crystallization of iPP. In this work, we have examined the radial growth rate of spherulites under some isothermal conditions for several iPP composites filled with nano- and microscopic silica particles. The spherulite crystallization behavior in iPP/nano-particles was considered according to the lamellar clustering process.

2. Experimental

2.1. Materials

The starting materials used as the matrix polymer were isotactic polypropylenes with a high isotacticity (98–99%) and different molecular weights: the weight average molecular weight $M_w = 260 \times 10^3$ and molecular weight distribution index $M_w/M_n = 5.65$, $M_w = 377 \times 10^3$ and $M_w/M_n = 8.14$, and $M_w = 490 \times 10^3$ and $M_w/M_n = 4.38$. These iPP polymers were donated by Chisso Corp.

Four commercial grades of silica particles, having an average particle diameter of about 16 nm, 26 nm, 100 nm, and 51 μm, were used as fillers in this work: the SiO_2 (Aerosil® 200) with an average particle size of 16 nm was donated by Aerosil Japan Co.; SiO_2 (NanoTek®) with an average particle size of 26 nm was purchased from Kanto Chemical Co.; SiO_2 (KE-P10) with an average particle size of 100 nm was donated by Nippon Shokubai Co.; SiO_2 (Crossfield® ES70X) with an average particle size of 51 μm and surface area of 316 m^2/g was donated by Asahi Kasei Co.

In addition, the surface modification of SiO_2 particles with a diameter of 26 nm was performed. The surface of the silica particles was modified with silane coupling agents to improve the miscibility with hydrophobic iPP matrix. Silica particles can be easily modified to change its surface nature from hydrophilic to hydrophobic using some silane coupling agents [14,15]. In this work, the surface modification with hydrophobic methyl (C1) and octyl chains was performed using trimethylchlorosilane (C1) and *n*-octyldimethylchlorosilane (C8), obtained from Gelest Inc., respectively.

2.2. Preparation of PP/SiO_2 nanocomposites

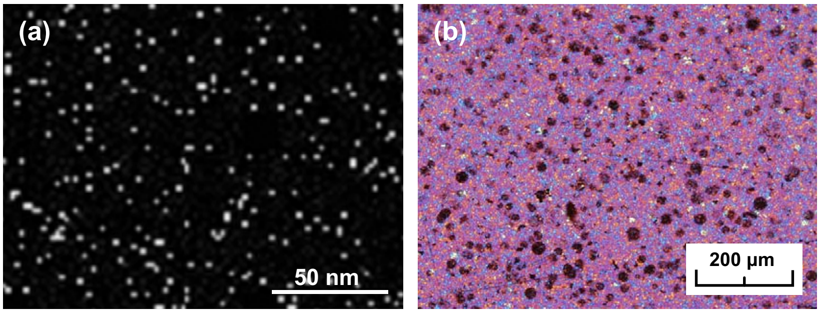
Composites were prepared by melt mixing SiO_2 particles with different diameters of 16 nm, 26 nm, 100 nm and 51 μm, respectively. Melt mixing was performed in a corotating twin-roller. The PP pellets were kneaded by mixing rollers at 180 °C for 5 min and then a given amount of SiO_2 was added into the kneaded PP. The mixture was kneaded at 180 °C for another 10 min. The samples thus prepared were collected during the cooling process of the roller and subsequently stored in a refrigerator. The content of SiO_2 in the PP/SiO_2 composites was changed from 0 wt.% to 5.0 wt.%.

2.3. Spherulite growth behavior of PP/SiO_2 composites

The polarizing optical microscope (Olympus, B201) equipped with a Mettler FP82HT hot stage was used to examine the isothermal crystallization processes of neat iPP and the composites. An optical polarizing microscope was used. The hot stage was held at a steady temperature of ±0.2 K by a proportional controller. The thin sample pieces were sandwiched between a microscope slide and a cover glass, heated to 503 K and kept at this temperature for 10 min to completely melt the crystallites. Then the samples were rapidly quenched to a given crystallization temperature and allowed to crystallize isothermally. The radius of a spherulite was measured as a function of time under the isothermal crystallization condition at the temperatures of 339, 403, and 407 K.

3. Results

The dispersion state in nanocomposite was characterized by a scanning electron micrograph (SEM-EDS) Si-mapping method [13]. As shown in Fig. 1(a) the SiO_2 nano-particles (16 nm) were clearly observed homogeneously dispersing in the iPP matrix and no obvious agglomerations of silica particles up to micron size scale were differentiated by human eyes through POM observation. Whereas, the dispersability of



iPP/SiO_2-16nm   iPP/SiO_2-51μm

Fig. 1. (a) A scanning electron micrograph (SEM-EDS) Si-mapping in iPP composites filled with silica particles having the size of 16 nm [13]. (b) Polarized optical micrograph pictures of iPP composites filled with silica particles having the diameter of 51 μm.

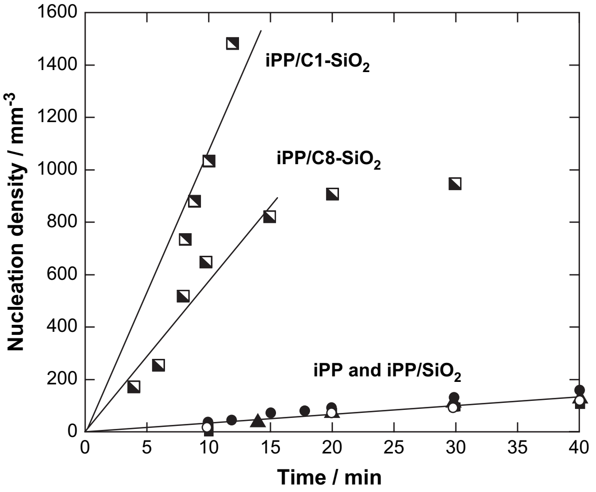


Fig. 2. Nucleation density calibrated by the volume of measured area in the POM under a fixed temperature of 403 K for iPP/SiO$_2$ composites filled with neat silica and surface-modified ones where ○: iPP; ▲: iPP/51 μm-SiO$_2$; ■: iPP/100 nm-SiO$_2$; ●: iPP/26 nm-SiO$_2$.

silica particles (51 μm) in the micro-composite was examined by polarizing optical microscope (POM) pictures. As shown in Fig. 1(b), it was clearly observed that isolated silica particles with the size of about 50 μm were randomly dispersed in the iPP matrix.

When each sample piece is set in the hot stage under the POM, spherulites begin to spontaneously appear. The overall crystallization process includes the spherulite growth and the primary nucleation. The primary nucleation process can be realized by counting the number of spherulites as a function of time. Fig. 2 shows the nucleation density calibrated by the volume of area measured in the POM at a fixed temperature. The nucleation rates of the composites filled with all neat silica particles were found to be almost in accordance with that of the neat iPP being independent of the size of particles, indicating that the neat silica particles have no ability to be the nucleus for iPP. This is likely because iPP is completely immiscible with the silica particles owing to hydrophilic surface of the silica particles. On the other hand, the addition of the hydrophobic silica particles, C1-SiO$_2$ and C8-SiO$_2$, markedly raises the primary nucleation rate, suggesting that the surface-modified silica particle can act as primary nuclei of iPP.

The linear spherulite growth rate for all iPP/SiO$_2$ composites and neat iPP was evaluated by measuring the spherulite radius as a function of time. In Fig. 3 an example of the measurement of the growth rate in radial direction is shown, which makes the time when the growth started as the starting point of the time axis. It was possible to reliably determine the growth rates of all the samples because of the linear relationship between the radius of spherulites and crystallization time. The linearity is also held in the composites with surface-modified particles (see Fig. 3(b)). These results, that the growth rates remained constant at a given temperature being independent of surface modification of silica particles, demonstrate that the SiO$_2$ concentration in the melt ahead of the growth front did not change throughout the growth and the silica particles were accommodated inside the spherulites rather than segregation to the boundary [16].

Growth rates measured isothermally at 407, 403, and 399 K are plotted against the content of SiO$_2$ particles in Fig. 4. The spherulite growth rates of iPP spherulites decrease significantly with increasing the SiO$_2$ content and markedly reduces with decreasing the particle size at any temperature. Furthermore, it is interesting to note that the linear growth rates of iPP/C1-SiO$_2$ and iPP/C8-SiO$_2$ are almost the same with that of iPP/SiO$_2$ as shown in Fig. 4(b) and the growth rate is independent of the surface modification of silica particles.

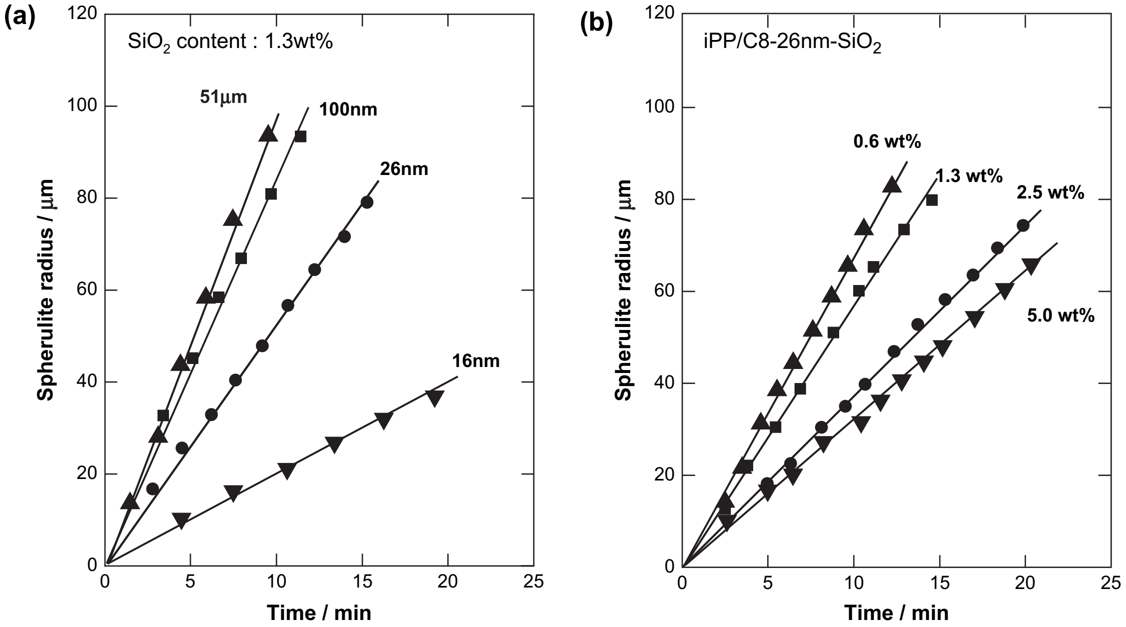


Fig. 3. The spherulite radius plotted against the crystallization time for iPP nanocomposites (a) filled with neat silica particles and (b) filled with surface-modified silica of 26 nm by octyl groups.

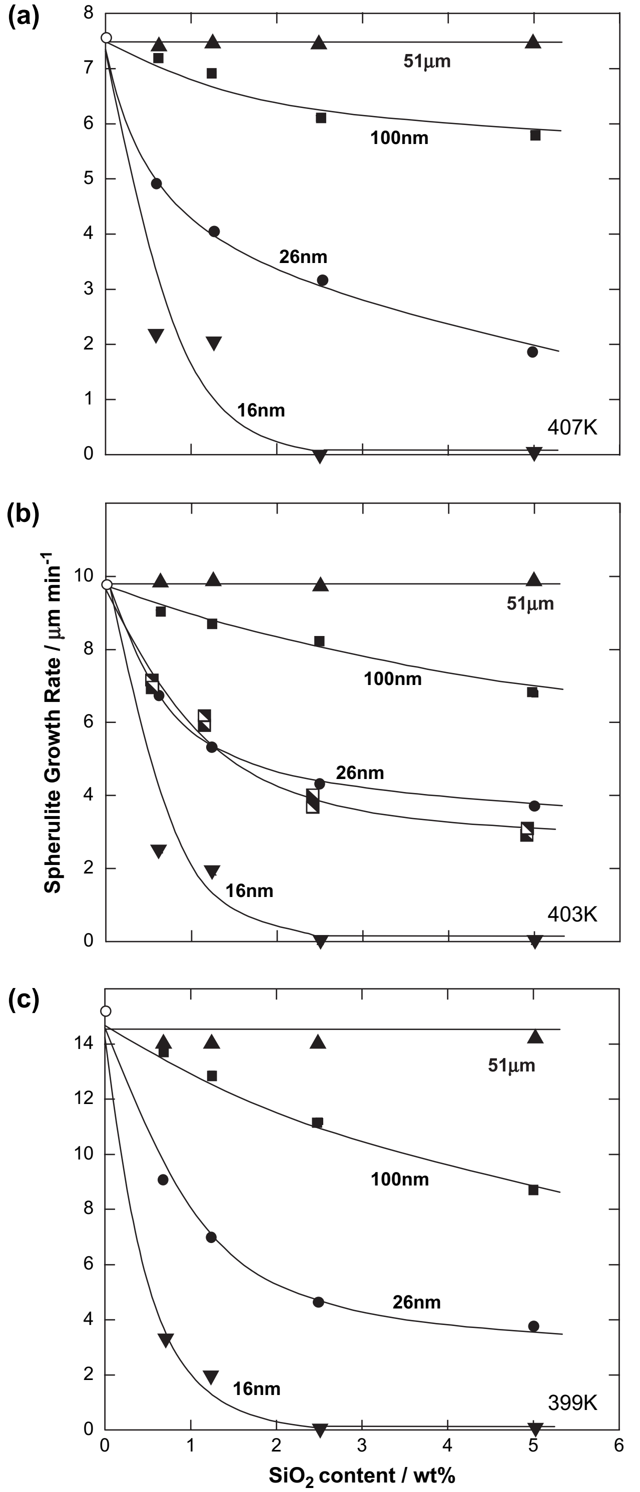


Fig. 4. Silica content dependence of the spherulite growth rates isothermally measured at (a) 407, (b) 403, and (c) 399 K. ▼: iPP/16 nm-SiO$_2$; ○: iPP; ▲: iPP/51 μm-SiO$_2$; ■: iPP/100 nm-SiO$_2$; ●: iPP/26 nm-SiO$_2$.

Assuming that particles are homogeneously dispersed in a matrix, the distance between the surfaces of adjacent particles d can be estimated by [17]

$$d=\left[\left(\frac{4\pi\sqrt{2}}{3\phi}\right)^{1/3}-2\right]r \tag{1}$$

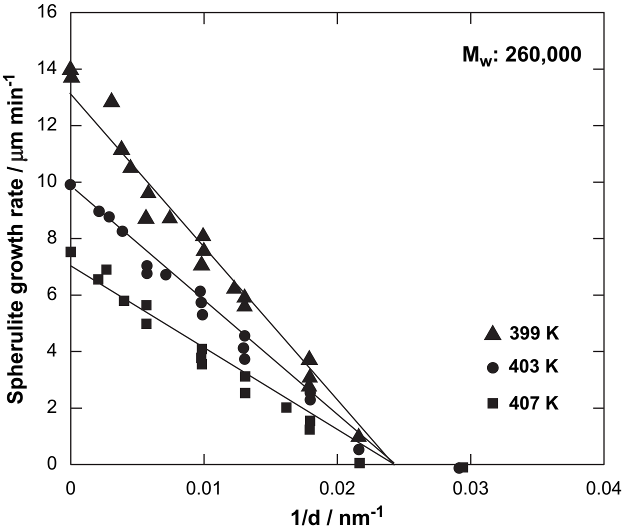


Fig. 5. Spherulite growth rate plotted against the reciprocal of the distance between adjacent silica particles for the composite of iPP with $M_w = 260 \times 10^3$.

where ϕ and r are the volume fraction and the radius of the particle, respectively. All the data were replotted against the reciprocal of the inter-particle distance $1/d$. It should be noted here that all data measured at each temperature fall on the each straight line and the slope of the line k decreases with increasing the crystallization temperature (see Fig. 5). In addition, it was found that the intercepts of these lines with the $1/d$ axis give a critical distance d_c which is independent of the temperature. Consequently, we found the following relation between the iPP spherulite growth rates G_C in the composites and the inter-particle distance at a given temperature:

$$G_C = G - k\frac{1}{d} \tag{2}$$

where G is the linear growth rate of the pure iPP. The addition of silica particles generally causes a reduction of the average distance between adjacent particles and the linear growth rates become zero at the inter-particle distance $d = d_c$. Then, we have

$$G = \frac{k}{d_c} \tag{3}$$

Our further attention about the slope k and the intercept d_c is to examine their molecular weight dependences. The linear growth rates for the iPP ($M_w = 377 \times 10^3$) based composites and the iPP ($M_w = 490 \times 10^3$) based composites were measured under a fixed temperature of 403 K. It was found that the linear growth rates of these composites decrease with an increase in the molecular weight M_w of matrix iPP over all the experimental range of silica content. Furthermore, the addition of silica on these iPP samples causes a drastic reduction in the linear growth rate in the same manner as for iPP ($M_w = 260 \times 10^3$). It was found that the slope of the line k is independent of the molecular weight of iPP and the value of d_c increases with an increase of the molecular weight M_w of iPP matrix, as shown in Fig. 6.

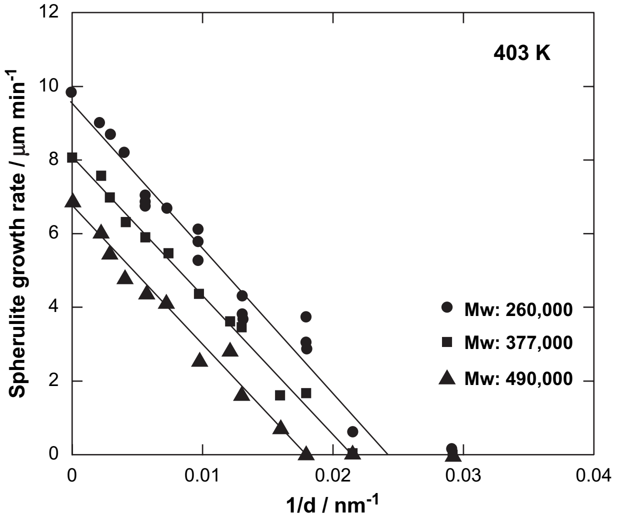


Fig. 6. Molecular weight dependence of spherulite growth rate, measured at 403 K plotted against the reciprocal of the distance between adjacent silica particles.

Here, we compare the values of d_c and the end-to-end distance of unperturbed chains of iPPs used in this work. As seen in Table 1, surprisingly, the values of d_c coincide with the end-to-end distance of the matrix iPP chains:

$$d_c \cong \langle r^2 \rangle^{1/2} \tag{4}$$

This indicates that the spherulite growth rate of the composites becomes zero when the inter-particle distance is less than the end-to-end distance of the iPP chains.

Combination of Eqs. (3) and (4) gives the following equation and the linear growth rate of iPP becomes proportional to $M_w^{-0.5}$:

$$G \cong k\langle r^2 \rangle^{-1/2} \propto M_w^{-0.5} \tag{5}$$

The resultant Eq. (5) drawn from our results for crystallization process in composites reached an empirical relation recently proposed by Umemoto et al. [18,19]. They demonstrated that the molecular weight dependence of the linear growth rate can be expressed as the power of −0.5 for folded chain crystallization process in various crystalline polymers.

4. Discussion

The kinetics of isothermal spherulitic growth has been 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. It is reasonable that this reduction in growth rate is attributed to a reduction in mobility or transportation of crystallizing units caused by the nano-spheres [16].

Table 1
End-to-end distance of the matrix iPP and the critical distance of its composites

$M_w \times 10^3$	$\langle r^2 \rangle^{1/2}$ (nm)	d_c (nm)
260	40.1	40
377	48.9	46
490	55.8	57

In the present case one point of interest is how the presence of spherical fillers affects the kinetics of the growth rate. Here, we consider the lamellar cluster model as previously demonstrated by Nitta–Takayanagi [11,12]. In our preceding papers, we proposed a lamellar clustering process to occur during the supercooling of PE and PP with a wide range of molecular weight to account for the yield behavior. The idea of occurrence of chain ends-exclusion process in the supercooled state led us to conclude that precursor units are spontaneously built up from the homogeneous texture of the melt and contain partially stiffened segments on the basis of Fischer's solidification process [20]. The precursor units, with a diameter similar to the space occupied by a single Gaussian chain, include many intertwining chains. The partially stiffened chain segments within the precursor units tend to align with their molecular axes in parallel in the supercooled state, forming a smectic packing as theoretically proposed by Zachmann [21]. Then the stiffened segments are cooperatively ordered to form crystalline lamellae within the precursor units. Thus, the solidified units are composed of stacks of several interleaved crystalline lamellae and amorphous layers. In the isothermal condition, they will move to the growth front in the quasi-solidified state and are ordered to form the lamellar clusters.

The thickness of the cluster units can be determined as the weight average value calculated from the probability that a chain penetrates a stack of lamellae of total thickness L. The average thickness of lamellar cluster is obtained by [12]

$$L_w = \frac{3}{4}\sqrt{\frac{2\pi}{3}}\langle r^2 \rangle^{1/2} \cong 1.08\langle r^2 \rangle^{1/2} \tag{6}$$

The lamellar cluster thickness was found to be almost equal to the end-to-end distance of unperturbed chains in the melt. This implies that the volume of the precursor or quasi-solidified cluster units is estimated to be L_w^3. This is likely since the precursor units are assumed to be built up by segregation process of chain ends in the supercooled state.

The reduction in growth rates due to the addition of silica particles cannot be fully understood by the classical crystallization kinetics based on the molecular transportation and secondary nucleation processes because polymer chains have enough space to diffuse to the crystallization front even if the inter-particle distance is on the size scale as the end-to-end distance of polymer chains.

The reduction in the linear growth rate can be explained by assuming that the precursor or solidified units act as the crystallizing units in isothermal crystallization kinetics. Thus, the reduction results from spatial confinement of the precursor units into small volumes between adjacent particles, leading to a retardation of the diffusive mobility of precursor or cluster units. Fig. 7 shows the schematic illustration of the solidification process of iPP/silica composites at the critical condition.

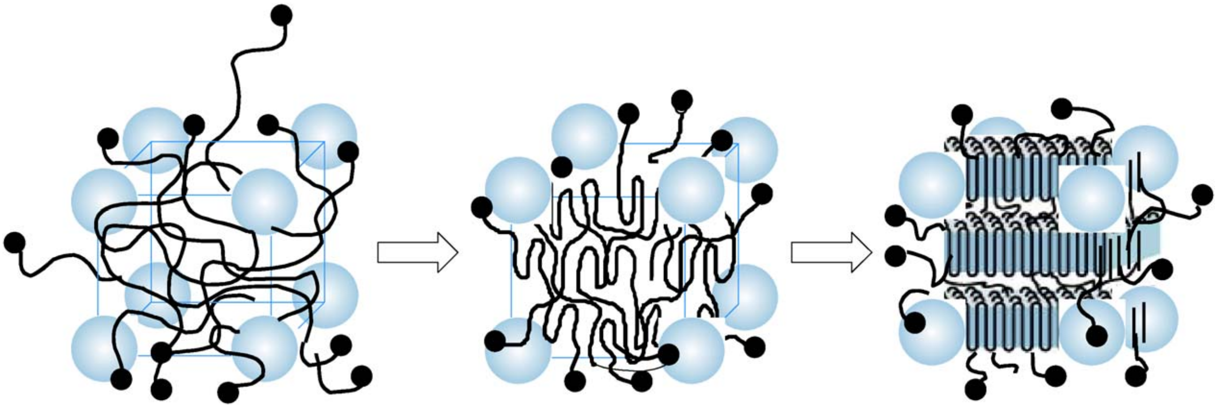


Fig. 7. Schematic illustration of the solidification process of iPP/silica composites at the critical condition that inter-particle distance equals the end-to-end distance of iPP chains.

Thus, we can assume that the spherulite growth rate of the composites approaches zero as the distance between adjacent particles approaches L_w. Consequently, the linear growth rate of pure iPP can be obtained by using $d_c = L_w$ in Eq. (3):

$$G = k L_w^{-1} \tag{7}$$

The lamellar cluster thickness L_w is independent of temperature and depends on the molecular weight while the parameter k is independent of molecular weight and depends on the temperature. Therefore, the kinetics for spherulite growth will be directly derived from the temperature dependence of the parameter k.

In one possible case, silica particles may be rejected to spherulite borders, causing an increase in nano-filler concentration in the pre-crystallized melt and, consequently, a gradual decrease in growth rate during crystallization. In this case, growth rates do not keep constant and should be saturated with time, which was not observed. The growth rate was constant at any temperature for all composites. The existence of this linearity in growth rate implies that the SiO_2 concentration in the melt ahead of the growth front does not change throughout the growth and that silica particles are accommodated inside the spherulites rather than the segregation to the boundary, as also demonstrated by Waddon and Petrovic [16]. Moreover, the linear growth rates of the composites filled with modified silica particles (26 nm), which act as crystallization nuclei and/or remain essentially within the body of the spherulite, almost accord with those of the composites filled with unmodified silica particles (26 nm) over all the experimental range of silica contents (see Fig. 5). This is consistent with the conclusion that the reduction in growth rates result from the spatial constraints on crystallizing units which are introduced by confining them in the restricted space between particles.

5. Conclusions

It was found that the linear growth rates of spherulites in composites of iPP filled with silica particles are reduced as the content of silica particles increases. The addition of silica particles generally causes a reduction of the average distance between adjacent particles and the linear growth rates become zero when the inter-particle distance reaches to the end-to-end distance of iPP chains. The reduction in growth rates may result from the spatial constraints on crystallizing units introduced by confining them to the restricted space between particles. This can be understood by considering the lamellar clustering process in which the precursor units, with a diameter similar to the space occupied by a single Gaussian chain, act as a crystallizing unit. As a consequence, the reduction in growth rate is attributed to a reduction in mobility or the marked increase of the activation energy of the precursor units restricted or confined by the particles. Furthermore, this crystallization process can explain the empirical relation [18] that the growth rate is proportional to $M^{-0.5}$. Takayanagi has previously proposed this empirical relation based on the activation entropy of molecular transport term [22]. It is very interesting that the changes in activation entropy under isothermal crystallization are reconsidered by the lamellar clustering process. We believe that further analysis based on the lamellar clustering process may throw a new physical insight into the crystallization kinetics in semicrystalline polymers. This will be discussed in our future studies.

In addition, considering that inclusion of the silica particles within the crystal is clearly impossible and that the diameter of silica particles used in this work is larger than the typical thickness of amorphous layer of the iPP, the nano-particles are likely to be incorporated into the intercluster region. This strongly suggests that the addition of nano-silica particles can improve the mechanical properties of iPP.

Acknowledgements

We would like to express our sincere thanks to Emeritus Professor M. Takayanagi of Kyushu University for many helpful comments and suggestions. We also acknowledge Miss N. Iwata (Kanazawa University) for her support in experiments.

References

[1] Sinha Ray S, Okamoto M. Prog Polym Sci 2003;28:1539.

[2] Perrin-Sarazin F, Ton-That MT, Bureau MN, Denault BJ. Polymer 2005;46:11624.

[3] Silvesta C, Cimmino S, Raimo M, Cargagna C, Capuano V, Kotsikova R. Macromol Symp 2005;228:99.

[4] Kato M, Usuki A, Okada A. J Appl Polym Sci 1997;66:1781.

[5] Maiti P, Hoai P, Okamoto M, Hasegawa N, Usuki A. Macromolecules 2002;35:2042.

[6] Svoboda P, Zeng C, Wang H, Lee LJ, Tomasko DL. J Appl Polym Sci 2002;85:1562.

[7] Szazdi L, Pukánszky Jr B, Vansco GJ, Pukánszky B. Polymer 2006; 47:4638.

[8] Yang KY, Li G, Sun Y, Feng D. Mater Lett 2006;60:805.

[9] Saujanya C, Radhakrishnan S. Polymer 2001;42:6723.

[10] Garcia M, van Zyl WE, ten Cate MGJ, Stouwdam JW, Verweij H, Pimplapure MS, et al. Ind Eng Chem Res 2003;42:3750.

[11] Takayanagi M, Nitta K, Kojima O. J Macromol Sci Phys 2003;B42:1049.

[12] Nitta K, Takayanagi M. J Macromol Sci Phys 2002;B42:107–26.

[13] Asuka K, Boping L, Terano M, Nitta K. Macromol Rapid Commun 2006;27:910.

[14] Iler RK. The chemistry of silica. New York: Wiley; 1979.

[15] Arkles B. CHEMTECH 1977;7:766.

[16] Waddon AJ, Petrovic ZS. Polym J 2002;34:876.

[17] Tyuzyo K, Harada Y. Kolloid Z 1965;201:66.

[18] Umemoto S, Kobayashi N, Okui N. J Macromol Sci Phys 2002;B41:923.

[19] Umemoto S, Hayashi R, Kawano R, Kikutani T, Okui N. J Macromol Sci Phys 2002;B42:421.

[20] Fischer EW. Polym J 1985;13:307.

[21] Zachmann HG. Pure Appl Chem 1974;38:79.

[22] Takayanagi M. J Polym Sci 1955;19:200.