

# Influences of polypropylene grafted to SiO<sub>2</sub> nanoparticles on the crystallization behavior and mechanical properties of polypropylene/SiO<sub>2</sub> nanocomposites

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**Abstract** Influences of polypropylene (PP) grafted to SiO<sub>2</sub> nanoparticles (7 nm) were studied on the crystallization behavior and the mechanical properties of PP/SiO<sub>2</sub> nanocomposites. PP for the matrix and grafting was synthesized in order to have an identical primary structure, aiming at their co-crystallization and resulting reinforcement of filler-matrix interfaces. The grafted PP chains improved the dispersion of SiO<sub>2</sub>, and notably accelerated nucleation in crystallization. It was plausible that the grafted chains whose one chain end was pinned to SiO<sub>2</sub> became nuclei of the crystallization (co-crystallization between the matrix and grafted chains), thus directly bridging between the matrix and SiO<sub>2</sub> nanoparticles. The Young's modulus and tensile strength were most improved by the grafted PP chains at low filler contents such as 2.3 wt%, whose origin was attributed to effective load transfer to SiO<sub>2</sub> through the co-crystallization-mediated bridging.

**Keywords** Polypropylene · Nanocomposites · Crystallization · Mechanical properties

## Introduction

Polypropylene (PP) materials have been widely used for a variety of fields such as automobile parts, packaging, and containers because of the advantages of low price, light weight, high melting temperature, and excellent processability and mechanical properties. They are also environmentally friendly with low production energy and high reusability/recyclability. Owing to these advantages, the production and application of PP materials have continuously expanded, in which compounding

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with other materials has played a key role. Among a variety of PP compounds, nanocomposites containing nano-sized inorganic fillers have attracted a great attention in the last two decades because they are expected to offer properties that are not realizable with micron-sized fillers [1].

Usuki and co-workers [2] reported the first successful polymer nanocomposite, Nylon 6/clay, with excellent properties: 87 °C higher heat distortion temperature and 4 times higher flexural modulus than those of the pristine polymer were achieved by adding only 5 wt% of nanoclay. With nano fillers, strong interaction is achieved between a matrix polymer and fillers or between fillers at a small content (usually less than 5 wt%) of fillers. For example, percolation thresholds for nanocomposites are considerably lower than those for micro-sized composites, which facilitates much more effective reinforcement with a small amount of fillers [3]. The glass transition behavior is also modulated by a small amount of nanofillers as a result of chain confinement [4]. For semi-crystalline polymers with higher-order structures, the size of nanofiller is smaller than or comparable to the size of spherulites or lamellar morphology, and therefore the addition of nanofiller can greatly change these structures. Nitta et al. [5] have reported that SiO<sub>2</sub> nanoparticles in PP depress the spherulite growth rate as the particle size decreases and as the SiO<sub>2</sub> content increases, while micro-sized SiO<sub>2</sub> (diameter of 51 μm) did not affect the spherulite growth rate. Moreover, spherulites were never formed when the theoretical interparticle distance between SiO<sub>2</sub> nanoparticles became shorter than the end-to-end distance of PP chains. Thus, nanocomposites exhibit several aspects that are not present in the conventional composites, being expected to give a new class of high-performance materials.

A huge demand from industry has motivated enormous efforts for the development of PP-based nanocomposites. However, the results obtained until now is far from satisfactory, compared with those achieved in other polymers such as nylon 6. One of the most serious problems for PP-based nanocomposites is poor compatibility between PP and inorganic fillers: polar inorganic fillers easily form large aggregates in apolar PP matrix. Early efforts were directed to achieve homogeneous dispersion of fillers, by adding a compatibilizer and/or by an organic modification of the filler surface, for example, using silane coupling agents or organic ammonium salts for clay. Usuki and co-workers [6] reported that the combination of maleic anhydride modified PP (MAPP) and organic ammonium salts resulted in significant exfoliation of nanoclays in PP. However, the degree of mechanical reinforcement was not sufficient with respect to potentially expected reinforcement. Garcia et al. [7] studied the effects of the filler dispersion on the mechanical properties of PP/SiO<sub>2</sub> nanocomposites. They found that the improvement of the dispersion of SiO<sub>2</sub> hardly affected the tensile strength. Bikiaris et al. [8] also showed that the addition of MAPP as a compatibilizer decreased the size of SiO<sub>2</sub> aggregates in PP, but only moderately improved mechanical properties. Accordingly, it is concluded that good dispersion of nanofiller is not enough to realize dramatic reinforcement of PP-based nanocomposites. In addition, the most commonly used MAPP compatibilizer is known to accelerate oxidative degradation of PP [9].

In situ composite formation is an alternative method to achieve good dispersion of fillers without any compatibilizer and organic modification [10]. In this method, matrix polymer is synthesized in the presence of nanoparticles to automatically facilitate the dispersion of the nanoparticles. Although several authors reported good dispersion of clay, SiO<sub>2</sub> or carbon nanotube in PP [10–12], the mechanical properties of the resulting nanocomposites were not sufficiently investigated. It is notable that the in situ method does not include a strategy to reinforce weak interface between PP and fillers.

One promising method to reinforce the polymer-filler interface is grafting of polymer chains to fillers, which has advantages of improved compatibility between fillers and matrix polymer and strengthened interfacial interaction through entanglements between grafted and matrix polymer chains. In addition, grafted polymer chains may decrease the aggregation tendency of fillers by their steric hinderance. Physical entanglement between grafted and matrix chains is quite attractive, since it is almost impossible to get effective chemical interaction between PP and fillers. Rong and Friedrich et al. [13–16] have synthesized PP-based nanocomposites using SiO<sub>2</sub> nanoparticles with a variety of grafted polymer chains such as polystyrene (PS), polybutylacrylate, polyvinylacrylate, and so on. However, these grafted chains did not induce large improvements of the mechanical properties of the formed nanocomposites. It is supposed that the immiscibility between PP and the grafted chains might not allow sufficient entanglement.

Based on these backgrounds, it must be preferable to graft PP chains onto nanofiller in order to acquire good miscibility with PP matrix. In employing PP itself as grafted chains, it should be noted that even PP chains can be immiscible with each other when they have different primary structures. Maier et al. [17] and Phillips [18] reported immiscibility between syndiotactic and isotactic PPs. Silvestri and Sgazi [19] reported possible immiscibility between isotactic and atactic PPs, depending on  $M_w$  of each component. In this sentence, stereo- and regio-structures of grafted PP chains should be identical to those of matrix chains. By fulfilling these requirements, resultant nanocomposites are expected to show much higher mechanical properties not only through entanglement but also through incorporation of grafted PP chains into crystallites of the matrix based on co-crystallization). Such nanocomposites with same grafted and matrix polymer chains were reported for PS and polyethylene (PE) [20–22]. In particular, a PE/PE-g-carbon nanotube nanocomposite showed excellent improvements of mechanical properties by the grafted PE chains: 1.6 times higher Young's modulus and 6.9 times higher elongation at breath than those of the ungrafted nanocomposite [22]. Differently from polymers such as PS and PE, radical graft polymerization is not available for PP, thus PP-grafted filler is not easy to synthesize.

In this study, terminally hydroxylated isotactic PP (PP-OH) having an identical structure with matrix PP was synthesized and grafted onto SiO<sub>2</sub> nanoparticles, so as to obtain the first PP-based nanocomposite having the same primary structure for the matrix and grafted PP chains. The crystallization behavior and mechanical properties of the nanocomposite were investigated by various techniques such as differential scanning calorimetry (DSC), polarized optical microscopy (POM), a tensile test, and dynamic mechanical analyses (DMA).

## Experimental

### Materials

*rac*-[dimethylsilylenebis(4,5,6,7)-tetrahydro-1-indenyl]zirconium dichloride was purchased from Wako pure chemical Co. Toluene and tetradecane were dried over the molecular sieve 13X before usage. Propylene gas of research grade and modified methylalumoxane (MMAO) were donated by Mitsubishi Chemical Co. and Tosoh Finechem Co., respectively. Aerosil 300 (the diameter of 7 nm and the surface area of 300 m<sup>2</sup>g<sup>−1</sup>) was employed as filler.

### Synthesis of PP and PP-OH

PP used as a matrix was synthesized with *rac*-[dimethylsilylenebis(4,5,6,7)-tetrahydro-1-indenyl]zirconium dichloride and MMAO in toluene ( $\text{Al/Zr} = 5000$  and  $[\text{Zr}] = 4 \mu\text{mol/L}$ ) at 0 °C for 1 h under a continuous propylene flow at 1 atm. PP-OH for grafting was synthesized by hydroxylation of the chain end of PP [23]. In detail, propylene was polymerized for 1 h under the above-mentioned conditions, and then oxygen gas was bubbled in the reactor at 0 °C for 1 h, followed by the addition of 1 M NaOH and 35% H<sub>2</sub>O<sub>2</sub> aqueous solution. The slurry was stirred for 30 min, to accomplish terminal hydroxylation of PP. The stereoregularity, weight average molecular weight ( $M_w$ ) and molecular weight distribution (MWD), and melting point of the obtained PP and PP-OH were measured by <sup>13</sup>C NMR, high-temperature size exclusion chromatography, and differential scanning calorimetry (DSC). The synthesized PP had a high isotacticity (91 mol% in mmmm),  $M_w$  of 307,000 with relatively narrow MWD about 2.6, and a high melting point ( $T_m = 160$  °C). PP-OH was found to have the primary structure and thermal properties completely identical to those of the matrix PP.

### Synthesis of PP-grafted SiO<sub>2</sub>

The terminal OH group of PP-OH was reacted with the silanol groups of SiO<sub>2</sub> at 200 °C in tetradecane for 7 h with stirring to obtain PP-grafted SiO<sub>2</sub> (PP-g-SiO<sub>2</sub>). An adequate amount of AO-50 (donated by ADEKA Co.) was added in tetradecane to avoid thermal degradation of PP during the reaction. The made PP-g-SiO<sub>2</sub> was washed repeatedly by hot filtration with *o*-dichlorobenzene at 145 °C to completely remove ungrafted PP chains, then rinsed by methanol, and finally dried in vacuo at 60 °C for 6 h. Successful grafting was confirmed by Fourier transform-infrared spectroscopy (FT-IR, FT/IR-6100, JASCO). The amount of grafted PP was evaluated by thermogravimetric analysis (TG, TG-50, METTLER), where the sample temperature was kept at 200 °C for 30 min to remove physisorbed water, and then increased up to 650 at 20 °C/min. The grafted amount was estimated from the difference of the weight loss in 200–650 °C between PP-g-SiO<sub>2</sub> and unmodified SiO<sub>2</sub>. SiO<sub>2</sub> was also modified by octadecyltrichlorosilane for the comparison (C<sub>18</sub>-SiO<sub>2</sub>). The C<sub>18</sub> modification lowers the surface energy of SiO<sub>2</sub> as the PP grafting

does, while the  $C_{18}$  group is unable to entangle and co-crystallize with the matrix PP. Thus,  $C_{18}$ - $SiO_2$  was utilized to exploit the relative importance between surface bulk properties (surface energy) and the molecular structure of grafted chains in the design of nanocomposites.

### Preparation of nanocomposites

Nanocomposites were prepared by melt mixing using a two-roll mixer at 20 rpm. PP pellets were kneaded at 185 °C for 5 min and then a specified amount of unmodified  $SiO_2$ , PP-g- $SiO_2$ , or  $C_{18}$ - $SiO_2$  was added. The mixture was further kneaded at 185 °C for additional 10 min. Thus, produced nanocomposites with a variety of filler contents (0–10 wt%) were hot-pressed into sample films with the thickness of 200  $\mu m$  at 230 °C and 20 MPa, and then quenched at 100 °C.

### Instrumentation

The dispersion of  $SiO_2$  nanoparticles in the matrix was monitored by a transmission electron microscope (TEM, Hitachi, H-7100). TEM specimens with the thickness of 100 nm were prepared by an ultramicrotome (Leica, ULTRACUTS FCS) equipped with a diamond knife (Diatome). The obtained TEM images were analyzed with an image analysis software (Image J software, NIH) to quantify the dispersion.

The crystalline structure and crystallinity of the nanocomposites were obtained by the wide-angle X-ray diffraction (Rigaku, Rint2500). Wide-angle X-ray diffraction (WAXD) measurements were performed in a reflection mode at room temperature with Cu  $K\alpha$  radiation operating at 40 kV and 30 mA. The scanning rate was  $1^\circ/\text{min}$  over  $2\theta$  of 10–30°. Sample films with a thickness of ca. 200  $\mu m$  were used.

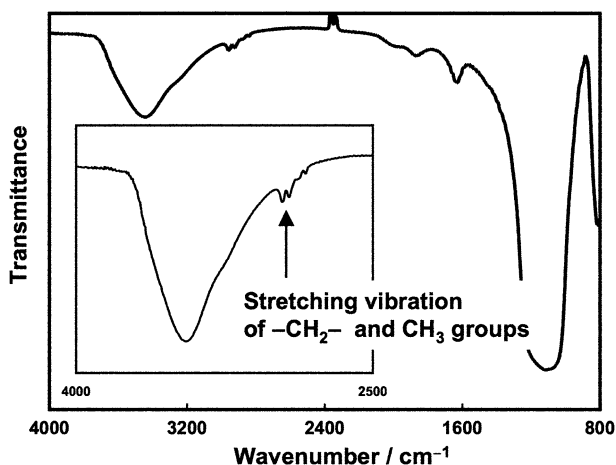
Isothermal crystallization was conducted at 128 °C with DSC (METTELER, DSC-822). Samples were kept at 200 °C for 5 min to erase a thermal history, and then cooled down to 128 °C at a rate of 20 °C/min. A crystallization rate was determined as an inverse of the half time of the crystallization (denoted as  $t^{-1/2}$ ). A nuclear density during isothermal crystallization at 130 °C was evaluated by POM (Leica, DMLB HC) equipped with an automated hot stage (METTELER, FP82HT).

Tensile tests were carried out at room temperature using a dumbbell-shaped specimen at a crosshead speed of 1.0 mm/min by a tensile tester (DAT-100, Abecks Inc.). Five measurements were performed for each sample. DMA (UBM, E4000) was conducted for the temperature dependence of oscillatory tensile moduli in the solid state ( $E'$ ,  $\tan\delta$ ). Measurements were performed in the temperature range from –80 to 170 °C with a heating rate of 3 °C/min and the frequency of 10 Hz. The size of a sample specimen was  $2 \times 8 \times 0.2 \text{ mm}^3$ . The frequency dependence of oscillatory shear moduli in the molten state ( $G'$ ,  $G''$ ) was measured by a parallel- and-plate rheometer (TA, AR2000ex) at 180 °C with a frequency range from 100 to 0.01 rad/s under  $N_2$  atmosphere. The diameter of the parallel plates was 25 mm. Each measurement was performed within a linear viscoelastic region.

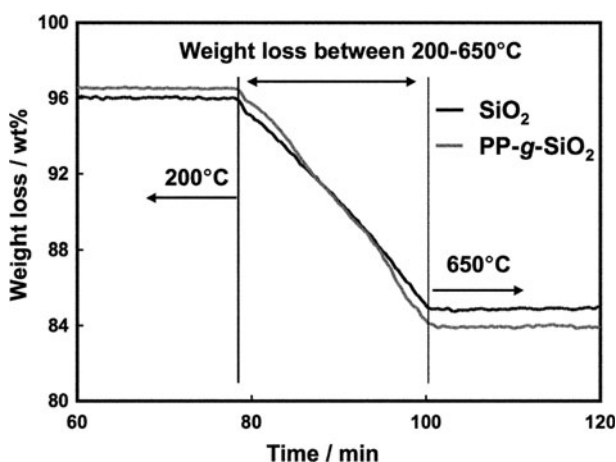
## Results and discussion

### Preparation of PP-*g*-SiO<sub>2</sub>

The FT-IR spectrum of synthesized PP-*g*-SiO<sub>2</sub> was measured after careful removal of ungrafted chains with hot *o*-dichlorobenzene (Fig. 1). The peaks at 2920 and 2950 cm<sup>-1</sup> (corresponding to the C-H stretching vibrations for the -CH<sub>2</sub>- and -CH<sub>3</sub> groups) indicate the successful grafting. TG analyses were performed to evaluate the amount of PP chains grafted on SiO<sub>2</sub> (Fig. 2). PP-*g*-SiO<sub>2</sub> exhibited 12.4 wt% of the weight loss between 200 and 650 °C. Referencing the weight loss



**Fig. 1** IR spectrum of PP-*g*-SiO<sub>2</sub>

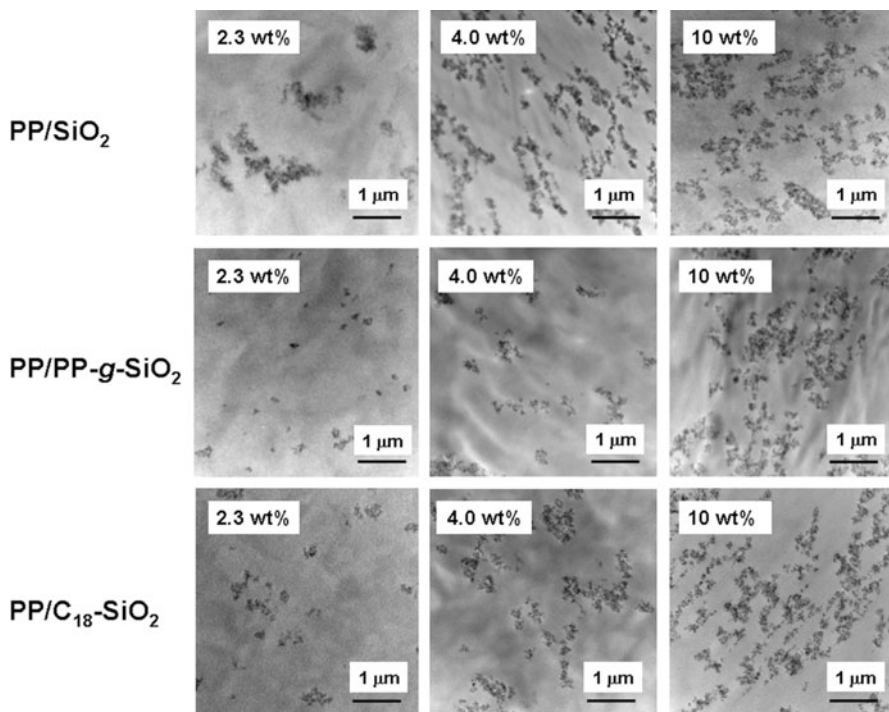


**Fig. 2** TG analysis of PP-*g*-SiO<sub>2</sub> and unmodified SiO<sub>2</sub>. The amount of grafted PP chains on SiO<sub>2</sub> was evaluated based on the weight loss from 200 to 650 °C

of 11.1 wt% for unmodified  $\text{SiO}_2$  in the same temperature range, the amount of the grafted PP chains was estimated as 1.3 wt%. Assuming a pore less and perfect sphere for the  $\text{SiO}_2$  particles, the number of the grafted chains was calculated as 1 chain/particle. The amount of the octadecyl group grafted on  $\text{SiO}_2$  was similarly obtained to be 7.5 wt%.

#### Dispersion state of fillers

The dispersion of unmodified  $\text{SiO}_2$ , PP-g- $\text{SiO}_2$ , and  $\text{C}_{18}$ - $\text{SiO}_2$  in the matrix was studied by TEM (Fig. 3). All the fillers formed small aggregates of 20–100 nm in the matrix. Up to the filler content of 4.0 wt%, the dispersion of PP-g- $\text{SiO}_2$  and  $\text{C}_{18}$ - $\text{SiO}_2$  was better than that of unmodified  $\text{SiO}_2$ . At the filler content of 10 wt%, the three kinds of fillers similarly formed large and extended aggregates. The better dispersion of PP-g- $\text{SiO}_2$  and  $\text{C}_{18}$ - $\text{SiO}_2$  was quantitatively confirmed by an image analysis. Table 1 shows the average areas of the aggregates, which are 50% smaller for PP-g- $\text{SiO}_2$  and 30% for  $\text{C}_{18}$ - $\text{SiO}_2$ . The average diameters are about 30% smaller for both PP-g- $\text{SiO}_2$  and  $\text{C}_{18}$ - $\text{SiO}_2$ . This result proved the effectiveness of the grafting of PP chains in improving the dispersion of fillers in the PP matrix, even though the grafted amount was as small as 1 chain/particle. The observed dispersion for the three kinds of fillers might be correlated with their cohesion abilities. The



**Fig. 3** TEM images of prepared PP-based nanocomposites. Filler contents were varied from 2.3 to 10 wt%

**Table 1** Size of SiO<sub>2</sub> aggregates

|                                                                                           | Sample                                      | Area/10 <sup>4</sup> nm <sup>2</sup> | Feret diameter/nm |
|-------------------------------------------------------------------------------------------|---------------------------------------------|--------------------------------------|-------------------|
| Approximately 400 aggregates of SiO <sub>2</sub> were analyzed and averaged by a software | PP/SiO <sub>2</sub> (2.3%)                  | 4.60                                 | 338               |
|                                                                                           | PP/SiO <sub>2</sub> (4.0%)                  | 5.03                                 | 340               |
|                                                                                           | PP/PP-g-SiO <sub>2</sub> (2.3%)             | 2.15                                 | 218               |
|                                                                                           | PP/PP-g-SiO <sub>2</sub> (4.0%)             | 2.62                                 | 230               |
|                                                                                           | PP/C <sub>18</sub> -SiO <sub>2</sub> (2.3%) | 2.82                                 | 250               |
|                                                                                           | PP/C <sub>18</sub> -SiO <sub>2</sub> (4.0%) | 3.52                                 | 250               |

modification by short alkyl groups is known to largely reduce the surface energy of SiO<sub>2</sub> [24], leading to better dispersion. On the other hand, the largely modified dispersion for PP-g-SiO<sub>2</sub> can be explained not only by reduction of the surface energy through the grafting, but also by steric hindrance from the grafted PP chains [13]. The way of the aggregation clearly depended on the kinds of the fillers. The aggregates of unmodified SiO<sub>2</sub> were larger and had an open or extended shape, while those of PP-g-SiO<sub>2</sub> and C<sub>18</sub>-SiO<sub>2</sub> were much smaller and more compact. Bartholome et al. [21] reported similar effects of grafted PS chains on the dispersion of SiO<sub>2</sub> in PS.

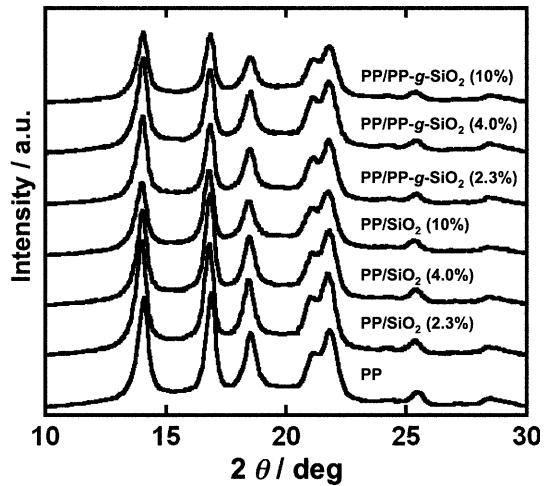
#### Crystalline structure and crystallization behavior

The WAXD patterns of pristine PP, PP/SiO<sub>2</sub>, and PP/PP-g-SiO<sub>2</sub> (Fig. 4) exhibited typical characteristics of the  $\alpha$ -form crystal with the peaks of  $2\theta = 14.07^\circ$ ,  $16.85^\circ$ ,  $18.51^\circ$ ,  $21.08^\circ$ , and  $21.77^\circ$  corresponding to (110), (040), (130), (111), and (131) reflections, respectively [25]. The other crystalline forms were never observed. Thus, SiO<sub>2</sub> nanoparticles and their modification had few influences on the crystalline structure of the PP matrix. The WAXD crystallinities ( $X_c$ ) summarized in Table 2 were quite similar for all the samples, which allowed us to fairly compare the mechanical properties of the different samples.

Isothermal crystallization of the nanocomposites was tracked by DSC to examine influences of the fillers on the crystallization behavior of the matrix (Fig. 5). Surface organic modification of fillers sometimes enhances a nucleating ability of fillers. It was found that the crystallization of PP was considerably accelerated by the addition of PP-g-SiO<sub>2</sub>: the crystallization rate was  $0.14 \text{ min}^{-1}$  for PP/SiO<sub>2</sub> at the SiO<sub>2</sub> content of 2.3 wt%, while that of PP/PP-g-SiO<sub>2</sub> was  $0.30 \text{ min}^{-1}$  at the same content. The C<sub>18</sub> modification of SiO<sub>2</sub> did not give such that significant enhancement of the nucleating ability. Thus, the high nucleating ability was originated by the molecular structure of grafted chains rather than the surface bulk nature such as surface energy.

The origin of the high nucleating ability of PP-g-SiO<sub>2</sub> was examined by POM, where the time-course increase of the nuclear densities was plotted during isothermal crystallization at 130 °C (Fig. 6). The nuclear density became more than twice by the addition of PP-g-SiO<sub>2</sub>, indicating that the increase of the crystallization rate by PP-g-SiO<sub>2</sub> was owing to the acceleration of the nucleation rather than the acceleration of the spherulite growth. On the other hand, unmodified SiO<sub>2</sub> hardly altered the nuclear density of pristine PP. Based on the result that the grafted

**Fig. 4** WAXD patterns of pristine PP and nanocomposites. Regardless of the filler contents, all the samples showed characteristic peaks of  $\alpha$ -form and other forms were never observed



**Table 2** Mechanical properties and crystallinities

| Sample                                      | Young's modulus <sup>a</sup> /MPa | Tensile strength <sup>a</sup> /MPa | $X_c^b$ /wt% |
|---------------------------------------------|-----------------------------------|------------------------------------|--------------|
| PP                                          | 347                               | 23.4                               | 55.1         |
| PP/SiO <sub>2</sub> (2.3%)                  | 347                               | 23.7                               | 55.6         |
| PP/SiO <sub>2</sub> (4.0%)                  | 364                               | 25.3                               | 52.9         |
| PP/SiO <sub>2</sub> (10%)                   | 416                               | 27.0                               | 51.4         |
| PP/C <sub>18</sub> -SiO <sub>2</sub> (2.3%) | 325                               | 24.1                               | 52.5         |
| PP/C <sub>18</sub> -SiO <sub>2</sub> (4.0%) | 332                               | 24.0                               | 51.8         |
| PP/C <sub>18</sub> -SiO <sub>2</sub> (10%)  | 362                               | 25.3                               | 51.5         |
| PP/PP-g-SiO <sub>2</sub> (2.3%)             | 369                               | 25.0                               | 54.3         |
| PP/PP-g-SiO <sub>2</sub> (4.0%)             | 374                               | 25.6                               | 52.2         |
| PP/PP-g-SiO <sub>2</sub> (10%)              | 439                               | 26.7                               | 52.2         |

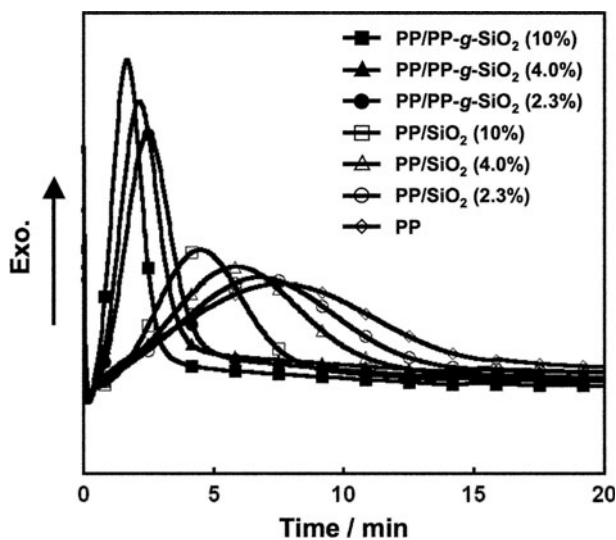
<sup>a</sup> Measured by tensile test

<sup>b</sup> Determined by WAXD

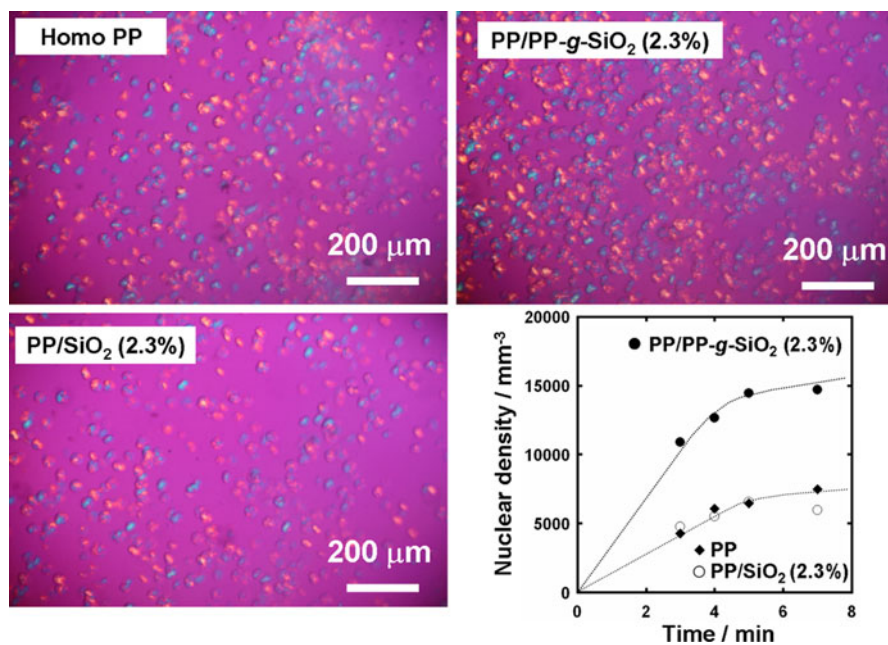
PP chains having the same primary structure with the matrix chains significantly enhanced the nuclear density; it was plausible that the crystallization of the matrix was initiated by the grafted chains with one chain end pinned to SiO<sub>2</sub>.

### Mechanical properties

Results of Tensile tests are summarized in Fig. 7 and Table 2. Unmodified SiO<sub>2</sub> hardly affected the Young's modulus and tensile strength at the lowest filler content, while increased these values above 4.0 wt%. The onset of the reinforcement at 4.0 wt% coincided with the formation of the percolation (described later). PP-g-SiO<sub>2</sub> showed the most notable reinforcement at the lowest content compared with unmodified SiO<sub>2</sub>. The degree of the reinforcement became closer to that for unmodified SiO<sub>2</sub> at higher contents, but always larger. Only the exception was the

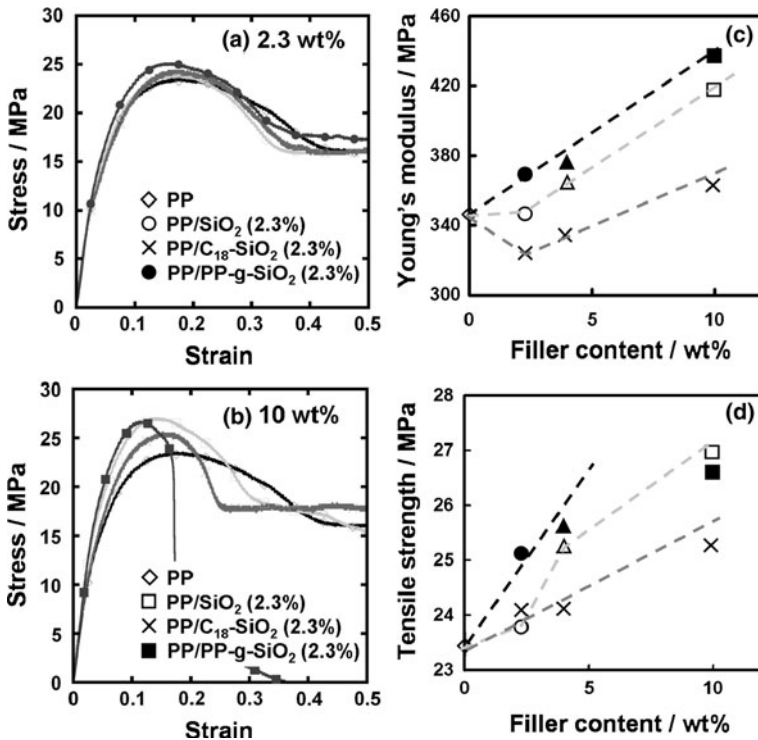


**Fig. 5** DSC curves for isothermal crystallization at 128 °C



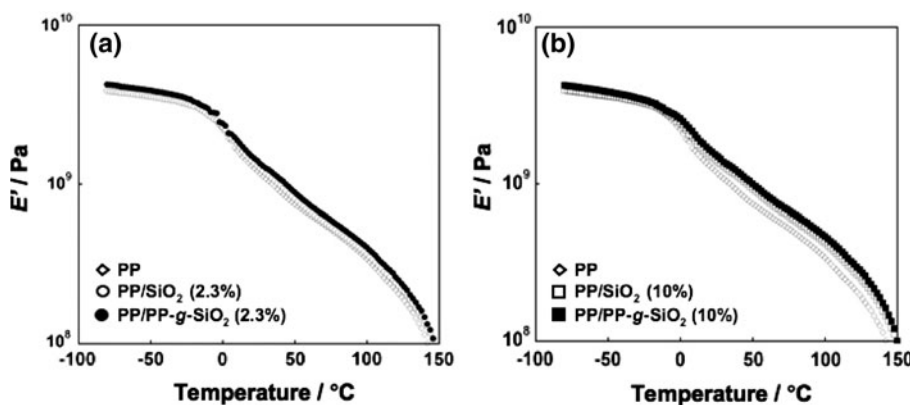
**Fig. 6** POM images in isothermal crystallization at 130 °C ( $t = 7$  min) and the time dependence of the nuclear density calculated by the number of nuclei in the pictures at each time

tensile strength at 10 wt%, where the break in elongation occurred in a very early stage for PP- $g$ -SiO<sub>2</sub>. The C<sub>18</sub>-modification of SiO<sub>2</sub> affected negatively, even though C<sub>18</sub>-SiO<sub>2</sub> showed the better dispersion than unmodified SiO<sub>2</sub>.

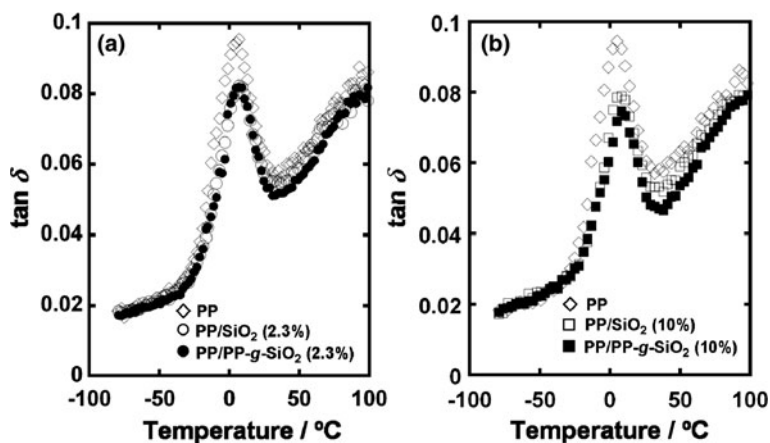


**Fig. 7** Stress–strain curves (cross head speed of 1 mm/min) at the filler content of **a** 2.3 wt% and **b** 10 wt%. **c** The Yang's modulus and **d** the tensile strength were plotted against the filler content

Rheological properties were evaluated to investigate interaction between the matrix and fillers. The temperature dependences of  $E'$  and  $\tan\delta$  are shown in Figs. 8 and 9, respectively. The glass transition temperatures ( $T_g$ ) determined from  $E''$  increased about 5 °C by modifications irrespective of the content and kind of the fillers (not shown). The  $E'$  values below  $T_g$  were almost the same among all the samples. The  $E'$  values above  $T_g$  were increased by the addition of both unmodified SiO<sub>2</sub> and PP-g-SiO<sub>2</sub> (Fig. 8). However, the ways of the increases were different between the two kinds of fillers: increase of the  $E'$  value from pristine PP was about two times higher for PP-g-SiO<sub>2</sub> compared with unmodified SiO<sub>2</sub>, while the advantage of PP-g-SiO<sub>2</sub> over PP/SiO<sub>2</sub> became much smaller at higher contents. These trends for  $E'$  are in line with the results of tensile tests. The peak intensity and area of  $\tan\delta$  at the glass transition generally correlate with the portion of the amorphous phase and/or the mobility of polymer chains therein [4]. Unmodified SiO<sub>2</sub> and PP-g-SiO<sub>2</sub> similarly reduced the peak intensity of  $\tan\delta$  (compared with pristine PP) (Fig. 9). As shown in the  $X_c$  values of Table 2, the amorphous portion was similar among all the samples. Hence, the peak reduction by the addition of the fillers must be ascribed by reduced mobility of the amorphous chains, which is known as a confinement effect by nanoparticles [4, 26, 27]. The frequency dependences of  $G'$  and complex viscosity  $\eta^*$  were shown in Fig. 10. A large difference was observed



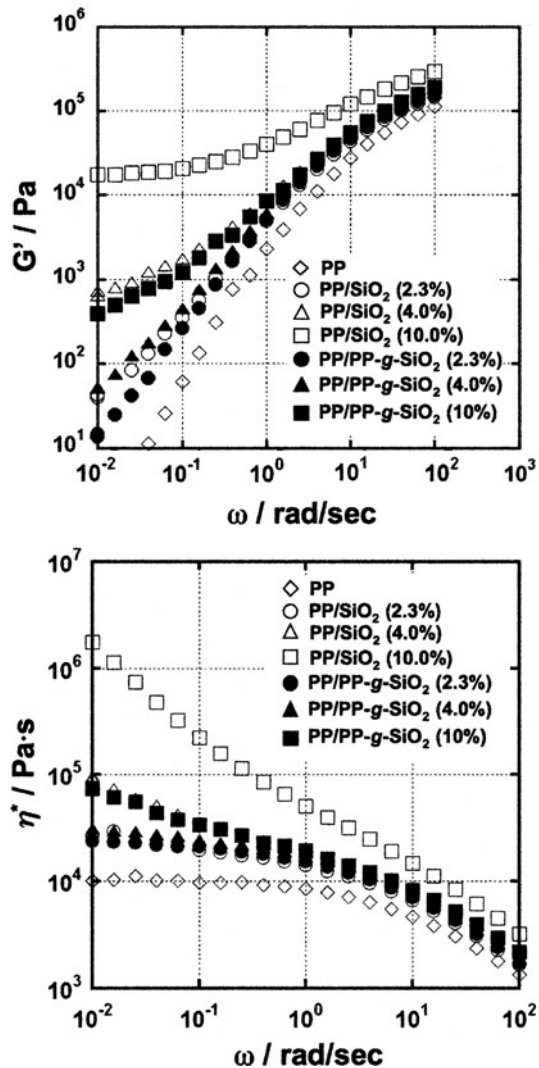
**Fig. 8** Temperature dependence of tensile storage modulus  $E'$  for pristine PP and nanocomposites. Measurements were performed in the temperature range from  $-80$  to  $170$  °C with a heating rate of  $3$  °C/min and a frequency of  $10$  Hz



**Fig. 9** Temperature dependence of loss tangent for pristine PP and nanocomposites. Measurements were performed in the temperature range from  $-80$  to  $170$  °C with a heating rate of  $3$  °C/min and a frequency of  $10$  Hz

between pristine PP and the nanocomposites in the low frequency region ( $< \sim 0.1$  rad/s). Both  $G'$  and  $\eta^*$  significantly increased by the addition of the fillers. At the filler content of 2.3 wt%, the two nanocomposites had similar  $G'$  values with terminal flow. However, the increase of  $G'$  was much more for unmodified  $\text{SiO}_2$  at the higher contents. A plateau appeared instead of the terminal flow at the content over 4 wt% for unmodified  $\text{SiO}_2$ , and at the content of 10 wt% for PP-g- $\text{SiO}_2$ . The appearance of the plateau in  $G'$  accompanied drastic increase of  $\eta^*$  by an order of magnitude. This phenomenon at higher filler contents is general for particulate nanocomposites, and indicates the formation of percolation network of fillers.

**Fig. 10** Frequency dependence of shear storage modulus  $G'$  (upper) and (bottom) complex viscosity  $\eta^*$  for pristine PP and nanocomposites. Measurements were performed at 180 °C with a frequency range from 100 to 0.01 rad/s under  $N_2$  atmosphere



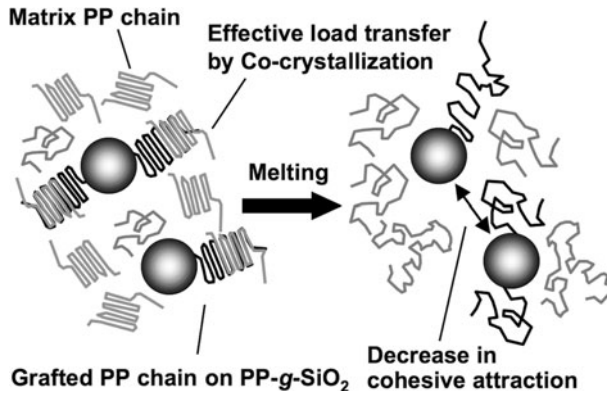
The percolation has been most precisely studied for polymer/clay nanocomposites, and percolation networks through direct connections among platelets such as “edge-to-edge” or “edge-to-face” have been reported [28–30]. On the other hand, it has been considered for polymer/SiO<sub>2</sub> nanocomposites that fractal structures formed by open aggregates of SiO<sub>2</sub> nanoparticles are responsible for the percolation [31]. As shown in Fig. 3, unmodified SiO<sub>2</sub> formed rather open aggregates in the matrix, while PP-g-SiO<sub>2</sub> and C<sub>18</sub>-SiO<sub>2</sub> existed as smaller and compact aggregates. The lower percolation threshold for PP/SiO<sub>2</sub> is clearly explained by this fact, where the percolation thresholds were from 2.3 to 4.0 wt% for unmodified SiO<sub>2</sub> and 4.0–10 wt% for PP-g-SiO<sub>2</sub>.

## Discussion

The obtained effects of the fillers are briefly summarized as follows. Modified SiO<sub>2</sub> (PP-g-SiO<sub>2</sub> and C<sub>18</sub>-SiO<sub>2</sub>) apparently improved the filler dispersion except at the highest filler content (Fig. 3). PP-g-SiO<sub>2</sub> and C<sub>18</sub>-SiO<sub>2</sub> made smaller but compact aggregates, while unmodified SiO<sub>2</sub> made network-like aggregates connected with each other. PP-g-SiO<sub>2</sub> showed the nucleation ability much higher than C<sub>18</sub>-SiO<sub>2</sub> and SiO<sub>2</sub> (Fig. 5). It was believed that the grafted PP chains initiate the crystallization of the matrix because of their lower mobility and to the same primary structure with the matrix. PP-g-SiO<sub>2</sub> showed the highest reinforcement in the tensile test at the lowest filler content (Fig. 7). On the other hand, the degree of the reinforcement was similar to that of unmodified SiO<sub>2</sub> over 4.0 wt%. The reinforcement by C<sub>18</sub>-SiO<sub>2</sub> was much poorer, in spite of the better dispersion of C<sub>18</sub>-SiO<sub>2</sub> than unmodified SiO<sub>2</sub>. SiO<sub>2</sub> and PP-g-SiO<sub>2</sub> similarly reduced the intensity of  $\tan\delta$  at the glass transition (Fig. 9), indicating that the confinement of the amorphous chains by SiO<sub>2</sub> nanoparticles was not affected by the grafted chains.  $G'$  of PP/SiO<sub>2</sub> at low frequencies was larger than that of PP/PP-g-SiO<sub>2</sub> in the molten state (Fig. 10), on the contrary to the higher Young's modulus and  $E'$  of PP-g-SiO<sub>2</sub> in the solid state. The disappearance of the terminal flow (corresponding to the formation of percolation network) occurred at a lower filler content for unmodified SiO<sub>2</sub> than for PP-g-SiO<sub>2</sub>. Hereafter, the mechanistic origin of the higher reinforcement by PP-g-SiO<sub>2</sub> in the tensile tests (Fig. 7) is discussed, for which C<sub>18</sub>-SiO<sub>2</sub> offers a useful reference.

Although the reinforcement mechanism in polymer-based nanocomposites has not been fully understood yet, the numerous efforts have identified plausible mechanisms into (i) strong interfacial interaction between matrix chains and filler particles, and (ii) percolation or network structures of filler particles. Load transfer to fillers based on these two mechanisms are also affected by the content, stiffness, aspect ratio, surface chemical nature, and dispersion state of fillers.

The percolation threshold for PP/SiO<sub>2</sub> lay within the filler content 2.3–4.0 wt%. The results of tensile tests for unmodified SiO<sub>2</sub> were well-correlated with the dependence of  $G'$  on the filler content: little reinforcement at 2.3 wt% before the percolation and sharp increases of the Young's modulus and tensile strength from 4.0 to 10 wt% after the percolation. Thus, the reinforcement for unmodified SiO<sub>2</sub> is believed to be mainly based on the percolation. On the other hand, PP-g-SiO<sub>2</sub> showed the most prominent reinforcement in the tensile test (compared with unmodified SiO<sub>2</sub>) at the lowest filler content, i.e., before the percolation. This suggests that some strong interaction between the matrix and filler particles was responsible for the observed reinforcement. Better dispersion of fillers has been believed to result in higher reinforcement because of more homogeneously distributed load transfer to particles. In this viewpoint, PP-g-SiO<sub>2</sub> was considered to be advantageous at lower filler contents. However, as was described in introduction, good dispersion of fillers is not a sufficient condition for the reinforcement. In fact, C<sub>18</sub>-SiO<sub>2</sub> with better dispersion than unmodified SiO<sub>2</sub> never showed notable improvements. These results claim the importance of the quality of the interaction between the matrix and filler particles. As in the results of DSC and POM



**Fig. 11** Schematic image of PP/PP-g-SiO<sub>2</sub> in solid and molten states

(Figs. 5, 6), the largest difference between PP-g-SiO<sub>2</sub> and C<sub>18</sub>-SiO<sub>2</sub> appeared in the nucleating ability of the fillers: the key factor for the nucleation was the molecular structure of grafted chains rather than the surface bulk natures. The considerably high nucleation ability of PP-g-SiO<sub>2</sub> suggested the crystallization of the matrix initiated from the grafted chains having the same primary structure with the matrix chains. In this way, we propose that the grafted chains are preferentially co-crystallized together with the matrix PP, and play a role of direct bridges between the matrix and filler particles for effective load transfer. This mechanism is supported by the poorer reinforcement in  $G'$  for PP/PP-g-SiO<sub>2</sub> than that of unmodified SiO<sub>2</sub> at the lower contents, where all crystallites were molten. The C<sub>18</sub> modification was not effective for both the percolation and co-crystallization, leading to the poorest reinforcement.

A schematic image of PP/PP-g-SiO<sub>2</sub> for both the solid and molten states is drawn in Fig. 11. Since the PP chains covalently grafted to SiO<sub>2</sub> particles preferentially co-crystallized with the matrix PP, the effective load transfer from the matrix to the fillers occurred in the solid state, resulting in the better mechanical properties even at the lower contents much before the percolation. On the other hand, the grafted PP chains gave better filler dispersion by steric hindrance without a large increase of complex viscosity in the molten state.

## Conclusion

In this study, a PP/SiO<sub>2</sub> nanocomposite having the same primary structure for the matrix and grafted PP chains was synthesized. PP-g-SiO<sub>2</sub> achieved much higher reinforcement than unmodified SiO<sub>2</sub>, at a low filler content (2.3 wt%). We have proposed a reinforcement mechanism that the grafted PP chains trigger the crystallization of the matrix and are imparted in the lamellae of the matrix, thus directly bridging between the matrix and filler particles for effective load transfer. On the contrary, the increase of the viscosity in melt by the addition of SiO<sub>2</sub> was partially suppressed with the grafted PP chains. In this way, to graft PP chains

having an identical structure to matrix chains can be a successful strategy to achieve significant reinforcement of PP-based nanocomposites, without sacrificing processability and light weight. Further improvements in the mechanical properties will be achieved by the optimization of the amount and structure of the grafted chains.

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