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Description	

Original Paper

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Effect of Silica on Sherulite Structure and Photo-oxidative Degradation Behavior in Polypropylene/Silica Nanocomposites

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Abstract

The physico-chemical interaction between hydrophobic polyolefin materials and originally hydrophilic inorganic nano-particles like surface hydroxylated SiO_2 has not been well understood up to now. In this study, the influences of particle size, content of hydrophilic SiO_2 nanoparticles on the isothermal growth rate of polypropylene (PP) spherulites in various PP/SiO_2 nanocomposites were investigated by polarized optical microscope equipped with temperature controlled hot stage. Moreover, photo-oxidative degradation behavior of the PP/ SiO_2 nanocomposites were investigated. It is most interesting to note that the addition of smaller SiO_2 nanoparticles effectively lowered the growth rate of PP spherulites in the composites and the spherulite growth rate became zero for the PP/16nm-SiO_2 nanocomposites with the SiO_2 content above 2.5 wt%. It was found that the sample without spherulite morphology is more stable to photo-degradation. Spherulite structure is considered to have the influence affect photo-oxidative degradation.

Keywords : Polypropylene/silica nanocomposite, Photo-degradation, Spherulite

1. Introduction

Nowadays, the development of various polymer-based nanocomposites with new properties has become one of the key research targets in the field of polymer materials from both academic and industrial points of view. It is quite important to develop high performance polymer-based materials with various outstanding properties. One of the most popular procedures of synthesizing polymer-based nanocomposites is to disperse various nano-sized inorganic particles into polymer matrix by melt mixing. Although a great number of polymer-based nanocomposites have been successfully synthesized up to now[1)-3)], a deep mechanistic understanding of physico-chemical interactions between inorganic nano-particles and polymer matrix has been far from being achieved. It has been reported that the mechanical and thermal properties[4)-13)] as well as many other performances[14), 15)] could be significantly improved for polyolefin-based nanocomposites compared with the original polyolefins.

Environmental durability is a key feature for polyolefin-based nanocomposites in their processing and usage due to their degradation. There are many factors influencing the degradation of polyolefin materials, such as photo-irradiation, thermo-degradation, oxidation etc., and their combinations. Within the various factors, the photo- and thermal-oxidation plays an important role. Thus, the study on photo- and thermal-oxidative degradation of polyolefin materials is always attracting attention in the field of polymer degradation and stability.

In this work, correlation of the spherulite structure and photo-oxidative behavior in terms of the size, content of silica particles were investigated.

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2. Experimental

2.1 Materials

Isotactic PP pellets with an isotacticity index (I.I.) of 98% were donated from Japan Polypropylene Corp.. Weight average molecular weight ($\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) are 26 × 10^3 and 5.6, respectively. AEROSIL@ 200 SiO_2 with an average particle size of 16 nm and surface area of $200m^2/g$ was donated from Aerosil Japan Co.. NanoTek@ SiO_2 with an average particle size of 26 nm and surface area of $110\,m^2/g$ was purchased from Kanto Chemical Co..

2.2 Preparation of PP/SiO_2 nanocomposites

Composites were prepared by melt mixing SiO_2 particles with different diameters of 16nm, 26nm and 100nm respectively. Melt mixing was performed in twin-roller. The PP pellets were kneaded by mixing rollers at 180 ℃ for 5 min and then a given amount of SiO_2 was added into the kneaded PP. The mixture was kneaded at 180 ℃ for another 10min. Then, the obtained mixture was pressed into a flat sheet at 230 ℃ under a pressure of $100kg/cm^2$ for 5 min using a compression-molding machine. Two kinds of PP/SiO_2 nanocomposites were prepared at the different cooling conditions ; (a) quenced at 100 ℃ (spherulites sample), (b) quenched at 0 ℃ then annealed at 100 ℃ for 24h under N_2 atmosphere (non-spherulites sample). The content of SiO_2 in the PP/SiO_2 composites was changed from 0 wt% to 5.0wt%.

2.3 Spherulite growth behavior of PP/SiO_2 nanocomposites

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 to ± 0.2 K by a proportional controller. A thin sample piece were sandwiched between a microscope slide and a cover glass, heated to 503K and kept for 10 min to melt completely 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 407K.

2.4 Photo-degradation of PP/SiO_2 nanocomposites

Photo-degradation experiments were conducted in the weather meter at 35 ℃ using four 550W xenon lamps. The oxidative degradation behavior was measured by FT-IR. Carbonyl growth in the region $1500\text{-}1800cm^{-1}$ region of the FT-IR spectrum is determined by using carbonyl absorbance defined as follow (see **Fig.1**).

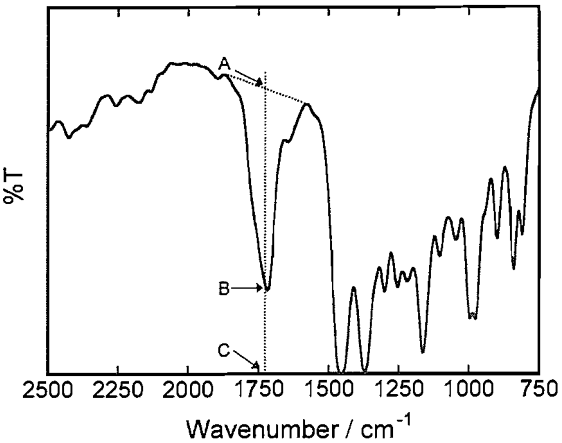

Fig.1 Typical FT-IR spectrum of oxidized PP film.

3. Results and discussion

Linear spherulite growth rate for all PP/SiO_2 nanocomposites and neat PP was evaluated by measuring spherulite radius as a function of time. An example of the measurement of growth rate in radial direction is shown in **Fig.2**, 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.

Growth rates measured isothermally at 403K is plotted against the content of SiO_2 particles in **Fig.3**. The spherulite growth rates of PP spherulites decreased significantly with increasing the SiO_2 content. It is interesting to note that the addition of smaller SiO_2 particles effectively lowered the growth rate of PP spherulite in the composites and the spherulite growth rate became zero for the PP/16nm-SiO_2 nanocomposites with the SiO_2 content above 2.5wt%.

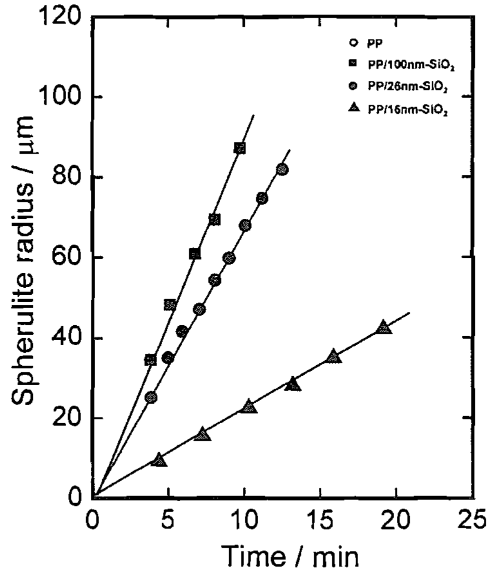

Fig.2 The spherulite radius plotted against the crystallization time for various PP/SiO_2 nanocomposites (SiO_2 content : 0.6 wt%).

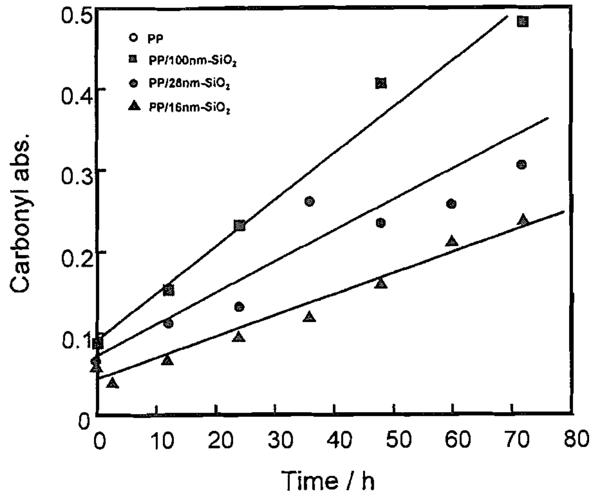

Fig.4 Carbonyl adsorption versus degradation time for PP and various PP/SiO_2 nanocomposites (SiO_2 content : 5 wt%).

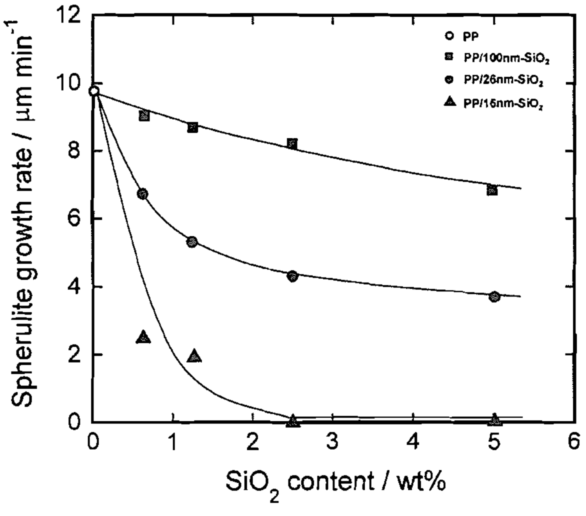

Fig.3 Effect of the SiO_2 content on the spherulite growth rates isothermally measured at 403K.

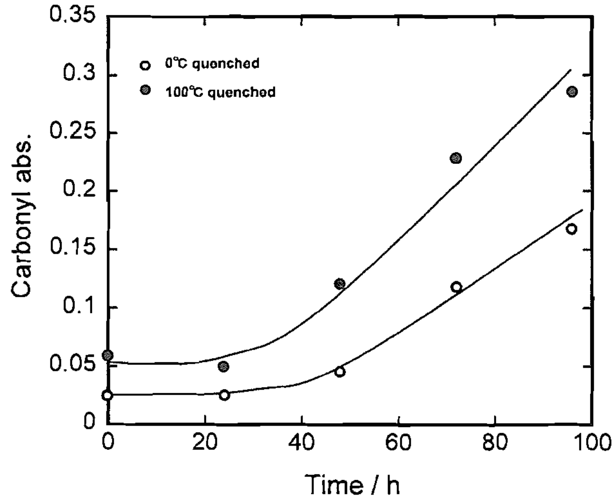

Fig.5 Carbonyl absorbance versus degradation time for various PPs.

Consequently, the PP/16nm-SiO_2 nanocomposite films has non-spherulite morphology.

Fig.4 shows the carbonyl index plotted against the photo-degradation time in the weather meter. The carbonyl index increases with increasing the SiO_2 particlesize. The addition of smaller SiO_2 particles effectively improved the degradation stability. The existence of spherulites morphology may have the important role for the phenomena. In addition, influence on photo-degradation for a sample with spherulite morphology and a sample without spherulite morphology was investigated. **Fig.5** shows the carbonyl absorbance plotted against the photo-degradation time in the weather meter. It was found that the sample without spherulite morphology is more stable to photo-degradation. It seems that since the interface of spherulites did not exist and diffusion of oxygen was restricted, photo-degradation stability became high.

4. Conclusions

It was found that the addition of smaller SiO_2 particles effectively lowered the growth rate of PP spherulite in the composites and the spherulite growth rate became zero for the PP/16nm-SiO_2 nanocomposites with the SiO_2 content above 2.5wt%. Moreover, it was found that the sample without spherulite morphology is more stable to photo-degradation. Spherulite structure is considered to have the influence on photo-oxidative degradation. This result indicates the real possibility to develop highly stable PP materials, which have been eagerly requested from various application areas.

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