

Effects of Nucleating Agent on Nonisothermal Crystallization of Syndiotactic Polystyrene

Joon-Yong Park*, Moo Hyun Kwon, Young Sil Lee and O Ok Park[†]

*Polymer Materials Lab., Samsung Advanced Institute of Technology,
103-6, Moonji-dong, Yusong-ku, Taejon 305-380, Korea
Dept. of Chem. Eng., Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-ku, Taejon 305-701, Korea
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Abstract—The effects of nucleating agent on nonisothermal crystallization were examined for syndiotactic polystyrene (SPS) using Differential Scanning Calorimetry (DSC). The crystallization peak temperature T_c , the crystallization rate parameter (CRP), the enthalpy of crystallization and melting, and the recrystallization behavior were compared between organic (DMBS, 1,3,2,4-dis-5-(3,4-dimethyl benzylidene) sorbitol) and inorganic (talc) nucleating agents. Both of the nucleation agents promoted the crystallization rate of SPS until some critical concentration of about 3,000 ppm. DMBS worked more effectively as a nucleating agent than talc, although the T_c showed lower level in SPS/DMBS than SPS/talc.

Key words: Syndiotactic Polystyrene, Crystallization, Recrystallization, Nucleation Agent, DMBS, Talc

INTRODUCTION

Syndiotactic polystyrene (SPS) is a new semicrystalline thermoplastic polymerized via homogeneous catalyst system [Ishihara et al., 1986a, b]. It has phenyl rings regularly attached to the polymer backbone chain. This regular structure allows SPS to crystallize and gives rise to a high melting temperature of about 270 °C. It also offers excellent chemical resistance. When SPS is reinforced with glass fiber of about 30 wt%, it shows good mechanical properties that can be comparable to the level of other engineering plastics. These merits enable us to expect that SPS will be a new engineering polymer with a niche at the middle to top of the performance polymer market [Dias, 1996].

In semicrystalline polymers, the crystallization behavior is quite important in their final properties. Numerous studies have been carried out about the isothermal crystallization of polymers based on the Avrami equation to investigate the isothermal crystallization kinetics. However, since isothermal crystallization is rarely used in practice and often restricted to a narrower temperature range, it is more practical to study the crystallization of polymers under nonisothermal conditions. To obtain the appropriate property for semicrystalline polymer, nucleating agents have generally been used. They change the crystalline size and crystallization rate while polymer is cooling down after processing. In general, nucleating agents lead to more uniform microstructure in polymer because of reduced spherulite size.

The degree of crystallinity of SPS after melt processing is typically 40% based on DSC and X-ray measurements [Gianotti and Valvassori, 1990]. The crystallization rate of SPS is much faster than that of isotactic polystyrene (IPS) and similar to that of polyethylene terephthalate (PET), but much slower

than that of polyethylene [Cimmino et al., 1991; Wessen, 1994]. The SPS is almost new material and only two companies produce it with small scale. It is very difficult to find any results about an effect of nucleating agent for SPS. Therefore, we chose nucleating agents used for Polypropylene (PP). Numerous results have been reported about the nucleating agent effect for PP. The typical nucleating agents for PP are sorbitol derivatives (organic) and talc (inorganic). While organic nucleating agents have been used to improve stiffness and transparency of PP, inorganic ones have been used to improve mechanical properties of PP and often used as an additive in large quantity, which results in higher crystallization temperature [Mitsubishi, 1996].

In this work, we have studied the nonisothermal crystallization behavior of SPS by comparing the melting/crystallization results of organic 1,3,2,4-dis-5-(3,4-dimethyl benzylidene) sorbitol (DMBS)/SPS and inorganic talc/SPS mixture. From the crystallization peak in various cooling rates, we obtained the crystallization rate parameter (CRP) which corresponds to the crystallization rate of polymer [Zhang, 1994]. It will contribute to the SPS processing as basic data. Studies on the crystallization form and the detailed kinetics remain as a future work.

EXPERIMENTAL

1. Materials

The SPS used in the present study was polymerized by Cp^* - $TiCl_3$ (pentamethyl cyclopentadienyl titanium trichloride)/MAO (methylaluminoxane) catalyst system at 50 °C (Al/Ti=1742) and separated from the non-SPS that was soluble fraction in boiling acetone ($M_w=204,800/g\text{-mol}$, PDI=2.08). The nucleating agents used in this study were commercial ones and their characteristics are summarized in Table 1.

2. Sample Preparation

The fine powder type of SPS was blended with each nucleat-

[†]To whom correspondence should be addressed.

E-mail: oopark@sorak.kaist.ac.kr

Table 1. Characteristics of used nucleating agents

| | Chemical name | Chemical formula | Appearance | T _m [°C] | Code |
|-----------|--|---|--------------|---------------------|----------|
| Inorganic | Talc (Magnesium silicate) | Me ₂ (Si ₄ O ₁₀)(OH) ₂ | White powder | 850 (Decomposition) | SPS/talc |
| Organic | 1,3,2,4-dis-5-(3,4-dimethyl benzylidene)sorbitol | C ₂₂ H ₂₄ O ₆ | White powder | 278* | SPS/DMBS |

*measured by DSC with a 10 °C/min heating rate.

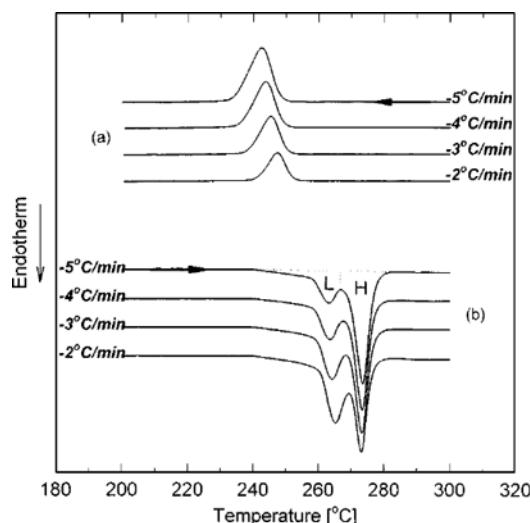
ing agent powder in a beaker by hand shaking for 10 min to disperse the nucleating agent uniformly in the SPS. The concentration of the nucleating agent was varied from 1,000 to 8,000 ppm. The samples with nucleating agent were then mixed by a rotational shear with $\dot{\gamma}=10$ s⁻¹ for 20 min in melt state under N₂ condition.

3. Measurements

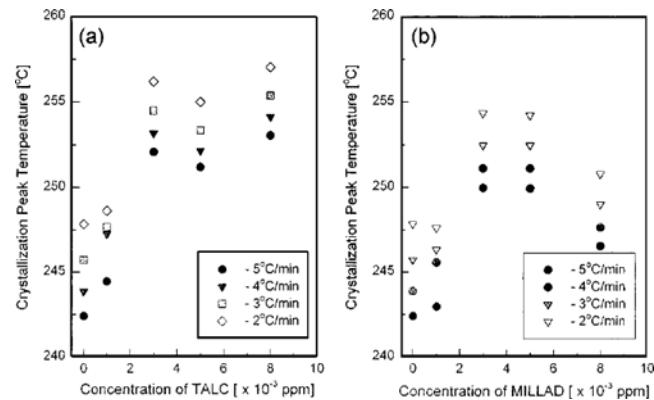
A DSC (DuPont TA 2010) was used for nonisothermal measurements. All runs were made under nitrogen gas merge. The nonisothermal crystallization experiments were carried out with various cooling rates (2, 3, 4, and 5 °C/min) until they reached a temperature of 200 °C. All cooling runs followed after premelting at 300 °C for 10 min. They were then reheated at a rate of 10 °C/min until 300 °C.

RESULTS AND DISCUSSION

Fig. 1 shows DSC thermograms of SPS with cycled cooling/heating procedure. As the cooling rate increases, the crystallization exothermic peak temperature, T_c, shifts to a lower value. Such a behavior of SPS is attributed to its shortened crystallization time corresponding to a faster cooling rate. At the heating scan with a 10 °C/min heating rate, it shows dual melting endothermic behavior. The lower melting peak shifts to a higher temperature with decreasing pre-cooling rate, while the higher melting peak does not change. The area ratio of the lower melting peak to

**Fig. 1. The DSC thermograms of SPS.**

(a) crystallization from 300 °C melt in various pre-cooling rates. (b) heating SPS pre-cooled, with a 10 °C/min rate from 200 °C. L: lower melting endotherm peak, H: higher melting endotherm peak.

**Fig. 2. Crystallization peak temperature, T_c, of SPS with nucleating agent as a function of nucleating agent concentration in various pre-cooling rates.**

(a) SPS/talc system, (b) SPS/DMBS system.

the higher one increases with decreasing pre-cooling rate. All thermograms for SPS containing nucleating agent have the same trend with that for neat SPS. In the following, the crystallization behavior of SPS containing nucleating agent is to be interpreted from these DSC thermograms.

Fig. 2 shows a change of T_c as a function of nucleating agent content with various cooling rates. The whole crystallization is composed of nucleation and a growth step. At low temperature, the nucleation step is dominant over the growth, but at high temperature the growth step becomes dominant. The addition of nucleating agent increases the nucleus density above the crystallization temperature and makes the crystallization peak shift to a higher temperature. However, at high contents over about 3,000 ppm, the increase of nucleus density was no longer effective. By comparing values of T_c for the SPS/talc with those of the SPS/DMBS, we could find that the T_c of the former is a little higher than that of the latter at all concentrations. The DMBS itself showed a melting temperature (278 °C with a heating rate of 10 °C/min) slightly higher than neat SPS. Therefore, the temperature at which DMBS acts as a nucleating agent would be lower than that of talc, because the talc is at a solid state during the crystallization of SPS.

There have been many suggestions to make a material parameter for directly comparing crystallization rates. Among them we adopted the crystallization rate parameter (CRP) proposed by Zhang et al. [1994]. From the nonisothermal crystallization thermograms, the width of the crystallization exothermic peak at half-height divided by the cooling rate yields the isothermal crystallization half-time, t_{1/2}, necessary for performing half a transition process at a given crystallization temperature. Polymeric material having a slower crystallization rate has a larger

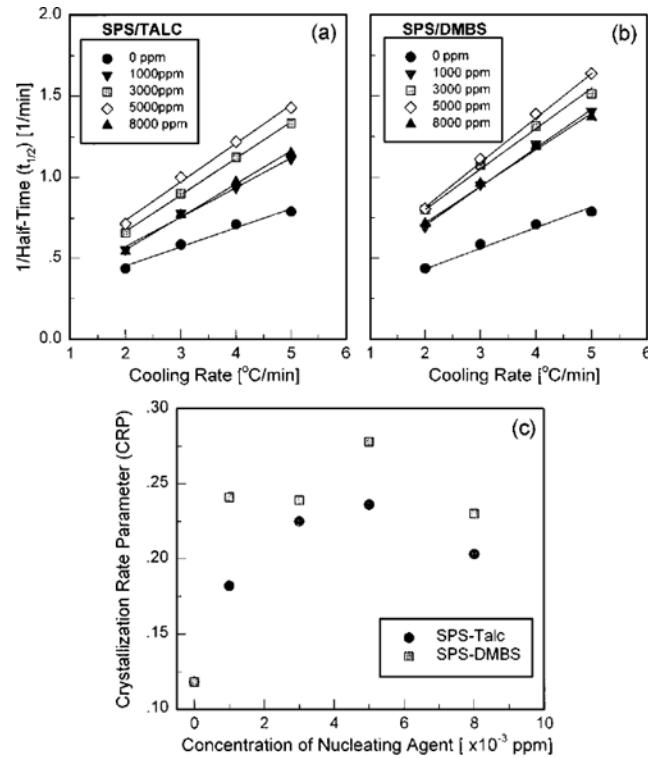


Fig. 3. Plots of reciprocal half-time, $1/t_{1/2}$, vs. pre-cooling rate for various concentrations of (a) SPS/talc and (b) SPS/DMBS systems, and (c) the crystallization rate parameter (CRP) as a function of the concentration of nucleating agent.

$t_{1/2}$. The CRP is determined by the slope in cooling rate vs. $1/t_{1/2}$ plot and corresponds to the crystallization rate of the system.

Fig. 3 shows the effect of nucleating agent on the CRP. With increasing the concentration of nucleating agent, the CRP increases but does not change significantly at high concentration of nucleating agent over 3,000 ppm. Comparing CRPs in each case, the CRP of SPS/DMBS is a little bit higher than that of SPS/talc. This means that the DMBS acts as a more efficient nucleating agent than talc does. This behavior is also shown in the Fig. 4. The enthalpy of crystallization, ΔH_c , presents the crystallinity of the sample. The nucleating agent enables SPS to crystallize more (talc-10%, DMBS-15%).

From the DSC thermograms of 10 °C/min heating rate after nonisothermal crystallization in various cooling rates, most of samples show dual melting endotherms. The area ratio of the two peaks in dual melting endotherm is influenced by the cooling rate during nonisothermal crystallization and by the addition of nucleating agent. With slower cooling rate, the lower melting peak shifts to a higher temperature and its area increases. The lower melting peak also shifts to a higher temperature with increasing the amount of nucleating agent. Many studies have explained the dual melting endotherms in terms of the recrystallization during heating cycle. Guerra et al. [1990] demonstrated that the dual melting endotherm of SPS was caused not by the change in crystalline form, but by the recrystallization of a portion having lower melting endotherm into a more perfect crystal, confirmed with wide angle x-ray diffractometry (WAXD)

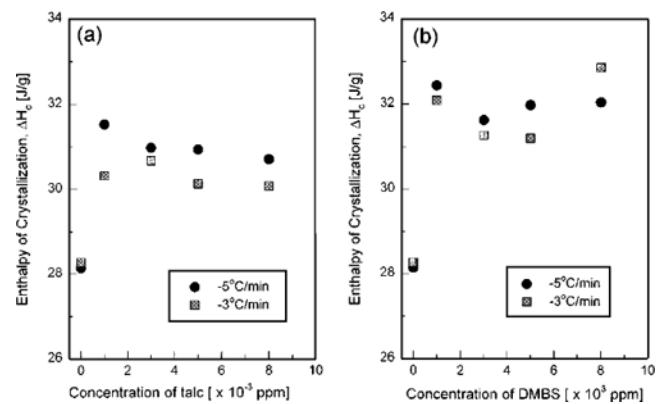


Fig. 4. Enthalpy of crystallization, ΔH_c , of SPS with nucleating agent as a function of nucleating agent concentration in 2 pre-cooling rates.

(a) SPS/talc system, (b) SPS/DMBS system.

at its melting region of about 270 °C. Sweet et al. [1972] explained that the change of the two peak area ratio in the dual melting endotherm in various conditions was attributed to the competition of melting and recrystallization of the portion having lower melting temperature, T_{mL} , in dual melting endotherm. This T_{mL} shifts to a lower temperature as the cooling rate is faster. The remaining portion of the crystalline form has the usual melting temperature, T_{mH} , and this temperature does not shift by changing cooling rate. Some imperfect

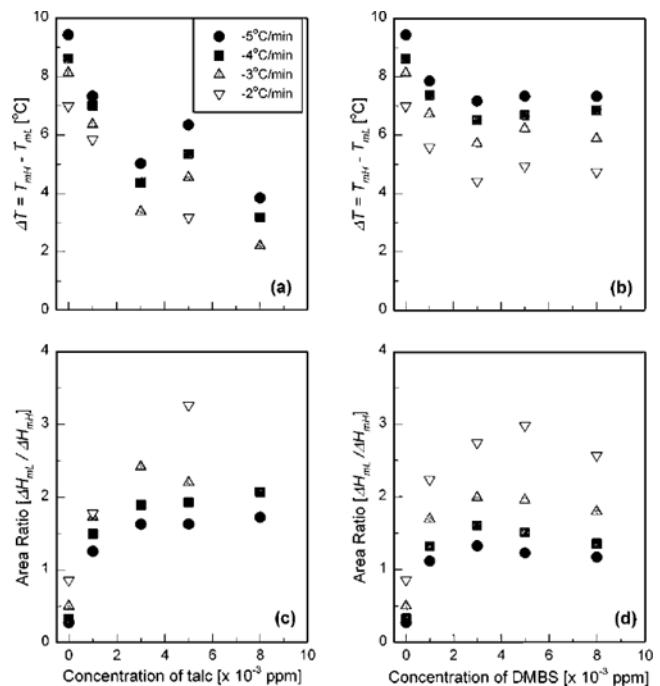


Fig. 5. Plots of $\Delta T = T_{mH} - T_{mL}$ (a and b), and the peak area ratio of lower melting endotherm to higher one (c and d) as a function of the concentration of respective nucleating agent in various pre-cooling rates.

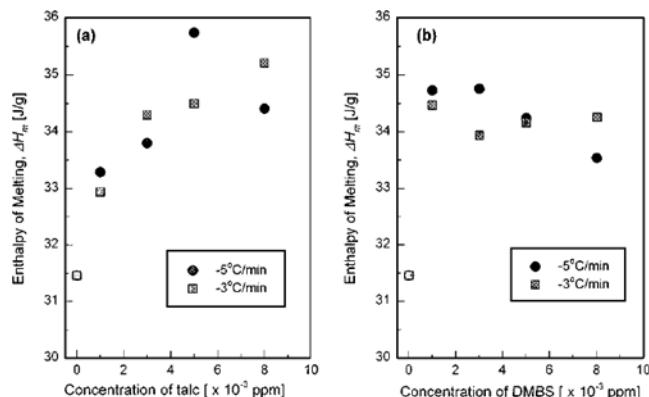


Fig. 6. Enthalpy of melting, ΔH_m , of SPS with nucleating agent as a function of nucleating agent concentration in 2 pre-cooling rates. (a) SPS/talc system, (b) SPS/DMBS system.

crystalline portion melts at lower temperature. As temperature rises, this portion rearranges into equilibrium state and this process is so-called 'recrystallization'. When temperature approaches a higher melting point, this portion starts to melt with the rest of the portion having a more perfect crystalline form. The recrystallization changes the peak area ratio of the lower melting endotherm to the higher one, represented by an enthalpy ratio, $\Delta H_{mL}/\Delta H_{mH}$. As T_{mL} shifts to a lower temperature, it has a stronger driving force ($\Delta T = T_{mH} - T_{mL}$) to recrystallize because it has more time to rearrange.

Fig. 5(a) and (b) show that the temperature difference ΔT decreases with slower cooling rate and the addition of nucleating agent because a more perfect SPS crystal is formed under these conditions. Therefore, the enthalpy ratio, $\Delta H_{mL}/\Delta H_{mH}$, increases with slower cooling rate and addition of nucleating agent. And these conditions produce more perfect crystal which does not have time to recrystallize. Here, we can also see that the DMBS makes the crystal more perfect and the effective concentration of nucleating agent is about 3,000 ppm. This result is consistent with a result of the SPS/atactic PS (APS) blend [Park and Park, 1998]. In that work, the APS hindered the crystallization of SPS.

Fig. 6 shows a total enthalpy of dual melting endotherm as a function of the concentration of nucleating agent. The melting enthalpy, ΔH_m , of SPS containing nucleating agent has a higher value than that of neat SPS. This is also consistent with the result from the enthalpy of exothermic crystallization. We did not observe the difference to depend on the type of nucleating agent.

CONCLUSION

The nucleating agents used in present study enhanced the crystallization rate of SPS and made the crystalline microstruc-

ture more perfect. This is manifested in higher T_c , higher CRP, and larger values of crystallization enthalpy and melting enthalpy. The amount of nucleating agent remained effective until about 3,000 ppm. The crystallization behavior was not promoted by further addition of nucleation agent. The effect of DMBS as a nucleating agent was a little more effective than that of talc in the nucleation of SPS, although the T_c showed lower level in SPS/DMBS than SPS/talc. This implies that the temperature at which DMBS acted as a nucleating agent was lower than that of talc, since DMBS had a melting temperature comparable to that of SPS. More detailed study for a crystalline structure remains for future study.

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