

실리카 나노입자 충전 폴리에틸렌 나프탈레이트의 특성

안선훈, 김성훈, 임승순, 이승구*

한양대학교 섬유고분자공학과, 기능성고분자신소재연구센터, *충남대학교 섬유공학과

Characterization of silica nano-particle filled poly (ethylene 2, 6-naphthalate)

Seon Hoon Ahn, Seong Hun Kim, Seung Soon Im, and Seung Goo Lee*

Department of Fiber and Polymer Engineering, Center for Advanced Functional Polymers,
Hanyang University, Seoul, 133-791, Korea

*Department of Textile Engineering, Chungnam National University, Daejeon, 305-764, Korea

1. Introduction

Poly (ethylene 2, 6-naphthalate) (PEN) has been used for a high performance engineering plastics such as fiber, film, and packaging, because of excellent physical properties and outstanding gas barrier characteristics [1-2]. However, the application of PEN is limited because PEN exhibits a relatively high melt viscosity. Recently, many researches for organic/inorganic composites by applying nano-particles to the polymer matrix have been carried out [3], and the nano-particles exhibited greatly improved mechanical and rheological properties [4]. Fumed silica nano-particles had extremely large and smooth non-porous surfaces, which could promote strong physical contacts between filler and polymer matrix. In this regard, rheological properties as well as mechanical and physical properties of PEN would be improved by applying small amount of silica nano-particles. However the research has been rarely performed about characterization of silica nano-particle filled PEN composites. In this research, silica nano-particles were melt blended to improve mechanical and rheological properties of PEN. Non-isothermal crystallization kinetics was adopted to investigate on the effect of silica nano-particles in PEN matrix during actual process condition. The study of non-isothermal crystallization kinetics, from differential scanning calorimetry measurements, has been performed using combined methods of Avrami and Ozawa methods. The spherulite growth rate, nucleating activity, and crystallization activation energy were also investigated.

2. Experimental

2.1 Materials and sample preparation

PEN (I.V. = 0.93 dL/g) was supported by Hyosung Co., and hydrophilic fumed silica (primary particle size is 7 nm) was purchased from Sigma Aldrich Co. Silica nano-particle filled composites were prepared using Haake rheomix 600 internal mixer at various silica contents (0.3~0.9 wt%). The melt compounding was performed at 275°C for 5 min, and rotor speed was 60 rpm.

2.2 Characterization

Melt viscosity was investigated using ARES (Advanced rheological expansion system, Rheometric scientifics Co.) with parallel plate type geometry at 275°C under the liquid nitrogen atmosphere, and the frequency was ranged from 0.05 to 300 Rad/s. The mechanical properties of silica nano-particle filled PEN composites were investigated using UTM Instron 4465 at a crosshead

speed of 1mm/min, and the gage length was 7cm. Non-isothermal crystallization behaviors of silica nano-particle filled composites were performed using Perkin-Elmer DSC-7, and the weight of all samples was kept in approximately 6mg. The samples were heated up to 300°C at a heating rate of 10°C/min under nitrogen atmosphere, and held for 5 min to remove previous thermal history. Non-isothermal crystallization kinetics was investigated by cooling of these samples at constant cooling rates from 300°C to 30°C such as 2.5, 5, 10, 15, 20, 25, and 30°C/min. Spherulite growth rate was calculated using polarized optical microscope equipped with a CCD camera (Nikon HFX-11A), and hot-stage (Mettler Toledo FP-82HT). By using a CCD camera, the spherulite growths of silica nano-particle filled PEN composites were monitored at isothermal crystallization conditions, and captured spherulite growth images for every 5 seconds. These captured images were analyzed using Image analysis (Media Cybernetics Co., Image-Pro®).

3. Results and Discussion

The total torque values of silica nano-particle filled PEN composites was decreased with the silica contents during the process, and the apparent viscosity was also decreased. In case of using silica nano-particles as the filler, they would act as a lubricant during melt compounding, because it had a spherical shape and smooth non-porous surface, which lowered friction coefficient [5]. It could propose the possibility for the improvement of processability and various applications of the nano-particle filled polymer composites. As shown in *Figure 1*, tensile strength and modulus were increased, while toughness and elongation were decreased by adding silica nano-particles. When the composites are under tensile stress, the force is transferred to silica particles through the interphase and the silica particles become the receptor of the tensile force. In this regard, mechanical properties of silica nano-particle filled PEN composites were improved by adding silica nano-particles [6].

Non-isothermal crystallization behaviors of PEN and silica nano-particle filled PEN composites are shown in *Figure 2*. As the cooling rate increased, the crystallization peak temperature (T_p) shifted to lower temperature both for PEN and silica nano-particle filled PEN. When the specimens were cooled down fast, a higher supercooling was required to initiate crystallization because the motion of PEN molecules could not follow the cooling temperature [7]. At a given cooling rates, T_p of silica nano-particle filled PEN composites shifted to higher temperature compared to pristine PEN. Overall crystallization time (t_c) was decreased with increasing the silica content at various cooling rates. The degree of crystallinity (X_c) of the composites was increased with the silica contents, because the polymer crystallized more perfectly in lower supercooling. Non-isothermal crystallization kinetics of silica nano-particle filled composites were analyzed using combined methods of Avrami and Ozawa theories. Liu et al. [8] proposed a new kinetic equation by combining Avrami [9] and Ozawa [10] equations. As the degree of crystallinity related to the cooling rate a and the crystallization time t (or temperature T), the relation between a and t could be built up at a given degree of crystallinity. Consequently, a new kinetic equation of non-isothermal crystallization is derived as below:

$$\log Z_t + n \log t = \log K(T) - m \log a \quad (1)$$

$$\log a = \log F(T) - b \log t \quad (2)$$

Where the parameter $F(T) = [K(T)/Z_t]^{1/m}$, with n the Avrami exponent calculated with the Ozawas method, and b is the ratio between the Avrami and Ozawa exponents, i.e., $b = n/m$. $F(T)$ refers to the value of cooling rate chosen at unit crystallization time, when the system has a defined degree of crystallinity. It can be seen that $F(T)$ has a definite physical and practical meaning. According to equation (1) at a given degree of crystallinity, the plot of $\log a$ against $\log t$ will

give a straight line with the intercept of $\log F(T)$ and the slope of b . The $F(T)$ values were increased with the relative degree of crystallinity, and the b was ranged from 0.95 to 1.11 and from 1.28 to 1.65 for PEN and silica nano-particle filled PEN composites, respectively.

Dobrev et al. [11] have suggested that a simple method to calculate the nucleating activity of foreign substrates in polymer melt. Nucleating activity (Φ) is a factor by which the work of three-dimensional nucleation decreases with the addition of other foreign substrate. If the foreign substrate is extremely active, Φ is approaching 0 and for inert particles Φ is approaching 1. For homogeneous nucleation from the melt near the melting temperature, the cooling rates can be written as,

$$\log r = A - B/2.3\Delta T_p^2 \text{ (homogeneous case)} \quad (3)$$

$$\log r = A - B^*/2.3\Delta T_p^2 \text{ (heterogeneous case)} \quad (4)$$

$$\Phi = B^*/B \quad (5)$$

Where r is the cooling rate; A is a constant; T_p is the degree of supercooling, i.e. $T_p = T_m - T_p$, T_p is the temperature corresponding to peak temperature of DSC crystallization curves. In these systems, nucleating activities of silica nano-particle filled PEN composites were calculated 0.95, 0.91, 0.88, and 0.71, respectively. From the results of the calculated nucleating activity, it could be seen that the nucleating effect of the filler were increased with the silica contents, which indicated that the fumed silica was effectively acted as a nucleating agent in PEN matrix.

Spherulite growths of PEN and silica nano-particle filled PEN composites were increased with the isothermal crystallization temperatures. The spherulite growth rates calculated from the slope of radius of spherulite against time plot were increased with the silica contents, because silica nano-particle acted as a nucleating agent in PEN matrix.

The crystallization activation energies of PEN and silica nano-particle filled PEN composites calculated using Kissinger's method [12] during non-isothermal crystallization process were determined to be 105, 91, 86, 79, and 75 kJ/mol, respectively. It can be seen that the crystallization activation energy of the composites were reduced with the silica contents than that of pristine PEN. From the above results, the silica nano-particles made the molecular chain of PEN more easily crystallized, and accelerated the overall non-isothermal crystallization process.

4. Conclusion

Silica nano-particle filled PEN composites were melt blended to improve mechanical and rheological properties of PEN. Total torque values and melt viscosity of the composites were decreased with the silica contents because it acted as a lubricant in PEN matrix. It could be propose the possibility for the improvement of processability and various applications of PEN. Tensile strength and modulus were increased with the silica content because silica particle became receptor of the tensile force and strong physical contact between the filler and the polymer. Crystallization peaks were shifted to the higher temperature, and the overall crystallization time was decreased with the silica contents. The degree of crystallinity of silica nano-particle filled PEN composites was increased with the silica contents. Combined method of Avrami and Ozawa theories were successful to describe the non-isothermal crystallization process of PEN and silica nano-particle filled PEN composites. Spherulite growth rate was increased with increasing the silica nano-particles, and the crystallization activation energies were decreased with the silica contents, which made the molecular chain of PEN more easily crystallized when the silica nano-particles added to PEN matrix. Therefore, silica nano-particles acted as a nucleating agent in PEN matrix, and the nucleating activities, which indicated the activities of the filler to the polymer matrix, were revealed that fumed silica nano-particles had a good nucleating effect on PEN.

5. Reference

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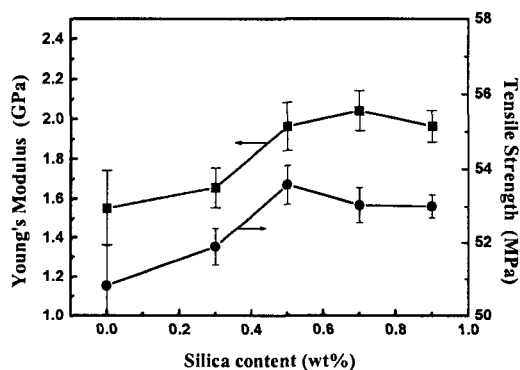


Figure 1. Tensile strength and modulus variations with increasing silica contents.

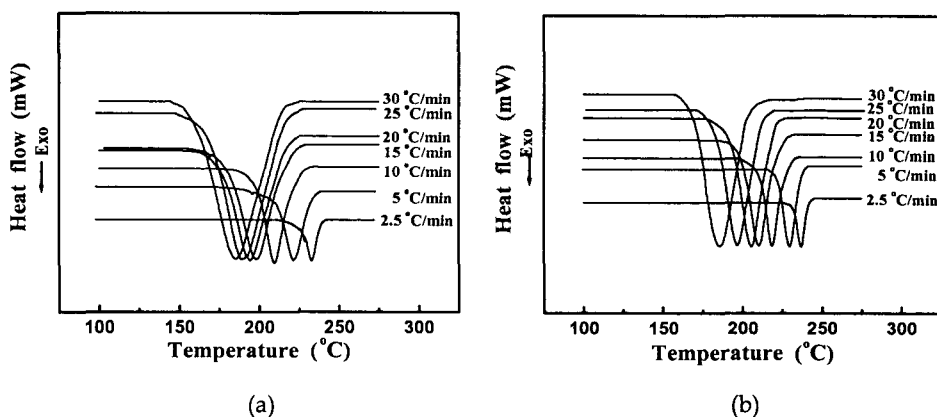


Figure 2. DSC thermograms of (a) PEN and (b) PEN/Silica 0.9 wt% during non-isothermal crystallization at different cooling rates.