Thermotropic Liquid Crystal Polymer or Silica Nano-particle Filled Polyester Composite Fibers

Seong Hun Kim,* Jun Young Kim, Seon Hoon Ahn
Department of Fiber & Polymer Engineering, Center for the Advanced Functional Polymers,
Hanyang University, Seoul, 133-791, Korea
(*E-mail: kimsh@hanyang.ac.kr)

Abstract

Ternary blend fibers (TBFs) based on melt blends of PEN, PET, and TLCP were prepared by melt blending and spinning to achieve high performance fibers. The reinforcement effect and the TLCP fibrillar structure resulted in the improvement of mechanical properties for TBFs. Molecular orientation was an important factor in determining the tensile strength and modulus of TBFs. Another part of this research is silica nano-particle filled PEN composites were melt-blended to improve mechanical and physicalproperties, and processability. The tensile modulus and strength were improved adding silica nano-particles to the PEN. The decreased melt viscosity by the fumed silica resulted in the improvement of the processability. The fumed silica may act as a nucleating agent in the PEN matrix.

Introduction

Thermoplastic liquid crystal polymers (TLCPs) are attractive because of their potential application as ultra-high strength fibers, and melt blends of TLCP and conventional thermoplastics have been extensively investigated due to their ease of processing and high performance [1-3]. As high performance polymers usually involve high cost and are difficult to process, it is very important to reduce their process cost without any decrease in their mechanical properties. Although various studies on the structure development during melt spinning and on the fundamental aspects of fiber formation have been carried out, little research and development into low cost-high performance fibers has been performed. In recent years, poly (ethylene 2, 6-naphthalate) (PEN) has been used for a high performance engineering plastics such as fiber, film, and packaging [1-3]. However, the application of PEN is limited because PEN exhibits high melt viscosity. Recently, many researches for organic/inorganic composites by applying nano-particles to the polymer matrix have been carried out [4], and the nano-particles exhibited greatly improved the mechanical and rheological properties [5]. 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. In part I, TBFs based on melt blends of PEN, PET, and TLCP were prepared by melt blending and spinning to achieve high performance fibers. Structure and property of TBFs were investigated using WAXD analysis, birefringence and density measurements, tensile testing, and SEM analysis. In part II, 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 spherulite growth rate, nucleating activity, and crystallization activation energy were also investigated.

Experimental

Part I. Thermoplastics used were PEN and PET with the intrinsic viscosity of 0.93 dL/g and 1.07 dL/g, respectively, and were supplied by Hyo Sung Co. TLCP used in this research was based on 80 mol% PHB and 20 mol% PET, and was purchased from Unitika Co. TLCP/PEN/PET ternary blends were carried out by melt blending in a Haake twin extruder, and were melt spun in the extruder with 4 holes spinneret. Mechanical properties of TBFs were measured using an Instron 4465 tensile testing machine. WAXD analysis was performed using a Rikagu Denki X-ray diffractometer. The birefringence and density of TBFs was measured using a Nikon polarizing microscope equipped with a K tilting compensator and density gradient column filled with carbon tetrachloride and *n*-heptane. The morphology of TBFs was observed using a Hitachi SEM model S-4200 scanning electron microscope.

Part II. PEN (I.V. = 0.93 dL/g) was supported by Hyo-sung 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%). Melt viscosity was investigated using ARES (Rheometric scientifics Co.). The mechanical properties of silica nano-particle filled PEN composites were investigated using a UTM Instron 4465. Non-isothermal crystallization behaviors of silica nano-particle filled composites were performed using Perkin-Elmer DSC-7.

Results and Discussion

Part I. The reinforcement effect of the polymer matrix by TLCP component and TLCP fibrilar structure with high aspect ratios could increase the mechanical properties of TBFs. It is expected that these highly oriented TLCP fibrillar structures and the development of those may improve the tensile strength and modulus of TBFs. The improvement of mechanical properties for TBFs suggested that annealing could improve the crystallinity of TBFs because the amorphous region was crystallized and that the crystalline structures of TBFs became more ordered and perfect by annealing. The increased apparent crystallite size was associated with development of larger crystallites and more ordered crystalline structures in the annealed TBFs with spinning speed. The density of TBFs was increased with spinning speed, which was attributed to both enhancement of the packing between the chains and to more densely packed fiber structures [6]. The increase in the birefringence with spinning speed resulted in the improvement of orientation of the chains along the fiber axis. The degree of crystallinity and density of TBFs would begin to increase rapidly at the birefringence value of approximately 0.095, and this region of rapid increase was considered as a break point, indicating the occurrence of the orientation-induced crystallization [7]. A linear relationship between birefringence and mechanical properties suggested that molecular orientation have greatly affected the tensile strength and modulus of TBFs.

Part II. The total torque values of silica nano-particle filled PEN composites were decreased with the silica contents during the process, and the apparent viscosity was also decreased. 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. As the cooling rate increased, the crystallization peak temperature (T_p) shifted to lower temperature both for PEN and silica nano-particle filled PEN, and at a given cooling rates, T_p of silica nano-particle filled PEN composites shifted to higher temperature compared to pristine PEN. Non-isothermal crystalliza-tion kinetics of silica nano-particle filled composites was analyzed using combined methods of Avrami and Ozawa theories. 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. 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.

Conclusions

In part I, the reinforcement effect of polymer matrix by TLCP and TLCP fibrillar structure with higher aspect ratios could increase the mechanical properties of TBFs. The increase in the apparent crystallite size in TBFs suggested that larger crystallites and more ordered crystalline structures were developed in the annealed TBFs. The increased density of TBFs was attributed to the effective between the chains in TBFs. Molecular orientation was an important factor in determining the mechanical properties of TBFs. In part II, silica nano-partiele acted as a lubricant in the PEN matrix, and promoted crystallization of the PEN. In these regards, crystallization rate and degree of crystallization were increased with the silica contents, and spherulite growth rate was also increased. From the above results, the silica nano-particles made molecular chain of PEN more easily crystallized, and accelerated the overall non-isothermal crystallization process.

References

1. S. H. Kim, S. W. Kang, J. K. Park, and Y. H. Park, J. Appl. Polym. Sci., **70**, 1065, (1998).
2. J. G. Lee and S. H. Kim, J. Korean Fiber Soc., **34**, 877 (1997)
3. J. Y. Kim, E. S. Seo, and S. H. Kim, Macromol. Res., **11(1)**, 62, (2003).
4. E. Reynaud, T. Jouen, C. Gauthier, G. Vigier, and J. Varlet, Polymer, **42**, 8759, (2001).
5. S. R. Raghavan and S. A. Khan, J. Rheol.,**36**, 1311, (1995).
6. W. Zhang, T. M. Nicholson, G. R. Davies, and I. M. Ward, Polymer, **37**, 2653 (1996).
7. J. Shimizu, N. Okui, and T. Kikutani, Sen'I Gakkaishi, 34, T-64 (1978).