Crystallization Behavior and Morphological structure of PEN/PET Blends and P(EN-ET) Copolymers

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INTRODUCTION

Although the demand of poly(ethylene terephthalate)(PET) is very large, better thermal and mechanical properties are desired for some application. Poly(ethylene 2, 6-naphthalate)(PEN) shows a great promise to fullfil this need. Naphthalate groups in the repeat unit provide rigidity to polymer backbone, thus, elevating the glass transition temperature, and enhance mechanical properties such as tensile modulus, creep resistance, etc. Unfortunately PEN has the high price and processing problem to be overcome. The ways to bring a settlement the problem would be to blend and to copolymerize PEN and PET. Especially, the deterioration of thermal and mechanical properties of PEN will occur If a lot of PET is introduced with PEN. Therefore in this article PET composition is limited less than 10%.

PEN is a semi-crystalline thermoplastic material with two reported crystalline structures. The first crystalline structure was reported by Mencik [1] and the other crystalline structure was reported by Buchner and Zachmann [2,3]. Thermal properties [4] and crystalline morphology [5] were also studied. Blending and transesterification studies between PEN and PET were reported Stewart et al [6].

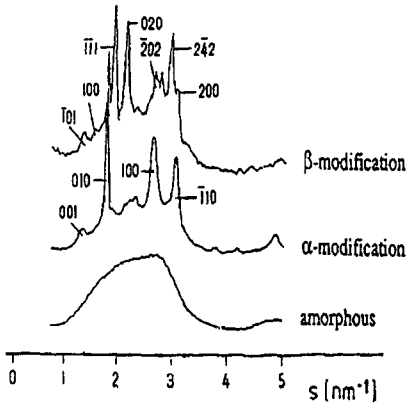
We investigate effects of presence of DMT on the morphological structures and crystallization behavior of PEN.

EXPERIMENTAL

Materials used in this study were poly(ethylene terephthalate)(PET), poly(ethylene naphthalate)(PEN), P(EN-ET) copolymers modified with DMT(2, 6, 8, 10 mol%), kindly supplied by KOLON co. Crystallization of PEN/PET blends and homo PEN, P(EN-ET) copolymers were performed isothermally in oil bath at 200 ℃, 250 ℃ for 1 hr, 13 hrs, respectively.

Thermal analysis was carried out from 50 ℃ to 300 ℃ at a heating rate of 10 ℃/min using a Perkin-Elmer DSC-7 with a nitrogen purge. Morphology of copolymers and homo PEN was observed by polarized microscopy(Nicon HFX-ⅡA). To obtain spherulite, samples were melted at 290 ℃ between two cover glasses of 0.15 mm thickness and 22 x 22 mm2 in site, crystallized in the same condition with isothermal crystallization. Wide angle X-ray diffraction(WAXD) patterns of samples isothermally crystallized were recorded on diffractometer(Rigaku Denki) with Ni-filtered Cu Kα radiation at 35 Kv and 35 mA.

RESULTS and DISCUSSION



Scheme 1 Wide angle X-ray profiles of α- and β-Modification.

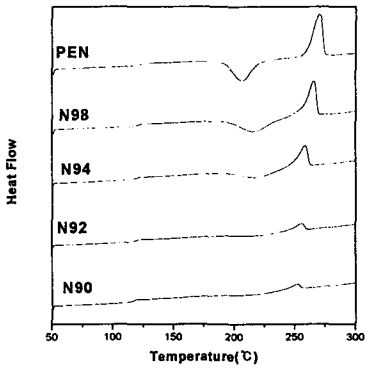


Fig. 1 DSC thermograms of PEN and P(EN-ET) copolymer

DSC thermograms of homo PEN and P(EN-ET) copolymer are shown in fig.1. With increasing the content of DMT, Tm and Tg have a tendency to decrease but

Tc increases. Also, crystallization peak becomes broad.

Scheme 1 shows WAXD profiles of these two different crystal structure. Buchner et al.[3] reported that crystal structures are influenced by melting and isothermal crystallization temperature. They observed that α-form appeared when PEN was isothermally crystallized below 210 ℃ and β-form did above 210 after the melt at 280 ℃. Also, β-form appeared when PEN was isothermally crystallized above 240 ℃ from the melt of 300 ℃.Fig. 2 shows WAXD patterns of homo PEN and P(EN-ET) copolymer isothermally crystallized at 200 ℃ for 1hr from 290 ℃. Homo PEN is crystallized in the α-form, which is consistent with the result reported by Buchner but in the case of P(EN-ET) copolymers, the β-form, (2-42) plane peak, begins to appears in the sample contained DMT 6 mol%(N94). Especially, N90(sample contained DMT 10 mol%) is crystallized mainly in the β-form. The only exception is the reflection corresponding to the very strong (010) reflection of the α-form. However, according to the (010) reflection just mentioned, a small amount of α-form seems to be present in this sample. This result indicates a change of unit cell from the α-form to the β-form as DMT content increase.

Polarized optical micrographs of PEN and P(EN-ET) crystallized at 200 ℃ for 1 hr are shown in fig. 3. As shown in the figure, homo PEN shows distinct maltese cross patterns. but with increasing the content of DMT, maltese cross patterns gradually fade. After all, maltese cross patterns disappear from N90 and then spherulites become segmented. According to X-ray investigations, this sample is crystallized in β-crystal structure including a small amount of α-form.

CONCLUSION

The crystallization behavior and morphological structures of PEN/PET blends and P(EN-ET) copolymers were investigated. PEN can be crystallized in two different crystal form called α and β the morphological structures show spherulitic and ellipitical shapes called amoeba.

At the isothermal crystallization temperature 200℃, homo PEN is crystallized in the α-form and shows distinct maltese cross patterns, while P(EN-ET) copolymer contained DMT 10 mol% (N90) is crystallized mainly in the β-form and exhibit segmental spherulites. It is supposed that the presence of DMT affect

morphological structure and crystallization behabor of PEN.

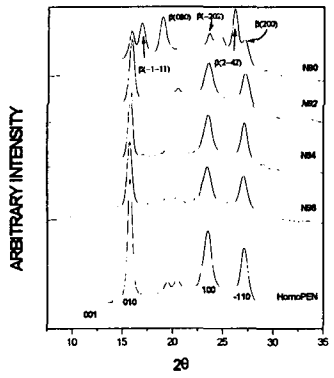
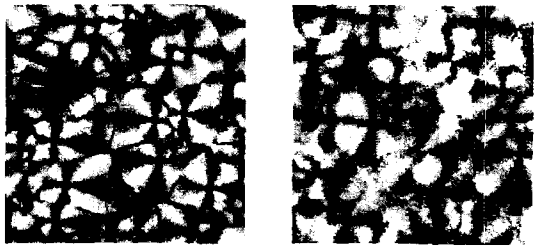


Fig. 2 WAXD patterns of P(EN-ET) copolymer crystallized at 200℃ for 1h



(a) Homo PEN (b) N98

(c) N94 (d) N92 (e) N90

Fig. 3 Fig.3 Polarized Optical micrographs of PEN and P(EN-ET) crystallized at 200℃ for 1hr

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