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Influence of soft segment content and chain length on the physical properties of poly(ether ester) elastomers and fabrication of honeycomb pattern and electrospun fiber

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ABSTRACT

Different series of poly(ether ester) (PEE) thermoplastic elastomers were synthesized using dimethyl-2,6-naphthalene dicarboxylate as hard segment, 1,4-butanediol as the chain extender, and three different soft segments of different molecular weights (MW), namely polycaprolactone diol (MW: 530 and 2000), poly(tetramethylene ether glycol) (MW: 1000 and 1800), and polycaprolactone-*block*-polytetrahydrofuran-*block*-polycaprolactone (MW: 2000). The composition of soft segment was changed from 30% to 50% with respect to the hard segment. The characteristic studies were focused to analyze the influence of the concentration and length of the soft segment content. In each series, 50:50 compositions of the hard and soft segments were found to show the best mechanical properties. In addition the physical properties of the elastomer were very sensitive to the type of soft segment. The elastomers prepared in this study were systematically characterized using various spectroscopic studies and thermal and mechanical analyses. As a means of discovering the feasibility of PEE elastomers as new functional materials honeycomb patterns and nanofibers have been fabricated by applying breath figures method and electrospinning, respectively, yielding uniform honeycomb structures and nanofibers of their diameter ranging from about 100 to 800 nm depending on the type of elastomer and the electrical potential employed .

1. Introduction

Since the early decades of the 20th century, researchers are focusing on finding an alternative to natural rubber that led to the discovery of various thermoplastic elastomers (TPEs) [1]. TPEs combine the functionality, performance, and properties of thermoset rubbers with the processability of thermoplastics. Natural rubbers are covalently linked, which make them nonreusable after being shaped or vulcanized. On the contrary, TPEs are cross-linked by secondary valence interactions such as van der Waals or hydrogen boding. This secondary valence cross-linking breaks down at an elevated temperature or under the influence of suitable solvents and will reappear on decreasing the temperature or removing the solvents. In principle, no damage to the material results from the breakdown and restoration of cross-linking [2,3].

In general, elastomers are composed of soft and hard segments, due to the incompatibility of these two blocks the hard one exhibit a tendancy towards crystallization and the soft segment, which imparts flexibility to TPE. The properties of block poly(ether ester) (PEE) elastomers are influenced by the sequence length of soft segment and the miscibility between the soft and hard segments. In addition, factors such as polymer morphology, crystallization behavior, and thermal history also influenced properties of the resulting copolymers [2]. Elastomers are innovative materials that have used in medical sector, packaging sector, constructions, and automobile industry. The versatility of these synthetic materials provides optimal adjustments to biomedical requirements [4–6]. Since their introduction, TPEs have been used in many important applications owing to their high degree of purity, recycling ability, and cost-effectiveness.

A variety of starting materials can be used to prepare block PEEs ranging from soft elastomers to relatively hard plastics, by varying the hard-to-soft segment ratio of materials. Majority of the works reported so far focus on the block PEEs based on poly(tetramethylene terephthalate) (PTT) or poly(tetramethylene isophthalate) (PTMI) as hard segments [7–12]. PTT possesses many advantages properties such as good tensile behavior, resilience, elastic recovery, and dyeability [13]. These characteristics make PTT highly suitable for engineering thermoplastic applications as fibers or films. Nevertheless, industrial applications demand significant enhancement in thermal behavior of PTT. Consequently, several studies were conducted to improve the heat resistance of PEEs. These studies highlighted the requirement of an aromatic diester

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monomer for hard segment [14–16]. Based on this, Wolfe et al. studied a series of block PEEs with poly(tetramethylene naphthalate) (PTMN) as hard segment [14].

Consequently, PTMN has recently attracted several investigators owing to its characteristic properties, either in pure state or in copolymer system. Ahn et al. studied the behavior of PTMN-poly(tetramethylene ether glycol terephthalate) PEEs based on the variations in hard segment [17]. For our study, we used dimethyl-2,6-naphthalene dicarboxylate (NDC) as hard segment and 1,4-butanediol (BDO) as chain extender. The use of more rigid naphthalate group in NDC is expected to improve the thermal behavior as compared to PTT [18]. We also explained the influence of the molecular weight of soft segment by synthesizing copolymers with three different soft segments, namely polycaprolactone diol (PCLD, MW: 530 and 2000), polycaprolactone-*block*-polytetrahydrofuran-*block*-polycaprolactone (PCL-*b*-PTHF-*b*-PCL, MW: 2000), and poly(tetramethylene ether glycol) (PTMEG, MW: 1000 and 1800). It is well known that PTMEG is one of the ideal soft segments for engineering elastomers. Hence, PTMEG was also used in this study. We synthesized different series of elastomers by varying the compositions of the hard and soft segments. The percentage of the soft segments was varied between 30% and 50%. The influence of soft segment length on the phase structure and thermal, mechanical and morphological properties of PEEs was also investigated in this study.

Hexagonally arranged pores known as honeycomb structured porous polymer films/membranes have been widely exploited in engineering, biotechnology and opto-electronics due to their versatility and robustness [19–21]. As a means of developing honeycomb structured thermoplastic elastomer films, attempts have been made to apply PEEs for breath figures technique. Electro-spinning has been demonstrated as a powerful technology that can be used to generate polymer fibrous materials with diameters ranging from tens of nanometers to several microns [22,23]. Electro-spun polymer nanofibers have significant importance in modern materials science for the technological developments. In addition to the application of PEEs as engineering materials, attempts have been made to utilize them in biomedical applications [24], since they reveal properties and behavior typical of the smart materials like shape memory effect due to their peculiar microstructure. In this sense trials have been made to fabricate electrospun PEE nanofibers employing typical electrospinning procedures.

2. Experimental

2.1. Materials

Polymerization grade of NDC and PTMEG (MW: 1000 and 2000) were donated by Kolon Plastics Co. (Gumi, Korea) and used them after drying. PCLD (MW: 530 and 2000), PCL-*b*-PTHF-*b*-PCL (MW: 2000), titanium tetrabutoxide (TBT; 97%), and Irganox 1010 purchased from Sigma–Aldrich were used as received. BDO (99%), hexane (99%), chloroform (99%), dichloromethane (99%), diethyl ether (99%), and ethanol (99%) were purchased from Dae Jung Chemical Co., Korea. Hexane, dichloromethane, diethyl ether, and ethanol were distilled over calcium hydride. Triflouroacetic acid (TFA) (99%) and 1,1,2,2-tetrachloro ethane (97%) purchased from Tokyo Chemical Industries(Japan) were used without further purification.

2.2. Synthesis of PEEs

The synthesis was carried out in a 1-L high-pressure reactor (Parr Instrument Company, USA) equipped with a vacuum pump, condenser, and cold trap for collecting the by-products. Poly(tetramethylene naphthalate)-*b*-poly(caprolactone diol naphthalate) (PTMN-*b*-PCLDN) PEEs were prepared by varying the NDC:PCLD weight ratios. The synthesis was involved by the transesterification of NDC by BDO and melt polycondensation with PCLD. Both the synthesis steps were carried out using TBT (0.3 wt% in relation to NDC) as a catalyst. Initially, the reactor was charged with NDC and BDO of desired ratio, followed by the addition of a thermal stabilizer (Irganox 1010, 0.5 wt% in relation to the total mass of comonomer) and TBT. The molar ratio of the diester (NDC) and diol (BDO) was maintained at 1:1.5. The trans-esterification reaction was carried out under nitrogen atmosphere at temperature range 160–210 °C for 90 min, and methanol was collected as a by-product. The conversion efficiency of the trans-esterification reaction was calculated by monitoring the amount of effluent methanol. When the distillation of methanol ceases, PCLD was added to the reactor together with TBT (0.15 wt% in relation to NDC) as catalyst. For the polycondensation reaction, the reaction temperature was increased to 250–255 °C, and the reaction was carried under vacuum. At 255 °C, the stirring torque change was monitored in order to estimate the melt viscosity of the product. The polycondensation reaction was carried out for 4–5 h depending on the weight content of PCLD segments. The product was extruded through a drain valve.

Poly(tetramethylene naphthalate)-*b*-poly(caprolactone-*b*-polytetrahydrofuran-*b*-polycaprolactone diol naphthalate) [PTMN-*b*-(PCL-*b*-PTHF-*b*-PCL)DN] and poly(tetramethylene naphthalate)-*b*-poly(tetramethylene ether glycol naphthalate) (PTMN-*b*-PTMEGN) elastomers were also synthesized using the same procedure.

2.3. Sample preparation

PEEs prepared by the abovementioned method were purified by precipitation method as follows. They were initially dissolved in chloroform, followed by precipitation in excess diethyl ether. Subsequently, the precipitate thus obtained was washed with ethanol and vacuum dried at 50 °C for 24 h. These purified samples were used for characteristic studies such as intrinsic viscosity, thermal and mechanical properties, electro-spinning, and fabrication of honeycomb patterns.

2.4. Fabrication of electro-spun fibers

Electrospun fibers were synthesized using NANO NC-ESR 100 (Nano NC, Seoul, Korea). The spinnability of the elastomers prepared in this study were analyzed by dissolving the samples in a mixed solvent of TFA and DCM (8:2) at room temperature, with gentle stirring for 6 h to form a homogeneous solution. Subsequently, a series of fibers at concentration of 30% w/v were electrospun to analyze the impact of electrospinning voltage on the morphology of the fibers. The electrospinning apparatus consisted of a 10 mL syringe connected to a syringe pump (Infusion type). The syringe pump was used to supply a steady flow of 1 μL/min of solution to the tip of the needle. A high-voltage power supply (ESN-HV60/ESN-HV30N) was used to apply a potential of 5–10 kV to the syringe needle. The inner diameters of the needles used were 0.23 mm. The target consisted of a grounded silicon wafer placed 18 cm from the needle tip to ensure that the fibers were dry upon collection at room temperature. Further analysis on the fiber morphology was made using scanning electron microscope (SEM, Hitachi S-3000H, Japan). Before the analysis, the samples were fixed to copper stubs using carbon adhesive tape and sputter-coated with 10 nm gold.

2.5. Fabrication of honeycomb pattern by breath figure method

For fabricating honeycomb pattern, PEE elastomers were dissolved in $CHCl_3$ ($0.4\ \mathrm{g\ dL^{-1}}$), and the solution thus obtained was