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Structure-properties relationships of novel poly(carbonate-*co*-amide) segmented copolymers with polyamide-6 as hard segments and polycarbonate as soft segments

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ABSTRACT

Novel poly(carbonate-*co*-amide) (PCA) block copolymers are prepared with polycarbonate diol (PCD) as soft segments, polyamide-6 (PA6) as hard segments and 4,4'-diphenylmethane diisocyanate (MDI) as coupling agent through reactive processing. The reactive processing strategy is eco-friendly and resolve the incompatibility between polyamide segments and PCD segments in preparation processing. The chemical structure, crystalline properties, thermal properties, mechanical properties and water resistance were extensively studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential scanning calorimetry (DSC), Thermal gravity analysis (TGA), Dynamic mechanical analysis (DMA), tensile testing, water contact angle and water absorption, respectively. The as-prepared PCAs exhibit obvious microphase separation between the crystalline hard PA6 phase and amorphous PCD soft segments. Meanwhile, PCAs showed outstanding mechanical with the maximum tensile strength of 46.3 MPa and elongation at break of 909%. The contact angle and water absorption results indicate that PCAs demonstrate outstanding water resistance even though possess the hydrophilic surfaces. The TGA measurements prove that the thermal stability of PCA can satisfy the requirement of multiple-processing without decomposition.

1. Introduction

Polyamides have been used in many fields due to their excellent performances such as outstanding process ability, thermal stability, mechanical properties and solvent resistance [1–3]. Polyamide elastomers are a kind of block copolymers, consisting polyamide as hard segments and polyester/polyether as soft segments [4], which have attracted considerable attentions in last decades. Compared with other hard segments in block copolymers, polyamide possess stronger hydrogen bonding that are well-suited for formation of strong physical crosslinks, which will improve the physical and chemical properties of polyamide based block copolymer such as mechanical properties, solvent resistance, thermal and dimensional stability [5]. Soft segments in polyamide elastomers typically include a low glass transition temperature (T_g) oligomer such as poly(tetramethylene oxide) (PTMO), poly(ethylene glycol) (PEG), poly(dimethyl siloxane) (PDMS), poly(butylene adipate) (PBA), polycaprolactone (PCL) etc, which will impart flexibility and rubber-like performance with the polyamide.

Li and coworkers [6] reported a series of novel aliphatic thermoplastic polyamide elastomers with different short polyamide-6 and PEG segments. The target products exhibited good thermal stability and mechanical properties. Lips, etc [7] synthesized a series of poly(ester-amide)s based on 1,4-butanediol, dimethyl adipate and a preformed bisamide-diol through melting polycondensation. The poly(ester-amide)s with different composition showed a regular change on thermal and mechanical properties. Kong and his group [8] prepared polyamide elastomers consisting polyamide 6 as hard segments and PTMO as soft segments. Meanwhile, they studied the influence of PTMO chain length on the performance of the products. Buckwalter et al. [9] described the synthesis and structure–property relationships of PDMS polyoxamide segmented copolymers with variable PDMS molecular weights. Gube et al. [10] prepared a series of block copolymers consisting alternating polycaprolactone/polyamide-12 in

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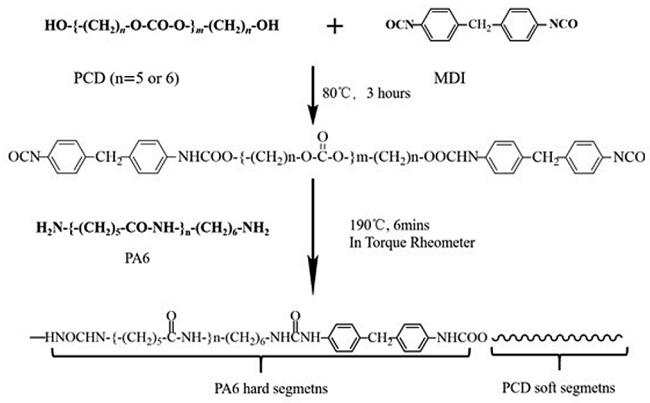

Fig. 1. The synthetic route of PCAs.

backbone, the results showed that samples with a high content of polycaprolactone showed high strain and good impact behavior. There are many researches on the preparation of polyamide elastomers with different soft segments. However, the polyamide elastomers with polycarbonate diol (PCD) as soft segments have not been studied in the previous research.

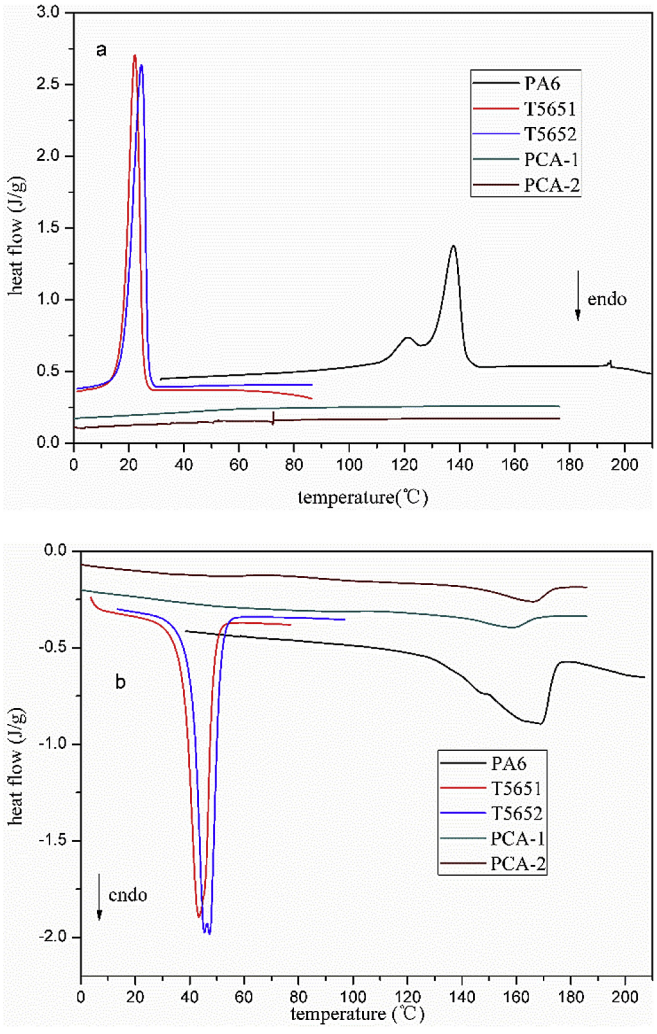

Fig. 2. The DSC results of PCD, PA6 and PCAs, a: cooling scan; b: heating scan.

Polycarbonate (PC) consists repeat -*O*—CO—*O*- units in backbone, which is insensitive to moisture but sensitive to original solvent [11]. Polyamide-6 is strongly resistant to most solvents and is sensitive to moisture [12]. Therefore, extensive researches on blends of polyamide-6 and PC have been conducted to obtain material which is resistant to organic solvents and insensitive to moisture [13,14]. However, the thermodynamically immiscible between PC and polyamide lead to the phase separation, which will affect the performance and restrict the application of the blends [15]. Polycarbonate diol (PCD) have the same repeat -*O*—CO—*O*- with PC, the PCD has been employed as soft segments to prepare the polyurethane in the previous research [16]. Therefore, it is expected to achieve the poly(carbonate-*co*-amide) (PCA) with excellent performance through incorporating the PCD with the polyamide-6 [17], which will simultaneously exhibit good solvent and water resistance due to the intrinsic nature of PCD soft segments and PA hard segments. In addition, the chemical bonds between PCD soft segments and PA hard segments will prevent the formation of phase separation. Moreover, the thermodynamically immiscible PCD soft segments and PA hard segments is favor to the formation of microphase separation, which will enhance the performance of PCA.

In this study, novel poly(carbonate-*co*-amide) (PCA) block copolymers with polyamide6 (PA6) as hard segments, MDI as coupling agent and PCD as soft segments are prepared through reactive process. The employment of PCD as soft segments in polyamide elastomers through reactive processing is reported for the first time. The reactive processing technology will avoid environmental pollution generated by the organic solvent in the preparation process. The chemical structure, crystalline properties, mechanical properties, water resistance and thermal stability of as-prepared PCAs are extensively studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential scanning calorimetry (DSC), Dynamic mechanical analysis (DMA), tensile testing, water contact angle, water absorption and Thermal gravity analysis (TGA).

2. Experimental

2.1. Materials

4, 4′-Diphenylmethane diisocyanate (MDI) was provided by Yantai Wanhua polyurethane Co., Ltd. (Shandong, China). Polycarbonate diol (PCD, T5651: $M_w = 1000$ g/mol; T5652: $M_w = 2000$ g/mol) was obtained from Asahi Kasei Corporation (Japan). T5651 and T5652 were prepared by random copolymerization of 1,5-pentanediol and 1,6-hexanediol. The reagents above are used as received. α.ω-amino polyamide-6 (PA6) with Mw of 1000 g/mol was synthesized according to previous study [4].

2.2. Preparation of poly(carbonate-co-amide) (PCA)

PCD and MDI were putted into three necks flask equipped with thermometer and stirrer at a molar ratio of 1:2, and the prepolyurethane was obtained after 2.5 h.

PA6 powder was dried at 80 °C for 24 h under vacuum before blending with prepolyurethane above at a molar ratio of 1:1, and then the blend was fed into HAAKE Torque Rheometer (Thermo Scientific, America) at 70 rpm at 190 °C for 6 min. The as-prepared poly(carbonate-*co*-amide) block elastomers were dried in a vacuum oven at 80 °C and standby application. PCA-1 and PCA-2 represent the reaction product with T5651 and T5652 as soft segments, respectively. The detailed synthetic route is shown in Fig.1.