Polymer 42 (2001) 9859–9862

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Thermal behaviour of poly(acryloyloxybenzoic acid)/nylon 6 blends

A.V. Sesha Sainath[a,*], T. Inoue[b], K. Yonetake[b], K. Koyama[a]

[a]Venture Business Laboratory of Yamagata University, Yonezawa 992-8510, Japan
[b]Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan

Received 14 May 2001; received in revised form 19 July 2001; accepted 23 July 2001

Abstract

The thermal behaviour of poly(acryloyloxybenzoic acid) (PABA)/nylon 6 (PA6) blends were investigated by differential scanning calorimetry. Melting point (T_m) of PA6 depressed with increasing PABA content. When PABA content was larger than about 60 wt%, second endotherm was observed above the T_m (first endotherm). Wide angle X-ray diffraction analysis suggested that crystallinity of PA6 was decreased with increasing PABA content. The second endotherm could be assigned to the melting of PA6–PABA complex. © 2001 Published by Elsevier Science Ltd.

Keywords: Poly(acryloyloxybenzoic acid); Nylon 6; Thermal behaviour

1. Introduction

Miscible polymer blends have received considerable interest in the past several decades, offering property profiles of both academic and industrial interests. The importance of specific interactions in achieving miscibility in polymer blends includes hydrogen bonding interactions. The role of hydrogen bonds in determining the phase behaviour of polymer blends is fascinating from a number of different viewpoints. Many researchers have carried out the effect of hydrogen bonding on the misciblility of polymer [1,2]. Kwei et al. studied many counterpolymers which contain proton acceptor groups such as poly(vinyl acetate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(vinyl methyl ether), poly(2,6 dimethyl-1,4 phenylene oxide), bisphenol A polycarbonate, poly(styrene-co-acrylonitrile), poly(dimethyl siloxane), a crystallizable polyester, an amorphous polyamide and two amorphous aliphatic polyesters [3]. Some miscible polymer blends have been found to undergo phase separation at elevated temperatures known as the lower critical solution temperature (LCST) behaviour, and the LCST is known to be sensitive to the specific interactions [4–6]. The electron donor–acceptor complexes of poly(*N*-butyl-3-hydroxymethylcarbazolyl methacrylate) with a series of poly(ω-hydroxylalkyl-3,5-dinitrobezoyl methacrylate)s are stable at below 229°C but show a decomplexation endotherm at this temperature [7].

Polymer composed of ethylene and acrylic acid, as well as poly(acrylic acid) itself, can form miscible blends with nylon 6 (PA6) [8,9]. Interest in these materials is attributed to their properties as membranes for separation of small molecules, for example, water/ethanol. Styrene/acrylic acid copolymers containing up to 20 wt% of acrylic acid have been melt blended with PA6, nylon 66, nylon 11 and nylon 12 (PA12). A correlation was observed between the acrylic acid content and the miscibility that did not depend upon the amide content of nylon. Complete miscibility with nylons, PA6 through PA12, may be anticipated for the copolymer with an acrylic acid content of 20 wt%. Hydrogen bonding interactions between poly(ethyl oxazoline) and ethylene–methacrylic acid copolymer were studied by Lichkus et al. [10]. In this paper, we report the thermal behaviours of poly(acryloyloxybenzoic acid) (PABA)/PA6 blends, in which both carboxylic acid and ester groups in PABA are expected to interact with amide group of PA6, using differential scanning calorimetry and a wide angle X-ray diffraction analyses.

2. Experimental

2.1. Reagents

4-Hydroxybenzoic acid (HBA), sodium hydroxide (NaOH), 1,4-dioxane, *N*,*N*-dimethylformamide (DMF), formic acid, methanol and ethanol were purchased from

---

[*] Corresponding author. Tel.: +81-238-26-3484; fax: +81-238-26-3499.
E-mail address: avssainath@vbl.yamagata-u.ac.jp (A.V. Sesha Sainath).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00534-1

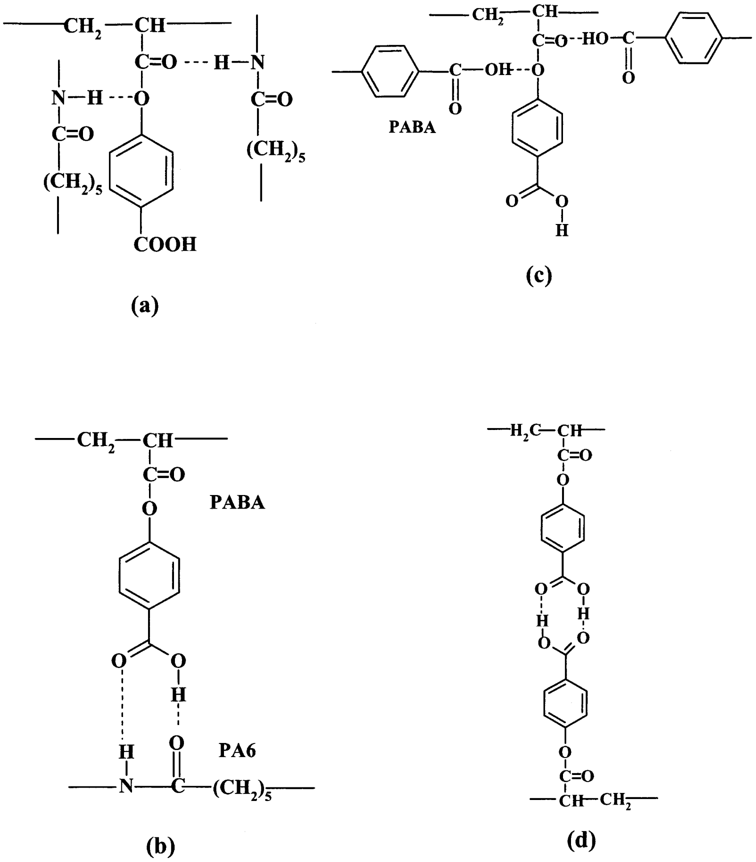

Fig. 1. Schematic diagram illustrating the possible interactions between PABA and PA6 and self-association of PABA.

Kanto Chemical Co., INC. Acryloyl chloride from Acrocs Organics and benzoyl peroxide from Aldrich were used. All the lab reagent grade materials used in this study were used as received. PA6 was obtained from Japan GE Plastics Co., Ltd.

2.2. Preparation of 4-acryloyloxybenzoic acid

To a well-stirred solution of HBA (13.14 g, 0.095 mol) and NaOH (7.7 g, 0.193 mol) in 50 ml of distilled water and 25 ml of dioxane was added 0.1 mol of acryloyl chloride, drop wise, at 8–12°C. After stirring at room temperature for 4 h, the reaction mixture was neutralized with dilute HCl solution. The solid ABA thus precipitated was filtered, washed with warm water, dilute HCl solution and water, successively, and recrystallized from ethanol. The yield of ABA was about 75%. The structure of ABA was analysed by FT-IR and ^{1}H NMR; FT-IR (KBr): 1743 cm^{-1} (ester C=O) and 1630 cm^{-1} (CH_2=CH–). ^{1}H NMR (DMSO-d_6): δ 6.2–6.65 (m, 3H, CH_2=CH–), and 8.1–7.3 ppm (m, 4H, ArH).

2.3. Preparation of poly(4-acryloyloxybenzoic acid)

ABA was polymerized as 2 M solution in DMF using benzoyl peroxide (1 wt% with respect to monomer) as an initiator at 70°C under argon atmosphere. The polymer was isolated after polymerization for 8 h by adding the reaction solution to excess of water, purified by reprecipitation from DMF solution into methanol/water mixture, and dried under vacuum. The yield of PABA was about 80%. The structure of the polymer was confirmed by FT-IR and ^{1}H NMR techniques. $M_w = 5.37 \times 10^3$; $M_w/M_n = 1.48$ from GPC in DMF.

2.4. Preparation of blends

The blends were prepared at weight ratios of 10/90, 15/85, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 (PABA/PA6). A typical procedure was as follows. PABA solution in DMF was added to a stirred solution of PA6 in formic acid. Exothermicity was observed at the early stage of mixing. Stirring was continued for 2 h at room temperature. Then, the solvent was evaporated at 50°C under vacuum. The samples were dried at 50°C under vacuum for one week. The resulting samples were stored in a desiccator.

2.5. Measurements

FT-IR spectra were measured on a Horiba FT-210 spectrophotometer at a resolution of 2 cm^{-1} for KBr specimens at room temperature and a minimum of 100 scans were signal averaged. ^{1}H NMR spectra were recorded on JEOL

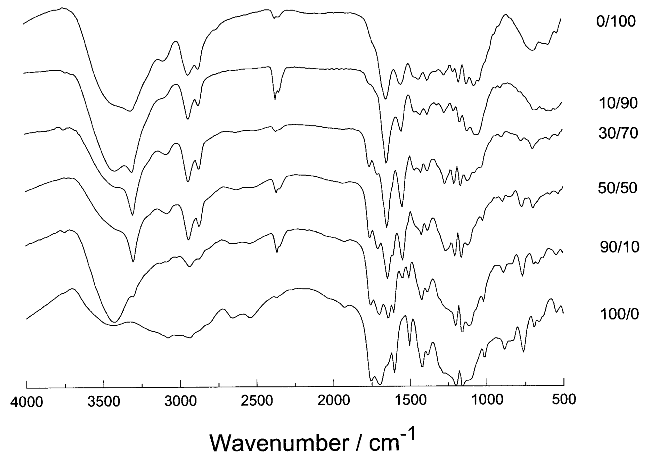

Fig. 2. FT-IR spectra of the PABA/PA6 blends.

EX 270 spectrometer. Thermal analyses were performed by a differential scanning calorimeter, Perkin–Elmer DSC7 at a heating rate of 10°C min^{-1} for under nitrogen. Typical procedures were as follows. First, the sample was heated from 10 to 150°C at 10°C min^{-1} and held at that temperature for 2 min. Then it was followed by rapid cooling to 10°C at about 100°C min^{-1} using ice/water mixture. Second, the sample was reheated to 280°C at 10°C min^{-1}. X-ray diffraction experiments were carried out by a RAD-rA diffractometer, Rigaku Denki Co. Ltd. Nickel-filtered CuKα radiation was employed. Wide-angle X-ray diffraction profiles were measured by a scintillation counter system with a 1.0 mm-diameter pinhole collimator and 1 × 1° receiving slit using a step scanning method (0.05° steps every 4 s).

3. Results and discussion

Fig. 1 shows the possible hydrogen bonding formations: intermolecular (a, b) and intramolecular (c, d). The FT-IR spectrum (Fig. 2) of PABA showed characteristic strong absorptions for free O–H stretching at 3440 cm^{-1}, hydrogen bonded O–H stretching at 3077 cm^{-1}, free C=O stretching centred at 1759 cm^{-1}, and hydrogen bonded C=O stretching centred at 1697 cm^{-1}, while the blends with PA6 showed that the free and hydrogen bonded C=O stretching peaks shifted to 1751 and 1705 cm^{-1}, respectively. These shifts should be caused by the interactions with N–H and O–H. The intensity of shifted hydrogen-bonded carbonyl stretching band increases with increasing PABA content. It indicates that interaction between PABA with PA6 is increasing with increasing PABA content. In PABA and its blends, the possible way of formation of free carbonyl groups are formed due to the formation of hydrogen bondings between hydroxyl with ester carbonyl and oxygen, in addition to free carboxylic acid group (Fig. 1).

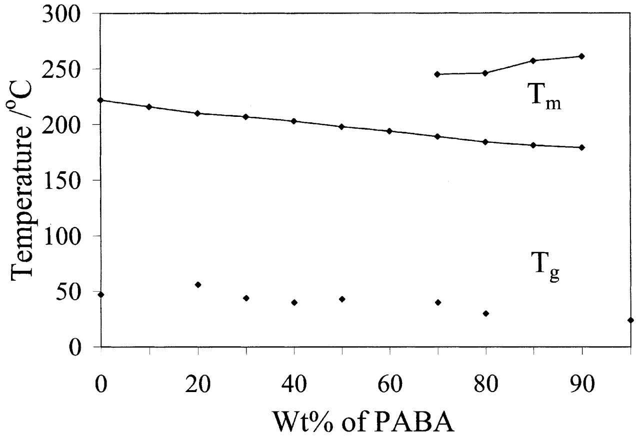

Fig. 3. T_g and T_m as a function of PABA content.

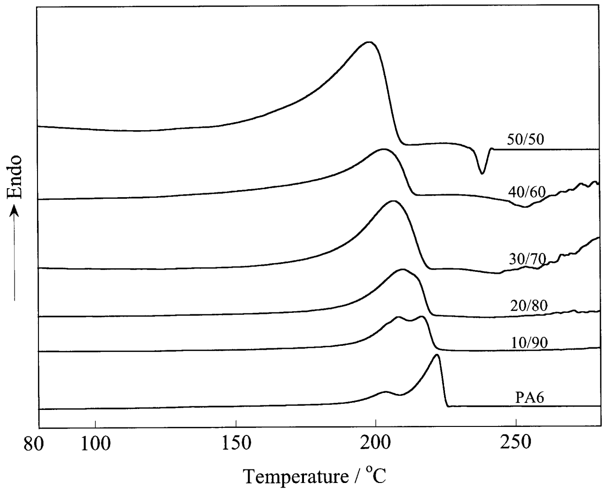

Fig. 4. DSC thermograms of PA6 and PA6-rich blends.

The glass transition temperatures (T_gs) and melt transition temperatures of PABA, PA6 and their blends are shown in Fig. 3. Figs. 4 and 5 show DSC thermograms. In blends, PA6 crystalline melting point depression is observed as compared to the pure PA6. Melting point depression increased with increasing PABA wt% in these polymer

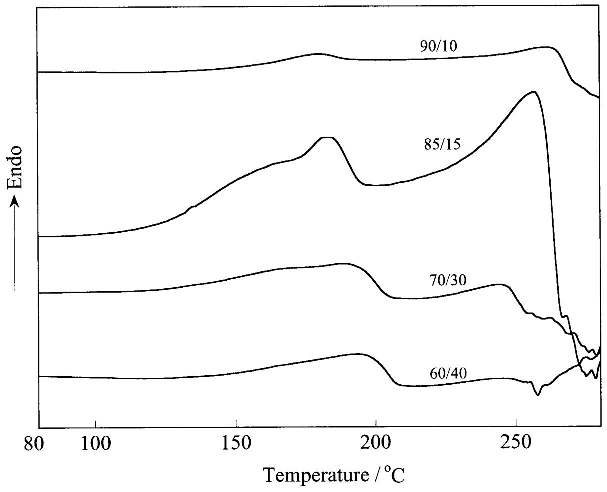

Fig. 5. DSC thermograms of PABA-rich blends.

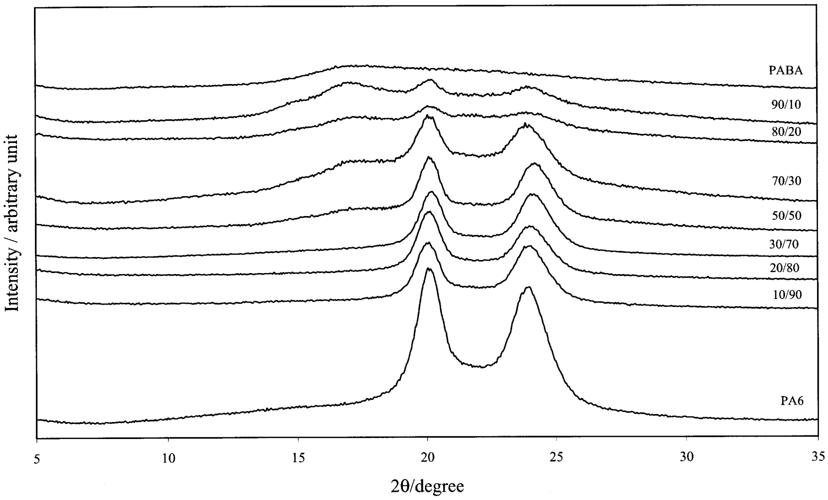

Fig. 6. WAXD profiles of PA6, PABA/PA6 blends and PABA.

blends. From 60 wt% of PABA systems onwards, two melting points (Fig. 5) were observed. First melting point can be assigned to PA6 crystallites and the second melting point could be assigned to the PABA–PA6 complex.

WAXD profiles of PA6, PABA and their blends are shown in Fig. 6. The WAXD profiles of PA6 indicated two crystalline peaks; in contrast, PABA exhibited amorphous nature. In the blends, the crystalline peaks decreased with increasing PABA content. However, the peaks positions did not change with PABA content. It implies that the structure of PA6 crystal does not vary in the blends. In PABA rich blends (PABA content ≥50 wt%), the third peak appeared at small angle. The intensity increased with increasing PABA content. It is clearly stronger than the amorphous halo of neat PABA. The third peak may be due to a stereo-regularity caused by the complex formation.

4. Conclusion

Blends of PABA with PA6 were prepared by solution blending. These blends showed single melting point up to 50/50 PABA/PA6 blends and afterwards, (from 60/40 PABA/PA6 onwards) showed two melting points. The low melting point was assigned to the PA6 crystalline melting while the higher one to PABA–PA6 complex melting. WAXD supported the presence of the complex phase.

References

[1] Ting SP, Pearce EM, Kwei TK. J Polym Sci Polym Lett Ed 1980; 18:201.
[2] Ting SP, Bulkin BJ, Pearce EM, Kwei TK. J Polym Sci Polym Chem Ed 1981;19:1451.
[3] Pearce EM, Kwei TK, Min BY. J Macromol Sci, Chem 1984;A21(8 & 9):181.
[4] Bank M, Leffingwell J, Thies C. J Polym Sci Polym Chem Ed 1972; 10:1097.
[5] Nishi T, Kwei TK. Polymer 1975;16:285.
[6] Kwei TK, Nishi T, Roberts RF. Macromolecules 1974;7:667.
[7] Rodriguez-Parada JM, Percec V. J Polym Sci Polym Chem Ed 1986; 24:579.
[8] Kuphal JA, Sperling LH, Robeson LM. J Appl Polym Sci 1991;42: 1525.
[9] Matzner M, Schober DL, Johnson RN, Robeson LM, McGrath JE. Permeability of plastic films and coatings. New York: Plenum, 1975 p. 125.
[10] Lichkus AM, Painter PC, Coleman MM. Macromolecules 1988;21: 2636.