Effects of Copolyester/Polycarbonate Blend Composition on the Thermal Diffusivity of Dye Transfer Printing

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ABSTRACT: The effect of the blend composition on the thermal diffusivity for blends of a poly(ethylene-*co*-cyclohexane 1,4-dimethanol terephthalate) (PETG) and a bisphenol-A polycarbonate (PC) that have been used as base films for a thermal dye transfer (TDT) printing system was examined. The inflection point in the thermal diffusivity measured by temperature wave analysis almost matched the inflection point of storage modulus measured by dynamic mechanical analysis. This result implied that the temperature dependence of thermal diffusivity related to the change in the microstructure of the PETG/PC blend. Furthermore, the correlation between the printing sensitivity and the thermal diffusivity at the actual thermal head temperature of TDT printing was found. The thermal diffusivity increased with increasing PC content, while the printing sensitivity decreased. The PETG/PC blend film suitable for the TDT printing base film could be obtained by adjusting the PC content in the blend. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 72–76, 2004

Key words: blends; polyesters; polycarbonates; thermal diffusivity; thermal dye transfer printing

INTRODUCTION

A thermal dye transfer (TDT) printing system is a color hard copy process that is capable of producing near photographic quality images. In this process, a thermal head is used to transfer a dye from a color ribbon onto a receiver paper, as illustrated schematically in Figure 1. It has been commercially used as video printers. A TDT printing sheet requires both good printing sensitivity and good heat resistance. Many patents and some papers concerned with the factors that determine printing sensitivities have been published.[1–3] One of the most important physical properties that influences the printing sensitivity is the thermal diffusivity of a base film. The dependence of printing sensitivity on the thermal diffusivity has been examined using the finite element prediction method.[4,5] From this prediction, greater decrease of thermal diffusivity is necessary to achieve better printing sensitivity.

In recent years, blends of poly(ethylene-*co*-cyclohexane 1,4-dimethanol terephthalate) (PETG) and polycarbonate (PC) have been used as the base film for a TDT printing sheet. PETG has a good processing property, but a low *Tg* and a low softening temperature. It has been attempted to improve the poor heat-resistance of PETG by blending it with PC.

It is well known that the thermal diffusivity of polymer blends depends upon the composition and the miscibility.[6–8] The miscibility can be assessed by the location of a peak top temperature of loss tangent (tanδ) measured by dynamic mechanical analysis (DMA), which is the most useful transition point in blend investigations.[9] The miscibility of PETG/PC blends was investigated by DMA in many reports.[10–14] However, the correlation between the thermal diffusivity and the blend composition of PETG/PC blends has not been examined yet.

In this study, the relationship between the blend composition and printing sensitivity was examined as a function of thermal diffusivity. First, the effects of blend composition on the dynamic viscoelasticity of PETG/PC blends and thermal diffusivity were investigated by DMA and "temperature wave analysis" (TWA) method, which was proposed by Hashimoto et al.[15–19] to measure the thermal diffusivity. And the correlation between the printing sensitivity and blend composition was discussed in the case of applying these blend polymers to base films of a TDT imaging system.

EXPERIMENTAL

Materials

PETG copolyester (Eastar PETG 6763, $\overline{Mn}$ = 26,000) was supplied by Eastman Chemical Company. It consists of cyclohexane dimethanol, ethylene glycol, and terephthalic acid in a molar ratio of approximately 1 /
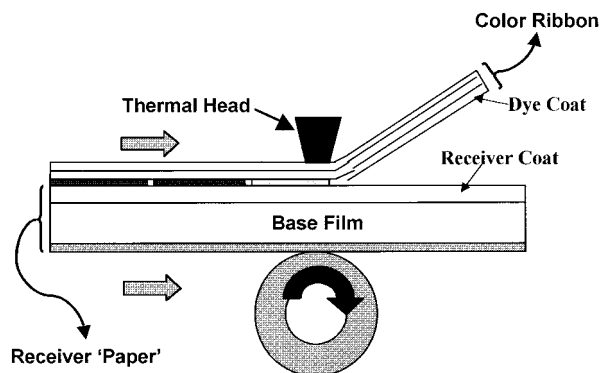
Figure 1 Schematic representation of thermal dye transfer imaging system.

2 / 3 according to the published information. Bisphenol-A PC ($\overline{Mn}$ = 17,300) was obtained from Sigma-Aldrich Co.

Specimen preparation

Polymer pellets were dried in a vacuum oven at 50°C for ca. 24 h. PETG and PC pellets were mixed in a mixing extruder (Imoto Machinery Co., Ltd.) at 270°C for 10 min to obtain desired composition blends. The extrudates were cut into small pieces and cooled. Films then were molded from these pieces by compression using a press apparatus (Toyo Seiki Seisakusho Co., Ltd.) at 270°C, 10 MPa for 3 min. Hot films were released to the atmosphere and quenched in cold water to form films with thickness of ~150 μm.

Dynamic mechanical analysis

DMA data were obtained at 1 Hz using a DMA 6100 mechanical spectrometer (Seiko Instruments Inc.). The static stress was 50 mN. The temperature was elevated from 0 to 180°C at 2°C/min. Specimen dimensions were 30 mm × 10 mm × 0.15 mm.

Thermal diffusivity measurements

The thermal diffusivity was measured by the TWA method developed by Hashimoto et al.[15]

The sample film was cut into a 7 mm × 12 mm piece. Gold was sputtered on both sides of the film to form thin layers. Each gold layer acts as a thermal heater and as a sensor for detecting the temperature wave signal. The temperature wave generated by the thermal heater diffuses across the sample in the direction of the thickness. The temperature wave signal at the other side was detected using a two-phase lock-in amplifier. The details of the thermal diffusivity measurements are described in Kurihara et al. [17].

The relationship between the frequency of the generated temperature wave and the phase delay of the signal at the other side is expressed by

$$\Delta\theta = -\sqrt{(\pi f/\alpha)}d - \pi/4 \qquad (1)$$

where $\Delta\theta$ is the phase delay, α is the thermal diffusivity, f is the frequency of temperature wave, d is the sample thickness, and $\pi/4$ is an instrumental constant.[15] From eq. (1) the thermal diffusivity can be obtained by measuring the phase delay of the temperature wave signal.

The measurements were made in the range from 30 to 200°C, at 0.4°C/min, 4 Hz, in the air atmosphere.

Printing sensitivity measurements

On to the respective sample film, the same receiver layer comprising an electron beam curable poly(urethane acrylate) resin and silicone oil was coated and cured by an electron beam radiation.[20] The printing sensitivity is influenced by the condition of the coated layer on the blend base film, depending on the composition of the used formation,[20] or irradiation dose. The same curing condition was employed in the receiving layer formation process.

The printing sensitivity was evaluated from the optical density (O.D.) of the printed image. A Machbeth RD-914 reflection densitometer was used for the O.D. measurement. A Nozaki Insatsu Shigyo Co., Ltd., NCP-300 was employed as the TDT imaging printer. All prints were made with original color ribbon setups.

RESULTS AND DISCUSSION

Relationship between thermal diffusivity and blend composition

The temperature dependence of dynamic viscoelasticity of PETG/PC blends is shown in Figure 2. PETG have a low Tg and a low softening temperature. The poor heat-resisting properties can be improved by increasing the PC content.

Two tanδ peaks were observed in all blend compositions, as shown in Figure 2. The two peaks in Figure 2 correspond to the PC-rich phase (higher Tg) and the PETG-rich phase (lower Tg), respectively. Since miscible polymer blends should exhibit a single Tg between the Tgs of pure components, these spectra imply a typical phase separation behavior of a polymer blend. Figure 3 illustrates the dependence of the peak temperatures of tanδ on blend composition. It is worthwhile to note that the higher Tgs are lower than the Tg of pure PC, while lower Tgs are almost the same as that of pure PETG. The higher Tg clearly increases with increasing PC content. It is clear that the PC-rich
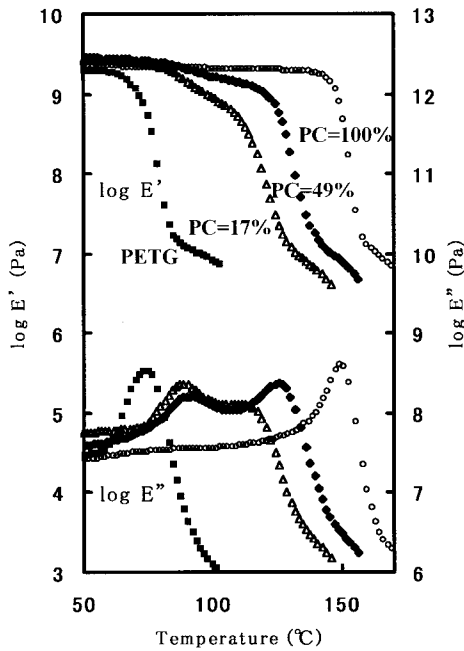
Figure 2 Temperature dependence of dynamic viscoelasticity for PETG/PC blend films at 1 Hz, 2°C/min. ■: PETG (PC = 0%); △: PC = 17%; ◆: PC = 49%; ○: PC = 100%.

Figure 4 Temperature dependence of thermal diffusivity for PETG/PC blend films at 4 Hz, 0.5°C/min.

phase is influenced by the PETG-rich phase. This phase separation behavior resembles the one reported by Samios and Kalfoglou.[14]

Figure 4 shows the temperature dependence of the thermal diffusivity of PETG/PC blend films. The thermal diffusivity increases with increasing PC content. The softening temperature of the blend also increases with increasing PC content at the same time, as shown in Figure 2.

Figure 4 also shows that the two inflection points of the thermal diffusivity were observed in the blend films. This tendency is similar to the temperature dependence of storage modulus (E′) in Figure 2. The two thermal diffusivitic transition points in Figure 4 cor-
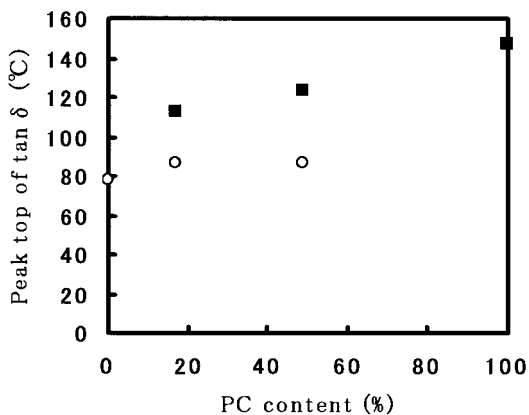
respond to the PC-rich phase (higher Tg_α) and the PETG-rich phase (lower Tg_α), the same as the tendency in Figure 2. Figure 5 presents the composition dependence of the thermal diffusivitic transition point in the blends. The higher Tg_αs increase with increasing PC content, while the lower Tg_αs are almost the same as the Tg_α of pure PETG. Therefore, analysis of the thermal diffusivitic transition point also confirms that the PETG/PC blends have the characteristics of phase separation blends.

As shown in Figure 6, the thermal diffusivitic transition point almost agrees with the viscoelastic transition point. This result implies that both transition phenomena reflect the same microstructural changes. Since the thermal diffusivity measured by the temperature wave signal in the direction of thickness correlates with E′ measured by the mechanical change in the direction of tension, these blend films are considered to be isotropic. The thermal diffusivity determined by TWA is a useful tool to probe the change in the microstructure in the blend the same as viscoelasticity determined by DMA.
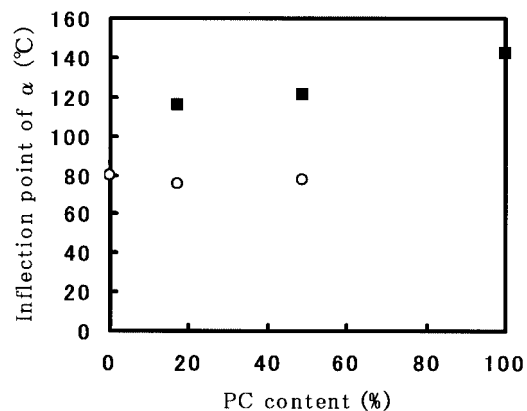

Figure 3 Composition dependence of viscoelastic transition for PETG/PC blend films. ■: higher Tg; ○: lower Tg.

Figure 5 Composition dependence of thermal diffusivitic transition for PETG/PC blend films. ■: higher Tg_α; ○: lower Tg_α.

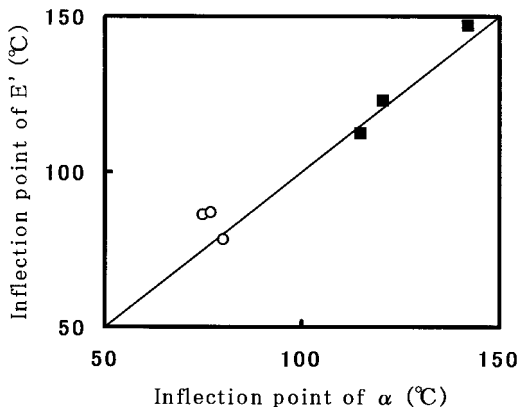**Figure 6** Relationship between viscoelastic transition and thermal diffusivitic transition for PETG/PC blend films. ■: higher Tg; ○: lower Tg.

Relationship between printing sensitivity and blend composition of a TDT base film

Figure 7 illustrates the relationship between the thermal diffusivity at 110°C and blend composition for PETG/PC blends. The actual temperature at a thermal head of the TDT imaging printer was estimated as 110°C. The thermal diffusivity of the blends tends to increase with increasing PC content in Figure 7. It is suggested that the thermal diffusivity can be controlled by the blend composition.

Thermal diffusivity is one of the most important physical properties that influence printing sensitivity for a base film of TDT printing. Figure 8(a) and (b) shows O.D. (printing sensitivity) as a function of the thermal diffusivity at 30 and 110°C, respectively. Some data of blends with white filler are included in both figures. TiO$_2$ fillers were mixed with PETG/PC blends in a mixing extruder. The influence of the filler on the printing sensitivity will be discussed later.

As shown in Figure 8(b), a good linear relationship seems to hold between the thermal diffusivity at the
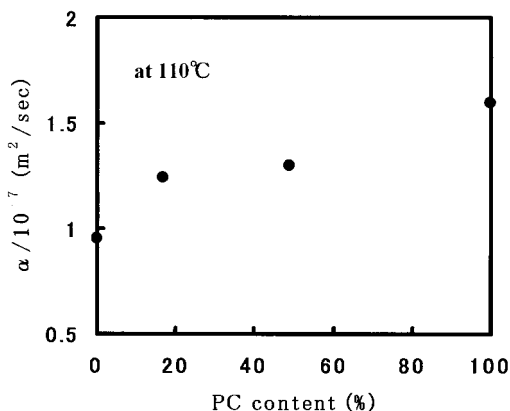

Figure 7 Thermal diffusivity as a function of blend composition for PETG/PC blend films.
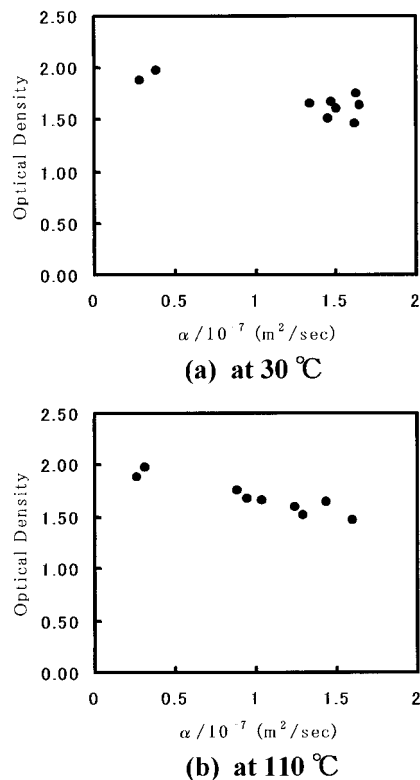

(a) at 30 ℃

(b) at 110 ℃

Figure 8 Printing sensitivity as a function of thermal diffusivity at (a) 30°C and (b) 110°C for PETG/PC blend films. Some data of blends with filler are included in figures.

thermal head temperature and printing sensitivity. However, the relationship is not recognized at 30°C [Fig. 8(a)]. As described in the preceding section, the dependence of the thermal diffusivity on temperature is governed by the microstructure in the blend composition. The difference between Figure 8(a) and (b) can be related to the difference of the temperature dependence of the transition in the blend. This result suggests that it is very important to measure the thermal diffusivity at the actual thermal head temperature to predict the printing sensitivity.

Figure 8(b) also shows that the printing sensitivity decreases with increasing thermal diffusivity at the thermal head temperature. Figures 7 and 8(b) imply that the printing sensitivity decreases with increasing PC content. Therefore, TDT printing prefers low PC content blends for a base film. The heat-resisting property of PETG can be improved by blending with PC, while printing sensitivity decreases. Suitable blend compositions exist for PETG/PC blend films from the point of TDT printing base.

It is necessary to control the blend composition and microstructure suitably, for TDT printing base films of PETG/PC blends. Although the poor heat-resistance of PETG can be improved by blending with PC, the PC content should be kept below 20% to maintain its good printing sensitivity.

CONCLUSION

The relationship between blends composition and printing sensitivity was examined as a function of thermal diffusivity to apply PETG/PC blends to TDT printing base films. The results are as follows:

1. Both the thermal diffusivitic transition behavior and the viscoelastic transition behavior reflect the same microstructural changes.
2. The printing sensitivity can be predicted by the thermal diffusivity at the actual thermal head temperature.
3. The PETG/PC blend film with both high softening temperature and good printing sensitivity can be obtained by adjusting the PC content suitably.

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