

The effect of cetyltrimethylammonium bromide on the coefficient of thermal expansion and optical transmittance of poly(ether sulfone) film

Nhat Tri Vo and Dukjoon Kim[†]

School of Chemical Engineering, Sunkyunkwan University, Suwon, Gyeonggi 16419, Korea

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Abstract—Cetyltrimethylammonium bromide (CTAB) was used as a stabilizing agent for PES films, and its effect on the coefficient of thermal expansion (CTE) and optical transmittance (OT) of PES films was investigated. The CTE of PES film decreased with increasing CTAB concentration up to 0.5 wt%, because of the improved intermolecular interaction between polymer chains via CTAB molecules. When 0.5 wt% of CTAB was added to the PES film, the CTE of polymer film decreased from 66 to 50 ppm/°C without noticeable reduction in OT. At such a low CTAB concentration range (<0.5 wt%), the glass transition temperature (T_g) and tensile strength increased with CTAB. At high CTAB concentration above 0.5 wt%, however, it had a negative effect on the properties of PES film - CTE increased but T_g and tensile strength decreased with it.

Keywords: OLED, Coefficient of Thermal Expansion, Optical Transmittance, Poly(ether sulfone), Cetyltrimethylammonium Bromide

INTRODUCTION

After the organic light emitting diode (OLED) was first reported by Tang and Van Slyke [1], it has gained much attention [2-5]. The typical OLED is composed of an organic layer between the cathode and anode deposited on a substrate. The substrate of OLED has often been made of glass, which is heavy and easily broken. In recent years, a flexible substrate has been requested by Guo et al. [6] and Salem et al. [7], as the bendable and rollable OLED displays are much more convenient [8], in many applications, such as lighting panels, electronic paper, mobile phones, and curved televisions [9]. Additionally, the flexible OLED display is light, thin, durable, and cost competitive by a continuous roll-to-roll processability [10].

Although flexible OLED displays have many applications, the flexible substrate is the biggest issue in their realization [11]. There are several types of available polymers for OLED substrate including polyethylene terephthalate (PET) and polyethylene naphthalene (PEN) [12]. These polymers have unique properties such as high transparency, good chemical and mechanical resistance, and high dimensional stability associated with low coefficient of thermal expansion (CTE), 15 ppm/°C and 13 ppm/°C for PET and PEN, respectively, from -55 to 85 °C [12]. However, as those special types of PET and PEN have some drawbacks in low glass transition temperature (T_g) and low cost competition, they cannot be used widely as flexible substrate. Another potential polymer to be used as flexible OLED substrate is polyether sulfone (PES) [13]. PES

has high OT (>89%), high T_g (about 220 °C), and excellent chemical and mechanical resistance with high cost competition. Nevertheless, the main drawback of PES is its high coefficient of thermal expansion (CTE) (54 ppm/°C in the temperature range from -55 to 85 °C). Therefore, to use PES as flexible substrate for OLED, reduction of the CTE is a prerequisite.

The common method to reduce the CTE of polymer is to use inorganic fillers [14-17]. The inorganic filler has a low CTE, and the interaction between polymer and inorganic filler possibly reduces the mobility of the polymer chain under thermal treatment. Inorganic filler also helps to decrease the free volume in the polymer matrix. Surfactants have also been used to aid enhancement of the CTE of the inorganic filler loaded polymers [18,19]. These surfactants can improve the intermolecular interaction between polymer chains, and decrease the free volume of the polymer matrix. CTAB is a low molecule surfactant that has a structure with positively charged head and aliphatic alkyl tail groups. The hydrophobic tail of CTAB can interact with the hydrophobic part of the polymer chain [20]. In the case of PES, the hydrophobic tail of CTAB can interact with the aromatic ring in PES backbone via hydrophobic-hydrophobic interaction. In addition, the sulfone group (O=S=O) of PES is a polar functional group that has negative charge on oxygen atom [21]. Therefore, the positive charge head of CTAB can possibly interact with the oxygen atom of the sulfone group. The interaction between CTAB and PES polymer chain might reduce the mobility of the PES polymer chain. In addition, CTAB is a low molecular weight organic surfactant; therefore, light scattering does not occur, and the CTAB molecules do not affect the transmittance properties of the PES film.

In this work, we added CTAB in the PES matrix to investigate its effect on the CTE and OT. Its effects on the thermal and mechanical properties were also studied.

[†]To whom correspondence should be addressed.

E-mail: djkim@skku.edu

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EXPERIMENTAL

1. Materials

Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich, USA. Dimethylacetamide (DMAc) was purchased from Samchun Pure Chemical Co. Ltd (Korea). Polyethersulfone (PES) was supplied by BASF Chemical Company (Germany).

2. Preparation of CTAB/PES Film

In a typical preparation, we first dissolved CTAB into 5 mL of DMAc under stirring at room temperature for 30 min. 1.4 g of PES was added into CTAB solution, and stirred at 50 °C for 6 h. Finally, we prepared the PES film with a Doctor Blade. To remove DMAc completely, PES films were dried in an oven at 60 °C for 12 h, at 120 °C for 12 h, and then at 170 °C for 24 h. In this film preparation process, we used different concentrations of CTAB from 0 to 2 wt%. All prepared films had a thickness of around 100 μm .

3. Characterization

We measured the CTE of PES films using a Seiko Exstar 6000 thermal analysis (TMA) machine. The samples were scanned from 30 to 150 °C, at the ramping rate of 5 °C/min. The absolute transmittance of these nanocomposite films was measured by an Agilent 8543 UV-Visible spectrophotometer (Agilent Technologies, California, USA). FTIR results were measured using the Thermo Scientific Nicolet iS 10 FT-IR Spectrometer (Thermo Fisher Scientific, USA). Tensile properties of the PES films were measured at room temperature using a universal tensile machine (UTM model 5565, Lloyd, Fareham, UK). The samples were cut into a 50 \times 10 (mm \times mm) sheet. Three measurements were carried out, and the average value was calculated. Finally, the T_g of PES films was measured using differential scanning calorimeters (DSC) model AutoQ20 of TA instruments at the ramping rate of 5 °C/min from 30 to 260 °C, and the data from the second run were used.

RESULTS AND DISCUSSION

1. Confirmation of Interaction between CTAB and PES

We prepared the CTAB/PES films with different concentration

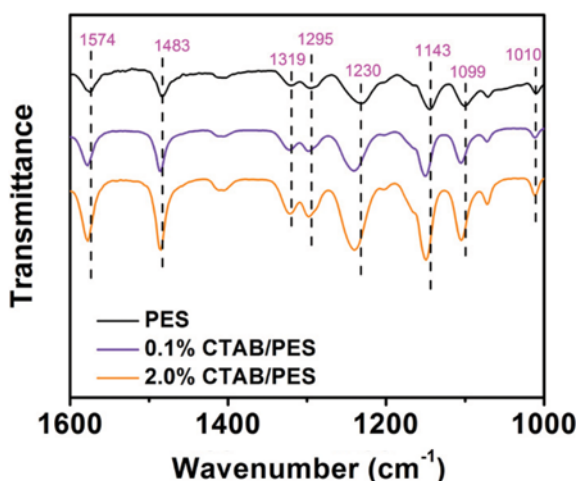


Fig. 1. FTIR spectra of PES, 0.1% CTAB/PES and 2.0% CTAB/PES films.

of CTAB, to investigate the effect of CTAB on the properties of CTAB/PES films. Fig. 1 shows FTIR spectra of the PES, 0.1% CTAB/PES, and 2.0% CTAB/PES films. In the spectrum of PES, the bands at 1,574 and 1,483 cm^{-1} are attributed to vibration of the aromatic ring on the backbone [22]. The IR bands at 1,319 and 1,295 cm^{-1} result from asymmetric O=S=O stretching, while the band at 1,143 cm^{-1} is from the symmetric O=S=O stretching of PES [23].

Interestingly, in the spectra of 0.1% and 2.0% CTAB/PES, the asymmetric O=S=O stretching bands are shifted to 1,322 and 1,297 cm^{-1} , respectively, and the symmetric O=S=O stretching is shifted to 1,149 cm^{-1} . The electrostatic interaction between sulfone group and CTAB head may increase the bond order in the sulfone group; therefore, the wave number was increased [24,25]. The FTIR shifts in the spectra of CTAB/PES films can confirm the presence of electrostatic interaction between the positively charged head of CTAB and the negatively charged oxygen atom of the sulfone group.

2. Effect of CTAB on the Optical Transmittance and CTE of PES Films

Fig. 2 shows the temperature dependence of the thermal expansion behavior of CTAB/PES films, while Table 1 shows the corresponding CTE values. The CTE of 0.1% CTAB/PES film decreases to 57 ppm/°C from that of the pristine PES film of 66 ppm/°C. By addition of 0.5 wt% of CTAB, the CTE of PES film decreased by 24.2%, as it decreased from 66 to 50 ppm/°C from 30 to 90 °C. Interestingly, when we added CTAB of more than 0.5 wt%, the result

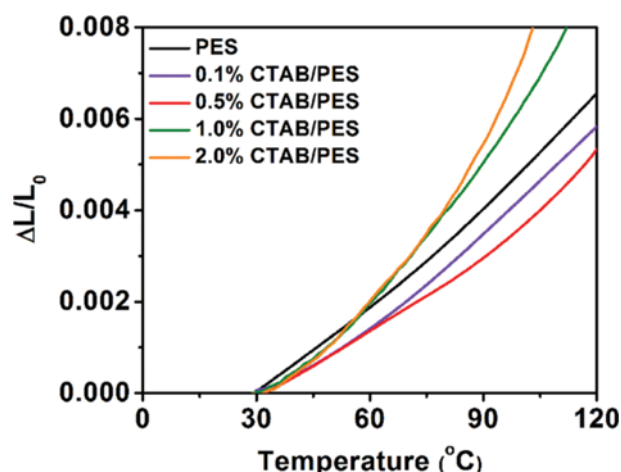


Fig. 2. Thermomechanical behavior of CTAB/PES films at different CTAB concentration. ΔL and L_0 are the displacement of length and the original specimen length, respectively.

Table 1. OT and CTE of CTAB/PES films at different CTAB concentration

Content of CTAB in PES (wt%)	OT (%) at 550 nm	CTE (30-90 °C) (ppm/°C)
0	87.8 \pm 0.2	66
0.1	87.5 \pm 0.1	57
0.5	87.9 \pm 0.1	50
1.0	86.4 \pm 0.3	84
2.0	85.7 \pm 0.3	90

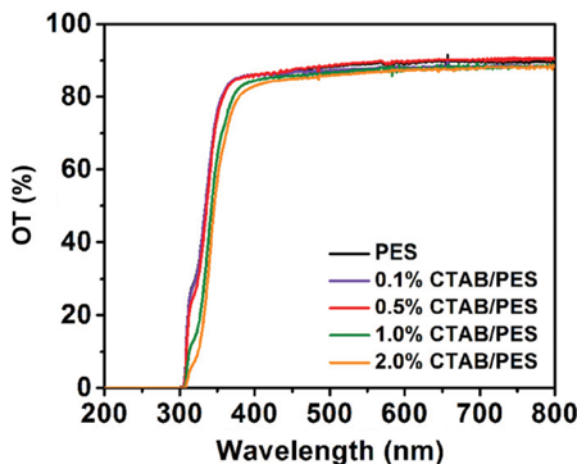


Fig. 3. OT of CTAB/PES films at different CTAB concentration.

was vice versa. When it was added up to 1 wt%, CTE increased to 84 ppm/°C; and if we further increased CTAB up to 2.0 wt%, the CTE of CTAB/PES film increased to 90 ppm/°C. We concluded that CTAB has a positive effect on the CTE at very low concentration level of up to 0.5 wt%, above which it has a negative effect on the CTE. We postulated from this interesting concentration effect that at low concentration of CTAB (<0.5 wt%), the CTAB molecules are well dispersed at a molecular level, which enhanced the interaction between PES molecules. As CTAB molecules filling up the free volume of PES matrix aid the interaction between polymer molecules, the packing densities of polymer matrix eventually increase. This positive effect on the CTE was observed when CTAB was introduced up to 0.5 wt%. However, when the CTAB amount was increased above 0.5 wt%, CTAB molecules aggregated to form micelles, or even larger clusters. Those solid CTAB clusters decrease the interactions between the polymer chains, and increase the free volume in the polymer matrix. Therefore, the CTEs of 1.0% and 2.0% CTAB/PES films were higher than the CTE of PES film.

Fig. 3 shows the variation of the OT of CTAB/PES films. As CTAB is small molecules dispersed in PES films, a small amount of CTAB added in PES did not significantly affect the OT of PES film. Table 1 shows that the slight decrease of OT of the film above 1% was caused by the formation of CTAB micelles or CTAB solid clusters in the PES film. As the CTAB solid cluster itself was highly transparent material, these CTAB solid clusters did not cause significant decrease in the OT of the PES film if the CTAB aggregate size is smaller than 50 nm, where light scattering is negligible.

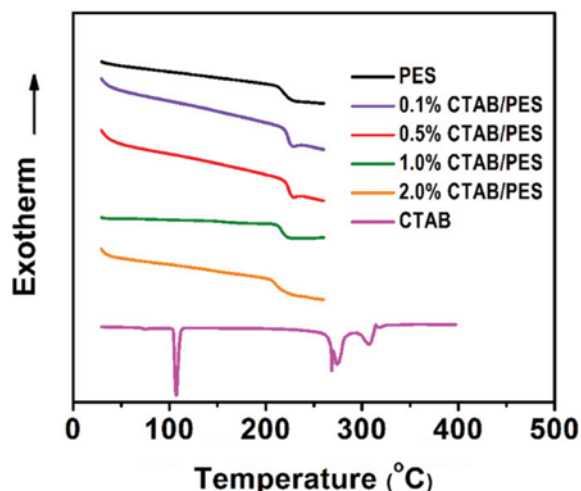


Fig. 4. DSC thermograms of CTAB/PES films at different CTAB concentration.

3. Effect of CTAB on the Thermal and Mechanical Properties of PES Films

To confirm the effect of molecular interaction between CTAB and PES, we measured the T_g of CTAB/PES films. Fig. 4 shows the DSC thermograms of CTAB/PES films at different CTAB concentrations. The T_g of PES film increased from 219.3 to 224.2 °C with increasing concentration of CTAB to 0.5 wt% (Fig. 4 and Table 2). However, when the concentration of CTAB was above 0.5 wt%, the T_g of CTAB/PES decreased with CTAB concentration, as the T_g of PES film reduced to 210.3 °C at 2.0 wt%, which is even lower than that of pristine PES. This interesting result is quite similar to the previous report by Leroux and Van Schalkwyk [26]. The higher T_g s of PES films at 0.1 and 0.5 wt% than the pristine PES film imply that CTAB plays an important role as an intermolecular enhancing agent for PES molecules via hydrophobic-hydrophobic and dipolar interactions bridged by them. As mentioned earlier, the hydrophobic interaction between the alkyl tail of CTAB and the aromatic ring on PES, and the electrostatic interaction between the polar head of CTAB and the oxygen atom in the sulfone group of PES restrict the mobility of PES films. When the CTAB concentration was higher than 0.5 wt%, the CTAB effect is quite different. At this CTAB concentration range, CTAB is not present in molecular structure, but present in aggregate or cluster structure. As CTAB has a melting temperature of around 105 °C, the solid clusters present in PES molecules at room temperature were feasibly melted to liquid, and thus acted as plasticizer at high temperatures near T_g .

Table 2. Glass transition temperature, tensile strength and tensile strain of CTAB/PES films

Content of CTAB in PES (wt%)	Glass transition (°C)	Modulus (MPa)	Tensile strength (MPa)	Tensile strain (%)
0	219.3	1416±85	75.1	8.93
0.1	222.1	1640±53	77.2	7.01
0.5	224.2	1867±71	84.1	6.21
1.0	215.1	1308±25	71.1	10.2
2.0	210.3	1235±38	59.6	11.0

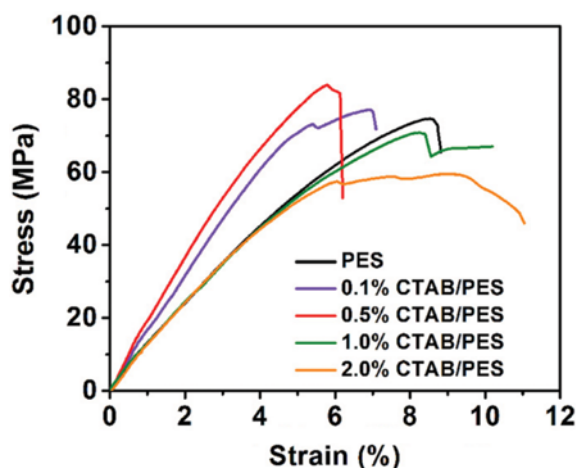


Fig. 5. Mechanical behavior of CTAB/PES films at different CTAB concentration.

($\sim 220^\circ\text{C}$) of PES. As this plasticization effect resulted in the reduction of T_g , the T_g s of PES films at 1.0 and 2.0 wt% CTAB concentration was even lower than that of the pristine PES film.

Additionally, the CTAB effect on the mechanical strength of PES film was investigated at varying CTAB concentration, and Fig. 5 shows the results. When 0.5 wt% CTAB was added, the tensile strength of PES film increased from 75.1 to 84.1 MPa, while the

tensile strain decreased from 8.93% to 6.21%. However, as we expected, at CTAB concentrations of 1.0 and 2.0 wt%, the tensile strength of PES film decreased to 71.1 and 59.6 MPa, respectively. Of course, at CTAB concentrations of 1.0 and 2.0 wt%, the corresponding tensile strains increased to 10.2% and 11.0%, respectively. This result can be explained by the same theory mentioned above. As we discussed, the interaction between CTAB and PES at 0.1% and 0.5% CTAB could enhance PES molecular interaction, and therefore increase the tensile strength but decrease the tensile strain of the films. However, at high concentration of CTAB (>0.5 wt% CTAB), the CTAB solid clusters cause mechanically weak defects in the film [27]. This defect structure in the polymer film decreases the tensile strength.

4. Theoretical Aspect of Interaction between CTAB Surfactant and PES

From the experimental results, we propose a model for the possible interaction between CTAB and PES molecules in the solution and the dry states of PES films prepared either at low concentration or high concentration of CTAB (Fig. 6). In the solution state of PES/CTAB in DMAc, the hydrophobic alkyl tail of CTAB surfactant moves toward the hydrophobic aromatic ring of PES molecule, but the polar head of CTAB moves away from it [28]. As the sulfone group of PES is a polar with negative charge on oxygen atom, there is electrostatic interaction with the positively charged head of CTAB. These hydrophobic and electrostatic interactions between PES and CTAB may increase the packing density of the

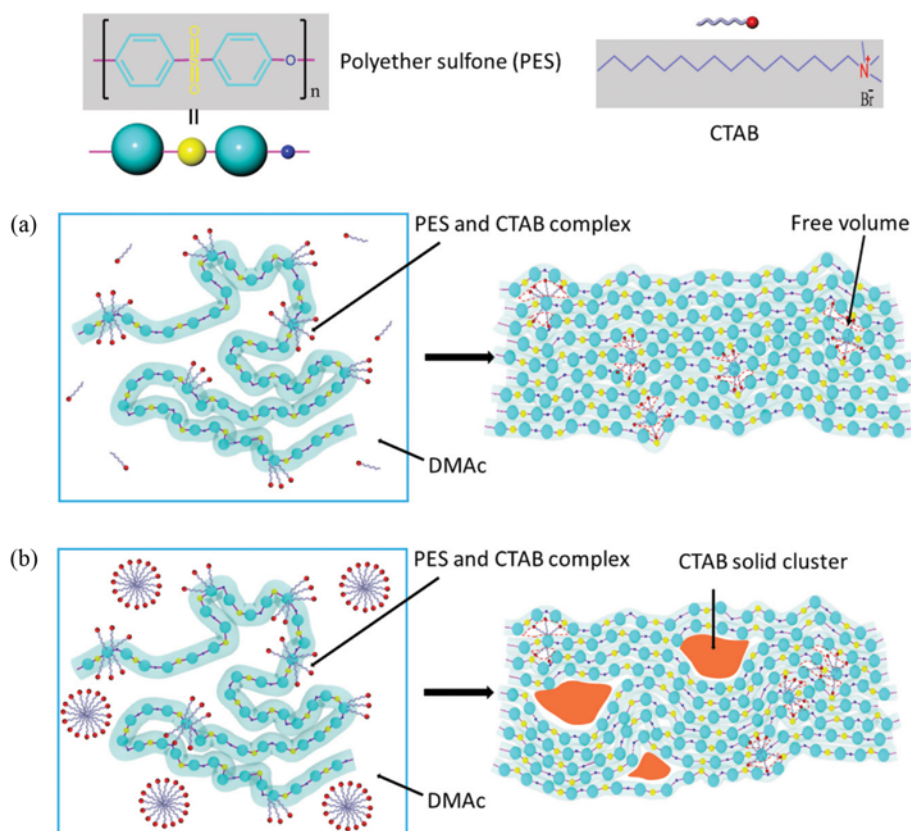


Fig. 6. The interaction model between CTAB and PES molecules in the solution and the dry film states at low concentration (a) and high concentration of CTAB (b).

polymer chain but decrease the free volume of polymer film.

However, at high concentration of the CTAB, the CTAB molecules may form free micellar structures composed of the alkyl chain core and the polar head shell in the solution state [29]. As those micelles are possibly aggregated in the films at further increased CTAB concentration, numerous CTAB micellar nanoclusters are formed and remain in the voids in the polymer structure in the dry state at room temperature. Those CTAB nanoclusters present in voids of dry polymer film eventually decrease the packing density of polymer chain. Those different states of CTAB molecules had different effects on the polymer film properties aforementioned.

CONCLUSIONS

A surfactant, CTAB, was added to PES films to investigate its effect on the CTE and OT of the film for OLED application. The FTIR results confirmed the hydrophobic interaction between the CTAB tail and the aromatic ring of PES and electrostatic interaction between the polar head of CTAB and the polar sulfone group of PES. At 0.1 and 0.5 wt% CTAB, the interaction between CTAB surfactant and PES decreased the CTE of PES film from 66 to 57 and 50 ppm/°C. Furthermore, the glass transition and tensile strength of 0.1% and 0.5% CTAB/PES were also higher than those of the pristine PES film. However, when CTAB concentration was higher than 0.5 wt%, the formation of free micelles in the solution resulted in the formation of CTAB solid clusters in the PES film at room temperature. Therefore, at 1.0 and 2.0 wt% of CTAB, the CTE of PES film increased to 84 and 90 ppm/°C. This CTAB concentration effect was also clearly observed in the thermal and mechanical properties of PES films. While the T_g and tensile strength increased with CTAB concentration up to 0.5 wt%, those decreased with CTAB concentration when it was above it.

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