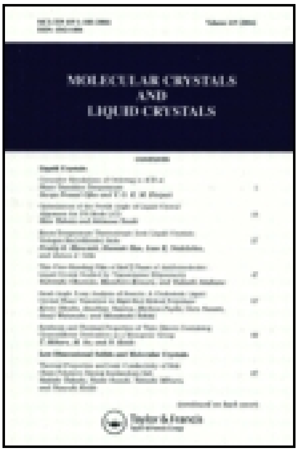

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Effects of Solvents on ITO Cracks in Ultrasonic Cleaning of ITO-Coated Flexible Substrates for Polymer Solar Cells

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We report an experimental optimization of the cleaning process in the fabrication of flexible polymer solar cells using an indium tin oxide (ITO) coated poly(ethylene naphthalate) (PEN) substrate. The effects of the solubility parameters of the cleaning solvents on the occurrence of ITO cracks have been systematically investigated. The experimental results showed that the ITO cracks caused during the ultrasonic cleaning process were mainly affected by differences between the solubility parameters of the solvent and that of the PEN substrate, not by direct interaction between the solvent and the ITO layer. Our results provide a simple method for reducing ITO cracks during wet cleaning processes by selecting solvents with solubility parameters which differ significantly from those of the flexible substrates.

Keywords: flexible substrate; cleaning solvents; ITO crack; solubility parameter

Introduction

Organic polymer solar cells have attracted much attention as promising candidates for the next generation of solar cells because of their various advantages such as inexpensive, light-weight, flexible, large area and renewable energy conversion devices [1,2]. The power conversion efficiency (PCE) of polymer solar cells has been greatly improved by the introduction of donor–acceptor bulk hetero junction (BHJ) structures, with PCEs of

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about 5% being achieved for single junction cells based on a poly(3-hexylthiophene):1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61} (P3HT:PCBM) blend [3–5]. There is still the potential to increase PCEs to above 10% by using low band gap materials and/or tandem cell structures [1,6,7]. Until now, most research has focused on improving the performance of cells based on ITO-coated glass substrates except for some cases.

For the commercialization of polymer solar cells to succeed, it will be necessary not only to improve their low PCEs and short life times, but also to produce large-area flexible modules, which is one of the potential advantages in organic-based solar cells compared to inorganic solar cells [8]. Flexible polymer solar cell technology requires flexible substrates. There are at present three choices for flexible substrates, which include plastics, thin glasses, and thin metal foils. A number of issues such as process temperature limitations, optical properties, thermal properties, and oxygen/water permeation properties need to be considered in the production of flexible polymer solar cells; a plastic substrate with an ITO electrode, as a result, has the greatest potential for achieving fully flexible devices. It is generally accepted that poly(ethylene terephthalate) (PET) and PEN, which are biaxially oriented semicrystalline films, have better thermal properties, mechanical properties, and solvent stability than amorphous films such as polycarbonate (PC), and poly(ether sulfone) (PES) [9].

Representative examples of flexible polymer solar cells have been demonstrated by Na et al. (ITO-free polymer solar cells on PET/modified polymer anode) [8], Al-Ibrahim et al. (normal flexible polymer solar cells on PET/ITO) [10], Hau et al. (inverted flexible polymer solar cells on a plastic substrate/ITO) [11], and Zhou et al. (ITO-free polymer solar cells on PET/bilayer polymer anode) [12]. These studies were carried out using plastic substrates with ITO deposited through a patterned metal shadow mask, using plastic substrates without an ITO patterning process, or using ITO-free substrates.

When flexible polymer solar cells are fabricated on ITO-coated plastic substrates, a wide range of solvents and chemicals for the cleaning and patterning processes can potentially be used. Some solvents can cause severe defects, such as ITO cracking, during ultrasonic cleaning processes, but little research has been done to identify the properties of plastic substrates which result in interaction with solvents to cause ITO cracks.

In this study, we investigate the effects of cleaning solvents on the occurrence of ITO cracks during ultrasonic cleaning processes, and discuss the interaction between the PEN/ITO substrate and the solvents in terms of the differences between the solubility parameters of the cleaning solvents and that of the substrate.

Experimental

Solvent Stability of ITO-Coated Flexible Substrates

A PEN substrate with an ITO layer (300 nm, 15 Ω/sq.) (PEN/ITO), used for flexible polymer solar cells, was purchased from Peccell Technologies, Inc., Yokohama, Japan. We investigated the solvent stability of the PEN/ITO substrate by ultrasonication of the substrate in various solvents for about 15 min. The solvent stability was evaluated from the formation of ITO cracks and the transmittance properties.

Measurements

Surface cracks on the ITO layer were observed by optical microscopy, and the transmittance was measured with a UV-Vis spectrometer (Lambda 750, PerkinElmer, Waltham, MA, USA). Current–voltage (*I*–*V*) measurements were performed using a Keithley model 2400

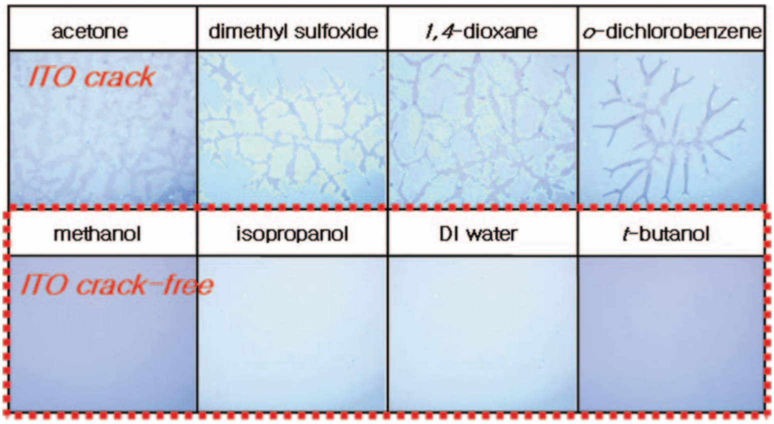


Figure 1. Optical microscopy images of ITO crack during solvent testing.

source meter (Keithley Instruments, Inc., Cleveland, OH, USA) with a two-probe distance of 3 cm, and the average resistance was calculated from the slope of the *I*–*V* data. All measurements were carried out under ambient conditions at room temperature.

Results and Discussion

As far as we know, ITO glass is cleaned by sequential sonication in acetone, deionized water (DI water), and isopropanol (IPA) to remove organic dust or other contaminants before the coating process of photo-active materials to make polymer solar cells. In our experiments, sonication in some solvents caused severe cracks in the ITO layer, as shown in Figure 1.

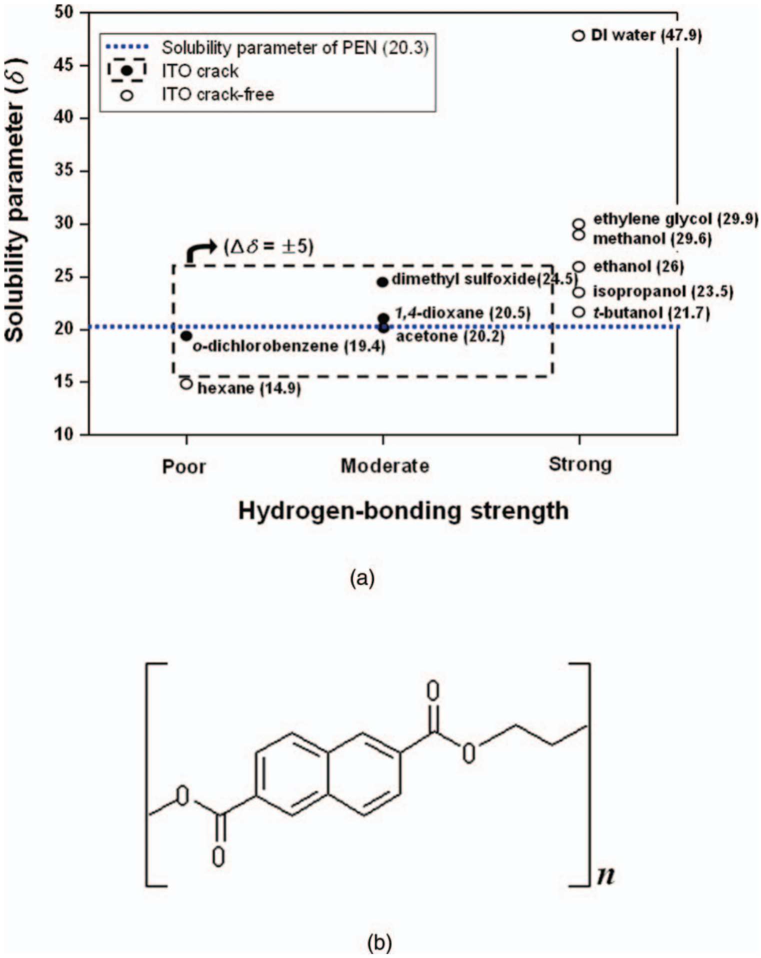
This weak solvent stability of ITO-coated plastic substrates is generally thought to be the result of the low deposition density of the ITO layer, and of poor adhesion between the polymer substrate and the thin ITO layer as a result of the relatively lower glass transition temperature (T_g, 120°C in the case of PEN) of the polymer substrate and the ITO deposition temperature being lower than that for deposition on a glass substrate. Moreover, the solvents which cause ITO cracking, such as acetone, have a much stronger chemical potential than those of methanol, ethanol, isopropanol, etc.

To investigate the interaction between the PEN/ITO substrate and the solvents, we examined ITO crack formation during sonication with 11 different solvents for 15 min. As shown in Figure 2(a), ITO cracks appeared only in solvents having both poor or moderate hydrogen-bonding strengths and a small difference between their solubility parameters and that of PEN ($\Delta\delta = |\delta_{\mathrm{PEN}} - \delta_{\mathrm{solvent}}|$).

The thermodynamic criteria of solubility are based on the free energy of mixing ΔG_{M} [13]. By definition $\Delta G_{\mathrm{M}} = \Delta H_{\mathrm{M}} - T\Delta S_{\mathrm{M}}$, where ΔH_{M} is the enthalpy of mixing, T is the temperature, and ΔS_{M} is the entropy of mixing. Two substances are mutually soluble if ΔG_{M} is negative. As ΔS_{M} is generally positive, there is a certain limiting positive value of ΔH_{M} below which dissolution is possible.

According to Hildebrand and Hansen [14,15], the enthalpy of mixing can be approximately calculated by the following equation:

$$\Delta h_{\mathrm{M}} = \varphi_1\varphi_2(\delta_1 - \delta_2)^2 = \varphi_1\varphi_2[(\delta_{\mathrm{d1}} - \delta_{\mathrm{d2}})^2 + (\delta_{\mathrm{p1}} - \delta_{\mathrm{p2}})^2 + (\delta_{\mathrm{h1}} - \delta_{\mathrm{h2}})^2]$$



(a)

(b)

Figure 2. (a) Relationship between ITO crack properties and solvents, according to solubility parameters [(J cm^{-3})$^{1/2}$] and hydrogen-bonding strengths. The figures in brackets denote solubility parameters from references 14 and 15, and that of PEN from reference 16. (b) Chemical structure of PEN.

where Δh_M is the enthalpy of mixing per unit volume, ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, δ_1 and δ_2 are the solubility parameters of components 1 and 2, and δ_d, δ_p, and δ_h are the solubility parameter components due to dispersion forces (van der Waals or London), permanent dipole interactions, and hydrogen bonds, respectively.

In a polymer–solvent system, if the difference between the solubility parameters is small, the polymer can swell in the solvent system. There are, however, some exceptions; if one of the substances involved contains strongly polar groups or hydrogen bridges, dissolution does not occur, even for $\delta_1 \approx \delta_2$. This is in accordance with the general rule that chemical and structural similarities favor solubility [13,14]. In our case, PEN has no strong hydrogen bridges, as shown by the chemical structure (see Figure 2b), thus

ITO cracks did not appear in strongly hydrogen-bonded solvents, even when the difference between the solubility parameters was small, for example, isopropanol, *t*-butanol, or ethanol.

In order to determine the dominant factor in ITO crack formation, we prepared three PEN/ITO samples. In the first sample, the PEN side was protected by a polyimide film (the ITO side was open, sample 1), in the second sample, the ITO side was protected (the PEN side was open, sample 2), and, in the third, there was no protection (both sides were open, sample 3). After sonication in acetone for 15 min, severe ITO cracks appeared in samples

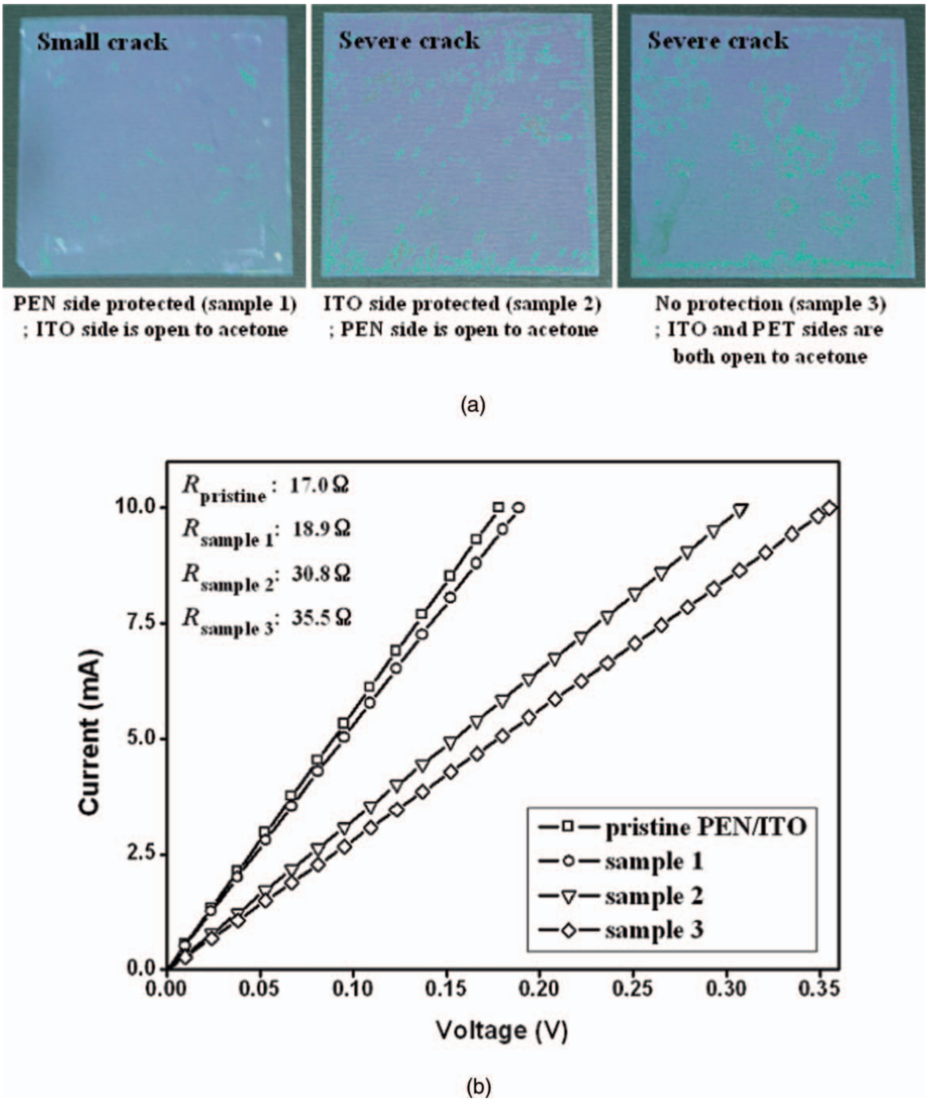


Figure 3. (a) Photographs of ITO cracks for three samples sonicated in acetone for 15 min. The differences among the three samples are noted below the photographs. (b) *I*–*V* graph and average resistances of three samples and a pristine substrate measured using an *I*–*V* meter with a two-probe distance of 3 cm.

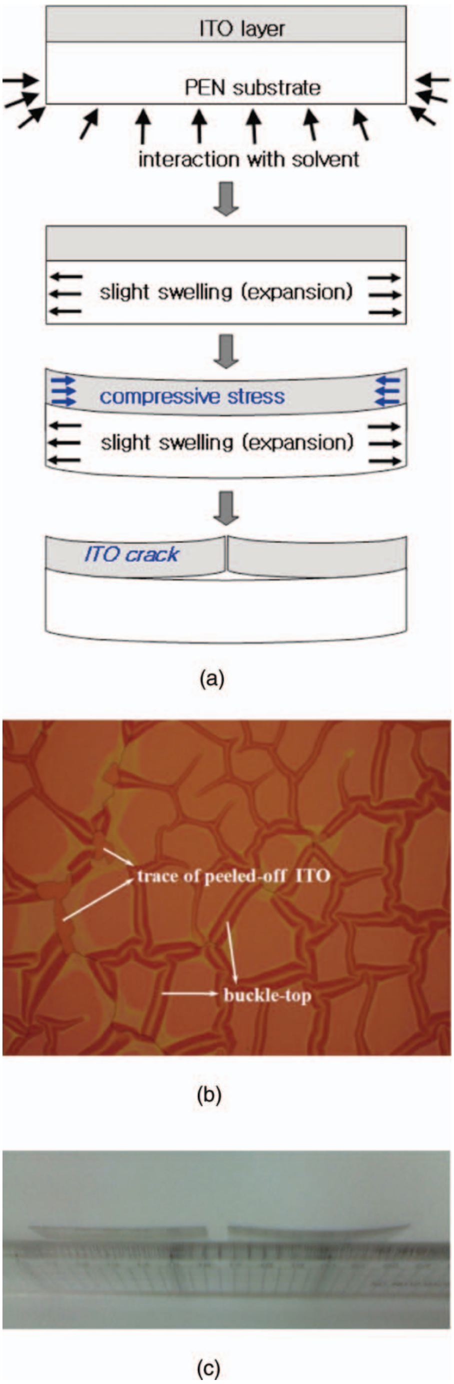


Figure 4. (a) A proposed schematic mechanism of ITO crack formation as a result of interaction between the plastic substrate and the solvent. (b) Optical microscopy image of ITO crack pattern (C) Photographs of stress-induced curvatures before (left) and after (right) ultrasonic cleaning of a PEN/ITO substrate (sample 3) in acetone (ITO layers are coated on the top side of the substrates).

2 and 3, but sample 1 had only a small crack, even although the ITO in sample 1 interacted directly with the acetone (see Figure 3a). Figure 3(b) shows the degree of ITO cracking, confirmed by the average resistance using the *I–V* meter with a two-probe distance of 3 cm. The trend in the average resistance for the three samples corresponded to that of the ITO crack images shown in Figure 3(a).

As a result, we can assume that if there was marginal swelling in the PEN substrate through interaction with a solvent, the ITO layer on the PEN substrate might be stressed and cracked as illustrated in Figure 4(a). Our crack image in Figure 4(b) shows a typical buckle-type crack with protruding buckle-top which is similar to the image in other literature [16]. This buckle-type crack is attributed to compressive stress in the ITO layer. When a thin brittle film such as oxide compounds adheres to a high elongation (or expansion) substrate, the thin film suffers a compressive stress as the underlying substrate expands due to its low expansion property [17,18]. In addition, as we showed in Figure 3(a), the solvent strongly interacts with the PEN substrate not with the ITO layer, thus the ITO suffers compressive stress as the PEN expands. Other indirect evidence for our proposed mechanism of stress-induced ITO cracking shown in Figure 4(a) is that we can see the stress-induced curvature in sample 3 after sonication in acetone (see Figure 4c). These crack-formation phenomena will be more severe in ITO substrates with large internal residual stresses between the ITO layer and the flexible substrate, especially in cases where the ITO layer thickness or the ITO deposition temperature has been increased in order to enhance the conductivity of the ITO layer.

We concluded that the dominant factor in ITO crack formation was the interaction between the solvent and the PEN substrate, based on their solubility parameters rather than on direct interaction between the ITO layer and the solvent. When treating a plastic/ITO substrate with solvents or chemicals, we suggest that it would be useful to introduce a solvent barrier layer ("hardcoat") on the back of the base film. This is already being applied to some commercially available amorphous-type substrates such as PES [9]; however,

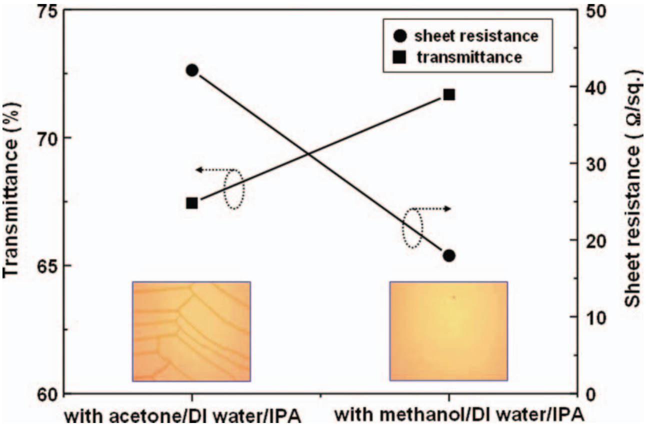


Figure 5. Transmittance and sheet resistance of PEN/ITO substrates cleaned in acetone/DI water/IPA or methanol/DI water/IPA. The inset pictures show an optical microscopy image of an ITO surface.

according to our experiments, it is more useful to adjust the type of solvent by considering its solubility parameters.

On the basis of our results, we changed the cleaning procedure to sequential sonication in methanol, deionized water, and isopropanol, each for 15 min. By applying our modified cleaning procedure, crack-free ITO could be obtained, as shown in the right-hand inset in Figure 5, without reducing the conductivity and transmittance of the PEN/ITO.

Conclusions

We report here an optimized cleaning process for plastic substrates for use in flexible polymer solar cells. We suggest that the ITO cracks which appeared during solvent-based ultrasonic cleaning processes might be affected by the difference between the solubility parameters of the solvents and that of the PEN substrate. Crack formation might also be partly the result of low density and poor adhesion properties of the ITO layer on the PEN substrate.

It is obvious that these factors are more critical in the fabrication of flexible polymer solar cells of large area because of the formation of large amounts of inherent residual stresses and defects during ITO deposition.

Acknowledgment

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