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We fabricated PEN substrates coated with photo-polymerizable acrylate layer to produce three dimensional network structures of barrier for the application of flexible display. Components for the photo-curable resin composed of multi-functionallized acrylates were synthesized, successfully. It is found that the photo-polymerized organic layer on PEN substrate could enhance surface properties of the pristine substrate. The surface roughness and optical transparency were measured to evaluate and optimize the organic/inorganic treatment on PEN substrate for application of flexible devices.

Keywords: barrier layer; flexible display; photo-polymerizable organic layer; plastic substrate; polyethylene napthalate substrate

INTRODUCTION

Recently, flexible displays using plastic substrates have attracted considerable attention for the use of ubiquitous environment due to

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their special features such as light-weight, flexibility, portability, and durability to compare with that of conventional displays. For flexible devices, typical glass substrates should be replaced with plastic or other bendable substrates to realize flexible and paper like devices [1]. Furthermore, the plastic substrate could offer the possibility of using low-cost device process such as roll-to-roll processing or printing technology which could reduce the cost for the device manufacturing [2,3].

However, plastic substrates for the flexible display must be equipped with many properties such as thermal resistance, transparency, coefficient of thermal expansion (CTE), hygroscopic expansion, retardation, surface roughness, permeation of O_2 and H_2O, resistance against chemicals and solvents used in display technology [4–6]. Moreover, plastic substrates must possess thermal stability at temperatures above 180°C, because they are exposed to such temperatures to deposit an indium tin oxide (ITO) electrode with a low electrical resistance and an optical clarity. To provide improved reliability at high operating temperatures, the UV-curable coating process with multi-functionallized acrylates, silicon containing compounds, or Novolac epoxy resins has been considered [3].

On the other hand, polyethylene napthalate (PEN) is one of prominent candidate for the plastic substrate for the application of flexible display which has high optical transparency, low CTE and low water absorption ratio to compare with that of other polymer substrate such as polyethylene terephthalate or polycarbonate.

In this paper, we fabricated plastic substrates coated with photo-polymerized acrylate layer and/or inorganic barrier layer to improve stability of moisture impermeability and surface roughness. Three or four functionalized photo-polymerizable acrylate monomers were selected and synthesized to fabricate the three-dimensional network structure on the pristine substrate which could improve the thermal stability and reduce water permeability.

EXPERIMENTAL

Synthesis of Curable Resins

(1) Pentaerythritol-tetra-acrylate, TM4A

A stirred mixture of pentaerythritol (1.00 g, 7.35 mmol), acryloyl chloride (3.2 g, 33.51 mmol), and triethylamine (3.4 g, 33.66 mmol) in THF (50 mL) was stirred for 3 h under N_2 atmosphere. The solution was then cooled, and the mixture was extracted twice with chloroform. The organic layers were washed with water. Removal of volatiles

under reduced pressure left a residue that was purified by flash chromatography (silica, CH_3Cl (70%)/hexane (30%), Rf 0.75), Yield: 50%, ^1H NMR ($CDCl_3$); δ 6.42 (d, 4 H, J = 17.1 Hz), δ 6.12 (dd, 4 H, J_1 = 11.1 Hz, J_2 = 17.1 Hz), δ 5.89 (d, 4 H, J = 10.2 Hz), 4.30 (s, 8 H).

(2) Pentaerythritol Tetratosylate

A mixture of pentaerythritol (5 g, 36.76 mmol) and p-toluenesulfonyl chloride (34.9 g, 183.8 mmol) in pyridine (100 ml) was stirred for 48 hours under N_2 atmosphere. The resulting white precipitate was filtered and washed with methanol. The solid was recrystallized from benzene to afford pure pentaerythritol tetratosylate (24.0 g, 31.98 mmol, 87% yield) as white crystals: mp 155°C. ^1H NMR (300 MHz, $CDCl_3$); 7.68 (d, 8 H, J = 8.7 Hz), 7.36 (d, 8 H, J = 8.7 Hz), 3.81 (s, 8 H), 2.47 (s, 12 H), IR (KBr) 3047, 2959, 2926, 1599, 1468, 1366, 1296, 1181, 1096, 976, 835, 666, 608 cm^{-1}.

(3) Tetra[(4-formylphenoxy)methyl]methane

A stirred mixture of pentaerythrityl tetratosylate (4.00 g, 5.31 mmol), 4-hydroxybezaldehyde (3.3 g, 26.5 mmol), and NaOH (1.06 g, 26.5 mmol) in DMF (20 ml) was heated at reflux for 24 h under an inert N_2 atmosphere. The solution was then cooled, and the mixture was extracted twice with methylene chloride. The organic layers were combined, washed with water and dried over $MgSO_4$ and crystallized from benzene/hexane; mp 180°C, yield: 65%, ^1H NMR (300 MHz,$CDCl_3$); δ 9.89 (s, 4 H), δ 7.84 (d, 8 H, J = 8.1 Hz), 7.05 (d, 8 H, J = 8.1 Hz), 4.49 (s, 8 H), IR (KBr) 3067, 2944, 2830, 2805, 2728, 1688,1599, 1578, 1508, 1318, 1244, 1215, 1159, 1055, 1036, 870, 835, 683, 618 cm^{-1}.

(4) TA4A

A stirred mixture of tetra[(4-formylphenoxy)methyl]methane (1.00 g, 1.81 mmol), methyl-triphenyl-phosphonium iodide (3.3 g, 8.15 mmol), and potassium tert-butoxide (1.1 g, 9.05 mmol) in dried THF (30 ml) was stirred for 6 h under an inert atmosphere of Ar gas. The solution was then cooled, water was added, and the mixture was extracted twice with chloroform. The organic layers were combined, washed with water. Removal of volatiles under reduced pressure left a residue that was purified by flash chromatography (silica, CH3Cl (70%)/hexane (30%), Rf 0.80), yield: 78%, ^1H NMR (300 MHz, $CDCl_3$), δ 7.31 (d, 8 H, J = 8.4 Hz), 6.87 (d, 8 H, J = 8.4 Hz), 6.64 (dd, 4 H, J_1 = 17.4 Hz, J_2 = 11.1 Hz), 5.59 (d, 4 H, 17.4 Hz), 5.12 (d, 4 H, 11.1 Hz), 4.35 (s, 8 H).

Preparation of Curable Resins

The photo-polymerizable resin were prepared by adding 3 wt% of diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide and 2-hydroxy-2-methyl-propiophenone mixture (50/50 wt%) as a photoinitiator into pentaerythritol triacrylate or pentaerythritol tetra-acrylate as a multi-functionallized monomer.

Coating and Irradiation Process

Thin and uniform film of resin on PEN film was prepared with the solvent casting method [6]. Then, the PEN substrate coated with curable resin were put in the UV irradiation apparatus and were irradiated for 30 min. The UV light source used for irradiation process is a lamp ($80\,W/cm^2$), which emits light in the near UV (characteristic wavelength, $340 \sim 360$ nm). The distance between samples and UV lamp was about 2 cm. The thickness of the cured film is 25 μm.

Measurements

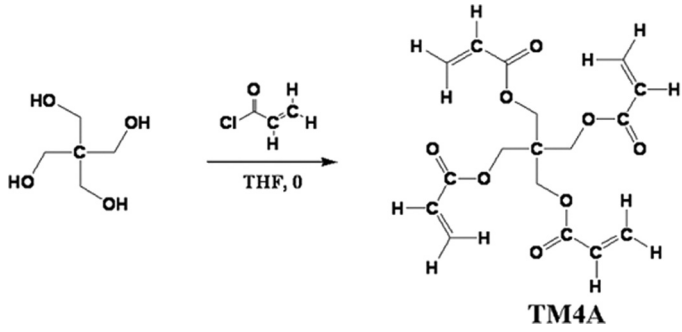
^{1}H-NMR and FT-IR spectra of synthesized compounds were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. UV-visible absorption spectra were obtained from Shimadzu UV-2100.

RESULTS AND DISCUSSION

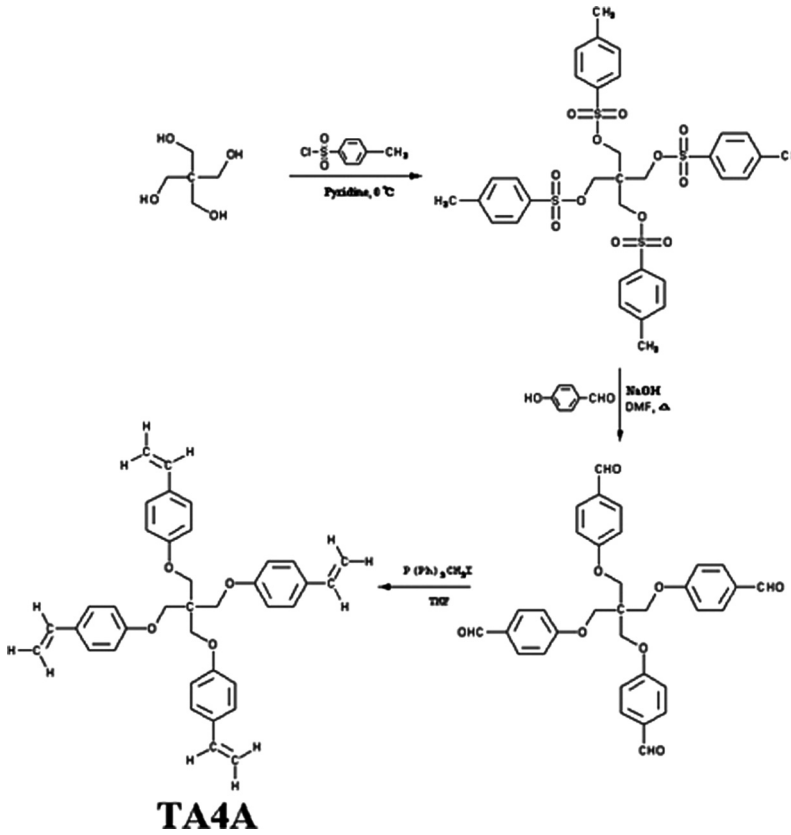
Synthsis of Multi-Functionallized Acrylates for the UV-Curable Resins

UV-curable resins are widely used for adhesives, inks and coating materials because of their advanced characteristics such as fast curing speed, conservation of energy, high efficiency and less pollution [7]. We designed and synthesized multi-functionalized acrylates as shown in Schemes 1 and 2 to prepare the UV-curable resins for the application of flexible substrates. Tetra-acrylated TM4A was synthesized from pentaerythritol and acryloyl chloride with moderate yield. In the case of TA4A containing aromatic moieties with tetra-acrylates, p-toluenesulfonyl chloride was used to produce intermediate for the target material.

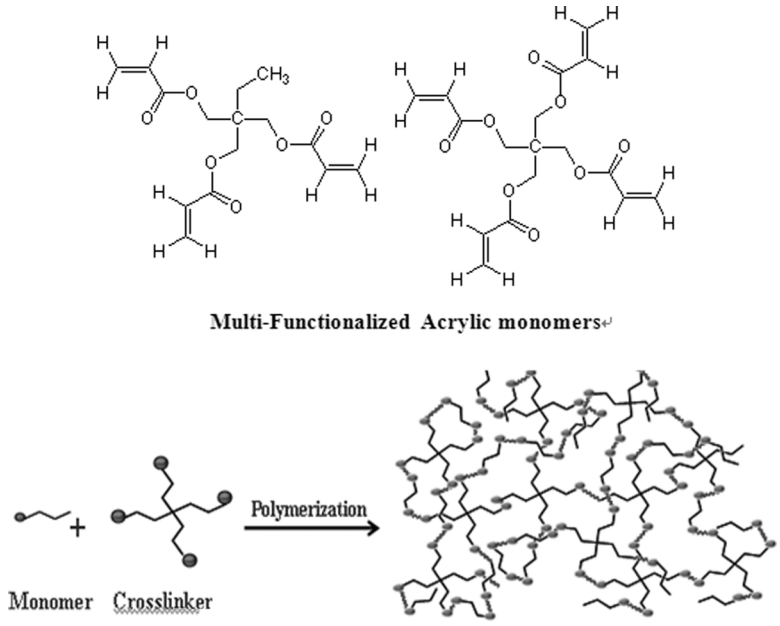
The chemical structures of the curable resin used in this study and three dimensional network of polymerized substrate were shown in Scheme 3, respectively. The UV-curable resins are prepared with



SCHEME 1 The synthetic procedure for multi-functionallized acrylate, TM4A for UV-curable resin.



SCHEME 2 The synthetic procedure for multi-functionallized acrylate, TA4A for UV-curable resin.



SCHEME 3 The chemical structures of the curable acrylates used in this study and three dimensional network of polymerized substrate.

mixtures of proper ratio of acrylates to control density and viscosity of resultant resins. The three dimensional network structure of resultant photo-cured resin could affect the transparency and thermal properties in the coated film.

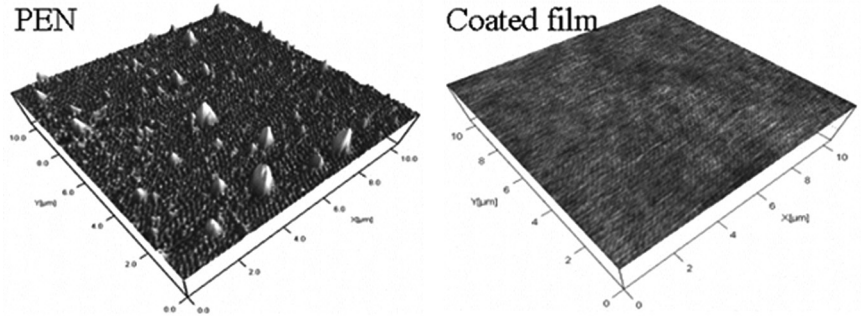


FIGURE 1 Surface roughness observation with AFM images over 30 micron square areas of base PEN film (left), and UV-cured PEN film (right).

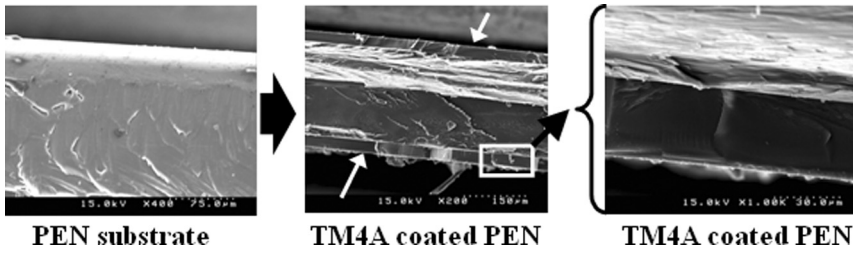


FIGURE 2 SEM image of the base PEN film and the delaminated acrylate resin coated on the both side of PEN base film.

We used the free radical type of photo-initiators such as diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide and 2-hydroxy-2-methyl-propiophenone mixture that could initiate cure to form a cross-linked network polymer as shown in Scheme 3.

Coating Resin for Flexible Substrate

We used the solvent casting method to coat UV-curable resins on the flexible substrate such as PEN film. Figure 1 shows the AFM image of the surface roughness of each substrates coated with different ratio of acrylates. Instead of base PEN substrate showed hole like defects of several 5 nm depth, the roughness of the UV-cured PEN substrate

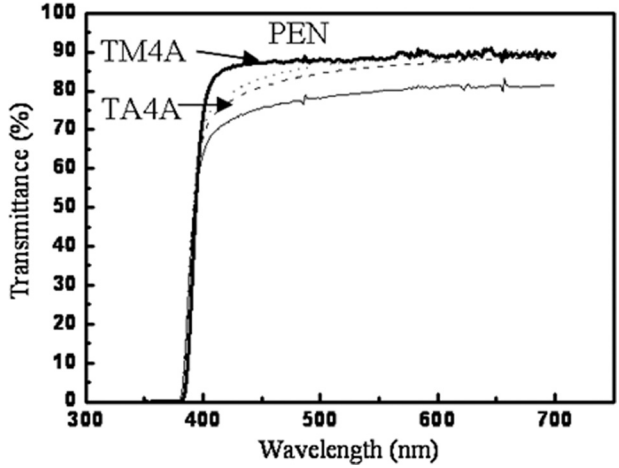
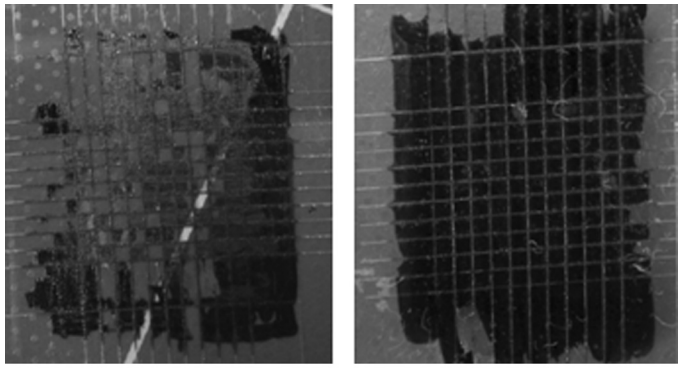


FIGURE 3 Light transmittances of coated PEN films with TM4A, TA4A and pristine PEN films.



(A) (B)

FIGURE 4 Grid adhesion test for the pristine PEN substrate (A) and coated PEN films with TM4A.

much improved which has an rms roughness of less than 3 nm as shown in Figure 1.

SEM image of the base PEN film and the delaminated acrylate resin coated on the both side of PEN base film were shown in Figure 2.

To utilize the coated film to display substrate, the film should be transparent in visible resion of wavelength. We measured the optical transparency in wavelength of 300 nm to 760 nm for the coated film which was compared with that of pristine PEN film as shown in Figure 3. In the case of TM4A resin, it showed more than 87% transparency in all range of visible wavelength that is almost same with that of the pristine PEN film which is enough to use it as a display substrate. However, the transparency of TA4A coated PEN film was decreased in 400–500 nm wavelength due to absorption property of benzosulfonyl group in TA4A. The grid adhesion test for the coated substrates was conducted with the treatment in 40°C, 90% RH for 24 hr [4], the result are shown in Figure 4. On the grids, the number of sections remaining without damage when the adhesive tape is removed is counted. The TM4A coated PEN film showed a good adhesion property (100/100) to compare with that of pristine PEN substrate.

CONCLUSIONS

We synthesized multi-functionallized acrylates to prepare photocurable resin which improved the surface properties of the plastic substrates of the flexible devices such as display and electro-optic

devises. We fabricated PEN substrates composed of sanwich-layered structure by using the photo-polymerizable acrylate resins. We found that the surface roughness, optical transparency and adhesion property of coated film were improved to compare with that of PEN base film which could contribute to the practical use of a flexible substrate. Further studies for the photo-polymerizable acrylates resins to evaluate barrier coating performance on plastic substrate are in progress. Also, the inorganic barrier coating is in progress to improve the permeation properties of O_2 and H_2O.

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