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Photo-thermal dual curing of acrylic anchor resins for screen printing

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ABSTRACT

Photo-thermal dual curing system was devised and applied to screen printing technology. New formulation of acrylic anchor resins contains a base polymer, which consists of hydrophilic units and solvent-absorbing units. As crosslinkers, multifunctional acrylates were employed. The acrylic anchor resins coated on poly(ethylene terephthalate) films were effectively cured by simultaneous photo-irradiation and baking below 80 °C. Printing resolution was strongly affected by the formulation of the acrylic anchor resins.

An 8-μm feature size silver circuit was successfully printed without defect on a poly(ethylene terephthalate) film having the acrylic anchor layer.

1. Introduction

Photo-thermal dual curing system [1–12] has been extensively investigated because of their wide applications, especially in the field of photosensitive materials which did not satisfy the demand of sensitivity and mechanical strength by only single exposure, especially to opaque materials. The photo-thermal dual curing system was achieved by the combination of photo-induced reaction and thermally induced reaction with different reaction mechanism [1–7]. Photo-induced radical polymerization was widely used due to high reactivity [1–11]. As thermal reactions, crosslinking of epoxy [1] and metal ions [2], ring opening polymerization of epoxy [3–5] and benzoxazine [6], and cyclotrimerization of cyanates [7] were reported. On the other hand, reactivity of photopolymerization can be enhanced by the assist of heat treatment [8–12]. The approach is quite effective to establish the system with high sensitivity [10]. Conversely, thermal curing reaction can be enhanced by the assist of photo-irradiation. Thus, the photo-thermal dual curing system offers benign conditions of curing required in the area of flexible electronics which contain thermoplastics such as poly(ethylene terephthalate) (PET) as a substrate.

Flexible electronics were fabricated by ink-jet [13–15] and screen-printing [16–19]. Especially, the fabrication of conductive circuits [14,15,17,18] or conductive layers [13,20] is very important as a component of flexible electronics. Thus, the effort to fabricate high-resolution circuits has been put with an aid of functional coatings such as poly(vinyl alcohol) [13], poly(acrylic acid) [14], and poly(4-hydroxystyrene) [17]. In practical use, it is desirable that the coating (anchor) layer is crosslinked to improve solvent resistance for subsequent fabrication process on the substrate. Thus, application of photo-thermal dual curing system is one of the candidates to enhance solvent resistance with increased productivity. However, to the best of our knowledge, there is no report on the fabrication of anchor layers by using photo-thermal dual curing system.

In this work, photo-thermal dual curing of acrylic anchor layer, subsequent screen printing, and fabrication of Ag circuit was carried out as shown in Fig. 1. We developed novel acrylic anchor resins composed of the mixture of multifunctional acrylates and base polymers which consist of hydrophilic units and solvent-absorbing units. Photo-thermal dual curing system was developed to accomplish curing of the anchor resin with benign conditions. Printing resolution was studied by screen printing using a high-resolution screen plate reported previously [18,19]. Printing resolution and surface free energies on the cured anchor resins were investigated in terms of the formulations and curing conditions of the anchor resins.

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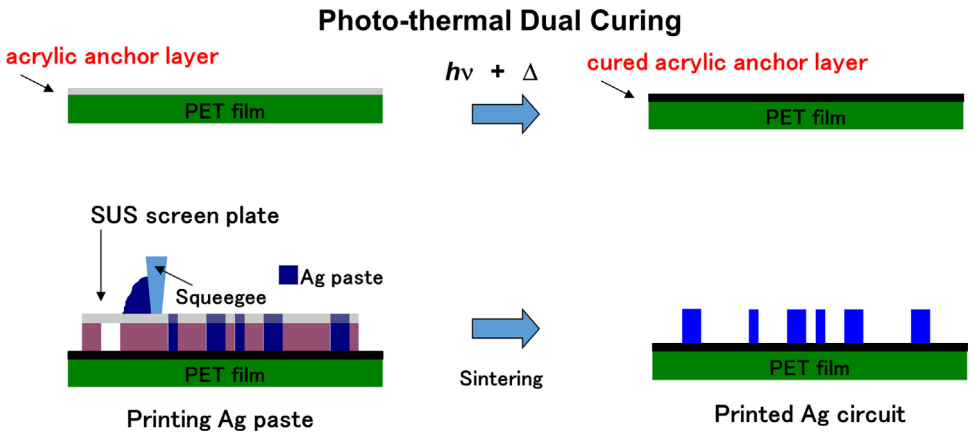

Fig. 1. Schematic illustration of photo-thermal dual curing of acrylic anchor layer, subsequent screen printing, and fabrication of Ag circuit.

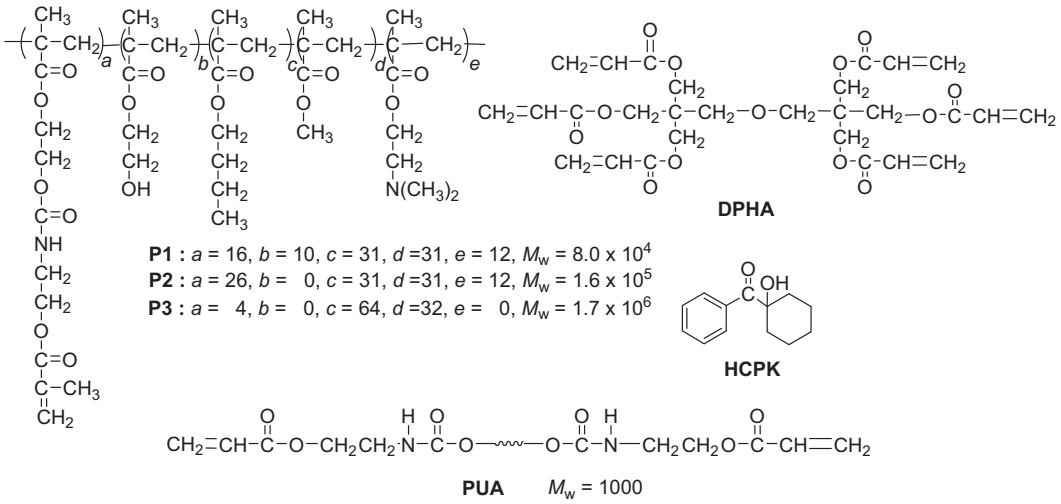

Fig. 2. Chemical structures of reagents used.

2. Experimental

2.1. Materials

Chemical structures of reagents used are shown in Fig. 2. Copolymers of 2-*N*-(2-methacryloxyethyl)aminocarbonyloxyethyl methacrylate, 2-hydroxyethyl methacrylate, *n*-butyl methacrylate, methyl methacrylate, and 2-*N*,*N*-dimethylaminoethyl methacrylate **P1** (product name: KV-2902), **P2** (product name: KV-2909), **P3** (product name: KV-2911), and crosslinkers dipentaerythritol hexaacrylate (DPHA, purity: >99%) and polyurethane diacrylate **PUA** (product name: UA-1282BK) were supplied from Shin-Nakamura Chemical Co., Ltd. A photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCPK, purity: >98%) and a thermal initiator 2,2′-azobis(isobutyronitrile) (AIBN, purity: >98%) were purchased from Tokyo Chemical Industries Co., Ltd.

2.2. Dual curing

Photo-thermal dual curing was performed as follows: methyl isobutyl ketone solution containing polymers, crosslinkers, and a photoinitiator (total content of the polymers, crosslinkers, and the photoinitiator: 20–24 wt%) was spin-coated on a silicon wafer. The film (thickness: about 0.5 μm) was irradiated using a xenon lamp (Asahi Spectra MAX-301, 300 W) with a 365 nm band-pass filter. During the irradiation, the film was baked using a conventional hot plate. The intensity of the light was measured with an Orc Light Measure UV-M02. UV–vis spectra were taken on a Shimadzu UV-2400 PC. FT-IR measurements of degree of polymerization were carried out using a Jasco FT-IR410 and by measuring the band intensities at 1630 cm^{-1} ascribed to C=C stretching of acrylates. The deviation for obtained conversions was less than 5%. Surface free energy of the film was determined using a contact angle meter DM-401s (Kyowa Interface Science Co., Ltd) using diiodomethane, 1-bromonaphthalene, and water as probes. The deviation for obtained contact angles was lower than 2°. Kitazaki–Hata equations [21] were applied to the calculations. The Kitazaki–Hata theory divides the surface free energy into dispersion, polar and hydrogen-bond components.

2.3. Screen printing

Evaluation of screen printing was carried out as follows: Acrylic anchor resins were coated on poly(ethylene terephthalate) (PET) films (Cosmoshine A4100, 125 μm, Toyobo Co., Ltd.) by bar-coating from solutions of methyl isobutyl ketone solution containing polymers, crosslinkers, and a photoinitiator (total content of the polymers, crosslinkers, and the photoinitiator: 20–24 wt%). The coated PET sheets (thickness: about 0.5 μm) were irradiated using a LED lamp which emitted a 365-nm light (CCS Inc. HLDL-50UV365-FN, 1.2 W). During the irradiation, the film was baked using a conventional hot plate. Screen printing was carried out using a

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