

UV-Activated Surface Modification of Photo-Cleavage Polymer for Contact Printing Applications

Edward K L Chan¹, Cheng Yang², Matthew M F Yuen¹

¹Department of Mechanical Engineering, The Hong Kong University of Science and Technology

²Department of Chemistry, The Hong Kong University of Science and Technology

Clear Water Bay, Kowloon, Hong Kong

edwardc@ust.hk, yangch@ust.hk, meymf@ust.hk, Tel: (852) 23588814

Abstract

Polymer electronics is an emerging technology for the last decade. For cost-efficient mass production and for thin, flexible polymer electronic systems, large area patterning processes may be an interesting option as an economic production method and will potentially play an important role in polymer electronics manufacturing. High resolution patterning methods for defining the separation between electrodes in electronic devices are important in manufacturing. The control of surface wettability during contact printing is an interesting approach because of its wide variety of applications. Stimuli-responsive surfaces make it possible to control the wettability of the surface and have been demonstrated by various methods, including UV light-irradiation.

Herein, a new strategy was demonstrated using free radical initiator to induce mold release between PDMS mold and the resins under UV irradiation. For example, by applying a thin layer of benzoyl peroxide (BPO) on PDMS surface, an increase of contact angle is achieved after UV irradiation. This method can be used as a transfer mechanism from mold to substrate. It was noticed that sufficient time of BPO deposition for the PDMS mold surface treatment is required for this strategy. Optimum concentration of BPO and suitable solvent system are concerns in the effectiveness of surface treatment. From this study, some preliminary insight in studying the controlling factors for the UV activation of free radicals on PDMS surface was shown. It can be shown that the molecular structure, polarity of materials, UV sensitivity of the free radical initiators, and solvent used, have direct effect on the efficiency of the wettability change under the UV irradiation. By knowing the controlling factors of UV assisted stimuli responses, printing can be improved and be applied in many other cases.

Introduction

Polymers are widely used in electronics as passive materials. For example, there are photoresist for etching and soldering, dielectrics, boards, materials for encapsulating, under-filler and coating, electrically and thermally conductive adhesives for electronic interconnecting. There are two major ways to lower the cost of electronics devices; firstly increasing the packaging efficiency of the ICs and secondly increasing the cost effectiveness by using volume production processes [1]. For a cost-efficient mass production and particularly for thin, flexible polymer electronic systems, large area patterning processes is a good choice and will most probably play an important part in polymer electronics manufacturing [2].

High resolution patterning methods for interconnects printing are important in view of the shrinking size of electronic devices. Although photolithography, electron beam lithography and other conventional techniques can achieve the required resolution, they are not very suitable to flexible electronics because they are expensive and generally require multiple steps with photo-resists, solvents and developers that are difficult to use with plastic substrates [2]. The contact printing method has the advantage of being a simple and chemical compatible process for flexible electronics.

Contact printing uses an element with surface relief (i.e. the stamp) to transfer material to a substrate. This approach has been used primarily to produce printed features that are 100 μm or larger. The printing process can be separated into two parts: fabrication of the stamp and use of this stamp to produce relief pattern features on a substrate surface. Usually, stamps are produced by replication against a master that has the desired relief features. A single master can generate many polymer stamps; each one of them can be used many times for printing. Its application to electronic systems that incorporate micron- or nanometer-sized features is not well explored. The property of the inks and the printing process restrict the classes of materials that can be patterned. The resolution is determined by the properties of the ink and its interaction with the stamp and/or substrate, the resolution of the stamp, and the conditions that convert the pattern of ink into a pattern of functional material. Pioneering work in contact printing was performed by Whitesides and co-workers [3-6], leading to subsequent application developments and studies of the process parameters.

On top of micro-contact printing, nano-transfer printing is a more recent high-resolution printing technique [7-9]. It uses surface chemistry as interfacial glues and release layers to control the transfer of solid material layers from relief features on a stamp to a substrate. However, there is less effort in studying the printing of polymer material by surface modification.

Contact printing using soft polymer mold still have some outstanding problems [10]. To ensure high efficiency of transfer of adhesive from the PDMS soft mold, controlling the surface wettability is therefore of major interest.

Epoxy Transfer Mechanism

shows the ideal printing procedure of contact printing. During dipping, the epoxy should be easily picked up by the PDMS mold using a higher surface energy of mold surface relative to the epoxy. While printing on the substrate, the PDMS mold surface should have a lower surface energy relative to the printing material to facilitate material transfer to the substrate.

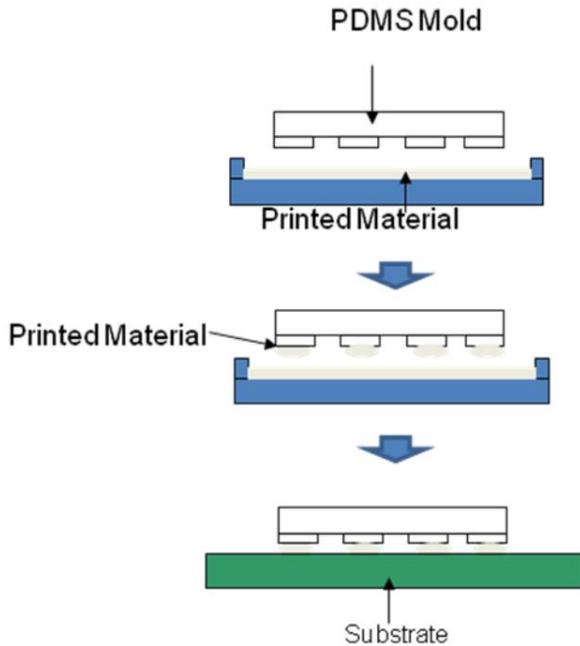


Figure 1 Contact Printing procedures

To enable this material transfer mechanism, control of surface wettability on mold surface is a key process. The control of surface wettability has demonstrated its wide variety of applications. Stimuli-responsive surfaces [11] make it possible to reversibly control the wettability of the surface and a number of approaches have been studied, including light-irradiation [12], use of an electric field [13], thermal treatment [14] and solvent treatment [15].

Among different controlling methods on surface wettability, light-irradiation probably is the most effective one especially in large volume production. In this paper, novel in-situ UV irradiation during contact is proposed. Under the UV irradiation, surface wettability of the soft mold is changed during contact and epoxy transfer is improved. In order to achieve surface modification under UV application, free radical initiators are used for the surface modification of PDMS mold. The strategy will be discussed in the following sections.

UV assisted wettability change by free radicals initiators

Since the desire printing mechanism is to have controllable wetting between the mold and epoxy, a surface having a relatively higher surface energy than the epoxy can help efficient material pick up during dipping. On the other hand, the PDMS mold surface should have a lower surface energy relative to the printing material in order to transfer the material on to the substrate. To facilitate this change of

wettability on the mold surface, Feng et al [16] used photosensitive semiconductors ZnO and SnO₂ nanoparticles on silicon surface to modify the surface by having a hydrophobic surface before UV irradiation and a hydrophilic surface after UV irradiation. However, the mechanism is an inverse to our proposed strategy and it took 5 hours to execute the significant wetting change. This is not acceptable for industrial process.

Radicals (often referred to as free radicals) are atomic or molecular species with unpaired electrons on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are chemically active. In this paper, free radicals is used as the surface modifier because it can be UV activated in a short time (less than 5 minutes) and the radicals is highly reactive in modifying the surface as wells as the epoxy [17]. The primary mechanism is given as follows:

1. The free radical initiator is deposited on to the mold surface as a thin layer via a weak hydrophobic interaction. Its polarity is between those of the PDMS and the epoxy resin, so the resin can be easily wetted to the mold with a low contact angle. After a few minutes of UV irradiation, the initiator molecule decomposes into two free radicals with higher polarity, and initiates the polymerization of the resin. The polymer chain starts to propagate and the viscosity starts to increase resulting in a larger contact angle.
2. Since the thin layer of initiator detaches from the PDMS substrate and merges into the resin, the wetting between the resin and the PDMS is rapidly decreased.
3. The decrease of wetting helps with the transfer of the epoxy from the PDMS surface.

Contact angle measurement of free radical treated surface under UV activation

Commercially available epoxy resins used in this study was Epon 828 (Shell Chemical Co.), which is commonly used as base resin in many polymer electronics system. Bulk PDMS soft mold was prepared be casting. Two hydrophobic type free radical initiators were chosen: benzoyl peroxide (BPO) (Figure 2) and azobisisobutyronitrile (AIBN) (Figure 3). Under UV irradiation, the double nitrogen bond inside AIBN and the single O-O bond in BPO will cleave leading to material release from the mold to the substrate

Contact angle measurements were conducted for the surface treated PDMS mold using the Digidrop contact angle meter to evaluate the wettability changes. Different concentration of free radical initiators were prepared by dissolving them inside 5ml of chloroform and hexane in a ratio of 1:5. Chloroform is used for dissolving the free radical initiators and hexane is used for better deposition of solution on PDMS surface as its surface tension is relatively lower than PDMS. Table 1 shows the surface tension of common solvent.

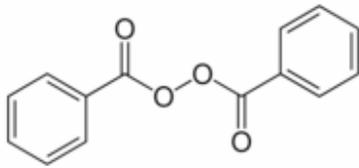


Figure 2 Chemical structure of benzoyl peroxide (BPO)

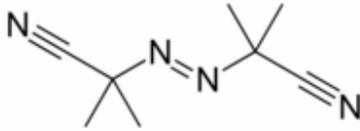


Figure 3 Chemical Structure of azobisisobutyronitrile (AIBN)

Material	Surface Tension
Hexane	17.89 dynes/cm
Chloroform	26.67 dynes/cm
Ethanol	21.97 dynes/cm
Toluene	27.93 dynes/cm
PDMS	19.8 dynes/cm

Table 1 Surface tension of common solvent

Three sample measurements were conducted for each case. UV irradiation was conducted by using a UVP UVL-28 2 mW/cm² UV lamp. The wave length of the UV lamp is 365 nm. Contact angle of Epon 828 droplet (6μL) for different UV irradiation time was measured. Effect for different dipping time of PDMS into the solution was also investigated. Lastly, a control experiment was conducted by measuring the contact angle between deionized water and treated PDMS surface.

Contact Angle Measurement Results

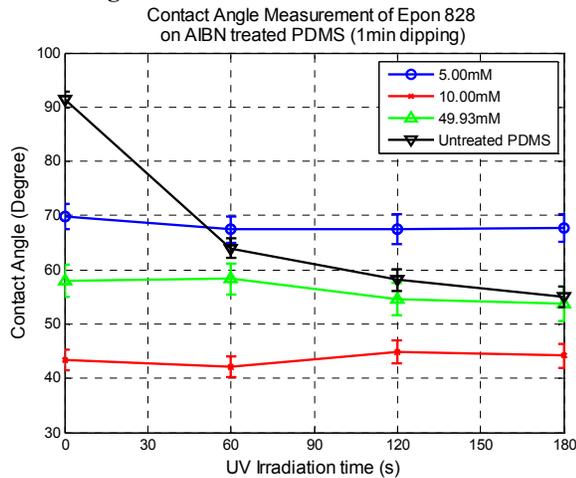


Figure 4 Contact Angle Measurement of Epon 828 on AIBN treated PDMS (1min dipping)

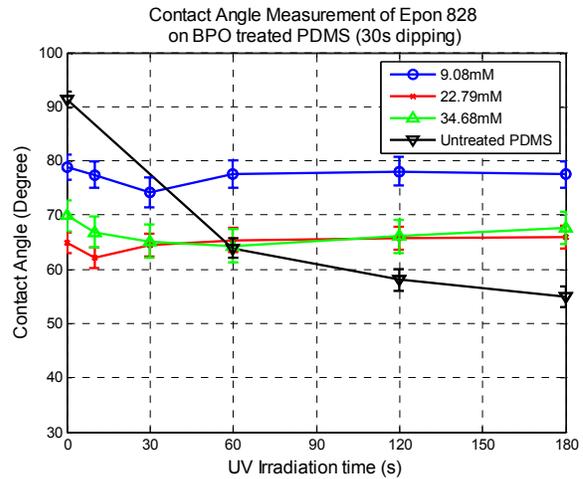


Figure 5 Contact Angle Measurement of Epon 828 on BPO treated PDMS (30s dipping)

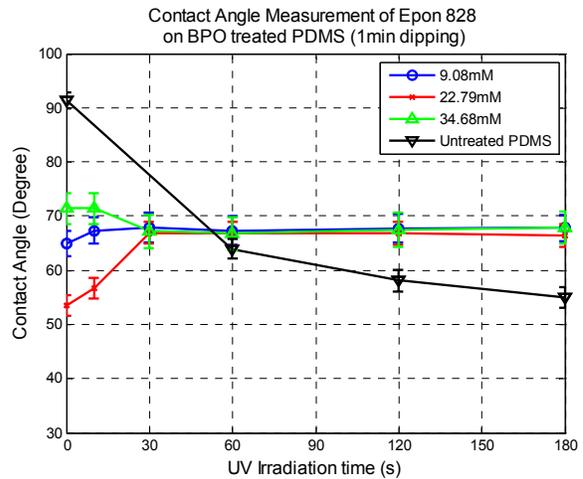


Figure 6 Contact Angle Measurement of Epon 828 on BPO treated PDMS (1min dipping)

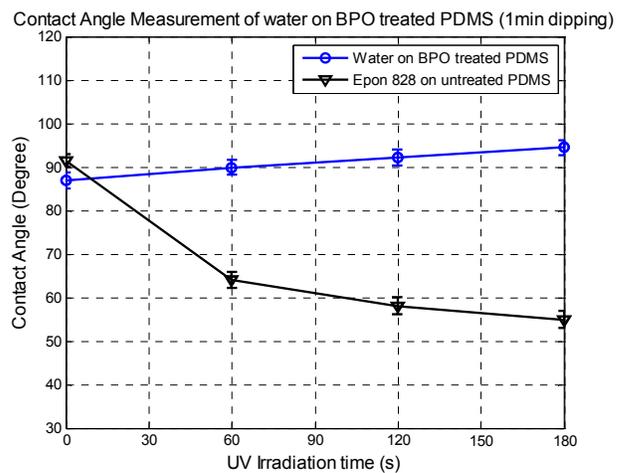


Figure 7 Contact Angle Measurement of water on BPO treated PDMS (1min dipping)

In Figure 4, contact angle of Epon 828 on different concentration of AIBN on PDMS was measured. First of all, the wetting became better after treatment of the PDMS surface, irrespective of the concentration of AIBN. However, the contact angle was not significantly affected by UV irradiation up to 3mins.

In Figure 5, contact angle of Epon 828 on different concentration of BPO on PDMS was measured. 30 seconds of dipping of PDMS was conducted. It can be shown that the wetting became better after treatment on PDMS surface, irrespective of the concentration of BPO. The changes of contact angle were not significant on different UV irradiation up to 3 mins of irradiation. This illustrates that insufficient time for the solution treatment on the PDMS surface will not facilitate efficient BPO deposition.

As there is no active bonding other than van der Waal's forces between BPO and PDMS surface, sufficient time of deposition will help deposition of BPO layer on PDMS surface. Therefore, we increased the dipping time for the PDMS mold in the BPO solution. In Figure 6, contact angle of Epon 828 on different concentration of BPO on PDMS was measured. 1 minute of dipping of PDMS was used. It can be shown that for small concentration of BPO treatment, a little increase of contact angle, i.e. poor wetting on PDMS, after 3 minutes of UV irradiation. When the concentration of BPO increases to 22 mM, the contact angle has significant increment (~10 degree) after 30 seconds of UV irradiation. However, the changes became steady after reaching such a saturation value. When the concentration of the BPO continues increasing, the initial contact angle also increases and the changes of wetting became insignificant. This may be due to too high concentration of BPO on the surface leading to uneven high concentration BPO region formed on the surface. After UV irradiation, some of the BPO was cleaved and reacted with the epoxy. This action will lower the contact angle slightly in the early irradiation stage.

In Figure 7, contact angle of water on BPO treated PDMS was measured. It can be shown that the BPO works in aqueous medium and increases contact angle under UV irradiation. On the other hand, for those PDMS without surface treatment, the contact angle decreases under UV irradiation.

Parameters Controlling UV-assisted wettability change

From the results above, the parameters controlling the UV activated wettability change can be summarized as follows.

For BPO structure, the BPO will form a thin layer on the PDMS with its benzene ring structure and is able to form regular 2D planar or π - π stacking, which alters the surface wettability uniformly. After UV irradiation, the O-O bond is broken forming two free radicals. The cleaved radicals will erect and merge with the resin chain due to a dramatic increment in polarity of BPO free radical. This will decrease the wettability of the resin on PDMS surface (Figure 8, Figure 9 and Figure 10).

On the other hand, AIBN does not induce much wettability changes in this system. This can be explained by the inability of AIBN to form a regular planar structure due to its steric effect. Also, the catalytic activity for epoxy polymerization is limited. Since AIBN has a higher polarity

than BPO, the contact angle with the resin are higher than that of BPO (Figure 4 and Figure 5).

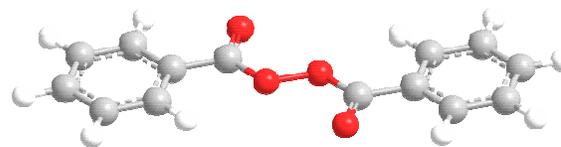


Figure 8 Planar structure of BPO (after energy minimizing using Chem3D.)



Figure 9 Illustration of the free radical formed from BPO

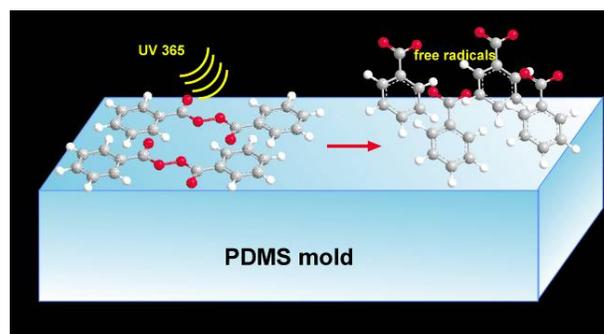


Figure 10 Illustration of radical formation process on the PDMS mold under UV irradiation

After UV irradiation, BPO forms the free radicals on the PDMS surface. The highly reactive and highly polarized free radicals then will react with the epoxy resin above the mold [18]. This will in turn erect the BPO structure and leads to worse wettability of the resin against the PDMS surface. Figure 10 illustrates the process.

In adopting this strategy, it is important to consider the polarity of the resin to ensure matching of the polarity of the free radical initiators and PDMS.

The UV irradiation time and its wavelength govern the absorption and effectiveness of bond breaking in the free radical initiators. As suggested by Labana et al [18], the absorption spectrum for the BPO is high in UV (<400nm) range. The matching of the UV wavelength or the dosage of UV will affect the activation of the free radical initiators on the PDMS surface. However, once the free radicals are formed, the wettability change is stopped as shown in the plateau region in Figure 6.

Since the PDMS surface is hydrophobic, the solvent for depositing the free radical layer is another parameters in this process. To form a uniform thin layer of initiator layer, a solvent should possess a lower surface energy than the PDMS surface and of medium polarity. One other concern is

the solubility of the initiators in the solvent. In this study, chloroform is used to dissolve the BPO and hexane is for dispersion of solution onto the PDMS surface.

Conclusions

In summary, UV activated free radicals initiator is used to modify the wetting between PDMS mold and the epoxy printing materials via a UV irradiation. This is the first exploration of using UV irradiation to decrease wetting between molding materials. Sufficient time of BPO deposition is required for this strategy but this can be improved by using derivatives of BPO to enhance bonding with PDMS surface. The results demonstrate a good potential to apply this strategy to contact printing.

References

- [1] R. Parashkov, R. Parashkov, E. Becker, T. Riedl, H. H. A. J. H. H. Johannes, and W. A. K. W. Kowalsky, "Large Area Electronics Using Printing Methods," *Proceedings of the IEEE*, vol. 93, pp. 1321-1329, 2005.
- [2] J. A. Rogers and G. Blanchet, "Patterning Techniques and Semiconductor Materials for Flexible Electronics," in *Flexible Flat Panel Displays*: John Wiley and Sons, 2005, pp. 198-217.
- [3] A. Kumar, H. Biebuyck, and G. Whitesides, "Patterning Self-Assembled Monolayers: Applications in Materials Science," *Langmuir*, vol. 10, pp. 1498-1511, 1994.
- [4] R. Jackman, J. Wilbur, and G. Whitesides, "Fabrication of submicrometer features on curved substrates by microcontact printing," *Science*, vol. 269, pp. 664-666, 1995.
- [5] Y. Xia, M. Mrksich, E. Kim, and G. M. Whitesides, "Microcontact Printing of Octadecylsiloxane on the Surface of Silicon Dioxide and Its Application in Microfabrication," *Journal of the American Chemical Society*, vol. 117, pp. 9576-9577, 1995.
- [6] Y. Xia and G. Whitesides, "Soft lithography," *Annu Rev Mater Sci*, vol. 28, pp. 153-184, 1998.
- [7] Y. Loo, -L., R. W. Willet, K. Baldwin, and J. A. Rogers, "Additive, nanoscale patterning of metal films with a stamp and a surface chemistry mediated transfer process: applications in plastic electronics," *Applied Physics Letters*, vol. 81, pp. 562-564, 2002.
- [8] Y. Loo, -L., R. W. Willet, K. Baldwin, and J. A. Rogers, "Interfacial chemistries for nanoscale transfer printing," *Journal of the American Chemistry Society*, vol. 124, pp. 7654-7655, 2002.
- [9] J. Zaumseil, M. A. Meitl, J. W. P. Hsu, B. Acharya, K. Baldwin, Y. Loo, -L., and J. A. Rogers, "Three-dimensional and multilayer nanostructures formed by nanotransfer printing," *Nano Letters*, vol. 3, pp. 1223-1227, 2003.
- [10] A. P. Quist, E. Pavlovic, and S. Oscarsson, "Recent advances in microcontact printing," *Analytical and Bioanalytical Chemistry*, vol. 381, pp. 591-600, 2004.
- [11] T. Russell, "Surface-Responsive Materials," *Science*, vol. 297, pp. 964-967, 2002.
- [12] K. Ichimura, S. K. Oh, and M. Nakagawa, "Light-driven motion of liquids on a photoresponsive surface," *Science*, vol. 288, pp. 1624-1626, 2000.
- [13] M. W. J. Prins, W. J. J. Welters, and J. W. Weekamp, "Fluid Control in Multichannel Structures by Electrocapillary Pressure," *Science*, vol. 291, pp. 277-280, 2001.
- [14] D. Crevoisier, P. Fabre, J. Corpart, and L. Leibler, "Switchable Tackiness and Wettability of a Liquid Crystalline Polymer," *Science*, vol. 285, pp. 1246-1249, 1999.
- [15] S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke, and M. Stamm, "Two-level structured self-adaptive surfaces with reversibly tunable properties," *J. Am. Chem. Soc.*, vol. 125, pp. 3896-3900, 2003.
- [16] X. J. Feng and L. Jiang, "Design and Creation of Superwetting/Antiwetting Surfaces," *Advanced Materials*, vol. 18, pp. 3063-3078, 2006.
- [17] G. Herzberg, *The Spectra and Structures of Simple Free Radicals: Introduction to Molecular Spectroscopy*: Dover Publications, New Ed edition, 1989.
- [18] S. S. Labana and Y. F. Chang, "Free-radical initiators as catalysts for aromatic amine-epoxy reaction," *Journal of Polymer Science, Part A-1: Polymer Chemistry* vol. 10, pp. 1861-1866, 1972.