Microsystem Technologies 9 (2003) 501–506 © Springer-Verlag 2003
DOI 10.1007/s00542-002-0289-0

Ultraviolet embossing for patterning high aspect ratio polymeric microstructures

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Abstract In ultraviolet (UV) embossing, a substrate with a coating of liquid or semi-solid UV curable resin mix is pressed against a patterned embossing mold. The resin mix is irradiated with UV before demolding of the hardened microstructures. UV embossing can be done at room temperature and low pressure. However, demolding of UV embossed high aspect ratio microstructures from a metallic mold is typically difficult since there is no differential thermal contraction between the mold and the embossing. Several factors have been identified to influence demolding of UV embossed microstructures: (1) Roughness of mold, (2) Taper angle of microstructures of mold, (3) Chemical interaction between mold and embossing, (4) Tensile and crosslinking shrinkage properties of the irradiated resin and (5) Uniformity of crosslinking process through the thickness of the molded microstructures. By controlling these five parameters, a microarray with an aspect ratio of 5 was demonstrated using a Formulation containing epoxy acrylate, Irgacure® 651, silicone acrylate and other acrylates. The embossed microstructures replicated the features of the mold very well. It was also shown that by controlling the amount of irradiation, the tensile modulus of the UV formulation increased whilst the elongation decreased. An optimum irradiation is needed for clean demolding from the mold without microcracking.

1 Introduction

Polymeric *m*icro-*e*lectro*m*echanical *s*ystems (MEMS) are important as low-cost alternatives to silicon-based MEMS technologies for a range of present and future commercially viable products. These include applications in Life sciences such as DNA microarrays or disposable devices on biocompatible substrate [1], micro-optics like diffractive optical elements or waveguide elements [2, 3] and display technology like optical backplane [4]. Making polymeric MEMS typically involves using a microstructured mold to shape the polymeric material with features in the micrometer range. In this paper, ultraviolet (UV) embossing is introduced as a technique for making polymeric MEMS components with high aspect ratio. The details of the process and the factors to consider for successful embossing are discussed.

Microstructures with high aspect ratio are needed in many applications since they offer a higher active area per unit substrate surface area, the possibility of higher packing density of microstructural elements and higher throughput in continuous flow systems due to higher cross-sections per unit substrate area [1]. Larger surface area and multilevel microstructures are particularly important for chemical or biochemical applications like microreactors, micromixers, chromatographic columns or DNA concentrators to allow long microchannel length for good analysis performance and multitasking within a small area. Similar considerations are important in micro-optics, for example in waveguide applications, which typically involve comparatively large devices with dimensions of several centimeters. Higher packing densities and planar multifunctionality are observed in trends of massive parallelization of MEMS functions [5] e.g. in DNA separations, protein microarrays, biosensors or nanowell-plates.

In UV embossing, a substrate coated with liquid or semi-solid UV curable resin mix is pressed against a patterned embossing mold (Fig. 1). The resin mix is irradiated with UV before demolding of the hardened microstructures. UV embossing offers many advantages. Firstly, UV curing is rapid and can involve curing on the order of tenth second time scales. Secondly, unlike thermal embossing, UV embossing is usually done at room temperature and low pressure. This is critical to the patterning of delicate substrates such as protein-encapsulated polymers or water-containing hydrogels for biomedical applications [6, 7]. Further, the requirements of the mold for such a process are less stringent and such molds can be duplicated economically from a master mold by electroforming [8] or machining on plastics. Thirdly, in contrast to photolithography, which is a batch process involving exposure and wet development in a clean room environment, UV embossing can be a roll-to-roll process outside the clean room environment (Fig. 2). Large areas of the patterns (up to a few meters long by a meter wide) can be

Received: 28 March 2002 / Accepted: 27 October 2002

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This research was supported by a Strategic Development Scheme fund (SDS 15/2001) from the Nanyang Technological University. The authors also acknowledge the kind contributions of chemicals by UCB Chemicals, Sartomer, Henkel (Singapore), Dupont (Singapore) and Ciba Chemicals and a microstructured mold by Dr R. C. Liang of SiPix Imaging (CA, USA). The second author acknowledges the financial support of Nanyang Technological University through a Research Scholarship.

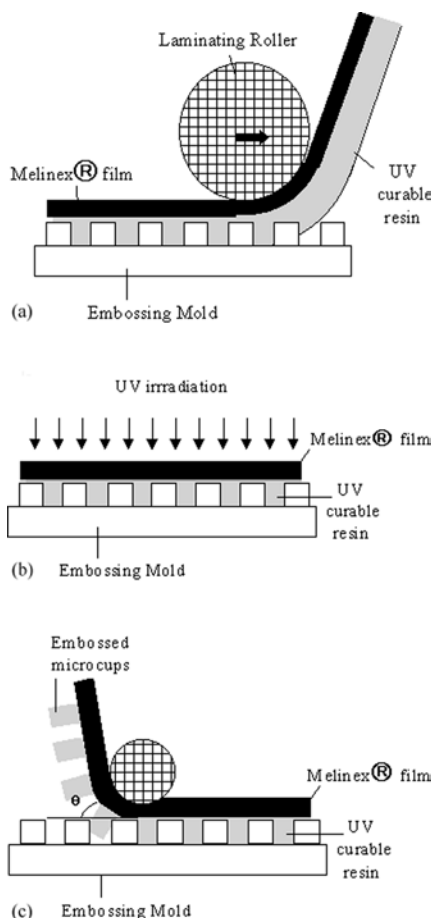


Fig. 1a–c. Schematic of UV embossing process. **a** Lamination, **b** UV irradiation and **c** demolding or peeling

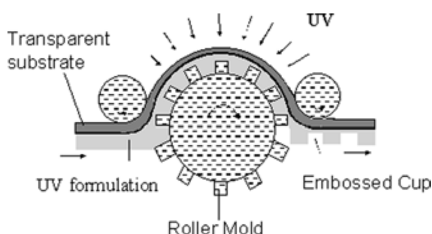


Fig. 2. Roll-to-roll UV embossing process

generated easily (Fig. 1) [3, 4]. Fourthly, the properties of the embossed polymer can be easily fine-tuned by the mix ratio of the components and made superior to those of the thermoplastic equivalents made by thermal embossing. Fifthly, UV embossing has been shown to produce parts with good dimensional replication due mainly to the fact that UV embossing may be done at low temperature [2]. UV embossing can be done at room temperature and low pressure and is suitable for applications where the patterning condition or material is restrictive. Patterning of biologically active molecules and on highly brittle indium tin oxide (ITO) patterned plastic substrate for biomedical and flexible display applications respectively are two such examples.

In spite of the advantages of UV embossing, there has been limited research reported thus far [2–4], especially for microstructures with aspect ratio more than one. High aspect ratio microstructures and nanostructures made by thermal embossing have been well studied [1, 9, 10]. There has been some recent work on *r*eaction *i*njection *m*olding (RIM) of UV curable resins [11]. Rudschuck et al. [12] has demonstrated UV embossing with highly tapered V-shaped grooves with aspect ratio of one. Harvey [2] claimed that reel-to-reel and flat bed embossing can produce microstructures with aspect ratio of 5 and 20 respectively; however no details of the process and materials or results were reported.

We had attempted to UV emboss microarrays with aspect ratios ranging from one to five. UV embossing of a microarray with aspect ratio of one was accomplished without much difficulty. However, as the aspect ratio increased, the UV cured microstructures tended to break in the mold during demolding. This paper summarises the results of our attempts to UV emboss a microarray with an aspect ratio of five from a nickel mold and identifies the factors contributing to clean repetitive demolding of the UV embossed microstructures from the mold.

2
Experimental setup and procedure

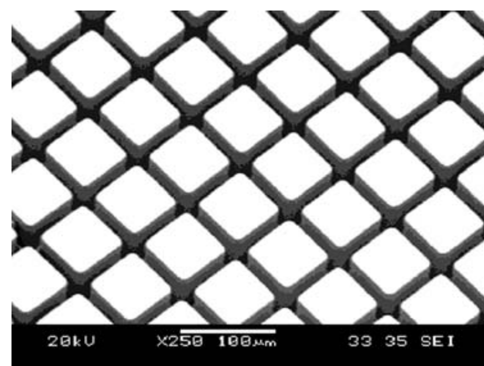
A nickel mold with an aspect ratio of 5 was prepared by exposing and developing a photoresist coating, specifically SU8 from MicroChem Corporation (MA, USA), on a metallized silicon wafer through a mask followed by electroforming nickel on the developed photoresist microstructure. More details can be found in the literature [8, 13, 14]. The mold was then coated with a hydrophobic release layer.

The schematic of the UV embossing is shown in Figure 1. The Formulation comprised UV curable epoxy and urethane acrylate oligomers, a crosslinker, hexane diol diacrylate (HDDA) as the viscosity reducer, a release agent and a photoinitiator (Table 1). Ebecryl 600, an epoxy acrylate from UCB Chemicals, was chosen for its high tensile strength and modulus after curing. Two different photoinitiators were investigated; they were Irgacure® 369 and Irgacure® 651 from Ciba. The UV transparency of the photoinitiators was also measured using an UV/VIS spectrometer, specifically a Shimaduz UVPC 3101.

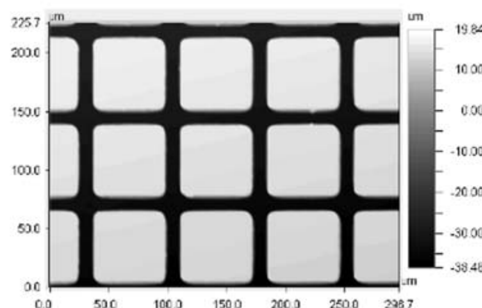
A 145-gage Melinex® 454 film which is an adhesion-promoted polyester film from Dupont, was used as the carrier for the UV curable resin. The UV transparency of this film was measured using the Shimaduz UVPC 3101. The UV formulation was dissolved in acetone to make a formulation with 67 weight percent solid content. The UV solution was coated on a sheet of Melinex® 454 using a Meyer rod Number 60. The coating was left standing in a hume cupboard for 15 min for the acetone to evaporate. The acrylate coated Melinex® film was then laminated on the mold at room temperature between rubber coated rollers. Then, it was UV irradiated with a flood UV exposure system with a Hg-lamp, specifically a 400 Watt PK 102 UV Lamp from I & J Fisnar Inc. The measured area-averaged UV intensity at 365 nm was 62 mW/cm^2. Various irradiation times, specifically 6, 8, 10 and 12 s were investigated. After irradiation, the embossed film was peeled off from the mold and care was taken to ensure that

Table 1. Composition of UV embossing

No.	Constituents	Description	Supplier	phr
1	Ebecryl 600	Epoxy acrylate	UCB Chemicals	35
2	SR 399	Dipentaerythritol pentacrylate	Sartomer	40
3	HDDA	Hexane diol diacrylate	UCB Chemicals	4.95
4	Ebecryl 210	Urethane acrylate	UCB Chemicals	14
5	Ebecryl 1360	Silicone acrylate	UCB Chemicals	6
6	Photoinitiator		Ciba	0.05
	Total			100.00



(a)



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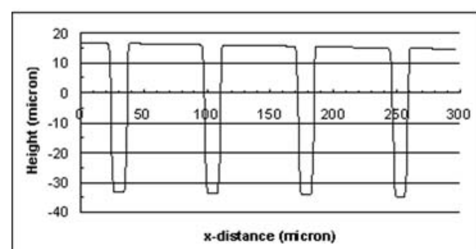

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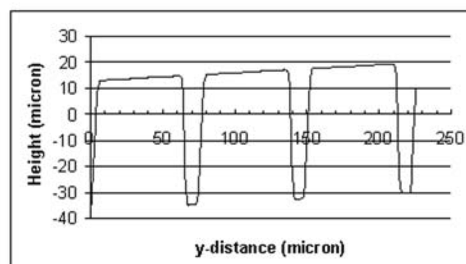

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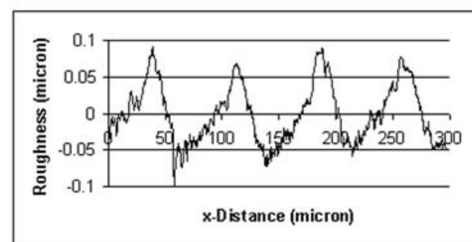
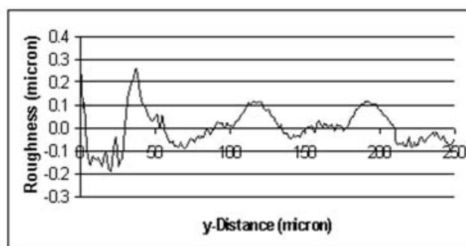


(e)



(f)

Fig. 3a–f. The mold. **a** 3D SEM micrograph, **b** lateral dimensions, **c, d** depth profile in x- and y-axes, **e, f** roughness of trench in x- and y-axes

the peeling angle (θ in Fig. 1c) was small. The surfaces of the replicated microstructures and mold were characterized using a scanning electron microscope (SEM) and an optical profilometer; the instruments used were Joel JSM-5600 and Wkyo NT 2000 respectively.

Tensile properties of the Formulation at various UV irradiation times were determined from rectangular thin strips cut from irradiated films made by compression molding of the formulation between two glass plates. The tensile test coupons were 100 mm by 10 mm and about 0.2 mm thick. The test was performed with an Instron 5565 using a speed of 3 mm/min and gage length of 50 mm.

3 Results and discussions

Figures 3a and 4a show the SEM micrographs of the mold and UV embossed microarrays with an UV irradiation time of 8 s. Figures 3b–f and 4b–f show the dimensions and roughness of the mold and the embossing respectively; these were measured using the Wkyo NT 2000. The mold had raised rectangular areas which were typically 56 µm by 57 µm on top and 66 µm by 68 µm at the valleys. The height of the raised areas was 50 µm. The corresponding lateral dimensions of the cavities of the embossed microarray were 54 µm by 55 µm and 65 µm by 66 µm. The lateral dimensions of the microcups were

slightly smaller because of crosslinking shrinkage. The trenches in the mold were typically 17–18 microns wide at the top and 7–9 microns wide at the bottom. The corresponding dimensions of the embossed microcups were 20–21 μm and 8–9 μm respectively. The height of the walls of the microcups was 50 μm. The root-mean-square roughnesses of the trench of the mold (Fig. 3e and f) and the corresponding top of the wall of microcup (Fig. 4e and f) were both about 100 nm. It can be seen that the embossing faithfully replicated the surface of the mold and was demolded without breakage of the micrometer-sized walls of the microcups. UV embossing results in good replication of the surface profile for four reasons: firstly, the viscosity of the formulation is low; secondly, the resin is cured while still in contact with the mold; thirdly, relaxation processes are inhibited as the crosslinking which occurs rapidly builds up the crosslinked network; and fourthly, the process is almost isothermal.

Figures 4a and 5 show the UV embossed microcups at various irradiation times of 8 and 12 s respectively. It was observed that an optimum UV irradiation of 8 s was needed for faithful replication of the mold without cracking. At high irradiation time of 12 s, microcracking of the walls of the microarray was observed. Several other problems can also be encountered during UV embossing. With very high viscosity, the molding may not fill the trenches of the mold completely. An effective hydrophobic release coating is needed on the mold to prevent the cured embossed resin from sticking to the mold during demolding and delaminating from the Melinex® substrate and. If the resin does delaminate and stick, this will result in permanent damage to the mold: it is very difficult to dissolve the cured resin in any solvent without damaging the mirrorlike finish of the nickel mold.

In thermal embossing, the differential thermal shrinkage of the polymer material and mold during cooling supports demolding. In contrast, UV embossing is an almost isothermal process and successful demolding depends strongly on the static force between the mold insert and the surface of the polymer, the sidewall angle and the elastic behavior of the polymer. The latter can be controlled before demolding by the amount of UV irradiation during embossing. UV irradiation can be continued after demolding for complete cure. Minimization of adhesion forces between the mold and the UV-embossed microstructures is crucial to ensure clean repetitive

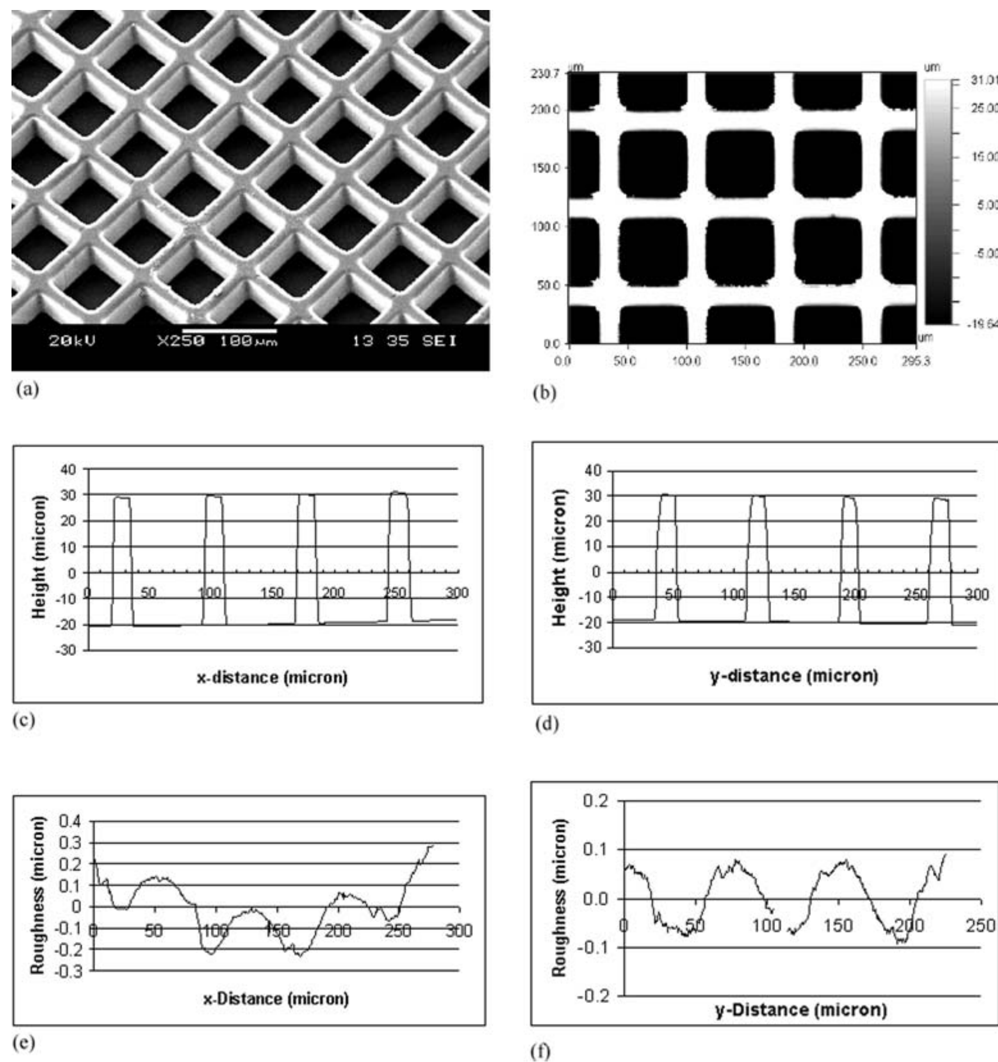


Fig. 4a–f. The molding **a** 3D SEM micrograph, **b** lateral dimensions **c, d** height profile in x- and y-axes, **e, f** roughness at top of embossed walls in x- and y-axes

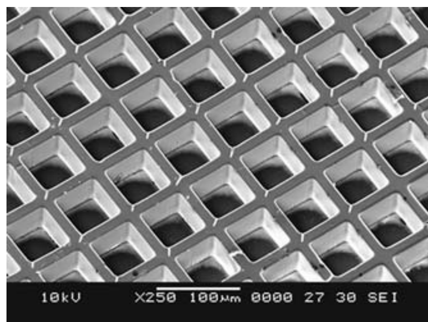


Fig. 5. SEM of microcups with excessive UV irradiation (12 s)

demolding. This and other factors for successful UV embossing of high-aspect-ratio microstructures which have been identified in our experiments are described below.

Sidewall angle

A vertical sidewall is desirous in many MEMS applications since it increases the opening area at the bottom of the microarray. However, in UV embossing, a small sidewall angle eases the demolding process. The sidewall angle of our mold was 6°. The mold was made by photolithography using SU8 which is a negative photoresist [13]. Changing the exposure for the SU8 will vary the sidewall angle of the mold.

Roughness of sidewall and bottom of trench

To obtain an undamaged microstructure, the frictional forces between the mold and the cured resin have to be minimized. The microstructure is destroyed if the frictional forces exceed the strength of the microcup walls. The surface of the raised area of the mold was very smooth and the roughest part of the mold was the valley of the trench; this had a root-mean-square roughness of about 100 nm. With other methods of mold fabrication like LIGA, a better surface roughness of about 10 nm RMS can be expected [1].

Chemical interaction between the mold and embossed resin

The nickel surface has a high surface energy and needs to be pretreated with a release layer before embossing. The mold was dip coated with the Frekote 700-NC before embossing. Also, the formulation contained silicone acrylate (Ebecryl 1360) which is a reactive release agent. Without this component or the equivalent, the embossed cured resin cannot be released from the mold.

Tensile and shrinkage properties of the embossed cured resin

For successful demolding, the strength of the embossed microstructures must exceed the frictional force need for demolding. Microstructure strength (and also brittleness) is controlled by the UV exposure, with increased exposure increasing both cured resin strength and brittleness. The force needed for demolding will depend on the surface roughness of the mold and the chemical interaction of the mold and the molding. However, excessive UV irradiation has to be avoided or shrinkage may lead to cracking and

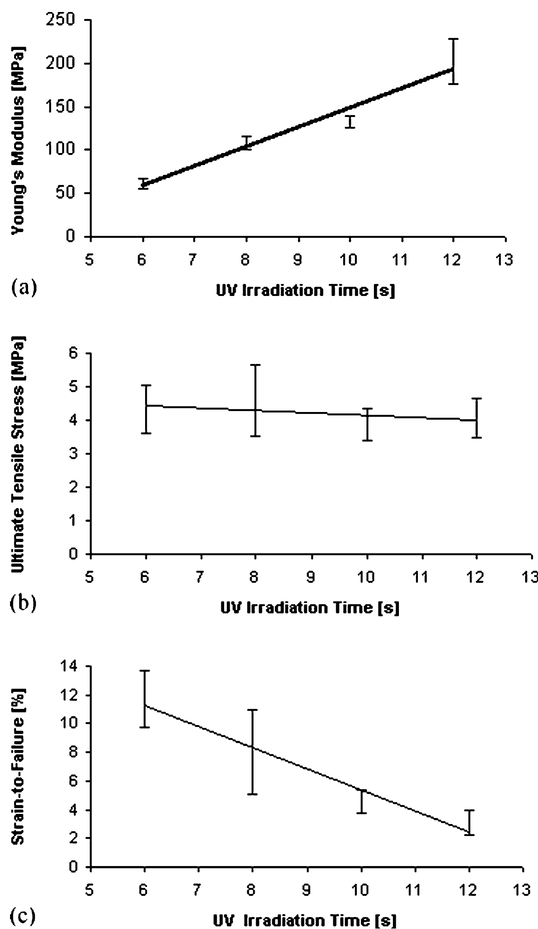


Fig. 6a–c. Variation of tensile properties of Formulation with UV irradiation time. **a** Young's Modulus, **b** ultimate Tensile Strength and, **c** strain-to-failure

breakage of the microcup within the mold. The tensile properties of the Formulation (Table 1) at different UV irradiation times were measured (Fig. 6). The strength appeared to vary little in the range explored. However, at low irradiation time, the film was relatively less stiff and had higher elongation-at-failure. With our formulation irradiated for 6 s, the modulus and elongation at break of the Formulation were about 60 MPa and 11% respectively. At 12 s, the modulus was about 180 MPa and 3% respectively. We found that UV embossing at 8 s produces microarrays with least microcracking and lowest defect frequency (Fig. 4a). With 12 s of irradiation, extensive microcracking was observed (Fig. 5).

Uniformity of the crosslinking process through the thickness of the microstructures

With UV embossing, the UV curable material has to have high transparency at the embossing depth of interest. The transmission of the 142-gage Melinex® film is shown in Fig. 7. It can be seen that the film is almost transparent to 365-nm UV light used for curing. Figure 7 also shows the transmission of Irgacure® 369 and Irgacure® 651. The transmission of 0.05 weight percent of Irgacure® 369 in HDDA varied from about 30, 75 to 90% at 330 nm, 350 nm and 365 nm respectively. In contrast, 0.05 weight percent

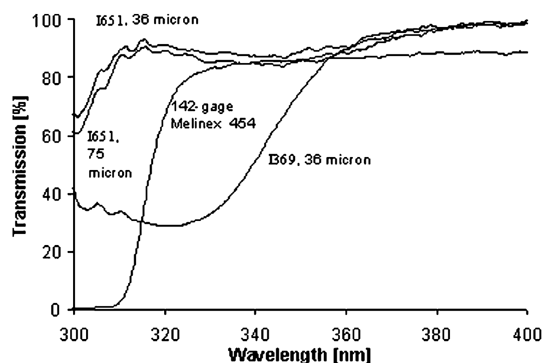


Fig. 7a–c. Optical densities of **a** Irgacure® 369, **b** Irgacure® 651 and **c** Melinex® 454

of Irgacure® 651 in HDDA was almost transparent in the wavelength range of 310–400 nm. Hence, Irgacure® 651 was used as the photoinitator for the UV embossing.

Various improvements can be made to further increase the aspect ratio of UV embossing. Controlling the demolding angle to be very small is expected to facilitate demolding of high aspect ratio UV embossing. A stronger material with low shrinkage is also desirable. The roughness of the mold can be made smaller with optimization of the photolithography conditions or other techniques of mold making such as LIGA. More studies are needed to understand the chemical interaction of the UV curable resin and the hydrophobic layer on the mold surface. Research is currently ongoing to demonstrate the possibility of embossing microstructures with aspect ratio of 10 or more.

4 Conclusion

It can been demonstrated that UV embossing can be used for patterning of high aspect ratio polymeric microstructures. A microarray with aspect ratio of 5 was UV embossed from a nickel mold. The embossing faithfully replicated the features of the mold. UV exposure time was optimized to yield adequate cured resin strength without excessive shrinkage. Other considerations for successful UV embossing were found to be the necessity of good transparency of the photoinitiator to permit uniform crosslinking at all depths in the resin, mold surface smoothness, mold microstructure taper angles and the preparation of the mold surface with a release coating. The technique is quick, economical and can be used for replication involving myriad varieties of UV curable polymers, especially in applications whereby low temperature and pressure are essential.

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