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Photo-curable resists for inkjet dispensing applied in large area and high throughput roll-to-roll nanoimprint processes

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ABSTRACT

We report two newly developed photo-curable resists specifically engineered for inkjet dispensing facilitating nanoimprint lithography (NIL) in a high-throughput environment. The viscosity of the novel NIL resists was adjusted especially to enable inkjet dispensing at room temperature. The novel resists can be applied either in NIL batch processes or in high throughput processes like roll-to-roll NIL (R2R-NIL). Batch-wise imprints were performed on various substrates as Si or plastics demonstrating the distinctive application versatility of the novel materials. The very fast curing speed of these materials is discussed in detail with the aid of FT-IR and photo-DSC measurements. The experiments demonstrate a high degree of double bond conversion of about 80% after curing and a fast curing in a few seconds even at a low radiation intensity of 0.2 mW cm^{-2}. The novel materials show excellent adhesion on different substrates and high optical transparency. The high throughput capability of the novel materials is demonstrated by R2R-NIL processes performed at a web speed of up to 30 m min^{-1}.

1. Introduction

Nanoimprint lithography (NIL) was invented in the mid 1990's by Chou and co-workers [1]. The very first approach of NIL, based on the softening of poly(methyl methacrylate) (PMMA) at 200 °C and a relatively high pressure of 13 MPa, was soon extended by a NIL process in which photo-curable resists are cross-linked by exposure to light at room temperature (RT) and much lower pressure [2]. Typically, both approaches use rigid substrates as well as rigid stamp materials and can be defined by a plate-to-plate NIL (P2P-NIL) technology. However, such P2P-NIL processes are only challenging applicable to large area imprinting or to high throughput production without affecting the production costs dramatically. Very recently, industrial interests have shifted alongside to alternative continuous process technologies which enable high throughput as well as patterning of large areas at lower fabrication costs. Suitable processes meeting these requirements are roll-to-roll (R2R) or roll-to-plate (R2P) NIL. These NIL processes are able to pioneer several nanostructured low cost products like wire grid polarizer, antireflection films, self-cleaning surfaces, or anti-friction coatings where no pattern transfer is necessary. Since the continuous NIL process is not unique in terms of process parameters and employed technologies, various roller tools are available and nearly every manufacturer uses individual process conditions. Such process conditions can vary from tool to tool by different exposure technologies (Hg bulb lamp or LEDs with different wavelength [3,4]), different stamp materials (Ni [5], Cu [6], stainless steel [7], or polymer stamps [3,8–11]), different substrate materials (polymers like PC [4], PEN [7], or PET [3]), or different technologies for the deposition of the photo-curable resist formulations (e.g. inkjet dispensing [8,12], slot die coating [13], gravure printing [14], or drop dispensing [3]).

Due to these variations in process technology, a photo-curable and R2R-NIL compatible resist has to fulfill a wide range of parameters in order to be widely applicable in different roller tools and on multiple substrate materials. Furthermore, not only the process conditions have to be addressed. The final coating has to be adaptable to a wide-range of applications. Therefore, the photo-curable material for example has to be highly transparent for optical structures (e.g. antireflection films), highly scratch resistant for permanent applications (e.g. antifriction films), or highly etch resistant for an adequate pattern transfer onto a substrate (e.g. wire grid polarizer) [5].

In this contribution, we present two novel photo-curable NIL resist formulations. They show a high potential to be widely applicable on various roller tools and they have physicochemical characteristics enabling a great number of different applications. We

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discuss the viscosity adjustment addressing different R2R compatible dispensing methods as well as the main properties of the liquid resist materials. Furthermore, the final material properties of the photo-cured resists are discussed in detail and the high throughput potential of the materials is demonstrated in a roller process. Since both formulations are mainly based on the same formulation they differ only in a very small amount of a surface active additive and reactive monomers, respectively. With this contribution it is shown that a material adjustment can easily be done by a small change in composition and adding additives to enable the customers' requirements without affecting the main material characteristics.

2. Experimental

2.1. Materials and characterization of the liquid formulations

All employed (meth-)acrylate monomers, additives, and photoinitiators of the formulations were used as received and were purchased from Sartomer Europe (France), Miwon Europe GmbH (Germany), BASF (Germany), or Eternal Chemical Co., Ltd. (Taiwan). A general overview of the used monomers and additives can be found in Table 1.

2.2. Preparation of unpatterned polymer films and their characterization

Employed 2-inch silicon wafers were cleaned in oxygen plasma before use and then coated with mr-APS1 [15]. All resist films were prepared by spin-coating on a DELTA 6 RC spin coater module from Süss MicroTec AG (Germany). The formulations were purified by filtration with 0.1 μm PTFE syringe filters prior to spin-coating, applying 3000 rpm for 30 s resulting in film thicknesses of about 1.9 μm. All coatings were cured in CO_2 atmosphere using a mask aligner from Süss MicroTec AG (Germany). Film thicknesses after curing were measured using a FTP 500 from Sentech Instruments GmbH (Germany). Advancing water contact angle measurements on Si/mr-APS1 [15] substrates were performed on a Surftens 4.3 apparatus from OEG GmbH (Germany).

2.3. P2P-imprint experiments for characterization of the imprinted patterns

Batch-wise imprints were conducted on a Nanoimprinter NIL-2.5 from Obducat AB (Sweden). Optical micrographs of imprinted structures were recorded using a BX51M microscope from Olympus K.K. (Japan) equipped with a Color View Soft Imaging System. The used stamps were in-house fabricated OrmoStamp® [15] replicas (a reference stamp featuring multiple structure architectures and a replica of a densely patterned 500 nm line & space (L&S) gratings with an aspect ratio (AR) of 1). Standard imprint conditions are as follows: filling time 20 s, filling pressure 0.7 MPa (machine limit), radiation intensity 32 mW cm^{-2} for 18 s at RT, followed by a manual separation of the stamp.

2.4. R2R-NIL experiments

Large area imprints were performed on a customized Basecoater R2R-NIL tool from Coatema (Germany). The resist was deposited by gravure printing (applying a 0.7 μm initial film thickness). Substrate material was PET Melinex 506, film thickness 50 μm from DuPont Teijin Films (USA) with a web width of 300 mm. Pneumatic pressure was 0.4 MPa and the imprint was conducted at RT. A Hg bulb lamp was used with a power of 20 W cm^{-1}. Stamp material was SEM fluorinated Ni.

2.5. Spectroscopic and calorimetric characterization

FT-IR analysis was performed on a Scimitar FTS2000 FT-IR spectrometer from Digilab, Inc. (USA) using a golden gate Mk II ATR (attenuated total reflection) system from Specac Limited (UK). For kinetic investigations a bluepoint 4 ecocure from Hönle AG (Germany) was used and the radiation was performed in Ar atmosphere at an radiation intensity of 0.2 mW cm^{-2}. The radiation was started manually 3 s after starting the data collection of the IR spectra. Photo-DSC experiments were conducted on a DSC822e from Mettler-Toledo Intl. Inc. (USA) using a Lightningcure™ L8868 from Hamamatsu K.K. (Japan) as light source (radiation intensity was 0.5 mW cm^{-2}). About 14 mg of the liquid samples were directly weighted into open Al crucibles and the heat flow and polymerization enthalpy were normalized, finally.

3. Results and discussion

3.1. Characteristics of the liquid formulations

Two different photo-curable resists were developed and characterized, namely mr-UVCur26SF XPA and mr-UVCur27SF XP. The specific material selection of monomers and additives was made due to final application aspects, adhesion to different substrates, low viscosity to fulfill inkjet dispensing requirements, and high curing speed potential. These both experimental formulations can either be used for permanent applications or as a dry etch mask on several substrates. Therefore, the monomers were selected due to high crosslinking density, fast curing speed, high optical transparency, high hardness, high RIE resistance and good adhesion to several substrates. A general overview of the different compositions is disclosed in Table 1.

Table 1
Summary of monomers and additives used for the formulation of the novel photo-curable NIL resists mr-UVCur26SF XPA and mr-UVCur27SF XP, respectively (R_1: H, R_2: CH_3), as well as the characteristic material properties and specific monomer concentrations.

Employed formulation components	Characteristic material property	Monomer concentration	
		mr-UVCur26SF XPA [%]	mr-UVCur27SF XP [%]
HC═C($R_{1,2}$)–(C═O)–O–CH_3–R_3–CH_3–O–(C═O)–C($R_{1,2}$)═CH	High cohesion, hardness, and glass transition temperature	30–50	30–50
HC═C($R_{1,2}$)–(C═O)-O–CH_3–R_4–CH_3–O–(C═O)–C($R_{1,2}$)═CH	Adhesion to flexible substrates	30–50	30–50
HC═C($R_{1,2}$)–(C═O)–O–CH_3–R_5	Viscosity reduction for inkjet dispensability	10–20	10–20
[HC═C($R_{1,2}$)–(C═O)–O–CH_3]$_{xy}$–R_6	High dry etch resistance	0	1–8
Surface active additive	Low surface energy	0	<1
Photoinitiator	Photo-curing	2–5	2–5