Improvement in the diffraction efficiency of a polymer using an ionic liquid

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Abstract: In this paper, photosensitive materials for information storage devices are presented. The polymers were prepared using surface relief-grating (SRG) fabrication with a diode-pumped solid-state (DPSS) laser of 532 nm, and the diffraction efficiency (*DE*) of the polymers were assessed with a low-power DPSS laser at 633 nm. However, the diffraction efficiency of the azo-functionalized epoxy-based polymer was low, even after 15 min of exposure. To improve the efficiency and reduce the time it takes for the *DE* measurements of the photosensitive polymer, the polymer was combined ionic liquids (ILs). Various ILs, *i.e*., 1-methylimidazolium chloride ([Mim]Cl) from the imidazolium family of ILs and diethylammonium dihydrogen phosphate (DEAP), triethylammonium 4-aminotoluene-3-sulfonic acid (TASA) and tributylmethylammonium methyl sulphate (TBMS) from the ammonium family of ILs, were investigated. For the first time, it was observed that *DE* dramatically increased the DEAP–polymer mixture in 4 min compared to the polymer (alone) and other polymer–IL mixtures. Therefore, DEAP IL could help improve the efficiency of *DE* measurements in a shorter time.

Keywords: photosensitive materials; diode-pumped solid-state; diffraction efficiency; ionic liquids; imidazolium IL; ammonium IL.

INTRODUCTION

Generally, the focus is on methods to store, generate, and transmit massive data at fast transfer rates at low costs.[1] Multiple technologies are currently used for information storage, and among them, the most prevalent include photosensitive materials. The optical reflection of photosensitive materials can be modified using the laser action, either in metallic or polymeric form.[1,2] Photopolymers and silver halide materials are used as holographic recording materials due to their high sensitivity and high resolution. Nevertheless, for a few years,

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polymers have been a key area of research due to their potential applications in various fields.[1–3] A polymer film, possessing unique properties of a photo-induced anisotropic effect and its nonlinearity is a promising holographic recording material. There are many interesting properties of polymers, such as their photo-induced birefringence, photo-induced phase transition and surface photomechanical deformation of thin films and relief-grating (SRG) formation.[4–9] These properties could be correlated with the photo-induced anisotropic effect, in which the *trans*-form of the azo group undergoes a transition to its *cis*-form through excited states. Irradiation of the interfering laser beams results in the appearance of sinusoidal surface patterns, which could then lead to the formation of SRG on the polymer films.[2,6] The unusual response of polymers occurs as a result of the passage of polymeric chains due to the free volume expansion in bulk driven by isomerization.[10] The force due to a dipolar interaction with the optically-induced electric field gradient, a translational worm-like diffusion as a result of photo-isomerisation of the azobenzene chromophores, along with the molecular alignment developing in a mean-field force enable the common occurrence of photo-mechanical effects in thin films.[11–14] These properties of the polymer allow them to be exploited in various application areas, such as for data storage devices.

On the other hand, polymers still lack a high quality in photo-induced anisotropy, which is essential for their practical use for optical storage. A large number of materials in combination with the peculiar properties of liquid crystals and azobenzene molecules, based on ionic interaction were proposed for this purpose for different applications in optics and information technologies.[15–17] A stable photo-induced birefringence in an azopyridine liquid crystalline polymer was reported.[18] Different excitation regimes of nonlinear absorption (NLA) were obtained for azo-containing ion liquid crystal polymer, reported in an early work.[19] The photo-orientation properties of liquid crystalline azo-dendrimer films were explored by Li *et al*. through pulsed irradiation.[20] ILs could be considered as classical molten salts having low-melting points.[21–24] The diverse chemical composition and structure are the most significant advantages offered by ILs, and thus, the desired properties can be attained by coupling various organic cations, with various inorganic or organic anions.[21–24] In recent years, an azo-containing IL–crystalline possessing reversibility and long-term optical storage was used by Pan *et al*.[25] In another work, the azo-containing IL–crystalline polymer and polymer film exhibited negligible nonlinear absorption and large nonlinear refraction.[26] Being influenced by both azo-containing IL–crystalline polymer and polymer research, the interaction between the synthesized epoxy-based polymer with ILs in an early work.[27] In this study, the imidazolium IL (1-methylimidazolium chloride) and ammonium ILs (diethylammonium dihydrogen phosphate (DEAP), triethylammonium 4-aminotoluene-3-sulfonic acid (TASA) and tributylmethylammonium methyl sulphate (TBMS)) were used to

investigated the surface relief grating (SRG) and diffraction efficiency (*DE*) for an epoxy-based azopolymer and polymer–ILs mixtures.

<div align="center">EXPERIMENTAL</div>

Materials

All other materials, reagents and solvents were purchased from Sigma–Aldrich Korea Ltd. and were used as received without further purification.

Characterization

Atomic force microscopy (AFM) images were obtained using an XE-100 AFM instrument (Park systems, Korea) operated in the non-contact mode. The laser experiment was conducted with a diode-pumped solid-state (DPSS) laser (Genesis CX-Series SLM; Coherent Lasers, Santa Clara, CA, USA).

The synthesis of the polymer and the ILs is illustrated in a previous work.[27] The polymer and the ILs are depicted in Fig. 1.
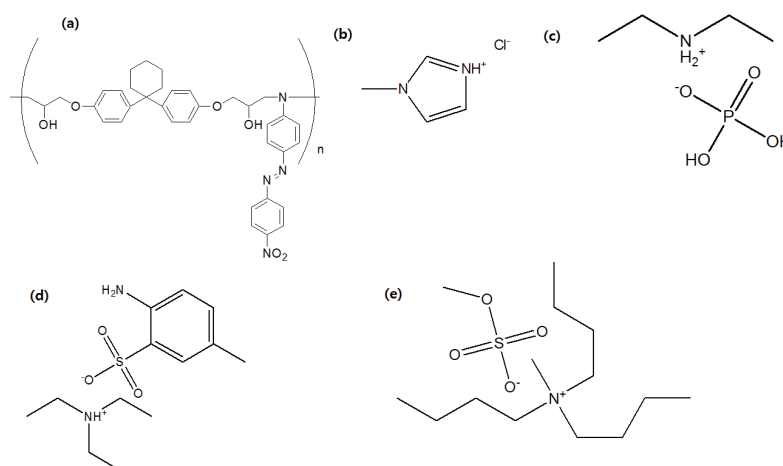

Fig. 1. Schematic representations of: a) epoxy-based azopolymer, b) [Mim]Cl, c) DEAP, d) TASA and e) TBMS.

Surface relief grating (SRG) formation and diffraction efficiency

Surface-relief-grating (SRG) measurements were performed using a previously reported procedure.[6,28] The light source was a linearly polarized diode-pumped solid state (DPSS) laser beam with a wavelength of 532 nm with 500 mW cm^{-2} light intensity (Fig. 2). The laser beam was split by a mirror and spatially filtered, expanded, and collimated with an intensity of 250 mW cm^{-2}. The grating formation was monitored with a low power DPSS laser at 633 nm by measuring the power of the first-order diffracted beam in the reflection mode in the real time mode during the writing process (Fig. 2). The writing beam and read-out beam were both p-polarized. SRG engraving was then performed under ambient conditions at room temperature, and the surface relief structure of the gratings on the polymer films was investigated *via* AFM. The diffraction efficiency (*DE*) was measured during the SRG formation with respect to the light irradiation time.[6]
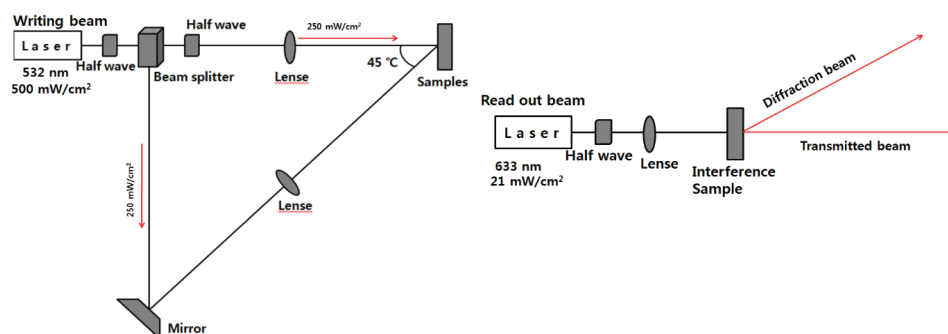
Fig. 2. Schematic diagram to determine the SRG and diffraction efficiency.

RESULTS AND DISCUSSION

SRG formation and DE *of polymer*

The epoxy-based azopolymer was synthesized according to a previously reported work.[27] The UV–Vis spectrum of the polymer was recorded. The spectrum showed a peak at ≈270 nm corresponding to π–π* transitions, and a peak at ≈510 nm due to the n–π* transition of azobenzene chromophores, as shown in Fig. 3a. The SRG formation behaviour of the polymer was studied using inscribing light produced by the DPSS laser, with the wavelength of 532 nm at an intensity of 500 mW cm^{-2}.
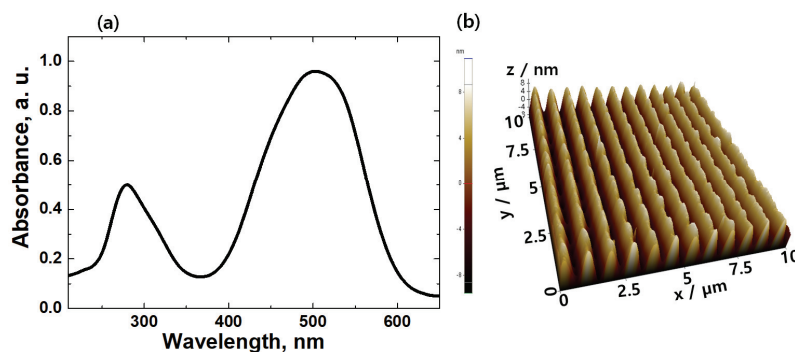

Fig. 3. a) UV-Vis absorption spectra of the epoxy-based azopolymer and b) AFM image of the SRG formation on the polymer film (The scan size for all images is: 10 μm×10 μm×5 nm).

To prevent the destruction of the SRG formation on the film, the exposure time was controlled to be as short as possible. The interference patterns created on the films that were used to engrave the SRGs could be attributed to the two p-polarized laser beams at a wavelength of 532 nm. Under this condition, the formation of an SRG was observed on the films of the polymer. As a result, an exposure time of about 15 to 20 min gave the best SRG. The AFM images of the

SRG that formed on the polymer films, which seem to be regularly spaced sinusoidal surface structures, are shown in Fig. 3b. The grating growth rates in the presence of the interfering laser beam irradiation were used to analyze the SRG formation and formed the basis for correlation studies with polymer structures and irradiation wavelengths. The low power DPSS beam at 633 nm was used to probe SRG engraving in a real time mode. The SRG formation was studied at room temperature, under ambient conditions. The thickness of the polymer film was 5 μm and the depth of the groves was 5 nm. The diffraction efficiency was measured during SRG formation with respect to the light irradiation time, as shown in Fig. 4a. The *DE* was found to be 0.05 % after 18 min, and it later decreased with increasing exposure time to the laser, as shown in Fig. 4a. To increase the *DE* and reduce the exposure time, a mixture of ILs with the polymer was prepared, as per a reported work.[27] Then, this combination of ILs and polymer was use to determine the SRG and diffraction efficiency (*DE*).
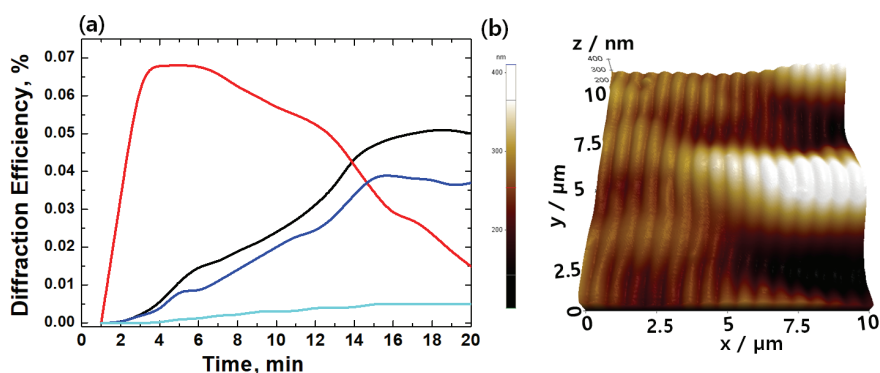

Fig. 4. a) Diffraction efficiency of the polymer (black), polymer + DEAP (red), polymer + TASA (blue) and polymer + [Mim]Cl (cyan); b) AFM image of SRG formation on a polymer + DEAP IL film (The scan size for all images is: 10 μm×10 μm×280 nm).

SRG formation for the combination of polymer and ILs

The SRG formation behaviour was investigated using spin-coated films of the polymer + IL mixture using the same experimental setup as used for the polymer alone (DPSS laser with the a wavelength of 532 nm and intensity of 500 mW cm^{-2}). The exposure time was controlled to be as short as possible to prevent the destruction of the SRG formed film. The diffraction efficiency of the first-order diffracted beam was measured in the real time mode, and the SRG formation was probed with a low power DPSS beam at 633 nm. The maximum efficiency of 0.04 % was observed for polymer + TASA in 15 min, thereafter, the efficiency started decreasing, as shown in Fig. 4. Whereas, the efficiency for the [Mim]Cl + polymer was found to be 0.005 % for 15 min. Moreover, TBMA +

polymer did not exhibit any *DE* during the experiments. On the other hand, the maximum efficiency of 0.07 % at 4 min was observed in the case of the protic IL DEAP, which showed strong interaction with the polymer. Later, the *DE* decreased with increasing the time of light irradiation. This might be due to the fact that after the exposure to the laser for more than 5 min, the interaction between the DEAP and the polymer decreased because of the longer exposure time to the laser, and this resulted in a heating effect that may breakdown the H-bonding between the polymer and DEAP. Furthermore, the polymer was further studied by atomic force microscopy (AFM). The AFM image showed that the polymer had an average roughness (R_a) of 4.0 nm while after interaction with DEAP, the R_a was ≈9.4 nm, as shown in Fig. 4b. Whereas, the R_a for TASA, TBMA and [Mim]Cl were found to be 0.04 µm, 4.89 nm and 15.61 nm, as shown in Fig. 5.
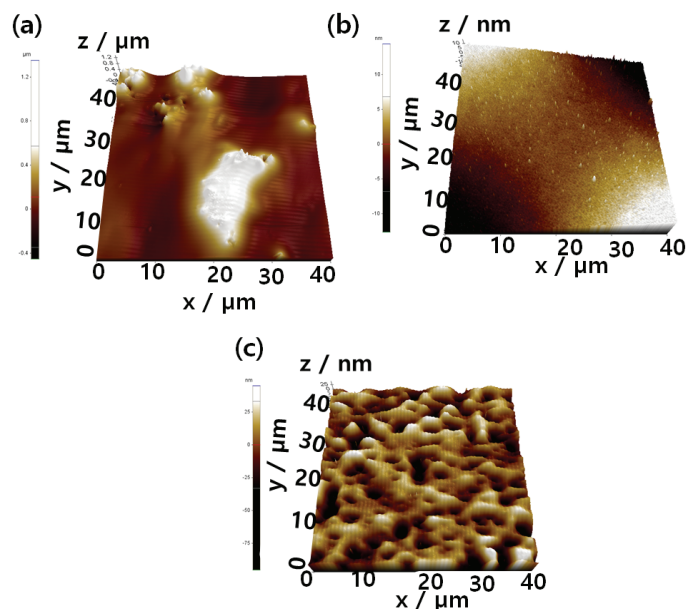

Fig. 5. AFM image of SRG formation on polymer +: a) TASA (the scan size is 40 µm×40 µm×0.8 µm); b) TBMA (the scan size is 40 µm×40 µm×8 nm); c) [Mim]Cl (the scan size is 40 µm×40 µm×20 nm) ILs film.

The diffraction efficiency of the polymer (alone) was ≈0.05 % for 18 min of exposure, with a low power DPSS beam at 633 nm, and the *DE* deceased slightly as a function of the laser exposure time (20 min). The *DE* of the polymer + DEAP was the highest among all the studied ILs with a lower exposure time. This property of the polymer + DEAP confers advantages in terms of fabrication of SRG using low intensity light for a short time. The decrease in efficiency with increasing exposure time might be due to disturbance in the H-bonds between

DEAP and the polymer. Moreover, the roughness is greater in DEAP + polymer, as compared to the TBMA + polymer, while less than [Mim]Cl + polymer and TASA + polymer. This shows that the roughness of the film is not an important factor for *DE* in the present study. Hence, the polymer + DEAP IL could be a good material for a holographic image. This is the first time that it has been shown that the polymer + DEAP combination could increase the *DE* in a shorter time, as compared to that of the polymer alone.

CONCLUSIONS

The extensive experimental data illustrates that the SRG on the polymer film was photofabricated using a DPSS laser of 532 nm. The *DE* of the epoxy-based azopolymer (alone) obtained using a 633 nm DPSS laser was found to be 0.05 % for 18 min. Furthermore, the *DE* analysis was checked using polymer + ILs and it was found that among all the studied ILs, DEAP showed the highest *DE* of 0.07 % in 4 min. Hence, these results seem to be beneficial to the field of polymer chemistry and holographic research.

ИЗВОД

ПОБОЉШАЊЕ ЕФИКАСНОСТИ ДИФРАКЦИЈЕ ПОЛИМЕРА ПОМОЋУ ЈОНСКИХ ТЕЧНОСТИ

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У овом раду су приказана истраживања фотоосетљивих материјала, који налазе примену у уређајима за складиштење информација. Површина полимерних филмова у облику рељеф-решетке (SRG) је припремана помоћу чврстог диодног ласера (DPSS) на таласној дужини од 532 nm. Ефикасност дифракције (*DE*) полимерних филмова је процењивана помоћу DPSS ласера мале снаге на таласној дужини од 633 nm. Међутим, ефикасност дифракције азо-функционализованог полимера на епоксидној бази је ниска, чак и након 15 min изложености ласерском зрачењу. Да би се побољшала ефикасност дифракције фотоосетљивог полимера и скратило време излагања ласеру, полимери су комбиновани са јонским течностима (IL). Изучаване су различите јонске течности, као што су 1-метилимидазолиум-хлорид ([Mim]Cl из имидазолиум фамилије IL) и диетил-амонијум-дихидроген-фосфата (DEAP), триетиламонијум-4-аминотолуен-3-сулфонске киселине (TASA) и трибутилметиламонијум-метилсулфата (TBMS) из амонијум фамилије. По први пут је нађено да се ефикасност дифракције за 4 min повећала за DEAP––полимерну смешу у поређењу са самим полимером и осталим полимер–јонским течностима. Стога, може се закључити да јонска течност DEAP доводи до побољшања дифракционе ефикасности и то за краћа времена.

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