Effective holographic recordings in the photopolymer nanocomposites with functionalized silica nanoparticle and polyurethane matrix

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**Abstract**

Effective holographic nanocomposites were developed by the surface-functionalized silica nanoparticles and two acrylate monomers/polyurethane (PU) matrix polymer. The functionalization was done with silane compounds carrying long alkyl chain or vinyl group. We evaluated the holographic nanocomposite films by the diffraction efficiency, volume shrinkage, optical loss, and the film morphology. It was found that acrylate monomers/PU system gave higher diffraction efficiency than those of two monomers due to the high refractive index mismatch between the acrylate-rich and PU-rich regions. With the modification of silica particle, up to 35% of particle loading was possible to give a maximum diffraction efficiency of 93.6% for a film of 20 μm in thickness, along with improved refractive index modulation and the sensitivity.

**Keywords:** Holographic Nanocomposite Photopolymer Functionalized nanoparticle Diffraction efficiency

1. Introduction

Holographic photopolymers have been receiving great attentions in optical data storage materials and display devices because of their high sensitivity, large dynamic range, high flexible formulation and one step process, and versatile applications [1–5]. Especially, the holographic photopolymer films with various monomers and polymer binder systems have been well established with high diffraction efficiency and sensitivity [6–11]. Poly(vinyl alcohol), poly(vinyl acetate), poly(methyl methacrylate), and cellulose acetate butyrate were applied as binder polymer in these systems. Despite of such broad studies, the mechanism of refractive index modulation in monomer and binder system has not been yet clearly understood.

It is known that the high refractive index modulation of holographic photopolymers could be achieved by the addition of inorganic materials due to their much-larger range of refractive indices [12,13]. These organic–inorganic nanocomposite holograms also have the high recording sensitivity, low shrinkage, and good dimensional stability. Many research groups have developed various holographic nanocomposites containing titanium oxide [14,15], silicone oxide [16,17], zirconium oxide [18,19], etc. These nanoparticles were at first dispersed in photopolymerizable mixtures, mainly acrylate monomers, which subsequently are irradiated by recording beams with interference patterns, and accumulated in low intensity regions. Among them, titanium oxide nanoparticle is the most common material in photopolymer nanocomposite films due to its high refractive index. However, high incoherent scattering as high as 20% with average particle size of 15 nm has been a significant loss of light. Therefore, to reduce the optical loss silicone oxide nanoparticle is often used owing to its small refractive index difference from polymer matrix.

Silicone oxide nanoparticles have a very large organophobicity, so the surface functionalizations with special agents having high organophilic moiety have been attempted to improve the dispersion property in various organic materials [20–22]. Recently, the nanocomposites with several organophilic nanoparticles have been studied in the optical devices [23,12]. On the other hand, polyurethane (PU) would be a suitable binder polymer in holographic photopolymers due to its great transparency, flexible formulation, and easily controlled properties.

As far as the present authors are concerned, binder polymer has not been used for the holographic photopolymers with nanoparticles. We first time introduced amorphous and low viscosity PU as a matrix polymer for acrylate monomers/polymer matrix system with silica nanoparticles. Two acrylate monomers, acrylate monomers/PU, acrylate monomers/PU/silica nanocomposites at various film compositions are encountered along with the surface modification of silica particles in an attempt to achieve high refractive index and low volume shrinkage. Surface modification was done by functionalizing the particle surfaces with octyltriethoxysilane (OTEOS) and vinyltriethoxysilane (VTEOS) via hydrolysis and condensation reactions. We have characterized the grating
formation mechanisms and holographic properties by diffraction efficiency, refractive index, sensitivity, volume shrinkage, and morphology.

2. Experimental

2.1. Materials

Polyurethane matrix polymer was prepared with poly(propylene glycol) (PPG, Mn 3000, KPG, Korea) and 1,6-hexamethylenediol (HDI, Aldrich). PPG was dried and degassed at 80 °C under vacuum for 3 h before use. HDI and dibutyltin dilaurate (DBTDL, Aldrich) were all extra pure grades and used without further purification. Tri(methylolpropane) triacrylate (TMPTA, Aldrich), ethyl hexyl acrylate (EHA, Aldrich), Rose Bengal (RB, Aldrich), and N-phenylglycine (NPG, Aldrich) were all extra pure grades and used without further purification. Tri(methylolpropane) triacrylate (TMPTA), provides the mixture with a high viscosity of polymer mixture. Multifunctional monomer, tri(methylolpropane) triacrylate (TMPTA), ethyl hexyl acrylate (EHA, Aldrich), Rose Bengal (RB, Aldrich), and N-phenylglycine (NPG, Aldrich) were used as received to form a photopolymer mixture. Hydrophilic silica with average primary particle size 40 nm (Aerosil® OX 50) was obtained from Evonik Degussa GmbH (Germany) and modified with octyltrialkoxyxiliane (OEOX), vinyltriethoxysilane (VTEOS), ethanol, and ammonia solution from Aldrich.

2.2. Preparation of photopolymer mixture

PPG was reacted with a molar excess of HDI in round-bottomed, four-necked flask equipped with a mechanical stirrer, condenser, thermometer, and nitrogen inlet. The reaction was carried out at 70 °C of oil bath in the presence of an organometallic catalyst (0.03 wt.% DBT based on the total solid) to form a polyurethane matrix polymer (Mn 12,000). 2-ethylhexyl acrylate (EHA) was used as monofunctional reactive diluents, which helps to reduce the viscosity of polymer mixture. Multifunctional monomer, tri(methylolpropane) triacrylate (TMPTA), provides the mixture with a high reactivity and the polymer with a highly networked structure. The composition of PU/EHA/TMPTA was varied with the experimental conditions. The hydrophilic silica nanoparticles or the modified nanoparticles were added to this mixture and magnetically stirred for 24 h. 0.3 wt.% of Rose Bengal (RB) was used as the photo-initiator for the holographic recording with an argon ion laser because it displays a broad absorption in the region of 450–560 nm and has a high triplet quantum yield. 1.8 wt.% of N-phenylglycine (NPG) was also added as co-initiator. The excited RB undergoes an electron-transfer reaction in which NPG functions as an electron donor, producing an NPG radical. Free radical polymerization is then initiated by the NPG radical. Detailed procedures are also available with our earlier publications [24].

2.3. Preparation of modified silica nanoparticle

After the dispersion of 7 g of hydrophilic silica (Aerosil® OX 50, 40 nm) in 500 mL of ethanol, 14.5 g of OTEOS or 10 g of VTEOS (5 times of the hydroxyl groups on the surface of nanoparticle which was assumed to be 1.5 mmol/g) was added. The excess OTEOS or VTEOS ensures that the most hydroxyl groups on the surface of silica nanoparticles are substituted. 70 mL of ammonia solution was then added immediately to the solution which was stirred for the next 24 h at room temperature. The suspension was centrifuged at 3500 rpm for 20 min. Then, the particles were redispersed in ethanol and centrifuged, which was repeated three times. The modified silica nanoparticles were collected through a vacuum at 60 °C overnight. Potassium bromide pellets of the modified silica nanoparticles were prepared and scanned using FT-IR Spectrometer (Nicolet IR200, Thermo Fisher Scientific).

2.4. Grating formation

Photopolymer mixture was sandwiched between glass plates by capillary action, which has a gap of 20 μm by bead spacer. The optical setup to establish the interference pattern on the photopolymer films consisted of two coherent laser beams (Ar-ion laser) of 514 nm, which have the same intensity and the fixed incident angle of 30° against the line perpendicular to the plane of the recording cell. The diffraction efficiency of the holographic gratings was measured with a photodiode using an Ar-ion laser. The diffraction efficiency is defined as the ratio of I_{diff}/(I_tr + I_{diff}), where I_{diff} is the intensity of the diffraction beam and I_tr is the intensity of transmission beam. Real time grating formation was monitored using a He-Ne laser probe at 633 nm since the material is not sensitive to red light. Detailed optical setup is available elsewhere [24]. The morphology of the grating was characterized by scanning electron microscopy (SEM, Hitachi S430).

3. Results and discussion

3.1. Grating formation of photopolymers

Polyurethanes have been widely used in various optical devices because of their good optical properties. We prepared and used the transparent PU base polymer as a binder in the acrylates/photo-
polymer system. Fig. 1 shows the scheme of holographic recordings in our system. The holographic recording would be built up by the polymerization and diffusion of acrylate monomers under the interference patterns of the recording beams. Since multi-functional monomer polymerize fast in the high intensity regions because of the larger acrylate concentration than mono-functional acrylate, these monomers diffuse in while mono-functional monomers diffuse out of the high intensity region due to the concentration gradient formed in situ. This leads to the formation of refractive index modulation along with the grating formation between the two acrylate polymers at constant volume system as shown in Fig. 1a. The refractive indices of monomers are 1.474 for TMPTA and 1.436 for EHA, and RIs of polymers are 1.527 and 1.489, respectively. On the other hand, with two monomers and the polymer matrix system (Fig. 1b), the concentrations of the acrylate monomers are lower than those of the two monomers system, which lowers polymerization rate. The acrylate monomers diffuse slowly in the early stage due to the high mixture viscosity. This in contrast augments diffusivity at the last stage due to the low rate of reaction and viscosity increase. The multi-functional acrylate primarily polymerizes in the high intensity regions, followed by the diffusion and polymerization of mono-functional acrylate to some degrees. Therefore the refractive index modulation is achieved between the acrylate-rich and PU-rich regions by the grating formation. The RI of PU matrix is 1.454, so the refractive index differences are expected to be greater than 1.

Fig. 2 shows the real-time diffraction efficiency for various monomer/PU compositions at three beam intensities. The two acrylate monomers system exhibited a short induction period which was related to the inhibiting effect of impurities and oxygen dissolved in the system [25]. The diffraction efficiency then reached a maximum values, followed by an asymptotic decrease to a constant value. Such early overshoots are indicative of the fast polymerization and the easy diffusion due to the high monomer concentration and the low viscosity. In the two monomers/PU system, the overshoots faded away due to the higher viscosity and lower polymerization rate than the two monomer system. The diffraction efficiency increased steadily to the maximum value which were induced from the high refractive index differences between the acrylate polymer-rich regions and the PU matrix-rich regions.

With regard to the effect of beam intensity, the diffraction efficiency is maximum at 70 and minimum at 140 mW/cm² (Fig. 2). It seems that at high enough intensity the diffusions of monomers do not follow fast rate of reaction due to the large viscosity rise while the rate of reaction is slow at low enough intensity (55 mW/cm²) [26,27].

Table 1 shows the steady-state diffraction efficiency, refractive index modulation, and sensitivity of the holographic gratings as a function of monomer/PU compositions. The refractive index modulation was determined from Kogelnik’s two-wave coupled-wave theory for an unslanted volume transmission grating as follows [28]:

$$\eta = \sin^2 \left( \frac{\pi \Delta n d}{\lambda \cos \alpha} \right)$$

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer/PU weight composition</th>
<th>Monomer weight composition</th>
<th>Diffraction efficiency ((\eta), %)</th>
<th>Refractive index modulation ((\Delta n))</th>
<th>Sensitivity (S, (10^{-2}) cm²/mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>10/0</td>
<td>TMPTA/EHA = 2/1</td>
<td>17.7</td>
<td>0.0035</td>
<td>1.67</td>
</tr>
<tr>
<td>S2</td>
<td>8/2</td>
<td></td>
<td>44.4</td>
<td>0.0059</td>
<td>2.81</td>
</tr>
<tr>
<td>S3</td>
<td>6/4</td>
<td></td>
<td>58.4</td>
<td>0.0071</td>
<td>3.38</td>
</tr>
</tbody>
</table>

Fig. 2. Real-time diffraction efficiency for various PU/monomer weight compositions at three beam intensity values ((a) 55 mW/cm², (b) 70 mW/cm², (c) 140 mW/cm²).
where Δn is the refractive index change, α is the Bragg angle, λ is the wavelength of the incident beam, and d is the sample thickness. The sensitivity was also calculated by the following equation:

\[ S = \frac{\Delta n}{l} \left( \frac{cm^2}{mJ} \right) \] (2)

where Δn is the refractive index change, t is the exposure time, and I is the light intensity. The holographic photopolymers in the presence of PU matrix exhibited the higher diffraction efficiency, the higher refractive index change, and the higher sensitivity than those of the acrylate photopolymers only.

3.2. Preparation of the modified silica nanoparticle

Fig. 3 shows a possible mechanism of the silica surface modification. The alkoxyl groups of OTEOS/VTESOS become OH groups by hydrolysis in water. These react with the OH groups on the surface of silica particles as results of dehydration condensation under NH3 catalyst. Then these compounds are immobilized on the particle surface and form networks.

FR-IR spectra of the modified silica particles are shown in Fig. 4. In the spectra of VTEOS, typical stretching vibration and bending vibration peaks of ethyl (−CH3, −CH2−) were found at 2700–3000 cm\(^{-1}\) and at 1300–1500 cm\(^{-1}\), which disappeared in VTEOS-modified silica through dehydration condensation between ethoxy and OH group. The characteristic peaks of ethyl in OTEOS still remained in OTEOS-modified silica due to its long alkyl chains. On the other hand OH stretching vibration peaks around 3400 cm\(^{-1}\) did not show any difference. It implies that OTEOS/VTESOS reacted with the OH groups only on the surface of silica.

3.3. Grating formation of photopolymer nanocomposites

The addition of inorganic nanoparticles to photopolymer mixtures inevitably augments mixture viscosity depending on the particle content, size, and the nanoparticle dispersion. Our choice for matrix was low viscosity PU to allow more of nanocomposite at appropriate mixture viscosity. Silica was used owing to its small refractive index mismatch with polymer matrix and low light scattering property. Aerosil OX 50 of RI 1.46 was used in this research. However, inorganic silica particles are usually aggregated in organic polymers and increase the mixture viscosity. So, we organically modified the silica by introducing OTEOS or VTEOS onto the particle surfaces via hydrolysis and condensation reactions. This is expected to alleviate particle aggregations and augment particle loading by interface modification.

On the other hand, silica particles in photopolymer mixtures are known to diffuse out of the polymerizing regions and accumulated in low intensity regions, which would positively affect diffraction [12,14]. Contrary to NP diffusion, almost the whole monomers are accumulated in high intensity region, so the refractive index difference between PU/NPs region and PU/acrylate polymer region would be greater. As expected, the diffraction efficiency of photopolymer films increases with the addition of untreated nanoparticles (Series A in Table 2). However, loading over 15 wt.% was not implemented due to the excessive particle aggregations and viscosity rise. When the particles were organically modified (Series B and C) loadings up to 25 (OTEOS) and 35% (VTEOS) were possible alongside substantial increases in diffraction efficiency with a maximum of 93.6% at 35% VTEOS.

Typical real-time diffraction efficiencies are seen in Fig. 5. At the same content of silica particle (15%), the initial rate of diffraction efficiency increases along A < B < C according to the hydrophobicity increase. However, as the particle content increases, the initial rate of diffraction decreases while the steady state efficiency increases monotonically. It seems that viscosity and hence diffusion dominates grating formation at the early stage while the steady state diffraction depends more on eventual grating formation.

On the other hand super hydrophobic silica with VTEOS was expected to participate in radical reaction. If it is, NPs somewhat migrate to polymerizing region and the diffraction efficiency is depressed compared to hydrophilic NP system. However DEs of series C are larger than those of series B because the diffusion velocity of large NP is smaller than monomer diffusion velocity. Also the mixture viscosity is very influential factor in grating formation.

3.4. Volume shrinkage

Typical organic photopolymer films containing acrylate monomers shows volume shrinkages during grating formation, which poses problems in the perfect and clear data recordings. The inorganic fillers are expected to reduce the volume shrinkage because of their high dimensional stability and to achieve the high diffraction efficiency. Fig. 6 shows the typical angular selectivity for the photopolymer films where the volume shrinkage is calculated by the following equation for slanted holographic grating [29]. Detailed data are shown in Table 3.

Degree of volume shrinkage \( \Delta \) is calculated as:

\[ \Delta = \tan \varphi \tan \varphi' \left( \tan \varphi' - \tan \varphi \right) / \varphi \]

where \( \varphi \) is the slanted angle at thickness \( d \), \( \varphi' \) is the slanted angle at \( d' \), and \( A/\tan \varphi' \) is the grating spacing. Volume shrinkage along with
the angular deviations from Bragg’s law by sample beam and reference beam, the slanted angle are shown. Volume shrinkage significantly decreases with the addition of matrix polymer (S1 vs. S3), and with the addition and increasing amount of particle. At the same content of particle, volume shrinkage decreases along A > B > C due to the finer dispersion of the particles which, on the other hand, is based on the effective surface modification. The actual film thickness after grating formation ($d_0$) was varied for $17 \pm 1.2 \ \mu m$ within the limit of volume shrinkage.

Furthermore, it should be mentioned that the optical loss of C35 was only 2.9% when calculated by $\text{OL} (\%) = 1 - (I_{diff} + I_{tr} + I_{refl})/I_0 \times 100$ ($I_0$: incident beam intensity, $I_{diff}$: diffracted beam intensity, $I_{tr}$: transmitted beam intensity, $I_{refl}$: reflected beam intensity).

### 3.5. Morphology

Typical grating formation morphologies of the holographic films are seen in Fig. 7. It is clear that matrix polymer is essential for grating formation (Sample S). The holographic films with silica nanoparticles appear the distinct grating formation between high and low intensity regions (Sample A, B, C). The holographic films containing hydrophilic silica are observed to have large aggregations, while the OTEOS-modified silica is evenly dispersed in the holographic film. On the other hand we have found some particle aggregations in the VTEOS-modified silica, which is induced by its reactive sites. However it doesn’t seem possible to conclude whether the particles exist in high or in low intensity region by SEM morphologies.
4. Conclusions

Acrylate monomer (TMPTA/EHA)/PU system gave higher diffraction efficiency than those of two monomers because of the high refractive index differences between the acrylate-rich regions and the PU matrix-rich regions. Also the former system exhibited the higher refractive index change, the higher sensitivity, and the clearer gratings than the latter one.

A maximum diffraction efficiency of 93.6% was achieved by incorporating 35 wt.% of silica nanoparticles. Such high loading was possible by introducing silane compounds with long alkyl chain (OTESOS) or vinyl group (VTEOS). The refractive index modulation and the sensitivity also increased with the addition of silica nanoparticles. On the other hands the diffraction efficiency in the early stage increased rapidly according to the addition of the hydrophobic moiety to silica.

The holographic nanocomposite films showed decreased volume shrinkages below those of no particles and two monomers system, with an optical loss of only 2.9%. 

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References