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Diffraction efficiency change in PVA/AA photopolymer films by photosensitive inorganic compound addition

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Abstract−The highest diffraction efficiency (DE) value after illumination and post-curing of photopolymer films were obtained at the SeO_2/Acrylamide (AA) Ratios of AA 3.0 g, SeO_2 1.0 g and the DE's were stable values of over 90%. By the addition of SeO_2, the maximum DE at the initial stage of illumination was reached at 300 seconds, which suggests SeO_2 slows down the photopolymerization of. DE variation curve for the optimum composition during extended-time illumination of 9,000 seconds resembles a sine curve due to the combination of the monomer diffusion and the photopolymerization, and the photopolymer film expanded at about 8% after photopolymerization due to monomer migration.

Key words: Photopolymer Film, Diffraction Efficiency, Acrylamide, Polyvinyl Alcohol, Photo Polymerization, Selenium Dioxide

INTRODUCTION

Recently, research on holographic recording material by optical recording has been attracting strong interest, and applications on digital recordings, watermarking, and hologram recording have been continuously conducted [1-3]. Holographic recording materials are silver halides, photographic emulsions, dichromated gelatin, photo resists, photopolymers, photochromics, photo thermoplastics, photorefractive materials. Among them, photopolymers which show high diffraction efficiency (DE) record images and data by the intensity modulations of recording optical light. Since photopolymers can be recorded by light exposure (self-developing), chemical treatments are not required for recording data or images and only drying processes are needed for manufacturing final products. Due to these advantages, photopolymers have be applied on various holographic optical elements (HOE) and films for security/surveillance holograms; also, they can be applied in the near future as media for holographic digital data storage (HDDS) and 3-D images, high speed optoelectric parts [4-6].

The fundamental theory of holographic recording with photopolymer can be explained as follows. Photopolymer consists of binding polymer, monomer, photosensitizing dye, and initiator. Upon exposure of laser light with holographic data photo polymerization can be initiated by absorbing energy and by sensitizing dye and decomposition of initiators. Holographic exposure produces spatial diffraction patterns due to photo-initiated polymerization [7]. A concentration gradient of un-reacted monomers between exposed and unexposed areas induces diffusion of the monomers from unexposed zone to exposed zone. This diffusion produces a compositional gradient, establishing refractive index grating, which makes it possible to record digital data or optical patterns. Reduction reaction of photo initiator proceeds when the film is illuminated by laser light of 532 nm wavelength. A photopolymerization reaction generally happens in three steps. The reaction mechanism is expected to follow three reaction steps as shown in Eq. (1). Polymer binder is not included in the reaction mechanism; however, the reaction speed and reaction process are severely influenced by the properties of the binders, mainly local viscosities [8-11].

$$\begin{aligned}&\mathrm{DYE}\rightarrow h\nu\rightarrow \mathrm{DYE}^*\\&\mathrm{DYE}^*+\mathrm{Am}\rightarrow \mathrm{Am}^*+\mathrm{LDYE}\\&\mathrm{Am}^*+\mathrm{M}\rightarrow \mathrm{P}\end{aligned}\tag{1}$$

DYE: photosensitizer
Am: photoinitiator
DYE^*: excited photosensitizer
LDYE: whitened photo sensitizer (decolored)
P: polymerization
Am: photoinitiator
Am^*: excited photoinitiator
M: monomer

When the volume of photopolymer film decreases upon light exposure, the shrinkage of exposed film may cause changes of the recording angle and reading angle due to the deviation of the Bragg angle. This shrinkage of film confines the recording density increase. To solve this film shrinkage problem, two kinds of shrinkage-free photopolymer material were introduced: photo-attaching or photo-detaching photopolymers in which monomers are attached on or detached from polymeric binders by light exposure, and ring opening photopolymers in which photopolymerization occurs through ring opening polymerization by cations generated from light-sensitive photoacid generators (PAG). These two photopolymers showed low shrinkage upon exposure (~0.5%); however, diffraction efficiencies are considerably lower and the research on enhancing diffraction efficiencies has been continuously pursued [12,13].

In general, reflection patterns in light-induced polymerizing photopolymers are explained as in Fig. 1. At first, lighted beams with reflection pattern by positive and negative interferences illuminated

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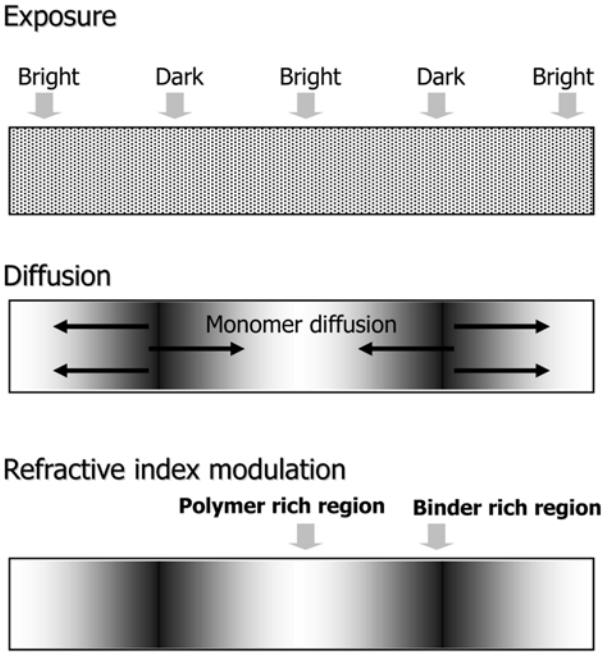

Fig. 1. Diffraction grating formation in holographic media after exposure.

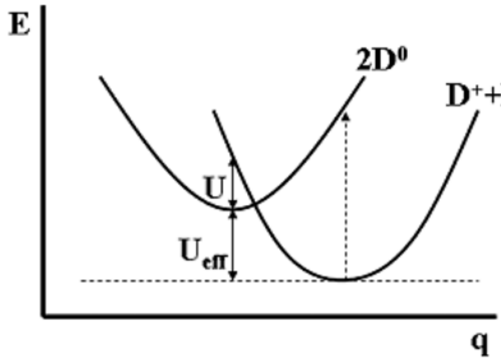

Fig. 2. Energy state by metallic bonding of selenium.

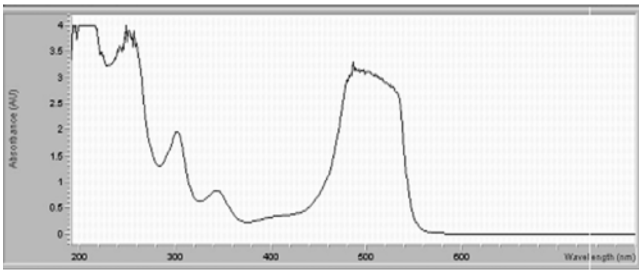

Fig. 3. Absorbance peak of Eosin Y.

the photopolymer film, and then photopolymerization took place on the area of positive interference of light. Monomer diffusion takes place due to the concentration differences between photo-polymerized zones of low monomer concentration and unpolymerized zones of high concentration.

Binding polymers must contain monomers and other ingredients in stable condition without phase separation throughout light-induced photopolymerization and must contain adequate viscosity for appropriate monomer diffusion with high transparency. As binding polymers for photopolymers, PMMA's, PVA's, siloxane polymers, and polycarbonates have been used. Among them, PVA's are water soluble and so the film manufacturing is more convenient; however, water and heat resistances of the films are low and there are few water soluble initiators for photopolymer synthesis. The popular initiator for PVA photopolymer is TEA, which has slow initiating speed, so activator is required to maintain proper polymerization speed. Since siloxane polymers have good thermal and photo stabilities and water resistance, they have attracted notice in photopolymer research. The solubility of siloxane polymers and monomers, initiators, and other ingredients is usually poor, so the solubility should be enhanced to develop commercial siloxane photopolymers [14-20].

Inorganic light-sensitive particle addition such as Kalcogenide materials has been attracting strong interest due to their unique photoactive characteristics and they are used as inorganic thin-film holographic storage materials. In this study, the effects of SeO_2 inorganic crystal addition are examined with green laser light (532 nm) sensitive PVA/AA-based photopolymer systems. SeO_2 crystals act as an oxidizing agent which is self reduced by light. SeO_2 crystals are used in this research to promote photosensitivity of dye and so enhance the photopolymerization characteristics (Fig. 2) SeO_2 crystals are considered to be introduced to prepare photopolymer systems in this research. Enhancements in optical characteristics and storage stabilities of photopolymer systems are examined by adding SeO_2 crystals as nano scale mixtures. The catalytic behaviors of inorganic photosensitive materials would be examined to develop optimized photopolymer for holographic recording [21,22].

MATERIALS AND METHODS

1. Materials

Components for the photopolymer system in this research are PVA for binder, acrylamide (AA) for photopolymerization monomer, TEA (triethanol amine) for initiator and Eosin Y for a photosensitizer which has high absorption on 488 nm-532 nm wavelength laser light as was shown in Fig. 3. Our previous research showed reliable response on holographic recording with these compositions [23-25]. SeO_2 crystals are selected as photo-oxidized inorganic crystals (Kanto Chemical Co., Inc). The molecular weights (Mw) of PVA polymer binders were selected as 89,000-98,000, which are considered to be the adequate internal viscosities for AA monomers to diffuse freely through the binding matrix of photopolymer films. In this experiment, high pure grade chemicals were used without further purification, since small amounts of impurities would not make any serious difference in density modulation upon photopolymerization.

2. Synthesis of Photopolymer Film

The first step of the synthesis of photopolymer films is the process of complete mixing of every component. PVA has to be heated to 80 °C to be melted and liquefied. Previously mixed solutions of AA, TEA, Eosin Y and SeO_2 are mixed with liquefied PVA to be clear solutions. In this experiment, PVA was heated first in a water bath without mixing other components for longer than 30 minutes, and then it was cooled to room temperature until it was used for mixing. AA, TEA, Eosin Y, and SeO_2 were completely solvated to be a transparent solution, and then mixed with cooled PVA for more than 2 hours with magnetic stirrer for high viscous PAV to be evenly mixed with other ingredients.

The composition variation experiments of the addition of SeO_2 inorganic particle were made in two different methods. Firstly, the optical characteristics of the films were observed with the variation of inorganic SeO_2 component, while other ingredients were kept constant. Secondly, total amounts of AA and SeO_2 were kept constant at 4.0 g, while the compositions of AA and SeO_2 differentiated relatively when the photopolymer films were prepared. The optical properties were detected afterwards. The compositions adopted in these experiments are shown in Tables 1 and 2. Photopolymer films without mixing SeO_2 were prepared and optically observed as standard samples for comparisons with other films with SeO_2.

Table 1. SeO_2 content variation experiment (Experiment 1)

No.	PVA (g)	AA (g)	TEA (ml)	Eosin Y (g)	Water (ml)	SeO_2 (g)
Std.	10	4	2	0.003	100	-
1	10	4	2	0.003	100	0.5
2	10	4	2	0.003	100	1
3	10	4	2	0.003	100	1.5
4	10	4	2	0.003	100	2
5	10	4	2	0.003	100	2.5
6	10	4	2	0.003	100	3

Table 2. AA+SeO_2 total content variation experiment (Experiment 2)

No.	PVA (g)	TEA (ml)	Eosin Y (g)	Water (ml)	AA (g)	SeO_2 (g)
Std.	10	2	0.003	100	4	-
1	10	2	0.003	100	3.5	0.5
2	10	2	0.003	100	3	1
3	10	2	0.003	100	2.5	1.5
4	10	2	0.003	100	2	2
5	10	2	0.003	100	1.5	2.5
6	10	2	0.003	100	1	3

3. Optical Characteristics Measurement Apparatus for Photopolymer Films

Most important optical characteristics for photopolymer films are DE (diffraction efficiency) and TE (transmittance efficiency). Angle selectivity, which is closely connected with storage density and recording sensitivity, may be the important optical character. High angular selectivity is required for photopolymer films for HDDS (holographic digital data storage); however, in low density holographic storage application, angular selectivity is not sensitive for recording property. DE was adopted as the reference property to decide the optical property of the photopolymer film in this experiment. There are two equations for the calculation of DE values. Eq. (2) is derived from the ratio of the intensity of diffracted beam and the intensity of original incident beam of the laser light. In Eq. (3) DE's are estimated from the ratio of the intensity of pure diffracted beam and the intensity of pure transmission beam in which scattered and diffracted beams before passing the photopolymer film, the reflected beam on the photopolymer surface, and the scattered beam inside the photopolymer film are not considered in this calculation. Eq. (3) is usually adopted for DE calculation in most research with an assumption of having high TE value of the films, so Equation (3) was utilized for DE calculation in this research [26].

$$\mathrm{DE}\ (\%) = \frac{\text{Diffraction beam intensity}}{\text{Incident intensity of the applied laser light}} \times 100 \qquad (2)$$

$$\mathrm{DE}\ (\%) = \frac{\text{Diffraction beam intensity}}{\text{Diffraction beam intensity} + \text{Transmission beam intensity}} \times 100 \qquad (3)$$

The optical characteristics measurement apparatus used in this research was the DE measurement apparatus designed by PrizmTech Co. as shown schematically in Fig. 4. This apparatus was composed

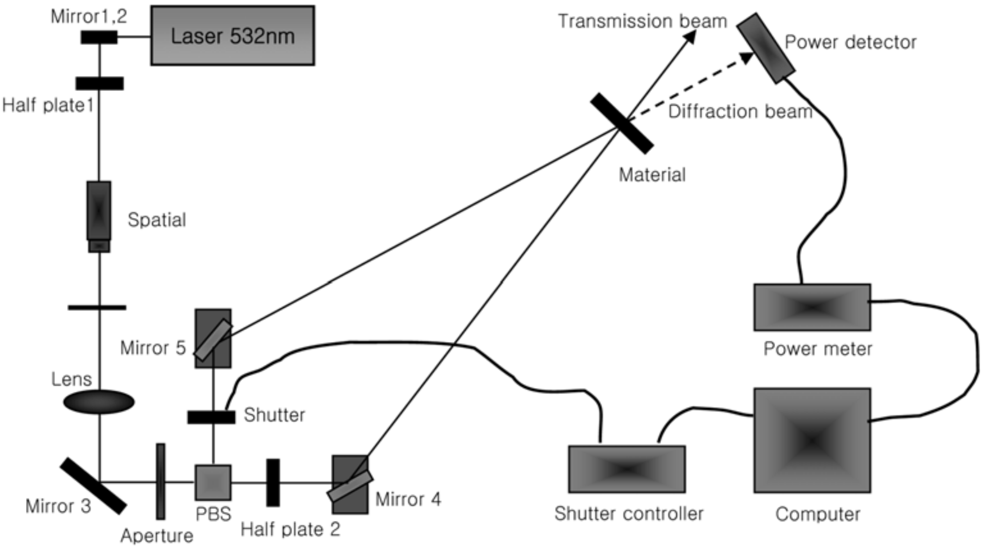

Fig. 4. Measuring systems for diffraction efficiency of photopolymer system.

of a laser of maximum power of 100 mW and wavelength of 532 nm, spatial filter, lens, PBS (polarized beam splitter), shutter, mirrors, power detector, and controller. In this research, the intensity of the laser light was fixed at 50 mW, the opening and closing times of the shutter were fixed at 3 s, 0.5 s, and the 2θ were fixed at 40° to obtain maximum diffraction efficiencies. The intensity of laser light, the opening times of the shutter, and 2θ values may be modified by operating conditions for the best results.

4. X-Ray Diffraction Measurement

XRD is applied for determining distances between atoms and atomic layers by illuminating X-ray to the material and observing the constructive interference of the diffracted X-ray. Usually, XRD is used for crystalline materials, which have ordered arrays of atoms. In this research, XRD was adopted to examine whether added SeO_2 is in crystalline state or amorphous state. RINT2000 (Rigaku) generates X-rays, D3 system (Bede) is attached for data processing.

RESULTS AND DISCUSSION

1. Diffraction Efficiency (DE)

DE's were obtained by manipulating the measuring system (Fig. 5) using MPAS operating program(S/W, prism tech.). After exposing for 3 seconds, the shutter was closed, and the intensities of diffracted beams of reference beams were measured. The above sets of measurements were repeated up to 300 times to get the DE value. The intensity of the beam was controlled at 50% of the maximum intensity of the laser (100 mW). DE's of samples in Experiment 1 (Table 1) are in Fig. 5.

In Fig. 5, maximum DE's were observed at 100-150 seconds for the standard sample without SeO_2, DE's dropped up to 30% at measuring time of 900 sec (15 minutes). This is a typical behavior of DE of conventional photopolymers. By the addition of SeO_2, the maximum DE reached slower at 300 seconds, which suggests SeO_2 slows down the photopolymerization of monomers by absorbing and storing light energy. At the initial photopolymerization stage, the density of exposed zone increases as the beam exposure continues. As the polymerization is completed and the monomers turn into polymers, the density of the exposed zone stays constant; however, the surroundings of the exposed zone keep polymerizing, so the density difference decreases. As the contents of SeO_2 increase, the DE's at 900 seconds increase because of the smaller decrease from the maximum DE values. This phenomenon can be explained as the effect of SeO_2, which first absorbs light energy and then transfers to initiate polymerization. By storing light energy, the efficiency increases and the photopolymerization slows down to allow more monomer to transfer from dark area to exposed area. As SeO_2 increases, the final DE's (after 900 seconds) increase. Table 3 shows the final DE's for every sample.

Table 3. Diffraction efficiency of samples after 15 minutes (Experiment 1)

No.	DE (diffraction efficiency, %)
Standard	28.5%
1	46.3%
2	48.8%
3	56.1%
4	88.8%
5	- (separation)
6	- (separation)

In Samples 5 and 6, phase separations occurred during drying the photopolymer films because the amount of AA and SeO_2, which were in powder form, exceeded the maximum solvation concentration in PVA. If the phase separations occurred, transparencies of the photopolymer films decreased, and the scattering of light and the diffraction of light were detected together. The diffraction of Samples 5 and 6 could not be observed due to the scattering of the samples.

The components of the photopolymer samples of experiment 2 (Table 2) were designed to determine optimum ratio of monomer and inorganic compound while avoiding phase separation between non-polar organic phase and polar organic and inorganic phases. With avoiding phase separation and scattering problems of the photopolymer films in DE measurements, the total amounts of powder

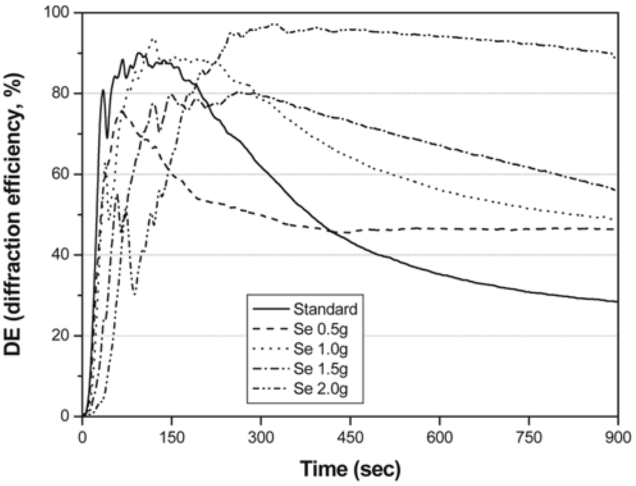

Fig. 5. Diffraction efficiencies of PVA/AA photopolymers with adding different amounts of SeO_2.

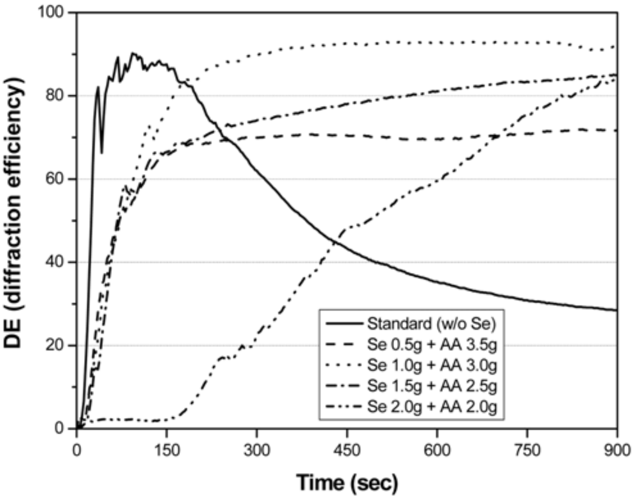

Fig. 6. Diffraction efficiencies of PVA/AA photopolymers with changing ratios of SeO_2 and AA.

components, AA and SeO_2, were fixed at the maximum value without the phase separation in Experiment 2. To get the optimum ratio between AA and SeO_2 several different ratios of AA/SeO_2 were selected and the DE's for each samples were observed; the experimental results are shown in Fig. 6. For sample 5 and sample 6 in experiment 1, DE's could not be measured because of the large scattering from the phase separation of added AA and SeO_2 with PVA binder. For sample 5 and sample 6 in experiment 2, DE's were too small to be accurately observed due to the small amount of added photopolymerizing monomer AA.

In experiment 2, DE's of sample 1, 2, and 3 showed stablegrowth and plateau after extended illumination past maximum DE values. However, sample 4 showed relatively late growth of DE compared to other samples. AA content of sample 4 was smaller than for other samples, because not enough AA was supplied for photopolymerization unless AA transferred from neighboring area by diffusion. So the low DE growth rates depended not only on the photopolymerization reaction rate but also on the diffusion rate of AA. The final DE values are summarized in Table 4 after 15 minutes of illuminations and post-curing of each sample; sample 2 of AA 3.0 g, SeO_2 1.0 g showed best DE characteristics and final stable values of over 90% continuously.

For the composition of sample 2 in experiment 2, which showed optimum composition in this experiment, a long time illumination experiment to observe DE variation was conducted, in which illumination time was 10,000 seconds. DE of over 90% was sustained throughout the illumination of 10,000 seconds, not like DE's of previous photopolymers without adding SeO_2 which were decreasing after 600 seconds. This stable tendency of DE values was shown for other samples, sample 1, and sample 3, of experiment 2. Fig. 7 shows DE variation curve for sample 2 in experiment 2 during illumination of 9,000 seconds. The fluctuation of the DE curve was considered to be the post diffusion of monomers and the change of density by rearrangements of polymer chains. However, these phenomena should be further studied to explain clearly.

Table 4. Diffraction efficiency of samples after 15 minutes (Experiment 2)

No.	DE (diffraction efficiency, %)
Standard	28.5%
1	71.7%
2	91.8%
3	85.0%
4	83.8%
5	- (no reaction)
6	- (no reaction)

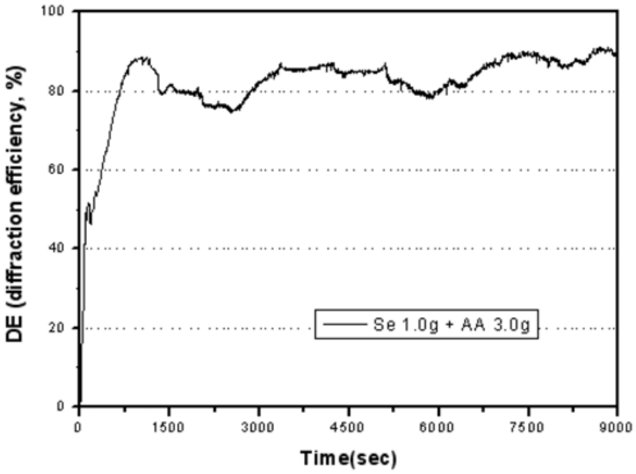

Fig. 7. Diffraction efficiencies variation curve for sample 2 in experiment 2 for 9,000 sec.

2. XRD (X-Ray Diffraction)

In Fig. 8(a), X-ray diffraction peaks of pure SeO_2 inorganic crystals are shown in which sharp crystalline peaks of SeO_2 from 20° to 50° were clearly found. Fig. 8(b) shows the X-ray diffraction peaks

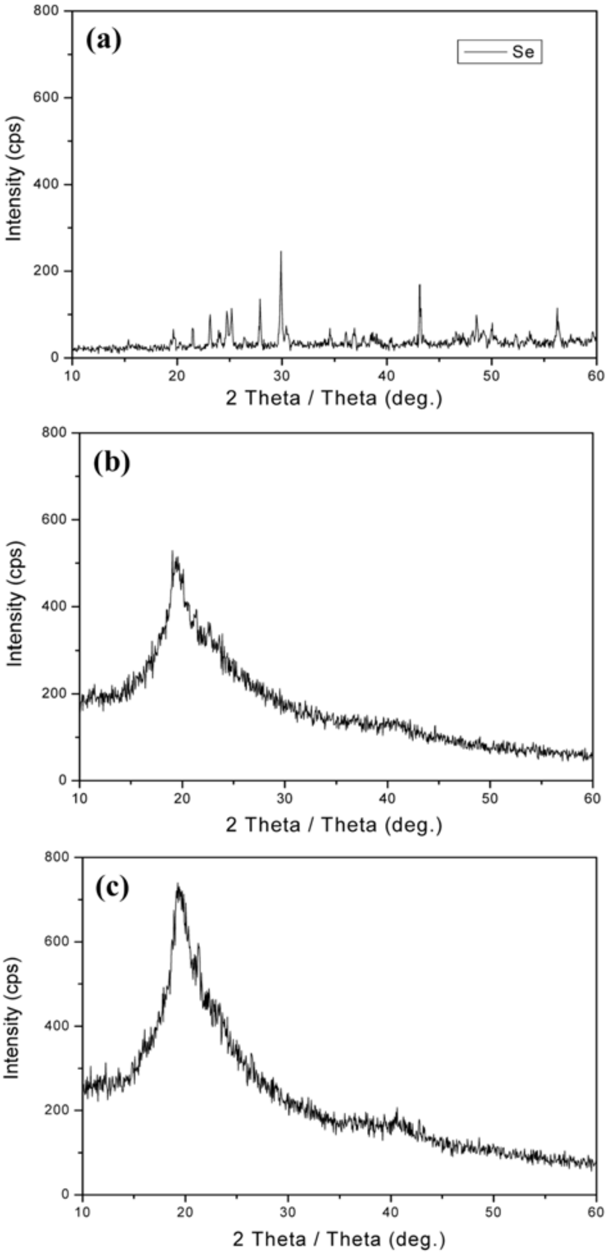

Fig. 8. XRD peak of SeO_2 crystals and photopolymer film.
(a) SeO_2, (b) Film without SeO_2 crystals, (c) Film with SeO_2 crystals

Table 5. Thickness of photopolymer film

No.	Thickness (μm)	No.	Thickness (μm)	No.	Thickness (μm)
1	97	8	101	15	91
2	95	9	95	16	95
3	94	10	97	17	97
4	98	11	99	18	96
5	95	12	95	19	98
6	98	13	94	20	95
7	96	14	98		
Average	96.2 μm		Deviation		±3 μm

Table 6. Thickness of film by photopolymerization

No.	Thickness (μm)	After (μm)	No.	Thickness (μμ)	After (μm)
1	97	105	11	99	111
2	95	101	12	95	103
3	94	101	13	94	102
4	98	106	14	98	106
5	95	101	15	91	95
6	98	106	16	95	102
7	96	105	17	96	103
8	101	113	18	97	105
9	95	100	19	98	106
10	97	103	20	95	105
Average		103.9 μm	Conversion rate		+ 8%

of photopolymer samples without adding SeO_2. The diffraction did not show crystalline sharp peaks; instead there was a broad curve which is typical for amorphous polymers. In Fig. 8(c), the X-ray diffraction of photopolymer sample with SeO_2 is shown. The sharp crystalline peak which was shown in crystalline SeO_2 disappeared; however, the peak at 20° increased greatly compared to (b). SeO_2 inorganic crystals were solvated in photopolymer since there was no crystalline SeO_2, and the SeO_2 mixed with organic photopolymer in smaller scale than X-ray crystalline size which can be included in nano-scale, and the polymer ordering showed improvement, which was shown through the increase of the peak at 20°.

3. Contraction Rate of Photopolymer Film on Photopolymerization

Thicknesses of photopolymer films were measured to estimate the contraction rate of photopolymer films during photopolymerization at illumination. Digimicro (ZC-101, NIKON Co.) was adopted for thickness measurements, which had accuracy of 10^{-4} mm, and the effective thickness was observed in 10^{-2} mm order in this experiment.

Thicknesses of the photopolymer films before illumination are summarized in Table 5. The films were made by dropping 2.0 ml-solution of photopolymer mixture on a slide glass and by drying for 72 hours at room temperature of relative humidity of 40%. The average thickness of the films was 100±10 μm, and the flatness of the films was so good as to minimize the scattering and the reflection at the film surface. Films were made with 100 μm thickness for faster drying and better surface quality. For preparing 100 μm films, a 2 ml photopolymer mixture was dropped on the glass. By volumetric calculation, the thickness of the film before drying should be 1.2 mm.

When photopolymerization proceeded by illumination, AA monomers were photopolymerized to produce poly-acrylamide. Synthesized poly-acrylamide chains were intercalated with PVA polymer binder because the monomers were permeated inside the PVA polymer binder. By this photopolymerization, monomers were used and so the concentration of the monomer decreased. During the photopolymerization reaction, monomer from the surrounding area migrated to the illuminated area where monomers are consumed for the photopolymerization and so the concentration of the monomer was low. By this migration and photopolymerization of the monomers, the photopolymer film expands during illumination as shown in Table 6. In other photopolymers using PMMA or epoxy as a binder, contraction of the photopolymer film on illumination observed due to photopolymerization of monomers soaked inside the binder, and this contraction sometimes became a cause for crack and surface problems like flatness and transparency. The photopolymer in this research, which was using PVA as a binder, expanded on illumination. High flexibility of PVA polymer enables monomer to migrate into the illuminated area from dark area of destructive interferences where photopolymerization did not take place. The flexible PVA binder expanded when AA monomers migrated to the illuminated zone. There was neither expansion nor contraction observed upon exposure of 10 minutes to sun light, which suggested that there were little changes of volume during photopolymerization of AA.

CONCLUSION

From this research, several new findings can be summarized as follows:

1. By the addition of SeO_2, the maximum DE reached slower at 300 seconds, which suggests SeO_2 slows down the photopolymerization of monomers by absorbing and storing light energy.
2. As the contents of SeO_2 increase, the DE's at 900 seconds increase because of the smaller decrease from the maximum DE values. This phenomenon can be explained as the effect of SeO_2, which first absorbs light energy and then transfers to initiate polymerization.
3. The final DE value after 15 minutes of illuminations and post-curing of sample 2 (AA 3.0 g, SeO_2 1.0 g) showed best DE characteristics and final stable values of over 90% continuously.
4. DE variation curve for sample 2 in experiment 2 during extended-time illumination of 9,000 seconds resembles a sine curve due to the combination of the monomer diffusion and the photopolymerization.
5. The sharp crystalline peaks which were shown in crystalline SeO_2 disappeared; however, the peak at 20° increased greatly compared to that of pure photopolymer. SeO_2 inorganic crystals were solvated in photopolymer since there was no crystalline SeO_2.
6. High flexibility of PVA polymer enables monomer to migrate into the illuminated area from dark area of destructive interferences where photopolymerization did not take place. The flexible PVA binder expanded about 8% when AA monomers migrated to the illuminated zone.

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