PHOTOREFRACTIVE COMPOSITES BASED ON ACRYLATE AND STYRENE TYPES OF TRIPHENYLAMINE POLYMER

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ABSTRACT

Two types of photorefractive (PR) composite based on acrylate and styrene type of triphenylamine polymer were fabricated. The PR performance was evaluated through diffraction efficiency, response and decaying time. These parameters could be obtained by applying degenerated four waves mixing method. The composite based on styrene type had faster response and decaying time while diffraction efficiency was only 16 %. The composite using acrylate type had slightly slow response results. However, the diffraction efficiency could reach 30 % and shelf-life was significantly improved.

Keywords: Composite, triphenylamine, photorefractive, polymer.

1. INTRODUCTION

Photorefractive (PR) polymer and composite, a fascinating materials for photonic applications, has attracted wide attention from optics and photonics researchers [1]. Owing to ability to continuously update holographic data, the material was considered as one of the potential approaches toward real-time three-dimensional display [2-5]. For a material which can perform PR effect, it must possess two characteristics, i.e. photoconductivity and nonlinear optical (NLO) property. These two are combined into a material by several ways [1, 6, 7]. However, the PR material under the form of a composite has been proven to be a versatile and feasible method. A chromophore, a birefringent molecule with high polarity, is added to create NLO property which is ability of changing refractive index under the affection of electric field. A photoconductive polymer is usually used as a dispersive matrix for the other components and to provide a photoconductive media. To assist charge generation which is very important for photoconductivity, a small amount of sensitizer is additionally added. The sensitizer is a molecule which absorbs light at the wavelength of laser source as writing beams. Another component is plasticizer. It was firstly used to reduce the viscosity for processing. After discovering orientational enhancement in PR effect [8], the plasticizer is also found to be important to improve PR effect significantly including PR response time [9, 10]. In addition to re-orientation speed, the PR response time strongly depends on photoconductivity [11-13]. To satisfy the requirement for applications, many composite and photoconductive material types were introduced and investigated [6, 14]. Triphenylamine-based PR composites have shown several interesting properties such as fast response [9, 15] and high diffraction efficiency [13]. The grating formed by electron transport at a moderate applied electric field was also reported by Giang *et al*. [16]. However, in most studies, the speed of grating formation process was the main concern to compare with the previous materials or to prove their superior in PR performance. For real-time applications, the writing and erasing processes have to be included in an investigation to have the best overall evaluation for each material. In this study, two types of triphenylamine photoconductive polymer, acrylate and styrene type were used to fabricate PR material. The acrylate type is poly(4-diphenylamino)benzyl acrylate)) (PDAA) and the styrene type is poly(4-diphenylamino styrene) (PDAS). The two composites had similar components to have a better comparison. The rising time and decaying time were investigated by degenerated four-wave mixing (DFWM) method. The ability to apply to future research shall be discussed.

2. EXPERIMENTAL SECTION

2.1. Materials and PR cells preparation

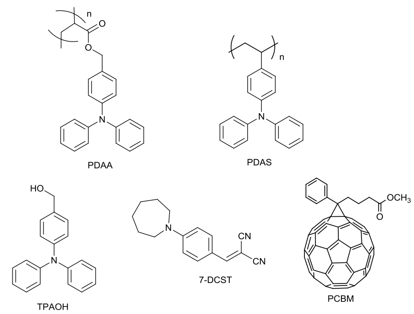

Figure 1. Chemical structures of components for PR composite

The polymer of PDAA or PDAS was weighed at an appropriate ratio comparing to other components and used as the main photoconductive matrix for the composites. (4-Azepan-1-yl)benzylidene)malononitrile (7DCST) was mixed into the composite with the role of NLO chromophore and provided the change in refractive index. (4-(Diphenylamino)phenyl) methanol (TPAOH) was added to reduce the viscosity of the composite matrix and supported the re-orientation of the chromophore. Phenyl-C61-butyric acid methyl ester (PCBM) was used as the sensitizer to enhance absorption property following by the charge generation at the used laser's wavelength. The chemical structures and abbreviations of each component are shown in Figure 1.

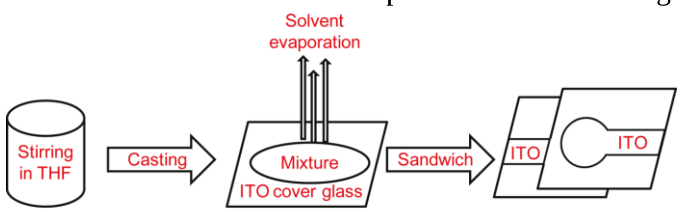

Figure 2. PR cells fabrication

All steps for PR cells preparation are summarized in Figure 2. The composites compound with ratio of PDAA/7DCST/TPAOH/PCBM (45/30/24/1) and PDAS/7DCST/TPAOH/PCBM (45/30/24/1) were dissolved in the solvent of tetrahydrofuran (THF). Then, solvent was evaporated under ambient atmosphere for 24 hours at the temperature of 70 ºC using a hot plate. The composite compound after drying was used to fabricate the PR cells. The composite was melted at 150 ºC on a hot plate and sandwiched between two indium tin oxide (ITO) covered glasses as described in Figure 2. A spacer was placed in the ITO glasses to control the thickness (90 µm). After the clear PR film composite was formed, the PR cell was quickly cooled down by a cold plate.

2.2. PR properties characterization

After successfully preparing the PR cells, they were used to characterize the PR performance. In this study, diffraction efficiency, response time and decaying time are the main focus. These properties could be evaluated by using degenerated four-wave mixing (DFWM) method. DFWM's geometry with optical system design is shown in Figure 3. In this geometry design, the laser from a 633 nm source (10 mW) went to a polarized beam splitter (PBS). Beam light from the laser source usually has *s* polarization which means the electric field direction is perpendicular to the plane of incidence. Therefore, only a very small part of the beam with *p* polarization (i.e. the electric field direction is parallel to the plane of incidence) could go through the PBS. This low intensity beam was used as a reading beam. A haft wave plate (HWP) was placed between the PBS and the laser source to control intensity of the reading beam. A strong intensity beam was reflected off by the PBS with *s* polarization. This beam was passed through a BS to have two writing beams with a same intensity. The two beams were directed by a mirror system to interfere at the position of PR sample. Electric field was applied to PR sample by a high voltage source. The reading beam was directed to counter propagate to one of the writing beams. Two different BSs were placed in the pathways of the writing beams to reflect the transmitted and the diffracted beam. The signals could be recorded by an oscilloscope.

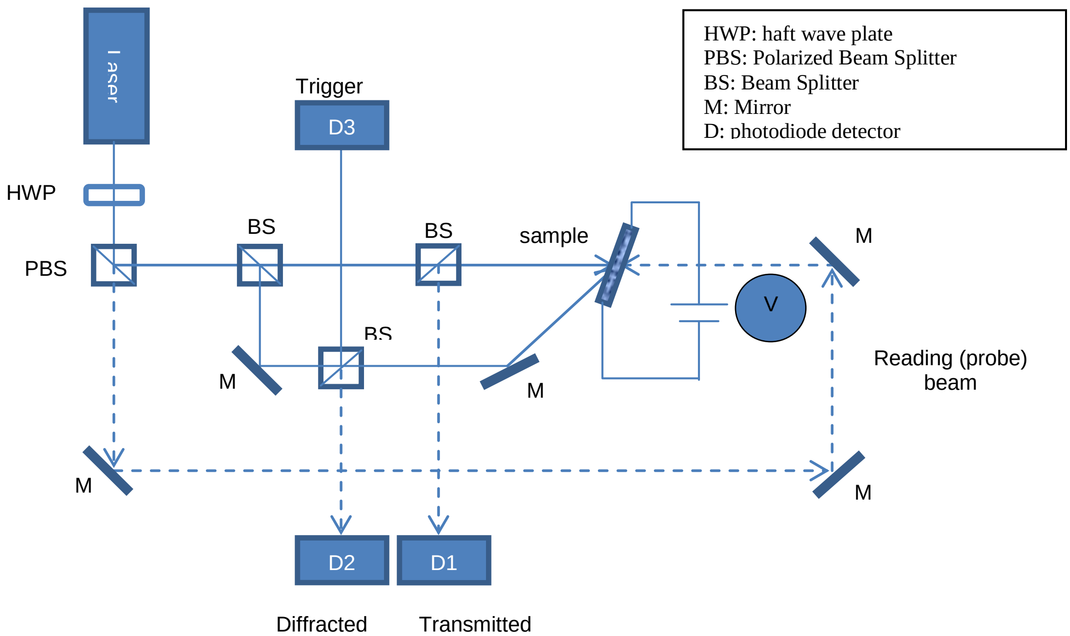

Figure 3. Optical geometry for DFWM

From the intensity of the transmitted beam (I_t) and the diffracted beam (I_d), the diffraction efficiency (η) was calculated using the equation: $\eta\% = \frac{I_d}{I_t + I_d} \times 100$

Response time or the time for building up the PR grating can be derived by observing growth of efficiency. Response time is the value represents the writing process. Therefore, the initial time when the light is turned on and directed toward the PR sample has to be determined. As can be seen in Figure 3, another detector was placed to catch the light reflected from one of the writing beams. The signal from this detector was used as a trigger to determine the initial time in the oscilloscope. Simultaneously, decaying time, i.e. the time required for the signal to return to initial value, could also be obtained from DFWM. By turning off one of the writing beams, the remained beam would homogenously illuminate the sample and erase the recorded holographic data. The decaying time represents the disappearance of the formed grating inside the sample. As a result, the erasing process could be evaluated by simply observing the decaying of diffraction efficiency signal.

3. RESULTS AND DISCUSSION

In the first experiment, the composite was PDAS-based material. Operating wavelength of 633 nm and applied electric field of 45 V/µm were used. The diffraction efficiency as the function of time for PDAS composite was shown in Figure 4. As can be seen, starting form the time which is equal 0, the signal was increased and reached the steady state in a very short time. The result indicated that the grating had been successfully recorded into the sample. After 3 s, one of the beams was off, the signal quickly returned to the initial value indicating that the formed grating was completely erased. As a result, the PR composite has been proven to possess updatable property which is very useful for real-time holographic applications.

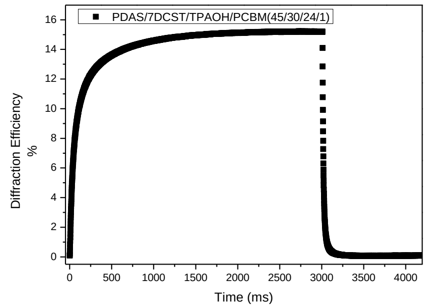

Figure 4. Diffraction efficiency as the function of time of the composite PDAA/7DCST/TPAOH/PCBM (45/30/24/1)

To have a better evaluation and comparison to other material, the rising signal was fitted with bi-exponential function to obtain response time parameter:

$$\eta = \eta_0[1 - m\exp(-t/\tau_1) - (1-\mathrm{m})\exp(-\mathrm{t}/\tau_2)]$$

where τ_1 , τ_2 are time constants with weighing factor of m ($0 \leq m \leq 1$) and (1-m), respectively.

The speed of PR response could be determined based on the dominant time constant, i.e. the constants has larger weighing factor. The decaying time could be also derived by fitting with a reversed bi-exponential function:

$$\eta = \eta_0[m\exp(-t/\tau_1) + (1-\mathrm{m})\exp(-\mathrm{t}/\tau_2)]$$

Figure 5 shows the fitting results for rising time and decaying time for PDAS composite:

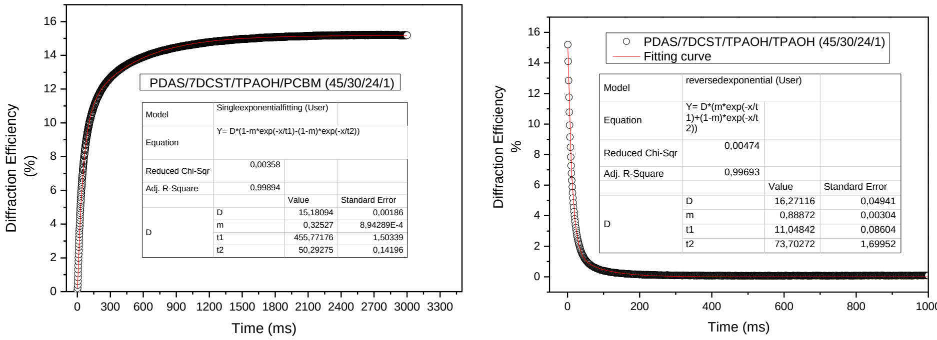

Figure 5. Rising and decaying of diffraction efficiency signal for PDAS based PR composite

As can be seen, the response time for PDAS composite was 50 ms while the decay time was determined to be only 11 ms. The diffraction efficiency could reach 16%. The results are very promising as the grating can be recorded and erased in a very short time with a moderate applied electric field (45 V/µm). However, the PR cell fabricated by PDAS-based composite was easily lost its transparency. The reason has been concluded as the recrystallization of highly polar 7DCST molecules in a relatively non-polar PDAS. Some samples even showed the sign of recrystallization in a few hours after preparation.

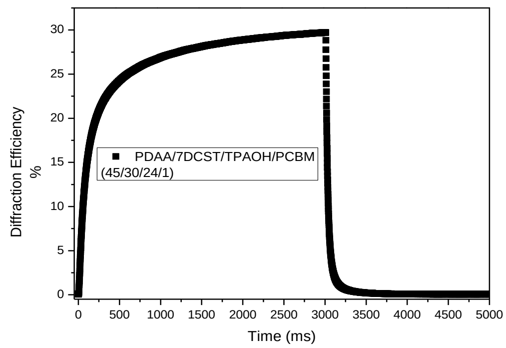

Figure 6. Diffraction efficiency as the function of time of the composite PDAS/7DCST/TPAOH/PCBM (45/30/24/1)

In the next experiment, the composite used was based on polymer of PDAA with the similar component. The DFWM result for PDAA-based composite was shown in Figure 6. Similar to the result obtained from PDAS composite, the PDAA-based composite also showed the ability to record and erase holographic information in a small amount of time. The rising and the decreasing signals were also fitted with the above bi-exponential functions. The results were shown in Figure 7.

The response time for PDAA-based composite was estimated about 93 ms. The decaying time was 24 ms based on the fitting result. As can be seen, both the response and the decaying time are slightly slower than PDAS-based composite. However, the diffraction efficiency was nearly 30 % and it is higher than efficiency achieved by using PDAS matrix at the same electric field. Besides, with the acrylate structure, the composite film using PDAA photoconductive polymer as a dispersive matrix is more stable against the recrystallization. The composite remained usable and maintained its transparency for a month after fabrication. Although with faster response, the problem of recrystallization in PDAS composite is not easy to be solved. There are a few suggestions and approaches proposed [1, 7, 17]. Some research directions require complicated synthesis of a new material [17]. However, none of those approaches could solve the stability without decreasing the PR performances. On the other hands, to have the faster PR response, there are many options which might effectively improve with more simple approach such as: shorter wavelength, stronger laser intensity or even larger plasticizer concentration.

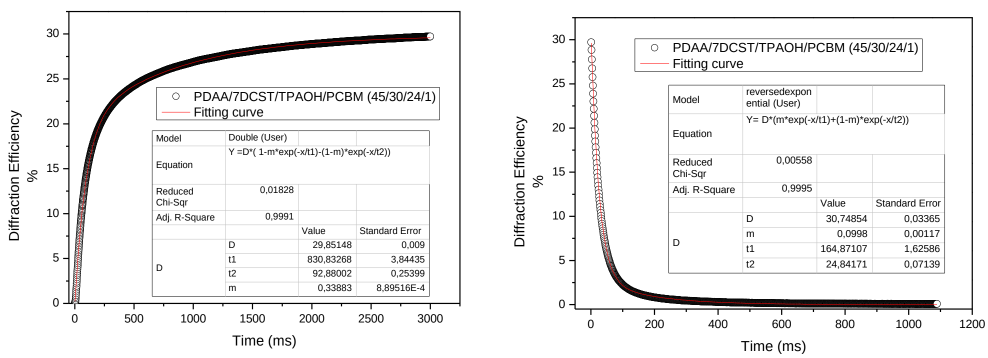

Figure 7. Rising and decaying of diffraction efficiency signal for PDAA-based PR composite

4. CONCLUSIONS

Two types of PR composite based on acrylate (PDAA) and styrene type (PDAS) of triphenylamine polymer were fabricated successfully. Clear PR cells were obtained. Using PDAS polymer as a dispersive matrix also reduced the shelf-life of PR cells. The clear cell was quickly turned into cloudy sample due to the recrystallization of 7DCST inside the matrix. The composite based on PDAS had response of 50 ms and decaying time was 11 ms. However, diffraction efficiency was only 16%. The composite using PDAA polymer had slightly slower response (93 ms) comparing to PDAS-based composite. Higher diffraction efficiency was achieved with PDAA (30%) and PR cells could be stored at room temperature in a longer time.

ACKNOWLEDGMENTS

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TÓM TẮT

COMPOSITE QUANG KHÚC XẠ ÁNH SÁNG TRÊN NỀN ACRYLATE VÀ STYRENE TRIPHENYLAMINE POLYMER

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Hai dạng composite quang khúc xạ ánh sáng trên nền acrylate và styrene triphenylamine polymer đã được chế tạo. Tính chất PR được đánh giá thông qua hiệu suất nhiễu xạ, thời gian đáp ứng và thời gian triệt tiêu. Các thông số này được khảo sát bằng phương pháp “degenerated four waves mixing”. Composite trên nền polymer dạng styrene có thời gian đáp ứng và triệt tiêu nhanh hơn trong khi hiệu suất nhiễu xạ chỉ đạt được 16%. Composite sử dụng polymer dạng acrylate có thời gian đáp ứng chậm hơn. Tuy nhiên, hiệu suất tán xạ có thể đạt đến 30% và thời gian lưu trữ cũng được cải thiện đáng kể.

Từ khóa: Composite, triphenylamine, quang khúc xạ ánh sáng, polymer.