New recording materials for the holographic industry

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ABSTRACT

This paper describes a new class of recording materials for volume holographic applications suitable to meet commercial manufacturing needs. These next-generation holographic photopolymers have the ability to satisfy the unmet demand for color and depth tuning that is only possible with volume holograms. Unlike earlier holographic photopolymers, these new materials offer the advantages of no chemical or thermal processing combined with low shrinkage and detuning. Furthermore, these materials exhibit high transparency, a high resolution of more than 5000 lines/mm and are environmentally robust. Bayer MaterialScience plans to commercialize these materials, which combine excellent holographic characteristics with compatibility to mass-production processes. In this paper, we will briefly discuss the potential markets and applications for a new photopolymer, describe the attributes of this new class of photopolymers, relate their ease of use in holographic recording, and discuss potential applications of such materials..

Keywords: holographic photopolymer, volume holography, hologram

1. INTRODUCTION

This paper introduces a new class of recording materials for volume holographic applications suitable to meet commercial manufacturing needs. There are diverse opportunities for holography, yet many of these have not been achieved commercially. Additionally, while embossed holograms play a key role in many of the current applications of holography, they suffer from some distinct disadvantages, including limited security and a lack of freedom in visual design.

Early holographic materials required cumbersome wet-chemical processing to develop the hologram after laser exposure. For this reason, there has long been the desire to have an ideal volume holographic material that offers easy processing, long-term stability, accuracy of grating reproduction and compatibility to standard industrial product-integration processes.

The introduction of the first generation of holographic photopolymers to the industry in the late 1980's marked the beginning of a new era of volume holography. Despite their advantageous properties, these materials failed to lead to a commercial breakthrough of holography on all fronts. One reason for this was the fact that these materials still required some wet or thermal post-processing after hologram exposure.

Because of the limitations of earlier material systems, there has existed an unmet demand, and the search for suitable volume holographic materials has continued. Table 1 lists the properties of an ideal holographic material.

Bayer MaterialScience has leveraged a material system that was initially developed for optical data storage and redesigned the chemistry to meet the additional needs of image holography and holographic optical elements without sacrificing performance. Bayer MaterialScience is developing its photopolymer to be easy to handle, with high diffraction efficiency, polychromatic, durable and customizable. This material will be simple to expose, with no wet or heat processing. This material is much closer to an ideal holographic material than other holographic materials as will be described in this paper.

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Table 1. Properties of an ideal holographic material.

Good Light Sensitivity
Flat Spatial Frequency Response
Bright Hologram
No Haze
No Absorption
No Shrinkage or Detuning
Industrially Available
Fast Hologram Formation
No Post-Processing Necessary
Stability (Environmental and Light)

Today, Bayer MaterialScience believes that new market dynamics, coupled with these next-generation photopolymers, will enable broad commercial breakthrough of volume holography. This paper covers the potential markets and applications for next-generation photopolymers, the needs for mass production in volume holography, and the material properties of these new materials.

2. MARKETS

There are a wide range of potential markets and applications for holographic photopolymer. In general, these can be classified into one of two categories based upon the function of the hologram or diffractive feature recorded in the photopolymer. In the first category, the hologram functions as an image. Examples of such markets are data storage, imaging and security. In the second category, the hologram functions as an optical element. Examples of such markets are projection, displays, solar energy concentrators, and sensors.

2.1 Markets where the hologram functions as an image

2.1.1 Data storage

The material developed by Bayer MaterialScience was initially developed for the application of holographic data storage by InPhase Technologies.[1,2] In optical data storage, the pages of information are written as images into the holographic media. To achieve high data storage density, a large number of images are written in the same area of the media by angular multiplexing. The details of this are better described elsewhere.[3] While the properties of the initial material were optimized for data storage, many of the fundamental needs are suitable for other forms of image holography. In holographic data storage, it is critical that the material have little scattering, very little shrinkage or detuning, high sensitivity, and excellent long-term stability. The underlying chemistry is used as foundation of the material development for other holographic applications. The technical merits of this are explained in section 4.2 below.

2.1.2 Image holograms

One of the earliest and most widely recognized uses of holograms is in the area of image holography. As with any other graphic technology, there are many potential uses of images generated with holograms. The diversity of applications that have been attempted or envisioned is as broad as the range of applications that printed media services. There are specific commercial examples of magazine covers, maps, trading cards, and book covers that have incorporated image holograms.

2.1.3 Security/authentication

The international market for security holographic devices has been valued over €300 million.[4] This is considered to be a still surprisingly low level of market penetration and parts of the brand protection business will most likely significantly grow over the next few years. Today a range of brand protection technologies is available with holograms being one of the most recognized primary brand protection technologies. It is estimated that brand protection/security holographic devices represent some 90% of the total market by value.[5]

Although examples of security/authentication products utilizing volume holograms exist, this business is currently dominated by surface-relief holograms due to their low cost of production. However, the level of security surface-relief holograms can provide is limited, and there is a significant demand for improved security features.[6] Security features based on volume holography have the potential to offer a greater level of security and incorporate new features that cannot be achieved in embossed holograms, such as color-invariant features and life-like full color. Volume holography is also more amenable to individualized holographic features, which are highly desirable for high security applications. And, finally, volume holograms based on photopolymers enable total product integration which is an obviously efficient counter-measure to counterfeiting.

2.2 Markets where the hologram functions as an optical element

While there exists a wide range of potential applications where the hologram can function as an optical element, only a few examples are given here.

2.2.1 Projection screens

Holographic projection screens have been developed and are currently fabricated with legacy volume holographic materials. These screens offer unique advantages over other types of projection screens, such as transparency and daylight compatibility. However, a key limiter to broader adoption of this technology is cost, due to the expense of fabrication with these legacy materials. A next-generation photopolymer that is able to achieve similar technical performance at a lower cost should enable expanded proliferation of this technology.

2.2.2 Holographic diffusers

Holographic diffusers are currently commercially available for a variety of applications, including architectural lighting, specialty lighting, rear-projection displays, and optical sensors, scanners and metrology equipment. Today, these applications are dominated by surface-relief holograms; however, volume holograms have the potential to achieve capabilities that are not possible in surface-relief holograms. Volume holograms produced in photopolymer can address some applications where higher performance is needed.

2.2.3 Head-up displays

Since the 1980's, volume holograms have been used in military aircraft for head-up displays[7]. While this has been an effective and sustainable use of holography, the market for such head-up displays is quite limited. There is increased interest in developing head-up displays for automotive and other transportation markets. Availability of material that is suited for such applications, both from a technical and cost perspective, is important to drive such opportunities to fruition.

As can be seen from this truncated list, there exist a wide range of opportunities for a next-generation photopolymer. As with any market opportunity, there are many factors that are necessary to be achieved to build a successful business including timing, material availability, process capability, suitable market channels, effective business strategies, and value-chain cooperation. However, it seems that there is currently an unmet demand for photopolymer materials and a willingness from a variety of companies in different industries to push volume holography forward.

3. MASS PRODUCTION

One of the key factors for the long-term success of any manufacturer of holographic materials is the large-scale adoption of holography in the marketplace and the subsequent creation of sustainable opportunities. As with any other product with broad commercialization, a method of cost-effective mass production must exist. Thus, a key enabling technology for the creation of sustainable holographic business is mass replication of holograms. For surface-relief holograms, embossing processes have been developed to enable large-scale proliferation of holograms in security, authentication, and decorative applications. Unlike surface-relief holograms, volume holograms cannot be replicated by mechanical processes such as embossing. While there have been several attempts to produce equipment capable of replicating volume holograms,[8-13] there does not exist a broad platform of holographic replication equipment in the market today. This is a significant impediment to broad commercialization.

3.1 Print media as model for holography

Although there are many differences between holography and traditional graphic images, the overlap of image holography with traditional printing and graphics is substantial. Both are often used to display graphical information. Image quality characteristics such as brightness, contrast, definition, color balance and resolution are used for both. Both have the potential for similar functionality in a variety of markets including advertising, packaging, security features, maps, decorative features, and artwork.

Prior to the invention of the printing press, all graphic images, whether text, illustration or artwork, were prepared as originals or as manually duplicated copies. While the cost of producing an original was high relative to the material costs, the cost of producing a replica was nearly as high, thus severely limiting the commercialization of graphics and text. Industries based on print media, which are quite pervasive in the society of today, didn't exist or were substantially limited in scope. It would be quite difficult to imagine a modern world that didn't have newspapers, magazines, catalogs, billboards, movie posters, flyers, commercial mailings, brochures, printed packaging, business cards, and most books. However, these would not be sustainable businesses without the advances in printing technologies that enabled mass replication of printed matter. Thus, the broad availability of both suitable materials and replication technology has been a key enabler to achieve broad-based commercialization of print media.

Conversely, the lack of both suitable material and replication technology has limited image holography. This is not to say that the replication technology has not been created or developed, but that this technology has not been standardized and widely adopted in the marketplace. It is difficult to discern the path that will move the business of image holography from its current state of limited scope to a pervasive technology that is integrated into the fabric of our society, but it is safe to assume that broad availability of materials and replication technology will be key to such success.

3.2 "Chicken or the egg" dilemma

Perhaps one of the most challenging aspects to enable the vision of broad-commercialization of holography is the dilemma faced between those who want to sell holographic materials and those who want to produce equipment for mass replication. In the absence of a suitable material for mass replication, there is no business case for fabricating equipment capable of mass replicating volume holograms. This would have been analogous to trying to invent the printing press is paper didn't exist. However, for the manufacturer of holographic materials, it is difficult or impossible to achieve sustainable volume sales of material without the equipment to support mass replication. This creates a "chicken or the egg:" dilemma for volume holography, because both need to develop and succeed in the marketplace to permanently establish volume holography as a commercial business.

We believe that this cycle can be broken by cooperative partnering between material manufacturers, replication equipment fabricators and hologram producers to achieve a total solution in which all parties win. Here, we focus on the material development necessary to accomplish this.

4. MATERIAL PROPERTIES

While it seems that a number of factors have contributed to the failure of earlier efforts to generate large-scale, sustainable business opportunities in holography, one of the key issues has been material challenges. In this respect, it is important that a suitable material for volume holography be broadly available to the marketplace. Here, we describe the attributes of our new photopolymer material that make it well-suited to support broad commercialization of holography.

4.1 Formats

While the expected format of the photopolymer product is a holographic film, a significant amount of the material development and testing has been done in sandwich coupon samples. Both of these formats are shown below in Figure 1.

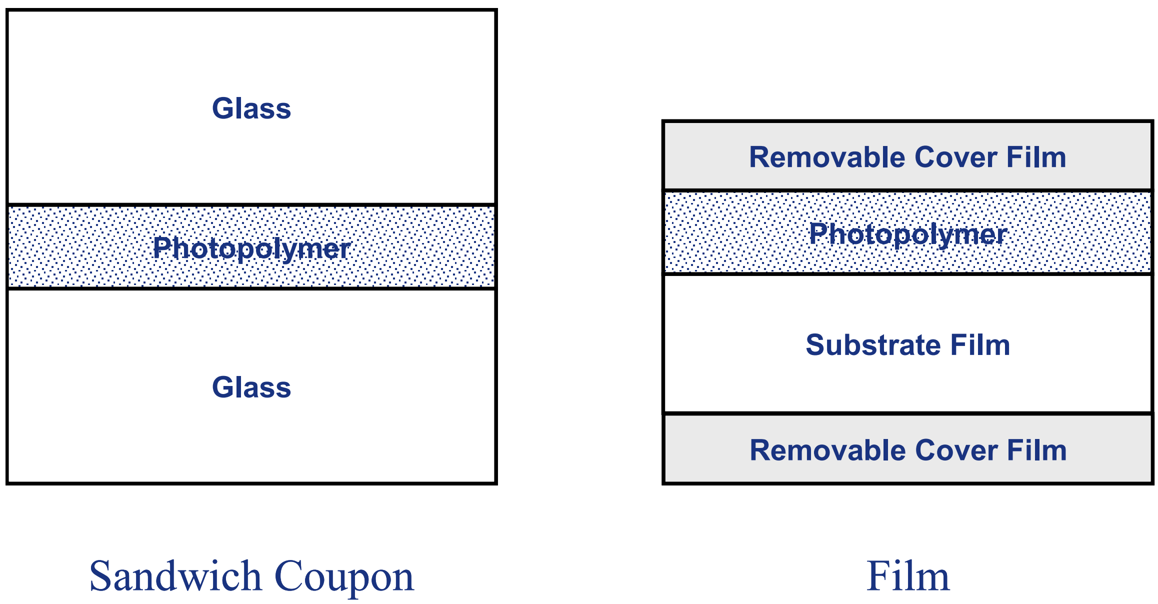

Fig. 1. Schematic showing the format of sandwich coupons and film samples fabricated with Bayer photopolymer material.

The substrate film of the holographic film format can be a wide variety of materials and can be chosen to support the requirements of target applications. To date, a low-birefringence polycarbonate and polyethylene terephthalate films are commonly used.

4.2 Working principle of the Bayer photopolymer

The photopolymer developed within Bayer MaterialScience is based upon an orthogonal two chemistry formulation. As is shown in Figure 2, the raw material is composed of two different polymer chemistries. The first chemistry is composed of the matrix precursors, which are cross-linked during the manufacturing process to form a stable matrix to host the photopolymer. The second chemistry is composed of the imaging components. These components are responsible for the hologram formation during exposure. The imaging components include functionalities for light absorption, initiation of the polymerization and polymerizable groups. The unexposed photopolymer, with fully formed matrix, can be stored, shipped and handled easily as long as light-safe conditions are used to prevent accidental photopolymerization. To record holograms, the photopolymer is exposed with laser irradiation to cause photopolymerization to occur. During the exposure, bright fringes from the interference of two or more beams of light initiate photopolymerization by activating neighboring imaging monomers. The polymerizable monomers diffuse within the matrix during the exposure until they react with an activated monomer or polymer chain. This process of polymerization in the bright regions and net diffusion away from the dark regions causes a refractive index modulation in the material. Once these monomers have fully reacted to form polymer chains, the writing chemistry is consumed and the hologram has fully formed within the material. No further processing is needed for complete hologram formation—photo-curing is only needed to fully bleach the absorbing species to gain optimal transparency. This process also ensures that the writing chemistry has been consumed. Since this photopolymer is based on two independent chemistries that can be tailored separately to optimize each aspect of the photopolymer, the matrix precursors can be chosen to yield optimal matrix properties, such as transparency, ease of processing and mechanical properties. The imaging components are optimized in parallel to provide the best holographic properties with minimal effect on the overall properties of the material. Therefore, the Bayer photopolymer can be tailored quite flexibly to address multiple customer requirements.

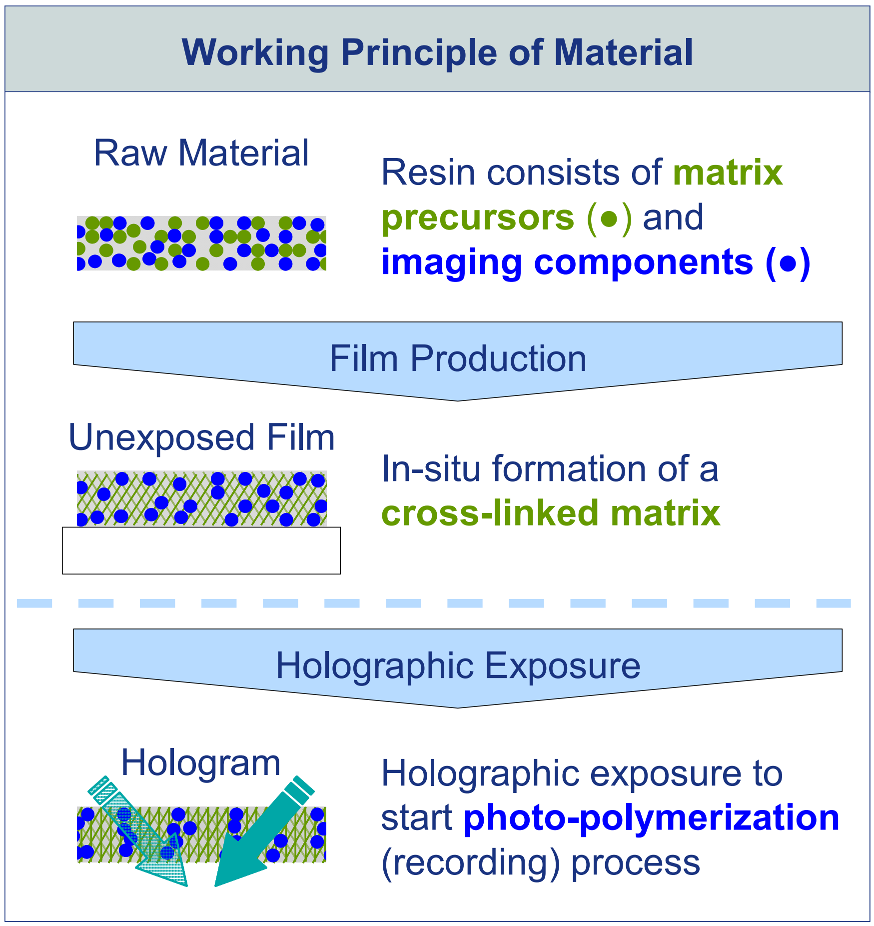

Fig. 2. Diagram showing the working principle of Bayer photopolymer film. The raw material is a resin that contains matrix precursors and imaging components. During film production, the matrix precursors are cross-linked to form a stable matrix system hosting the imaging components. This film product is stable until exposed to light. During the recording process the film is exposed to suitable light to initiate the photo-polymerization that forms the hologram structure.

4.3 Holographic performance

Bayer MaterialScience has produced monochromatic and panchromatic experimental materials in both sandwich coupon and film format. While specialized formulations have been achieved to address specific applications, the panchromatic material serves the broadest range of applications. As such, the performance of this formulation will be addressed here, unless otherwise noted. This panchromatic material is sensitive across the majority of the visible spectral range, with peak sensitivity in the red portion of the spectrum.

Figure 3 shows Bragg curves for holograms recorded in photopolymer at red (633 nm) and green (532 nm) wavelengths along with curve fits to Kogelnik models[14]. As can be seen from this figure, the experimental data closely matches the Kogelnik model, indicating that there is a very high optical quality from these materials. These results also prove that the material system has the potential to achieve Δn above 0.03. While the current photopolymer in film format does not yet reach this level of performance, it is anticipated that the commercialized product will exhibit holographic performance exceeding this value. Although the data shown here is for red and green light only, the material has a similar performance at 405 nm and 476 nm. In addition, also near UV sensitive material is available.

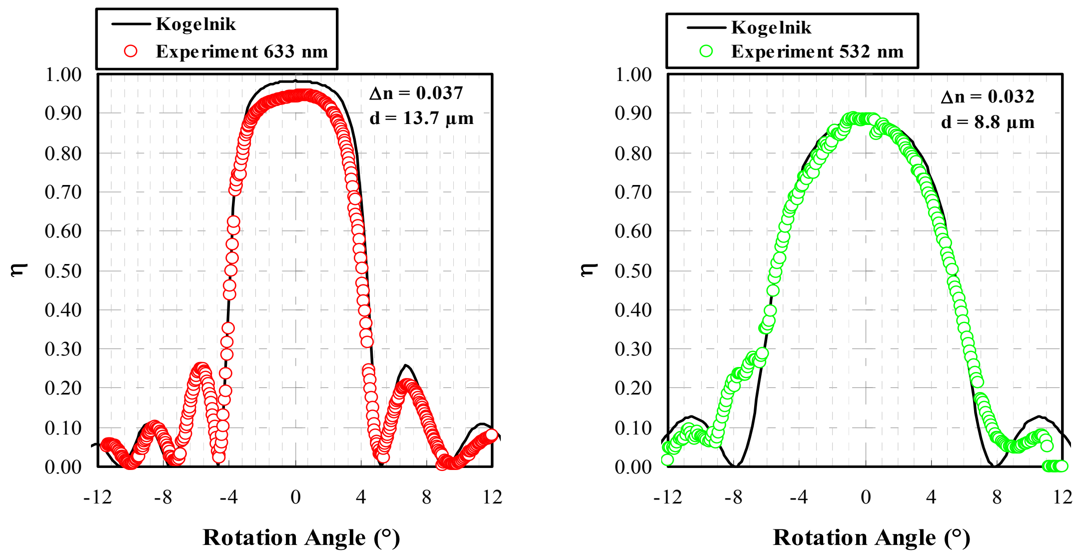

Fig. 3. Bragg curves (diffraction efficiency vs. rotation angle) for holograms recorded in sandwich coupon samples of photopolymer at 633 nm (left) and 532 nm (right). Overlaid on each set of data are best-fit curves from Kogelnik models.[14] For the data taken at 633 nm, optimization of the Kogelnik model yielded a calculated Δn of 0.037 and a thickness (d) of 13.7 µm. For the data taken at 532 nm, optimization of the Kogelnik model yielded a calculated Δn of 0.032 and a thickness of 8.8 µm.

In Figure 4, build-up curves for the RGB-sensitive photopolymer is shown for both red (measured at 633 nm) and green (measured at 532 nm) exposures. For the red testing, saturation is observed for total dosages above 10 mJ/cm^2. For the green testing, saturation is observed for total dosages above 80 mJ/cm^2. Blue testing at 476 nm requires total dosages above 200 mJ/cm^2 to reach saturation.

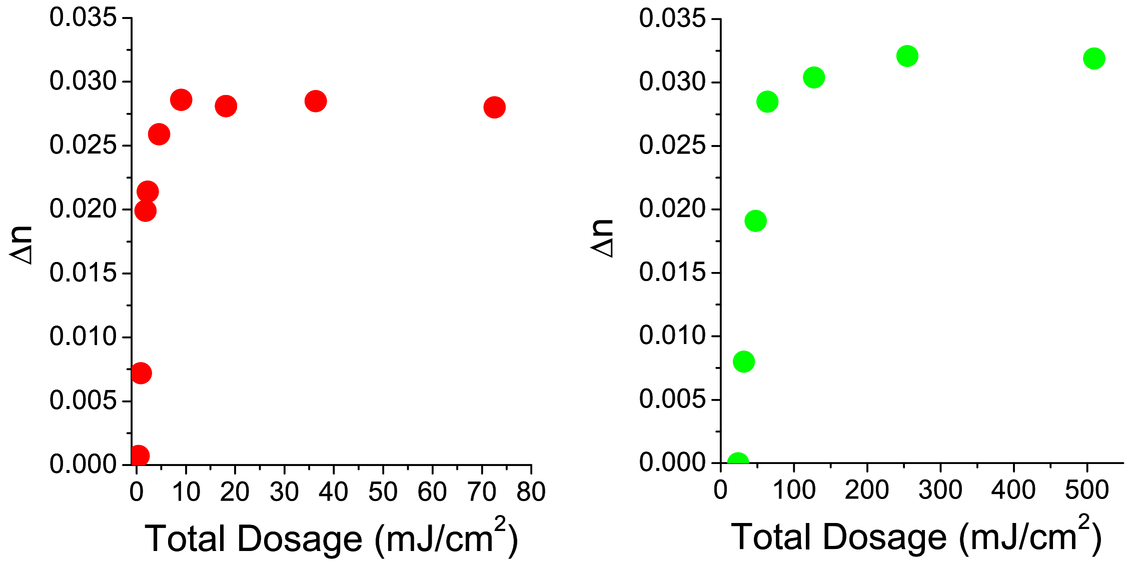

Fig. 4. Graphs of Δn vs. total dosage for holograms recorded in sandwich coupons of photopolymer at 633 nm (left) and 532 nm (right).

The superior transmission property of the Bayer photopolymer is shown in Figure 5. Transmission of 90% can be achieved in the photopolymer after flood curing. While the data presented here is for UV photo-curing with a mercury lamp, similar transparency is obtained for white-light photo-curing with similar dosages. Water-clear appearance of the

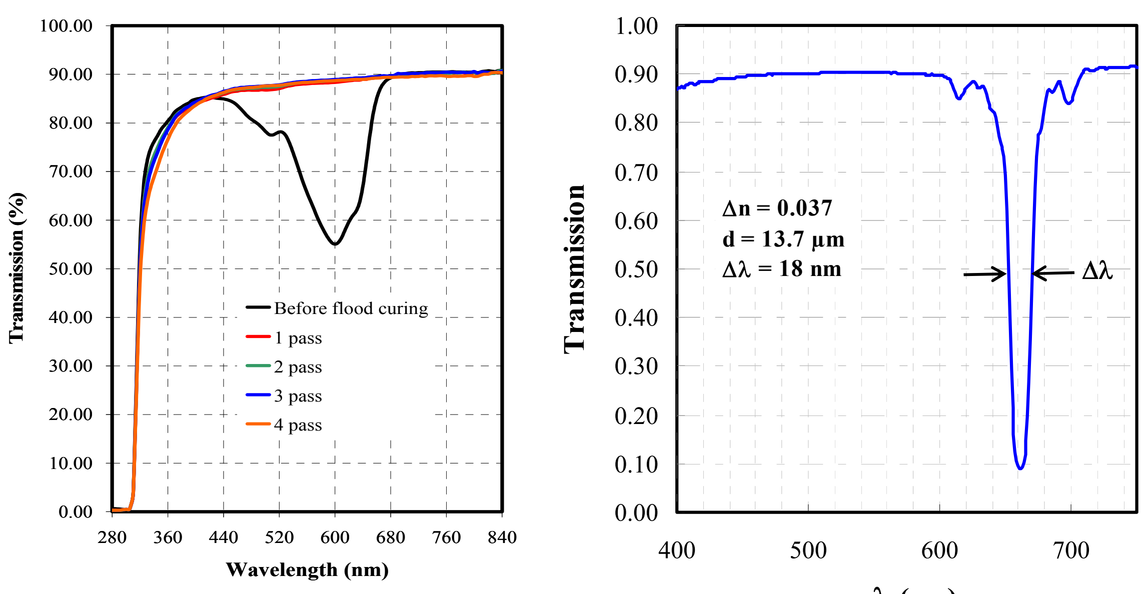

Fig. 5. Graphs showing the transparency of the material after photo-curing (mercury lamp delivering a dosage of $5J/cm^2$ per pass). The left-hand graph shows the transmission vs. wavelength of a sample of photopolymer before and after several passes of photo-curing. No hologram was recorded in this sample so that the inherent transparency of the material could be shown. The right-hand graph shows the transmission characteristics of a sample of photopolymer with a holographic grating recorded in the material after a single pass of photo-curing.

film has been achieved with tungsten lamp photo-curing, sunlight photo-curing and UV photo-curing. This high level of transparency not only enhances the visual appearance of holograms produced in the material, but it also enables some applications such as holographic features registered to printed images.

4.4 Film properties

The properties obtained in the current experimental films have not yet reached the performance achieved in sandwich coupons; however, we are confident that similar levels of holographic performance will be achieved in film as the development effort progresses. Film format offers many processing and cost advantages over sandwich coupons, so we intend that the initial products will be holographic films.

Our current films offer significant features to potential customers and end-users. This is shown in Table 2, where the properties are compared to those of an ideal holographic material. We have achieved monochromatic and panchromatic films with sensitivity spanning the range 355 nm to 670 nm. Our current materials have a peak sensitivity in the red (saturation is achieved for total dosages greater than 15 mJ/cm^2). These materials form bright holograms, due to the combination of high transparency, low scatter and strong gratings. These materials, which have $\Delta n = 0.016$, compare favorably with other materials, including photopolymers, with higher Δn due to the excellent optical properties of the Bayer photopolymer. The Bayer photopolymer is capable of achieving transmission above 90% in the film samples.

Table 2. Comparison of Bayer photopolymer with properties of an ideal holographic material.

Good Light Sensitivity	✓
Flat Spatial Frequency Response	✓
Bright Hologram	✓
No Haze	✓
No Absorption	Very Low
No Shrinkage or Detuning	Low
Industrially Available	Planned*
Fast Hologram Formation	✓
No Post-Processing Necessary	✓**
Stability (Environmental and Light)	✓

*While it is planned that Bayer MaterialScience will manufacture a product from these experimental materials and that this product would be generally available to the marketplace, this material is not currently industrial available. Furthermore, Bayer MaterialScience cannot make warrantees about specific future product(s) or their availability.

**Although no post-processing is needed for hologram formation, UV or visible light photo-curing is required to achieve optimal transparency.

Probably the most important aspect of a holographic film is the ease of processing. In principle, any material that can be produced as rolls of film should be suitable for mass production; however, the realities of processing challenges have severely limited earlier attempts to mass produce holograms cost effectively. The addition of chemical or thermal post-processing leads to more complicated processing equipment, more factors to control and higher loss due to yield. With the Bayer photopolymer film, the hologram is fully formed after optical exposure. This not only greatly simplifies the production equipment, but it also allows for much faster feedback of the quality of the resultant hologram to prevent significant yield loss.

Experimental films are produced today on a pilot-scale roll-to-roll coating machine. These sample holographic films are typically produced with photopolymer thickness between 10 and 60 μm. Our standard substrate is a 175 μm thick, low birefringence polycarbonate film. Because of the size of the coating machine, our typical coated width is 20 cm; however, Bayer MaterialScience anticipates producing holographic film product at widths up to 160 cm.

5. SUMMARY

It is clear that there exist a large number of potential applications for volume holographic materials, if the appropriate material can be developed along with equipment and processes for mass replication. The development of mass replication cannot occur in the absence of a suitable volume holographic material. To achieve sustainable, broad commercialization of volume holography, both of these critical facets are needed. Here, we describe the development of a next-generation photopolymer material that we believe is well suited to address this unmet need in the marketplace. These new materials offer no chemical or thermal processing, high transparency, high resolution, environmental stability and low shrinkage and detuning. The ease of handling, coupled with their strong holographic performance makes these materials well suited to enable a broad commercial breakthrough in volume holography.

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