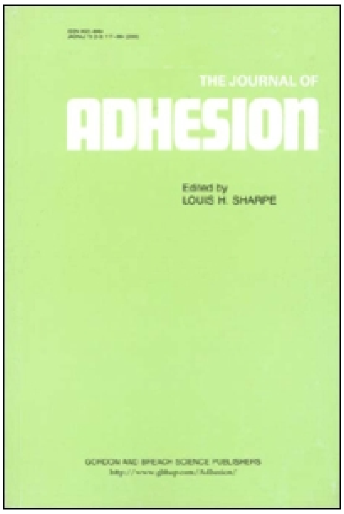

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Electrooptical Light-Management Material: Low-Refractive-Index Hydrogels

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A prototype synthetic hydrogel that has a low refractive index (<1.35) and is optically clear has been developed [1]. The refractive index is a key feature in the application of optical polymers, and this hydrogel is particularly useful for light-transmitting devices. The ultraviolet-light-curable hydrogel formulation contains more than 90% water (plus water-soluble oligomers, photoinitiator, and surfactant). UV cures it instantly at 425 mJ/cm^2 at a thickness of less than 10 mm, giving a firm hydrogel with a modulus of 2.3×10^3 dyn/cm^2. This hydrogel has utility in light-management applications.

Keywords: Electrooptics; Hydrogel material; Light-management materials; Low refractive index; Rheology; UV curing

INTRODUCTION

The objective is directed to the development of supportive materials useful in light-transmitting devices that help control light distribution, *i.e.*, low reflectance and low interference. Currently, for applications where there is a significant distance between the components of the light transmitting devices, *i.e.*, lens (or lenses) and other components, the medium is air and the components are mechanically supported. Air is a poor supporting medium. Replacing air with supportive material is achieved by employing hydrogels with low refractive index (< 1.35) to obtain the desired light distribution. The purpose of this

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article is to develop a hydrogel material having the desired physical properties of refractive index, light transmittance, and mechanical strength to help support and adhere a light-transmitting device to the lens (*i.e.*, a secondary lens or light-management plastic films).

An example of an application where a low-refractive-index material has utility in obtaining the desired light distribution is a rear projection screen for a television (back-lit projection screen). The Fresnel collimating lens for use with a projection screen should maintain the capability of effectively collimating light to provide more uniform brightness across the screen. It is generally advantageous to increase the difference between refractive indices of the Fresnel lens and medium or support material to help control light distribution (Figure 1). This can be achieved by using a low-refractive-index material to help support and adhere the secondary component to the Fresnel lens. The Fresnel lens material is glass or poly(methyl methacrylate) with refractive indexes of 1.53 and 1.49, respectively.

Noting the refractive index of the Fresnel lens material, a significant difference would be a refractive index of less than 1.4 for the supportive material. Materials with a refractive index of less than 1.4 are limited. There are only air, water, and fluoropolymers (Table 1).

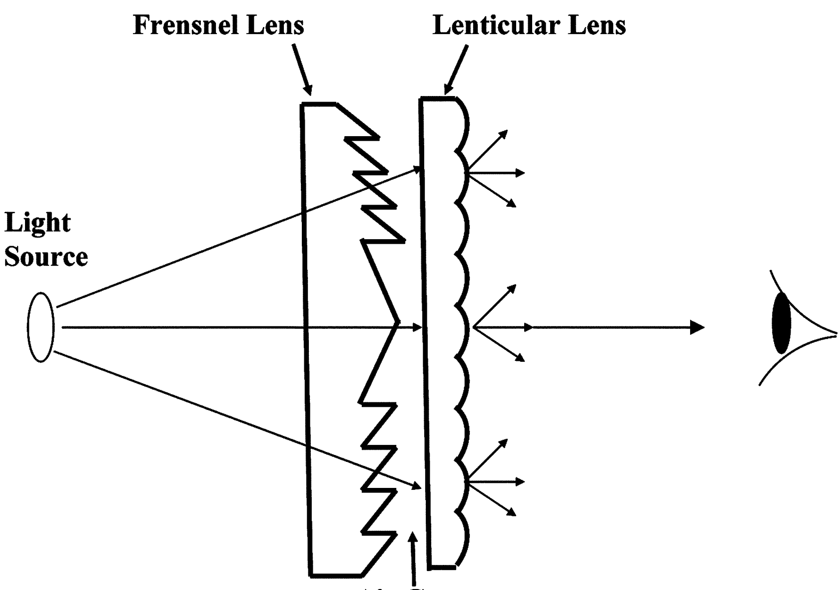


FIGURE 1 Typical component setup of a rear projection screen.

TABLE 1 Refractive-Index Materials

Material	Refractive index
Air (vacuum)	1.00
Water	1.33
Poly(tetrafluoroethylene)	1.35–1.38
Poly(dimethylsiloxane)	1.43
Poly(oxyethylene)	1.45
Polyacrylates	1.46–1.47
Poly(ethylene)	1.51
Poly(butadiene-co-styrene)	1.53
Glass	1.53
Poly(ethylene terphthalate) (PET)	1.64

Lorentz–Lorenz Equation and Correlation Model of Groh and Zimmerman

The relationship among refractive index, molar refraction, and molar volume is shown in the Lorentz–Lorenz equation [2,3]:

$$\frac{(n_D{}^2 - 1) \times M_G}{(n_D{}^2 + 2) \times \rho} = R_L \qquad (1)$$

where n_D is the refractive index, M_G is the repeating unit molecular weight, ρ is the density, and R_L is the molar refraction.

It can be observed from Equation (1) that a low refractive index can be achieved either by lowering the molar refraction or increasing the molar volume.

Groh and Zimmerman plotted the ratio of molar refraction, R_L, to molar volume, V_L, for different atoms present in organic polymers [4] using previously published data [5–7]. In spite of the broad range of values for each atom, due to different binding structures, and varying chemical environments, it is apparent that fluorine and to a lesser extent oxygen lower the refractive index of a compound [8].

BACKGROUND

Refractive Index of Fluoropolymers

We investigated the use of fluoropolymer adhesives [9] as low-refractive-index media. Based on the theoretical concept for optically clear polymers, the molecular structure to investigate had fluorination on the bulky polymer side chain (to increase the molar volume and to decrease the molar refraction by fluorination), rather than the more typical fluorinated polymer main chain [*e.g.*, poly(tetrafluoroethylene), which is hard and crystalline].

The side-chain-fluorinated acrylate monomers used in this work were PDFA (1*H*,1*H*-pentadecafluorooctyl acrylate, Synquest Laboratories, Alachua, FL, USA) and HFBA (1*H*,1*H*-heptafluorobutyl acrylate, Synquest Laboratories).

For a series of fluoroacrylic copolymers, a correlation of refractive index with the percentage of fluorine was observed; the higher the percentage of fluorine, the lower the refractive index. To achieve a polymer with refractive index of less than 1.36, the percentage of fluorine content has to be more than 57%. The fluoroacrylate monomers are expensive.

Details of this work have also been published previously [8].

Low-Refractive-Index Hydrogels

There is one light-receiving device that uses water as a medium—the eye. The eye actually uses a natural hydrogel as the medium and has a refractive index of 1.336. We also investigated and developed the use of hydrogels as a low-refractive-index medium. Figure 2 shows the use of polymeric hydrogels: a 2-hydroxyethyl methacrylate (HEMA)/ methacrylic acid (MAA) copolymer [10], a high-molecular-weight

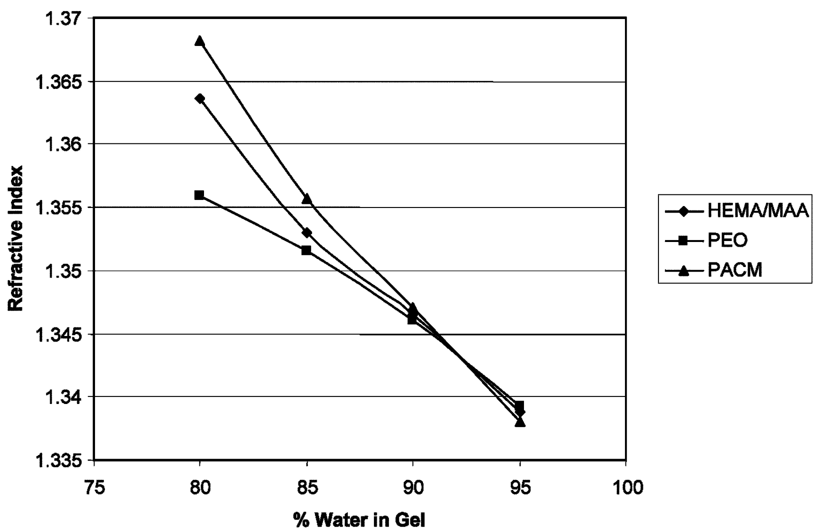


FIGURE 2 Refractive index of polymeric hydrogels as a function of percentage of water.

poly(ethylene oxide) (PEO) available from Union Carbide (Danbury, CT, USA) POLYOX® WSR-205 [1], and a polyacrylamide (PACM) available from BetzDearborn (Trevuse, PA, USA) POLYLOC® AP1142 [1]. Water is very effective in making a low-refractive-index medium, but to get below 1.35 the hydrogel would have to contain more than 85% water and the refractive index would be almost independent of the nature of the hydrophilic polymer. This indicates that water is the key refractive index contributor for these samples. Hydrogels are a very cost-effective product, but these polymers are not likely candidates because the mechanical strength is poor and it is difficult to make these hydrogels free of bubbles.

EXPERIMENTAL

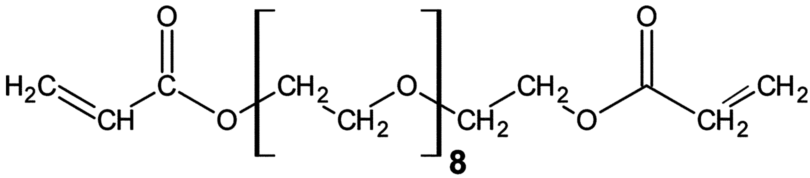
Based on the need for a cost-effective low-refractive-index material, a hydrogel was developed that was easily processed and had good mechanical strength [1]. The formulation included UV-curable poly(-ethyleneglycol) acrylate oligomers, UV photoinitiator, and surfactant. Twelve grams of formulation were weighed into an aluminum dish (57 mm in diameter × 14 mm high), and formulations were UV irradiated with two passes at 50 ft/min under a Fusion Systems (Gaithersburg, MD, USA) D-bulb at 850 mJ/cm^2. The UV curing raised the formulation temperature by 5°C (23°C to 28°C), but there was negligible water loss of the hydrogel.

Viscoelastic Properties Measurements

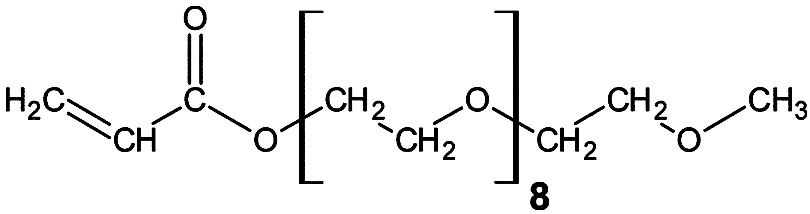
The viscoleastic properties of different hydrogel samples were measured on the Rheometrics (Piseataway, NJ, USA) Dynamic Spectrometer (RDS-7700) at room temperature and 50% relative humidity over a frequency range of 0.01 to 100 rad/s. Samples tested were in the form of a disk of 25 mm in diameter with a thickness of 1–2 mm. The strain employed was about 1%.

MATERIALS

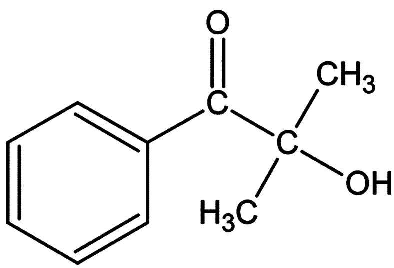
See Schemes 1–4 for materials. Figure 3 shows the use of UV-curable, water-soluble oligomers for making hydrogels at three different oligomer 1–oligomer 2 ratios as described in Table 2. It is interesting to note that there is hardly any refractive-index variation for these three oligomer blends, confirming that water is the dominating refractive-index contributor; to have a refractive index of about 1.35, at least 85% of water in the gel is needed.



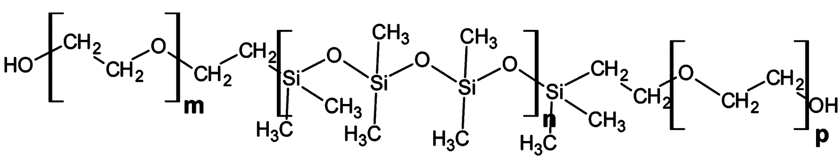
SCHEME 1 Oligomer 1: poly(ethylene glycol) (9) diacrylate (Sartomer, Exton, PA, USA, SR 344).



SCHEME 2 Oligomer 2: methoxy poly(ethylene glycol) (9) monoacrylate (Osaka Organic Chemical, Osaka, Japan, MPE 400A).



SCHEME 3 UV initiator: 2-hydroxy-2-methyl-1-phenylpropan-1-one (Ciba-Geigy, Basel, Switzerland, Duracure® 1173).



SCHEME 4 Surfactant: poly(ethylene oxide)-*block*-poly(dimethlsiloxane)-*block*-poly(ethyleneoxide) (Dow Corning, Midland, MI, USA, 193).

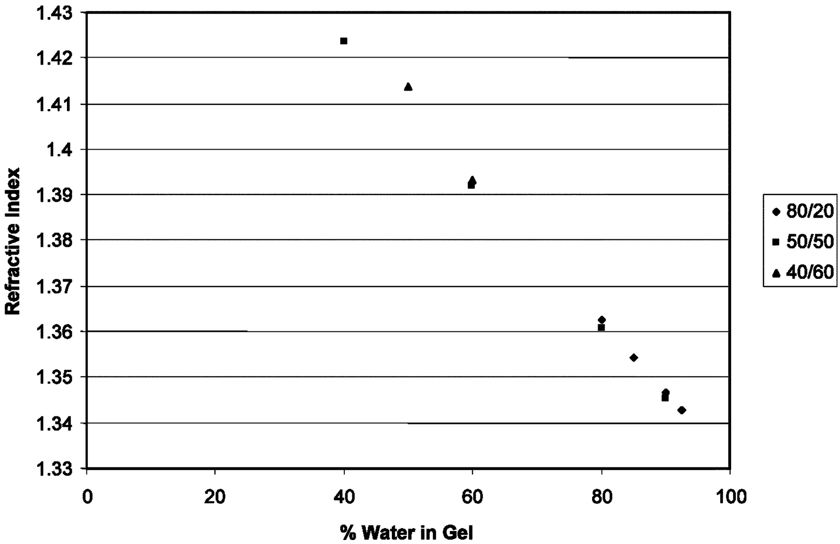


FIGURE 3 Refractive index of UV cure PEG hydrogels as a function of percentage of water.

Rheological Properties

Figures 4 and 5 show the frequency dependence of G′ (dynamic storage modulus) and tan δ (viscoelastic index) as a function of water content, respectively. It is noteworthy that for samples containing the 40% and 60% water, there is a significant frequency dependence of G′ indicative of its viscoelastic nature. This is consistent with the rather high values of tan δ, 0.5 to 2.0, in this frequency range. As the water content increases to 80%, the G′ value is only slightly affected but it remains fairly constant with frequency, suggestive of a rubbery plateau consistent with the sharp drop in tan δ values (<0.2). With further increase of water content to 90%, there is an almost two-decade drop in G′ values, and it is again frequency independent, consistent with the further drop in tan δ values to less than 0.1. At 95% water content, the G′ values further drop one decade but still maintain reasonable structural integrity and cohesive strength with G′ values close to 10^3 dyn/cm^2. The G′ and tan δ profiles are quite flat and low. Such a sharp drop in G′ values at more than 80% water most probably can be attributed to the lower cross-link density of the gel whose cohesive strength is dominated by the water matrix.

The observed G′ and tan δ crossovers can probably be attributed to the merging or intersection of the onset glass transition (as evidenced

TABLE 2 Formulations and Dependence of Refractive Index with Percentage of Water in Hydrogels

Oligomer ratio	Oligomer 1	Oligomer 2	UV initiator	Surfactant	Water	Total (g)	Water in gel (%)	RI
80/20	6.0	1.5	0.2	0.01	92.5	100.2	92	1.3427
80/20	8.0	2.0	0.3	0.02	90.0	100.3	90	1.3466
80/20	12.0	3.0	0.5	0.02	85.0	100.5	85	1.3543
80/20	16.0	4.0	0.6	0.03	80.0	100.6	79	1.3625
60/40	16.0	24.0	1.5	0.04	60.0	101.5	59	1.3933
60/40	20.0	30.0	1.5	0.03	50.0	101.5	49	1.4136
100/0	5.0	0.0	0.15	0.015	95.0	100.2	95	1.3399
50/50	5.0	5.0	0.3	0.06	90.0	100.4	90	1.3452
50/50	10.0	10.0	0.6	0.12	80.0	100.7	79	1.3607
50/50	20.0	20.0	1.2	0.24	60.0	101.4	59	1.3919
50/50	30.0	30.0	1.8	0.36	40.0	102.2	39	1.4237

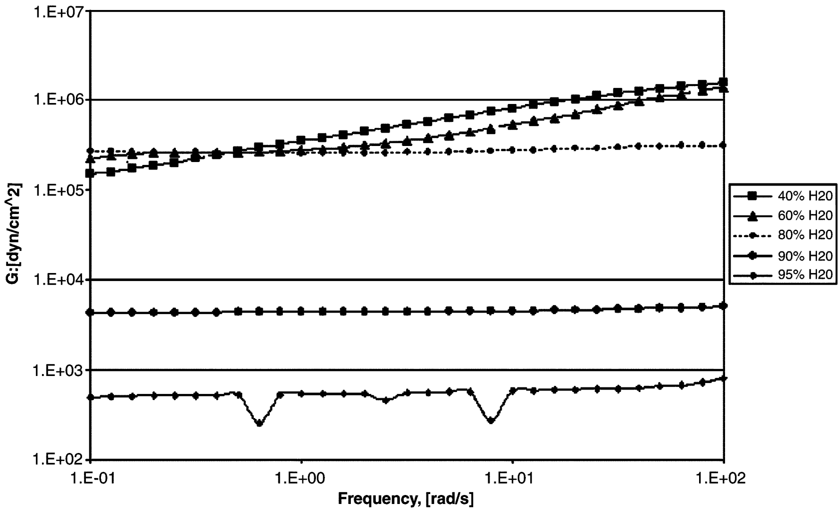


FIGURE 4 Frequency dependence of G′ as a function of water content.

by the low-water-content or high-polymer-content samples) and the plateau regions (as evidenced by the high-water-content or low-polymer-content samples).

To prepare a gel with a reasonable mechanical strength, it is recommended that the percentage of water in the gel be around, or less than,

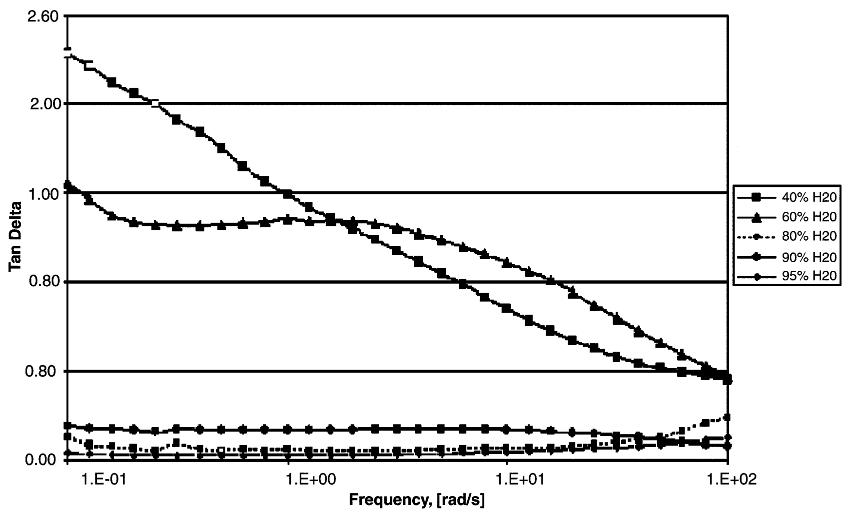


FIGURE 5 Frequency dependence of tan δ as a function of water content.

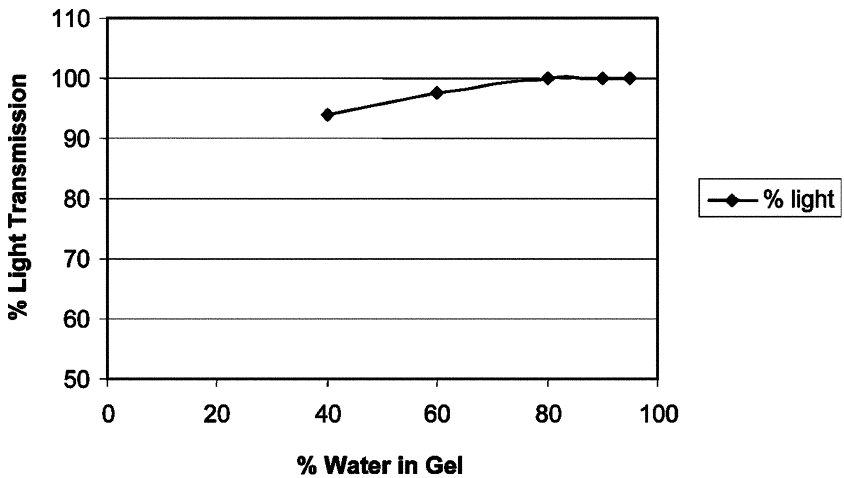


FIGURE 6 Percentage of light transmission as a function of percentage of water in gel.

90%, because this would provide some reasonable structural integrity for the attachment of the secondary component to the Fresnel lens as depicted in Figure 1.

Optical Properties

Figure 6 shows the percentage of white light transmission of the 50/50 UV-cured oligomer. There is a gradual increase in the percentage of light transmission with an increase in the percentage of water in the gel.

At 80% water or more, the gel is virtually transparent.

Table 3 summarizes the rheological and optical properties of a 50/50 oligomer ratio hydrogel containing different weight percentages of water.

TABLE 3 Rheological and Optical Properties of 50/50 Oligomer-Blend Gels at Different Weight Percent of Water

Oligomer ratio	Water content (wt %)	G′ at 1 rad/sec (dynes/cm^2)	tan δ at 1 rad/sec	Refractive index	Light transmission (%)
50/50	40	3.30E + 05	1.6	1.4237	93.8
50/50	60	2.70E + 05	1.4	1.3919	97.6
50/50	80	2.70E + 05	0.19	1.3607	100
50/50	90	4.50E + 03	0.028	1.3452	100

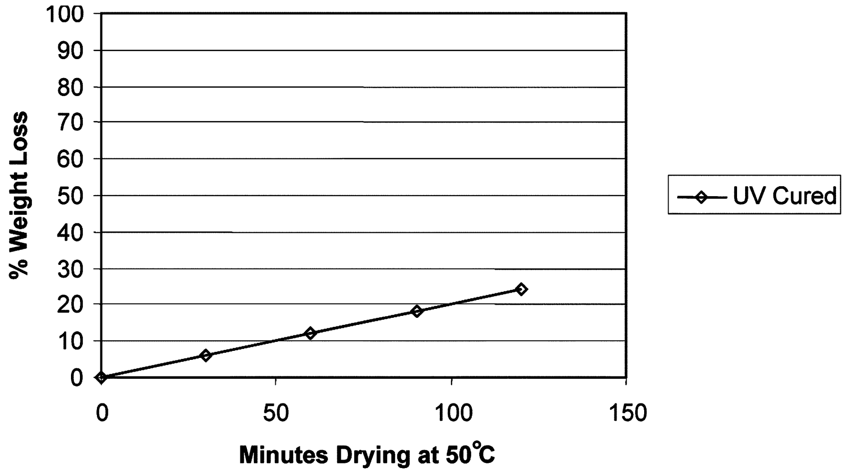


FIGURE 7 Hydrogel water loss as a function of drying time at 50°C.

Water Evaporation Issue

Figure 7 shows the percentage of weight loss as a function of time when the gel dried at 50°C. There is an approximately 25% weight loss after 2 h of drying, due to the water evaporation from the gel.

Figure 8 compares the weight loss of the gel (containing 1.4 g of polymer) *versus* a plain water sample. After 5 days of drying at

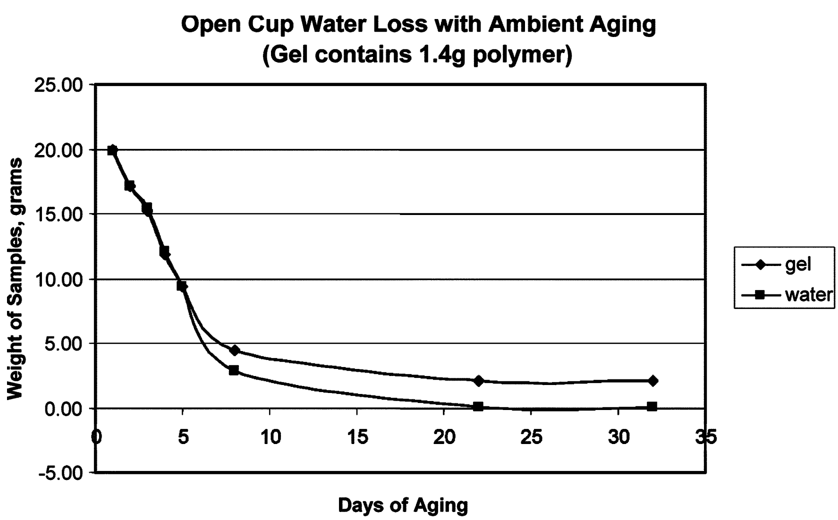


FIGURE 8 Hydrogel water loss as a function of ambient aging time.

ambient temperature, both the gel and the water samples lost about 50% of weight. However, with prolonged standing, the water totally evaporated (100% weight loss) after 25 days. The gel still maintained more than 10% of its weight, due most probably to the involatility of the polymer together with some entrapped water molecules, which might be strongly hydrogen bonded with the polymer.

To alleviate the water evaporation issue, it might be useful to form a very thin skin (*e.g.*, nanocoating) at the outside of the structure so as to provide a barrier against the water evaporation that does not affect the optical transmission. In addition, this optical adhesive might be used in a constantly moist environment.

CONCLUSIONS

In summary, we have demonstrated the feasibility of making a UV-light-curable hydrogel formulation containing more than 80% of water with excellent light transmission and reasonable cohesive strength for attaching the secondary component to the Fresnel lens. The low refractive index of about 1.35 would enable this optical adhesive to find utility in light-management applications.

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