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# Mechanical behavior of holographic material in a high vacuum and with temperature changes

Antonio Fimia<sup>a</sup>, María J. Méndez<sup>a</sup>, Manuel Ulibarrena<sup>a</sup>, Ricardo Mallavia<sup>a</sup>, Tarsicio Beléndez<sup>a</sup>, Isabel Cabeza<sup>b</sup> and Fernando Rodríguez<sup>b</sup>

<sup>a</sup>Universidad Miguel Hernández, Avd. Ferrocarril s/n,  
03202 Elche (Alicante), Spain.

<sup>b</sup>Construcciones Aeronáuticas S.A, Avda. Aragón 404,  
28022 Madrid, Spain.

## ABSTRACT

Evaluation of the mechanical properties of films of the materials currently employed for recording diffractive optical elements is very important in order to foresee their mechanical behavior during the photochemical processing following recording of the interference pattern. This will also provide information about the mechanical and thermal stability of holograms recorded on these materials, which may be tested in the different environments in which the final application of the optical element will be used. For quantitative evaluation of these properties in an acrylamide based photopolymeric system, a study was carried out on layers of films of polyvinylalcohol and polyvinylalcohol mixed with triethanolamine. Layers coated on glass substrate were subjected to both a high vacuum and temperature changes. Real time measurements of optical path variations in the film were performed using a vacuum interferometric measurement system.

**Keywords:** Photopolymer, polyvinylalcohol, vacuum, temperature changes, holographic recording materials

## 1. INTRODUCTION

Photopolymer materials employed to manufacture holographic optical elements (HOEs) are widely used nowadays due to their advantages over traditional holographic recording materials. One of the more advantageous features is the possibility of controlling the composition and structure of the layer when the material is made by the researcher himself. This would be of help in matching the requirements of the HOE application with the material employed to manufacture it.

Any variation of the recording conditions of an HOE for the reconstruction gives rise to optical aberrations. These aberrations affect to image quality.<sup>1,2</sup> Variations in the environmental conditions of any material where an HOE has been recorded modify the physical dimensions and properties of the layer. This changes the internal geometry of the interference planes recorded, thus affecting the HOE's performance. It is therefore important to know the relationship between thermomechanical properties of the material and the optical properties of the HOE.

Recent reliability studies for HOEs made with the Dupont photopolymer HRF-600 have been carried out by Yeh *et al.*<sup>3</sup> Tests included thermal-shock, thermal-cycling, humidity and burn-in tests. The authors found that the average diffraction efficiency decrease for these HOEs was less than 5%. Wu *et al.*<sup>4</sup> carried out experiments to study the behavior of the Dupont photopolymer in terms of its mechanical and thermomechanical properties and the effects on optical efficiency. They found that a temperature change caused a change of 22% in the diffracted optical power. Also, Dhar *et al.*<sup>5</sup> studied the temperature-induced changes in plane-wave holographic gratings recorded in an acrylate-based photopolymer medium. Shifts of  $\pm 0.2$  degrees in the Bragg angle occurred at different temperatures.

Mckay and White<sup>6</sup> discussed the effect of space environments on dichromated gelatin holograms. The weight loss after exposure to a vacuum environment was 3.7%. The majority of weight loss was associated with loss of absorbed water vapor. This leads to a wavelength shift.

In our study we deal with layers of material where no HOE has been recorded. For this study we used an acrylamide based dry film which we made ourselves.<sup>7</sup> In order to understand its behavior under space conditions preliminary studies were developed using a series of thermal-vacuum tests. Initial data were obtained for partial

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Further author information: (E-mail: a.fimia@umh.es, Telephone:34 96 6658690, Fax:34 96 6658793)

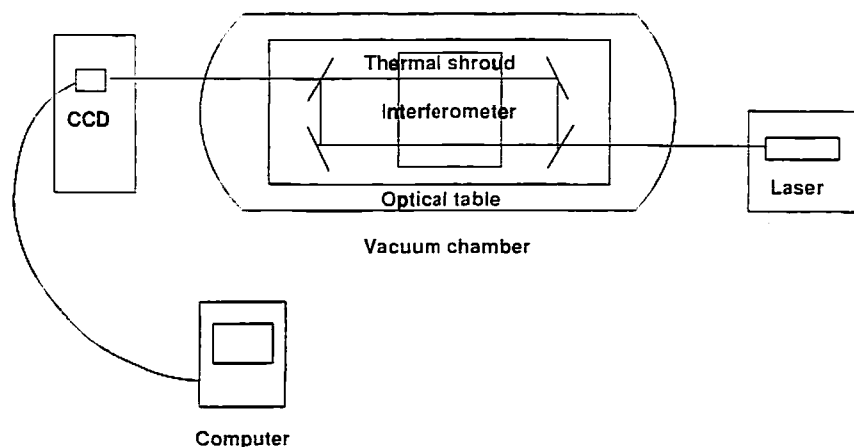


Figure 1. General setup view.

compositions of the material. This study helps us understand the thermomechanical performance of the whole layer, enabling us to optimise it in accordance with the final requirements of the HOE.

The same vacuum and temperature tests were also applied to gelatin layers as an example of conventional holographic material.

## 2. EXPERIMENTAL SETUP

### 2.1. Films Composition and Manufacture

The materials used in the manufacture of photopolymer dry films were polyvinylalcohol (PVA) supplied by Riedel-de-Häen ( $M_w \simeq 25,000$ ), triethanolamine (TEA), available from Sigma and a sensitizer, bengal rose (BR), from Panreac. All the components were of the highest grade available and used without any further purification.

To make PVA-BR layers, we took 40 ml of an aqueous solution of 13% PVA by weight (6.5 g in 50 ml). We added 2 ml of an aqueous solution 6.25 mM of BR and 7 ml of water to obtain 49 ml of final solution. From here on we shall refer to these layers as PVA layers. To make PVA-TEA-BR, we also took 40 ml of an aqueous solution of 13% PVA by weight. We added 2 ml of an aqueous solution 6.25 mM of BR and 7 ml of an aqueous solution of TEA (5 ml of TEA / 25 ml of  $H_2O$ ) to obtain 49 ml of final solution. From here on we shall refer to these layers as PVA-TEA layers.

Films were prepared by coating the solution over a 20 cm x 40 cm glass plate with an automatic device supplied by Neurtek, giving an initial thickness of 500  $\mu m$ . The solutions were dried for 48 hours in the dark under normal laboratory conditions (40 – 60% relative humidity and 22-25  $^{\circ}C$ ). The resulting thickness of the films were measured with a Pennig Ionization Gauge (P.I.G. 455) apparatus supplied by Neurtek. The thickness was  $30 \pm 5 \mu m$  for PVA films and  $70 \pm 5 \mu m$  for PVA-TEA films.

As a reference material for this study we used a gelatin layer derived from Agfa 8E type plates, after removal of the silver and sensitizers.

### 2.2. Optical Measurement System

A Mach-Zehnder interferometer was used to measure the optical path variations for testing all materials. The use of interferometry has two important advantages: it provides high resolution, and it is a non-contact method. The polymer does not suffer any mechanical stress due to the measurement method.

Fig. 1 shows a general scheme of the setup.

The light source is a HeNe frequency stabilized laser emitting at 633 nm. Its beam is filtered and collimated in order to produce a spot diameter of 10 mm. The laser beam enters the chamber through an optical quality glass

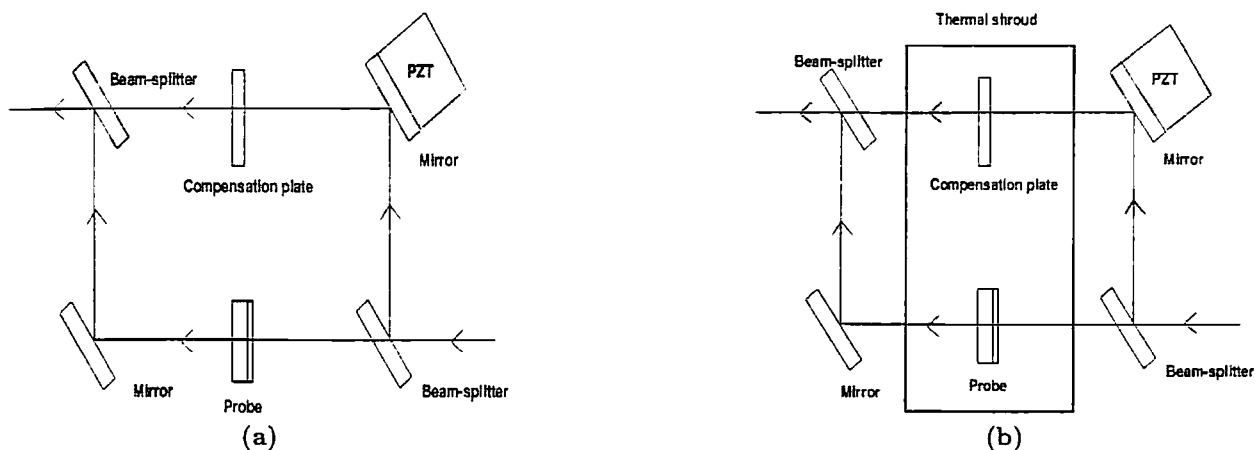


Figure 2. (a) Mach-Zehnder interferometer and (b) thermal shroud configuration.

window and is deflected inside the chamber so it can reach the interferometer. The interferometer (see Fig.2(a)) is mounted on an optical table inside the vacuum chamber. At the exit of the interferometer the two beams interfere forming a pattern of parallel fringes. This image reaches a CCD camera where it is processed. The interferometer is inside the vacuum chamber, while the HeNe laser with its collimation optics and the CCD camera are outside the chamber.

A detailed view of the interferometer is shown in Fig.2(a). The reason for using a Mach-Zehnder interferometer is that it has two different beams, one for the test probe, and the other for a compensating glass plate, so the effect of the test material can be clearly discerned from that of the substrate.

The interference beam leaves the vacuum chamber and goes through another optical quality glass window. The image formed on the CCD is digitized and processed in real time. By following the displacements of the fringes, the optical path difference (OPD) between the reference and the probe beams can be measured. The setup together with the processing software allows a resolution of  $0.03 \mu m$  for the OPD. In order to determine the sign of the OPD change, the interferometer needs to be calibrated. Such calibration consist in moving the mirror of the reference beam with a piezoelectric translator (PZT). To determine the sense of the movement of the fringes, the length of the reference beam is changed according to a calibration procedure.

The thermal environment is confined within two thermal shrouds which form an elliptical cylinder both bases of which are closed with multi-layer insulator blankets. The probe and the reference glass are inside the shroud (Fig.2(b)). All the optical equipment is outside at ambient temperature ( $22^{\circ}C$ ).

The temperature of the probe, the glass of reference and the optics of the interferometer are measured by means of Type-T thermocouples. The environmental conditions are achieved by means of an independent thermal-vacuum control system. In accordance with the specified test conditions a measurement loop starts. Every loop consists of the following steps: digitizing an interferometric image, processing it to get its most significant parameters, measuring the temperatures, and saving all these data to a file. The loop repeats this measurement process continuously until the test finishes.

### 2.3. Test Conditions

Two kinds of tests were applied to all the sample plates. After placing the plate inside the OMS and obtaining a vacuum, temperature variations starts.

Vacuum test data are continuously obtained starting at 150 mbar and rising to a value of  $3.10^{-5} mbar$ . It takes 5 hours for the OMS to reach this pressure, which is maintained until the test is completed. Fig.3 shows the history of the vacuum test.

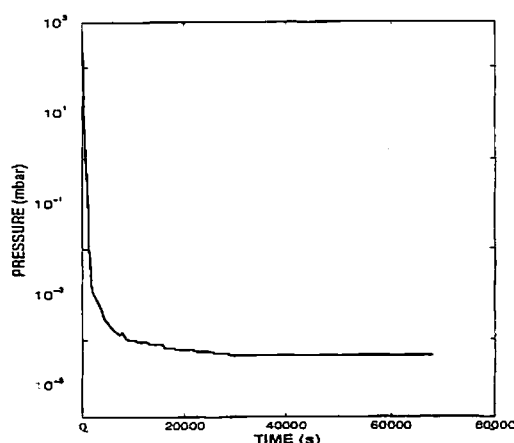


Figure 3. History of the vacuum test.

Test conditions of the temperature change test for PVA and gelatin films:

The initial temperature of the sample is 21 °C, which is maintained for 20 min. The sample is then heated to 79 °C for 15 min (40 min in the case of the gelatin sample). The temperature is increased at a rate of 3 °C/min. When this process is finished, the sample is cooled to 23 °C. The temperature is decreased at a rate of - 3 °C/min. The test is completed in approximately 1 hour and 30 min.

Test conditions of the temperature change test for PVA-TEA films:

The initial temperature of the sample is 22 °C, which is maintained for 15 min. The sample is then heated to 40 °C for 20 min. Subsequently, it is heated to 60 °C for 20 min and to 80 °C for 90 min. Later the sample is cooled to 24 °C. The temperature is both increased and decreased at a rate of  $\pm 2$  °C/min. The test is completed in approximately 4 hours.

Test conditions of the thermal cycling test for PVA-TEA films:

The initial temperature of the sample is 25 °C which is maintained for 10 min. The sample is heated to 50 °C for 10 min and then cooled to 25 °C for 10 min to complete a cycle. The temperature is both increased and decreased at a rate of  $\pm 3$  °C/min. The test is completed in approximately 2 hours and 40 min.

### 3. RESULTS

#### 3.1. PVA Films

Fig.4(a) shows the optical path difference as a function of time when the sample is subjected to a vacuum. After 13 hours the final optical path variation is 0.43  $\mu\text{m}$ . The layer undergoes a contraction probably due to a loss of material from the layer which is later recovered. After 5 hours, the pressure reaches a constant value, but the layer keeps changing. This may be due to the viscoelastic properties of the material.

Fig.4(b) shows the OPD variation when the sample is heated to 79 °C. A delay is observed between OPD variation and the rise and fall in temperature. The sample's thickness does not return to its initial value. This may be blamed, as in the former case, on the viscoelastic properties of the material. When room temperature is reached, an OPD is detected as though the material has a thermal memory.

#### 3.2. PVA-TEA Films

Fig.5(a) shows the OPD variations with time of PVA-TEA films subjected to the vacuum test. A final OPD of 0.38  $\mu\text{m}$  was obtained after an 18 hours test. An initial contraction was noted followed by the recovery of this loss in thickness of the layer.

Fig.5(b) shows the OPD variation with time when the sample is subjected to thermal variations. Note that the increase in thickness is greater in the last step (from 60 to 80 °C) than at the other temperatures.

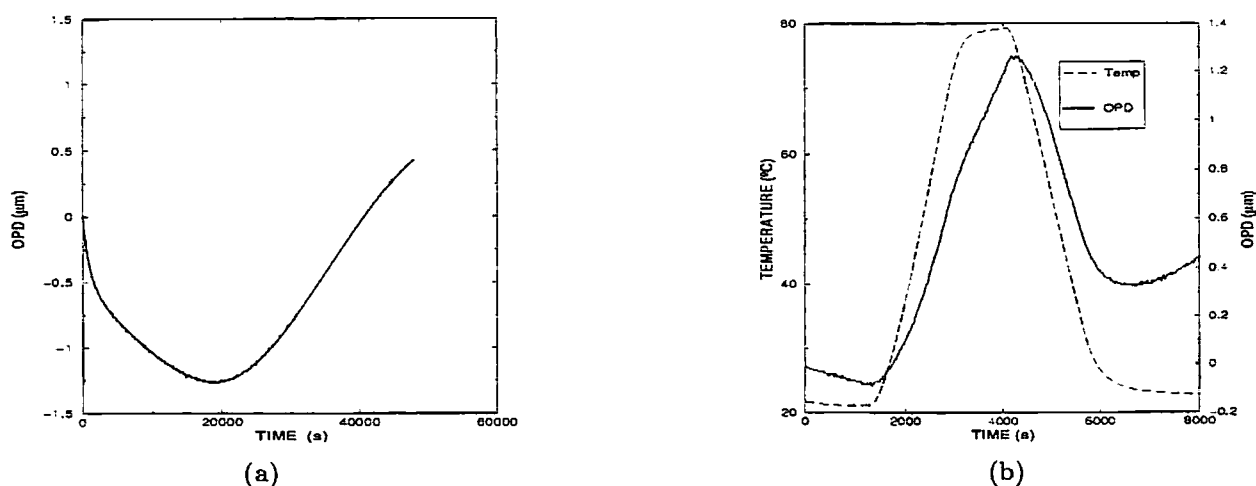


Figure 4. PVA film subjected to (a) a vacuum and (b) temperature changes.

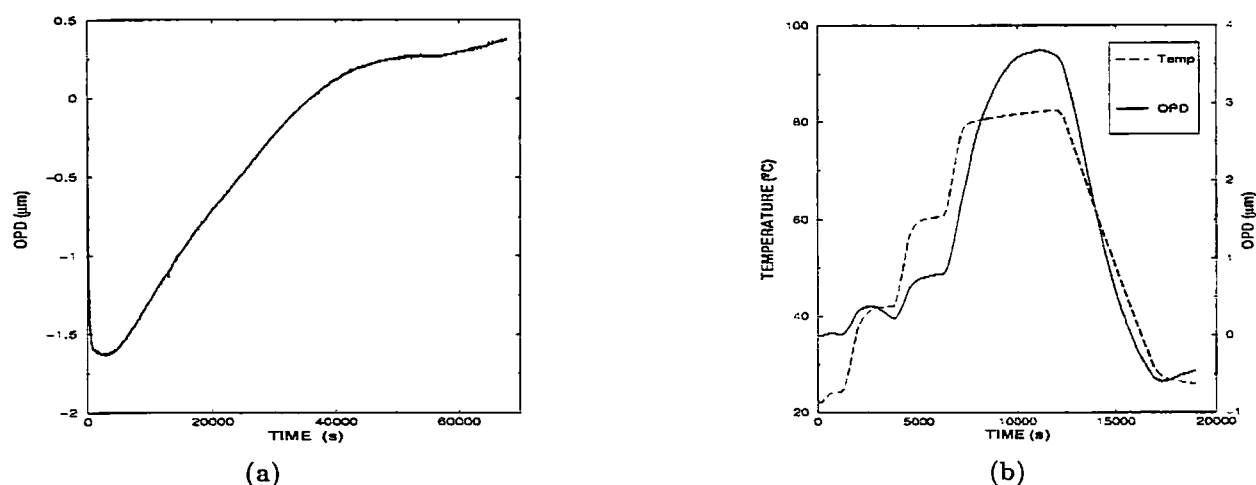


Figure 5. PVA and TEA film subjected to (a) a vacuum and (b) temperature changes.

### 3.3. Gelatin Films

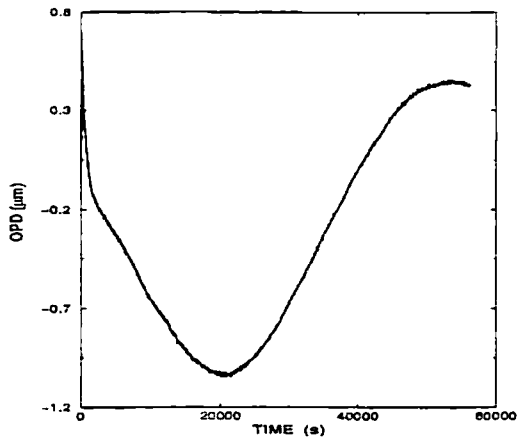
Fig.6(a) shows the OPD variations with time of gelatin films subjected to the vacuum test. A final OPD of  $0.43 \mu\text{m}$  was obtained after a 15 hours test. An initial contraction was noted followed by a recovery of this loss in thickness of the layer.

Fig.6(b) shows the OPD variation with time when the sample is subjected to thermal variations. The behavior of the film is different from those previously studied, since it does not show a return to its initial thickness.

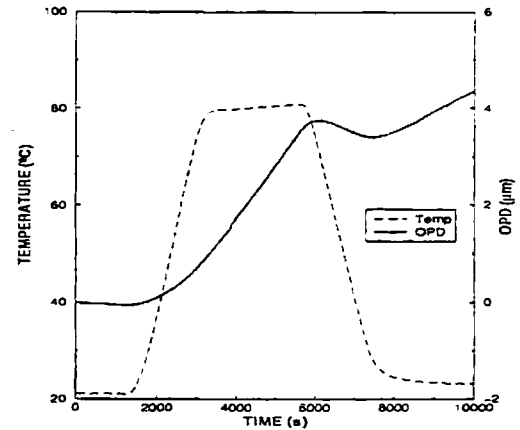
### 3.4. Comparison of films

Fig.7(a) shows the comparison between all three layers of the different materials tested in vacuum conditions. Fig.7(b) shows the comparison between the thermal-vacuum response of PVA and gelatin.

We observe a similar behavior in all layer when a vacuum is applied. All materials suffer an initial contraction probably due to water loss in the PVA and gelatin layer, and water and TEA loss in the PVA-TEA layers. Thickness variations are greater in the PVA-TEA layer due to the plasticising effect of TEA, thus giving thicker layers. This effect would explain how a small loss of TEA from the layer contributes greatly to a higher OPD variation.

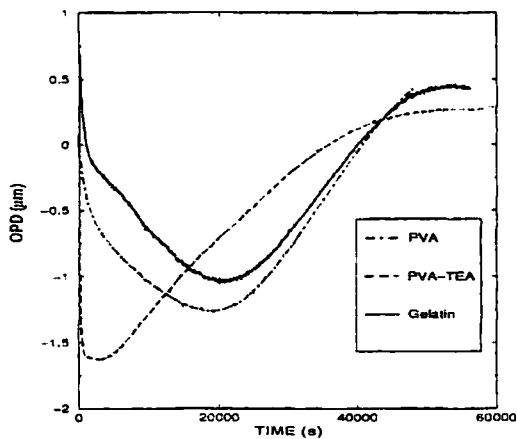


(a)

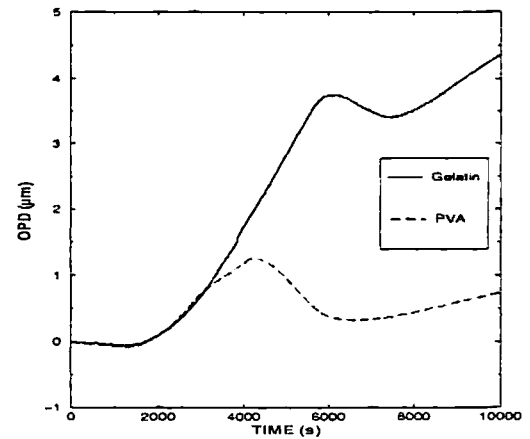


(b)

Figure 6. Gelatin film subjected to (a) a vacuum and (b) temperature changes.



(a)



(b)

Figure 7. Comparison of films subjected to (a) a vacuum and (b) temperature changes.

There is a difference between the behavior of PVA and that of gelatin layers when subject to temperature changes. The gelatin layer does not return to its initial thickness. The OPD variation is of the same order as its thickness. It may be that the three-dimensional structure of the gelatin layer is broken so it cannot return to its initial shape. The melting point of gelatin is about 40 °C<sup>8</sup> and we applied higher temperatures than this in the temperature test.

### 3.5. Thermal Cycle with PVA-TEA Samples

Fig.8 shows a thermal cycling test of PVA-TEA samples in vacuum conditions. OPD response with time is very quick, although some variations can be seen as the sample is subjected to more cycles.

## 4. THEORETICAL MODEL

Theoretical approximation of the behavior of the material was attempted with a finite element analysis. Finite element modelling (FEM) was performed using two-dimensional viscoelastic elements in ANSYS 5.4. The test case modelled consisted of a bi-layer structure composed of PVA as a thin film and glass as the substrate. Fig.9 shows the comparison between experimental and theoretical data of PVA variations in thermal-vacuum test.

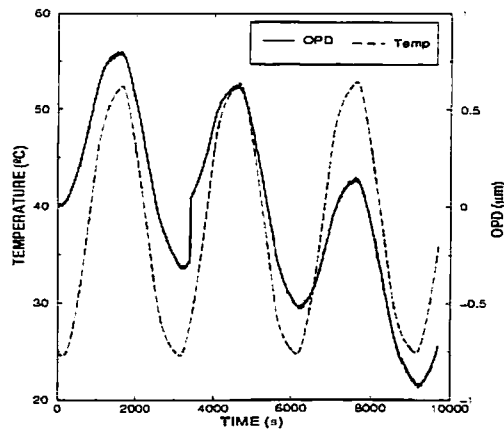


Figure 8. PVA and TEA film thermal cycling test.

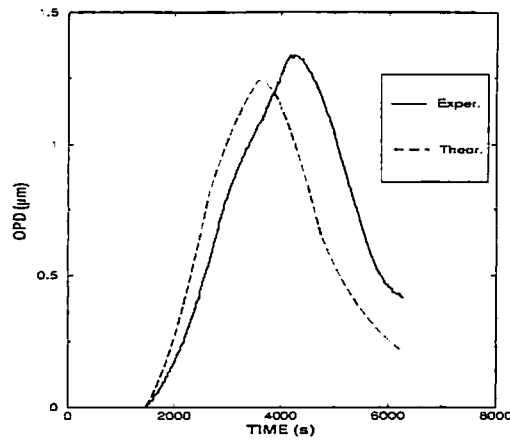


Figure 9. Theoretical variations vs. experimental variations for PVA film.

In order to match the experimental results with the theoretical ones, some assumptions were made:

1. The material shows viscoelastic properties.
2. The material is constrained due to the substrate, therefore the effect of the vacuum and temperature change is on the through-plane.<sup>9</sup>
3. The data used for polymer material correspond to bulk material properties.<sup>10,11</sup>
4. The algorithmic details of the integration are identical to those proposed in Ref. 12.
5. Vacuum and temperature data were the same as those of the experimental test conditions.

With these assumptions, we get the fitted values for this model shown in Table 1.

Parameters of glass substrate used in FEM are values found in MEMS Material Database from MEMS Clearing-house (<http://mems.isi.edu>).

## 5. CONCLUSIONS

During our work with the material we noticed the influence of a vacuum and temperatures variations on the layer. In the course of the vacuum test, we noticed a decrease in the optical path probably due to a loss of material from the layer. Later the layer tends to recover this loss, although it is never completely accomplish. This effect is to be blamed on the viscoelastic characteristics of the material. When a high vacuum is reached, thermal variation starts. The material shows a delay in response after both the increases and decreases in the temperature. When this thermal variation is finished and the system is at room temperature, the layer is not stable and optical path variations are still detected.



Table 1. Viscoelastic properties of the material

Thermal expansion coeff. in liquid state	28.6E-5 ( $^{\circ}\text{K}^{-1}$ )
Thermal expansion coeff. in glass state	9.1E-5 ( $^{\circ}\text{K}^{-1}$ )
Poisson Ratio	0.3
Young Modulus	650 (MPa)
Activation energy	350 (KJmol $^{-1}$ )
Relaxation times	850 (s)
Bulk modulus	508.5 (MPa)
Shear modulus at time=0	234.6 (MPa)
Shear modulus at time=infinity	0

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### REFERENCES

- [1] A. D. Gara and F. T. S. Yu, "Effect of emulsion thickness variations on wavefront reconstruction", *Applied Optics*, 10, pp. 1324-11328, 1971.
- [2] A. Beléndez Vázquez, "*Influencia del medio de registro en las características de los elementos ópticos holográficos*", PhD. Thesis, Universitat de Valencia, Valencia, 1990.
- [3] J. Yeh, A. Harton and K. Wyatt, "Reliability study of holographic optical elements made with DuPont photopolymer", *Applied Optics*, 37, pp. 6270-6274, 1998.
- [4] S. X. Wu, C. S. Cheng, T. Huang, S. Qin, J. Yeh, Q. Gao, A. Chen, C. P. Yeh, A. Harton and K. Wyat, "An experimental study on mechanical, termomechanical, and optomechanical behaviors of holographic materials", *Proc. SPIE*, 3294, pp. 145-151, 1998.
- [5] L. Dhar, M. G. Schnoes, T. L. Wysocki, H. Bair, M. Schilling and C. Boyd, "Temperature-induced changes in photopolymer volume hologram", *Applied Physics Letters*, 73, pp. 1337-1339, 1998.
- [6] A. McKay and J. White, "Effects of simulated space environments on dichromated gelatin hologram", *Optomechanical design of laser transmitters and receivers*, 1044, pp. 269-275, 1989.
- [7] S. Blaya, L. Carretero, R. Mallavia, A. Fimia, R. Madrigal, M. Ulibarrena and D. Levi, "Optimization of an acrylamide-based dry film used for holographic recording", *Applied Optic*, 37, pp. 7604-7610, 1998.
- [8] D. Meyerhofer, "Dicromated gelatin", *Holographic recording materials*, H. M. Smith, pp. 77-78, Springer-Verlag, 1998.
- [9] J. B. Lee, M. G. Allen, T. C. Hodge, S. A. Bidstrup and P. A. Kohl, "Modeling of substrate-induced anisotropy in through-plane thermal behavior of polymeric thin films", *Journal of Polymer Science: Part B: Polymer Physics*, 34, pp. 1591-1596, 1996.
- [10] M. L. Cerrada García, "*Propiedades mecánicas, comportamiento viscoelástico y anisotropía de copolímeros de alcohol vinílico y etileno*", PhD. Thesis, Universidad Complutense de Madrid, Madrid, 1995.
- [11] Strain Gage Measurements on Plastics and Composites from Measurement Group, <http://www.measurementsgroup.com>.
- [12] R. L. Taylor, K. S. Pister and G. L. Goudreas, "Thermochemical analysis of viscoelastic solids", *International Journal for Numerical Methods in Engineering*, 2, pp. 45-59, 1970.