

Photo differential scanning calorimetry, UV thermal mechanical analysis and UV dynamic mechanical analysis of light cured acrylics

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Polymers and composites cured by ultraviolet light exhibit similar shrinkage on curing as those cured by heat, with the associated distortion in the product shape. We report results pertaining to the effects of light intensity and temperature on the properties of the cured acryl resin materials. Ultraviolet differential scanning calorimetry and ultraviolet dynamic mechanical analysis were performed. The degree of distortion was measured by the displacement of the static probe position in the dynamic mechanical analysis. The results are represented as time–intensity–transformation diagrams and as three-dimensional plots of intensity, temperature and time. The largest distortion is seen when high intensity light is used to cure the sample through the gelation point. Curing the sample using low intensity light until gelation and then completing the cure at higher intensities result in minimal distortion.

Keywords: Polymer curing, Curing shrinkage, Differential scanning calorimetry, Dynamic mechanical analysis, Time–intensity–transformation curing diagram, UV curing

Introduction

Network polymers have a very wide range of applications.¹ Network formation is variously called cross-linking, curing or vulcanisation in the case of natural rubber. The term curing will be used in this article. The curing of epoxies,^{2–7} other thermosets and thermoset based composites^{8–11} is most often performed by providing heat, a procedure called thermal curing. Another option is photocuring. It is also called light curing or optical curing and consists of the application of irradiation; ultraviolet (UV) light is used often, but sometimes an electron beam or gamma radiation¹² is used instead. In both types of curing processes, either bulk materials or else films and coatings can be cured. Photo initiated systems have several advantages: short curing times, low amounts of volatile organic compounds and relative ease of application.¹³

One problem with both photocured and thermally cured materials is that curing causes shrinkage in

samples.¹⁴ The shrinkage can be as much as 6 vol.-% in aerospace composites. In photocured materials, shrinkage leads to a significantly higher amount of residual stresses, misshapen parts and increased failures in use. Finding a remedy is complicated by several factors. Curing is a function of temperature and time; there is an equation representing the effects of both.¹⁵ At the fundamental level, the progress of curing depends on the functional groups present.¹⁶ During curing, two distinct phenomena occur, i.e. gelation and vitrification.^{17–19} These two phenomena can be separated, but such separation requires application of two different techniques,¹⁹ namely, temperature modulated differential scanning calorimetry and dynamic mechanical analysis (DMA).

In this situation, we have decided to investigate whether the shrinkage during photocuring can be mitigated. A commercial obturation resin used in dentistry was the material studied. As already noted, differential scanning calorimetry (DSC) and DMA are the techniques used often to characterise the progress of curing,^{14,19–22} and we have used them. These techniques have been described in some detail by Lucas and her colleagues,²³ by Gedde²⁴ and by one of us,^{25,26} and the DSC was also described by Saiter and co-workers.²⁷

Experimental

The material used was a commercial dental resin used for filling cavities. Donated to us by the University of Colorado Dental School, the material consists of a N,N-dimethylaminoethyl methacrylate and bis-glycidyl

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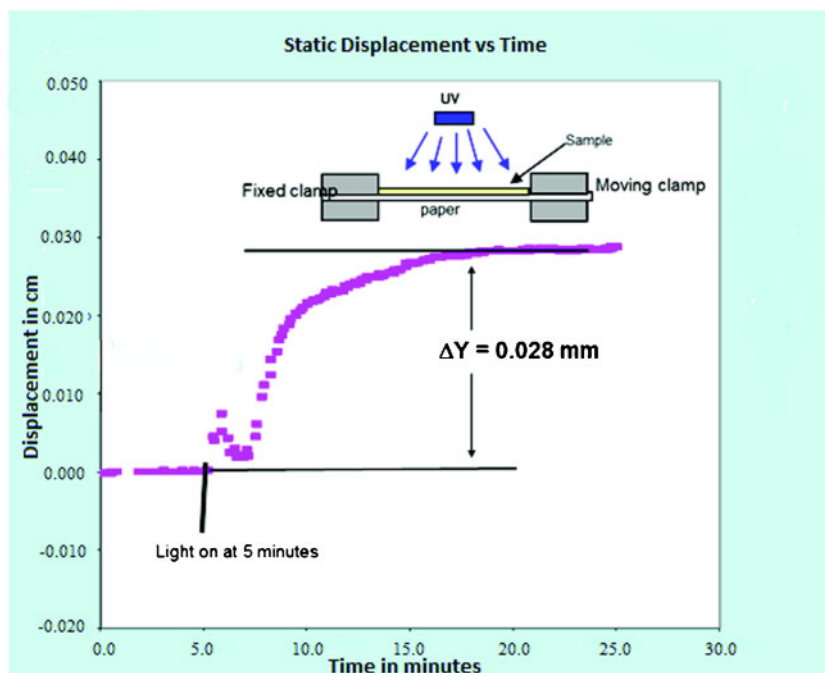
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1 Determination of sample distortion by DMA under UV irradiation, showing change in sample size as measured by static position of DMA probe: work was performed at 25°C and 365 nm

methacrylate in a mixture of 60 and 40 wt-% respectively. No silicate fillers were present. This represents a fairly standard composition for dental obturation materials.

The PerkinElmer Diamond DSC was used with liquid N₂ (LN₂ cooling attachment) purge and recirculation cooling (−20°C). One of the advantages of power compensation DSC is that it controls temperature and measures energy. This means that the temperature spikes seen sometimes in heat flux DSC do not happen when using this particular apparatus with adequate cooling as the instrument controls sample temperature. The modified DSC was fitted with a specialised lid to allow the light source to reach the material tested. The UV energy used in the DSC was measured and calibrated using graphite targets.²⁰ Samples for DSC experiments were weighted before and after runs, showing little to no weight loss across the run. For the optically curing system used here, weight loss was ~0.05% in the worst case. Results from DSC runs were used to measure the energy of cure, the activation energy of the curing reaction and the glass transition temperature T_g of the cured samples. Details of this approach may be found in the work of Gabbott.²⁸

The PerkinElmer DMA8000 with LN₂ cooling attachment was used to test the mechanical properties

and to track deformation. Distortion of the samples was measured in the DMA by tracking the static position of the probe (see Fig. 1). The T_g and the progress of curing the samples were evaluated by DMA. Since UV light generates heat, cooling during DMA testing is especially necessary so that temperature remains fairly constant during the run. Without effective cooling, temperature spikes can give the impression in the DMA results that a modulus change has occurred. We found that cooling with liquid nitrogen provides sufficient control to prevent the said abnormalities within the data, and no temperature drift was seen in the DMA samples. The LN₂ cooling attachment is controlled by the DMA firmware and maintains sample temperature by adjusting the flowrate of LN₂. We recall that in DMA, a sinusoidal stress σ is applied as a function of time t

$$\sigma(t) = \sigma_0 \sin(2\pi vt) \quad (1)$$

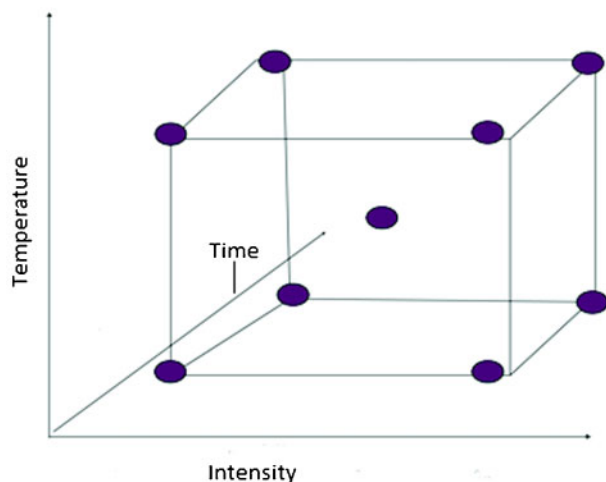
where v is the frequency in hertz (cycles/s). The result of the imposition of the sinusoidal load results in the following behaviour of the strain ε

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi vt - \delta) \quad (2)$$

The results provide us with the storage modulus E' representing the elastic (solid-like) behaviour and the loss modulus E'' representing the viscous flow (liquid-like)

Table 1 Experimental conditions and results from factorial design experiments

Temperature/°C	Intensity/W cm ⁻²	Time/min	$t_{\text{gel}}/\text{min}$	$t_{\text{vit}}/\text{min}$	Delta Y	Per cent cure
25	110	30	0.1	11	0.019	95.4
50	110	30	0.1	10	0.016	96.3
25	40	30	0.4	14	0.003	89.1
50	40	30	0.4	13	0.004	90.3
50	40	10	0.4	13	0.004	90.8
25	40	10	0.5	15	0.003	90.1
25	110	10	0.1	15	0.013	96.7
50	110	10	0.1	10	0.015	97.0
37.5	75	20	0.3	12	0.006	94.6



2 Graphical representation of factorial design used: this design is referred to as 2^3 centred factorial design, and boundary points of region of interest are measured as is centre point of experimental conditions²⁹

behaviour.^{23–26} Sometimes, one works also with $\tan \delta = E''/E'$.

Samples were prepared by coating the material on paper backing and then run in single cantilever geometry. A light emitting diode (LED) curing unit from Digital Light Labs, Knoxville, TN, USA, was used with a 365 nm LED source. Light was applied to the samples under temperatures of 25, 37.5 and 50°C for times ranging from 10 to 30 min and at intensities of 40–110 W cm⁻². Light intensity was measured in the DMA using a radiometer to calibrate for intensity. More information on the curing of photo initiated materials in DMA can be found in Ref. 26.

Following standard experimental design protocols,²⁹ we used a factorial design to define the conditions run in the experiment to characterise both the amount of cure and the degree of distortion as functions of light intensity, exposure time and temperature used. This approach allowed us to minimise the number of experiments used to characterise the material.

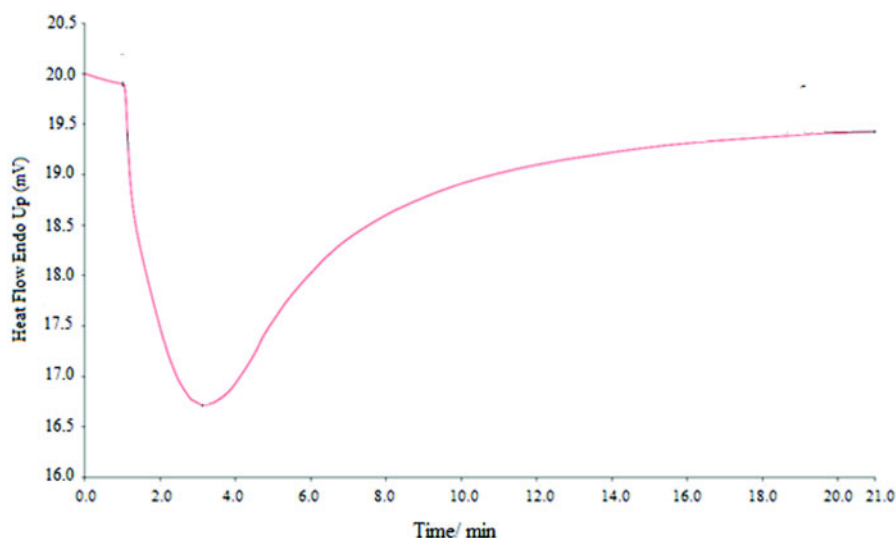
Experiment conditions are reported in Table 1 in the first three columns. These values can be graphically envisioned as the points shown in Fig. 2. A commercial software package Design-Ease was used to analyse the results (Stat-ease Software, Minneapolis, MN, USA).

Results and discussion

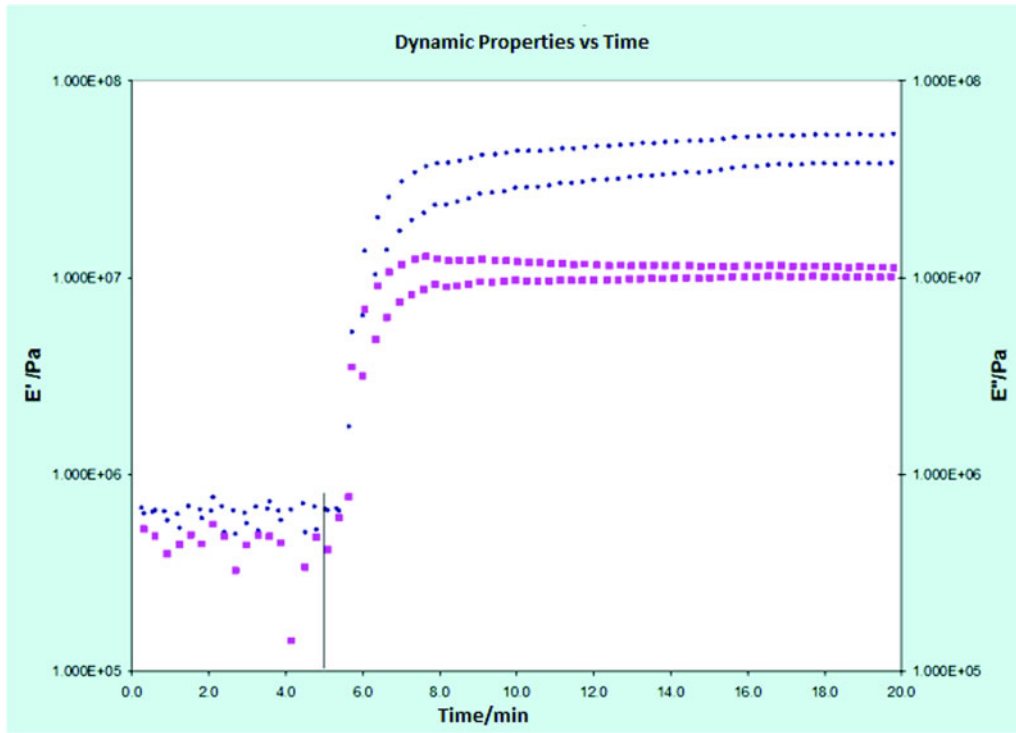
Analysing the results, we need to remember that most materials reach functional mechanical strength at <100% cure.³⁰ In most cases, reaching a value above the T_g^c (critical glass transition value where the material begins to act as a high polymer) gains sufficient strength for most uses. However, it is important to remember that other physical properties do not always track strength.³¹ Hence, the relationship of degree of cure to a particular property will need to be determined for the system of interest.

Examples of the data obtained from DSC and DMA are shown in Figs. 3 and 4 respectively. The enthalpy change is used to calculate the degree of cure by dividing a given value during the process by the value for complete cure.²⁸ This gives the amount of uncured material.

The method that we use is easier than the volumetric method used in thermomechanical analysis and can be applied in the same run as measuring gelation and vitrification temperatures. A variety of trials were undertaken, and we found that the gelation of the sample varied widely, depending on the intensity of the light. With a high intensity of light, there was significant distortion of the sample, as opposed to a low intensity of UV, where very little shrinkage of the sample occurred. The same occurred on the vitrification of the sample, but on a much higher order of magnitude. Since an initial high intensity of UV light causes rapid deformation of the sample, we are able to conclude that both gelation and vitrification occur almost simultaneously at high intensity. Gilham has developed time–temperature–transformation diagrams³² for the process of curing.³³ Following his example, we have developed from our results time–intensity–transformation relationships.



3 Differential scanning calorimetry results from typical photocure experiment: DSC data were used to calculate residual cure by measuring enthalpy of exothermic reaction and comparing to known value for 100% curing; in this instance, it was cured at 365 nm and 25°C



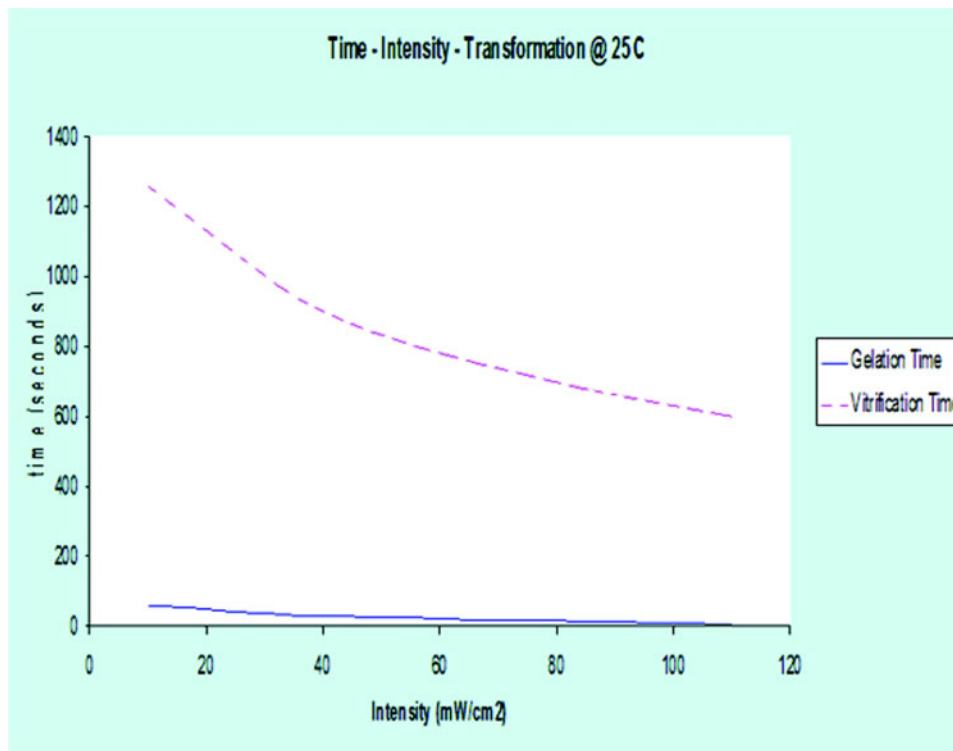
4 Dynamic mechanical analysis results from typical photocure experiment at 25°C and 365 nm. Mark at 5.0 min indicates initialisation of light. Results were used to calculate time of gelification t_{gel} , time of vitrification t_{vit} and distortion of sample. Small dots represent storage modulus E' , and filled squares represent loss modulus E''

Needless to say, intensity pertains here to the UV light intensity in curing.

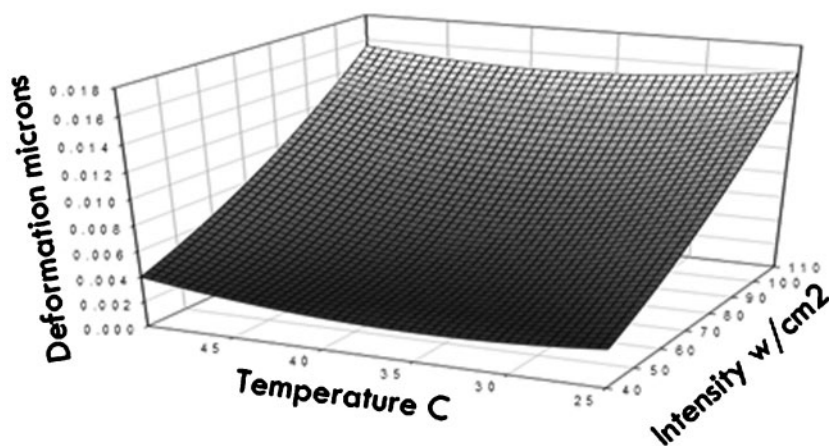
Since ultimately the goal is to minimise the distortion of the material as much as possible, we determined that the best method to use was low intensity UV light to photocure the sample at the beginning of the experiment,

and then after to increase the UV light significantly in order to finish the vitrification of the sample. The results are also reported numerically in Table 1. The factorial design shown schematically in Fig. 2 was used.

First, from the results in Table 1, an intensity equivalent of the Gilhams–Enns or time–temperature–transformation



5 Time–intensity–transformation diagram showing how intensity and time interact to cause vitrification and gelation: this example is at 25°C and 365 nm



6 Response surface mapping showing distortion of sample Z as function of intensity X and temperature Y: shading represents similar distortion values with darkest shades indicating least distortion

diagram was generated, as shown in Fig. 5. This displays how the transitions in the material are affected by a constant intensity at 25°C. Note that at high intensities the gelation occurs almost instantly.

Then, we have developed a cure profile to minimise distortion for reasonable curing times. Finally, the distortion was plotted as a function of temperature and light intensity (Fig. 6). We find that temperature has little effect; the higher the intensity of the light, the greater distortion is seen in the material. Based on this, we tried low intensity light until gelation and then finishing the cure with higher intensity and found that such procedure minimised the changes in the sample shape. Finally, the distortion was plotted as a function of temperature and light intensity (Fig. 6). In the case of these materials, the response surface is smooth and well behaved.

The results displayed in Fig. 6 show that temperature has only little effect on sample distortion. This can be summarised as the higher the intensity of the light, the greater distortion is seen in the material. Based on this, we have tried low intensity light until gelation and then finishing the cure with higher intensity; this procedure minimised the changes in the sample shape.

Brief survey of results

We recall the role of DSC in the evaluation of the effects of UV irradiation on the photostability of drugs.³⁴ The DSC turned out to be a reliable and convenient technique for the purpose.

The use of an experimental design approach to the characterisation of a light cured acrylic resin has promise for allowing characterisation of the shrinkage, curing time, time to gelation and time to vitrification to be obtained from one sequence of experiments. Interestingly, the greatest driver for distortion was the intensity of the light, indicating that the initial network formation is vital to controlling this. By utilising a variation of the Gillham diagram and response surfaces, it is possible to determine the best conditions for a minimally distorted product from a UV driven cure.

With this new approach of analysis, including photo differential scanning calorimeter, UV thermomechanical analysis, and UV DMA, it was possible to find which parameter had the greatest effect on the curing of acrylic

resins. We believe that our findings will be generally applicable for other light curing materials.

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