

Analysis of internal stresses in polymers obtained by photopolymerization

TP Photopolymérisation for MSE-360 : Science des polymères

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Introduction

UV light curing dates back to the 1940s, with the development of styrene polyester-based inks. In the 1960s, the wood industry used the photopolymerization process for varnishes, which is still one of the main applications of light-curing resins. Today, these resins are used in many areas, as shown in Figure 1, such as printing inks, varnishes and protective coatings for all types of substrates (Decker 1987), for lithography applications in microtechnology (Geiser 2010), for 3D printing (Bagheri 2019) and in composite formulations for dental restoration (Carioscia 2005).

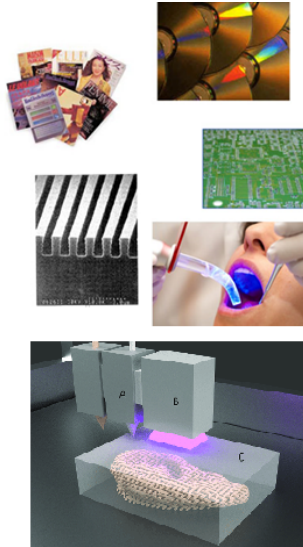


Figure 1 : Examples of light-cured resins (inks, protective layers, microelectronics, dentistry, 3D printing)

The curing process in UV or visible light is faster than thermally-induced processes and is usually performed at room temperature. There are radical systems (acrylates, polyesters, thiol-enes) and cationic systems (epoxides, vinyl-ethers), whose main characteristics are listed in Table 1. Acrylates are the more commonly in use because of their very high reaction rates and the large variety of available molecular structures with unique properties.

The aim of this practical work is to analyze internal stresses which develop in photopolymerizable layers deposited on aluminium substrates following exposure to UV irradiation. The experiments involve measuring the deflection of aluminium strips coated with resin and calculating the stress from the beam theory.

Table 1 : Characteristics of photopolymerizable acrylate and epoxide resins (Decker 1978)

	Acrylate resins	Epoxide resins
<i>Mechanism</i>	Radical	Cationic
<i>Growth</i>	Chain	Step
<i>Network</i>	Heterogeneous	Homogeneous
<i>Oxygen inhibition</i>	Sensitive	Not sensitive
<i>Humidity/bases inhibition</i>	Not sensitive	Sensitive
<i>Dark cure</i>	Very limited	Significant
<i>Polymerization speed</i>	Very fast	Moderate
<i>Shrinkage</i>	High	Low
<i>Toxicity</i>	Low	Low
<i>Conversion at gel point</i>	1 - 15 %	30 - 70 %

Theoretical basis

The polymerization of UV resins is accompanied with the phenomenon of shrinkage, giving rise to the development of internal stresses when the resin is confined, on a substrate for example. These stresses are responsible for problems of dimensional stability and even mechanical integrity (delamination, fracture etc.). Internal stresses can also occur during solvent evaporation, phase transformations and coalescence reactions as shown in Figure 2.

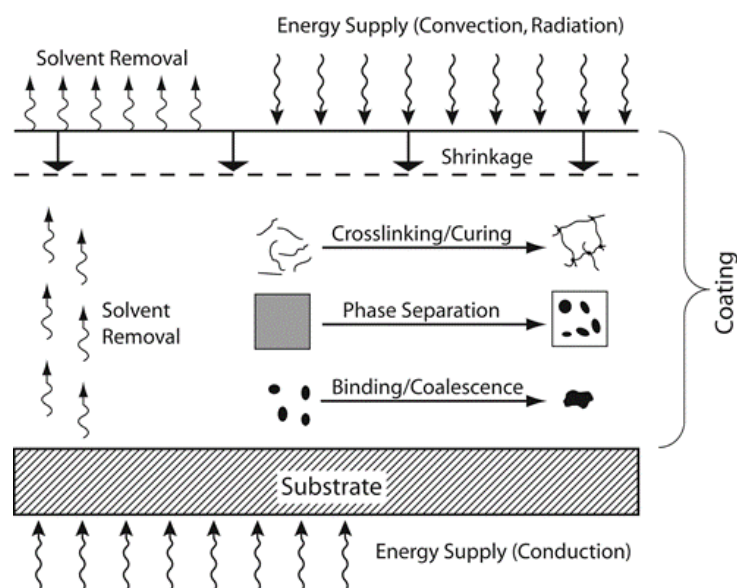


Figure 2 : Mechanisms responsible for shrinkage during the processing of polymeric coatings (Payne, 1998)

Shrinkage due to chemical reactions – chemical shrinkage

Before the gel point, the polymer in a liquid state can contract freely. When the relaxation time of the forming polymer becomes too long for the material to contract freely, the stresses become measurable. The volume of the polymer is then no longer in equilibrium. Therefore, the level of internal stress generated during polymerization does not only depend on the contraction of the material, but also on the rate of contraction and viscoelastic relaxation processes, which are strongly dependent on the rate of reaction between the functional groups (Schmidt 2007).

If the polymerization is carried out at a temperature above the glass transition temperature of the polymer, the formed material will be in a rubbery state throughout the reaction and the chemical shrinkage stresses will remain low (except in the case of three-dimensional confinement, as the liquid is incompressible). On the other hand, if the polymerization is carried out at a temperature lower than the glass transition of the polymer (which is generally the case for UV resins), the material will vitrify during the polymerization. This results in chemical shrinkage stresses that can be very high and may even lead to cracking.

Shrinkage due to cooling – thermal shrinkage

When processing thermoset resins, thermal stress is generated during the cooling process. As photopolymerization is done at room temperature, such stresses can be avoided or limited (except in case of exothermic effects).

Calculation of internal stresses: case study of a resin layer on a substrate

In the case of a layer on a substrate, the internal stress is expressed as follows:

$$\sigma_i(t) = 2 \int_0^t G(t) \frac{\partial c}{\partial t} dt + 2 \int_{T_c}^{T_f} G(\alpha_s + \frac{\partial c}{\partial T}) dT \quad (1)$$

where c represents the contraction or shrinkage of the polymer (chemical or thermal), G is the shear modulus, α_s the thermal expansion coefficient of the substrate and T_c and T_f are the temperature of curing and end of processing, respectively.

The first part on the right side of the equation represents the stress due to the chemical shrinkage that occurs during polymerization, while the second part represents the stress related to thermal shrinkage, which occurs during the cooling process, when the polymerization is done at high temperatures.

In this geometry layer/substrate, the contraction of the layer is connected to its free linear contraction S_L , to its Poisson coefficient ν_c and to the thermal expansion of the substrate as follows:

$$d_c = 2 \frac{\nu_c}{1-\nu_c} \alpha_s dT + \frac{1+\nu_c}{1-\nu_c} dS_L \quad (2)$$

Table 2 shows the volumetric shrinkage of various polymers, which depends on the reaction mechanisms of those materials. Thus, epoxides, which undergo ring opening, generally have a lower shrinkage than the acrylates. Alongside the development of new chemistries, many strategies have been proposed to reduce the level of internal stresses such as the optimization of the processing to activate viscoelastic relaxation processes or the introduction of nanoparticles transparent to UV light (Geiser 2009).

Table 2 : Volume shrinkage of different polymers

	Volume shrinkage	Reference
Thiol-ene	7%	Carioscia 2005
TGDDM (epoxide)	10%	Eom 2002
Polydimethylsiloxane	15%	Govindaraju 2005
DPHA (acrylate)	18%	Klang 2006

Presentation of the bending bilayer strip test

A conventional method to evaluate internal stresses in layers is to measure the deflection (or bending) of an elastic polymer/substrate bilayer strip (e.g., wafer, disk, beam). In the beam bending method, a thin layer of resin is deposited on a metal substrate in the form of a lamina and then the resin is cured. The curvature of the metal strip allows the measurement of the internal stress within the resin layer. The experimental setup used in this practical work is schematically shown in Figure 3 and consists of a support frame with two points on which the metal strip is placed. The radius of curvature is calculated from the deflection δ , which is measured with an inductive sensor:

$$R = \frac{4\delta^2 + L^2}{8\delta} \approx \frac{L^2}{8\delta} \quad (3)$$

where L is the distance between the two supporting points (150 mm). The sensor's weight (0.5 g) may induce an error in the calculation. This error, being less than 1%, will be ignored in the present work.

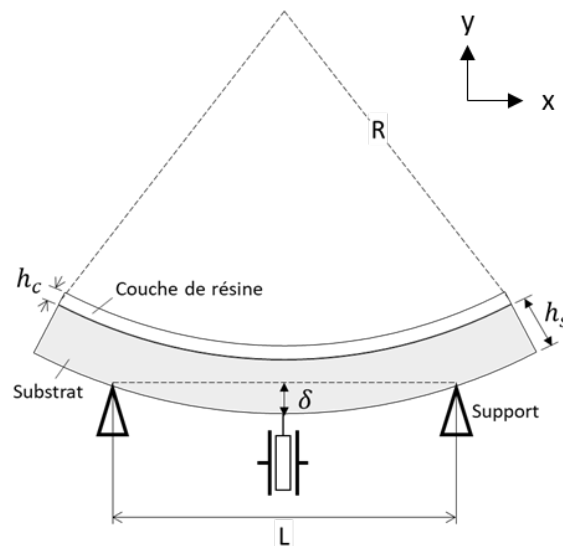


Figure 3 : Schematic representation of the bending bilayer strip test

Several models have been developed in order to calculate the internal stress from the curvature of the bilayer strip. The elastic properties of the polymer layer and the metallic substrate, and the geometry of the system are taken into account.

The Stoney model (1909) is the first known:

$$\sigma_i = -\frac{E_s h_s^2}{6R h_c} \quad (4)$$

where E_s is the Young modulus of the substrate, h_c and h_s are the resin layer's thickness and substrate's thickness, and R represents the radius of curvature that is measured.

The “-” sign results from the convention that the tensile stresses are positive and vice versa for compressive stresses. Stoney model provides a good approximation of the stress when $h_c \ll h_s$ and has the advantage to not depend on the elastic modulus of the polymeric layer, which is generally unknown and evolves during polymerization.

In case the elastic modulus of the cured layer during photopolymerization is known (when obtained through photo-rheological experiments for instance), a more accurate model, that takes into account the plane strain effects, is given by Inoue and Kobatake (1958):

$$\sigma_i = -\frac{E_s h_s^2}{6R h_c} \left(\frac{(1-ab^2)(1-a) + (ab(b+2)+1)^3 + a(ab^2+2b+1)^3}{2(1+b)(1+ab)^3} \right) \quad (5)$$

where $a = E_c/E_s$ (E_c being the Young modulus of the resin layer) and $b = h_c/h_s$.

Experimental part

The goal of this practice work's experimental part is to obtain a graph showing the evolution of the internal stress as a function of time for two types of polymeric resins:

- Photopolymer hyperbranched polyester acrylate with 6 wt.% photoinitiator TPO
- Cycloaliphatic epoxy photopolymer with 3 wt.% photoinitiator O250 and 1 wt.% thioxanthone.

The substrate is a 0.3 mm thick aluminium strip, whose width and length are about 8 mm and 180mm, respectively (the distance between the two support points of the setup being equal to 150 mm). Young's modulus of aluminium is equal to 72 GPa.

The experiment takes place as follows:

1. Place the sewing thread through the sensors hook without moving it (position of the sensors should be around -5 - 0 mm).
2. Shorten (to 180 mm) and clean the aluminium strip with a solvent (acetone or isopropanol) and let it dry.
3. Apply a thin layer of the chosen resin on the strip. Be careful not to apply resin on the backside of the strip (remove excess if necessary with dry paper).
4. Place the strip on both supporting points of the setup.
5. Tie the inductive sensor to the sample with the sewing thread. The sensor should be close to the strip (hanging), but not too tightly fixed to the strip.
6. Check that the shutter of the UV lamp is closed.
7. Move the setup inside the chamber and set the sensor's height to zero.
8. If it is the first measurement, turn on the UV light and wait 3 minutes for the heating of the lamp.
9. Start the data acquisition at the same time you open the shutter
10. Close the shutter once the deflection stabilizes (about 3-5 min), but let the data acquisition continue about 3 more minutes and then end the experiment.
11. Measure the thickness of the polymerized layer + metal strip (ideally from 5 different locations of the same strip to obtain the mean and the standard deviation)
12. The program gives you in a text file: time [s], deflection [mm] and temperature [°C]. Draw the graphs: (a) deflection vs time, (b) temperature vs time and (c) the internal stress, calculated using Stoney's equation (Equation 4) vs time.

The experiment should be carried out 2-3 times for each resin.

Questions to be addressed in Results and Discussion

- Measuring the deflection as a function of time allows us to calculate the evolution of the internal stress as a function of time. Are the measurements reproducible? Do the orders of magnitude of the calculated stresses seem reasonable? (Compare with literature references)
- Are the stresses in tension or compression? What could be the consequences of such stresses in practice?
- How can we distinguish the effects of chemical shrinkage from the ones of thermal shrinkage? How do these two phenomena affect the internal stress in theory and according to the experiments?
- What are the observed differences between the two types of resin (time for the reaction to start, final internal stress level, thickness of layer, etc.). Are your observations consistent with Table 1 and Table 2 ?
- According to Table 1, the photopolymerization of acrylate resins is inhibited by oxygen. Did you observe it during the experiments? How and why? How can you improve the polymerization conditions to avoid it?

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ANNEXES

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