A Simple and Inexpensive Method to Measure Photopolymerization Shrinkage Stress

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Polymerization shrinkage is important for many applications since it leads to residual stresses, which can deform a system and undermine its optical or mechanical properties. This paper describes a simple, inexpensive and effective method for characterizing polymerization shrinkage stresses in photopolymerized coatings. The method, which is based upon the deflection of a thin brass cantilever, can be used with any initiating light source, and is ideally suited for screening of monomer formulations since it can quickly and easily generate comparative data. The theoretical basis and design of the apparatus is presented and considerations for accurate stress measurements are discussed.

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Introduction

Photopolymerization has recently become an industrial standard in many high throughput applications because of its efficient use of light energy to rapidly initiate polymerizations at room temperature. Both free-radical and cationic photopolymerizations[1,2] are used in applications that range from thin coatings to thick films,[3,4] and from emulsion polymerizations[5,6] to nanostructured materials produced using lyotropic liquid crystals.[7] Photopolymerization is also an area of active research designed to address current issues and enable new applications. Examples include research on methods for overcoming oxygen inhibition,[8] and new initiation systems using less energetic visible light.[9]

The density of the final polymer coating is invariably greater than that of the original monomer liquid, and the resulting polymerization shrinkage stress may deform the coated product or undermine its optical or mechanical properties. For example, the coating could warp low modulus substrates or cause delamination or micro-crack formation.[10] The polymerization stresses developed in a given system depend upon a number of factors, including the molar volume change upon polymerization, the conversion profile, the geometry of the system, the modulus of the cured material and the modulus of the substrate or confinement. For many applications, a simple, inexpensive and effective method for measuring the polymerization shrinkage stress in photopolymerized coatings is important because it will allow the shrinkage stress resulting from different monomer formulations to be quickly compared for screening purposes. This paper describes such a method for characterizing polymerization shrinkage stresses in photopolymerized coatings. The method, which is based upon the deflection of a thin brass cantilever, can be used with any initiating light source and photopolymerization system.

Principles of the Cantilever Method for Coating Stress Measurements

The measurement of polymerization shrinkage stress through the deflection of a cantilever is a simple concept illustrated schematically in Figure 1. Polymerization of the coating leads to shrinkage in the plane of the cantilever. Because the coating is constrained by adhesion to the cantilever, a stress is transferred to the cantilever, causing it to deform. Cocoran, *et al,* studied stresses in organic coatings in the 1960s and developed a relationship between the cantilever deflection and internal stresses in the organic coating. This relationship was based on Stoney's equation[11,12] and includes the moduli and Poisson ratios of the coating and the cantilever.

Equation 1 shows a modified version of Corcoran's relationship that will be used in this paper:

Equation 1

$$S=\frac{hE_s t^3}{3L_s L_c c(t+c)(1-Y_S)}+\frac{hE_c(t+c)}{L_S L_C(1-Y_C)}$$

In this equation, S represents the internal stress; h is the deflection of the cantilever; E_s and E_c correspond to the modulus of elasticity for the substrate and coating, respectively; Y_s and Y_c are Poisson's ratio of the cantilever substrate and the coating, respectively; L_s denotes the length of the substrate between the edge point at which it is clamped and point at which deflection is measured; L_c is the length of the coating; t denotes the thickness of the cantilever substrate; and c represents the thickness of the coating. The second term in Equation 1 gives a value for the stresses removed as a result of the cantilever deformation while the first term gives a value for the stresses remaining in the coating.[13] Equation 1 is based on the assumption that the coated portion of the cantilever lies centered along the cantilever's length.

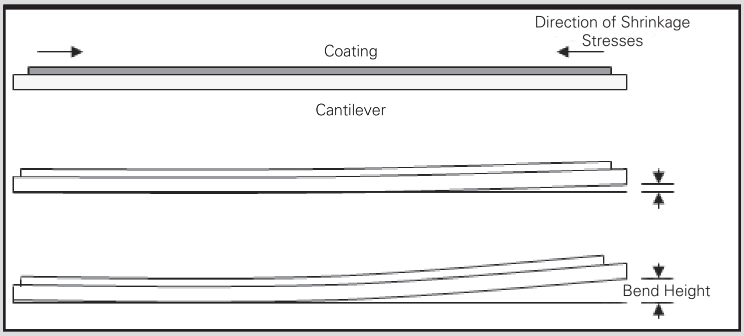
Selection of Cantilever Materials and Dimensions

The dimensions and mechanical properties of a cantilever for stress measurements depend upon the magnitude of the stress to be measured. It is desired that the cantilever deflection be easily measurable, but remain within the elastic deformation regime. In addition, it is imperative to have good adhesion between the substrate and polymer coating, and the cantilever must not react with nor dissolve in the monomer liquid. Many plastic substrates were eliminated due to the latter consideration. Based upon all of these considerations, a brass cantilever substrate was chosen with characteristics listed in Table 1. With this design, photopolymerization shrinkage stresses generated by acrylates lead to cantilever deflections on the order of 10 mm.

The selected brass alloy was obtained in a standard roll, and cantilevers were cut to the desired length using a small precise table-mounted shear. To ensure adhesion between the cantilever and the coating, each brass cantilever was thoroughly cleaned using the following procedure. Oils from machining and handling of the brass were removed by washing in soap and water, followed by a rinse in de-ionized water then a rinse with acetone before being stored in sealed vials of acetone.

FIGURE 1

Schematic of polymerization shrinkage stress in the plane of a coating causing a vertical deflection of a cantilever



Stress Measurement—Setup and Procedure

Photopolymerizations were initiated using a 1,000 W Hg/Xe arc lamp equipped with optics (Newport Corporation, Irvine, Calif.), which directed the light downward toward the substrate. A mechanical shutter was used to control the length of illumination and the light was passed through a water-cooled IR filter to reduce heating from the lamp. A cantilever holder was machined from a block of poly(vinyl chloride) and used to secure one end of the brass cantilever so that the free end could be measured

TABLE 1

Brass cantilever properties

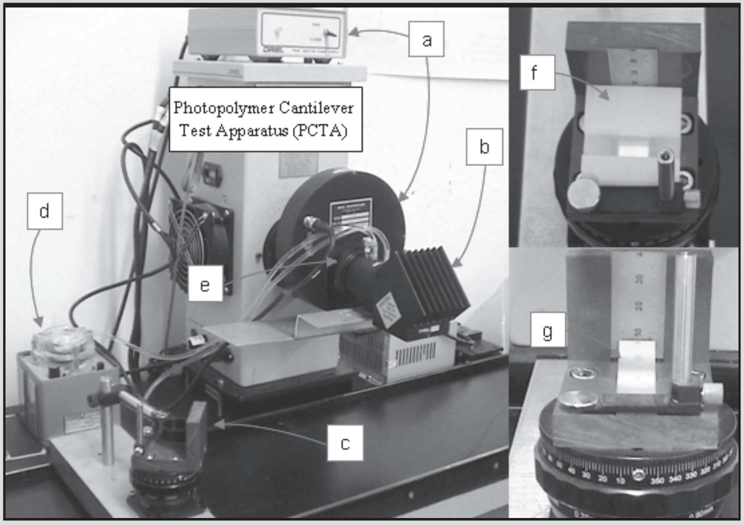
Description	Formable Cartridge Brass (Alloy 260), 25 ft roll, McMaster order #90355K223
Thickness	0.051 ± 0.008 mm (0.002 ± 0.0003 in)
Width	12.7 mm (0.5 in)
Length	5 cm

using the mounted rule. A picture of the experimental apparatus is shown in Figure 2 along with a diagram in Figure 3 showing a detailed view of the custom-machined parts. In Figure 2, the cantilever holder is shown in the position where monomer is applied. The aluminum platform, including the cantilever holder and optional filter holder, is slid into place beneath the lamp prior to illumination.

The repeatable application of the monomer to the cantilever substrate was found to be an important step in the stress measurement process. Consistent application was ensured using a micropipette to apply precise amounts of monomer (20 µL) to the substrate, and a custom machined guide to spread the monomer over a specified area measuring 1/2" by 3/8" in a specified location in the center of the brass cantilever substrate. Figure 3 shows the various custom machined components. The two thumbscrews are used together for tightening the cross member, which holds down one end of the cantilever strip. The white applicator guide is used along with a micropipette in order to consistently apply the monomer coating, which is to be photopolymerized and subsequently measured for stress. The machined guide is removed before photopolymerization occurs, so as not to hinder the deformation of the cantilever substrate.

FIGURE 2

Pictures of the cantilever setup for the stress measurements reported in this contribution



(a) shutter device (b) light beam turner (c) cantilever holder (d) water pump (e) water-cooled IR filter (f) application guide (g) deflected cantilever

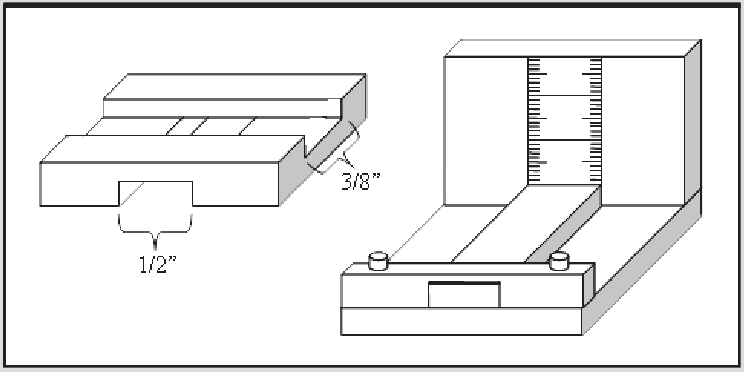
In the first step of the stress measurement procedure, a single brass strip is removed from the storage media and dried using a delicate task wipe to remove the solvent. The brass strip is then inserted into the holder so that the curvature of the strip is concave up. Next, the machined guide is placed atop the strip and monomer is applied in a defined area. Then, the machined guide is removed and the bend height of the cantilever due to natural curvature of the strip is recorded. The coated cantilever strip is then centered beneath the lamp by sliding the holder into place. With the optics aligned and focused properly, the coating is illuminated for a specified amount of time to give consistent monomer conversion between samples. The bend height for both the left and right side of the cantilever strip is measured and recorded. The original bend height is subtracted from that measured after polymerization to obtain net deflection of the cantilever. These values can either be compared between experiments to show which systems result in greater stress, or they can be used in Equation 1 to obtain a stress value.

Conclusions

In this contribution, a simple and inexpensive cantilever apparatus for photopolymerization shrinkage stress measurements is described. The apparatus, which is designed for stresses typically encountered in photopolymerizations of acrylates, can

FIGURE 3

Diagram showing both the cantilever holder and the application guide



provide a very consistent means of comparing the shrinkage stresses that arise from different coating formulations. The method can be used with any initiating light source, and is ideally suited for screening of monomer formulations since it can quickly and easily generate comparative data. This apparatus and method will be used in a future contribution for a systematic study of photopolymerization shrinkage stress. ◗

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