

The Effects of Processing Variables on Stress Development in Ultraviolet-Cured Coatings

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ABSTRACT: A cantilever deflection technique was used to monitor stress development during ultraviolet photo-cure of acrylate coatings to the glassy state. Two coating systems were studied: a trifunctional monomer (trimethylol propane triacrylate, TMPTA) and a tetrafunctional monomer (pentaerythritol tetraacrylate, PETA). Both were photoinitiated with 2,2-dimethoxy-2-phenylacetophenone (DMPA). Average in-plane stresses of up to 30 MPa were measured upon curing at room temperature. The rate and magnitude of stress development rose with the photoinitiator concentration and with light intensity. Curing with more strongly absorbed light had similar effects. Light absorption caused decreased stress magnitudes in thicker coatings. Somewhat unexpectedly, the rate and magnitude of stress development increased with monomer functionality even though the conversion fell. Moreover, curing thick coatings with high radical concentrations (strongly absorbing light and large photoinitiator concentrations) caused ripple defects to form. With the appearance of these defects, stress ceased to rise with the photoinitiator concentration. Fourier transform infrared spectroscopy was employed to monitor conversion and to help understand these stress development trends. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1267–1277, 1997

Key words: coating stress; photoinitiation; deflection measurement; coating defects; ultraviolet curing

INTRODUCTION

Radiation-cured multifunctional polyacrylate coatings are growing in use because they can cure quickly to glassy coatings with no emission of volatiles and with excellent thermal and mechanical stability.^{1–3} Ultraviolet (UV)-curing is currently used in adhesives, protective layers, dental restorative materials, and photoresists.^{1–3} The demands of these applications have led to an increased need to characterize coating properties, particularly

the stress produced during cure.^{4–7} Stresses can lead to defects (e.g., buckling, cracking, curling, delamination) that degrade the final coating quality.^{8–11} Since stresses and subsequent defects limit a coating's performance and quality, the measurement and control of stress development in solidifying and solidified coatings can help to optimize material selection and curing process design.^{11–15}

Most coatings prepared from a liquid (solution or dispersion) develop stress as the liquid transforms into an elastic or viscoelastic solid. Since the coating adheres to a rigid substrate, shrinkage can occur only in the thickness direction. The constrained or frustrated volume change in directions parallel to the substrate leads to an in-plane tensile stress. Moreover, in complex formulations, shrinkage and stress can be amplified by

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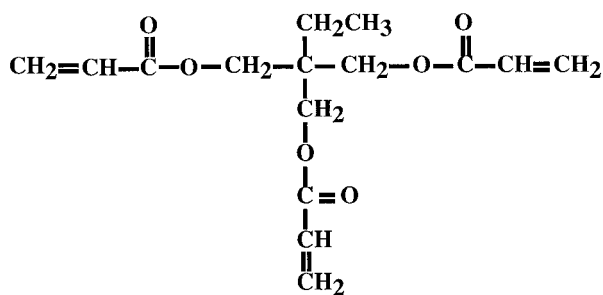
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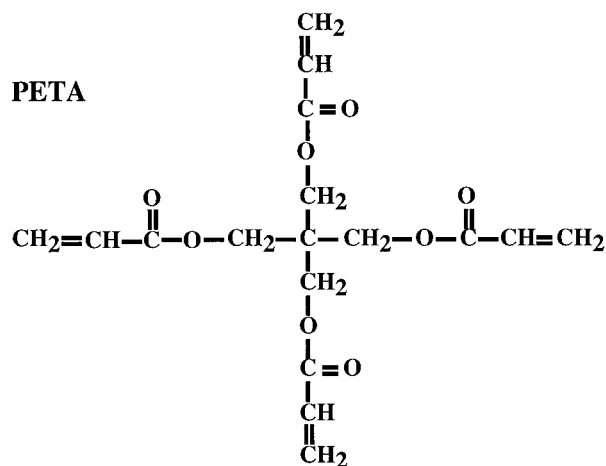
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TMPTA



PETA



DMPA

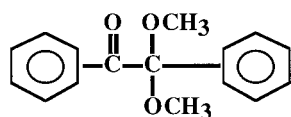


Figure 1 Chemical structures of TMPTA, PETA, and DMPA.

solvent loss, particle binding/curing, temperature changes, foreign particles, nonuniform drying conditions, thermal gradients, and degradation.

Multifunctional monomers are added to coating formulations to enhance solidification rates, increase glass transition temperatures (T_g s), and produce higher modulus and more chemically resistant coatings.^{2,3,16-18} In the simplest formulations (no solvent, particles, plasticizers, etc.), only liquid monomers with small amounts of photoinitiator are coated and then polymerized with UV light. However, even in these simple formulations incomplete conversion can complicate design. It is difficult to assess the conversion- and rate-dependent apparent T_g , modulus, etc.¹⁹ These mechanical properties are known to be affected by monomer functionality and processing variables—photoinitiator con-

centration, light intensity and wavelength, and coating thickness.

The effects of processing variables on monomer conversion have been reported,^{1,2,7,17,19} but there has been no work quantifying their effects on stress development. In this report, we describe the measurement of stress development rate and stress magnitude in coatings of multifunctional acrylates cured with UV light as a function of coating composition (i.e., monomer functionality and photoinitiator concentration) and other processing variables.

EXPERIMENTAL

Coating Preparation

The multifunctional monomers used for this study were trimethylol propane triacrylate (TMPTA; Aldrich Chemical Co., Milwaukee, WI) and pentaerythritol tetraacrylate (PETA; Sartomer, West Chester, PA). Their chemical structures are shown in Figure 1. Coatings were prepared from the acrylate monomers with dissolved photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA; Aldrich Chemical Co., Milwaukee, WI). Monomer and DMPA were mixed in the dark so as to limit pre-experimental curing. The photoinitiator amount used varied from 0.02% to 2% of the total functional group concentration. To minimize oxygen inhibition of radicals, nitrogen was bubbled through each solution before coating, and curing took place in a nitrogen atmosphere. At very low photoinitiator concentrations (<0.10%), there was some variability in the “pre-solidifica-

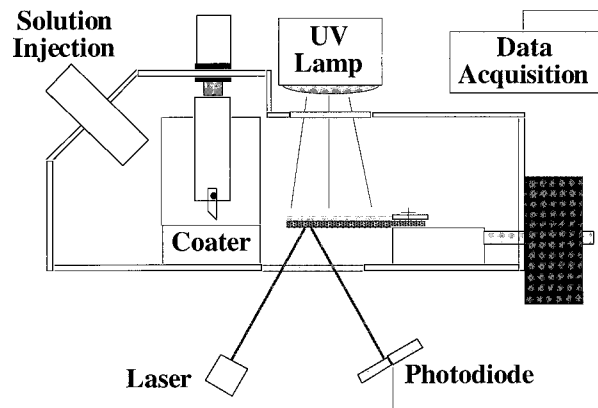


Figure 2 The stress measurement apparatus: a controlled environment combination draw-down coater and cantilever stress measurement device.

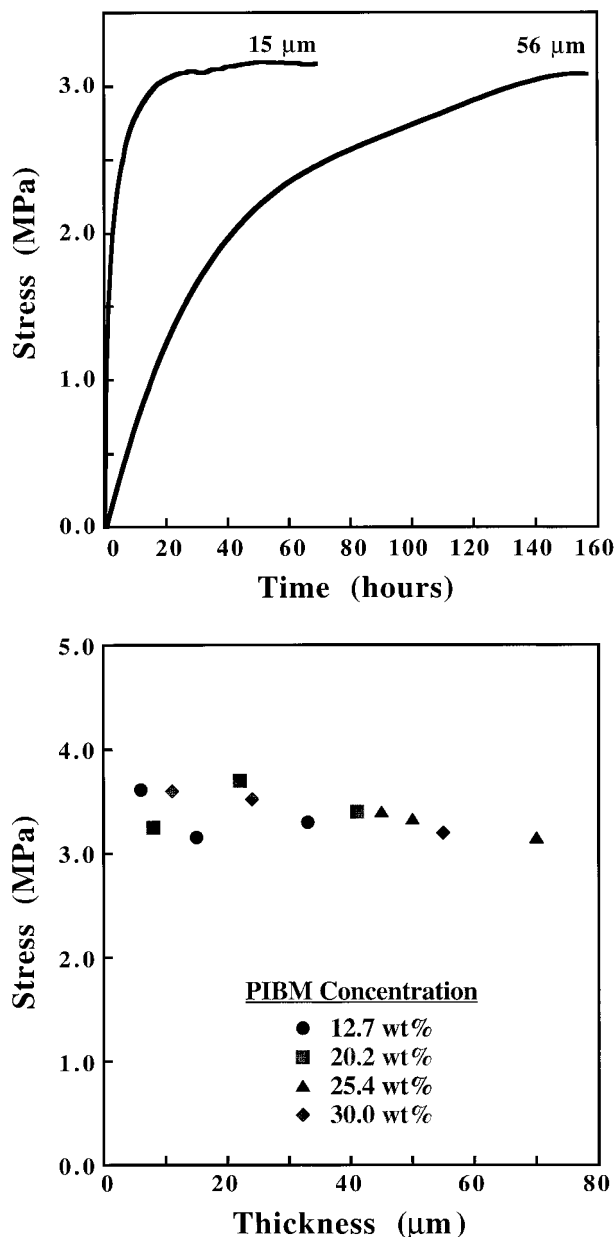


Figure 3 Stress development in solvent cast PIBM coatings. Coating liquids were 25 wt % PIBM in toluene (top only).

tion" period (see below) due to the inhibitor present in the as-received monomer, but the removal of dissolved oxygen sufficed to ensure that this variability did not affect the relevant stress and conversion trends. Industrial practice frequently addresses this sensitivity problem simply by curing with very high light intensities rather than curing in an inert atmosphere.²

An automated draw-down coater was used to meter coating thickness at a constant coating speed (~ 0.70 cm/s). Coating thickness was var-

ied from 10 to 200 μm . Coatings were prepared on steel feeler gauge stock inside the stress measurement apparatus (Fig. 2). The steel substrates, with thicknesses between 0.35 and 0.45 mm, were cut to clamped dimensions of 45×6 mm. Cantilever length-to-width ratios were chosen (based on finite element analysis) so as to avoid significant effects due to cupping. Two UV pencil lamps with wavelengths of 254 and 365 nm (Spectronics Corp., Westbury, NY) were used to cure the coatings. Light intensity was adjusted by changing the lamp-to-coating distance. The light intensity was monitored with a radiometer. All coatings were exposed to UV light in a nitrogen atmosphere at room temperature ($\sim 21^\circ\text{C}$). Since the purpose of the work was to look at the transient behavior of the coatings, ultrafast curing (i.e., high UV intensities) was not desired. Instead, low light intensities ($<1000 \mu\text{W}/\text{cm}^2$) were used to allow for observation of small changes in stress evolution and stress magnitude during curing.

Stress Measurement

A controlled environment coating and stress measurement apparatus based on a cantilever deflection measurement principle was used to study stress development. A schematic of the device is shown in Figure 2. Deflection was measured with an optical lever consisting of a small HeNe laser, a position sensitive photodiode (#DL-10; UDT Sensors, Inc., Hawthorne, CA), and various intermediary optics. All data were acquired via computer.

The end deflection of the clamped beam is related to the average in-plane stress in an adhered coating by

$$\sigma = \frac{dEt^3}{3zL^2(t+z)(1-\nu)} \quad (1)$$

where E and ν are the elastic modulus and Poisson's ratio of the substrate, respectively; t and L are the thickness and the clamped length of the substrate, respectively; z is the coating thickness; and d is the end deflection of the cantilever.¹² Equation (1) is valid as long as the measured deflections are small relative to the substrate thickness and as long as the elastic modulus of the coating is much less than the substrate modulus. Edge effects due to stress concentrations were avoided by maintaining sufficiently large sample areas relative to the coating thickness.

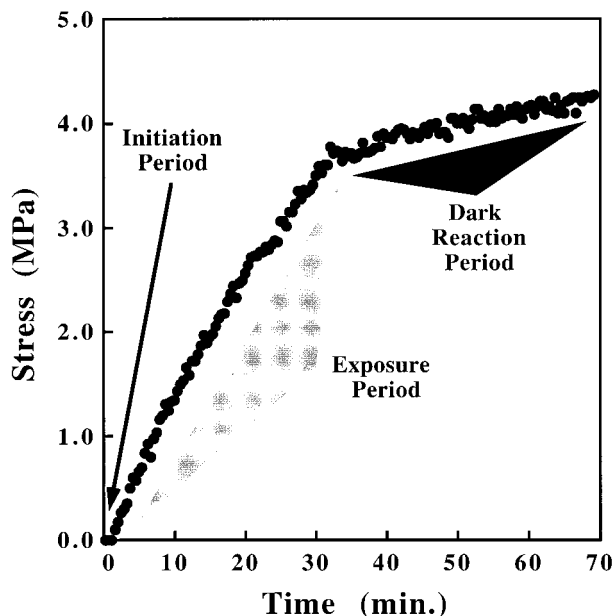


Figure 4 Typical stress evolution for TMPTA prepared and cured using base-case conditions. See Table I.

Conversion Measurement

A Magna 750II FT-IR (Nicolet Instrument Co., Madison, WI) was used to monitor conversion during curing. Coating solutions were sandwiched between two sodium chloride plates separated by a Teflon spacer and were then exposed to UV light (in a nitrogen atmosphere at room temperature). Spectra were taken at periodic intervals to monitor the drop in absorbance of reactive monomer double bonds, allowing calculation of conversion from characteristic peak areas.^{1,7} All samples (for both stress and conversion measurements) were exposed to equal light intensities. If conversion and stress were directly compared (as in Fig. 5), the conversion sample was approximately one-half as thick as the coating used in the stress measurement. This was done in order to account for reflection of UV radiation from the steel substrate.

Measurement Validation

To test the stress measurement technique, stress in solvent-cast thermoplastic coatings was mea-

Table I Base Case Experimental Conditions

Monomer	TMPTA, trifunctional
Photoinitiator concentration	0.20 mol %
Radiation wavelength	365 nm
Radiation intensity	210 $\mu\text{W}/\text{cm}^2$
Coating thickness	25 μm

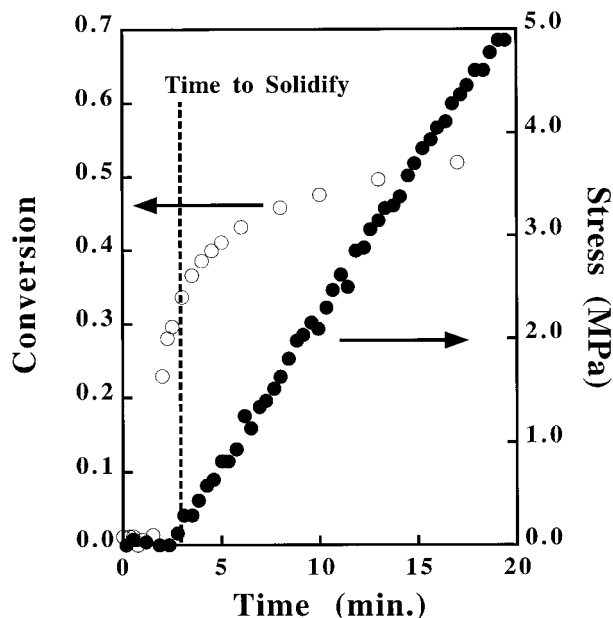


Figure 5 Stress evolution and percent conversion versus irradiation time for base-case conditions. See Table I for conditions. Note: Conversion sample is one-half as thick as the coating used for the stress measurement in order to account for reflection of UV light from the steel substrate.

sured. Coatings of polyisobutyl methacrylate (PIBM; Elvacite 2045, ICI Acrylics, Inc., Wilmington, DE) were prepared from toluene solutions (12 to 40 wt % PIBM). Stress was monitored during drying in a nitrogen stream (50 mL/min) at 21°C and 30% relative humidity. Thicker and more concentrated coatings dried more slowly and hence developed stress more slowly [Fig. 3(top)], but all coatings reached the same maximum stress value of 3.30 ± 0.40 MPa [Fig. 3(bottom)]. These results agree with previously published work by Croll¹⁴ and Perera and colleagues.¹⁵

RESULTS

Figure 4 shows a typical stress profile for a UV-cured multifunctional acrylate coating. A short period is observed during which no stress develops because the coating has not yet solidified. As conversion increases, the elastic modulus of the liquid coating grows and the polymer relaxation rate slows until stress can be supported in a solid-like fashion. After this "solidification," further monomer conversion elevates the modulus (and the apparent T_g ¹⁹) and hence the stress. Even after the light is turned off (~ 30 min in Fig. 4), stress continues to grow, though less quickly, because

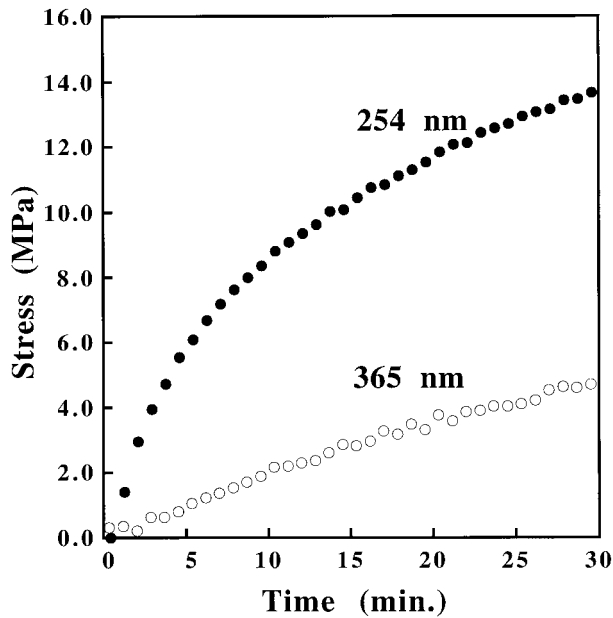


Figure 6 Comparison of stress for TMPTA coatings cured with different UV wavelengths (all other conditions were base-case).

radicals already present continue to react during this “dark period.”

In all of the following results, the irradiation is kept continuous and stress is shown as a function of irradiation time. The coating stress depends on monomer functionality, photoinitiator content, light wavelength and intensity, and coat-

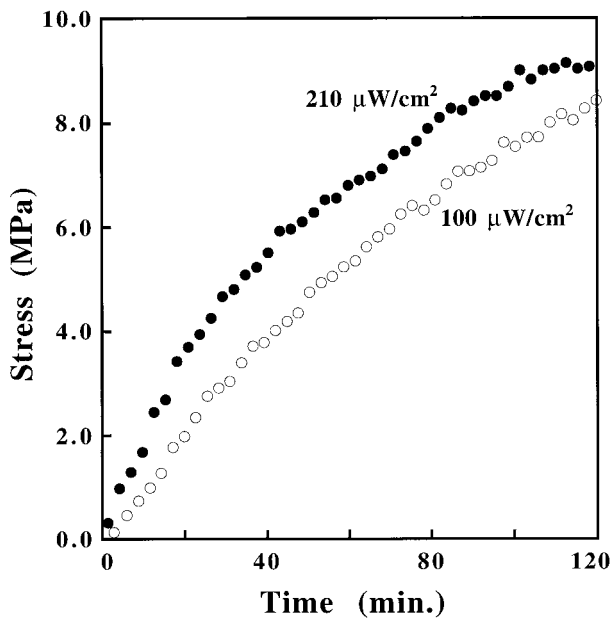


Figure 7 Intensity effects on stress in TMPTA coatings (all other conditions were base-case).

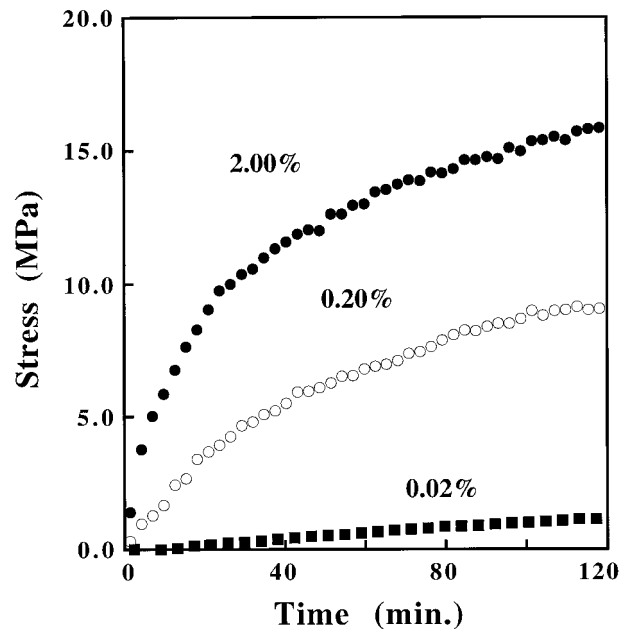


Figure 8 Comparison of stress in TMPTA coatings containing different photoinitiator concentration (all other conditions were base-case).

ing thickness. To facilitate discussion of these variables, a base case will be considered first (see Table I); thereafter, the effect of changing processing variables from the base conditions will be described.

Base Case

Figure 5 shows the development of stress and conversion with continuous irradiation of a TMPTA coating under base-case conditions. These conditions are selected to clearly reveal the most salient features of the study. Significant stress develops only after about half of the maximum conversion is reached. As irradiation continues, the produced stress climbs more quickly than the conversion. Exposure much beyond the point of solidification for such coatings fails to produce significantly more conversion, but it dramatically increases the stress.

In multifunctional monomer systems, it is thought that the limited conversion is due to rapid network formation (gelation and/or vitrification), which causes diffusional (both translational and segmental) resistance to propagation.^{1,7,19} We show here that what little conversion can be achieved beyond solidification comes with a high stress penalty. It has been shown that the limited conversion, and so the stress, might be addressed by decreasing the volumetric crosslink density (by

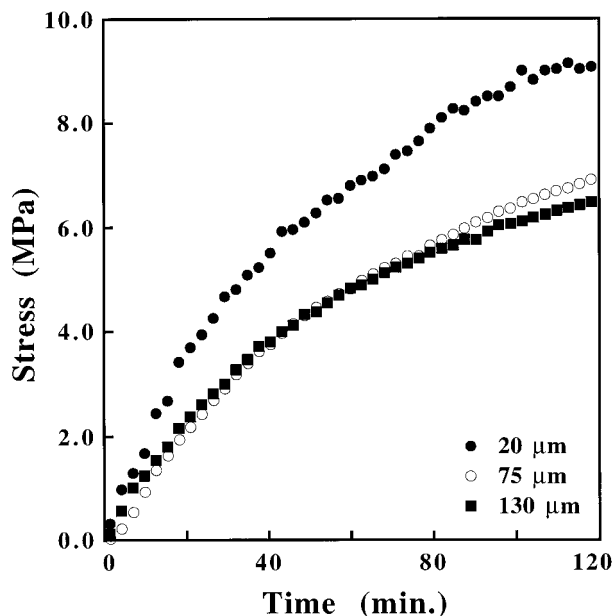


Figure 9 Thickness effects in TMPTA coatings containing 0.20% DMPA (all other conditions were base-case).

adding spacer groups in the monomer), adding solvent, and raising reaction temperature.^{19–21} All of these approaches help to maintain polymer segment mobility through to higher conversion. The stress measurements here can be helpful in designing optimal processing conditions.

Process Variables

In the following, individual process variables are changed, one at a time, from the base case. To study the effects of light wavelength, the UV source was changed to 254 nm, for which DMPA has an absorption coefficient two orders of magnitude greater than at 365 nm. The stress was much higher in coatings cured at 254 nm than at 365 nm (Fig. 6), as was the final conversion (71% versus 66%). Curing with lower intensities (half of the base-case intensity) decreased both stress and conversion (Fig. 7). Increasing the photoinitiator concentration increases both stress and conversion (Fig. 8). Decreasing the coating thickness increases the stress and conversion (Figs. 9 and 10). Moreover, similar trends are observed for the tetrafunctional monomer as for the trifunctional monomer (not shown).

These results correlate well with previously reported trends in reaction rates. Indeed, the thickness trends have been reported for UV photore-sists.^{7,22} In each case where the processing vari-

able increases the reaction rate, higher stress is observed (this is discussed in greater detail below). Kloosterboer and others have already shown that faster reaction can lead to higher conversion.⁴ The new finding here is the measurement of the degree to which the conversion trend is accompanied by the penalty of higher stress.

A notable exception to the general trend occurs when several process variables are changed at once from the base-case conditions. Curing thick coatings with strongly absorbed light (254 nm) and with high photoinitiator concentrations creates surface ripple defects. Under these processing conditions, the stress value is no longer sensitive to the photoinitiator concentration (at a given thickness). However, the surface ripples change in size scale, particularly with thicker coatings (Fig. 11). Ripples ranged in height from 1 to 15 μm , as measured by a Dektak IIA surface profiler.

Monomer Functionality

In the variations from the base case described above, we find correlated changes in conversion and stress. However, if all process variables are kept the same but the monomer functionality is switched, a striking new trend is observed. Changing from the base-case trifunctional mono-

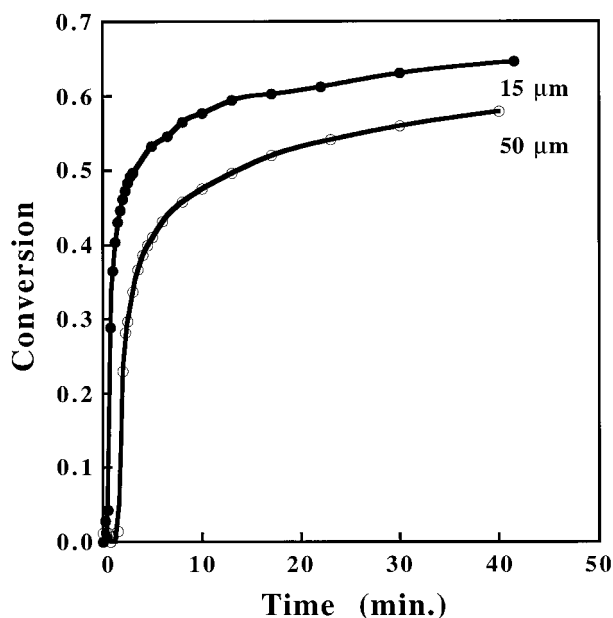


Figure 10 Conversion differences due to UV absorption in TMPTA samples of varying thickness. Samples contained 0.20% photoinitiator and were cured with 365 nm light at an intensity of 210 $\mu\text{W}/\text{cm}^2$.

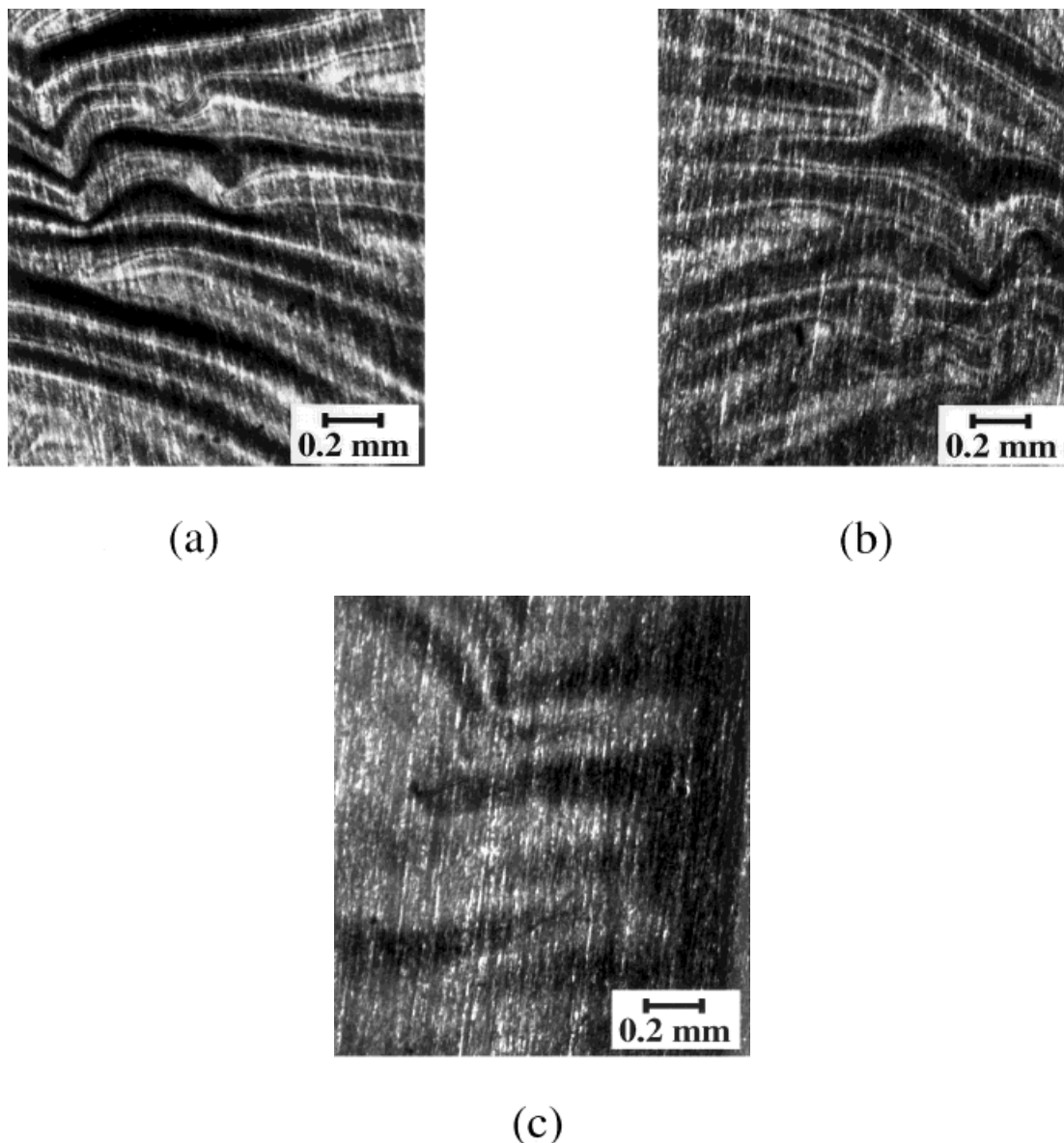


Figure 11 Ripple defects in TMPTA coatings. Defect size decreased with coating thickness: (a) $130\ \mu\text{m}$, (b) $86\ \mu\text{m}$, (c) $30\ \mu\text{m}$. All coatings shown contained 2% photoinitiator and were cured using a 254 nm lamp with an intensity of $500\ \mu\text{W}/\text{cm}^2$.

mer (TMPTA) to the tetrafunctional monomer (PETA) results in a larger coating stress (Fig. 12), but this is accompanied by a lower conversion (compared with the TMPTA conversion).

One reason this is surprising is that in solvent-cast polymer coatings, the final stress grows (in general) as the pure polymer T_g increases.^{23,24} However, Anseth and associates,^{7,19} showed that the apparent T_g of poly-TMPTA is larger than that measured for poly-PETA when cured under similar conditions; they attribute the higher T_g to more complete conversion. Higher conversions are common in low functionality systems because

slower solidification allows monomer and radicals to remain mobile. For this reason shrinkage and stress measurements cannot be used to monitor conversion. The results in Figure 12 demonstrate, then, that in this case conversion (and thus, apparent T_g) is not a sufficient predictor of stress in these systems.

DISCUSSION

The cantilever deflection method used here gives a measure of the average in-plane stress in a

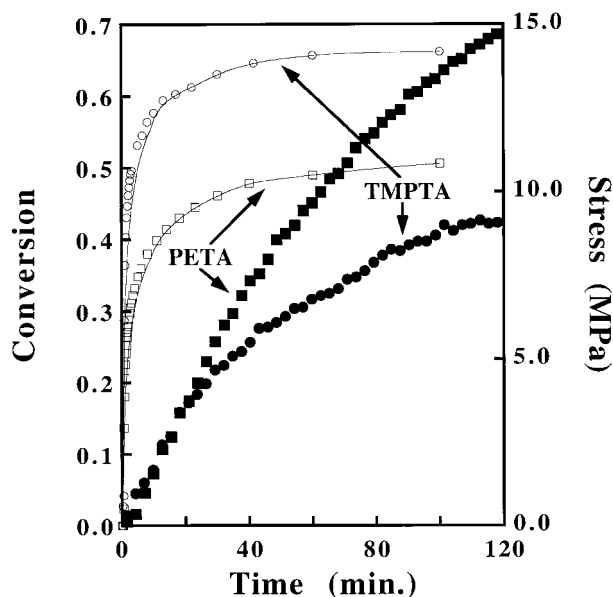


Figure 12 Stress evolution and conversion curves for TMPTA and PETA cured under base-case conditions. Conditions, except for monomer, given in Table I. Closed symbols are stress curves; open symbols are conversion curves; circles are TMPTA; and squares are PETA.

coating adhered to a substrate. A simple elastic interpretation of stress treats post-solidification shrinkage as a strain, ε . The stress is then related to the strain by

$$\sigma = \frac{E_c \varepsilon}{1 - \nu_c} \quad (2)$$

where E_c and ν_c are the elastic modulus and Poisson's ratio of the coating, respectively. Stress develops during a solidification process because the material is unable to shrink (due to adhesion to a substrate) to a stress-free state. While the strain, ε , in conventionally drying coatings depends on the difference between the solvent content at the point of solidification and the solvent content at the end of drying,^{14,15} strain in polymerizing coatings (with no volatile species) depends on the difference, caused by crosslinking, between the free volume at the point of solidification and that at the end of cure. Moreover, in both drying and curing, stress depends on the time-dependent (and poorly quantified) elastic modulus, E_c . The transient microscopic in-plane stress and modulus are not well-known functions. Studies such as the present one will serve to allow future models to be developed for these functions.

To explain the changes in stress due to varying

wavelength, intensity, photoinitiator concentration, and thickness, it is useful to review how the polymerization rate should be expected to change. Models for multifunctional polymerization near and beyond solidification are still under development, but it will suffice here to examine a simple model applicable to early stages of reaction. If we assume that irradiation has continued long enough to allow a pseudo-steady-state concentration of radicals to be established, but not so long as to allow changes in diffusion resistance to any recombination termination or propagation reactions, then we may postulate how the polymerization rate will change with the intensity of incident light at the photoinitiating wavelength, I , in watts/cm² (often intensity, expressed as I_0 , has units of moles of light quanta per liter-second); the photoinitiator absorption coefficient at the wavelength delivered, α ; and the photoinitiator concentration, $[PI]$. The average conversion rate is proportional to

$$\frac{1}{z^{3/2}} \sqrt{\frac{\lambda \phi (1 - e^{-\alpha [PI] z})}{N h c}} \quad (3)$$

where N is Avogadro's number, h is Planck's constant, c is the speed of light, λ is the radiation wavelength, and ϕ is the quantum yield of the photoinitiator, which should depend on α .²⁵ Note that we have divided by the coating thickness to arrive at the average conversion rate. The term in parentheses accounts for the attenuation of light power through the coating thickness, assuming that the photoinitiator is the only absorber.^{2,25,26} We see that the average rate should increase with the absorptivity (i.e., at 254 nm compared with 365 nm), with light intensity, and with photoinitiator concentration. The conversion rate averaged through the coating thickness will decrease in thicker coatings (though the total rate, R_p , plateaus at a limiting value at high thickness). Equation (3), although limited in accuracy, does show qualitatively that the conversion should increase for more strongly absorbed wavelength, higher intensity, and higher photoinitiator concentration. The conversion should decrease with coating thickness because of attenuation of light through the coating medium.²⁵

The higher stress in coatings cured with a shorter-wavelength light can be explained with the conversion trends. The absorption coefficient for the photoinitiator at 254 nm, α_{254} , is 1.1×10^4 L/mol · cm; that at 365 nm, α_{365} , is two orders of magnitude smaller. The larger stresses and faster

stress development rates with 254 nm light are associated with the faster reaction rates. Curing with higher intensities of the same wavelength (Fig. 7) and higher photoinitiator concentration (Fig. 8) produces a similar effect. Faster polymerization rates have been shown to lead to higher conversion, and it has been postulated that this is because fast reaction allows more excess free volume to remain in the system (thereby allowing easier segment diffusion).^{4,7,19} However, we show here that this same trend produces a great deal of stress in the coating.

The measured stress is lower for thicker samples, which also reach lower conversion levels due to significant light absorption (Fig. 10) as suggested by eq. (3). This is consistent with the conversion trends discussed above, but a new phenomenon needs further consideration. Applications for UV-cured coatings typically require properties (e.g., good solvent resistance and high T_g) that are attained only if there is uniform polymerization through the entire coating thickness. Naturally, strong attenuation of light through the coating not only decreases the average conversion but also produces an undesirable gradient. Gradients in conversion due to significant absorption in thick samples have been documented in the literature.^{7,22,27} Conversion data taken on samples of different thickness support the idea of a solidification gradient (Fig. 10). When such a gradient develops, the upper portion of the coating can solidify first and shrink without constraint because the slower-reacting region below it is still fluid. Only when the region of the coating nearest the substrate solidifies will stress begin to develop. The final measured stress is then lower (all else but thickness remaining the same) since the early shrinkage occurred without adhesive constraint to the substrate.

The formation of defects in some of the coatings studied might be attributed to this type of a solidification gradient. When coatings containing large amounts of DMPA ($\sim 2\%$) were cured with 254 nm light, surface ripples were observed (Fig. 11). One could imagine the following scenario: Due to radiation absorption effects, the material nearest the coating surface solidifies first and shrinks unconstrained. Later, as the coating near the substrate solidifies, it also begins to shrink but the shrinkage is now constrained by adhesion to the substrate. Cohesion of this region with the already-solid and already-shrunk material above causes compression of the coating nearest the surface. In the extreme case, the top of the coating deforms plastically into ripples.

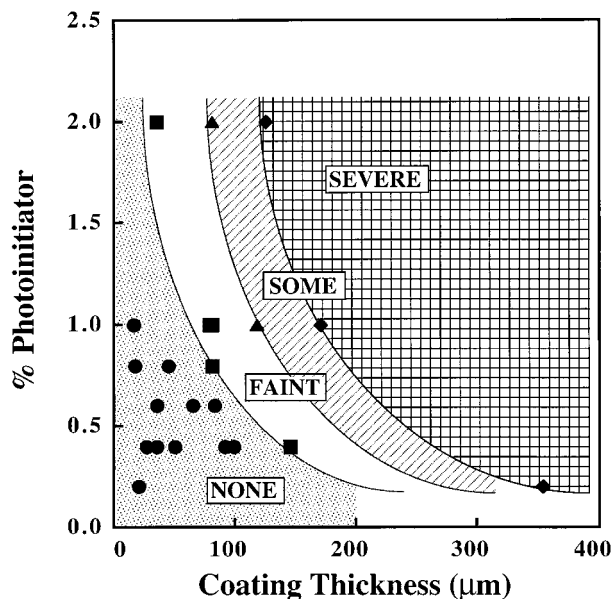


Figure 13 Defect regime map for TMPTA coatings cured with 254 nm light at an intensity of $500 \mu\text{W}/\text{cm}^2$.

Further study of coatings with different thicknesses and photoinitiator concentrations showed that the defect height increases with $[PI]$ and c as shown in the defect regime map in Figure 13. It makes sense qualitatively that higher amounts of photoinitiator and thicker coatings will result in more severe solidification gradients. In fact, ripple defects are common in the UV coating industry for coatings containing fillers and pigments, which limit UV penetration by absorbing light.²

If the above hypothesis is correct, oxygen can help with this defect problem. Oxygen inhibits radical effectiveness; therefore, curing at the coating surface will be slower in air, reducing the solidification gradient due to absorption. Indeed, coatings cured in air instead of nitrogen were always defect-free.

If surface uniformity is not critical, the ripple defects can be useful in that they represent a limit in the stress. In Figure 14, stress (after 30 min. light exposure) is plotted versus thickness for coatings cured under conditions leading to a solidification gradient. The solidification gradient, enhanced by DMPA's higher absorption coefficient at 254 nm, leads to smaller stresses in thicker coatings. Moreover, at a specified thickness, the stress no longer increases with photoinitiator concentration (compare with Fig. 9)! One could accelerate solidification and increase conversion by increasing the photoinitiator content without paying a stress penalty.

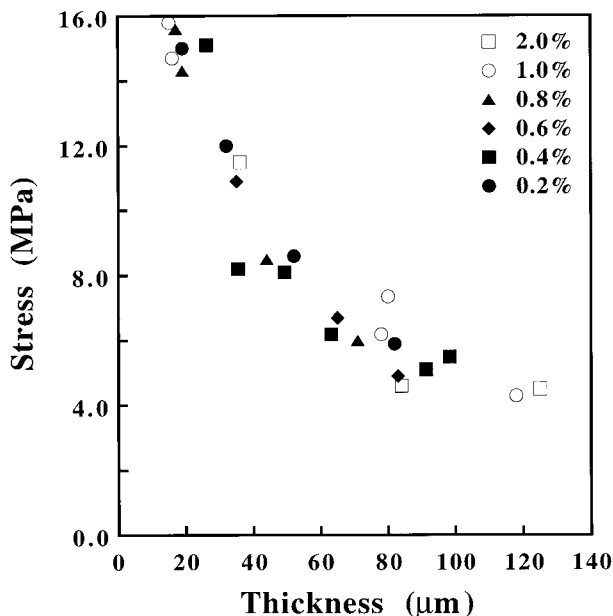


Figure 14 Lack of dependence of stress on photoinitiator concentration due to an enhanced solidification gradient. Plotted stress is magnitude after 30 min. of curing with 254 nm light.

There is quite a different trend when the monomer functionality is increased (keeping all other process variables at base-case conditions). The tetrafunctional (PETA) coatings developed larger stresses than the trifunctional coatings, even though the conversion was lower (Fig. 12). The lower conversion is consistent with past work which shows that faster solidification in high functionality systems significantly reduces radical mobility; in turn, this limits conversion and glass transition values.¹⁹ It is interesting to note, though, that the two monomers do establish a similar molar crosslink density—about 2 moles of crosslinks for every mole of monomer (under base-case conditions).

A common mistake is to assume that once it is solidified, a material is done shrinking. In fact, it is the constrained shrinkage *after* solidification that determines coating stress magnitudes. Here the operating definition of “solidification” is the point at which the elastic modulus is large enough, and the polymer relaxation slow enough, to support a stress that cannot relax on the time scale of the curing process. The modulus of these materials continues to rise even after a material becomes solid, due to further crosslink formation, and the stress grows accordingly. Although it is known that the tetrafunctional system should solidify faster than the trifunctional, this also creates the undesirable opportunity for more post-

solidification shrinkage. In terms of free volume, faster reaction (due to the greater functionality of PETA) will result in slower volume relaxation. As a result the conversion increases outpace the volume changes, leaving excess volume upon solidification. The increased volume allows greater post-solidification mobility of the reactive species and thus, more shrinkage beyond vitrification relative to the slower-reacting TMPTA. A more careful analysis of solidification and mechanical property changes during curing will be the subject of ongoing research.²⁴

CONCLUSIONS

The cantilever deflection technique allowed measurement of the average, in-plane stress during curing of multifunctional acrylate coatings. The stress development rate and stress magnitude depended on light wavelength and intensity, photoinitiator content, and monomer functionality. The coating thickness affected stress due to light-absorption effects. Defect formation when curing with highly absorbed light and high photoinitiator concentration was associated with a limited maximum stress value at a given coating thickness.

The present results can be useful in the design of reactive coating design. Care should be taken not to over-irradiate coatings; irradiation after vitrification will only marginally increase conversion but will seriously increase stress. By slowing reaction rates and by introducing solidification gradients, it is possible to reduce coating stress—at the expense of conversion. The trifunctional TMPTA offers higher conversions and smaller stresses than the tetrafunctional PETA. Other means, such as addition of plasticizers to the coating formulation, should be used to further increase conversion while reducing coating stress. Processing temperatures can also be used to facilitate conversion increases. The design of such approaches will also need to account for the final coating modulus, since plasticizers or other low-molecular-weight additives will limit the modulus and increase the likelihood of conversion-rate gradients through the coating thickness. Finally, when increasing functionality to encourage faster solidification, special care must be taken to avoid stress.

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