Stress Buildup in Ultraviolet-Cured Coatings: Sample Thickness Dependence

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ABSTRACT: Stress buildup in ultraviolet radiation-induced coating can vary significantly as a function of processing conditions. Depending on radiation intensity and photoinitiator concentration, the average stress in the film may either increase or decrease with film thickness. On the basis of the current study on trimethylolpropane triacrylate (TMPTA) together with data reported previously, we conclude that the two main factors affecting stress in radiation curable coatings are (i) degree and distribution of cross-linking and (ii) temperature at solidification point. In certain experimental conditions, an uneven distribution of the conversion within the film may occur, leading to a decrease of the average film stress with increasing film thickness. In contrast, the temperature jump in the sample when irradiated may lead to an increase of the ultimate stress with film thickness.

Introduction

Polymer coatings are well recognized to be an important field of study from both fundamental and practical perspectives.[1] Among the many methods for preparing polymer coatings, radiation curing ranks among the most effective and environmentally friendly.[1,2] Polymer coating quality is strongly affected by the magnitude of internal stress that develops as the liquid (solution or dispersion) transforms into an elastic or viscoelastic solid. Since the coating by definition adheres to a substrate, shrinkage can occur only in the thickness direction. The constrained or frustrated volume change in the direction parallel to the substrate leads to an in-plane stress which can ultimately lead to defects such as buckling, cracking, curling, and delamination, all of which degrade final coating quality.[3−8]

Several experimental techniques have been employed to determine stress in thin coatings.[6,9] It should be noted, however, that all existing methods measure the stress averaged over film thickness. The quality of polymer coatings, however, depends not on the average stress but on stress distribution with the distance from the coating/substrate interface. For example, fracture toughness, depends on the maximum stress value at the interface, not on the average one. Adhesion to the substrate depends on the stress of the interface layer only, also not on the average stress in a coating.

One possible route to obtain stress distribution within the film is to analyze stress dependence as a function of coating thickness. Stress−thickness dependencies have been determined for several films prepared by the solvent-casting technique,[6,10−12] aqueous gelatin,[13] and metallic coatings.[14,15] Depending on the type of coating and the preparation method, the average internal stress may increase,[15] decrease,[14] or remain independent of film thickness.[10−12] Unfortunately, only a limited number of studies address stress−thickness dependence associated with radiation curable coatings.[12] Our previous study was devoted to the onset of stress buildup in ultraviolet-cured coatings and a correlation of stress with molecular architecture.[16] The present goal is to obtain stress−thickness data under different experimental conditions. Our results are reported here.

Experimental Section

Our radiation-cured coatings start with a monomer, trimethylolpropane triacrylate ($(H_2C{=}CH{-}C(O){-}OCH_2)_3C{-}C_2H_5$, TMPTA), and a photoinitiator, 2-benzyl-2-(dimethylamino)-4′-morpholinobutyrophenone, sold commercially as Irgacure 369. Both components were purchased from Aldrich and used as received. The concentration of photoinitiator in the formulation varies and is specified below.

Coating stress was measured using the experimental techniques discussed previously. In this method, the deflection of a cantilever serves to monitor the stress buildup.[9,10,12,17−19] The entire experimental setup, including a Specac external reflection assembly, ultraviolet radiation introduced by a liquid light guide, and coupling optics, can be accommodated in the experimental chamber of our Perkin-Elmer system 2000 Fourier transform infrared spectrometer. The combination of techniques permits simultaneous measurement of the stress buildup and polymerization kinetics. As the experimental technique has been described previously,[16] only information relevant to the current study is presented here. Steel shims (0.107 and 0.31 mm thick) and Si (100) wafers (0.50 mm thick) were utilized as cantilevers. The steel cantilevers (5 × 0.5 cm) were cut from a sheet of 0.6 × 0.3 m. The long axis of the cantilever is parallel to the long axis of the overall sheet. The dimension of Si(100) cantilevers were 9 × 0.9 cm. The modulus of the materials was determined using beam deflection measurements.[20] The obtained magnitudes are 175 ± 15 and 160 ± 10 GPa for steel and Si wafers, respectively. Before use, the cantilevers were cleaned first with toluene and then by heptane.

A 3010-EC Dymax ultraviolet lamp was used as the radiation source. This radiation source employs a 100 W, short arc mercury vapor bulb exhibiting radiation mostly in the 320−390 nm region. The ultraviolet energy was measured by the IL390B Light Bug radiometer (International Light) and adjusted by changing the source-to-sample distance.

Spectral resolution of infrared spectra was maintained at 4 cm^{-1}. To prevent the chemical reactions from being inhibited by oxygen, the experimental chamber was flushed with dry nitrogen gas. The ambient temperature was maintained at 25 °C. Film temperature was monitored by a miniature (180 μm thick) chromel−alumel thermocouple placed directly into the cured film. The coating thickness (8−150 μm) was determined

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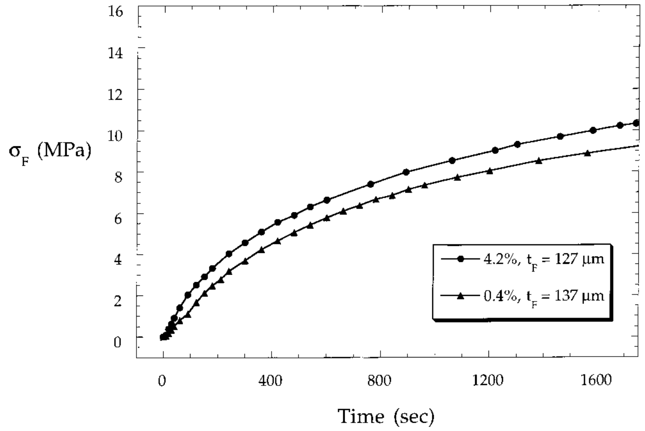

Figure 1. Stress development obtained for thick TMPTA films at 0.26 mW cm^{-2} and different photoinitiator concentrations.

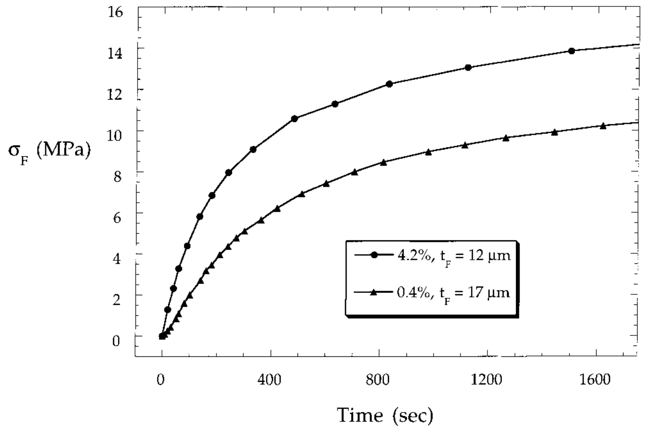

Figure 2. Stress development obtained for thin TMPTA films at 0.26 mW cm^{-2} and different photoinitiator concentrations.

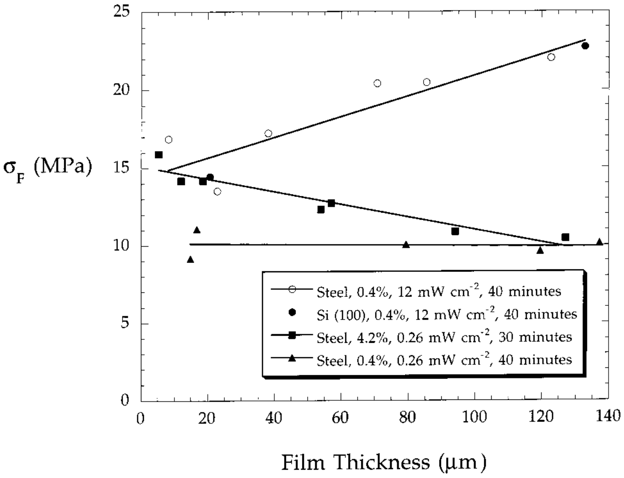

Figure 3. Stress in TMPTA films vs film thickness at different experimental conditions. Open symbols correspond to steel substrates; closed symbols correspond to Si (100) substrates, 0.4% of photoinitiator, 12 mW cm^{-2}, and 40 min of radiation.

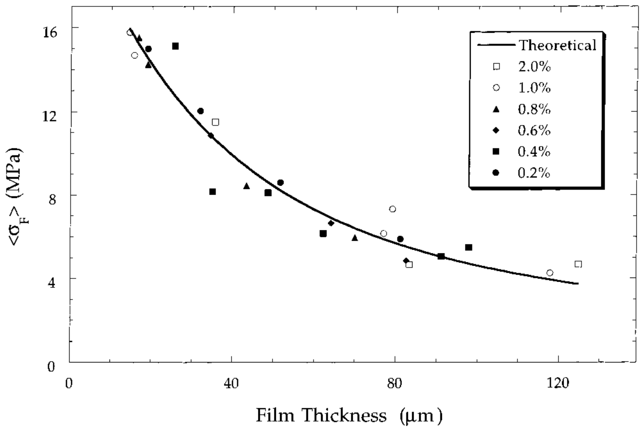

Figure 4. Stress in a trimethylolpropane triacrylate coating as a function of the film thickness. The values obtained after 30 min of curing with 254 nm light. The radiation intensity was 0.21 mW cm^{-2}, and the concentration of the photoinitiator (2,2-dimethoxy-2-phenylacetophenone) varied between 0.2 and 2.0%. The circles correspond to the experimental data, [12] and the solid line is the fit by eq 4.

from weight measurements. Attenuated total reflectance (ATR) infrared spectroscopy was employed to monitor composition variation in the film from the film/air interface inward. A Harrick Scientific reflectance unit incorporating a KRS-5 crystal is used for this purpose. The depth of penetration of the infrared beam in ATR experiments is of the order of 1 μm, much less than film thickness.

Stress (σ_F) in radiation-cured coatings is known to depend on the type of photoinitiator, its concentration, radiation intensity, radiation frequency, and exposure time.[12,16] Thus, to determine the dependence of stress on film thickness (t_F), consistency in experimental conditions is required. In the current study, all experiments were conducted using the same photoinitiator and ultraviolet source. Two photoinitiator concentrations (0.4 and 4.2 mol %) and two intensities (0.26 and 12.0 mW cm^{-2}) were employed. The radiation was applied for 30 min for coatings containing 4.2 mol % photoinitiator and 40 min for the rest. In some cases, when both high photoiniator concentration and radiation intensity were employed, stress was sufficiently high to cause film cracking. The stress measured at different photoinitiator concentrations and the same radiation dosages of defect-free films are shown in Figures 1 and 2. The data obtained for different radiation intensities are shown in Figure 3.

Results and Discussion

As shown in Figures 1−3, experimental conditions can significantly affect the stress measured in coatings. Surprisingly, using different experimental conditions it is possible to obtain both positive and negative slopes of the stress−film thickness dependence. Variation in photoinitiator concentration can affect the stress buildup rate for thin coatings. For thicker coatings, the effect seems to be rather small. Using higher radiation intensity leads to an increase of stress with t_F. In contrast, at lower incident intensities, σ_F decreases with t_F (at 4.2% of photoinitiator). Furthermore, the stress buildup may not even be dependent on film thickness. Unfortunately, only limited data are available (Figure 4) on stress−thickness dependencies for ultraviolet cured coatings.[12]

To consider quantitatively the different σ_F−t_F dependence measured, the assumptions used in stress analysis need to be validated. First, assessing the adhesion of coating to the underlying substrate is important. Second, the change in molecular architecture, i.e., the degree of cross-linking, is usually assumed to be uniform in the film. The exact distribution within the coating must then be established. As sample temperature is raised when radiation is applied, the effects of thermal history in film processing must also be considered.

The most fundamental assumption that is employed in stress analysis is that a nonslip boundary condition exists at the interface between coating and substrate. If adhesion of the coating to substrate is imperfect, then

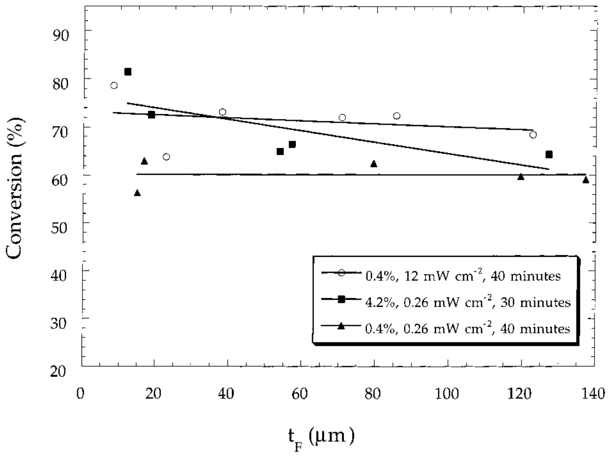

Figure 5. Average conversion of the vinyl groups at different experimental conditions. The error associated with these spectroscopic measurements is less than 2%.

a deformation, even slight, of the film with respect to the interfacial boundary should be observed. Such relative movement is more significant for thicker coatings since mechanical perturbations of the system are larger and may produce a negative slope for the $\sigma_F - t_F$ dependence.

To check the effect of adhesion, we compared the results obtained with steel and Si (100) cantilevers, keeping all other experimental conditions the same. It is known that extremely good adhesion can be achieved for the Si cantilever. If adhesion properties differ, measured stress should differ as well. As can be seen from Figure 3, the results obtained using different cantilevers are in good agreement with each other. The data strongly suggest that for both types of cantilevers the nonslip boundary condition is fulfilled.

Although a uniform composition is usually assumed, the fact that ultraviolet radiation intensity is absorbed throughout its path as it propagates the film, an uneven distribution of monomer conversion must exist. The conversion is expected to be highest at the outer surface of the coating and lowest at the coating-substrate interface. A decreasing exponential function would typically be expected. It should be noted, however, that the exact degree of conversion as a function of penetration depth could not be calculated in a straightforward manner, as several other factors have to be considered. These include inhibition of the reaction by residual atmospheric oxygen and molecular diffusion during the curing process. In many cases (including our data), the ultraviolet radiation passes the film twice since it is reflected from the substrate surface. If the degree of cross-linking decreases from the film surface, a negative $\sigma_F - t_F$ dependence is then expected.

In our previous study, infrared spectroscopy was used to follow the conversion from monomer to polymer. Specific spectroscopic features associated with monomers and polymers can easily be identified. The most convenient feature that can be monitored is the unreacted vinyl groups at 1949 cm^{-1}. The results for various film thicknesses are shown in Figure 5. It can be seen that there is no prominent dependence of the average conversion on t_F for systems with low photoinitiator content, 0.4%. In contrast, the average conversion decreases with film thickness when the formulation contains relatively high photoinitiator content, 4.2%. Contrary to the usually assumed uniform distribution, our data suggest an uneven conversion in thick film may be responsible for the negative slope of the $\sigma_F - t_F$ dependence.

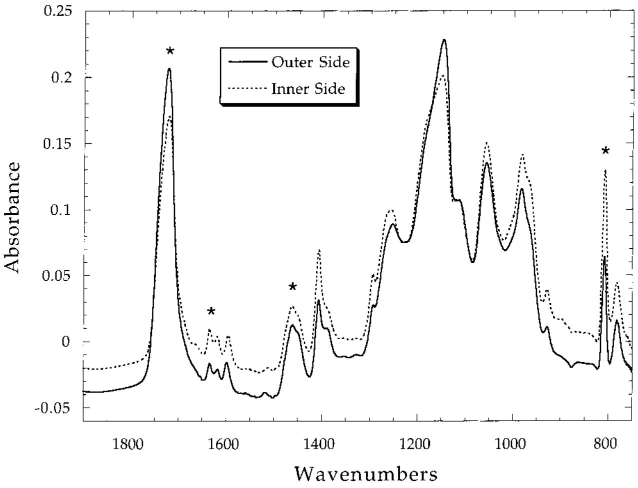

Figure 6. ATR spectra of inner and outer surface of a TMPTA film obtained at 4.2% of photoinitiator, 0.26 mW cm^{-2}, and 30 min of radiation. The film thickness is 94 μm. Stars mark the bands used in our analysis.

We have further used attenuated total reflectance spectroscopy to characterize the conversion distribution in the film. In this case, the film is removed from the substrate with a razor blade. ATR spectra obtained from opposite sides of the film (4.2% of photoinitiator) are shown in Figure 6. To analyze the data, we compared the integrated intensities of the bands at 1721, 1462, 1635, and 807 cm^{-1}. The intensities of the former two bands assignable to carbonyl stretching and CH_2− and CH_3 bending vibrations, respectively, do not change significantly with conversion[16] and hence can be used as reference. The latter two bands are assignable to unreacted vinyl groups. The ratios of these bands relative to the first set of two bands can be used to monitor the degree of conversion. When 4.2% photoinitiator is used, in passing from the outer to the inner surface, the relative intensity of the vinyl bands was found to increase by a ratio varying from 1.4 to 1.9. The implication is that fewer vinyl groups are consumed near the coating−substrate interface in comparison to the film surface. Since the average conversion is known (~65%, see Figure 5; the error associated with this measurement is less than 2%), it is possible to approximate the conversion at the film surface (~73 and 56% for outer and inner surfaces, respectively). The ATR spectra of films obtained at 0.4% photoinitiator were also studied. For these films, no measurable difference was detected between the spectra of the inner and outer sides. It is possible to conclude then that for these films the degree of conversion is almost the same over the film thickness, as shown by Figure 5.

We previously demonstrated that stress in multifunctional acrylate coatings strongly depends on the degree of conversion.[16] Due to the lower conversion at the film/substrate interface, the stress in the ultraviolet cured coatings containing 4.2% of photoinitiator is at a minimum. This in fact may lead to unexpected physical properties such as preventing coatings from delaminating and enhanced durability.

Another factor that needs to be taken into account in the analysis of stress distribution is thermal history. A temperature jump is also expected during polymeriza-

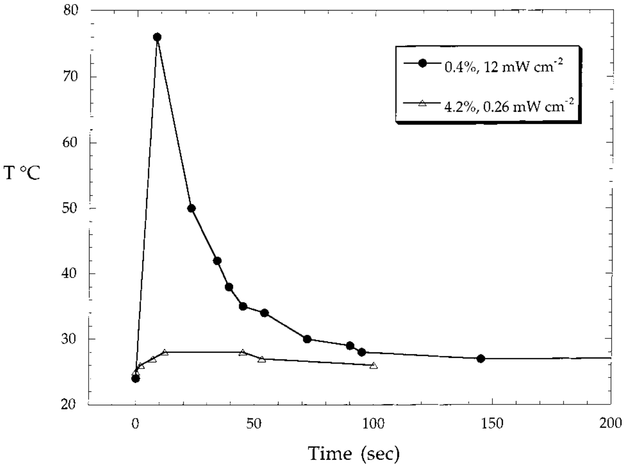

Figure 7. Temperature behavior in various TMPTA films.

tion. This comes from the fact that polymerization of vinyl monomers is an exothermic process releasing 14–20 kcal mol^{-1} of thermal energy per reaction. The temperature jump at a localized region produces a volume expansion of the liquid monomer. When the system approaches the gel point, the sample solidifies into a viscoelastic form, causing stress to develop. After the onset of gelation, the coating tends to shrink due to the further conversion of vinyl groups. At this point, reaction kinetics and heat transfer to the substrate and surrounding atmosphere govern the overall film temperature. Ultimately, the reaction slows, and the film temperature tends to approach that of the ambient value. This sample cooling causes the appearance of additional tensile stress, since the volume expansion coefficient of the coating is normally larger than that of the substrate. Thus, it is important to take this temperature jump into account when considering stress buildup in coatings. On the basis of surface-to-volume considerations, it is evident that the temperature effect should be more significant in thicker coatings, producing a positive slope of the $\sigma_F - t_F$ dependence.

The temperature behavior in relatively thick coatings ($t_F \geq 200\ \mu$m) was monitored by embedding a miniature thermocouple (~5 mm long and 180 μm thick) directly into the coating. This setup is sufficient accurate and sensitive to record the temperature jump in the coating. The observed temperature behavior is shown in Figure 7. Using the incident radiation intensity 0.26 mW cm^{-2}, the maximum temperature increase is less than 3 deg. Using 12 mW cm^{-2}, the sample temperature may increase by as much as 50 deg. Even without sample present, the temperature rise of the substrate is 2–3 deg when a 12 mW cm^{-2} ultraviolet radiation is employed. The effects of this temperature jump on coating stress can be significant. Two TMPTA coatings of different thickness but cured under similar conditions (t_F = 8.2 and 122 μm; 0.4% photoinitiator and 12 mW cm^{-2}) were analyzed, and results are shown in Figure 8. It can be seen that both samples exhibit extremely similar behavior, confirming the fact they are uniformly cured. The average slope of the dependence is ca. 0.2 MPa/K. Thus, the 20–50 K temperature jump at the solidification point may increase the ultimate stress by 4–10 MPa.

The uneven distribution of the monomer conversion and the temperature jump during irradiation are the two principal factors affecting stress buildup. In this study, we have successfully separated these effects. At

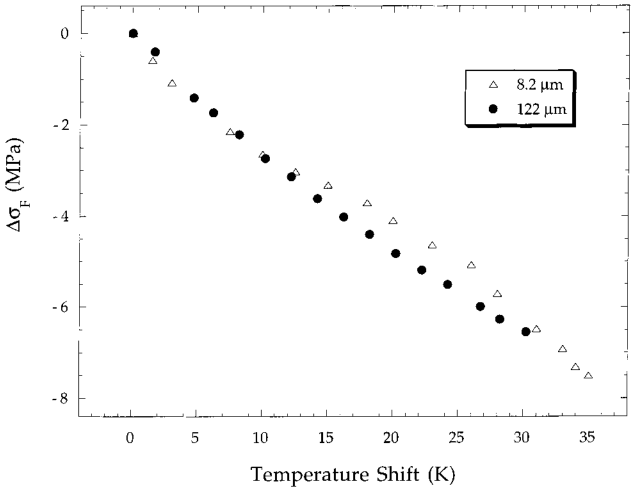

Figure 8. Temperature-induced stress shift in TMPTA coatings obtained at 0.4% of photoinitiator, 12 mW cm^{-2}, and 40 min of radiation. Both coatings are on steel substrates.

weaker radiation intensity (0.26 mW cm^{-2}), the temperature effect is negligible, making only the uneven conversion distribution significant. A negative $\sigma_F - t_F$ dependence is then produced as shown in Figure 3. No dependence of σ_F on t_F is observed for 0.26 mW cm^{-2} and 0.4% photoinitiator, since at such small concentrations of photoinitiator, the 8–150 μm thick films transmit most of the ultraviolet radiation in the 320–390 nm range. At higher radiation intensity (12 mW cm^{-2}, 0.4% of photoinitiator) the temperature jumps significantly, producing a positive slope of the $\sigma_F - t_F$ dependence.

The uneven conversion distribution may be taken into account in a quantitative fashion, however. It should be noted that the uneven distribution originates from the absorptivity of the photoinitiator and can be altered by either increasing photoinitiator concentration or using a radiation causing higher absorptivity. The latter can be achieved by using a higher frequency ultraviolet radiation as done previously.[12] In that study, 254 nm frequency radiation was utilized. It is known that in this spectral region the absorptivity of 2,2-dimethoxy-2-phenylacetophenone is significantly higher than that in the 320–390 nm region.[12] It should also be noted that, in the case of very high absorptivity of the system, the reaction kinetics may become diffusion limited. Generally speaking, the conversion of vinyl groups, P, as a function of film depth, y, can be modeled as follows:

$$P(y) = P_0 \exp(-\alpha y) \tag{1}$$

where P_0 is the conversion at the outer surface and α is a coefficient that depends on the absorptivity and diffusion constant. The average conversion in the system can be determined from eq 1:

$$P_{av} = \int_0^{t_F} P(y)\,dy = \frac{P_0}{t_F \alpha}(1 - \exp(-\alpha t_F)] \tag{2}$$

Average stress in the coating is proportional to cross-link density that is a function of conversion. TMPTA is a hexafunctional monomer for which the following has been previously obtained:[16]

$$\sigma_F \sim P^3(4 - P) + 4P_C^{\ 2}P(P_C - 3) + P_C^{\ 3}(8 - 3P_C) \tag{3}$$

In this expression P_C is the vinyl group conversion at the gel point which for TMPTA equals 0.23 ± 0.02.[16] In the vicinity of P_0, eq 3 can be represented as power series of $(P - P_0)$. As determined from ATR spectra, 0.7 is a reasonable estimate for P_0. Substituting P_0 and P_C in the power series and assuming that inside the film $(P_0 - P)$ does not exceed 0.15, the linear term in the power series accounts for more than 80% of the changes of σ_F with P. Thus, the average stress in the film, $\langle\sigma_F\rangle$, can be derived as

$$\langle\sigma_F\rangle = \frac{\sigma_0}{t_F\alpha}(1 - \exp(-\alpha t_F)) \qquad (4)$$

Equation 4 can be verified with experimental data. We fitted the stress values reported previously,[12] using eq 4. The result is shown as the solid curve in Figure 4. As can be seen, the functional form of eq 4 reproduces experimental data quite satisfactorily. The curve fits permit determination of the parameters in eq 4: $\sigma_0 = 22 \pm 1$ MPa and $\alpha = 0.048 \pm 0.001\ \mu\text{m}^{-1}$. The former parameter is the stress magnitude at the film/air interface. Comparing σ_0 with the $\langle\sigma_F\rangle$ values from Figure 4, the stress at the boundary may be seen to be several times higher than the average stress in the film. The practical consequence of this finding is that by increasing film thickness one can avoid high internal stress in coatings and hence prevent cracking.

Conclusions

From data obtained in this study and taking our previous results into account, it follows that two main factors affect stress in radiation curable coatings: (i) degree of cross-linking and (ii) temperature at the solidification point. The degree of cross-linking is governed by the type of photoinitiator, its concentration, and absorptivity. In certain cases, an uneven distribution of the conversion may occur that leads to a decrease of the average film stress with increasing film thickness. In contrast, the temperature jump may lead to the increase of ultimate stress with film thickness.

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