

Curing Mechanisms Affecting Curl in UV-Coated Laminate Constructions of Semi-Rigid Materials

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ABSTRACT

Geometric flatness in laminate constructions of semi-rigid materials depends strongly upon achieving the correct balance of shrinkage stresses in the various layers of the laminate. Improper stress balancing about the neutral axis results in curl toward the side possessing the larger shrinkage stress. This is especially important when the semi-rigid laminated materials are topcoated and backcoated with UV-curable resins because variations in UV-curing conditions can significantly alter the shrinkage stresses present in the cured coatings. The present study examines the critical UV-curing parameters associated with curl in such constructions (specifically, with a UV-topcoat and a UV-backcoat applied to a semi-rigid PVC substrate material). The effects of N₂ vs. air environment, UV energy dose, UV irradiance, coating weight (film thickness), photoinitiator level, and the substrate temperature during UV-curing are investigated and related to observed curl measurements. We have found that many samples display an unexpected and substantial increase in curl upon subsequent thermal annealing, and that the magnitude of the curl after annealing varies depending on curing conditions. In order to better understand the curing mechanisms responsible for these effects, FTIR-ATR, FTIR-transmission, Real-time FTIR, and Thin Film Calorimetry experiments were used to relate degree of cure to the observed curl behaviors and thereby provide a more fundamental understanding explaining the effects of UV-cure conditions on curl in UV-coated semi-rigid laminated structures.

INTRODUCTION

It is well known¹⁻³ that UV-coatings are subject to volumetric shrinkage upon cure, where the magnitude of shrinkage depends upon acrylate functionality and percent conversion (which together determine crosslink density), cured film modulus, glass transition temperature, etc. Moreover, end-use properties of the cured-film, such as the resistance to stains, chemicals, scratching, and abrasion, tend to increase with crosslink density. Maximizing these properties results in high shrinkage. Rigid substrates such as metal or wood can be coated with highly shrinking UV-materials without detrimental curling effects, whereas flexible substrates such as thin polymer films will be expected to exhibit significant curling. Semi-rigid substrates coated with highly shrinking UV-materials, on the other hand, will show curling effects intermediate between these two extremes.

A typical example of a semi-rigid substrate is a thick planar sheet of inorganic-filled polymeric material. Such materials are characterized by their room temperature rigidity (resistance to high strain rates) in tension and flexure, their ability to slowly creep under loads at typical ambient temperatures (cold flow or cold conformance), and their temperature sensitivity that leads to a great decrease in rigidity with modest temperature increase. In the present study, polyvinylchloride (PVC) floor tiles have been examined as an example of a semi-rigid substrate material. In particular, the curling behavior of these filled-PVC substrates upon application and curing of UV-topcoats and UV-backcoats was investigated as a function of several UV-curing parameters. These curing parameters include coat weight (film thickness), UVA dose, UVA peak irradiance, photoinitiator level, atmospheric environment during cure, and temperature at the start of cure. It is important to note that after the laminating and coating processes have been completed on these types of PVC floor tiles, it is customary to thermally anneal the tiles in order to relieve residual internal stresses. As a result, the effect of thermal annealing on the curl behavior of these UV-coated PVC tiles has also been investigated in the present work. Finally, the UV coatings have been further studied using FTIR, SEM, Real-Time FTIR, and Thin Film Calorimetry in order to correlate degree of cure to curl.

EXPERIMENTAL

Sample Tile Preparation, UV materials, and UV-Curing.

All tile samples were prepared such that various backcoat conditions were tested on a constant upper-layer construction. This upper layer construction consisted of about 7 mils total of cured UV-topcoat and other stress-carrying films sitting atop a 152 mil thick center substrate of semi-rigid, CaCO₃-filled PVC tile base. To this standard construction, UV-curable backcoat films were applied at known coat weights using an airknife application process. Following backcoat application at room temperature, the wet, coated tiles were placed in a dark convection oven for approximately 2-4 min to bring the wet backcoat to the desired curing temperature (defined here as the temperature at which the uncured coating first enters the UV-processor). Curing was accomplished using a Fusion UV Systems, Inc. Light Hammer UV-processor equipped with 2 rows of medium-pressure mercury H-bulbs (primary emissions at 254, 313, and 365 nm). While exact backcoat film thicknesses are a function of coat weight, the nominal thickness is on the order of 1 mil. The finished tile construction as shown in Fig. 1A has a total dimension of roughly 16 in by 16 in by 0.160 in.

Specific details regarding the composition of the upper layers are proprietary. The backcoats consisted of either 1 wt% or 10 wt% Darocur[®] 1173 photoinitiator (available from Ciba Specialties)

blended with trimethylolpropane triacrylate (TMPTA, available from Sartomer as SR-351 monomer). Cure environments were either air (21% oxygen) or N₂-inerted (about 0.7 % oxygen as measured by a Thermox CG1000 O₂ meter, Ametek, Inc.). UVA dose and irradiance measurements were made with a PowerMap Radiometer (EIT, Inc.). Except where indicated, cure temperature was 120 °F (49 °C) and irradiance was approx. 900 mW/cm².

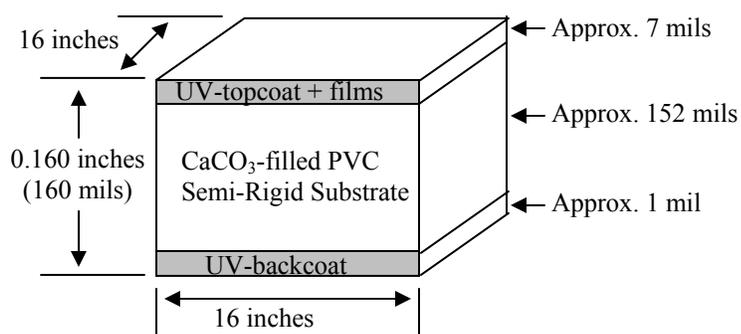


Figure 1A. Sample Construction

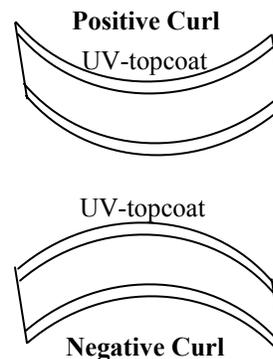


Figure 1B. Curl Definition

Curl Measurements

Immediately after UV-curing of the backcoat, tiles were placed on a flat surface at room temperature with the backcoat facing upwards to allow for backcoat curling with as little interference as possible from the weight of the tile. After a 24 hr equilibration period, curl measurements were made with the tile placed on a flat granite plate using a stand-mounted micrometer equipped with a spring-loaded displacement foot. The measuring foot is balanced such that tile displacements are not significantly affected by the force applied by the foot. The corner displacement of the tile above the granite surface is defined as “Lift,” the displacement of the same corner when depressed against the granite surface is “Gauge,” and, thus, Curl = Lift – Gauge. The curl at all four corners is averaged and reported as “negative curl” when the backcoat is face-up, then the tile is turned topcoat-up to measure the “positive curl.” The final curl value for a given condition is reported as the larger of the front curl vs back curl, such that a positive curl results for curl in the direction of the topcoat, and negative curl results for curl in the direction of the backcoat (see Fig 1B).

Thermal Annealing

After unannealed curl measurements were obtained, the tiles were placed in a convection oven at 125 °F (51 °C) for 48 hrs. To minimize weight effects on the curling behavior of the various backcoat test conditions, the tiles were again placed with backcoat facing-up, and each tile was placed on an individual shelf such that no external weight was present and the individual sample had sufficient clearance to curl. After removal from the annealing oven, the tiles were equilibrated with the backcoat facing-up at room temperature for 24 hrs before measuring annealed curl.

FTIR and SEM Measurements

Fourier Transform Infrared (FTIR) spectroscopy was used in both transmission mode and Attenuated Total Reflection (ATR) mode. Specifically, the surfaces of the cured backcoat on tile samples were measured with FTIR-ATR (ZnSe crystal) both before and after annealing. For transmission measurements, thin films of optically equal thickness were cast directly onto NaCl crystals, cured with the UV-processor, and measured by FTIR before and after annealing. In both cases, a Perkin-Elmer Spectrum 2000 FTIR was used with spectral resolution of 4 cm^{-1} and 32 signal-averaged scans. Degree of cure was calculated as % conversion of the acrylate band at 808 cm^{-1} (assigned to the $\text{CH}_2=\text{CH}$ — twisting mode of the acrylate group⁴), relative to its initial integrated area in the wet, uncured coating. While no internal standard was required for the transmission samples due to the use of the same sampling spot for each measurement, the ATR calculations were normalized using the band at 1465 cm^{-1} (assigned to the $\delta_s[\text{CH}_2]$ bending/scissoring mode of the polymer backbone⁵) as an internal standard. Backcoat film thicknesses cured on the tile samples at the various tested coat weights were measured with a JEOL JSM-35CF scanning electron microscope (SEM) operating at 25 kV of accelerating voltage, magnifications of 500x and 1000x, a working distance of 39 mm, and sputter coating the samples with gold.

Real-Time FTIR and Thin Film Calorimetry

To further corroborate the relative degree of cure of the backcoats cured at different photoinitiator (PI) concentrations and in different environments, both Real-time FTIR (RT-FTIR) and Thin Film Calorimetry (TFC) tests were conducted using a high pressure mercury bulb. For the RT-FTIR studies, thin films were cast onto NaCl crystals and the UV-curing conversion tracked in real-time. For the TFC tests, backcoat films were sandwiched between very thin glass cover plates, and the heat evolution during reaction was tracked in real-time. Details of the experimental procedures may be found elsewhere for both RT-FTIR⁶ and TFC⁷.

RESULTS

An overview of the raw curl data is given in Figures 2A and 2B for curl before and after annealing, respectively (curl values have been zeroed relative to their initial values of approx. +25 mils of positive curl). The effect of backcoat weight is clearly the dominant factor in these plots. However, the spread of data points about the coating-specific curl curves (curves which are averaged with respect to UVA energy dose) indicates that UVA energy dose is an important parameter for curl, as well. It is also obvious that the 1% photoinitiator (PI) coating cured in N_2 exhibits significantly less curl before and after annealing than the 10% PI coatings, both of which are of similar magnitude. Note also that there is no data for a 1% PI coating cured in air due to insufficient surface cure for a tack-free film. Finally, the hashed/shaded curve in Fig. 2B has been drawn to roughly project the likely curl behavior for the 10% PI coatings at high coat weights after annealing, since the measured (negative) curl was found to have been greatly reduced in magnitude due to cracking of the film after annealing for coat weights greater than 5 grams (presumably from locally exceeding the strain to break in the backcoat by thermal expansion/contraction of the laminate during the annealing cycle).

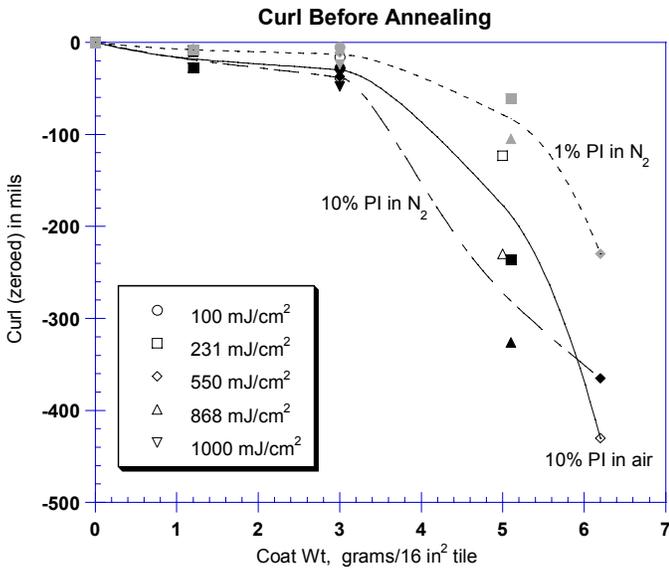


Figure 2A. Curl Before Annealing

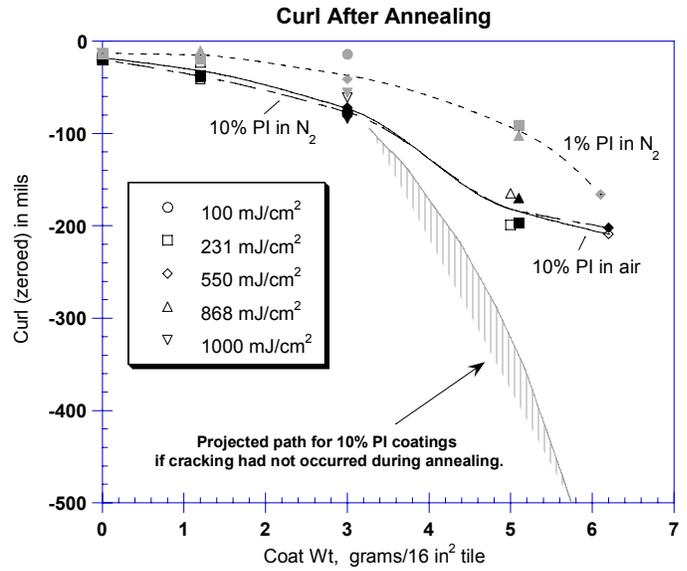


Figure 2B. Curl After Annealing

These figures demonstrate that curl is changing during thermal annealing. To see this effect more clearly, the curl of a single coating before and after annealing (and backcoat cured at two different energy levels) is given in Figure 3. Here it may be seen that the backcoat cured at low energy changes the negative curl of the tile by about -50 mils, while the annealing effect at higher energy is reduced to about -30 mils. For reference, curl values exceeding about +/- 10 mils are considered “out-of-plane” in practical flooring application, where positive curl is especially problematic. Note that coat weights in this figure have been kept within a range that prevents cracking.

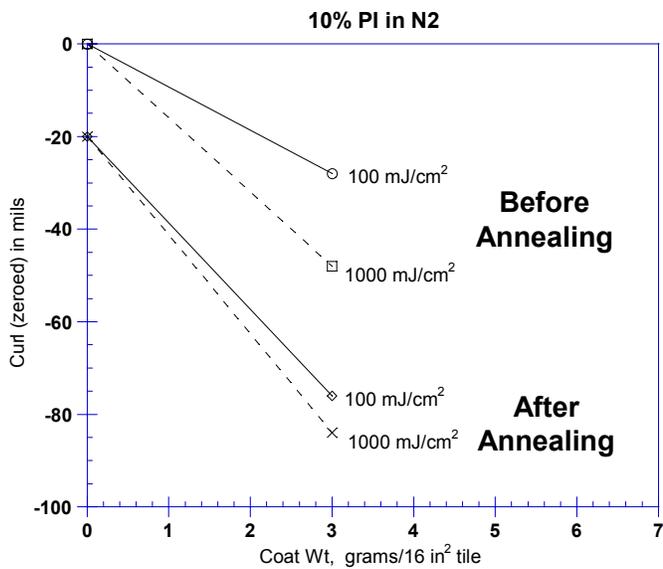


FIGURE 3. Illustration of the change in curl upon annealing.

This change in curl upon annealing may be visualized more readily by looking at the variable of curl change (= annealed curl – unannealed curl) as a function of the process parameters. Plots of curl change are presented in Figures 4A and 4B. The 3D figures were constructed using a Design-of-Experiments software package (Design Expert by Stat-Ease, Inc.), where the tiles with cracked backcoat films after annealing were rejected. Data at coat weights above 5 grams have thus been extrapolated from the response surface model (2-factor interactive) to give a sense of what the probable curl change behavior should be in the high coat weight region. Also, note that the curl change response surface for the 10%PI-Air coating that is shown in Fig. 4A is very similar to the 10%PI-N₂ (not shown). However, these coatings (10%PI) have significantly more change in negative curl upon annealing than the 1%PI-N₂ coating (Fig. 4B). Thus, not only are the 10%PI coatings equilibrating to a higher absolute magnitude of negative curl after annealing compared to the 1%PI coating (e.g. see Fig. 2B), but the 10% PI coatings are also achieving these large negative curls via greater curl changes during annealing compared to the 1% PI coating (e.g., Fig. 4A vs. 4B).

Interestingly, based on Figs. 3 and 4A/4B, the energy-dependence of curl change upon annealing appears to be somewhat greater than the energy-dependence of the curl magnitude itself (Fig. 2A/2B). Also note that at low coat weights 80-100% of the final curl develops during annealing, but as coat weight increases this value drops to 20-40%. Thus, greater coat weight achieves more of its final curl at cure and is proportionally less dependent on annealing even though the magnitude of curl change on annealing is still higher at higher coat weights.

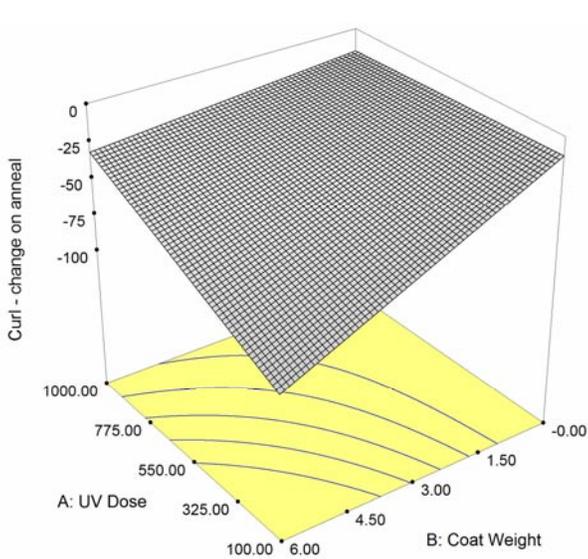


Figure 4A. Curl Change upon Anneal (mils) for 10%PI-Air

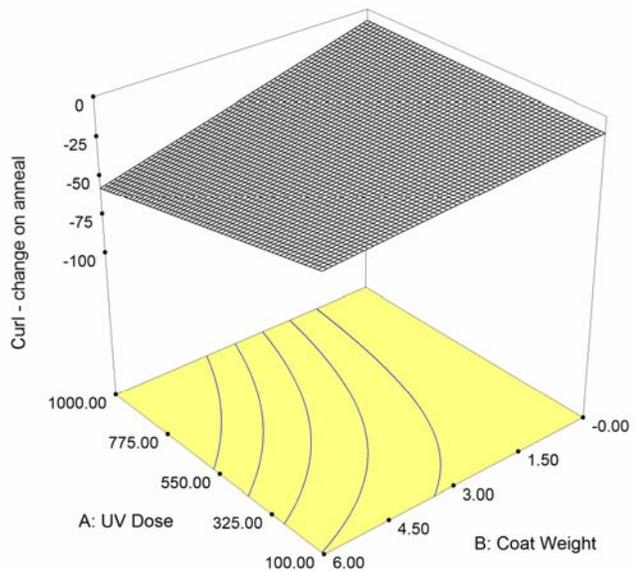


Figure 4B. Curl Change upon Anneal (mils) for 1%PI-N₂

** Note that the offset from zero curl at zero coat wt. in Fig. 4A/4B arises from about -15 mils of curl change upon annealing originating in the upper layers of the laminate.

Finally, the effects of irradiance and temperature on annealed curl (in this case, absolute values of zeroed negative curls) are presented in Figures 5A and 5B. These results indicate that annealed curl is relatively insensitive to irradiance in thin, highly crosslinked clearcoats such as the backcoats presently studied. The values of annealed curl depend somewhat on dose, since the 1000 mJ/cm² dose in most cases leads to greater annealed curl than when 100 mJ/cm² doses are used. However, as seen previously, the PI level appears to have a greater role in determining the annealed curl (higher PI gives higher curl). These trends and the values associated with them are generally repeated at all three irradiances. Similarly, the 80 °F and 120 °F annealed curls are similar in the trends between coatings, but the 150 °F samples exhibit significantly lower annealed curls. While increased cure rates may play a role in this effect, it would be expected to increase the annealed curl rather than decrease it based on the dose-dependency seen before. Instead, inspection of the backcoat films for these samples revealed much greater wet coating penetration into the substrate and subsequently a thinner contiguous backcoat film compared to the lower temperature samples. Thus, the temperature effect of lower curl at higher cure temperature seems more likely to be caused by viscosity reduction and mobility into the substrate, which reduces film thickness (i.e. the percentage of coat wt that is “effective” for curl has been reduced).

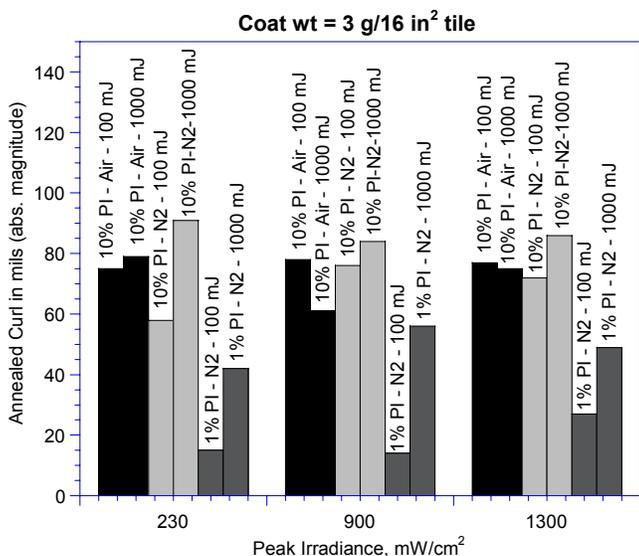


Figure 5A. Effect of Irradiance on Annealed Curl

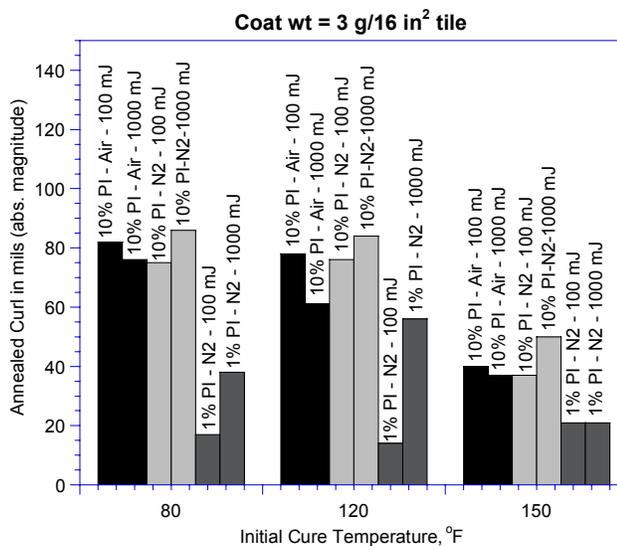


Figure 5B. Effect of Cure Temperature on Annealed Curl

DISCUSSION

The results presented above have generated two fundamental questions regarding curl in UV-coated semi-rigid laminates: a) why does the curl change so dramatically upon annealing (50+ mils in some cases), and b) why do some coatings equilibrate to much higher magnitudes of negative curl than others?

The mechanism of curl change during annealing is primarily related to the semi-rigid nature of the substrate (the thick, mineral-filled PVC center layer of the tile construction). This is because the substrate has the ability to deflect in curvature immediately after application and curing of the UV-backcoat, but will yield significantly further once its modulus decreases at annealing temperature. Figure 6 illustrates the way in which the internal stresses of a highly shrinking, crosslinked, high modulus UV-topcoat and backcoat oppose each other via bending moments through the center substrate (see the references on laminate curl^{1,8} for additional theoretical details):

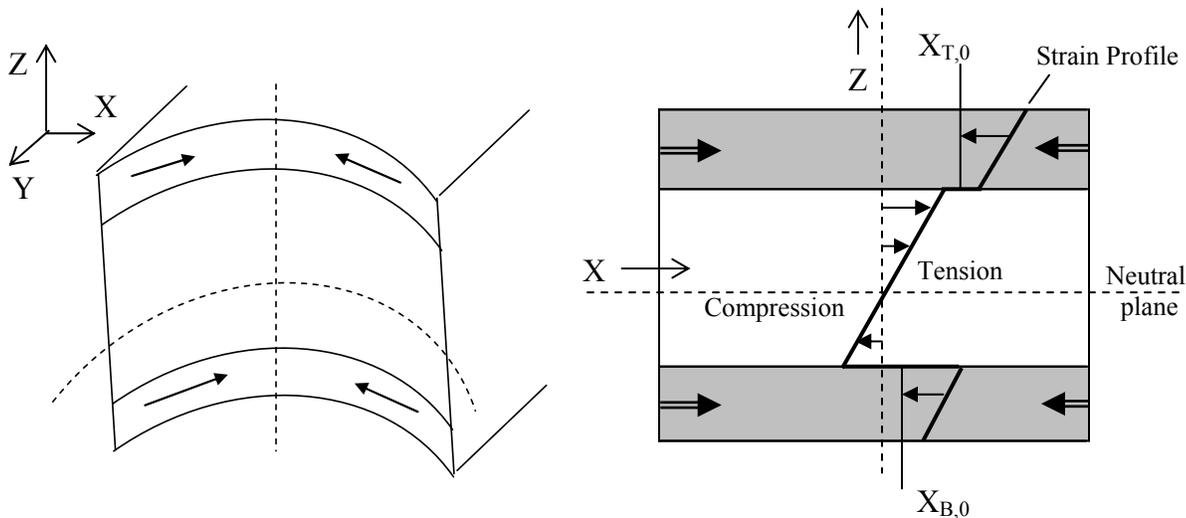


Figure 6. Mechanics of Laminate Bending.

Note that the semi-rigid center substrate has been forced into a state of tension above the neutral plane and into compression below the neutral plane, and therefore acts as a beam to resist deflection (if the coatings were removed this center layer would return to its internal equilibrium state of non-deflection). The UV-coatings, on the other hand, are both in a state of tension because they have reached a static equilibrium such that the backcoat has strained the topcoat away from its natural free-film equilibrium shrinkage, $X_{T,0}$, via its bending moment (leaving it with a restoring force favoring further strain shrinkage), while the topcoat has done the same to the backcoat. At room temperature, the reaction forces driving the center substrate to be flat eventually balance the shrinkage forces of the UV-coatings such that the UV-coatings can only achieve a portion of the curvature they would otherwise obtain (e.g., if the laminate were a 2-ply of the coatings alone). However, the coatings are able to seek a more direct equilibrium with each other when the semi-rigid center substrate is softened during annealing. This is the primary mechanism of curl change during annealing.

Another factor that must be considered while investigating the mechanism of curl change during thermal annealing is the possibility of additional “dark cure” of the backcoat. In particular, Kloosterboer⁹ showed that trapped radicals can be released by heat for further polymerization for as long as several months after the initial UV-cure. Therefore, in the present study the % acrylate conversion was studied by FTIR before and after annealing to determine if any additional curing was occurring in the annealing process. Both ATR analysis of cured films on the tiles themselves and transmission studies of thin films cast on NaCl crystals indicated no significant additional cure upon annealing in the case of the 10% PI coatings (air and N₂ cure both giving up to 90% conversion in optimal curing conditions with no more than a 2-4% increase during annealing). However, the 1% PI coating did experience 10-20% increase in conversion during annealing, depending on condition. This finding is especially validated by the transmission studies, where it was possible to measure 1% PI cured in air and N₂ at 550 mJ/cm². These 1% PI studies showed a change from 66% to 71 % conversion (7.6% increase) for N₂ cure, and a change from 54% to 63% conversion (17% increase with a transition to tack-free surface) for cure in air. Nevertheless, this increase in % conversion during annealing with the 1% PI coating is apparently insufficient to cause a large change in curl, since the previous data shows the relative ineffectiveness of the 1% PI coatings both before and after annealing. As a result, it appears that the primary mechanism for curl change upon annealing is the softening of the semi-rigid center substrate to allow for more direct force balancing between the topcoat and backcoat.

The second fundamental question raised by the curl results concerns the driving force behind the different annealed curl values in their final states. Consistently, the lower PI coating yields much lower annealed curl values. This is best explained in terms of % conversion of acrylate, which when increased will tend to likewise increase crosslink density, shrinkage and modulus to create greater curl force for a given substrate. This idea was tested using FTIR (ATR and transmission), Real-time FTIR, and Thin Film Calorimetry. The FTIR-ATR and transmission results were discussed above and the results from the other techniques are presented in Figures 7A, 7B, and 7C. In all cases, increased dose and, especially, increased PI level results in higher % conversion of acrylates. As a general trend this is expected, but it is interesting to note the utility of quantitative analysis in regard to the annealed curl results. Firstly, repeated measurements by multiple techniques have confirmed conversions in the 80-90% range for the 10% PI coatings. This is surprising in the case of air-cured coating due to oxygen inhibition. Most likely, these high conversions are a result of the very thin, clear films being cured under a relatively intense UV source that can overcome both oxygen inhibition, optical density effects, and photoinitiator screening. Even the RT-FTIR can achieve 80% conversion at very low irradiance in air with high PI and a thin film (films for the various techniques ranged from 10 to 30 microns as measured by SEM). Secondly, by quantifying the conversion with these cross-validated FTIR methods it is possible to show that conversion drives the ultimate annealed curl. This is shown in Figure 8. Note that the previously discussed insensitivity of curl to “dark cure” in initially low conversion films (1% PI) is likely due to the relatively small change in absolute % conversion before and after annealing (for example, an 11% increase from 54% initial conversion yields only 60% annealed conversion).

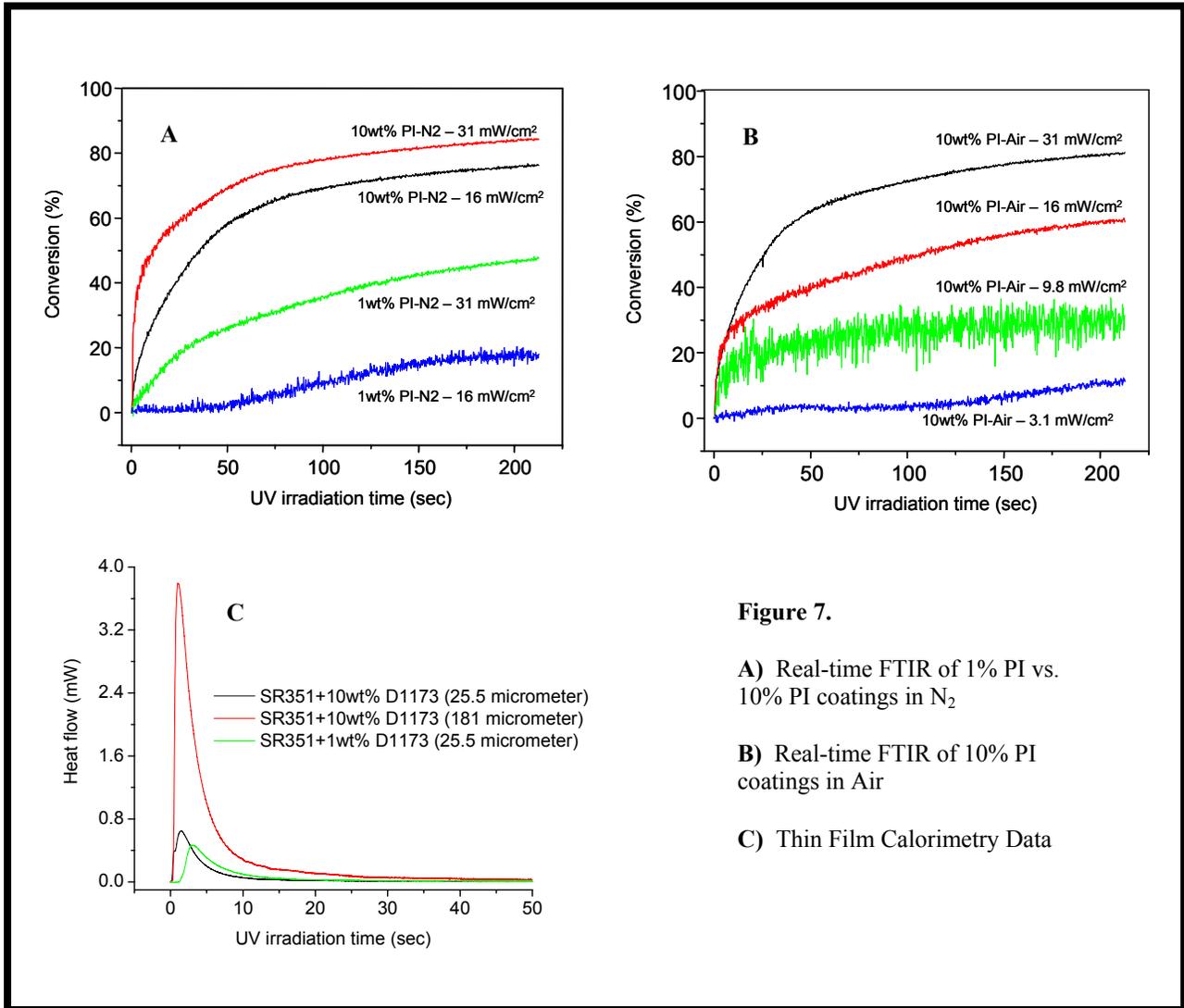


Figure 7.

A) Real-time FTIR of 1% PI vs. 10% PI coatings in N₂

B) Real-time FTIR of 10% PI coatings in Air

C) Thin Film Calorimetry Data

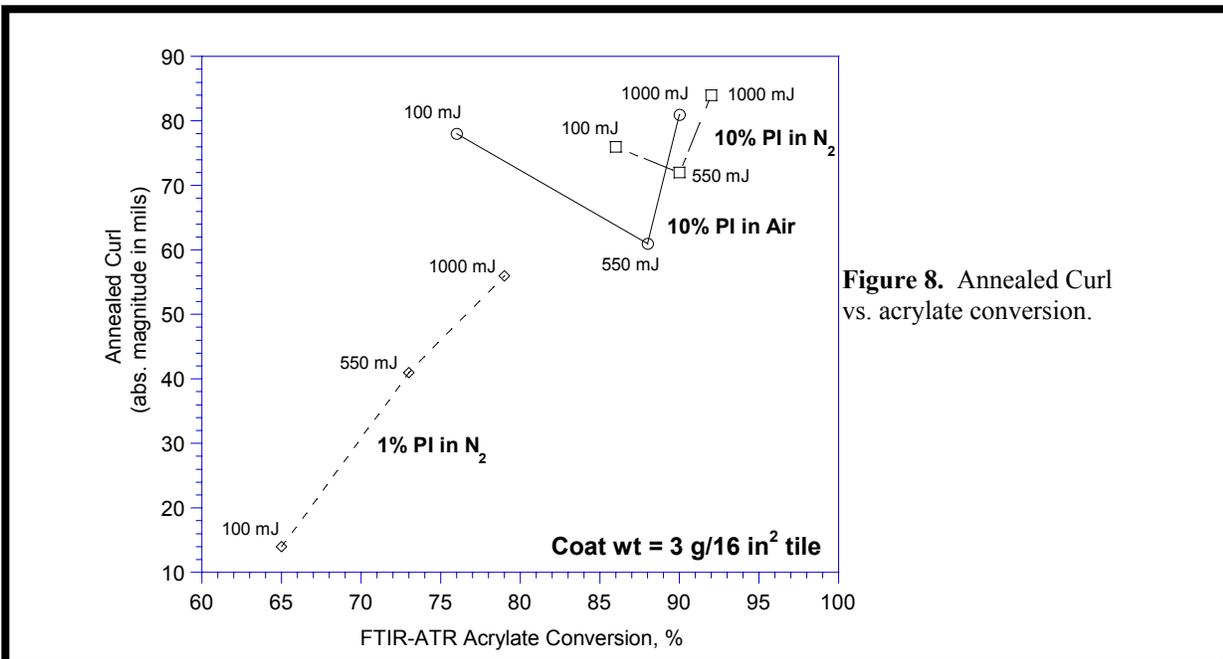


Figure 8. Annealed Curl vs. acrylate conversion.

CONCLUSIONS

The present study has investigated the important parameters governing curl in the processing of UV-coated, semi-rigid laminate materials. It was discovered that two primary mechanisms are involved in this process. First, there is a mechanical force balance between the UV-topcoat and UV-backcoat that is damped by the presence of the semi-rigid center substrate. This has the effect of allowing for a partial curvature to be achieved immediately upon UV-curing as the center layer has some semi-rigid deflection ability. However, full curl is not achieved until thermal annealing has softened the center layer to allow the coatings to balance against each other in a more direct manner. Coating weight (film thickness) is a dominant factor in determining how much curl is achieved immediately versus how much is achieved after annealing, although UV energy dose has some effect as well (higher doses can achieve more of the final curl before annealing just like higher coat weights). The second fundamental issue is the magnitude of the driving force for the final annealed curl itself. This was found to be directly related to % conversion of acrylate crosslinking groups, with a significant change in annealed curl occurring over a range of 50-90% conversion (higher curl at higher conversions). In turn, the conversion is increased most significantly by higher UV dose and photoinitiator (PI) concentration. Curl was relatively insensitive to peak irradiance and cure temperature at the levels and thin film thicknesses used in this study. Finally, some evidence for an increase in conversion during annealing of low PI coatings suggests that a measure of thermal “dark cure” is possible for films with initially low conversions (less than 75%), but the significance of this effect in determining annealed curl appears to be rather weak due to the relatively small change in absolute % conversion before and after annealing.

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