DIRECT COMPARISONS BETWEEN HIGH AND LOW UV INTENSITY IRRADIATION ON ACRYLATE DOUBLE BOND CONVERSION

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ABSTRACT OF PAPER
In this study, the influence of UV light intensity (I_0) from different UV irradiators was evaluated with respect to the depth profile (Cd) of double bond conversion in acrylate based formulations. The UV irradiators evaluated in this study include conventional arc lamps, fluorescent lamps and microwave powered lamps. The investigation was performed at a constant UV dose in order to compare the "curing efficiencies" between the irradiators after delivering equal amounts of photons, but in a very different time scale. At low light intensity conditions, increasing the total dose does not reduce the oxygen inhibition seen at the surface of the exposed film. The purpose of the study was simply to define conditions for optimization and also to give predictions for control of physical properties of the photopolymerized films. All photopolymerizations were carried out in air using the single laminate condition at various film thickness [1.2]. Degrees of C=C conversion were obtained by the use of FTIR.

1. INTRODUCTION

In two previous papers, I_a was kept constant by variation of I_0 and [PhI], simply by using the relation $\mathbf{I_a = Const.\bullet I_0 \bullet [PhI]}$ **(1).** I_a is the absorbed light intensity at different thickness of the film. I_0 is the UV light intensity at the surface of the film. [PhI] is the concentration of photoinitiator in the UV curable formulation. A constant value of I_a can thus be obtained by applying the following equation [1,2]:

$$\mathbf{[PhI]_{high} \cdot I_{0\ low} = [PhI]_{low} \cdot I_{0\ high}} \quad \mathbf{(2)}$$

In this study, the total dose or delivered energy is kept constant (mJ/cm^2). However, the time to deliver equal energies are very different due to variations in I_0 among the various irradiators investigated. Furthermore all formulations are photopolymerized keeping the [PhI] constant. This situation will therefore be quite different from previously reported [1, 2, 3]. In order to obtain the same delivered energy in the comparison between the irradiators the following ratios were kept constant:

$$\mathbf{I_{0(high)} \bullet t_{EXP.(short)} = I_{0(low)} \bullet t_{EXP.(long)}} \quad \mathbf{(3)}$$

2. EXPERIMENTAL

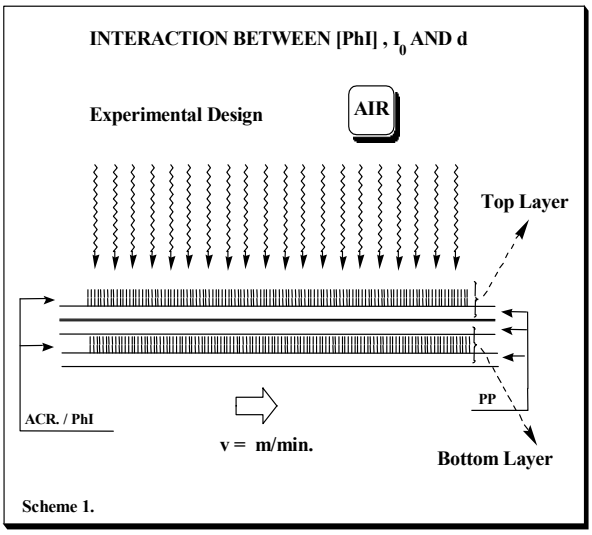
In Table 1 is displayed the maximum light intensity readings ($\mathbf{I_{0MAX}}$) using a UV Power Map unit from EIT. The Microwave* D, H and the Arc lamp** were monitored at 6-7 m/min. The QUV*** was measured in a static mode.

Table 1 UV intensity ($I_{0\ Max.}$, mW/cm^2) comparison of different UV light sources

	Microw.*D[1]	Microw.*D[1] (with Pyrex)	Microw.*H[1]	Arc**[2]	QUV***3 (315&351)
UVA	4855	3712	2296	106	5
UVB	1406	52	2002	0	0.2
UVC	150	34	242	0.5	0.1
UVV	2914	2668	2074	23	0.8

1.Measured at focus
2.Measured at 1" from screen to belt
3.Measured at 2" from bulb

The photopolymerization conditions used for the FTIR analysis are described in references [1,2]. A "single laminate model" was shown in **Scheme 1**. Film thickness of both top layer and bottom layer were 12 microns. Since all the photopolymerization were accomplished in an air simulating set-up, the top film layer was cured under O_2 diffusing conditions, which is identical to practical curing in air and consequently the "bottom" layer is now polymerizing under O_2 free diffusive conditions between the two PP films. This fairly simple arrangement is also a good approximation to what is actually occurring in air curing at the bottom of photopolymerizing medium.



Scheme 1.

3. RESULTS AND DISCUSSION

3.1. Comparison between Microwave* D and Arc lamp**

Exposures at equal dose conditions

The ratio in I_{0MAX} in the UVA area between Microwave* D and Arc lamp** is according to table 1 46:1. The corresponding ratio in dose readings is 14:1. This is due to the very much broader irradiation profile from Arc lamp**. In order to perform the photopolymerizations at equal energy delivery (dose), the exposure time for the Arc lamp** irradiations are therefore 14 times longer as compared to the Microwave* D exposures. In Figure 1 is shown the C=C acrylate conversion as a function of exposure time (belt speed in m/min) for the Microwave* D irradiator. As expected a very small if any difference can be seen between the top layer and the bottom layer as a function of exposure time. A high total degree of conversion (≈ 90 %) at 40 and at 100 m/min, clearly indicates a very efficient "curing" process.

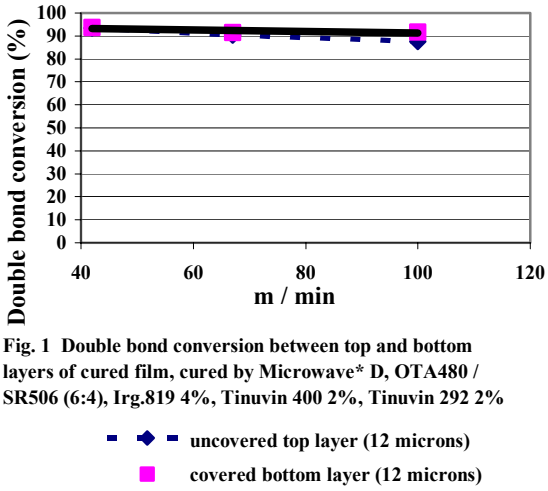


Fig. 1 Double bond conversion between top and bottom layers of cured film, cured by Microwave* D, OTA480 / SR506 (6:4), Irg.819 4%, Tinuvin 400 2%, Tinuvin 292 2%

In Figure 2 is outlined the C=C acrylate conversion for the parallel curing experiments using the Panacol irradiator. At belt speeds of 3, 5 and 7 m/min., one obtains the equal doses as for the previous exposures using the Microwave* D system. Already at longer exposure times (3 m/min) and in the bottom layer the Arc lamp** shows a reduced degree of C=C conversion, 93 % to 82 % and at 7 m/min it is below 80 %. The predicted differences in C=C conversions due to the huge differences in I_{oMAX} between these two irradiators are very obvious when comparing the situation for the top layers, where the oxygen inhibition for Arc lamp**l system very apparent.

The actual FTIR readings show that at 3 m/min it is less than 60 % and at 7 m/min it is 50 %. These values will clearly indicate that the "upper" surface region of the top layer is uncured and "tacky" in appearance.

A more careful inspection of the spectral distributions for these two irradiators will show the presence of high light intensity also in the UVB and UVC regions for the Microwave* D lamp, which is not the case for the Arc lamp**. In order to compare the C=C conversions at "similar" spectral distributions, a Pyrex filter was used in front of the Microwave* D lamp and thereby filtering out the UVB and UVC emissions.

By comparing the C=C conversions in Figure 1 and 3, the short wavelengths influence can be slightly notified. Although the bisacylphosphine initiator (Irg. 819) has a very strong absorption in the 300 nm area, the "long-tailed" absorption between 350 and 420 nm seems to be quite enough for an "acceptable degree of cure". The very small difference seen is also of course due to the fact that the UV absorber (Tinuvin 400) strongly absorbs in this wavelength area. The reduction in degree of conversion in the bottom layer is minimal (1-2%) as expected. In the top layer a reduction in conversion is now clearly noticeable (≈ 5-10%), but still not very depent at these exposure times (40-100 m/min).

However, the interesting comparison is still to be seen in Figure 2 and 3, where the strong influence of I_0 is shown. By curiosity only, the top layer cured under the Pyrex Microwave* D set-up has the same degree of conversion as the bottom layer for the Arc lamp** (≈ 80 %). Again, showing the dramatic influence in conversion in air by the use of a high intensity irradiator.

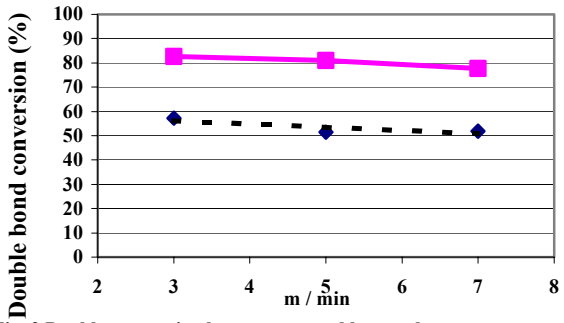
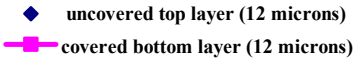


Fig. 2 Double conversion between top and bottom layers of cured film, cured by Arc lamp at 1.1", OTA480 / SR506 (6:4), Irg. 819 4%,Tinuvin400 2%, Tinuvin 292 2%**



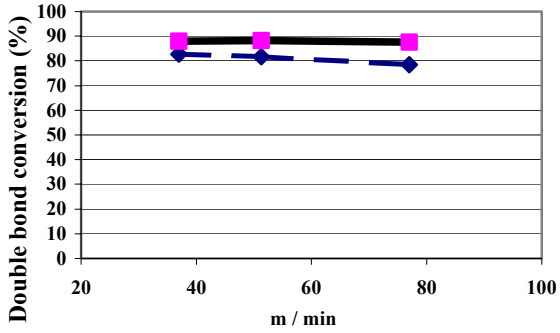


Fig. 3 Conversion between top and bottom layers of cured film, cured by Microwave* D with pyrex, OTA480 / SR506 (6:4), Irg. 819 4%, Tinuvin 400 2%, Tinuvin 292 2%

Exposures at increased dose conditions

An investigation was carried out in order to find out whether an increased total dose of exposure could compensate for the very low I_0 generated by the Panacol lamp. If that was possible, one would expect to see a slow approach towards the high degrees of conversion obtained by the use of the Microwave* D/Pyrex set-up. At 7 m/min using the Arc lamp** the coating receives the same energy as passing under the Microwave* D at a belt speed of 98 m/min. From the C=C conversion as displayed in Figure 4, it is quite obvious that increasing the total dose by a factor of 3 simply by exposure the coating 3 times at 7 m/min, no increase in C=C conversion in the bottom layer could be detected (78% to 79%).

In the top layer an increase in conversion could clearly be seen, an increase from 52 % to 66 % was recorded. However, by comparing the corresponding high degrees of C=C conversions in the two layers using the Microwave* D and Microwave* D/Pyrex irradiators under these experimental conditions, the threefold increase in total energy delivery could not compensate for the low I_0 emission from the Arc lamp**. The actual values are 92 % versus 79 % for the bottom layer and 87 % versus 66 % for the top layer. As mentioned earlier, a total C=C conversion of 66 % in the top layer will again indicate that the "upper" surface region is almost uncured.

Even though an increase can be detected at higher dose levels in the top layer for the Arc lamp**, it also implies that the surface is much more oxidized and therefore an initial state of degradation is initiated, which might sacrifice the outdoor stability.

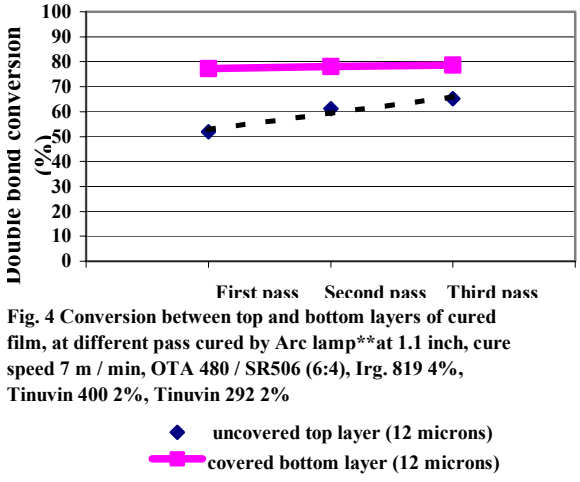


Fig. 4 Conversion between top and bottom layers of cured film, at different pass cured by Arc lampat 1.1 inch, cure speed 7 m / min, OTA 480 / SR506 (6:4), Irg. 819 4%, Tinuvin 400 2%, Tinuvin 292 2%**

3.2. Comparison between Microwave* D and Microwave* D with Pyrex versus QUV*** Chamber 313/351

Exposures at equal dose conditions

The QUV Chamber consists of two 40 W fluorescent lamps with emission spectra at 313 and 351 nm. Due to the different lamp designs, the comparison was made in the static state for the QUV Chamber and the C=C conversion measurements were therefore calculated from exposure time in order to maintain the criteria postulated in equation **(3).**

The exposure times from varying the belt speed for the Microwave* D and Microwave* D/Pyrex installations versus the static exposure times in the QUV*** Chamber are shown in Table 2 and the Gauss-Boltzman distribution profile for the Microwave* case is approximated to "rectangular" pulse with a pulse width of 1.2 cm.

Table 2. t_{EXP} versus equal UVA Dose (mJ/cm^2) for Microwave*D and QUV* Chamber**

Microwave*D	Microwave* D / Pyrex	QUV***
8 msec. / 96	11 msec. / 101	22 sec. / 90
13 msec. / 144	16 msec. / 135	30 sec. / 135
17 msec. / 192	23 msec. / 189	45 sec. / 198

In Figures 5 and 6 are plotted the C=C acrylate conversion as a function of equal energy delivery (dose) for the QUV*** Chamber and the Microwave* D irradiation cases. A careful examination of the extremely huge differences in the C=C conversion data will again emphasize on the importance of I_0 in reduction of the oxygen inhibition. At high dose levels (190 mJ/cm^2) the difference is rather modest, 88 % versus 93 %. For the top layer, the differences are almost characterized as "well cured" to "uncured" ! The real gap in between the two recordings are at a high dose level less than 30 % versus 93 % ! Such a low degree of conversion causes the surface to be very tacky if not "wet" in appearance. Even more amazing is the fact that for the Microwave* D exposures the degree of conversion is the same for the top and bottom layer. It is also well worth to focus on the fact that the QUV*** exposure times are more than 2000 times longer for QUV*** irradiations.

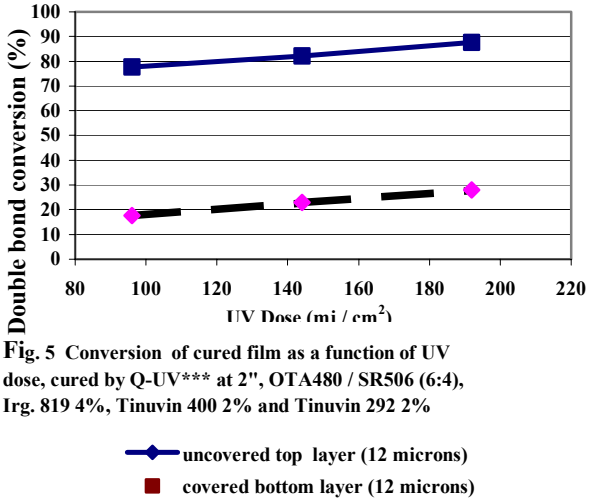


Fig. 5 Conversion of cured film as a function of UV dose, cured by Q-UV* at 2", OTA480 / SR506 (6:4), Irg. 819 4%, Tinuvin 400 2% and Tinuvin 292 2%**

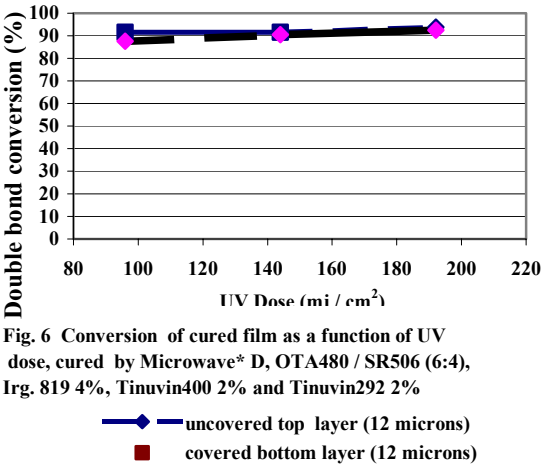


Fig. 6 Conversion of cured film as a function of UV dose, cured by Microwave* D, OTA480 / SR506 (6:4), Irg. 819 4%, Tinuvin400 2% and Tinuvin292 2%

The comparative data using the Microwave* D/Pyrex set-up installation as a function of delivered dose (Figure 7.) does not change the previous picture as out lined above in the 3.1. section, where the Arc lamp** was examined. Again, the small deviations seen are also in case due to the balance between the competing photon absorption between the photoinitiator (Irg. 819) and the UV absorber (Tinuvin 400) as described earlier.

Exposures at increased dose conditions

As a matter of curiosity only, the QUV*** Chamber experiments were extended to exposure times 10 to 60 times longer than the equal dose exposure time predicted just to verify that longer exposure times could not at all compensate or reduce the severe oxygen inhibition always present for the very low I_0 readings typical for this type of irradiating system. The results

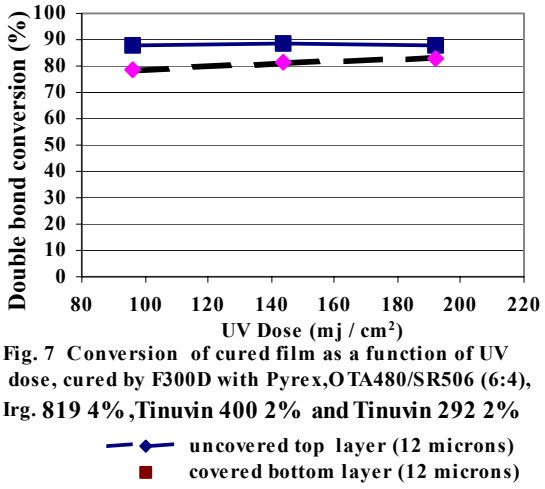


Fig. 7 Conversion of cured film as a function of UV dose, cured by F300D with Pyrex,OTA480/SR506 (6:4), Irg. 819 4%,Tinuvin 400 2% and Tinuvin 292 2%

from the heavily extended exposure times are displayed in Figure 8. Not surprising, but nevertheless overwhelmingly clear is the fact that for 40 minutes of exposure time (2400 sec.), the top layer C=C conversion is still below 60 %!

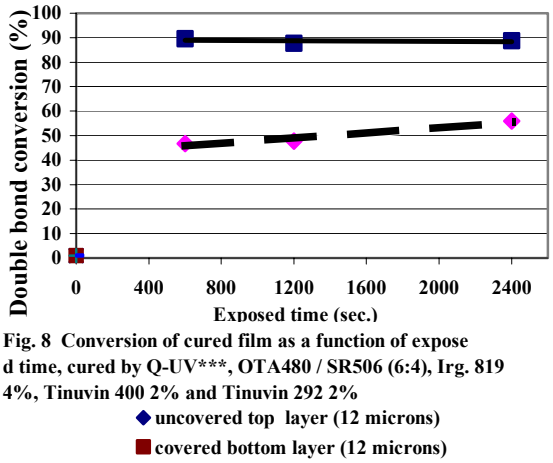


Fig. 8 Conversion of cured film as a function of expose d time, cured by Q-UV*, OTA480 / SR506 (6:4), Irg. 819 4%, Tinuvin 400 2% and Tinuvin 292 2%**

4. CONCLUSIONS

This investigation has been focused on the strong influence of high light intensity (I_0) as it is related to total degrees of C=C conversion, uniformity of cure, depth profile in cure response and reduction of oxygen inhibition. It is obvious from the results obtained from the various irradiators used in the examination that for lamps emitting UV radiation at low I_0 an increased dose even in orders of magnitude no compensation in degree of C=C conversion can be achieved. In this investigation it is further illustrated that the presence of UV absorbers and the high demands for outdoor stability (resistance to UV degradation) in combinations with the presence of PhI`s could be well balanced and the curing performance characteristics required can be fulfilled by the use of high I_0 only.

5. REFERENCES

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Microwave* lamp is made by Fusion UV Systems, Inc. F300 H or F300 D lamp was used in this research.
Arc lamp** is made by Panacol-Eloso.
QUV*** chamber is made by Q-panel Lab Products.