Using A New Approach To Analyze A Depth Profile Of Double Bond Conversion In Model Formulations And Commercial Formulation

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ABSTRACT OF PAPER

A new approach of analyzing the depth profile of double bond conversion as a function of film depth has been discussed. By using a combination of statistical calculation and traditional FTIR, a new approach to analyze the depth profile of conversion "layer by layer" in the characterization of photopolymerization was explored. Utilizing a formula **$(X_1 + X_2 + \ldots\ldots X_n) / n$ = Average conv. n = 1,2,3…. n:** a number of layer (5μm), an average conversion of any 5μm depth could be calculated from prior 5μm conversion and total average conversion. More detail information of photopolymerization, such as the depth profile of conversion and a difference in conversion between the top 5 microns and the bottom 5μm in a 25μm film as a function of film depth was obtained. This investigation was accomplished using a variation of film depth, non-photo bleaching PhI (Irg. 184) as well as the concentration of PhIs in the presence of air and in absence of air. A commercial formulation also was analyzed using this new approach. Results of analyzing double bond conversion between traditional FTIR and the new approach (statistical calculation / FTIR) were compared.

1. INTRODUCTION

In the UV curing processes, it is well known that double bond conversion at different depths of a film is not uniform because there are an oxygen inhibition in outermost part of a cured film and an inner filter effect in a bottom part of a cured film. Surface tackiness and a wet approach at an interface between coatings and substrates are a big challenge for the current UV curing industry. To study a depth profile of double bond conversion in a UV cured film enables formulators to further understand the photochemistry of UV curing and to improve cured film properties. Analyzing double bond conversion is a key technology for a performance characterization of photopolymerization and for quality control of the UV curing processes. FTIR, RTIR and Photo-DSC are very important methods for monitoring the UV curing processes. However, all of these methods can only analyze a total average double bond conversion throughout the entire film. There are only a few papers aiming to study the depth profile of double bond conversion as a function of film depth using different analytical instruments (1). In 2002, Tom Scherzer reported a depth profiling as a function of degree of cure during the photopolymerization of acrylates studied by real-time FTIR-ATR spectroscopy (2). A conversion was analyzed only in a narrow layer (1-2μm) at the bottom of the coatings, which does not give the total profile of conversion across the cured films. In 1997, a depth profiling of radiation curable coatings was investigated by W. Schrof (3) using a confocal Raman spectroscopy. Recently, Julie L.P. Jessop studied a conversion distribution along different depths of a cured film using a confocal Raman spectroscopy (4). A conversion of 2μm depth film in a cured film can be studied by using confocal Raman technology. In our previous papers (5,6,7), a double or single laminated model was used to study the inner filter effect on absorbed UV light intensity (I_a) and oxygen inhibition at the surface of cured films. Using the double or single laminated model, a film needs to be separated physically to different layers by using PP films. In 2006, we first reported a new approach of using a combination of statistical calculation and traditional FTIR to analyze a double bond conversion layer by layer, using a photo-bleaching Irg. 819 as a PhI (8). This study focuses on using a new approach to analyze a depth profile of double bond conversion of model formulations using a non-photo bleaching Irg. 184 as a PhI and a commercial formulation.

2. EXPERIMENTALS

2.1. Materials

Acrylates: EB 8402 is a difunctional acrylated aliphatic urethane from UCB, $M_w \approx 1{,}000$.
SR506 is isobornylacrylate from Sartomer.

Commercial formulations 1(CF1): Recommended coating thickness is 2-10μm for OPV (Over Printing Vanish) application for plastics.

Photoinitiators: Irgacure 184 from CIBA.

Irradiators: A Fusion LH6H lamp was used throughout the entire evaluation.

2.2.Photopolymerization conditions

A clear coating formulation, based on EB8402 / SR506 (3:7) with Irg. 184, was used as model formulation in presence of air. The formulation was coated on a substrate, such as PP-films. The film thickness applied throughout this investigation was 5μm, 10μm, 15μm, 20μm and 25μm, respectively. A series of drawdown bar was used to control the film thickness.

2.3. Analysis

FTIR analysis was carried out using a Spectrum 2000 spectrometer from Perkin – Elmer.

3. RESULTS AND DISCUSSION FOR MODLE FORMULATIONS

3.1.A depth profile of conversion as a function of film depth and [Irg.184]:

For a formulation using photo bleaching Irg. 819 as a PhI in absence of air, its depth profile of the double bond conversion is virtually unchanged and in presence of air, its depth profile of the C=C conversion is increased from the outermost to the bottom of a cured film (8). Its peak of the conversion (highest conversion) is in the bottom of a cured film in presence of air. It is very interesting to study a distribution of a depth profile of conversion along with various depths of a cured film using non-photo bleaching Irg. 184 as PhI in a formulation.

In order to study the oxygen diffusion and the inner filter effect, a comparison test between laminated films (no oxygen inhibition) and un-laminated films (in air) was performed. One piece of PP film was placed in front of "cured film" for the air curing system in order to run a fair comparison test. The distance between the PP film and coating is about 1 cm, so the front side of coating is still under influence of oxygen inhibition. The film thickness was varied by 5µm increments. The formulation is EB8402 / SR506 (3:7) with Irg. 1840.4%. From Fig. 1, one can see that the C=C conversion in a laminated film (in absence of oxygen) as a function of film thickness is decreased when the relative thick films (15-25µm) are cured because of the inner filter effect of Irg. 184. For a formulation using non-photo bleaching Irg. 184 as a PhI in absence of air, the conversion of thin film is higher than that of thick film due to the inner filter effect. The inner filter effect cannot be observed in the thin film (5-15µm). Each curve in Fig. 1 represents five different average double bond conversions for five different thickness films.

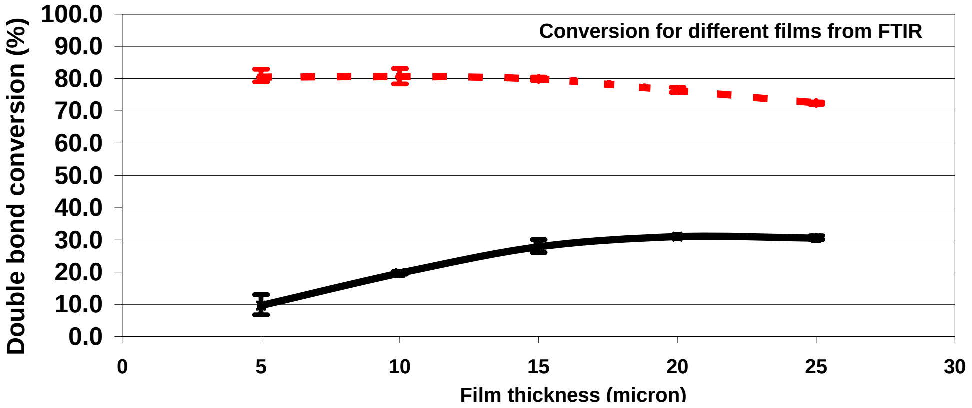

Fig. 1 Double bond conversion as a function of film thickness, EB8402/SR506 (3:7), Irg. 184 0.4%, 67 mpm

By curing in presence of air, the average double bond conversion can be increased from 10% for a thin film (5µm) to 30% for a thick film (25µm). Even for a total 25µm film, an real oxygen inhibition at the outermost layer of the film has not been reduced by increasing film thickness. A major contribution of increasing average double bond conversion results from the underlying layers beyond the oxygen diffusion affected region. Due to a balance of reducing the oxygen inhibition and increasing the inner filter effect from 20µm to 25µm film, the total average of the conversion is not changed for these two films.

By using the new approach to analyze the depth profile of conversion by each 5µm for a 25µm film, some interesting results can be demonstrated. When the film is 5µm, the conversion in presence of air is 9.67%. X_1 = 9.67%. Subsequently, it was supposed that the double bond conversion (X_1 = 9.67%) of this 5µm film is equal to the conversion of a top 5µm film of 10µm thickness film (2 X 5µm). By utilizing the formula **$(X_1 + X_2) / 2$ = Average conversion (19.68%)**, the conversion (X_2) of the bottom 5µm film can be calculated. X_2 = 29.69%. By using the formula **$(X_1 + X_2 +\ldots\ldots X_n) / n$ = Average conv**. **n** = 1, 2,3…**n** is a number of layer (5µm), the average conversion of any 5µm section can be calculated from prior and total average conversion. Following table 1 is a calculation result of each 5µm thickness for a 25µm film in the presence of air.

Table 1. Depth profile of double bond conversion as a function of film depth in presence of air at 67 mpm

Film Thickness	Ave. Conv.	Top 5	Second 5	Third 5	Forth 5	Fifth 5
5μm	9.68%	9.6%				
10μm	19.68%	9.68%	29.68%			
15μm	27.83%	9.68%	29.68%	44.13%		
20μm	30.97%	9.68%	29.68%	44.13%	40.39%	
25μm	**30.56%**	**9.68%**	**29.68%**	**44.13%**	**40.3%**	**28.93%**

Table 2. Depth profile of double bond conversion as a function of film depth in absence of air at 67 mpm

Film Thickness	Ave. Conv.	Top 5	Second 5	Third 5	Forth 5	Fifth 5
5μm	80.40%	80.40%				
10μm	80.58%	80.40%	80.76%			
15μm	79.95%	80.40%	80.76%	78.69%		
20μm	76.35%	80.40%	80.76%	78.69%	65.55%	
25μm	72.49%	80.40%	80.76%	78.69%	65.55%	57.05%

In table 2, the calculation result of each 5μm thickness for a 25μm film in absence of air is calculated. In Fig. 2 is plotted the depth profile of C=C conversion of a 25μm film in absence and presence of air form Table 1 and Table 2. For a formulation using non-photo bleaching Irg. 184 as a PhI in the absence of air, the conversion of the top 5μm is higher than that of the bottom 5μm (80.40% vs 57.05%) in a 25μm film. Apparently, there is a turning point (at 15μm depth) of the conversion in this depth profile curve of conversion in a 25μm film cured in the absence of air, which means that the film depth from 15 to 25μm are under an influence of the inner filter effect.

For the film in presence of air, photopolymerization from 5 to 15μm is under strong influence of oxygen inhibition. Deeper than 15μm depth, a clear inner filter effect from the film is observed. For a formulation using non-photo bleaching Irg. 184 as a PhI in presence of air, there is a peak conversion (highest conversion) at 15μm depth (third 5μm in table 2) in the depth profile curve of conversion due to the least oxygen inhibition and least filter effect (44.13% vs 9.68% and 28.93%) in this depth. For this film depth (15μm), there is the least oxygen inhibition and filter effect than rest depths of the 25μm cured film.

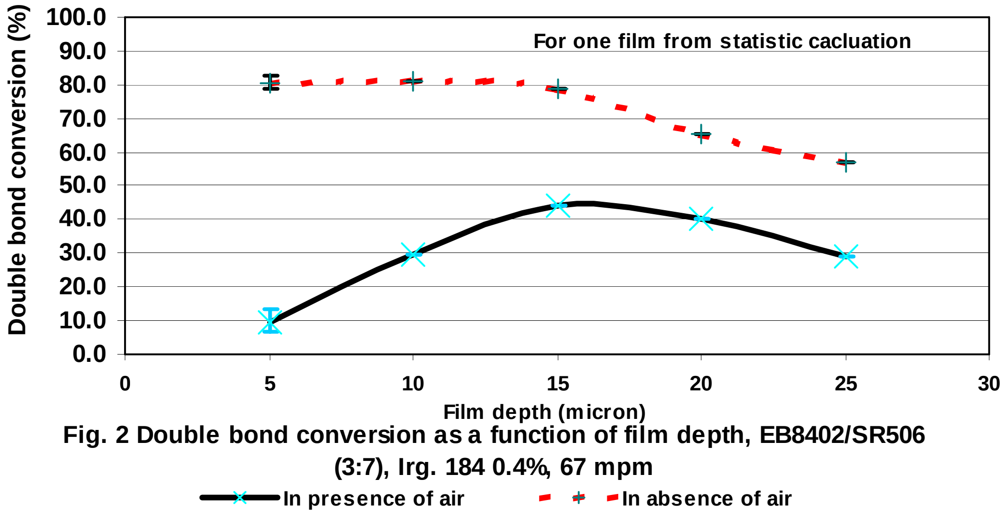

Fig. 2 Double bond conversion as a function of film depth, EB8402/SR506 (3:7), Irg. 184 0.4%, 67 mpm

3.2. A depth profile of conversion as a function of film depth and curing speed:

In Fig. 3 is shown the double bond conversion as a function of curing speed (exposure time) and film thickness. Reducing curing speed from 67 m/min to 33 m/min, there is no change of the C=C conversion of a thin film (5µm) due to the oxygen inhibition. A benefit of increasing the conversion (30% vs 54%) of a thick film (25µm) has been observed. Increasing UV dose (mJ /cm^2) cannot reduce the oxygen inhibition at the thin film (5µm), however it improves the conversion of the underlying layers without or with much less the oxygen inhibition.

By using a combination of statistic calculation and FTIR result from Fig. 3, Fig. 4 is plotted as a depth profile of C=C conversion as a function of curing speed and film depth. It is very noticeable that the peak conversion (highest conversion) has been shifted from 15µm depth to 20µm depth for the same formulation, by decreasing a curing speed from 67 mpm to 33 mpm. By analyzing an average conversion using a traditional FTIR method, 24% increasing conversion for a 25µm film (from 30% to 54%) in Fig. 3 can be shown. By using this new approach to analyze the conversion “layer by layer”, 39% increasing conversion of bottom 5µm is shown (from 29% to 68%) for this 25µm film as expressed in Fig. 4.

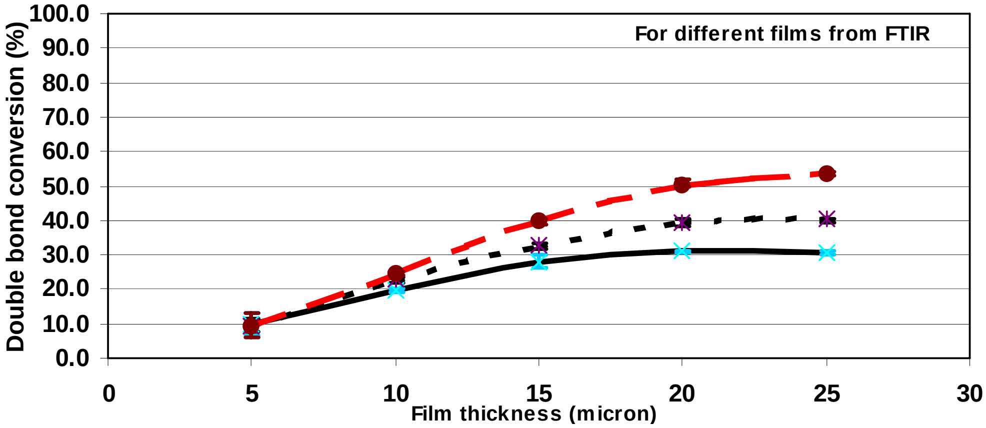

Fig. 3 Averge double bond conversion as a function of film thickness and curing speed, EB8402/SR506 (3:7), Irg. 184 0.4% in air

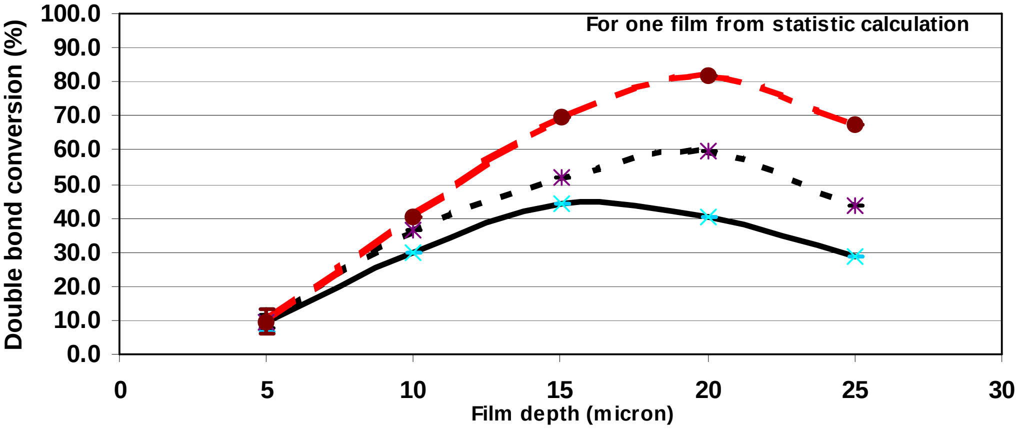

Fig. 4 Double bond conversion of each bottom 5 microns as a function of film depth and curing speed, EB8402/SR506 (3:7), Irg. 184 0.4% in air

3.3. A depth profile of conversion as a function of film depth and [PhI]:

PhIs are an important linkage between UV light and UV curable oligomers as well as monomers. The [PhI] level frequently need to be adjusted in order to improve physical properties of cured films. So, it is important to look into an effect of [PhI] on double bond conversion at different depths of cured films in order to fully understand photopolymerization. In Fig. 5 is shown that the influence of [Irg. 184] and film thickness on average double bond conversion. By increasing [Irg.184], an increase in average double bond conversion for a thin film (5µm) and thick film (25µm) can be detected. A flat conversion platform is reached when a film thickness is increased from 20µm to 25µm due to a balance of reducing the oxygen inhibition and increasing the filter effect. With the new approach, one can study distribution of a double bond conversion as a function of each 5µm individually. In Fig. 6 is displayed that increasing [Irg. 184] from 0.4% to 4%, both top 5µm conversion and bottom 5µm C=C conversion have been increased. The peak conversion (highest conversion) is still in the middle depth (third 5µm) of 25µm cured film because there is the least oxygen inhibition and inner filter effect in this depth of a cured film. For each conversion curve of a 25µm film from these clear formulations, depth of the film lower than 15µm is mainly under an influence of the oxygen inhibition; depth of the film higher than 15µm is mainly under an influence of the inner filter effect.

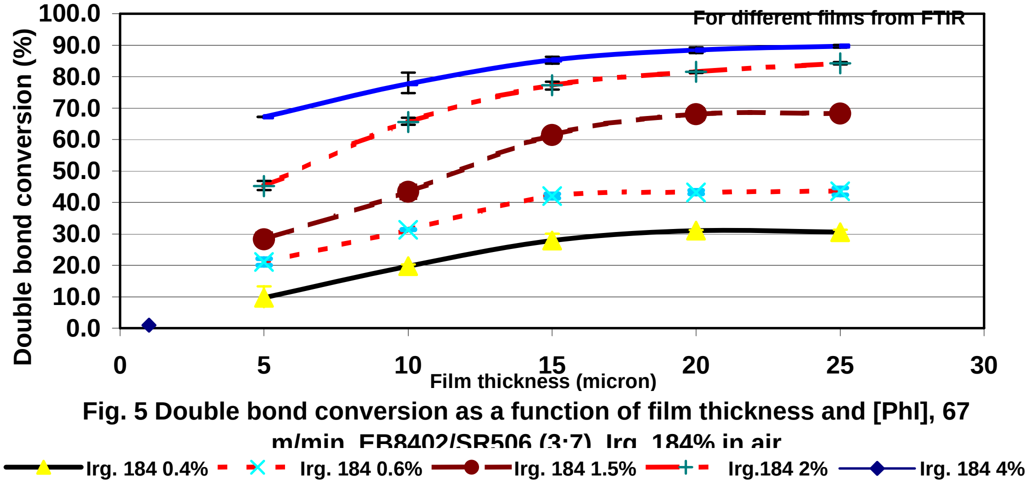

Fig. 5 Double bond conversion as a function of film thickness and [PhI], 67 m/min, EB8402/SR506 (3:7), Irg. 184% in air

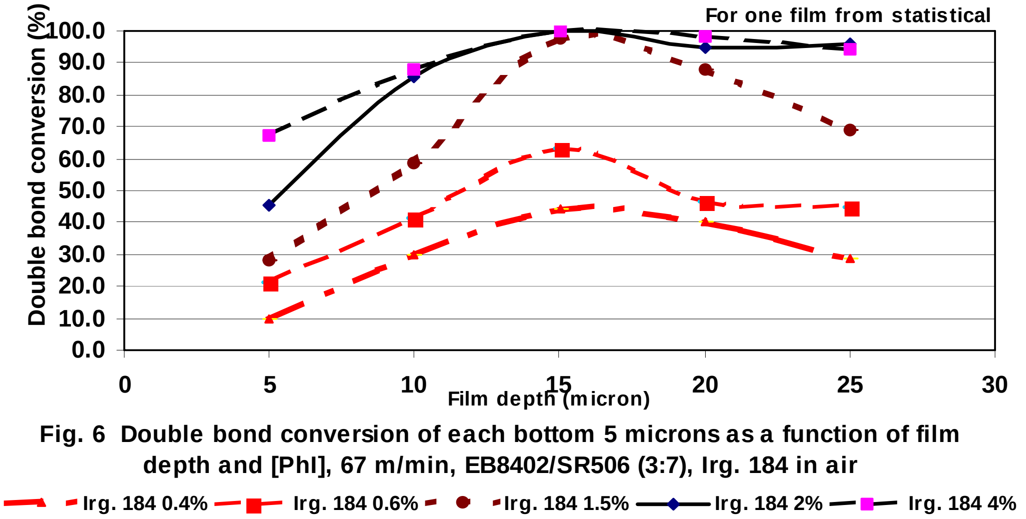

Fig. 6 Double bond conversion of each bottom 5 microns as a function of film depth and [PhI], 67 m/min, EB8402/SR506 (3:7), Irg. 184 in air

3.4. A depth profile of conversion as a function of film depth and I_0 (mW/cm^2):

An average C=C conversion as a function of UV light intensity (I_0) and film thickness is displayed in Fig. 7. In this study, the same UV spectral distribution (LH6H) but four different power settings (I_0) and an equal UV dose (mJ/cm^2) were used. Increasing film thickness can increase the conversion of a thicker film than 5µm. The average double bond conversion of a thin film (5µm) and thick film (25µm) is increased, simply by increasing I_0 (mW/cm^2) from 416 mW/cm^2 to 2315 mW/cm^2.

In Fig. 8 is shown the depth profile of the double bond conversion as a function of I_0 and film depth from the "new approach". In Fig. 8, each curve represents a distribution of the C=C conversion of each 5µm depth in a total 25µm film with an equal UVA Dose (mJ/cm^2). From the data in Fig. 8, the following clear informative remarks can be concluded for this formulation:

i. A benefit of a high I_0 (mW/cm^2) / short exposure time is at the outermost part (top 5 microns) of a cured film. Surface curing (top 5µm) is mainly improved from 20% to 46% when I_0 is increased from 416 mW/cm^2 to 2315 mW/cm^2. Once again, an influence of I_0 (mW/cm^2) on reducing oxygen inhibition can be clearly demonstrated.

ii. For the conversion curve using a high UV intensity / short exposure time, there is a peak conversion in the middle (15µm depth) of the cured film.

iii. For the conversion curve using a low UV I_0 / long exposure time, there is a peak conversion in or near bottom 5 micron depth of the 25µm cured film.

iv. For this clear formulation, there is no change of the conversion from forth 5 microns to fifth 5µm (bottom 5µm) for the 25µm film.

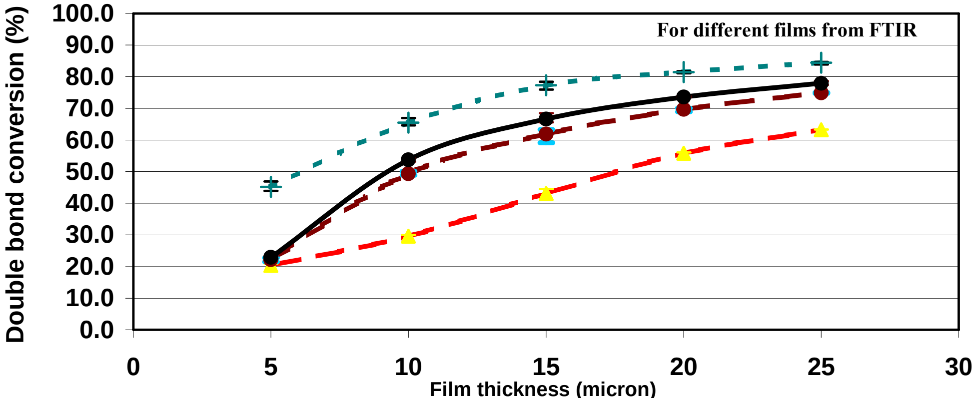

Fig. 7 Double bond conversion as a function of film thickness and I_0 (mW/cm^2), equal UVA Dose (mJ/cm^2), EB8402/SR506 (3:7), Irg. 184 2% in air

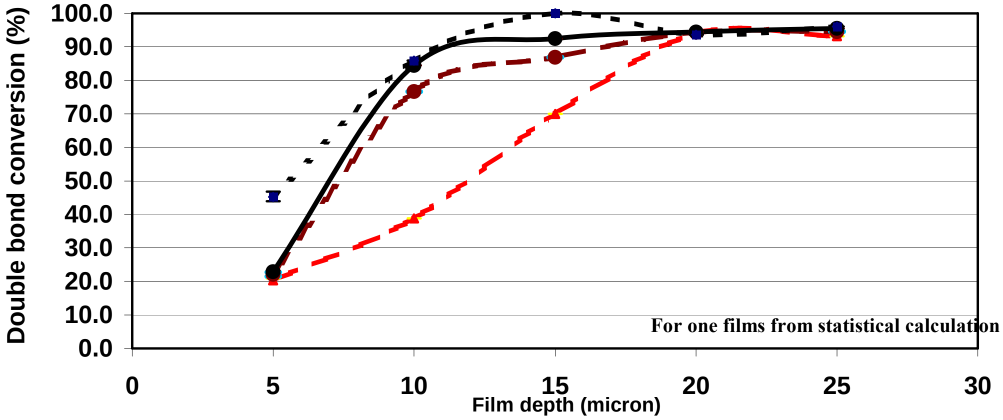

Fig. 8 Double bond conversion as a function of film depth and I_0 (mW/cm^2), equal UVA Dose (mJ/cm^2), EB8402/SR506 (3:7), Irg. 184 2%,one scan in air

4. RESULTS AND DISCUSSION FOR COMMERCIAL FORMULATION

A commercial formulation from a formulator was analyzed using the new approach. Concentration of [PhI] and what PhI are used in this formulation is unknown. However, the depth profile of C=C conversion from this "off-the-shelf" commercially available formulation is very similar to that from known module formulations discussed above, in which a benefit of a high UV intensity lamp in reducing the oxygen inhibition was shown, even if with equal UV Dose. The depth profile of the conversion for this commercial formulation has been studied.

4.1. Depth profile of conversion of CF1 as a function of film depth and I_0(mW/ cm^2):

CF1 was cured using the same UV spectral distribution (LH6H) but four different power settings (UV light intensity) and an equal UV dose with four different curing speeds. An effect of a film thickness and I_0 (mW / cm^2) on total average double bond conversion is outlined in Fig. 9. The film thickness was varied by 5µm increment. In Fig. 9 is shown five different group tests for five different thickness films. By increasing the film thickness, one can find an increase in the average conversion, which results from a major contribution from the deeper part of the cured films, but not the top 5µm exposed to air directly. Overall, the high double bond conversion from different films can be obtained by using a high I_0 (mW / cm^2) lamp. The C=C conversion of the thin film (5µm) can be increased faster than that of the thicker film (25µm), by increasing the I_0 (mW / cm^2) from 216 mW / cm^2 to 2315 mW / cm^2, due to reducing the oxygen inhibition.

All results in Fig. 9 are the total average conversion of different films. By using the new approach (a combination of traditional FTIR and statistical calculation) to analyze the depth profile of conversion by each 5µm, some interesting results can be demonstrated.

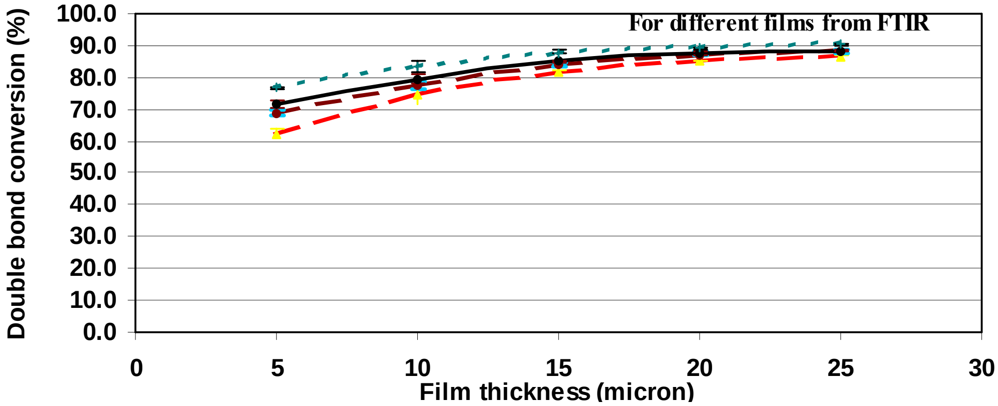

Fig. 9 Double bond conversion as a function of film thickness and I_0 (mW/cm^2), with equal UV Dose (mJ/cm^2), CF1 OPV in air

When the film is 5µm, the conversion from a low UV intensity condition (416 mW / cm^2) is 62.36%. By using a formula such as: $\mathbf{(X_1 + X_2 + \cdots X_n) / n}$ **= Average conv.**, the conversion of each 5µm section can be calculated from prior and average conversion for a one film. Table 3 is a statistical calculation result of each 5µm thickness for a 25µm film.

Table 3. **Depth profile of conversion of CF1 as a function of film depth using equal UV Dose (mJ /cm^2)**

Film Thickness	Ave. Conv.	Top 5 micron	Second 5 micron	Third 5 micron	Forth 5 micron	Fifth 5 micron
5μm	62.36%	62.36%				
10μm	74.37%	62.36%	86.38%			
15μm	81.87%	62.36%	86.38%	96.87%		
20μm	85.13%	62.36%	86.38%	96.87%	94.91	
25μm	86.65%	62.36%	86.36%	96.87%	94.91	92.87

From table 3 and similar data, as expressed in Fig. 10 can be plotted a depth profile of double bond conversion as function of a film depth and I_0 (mW / cm^2) for a 25μm film of CF1.

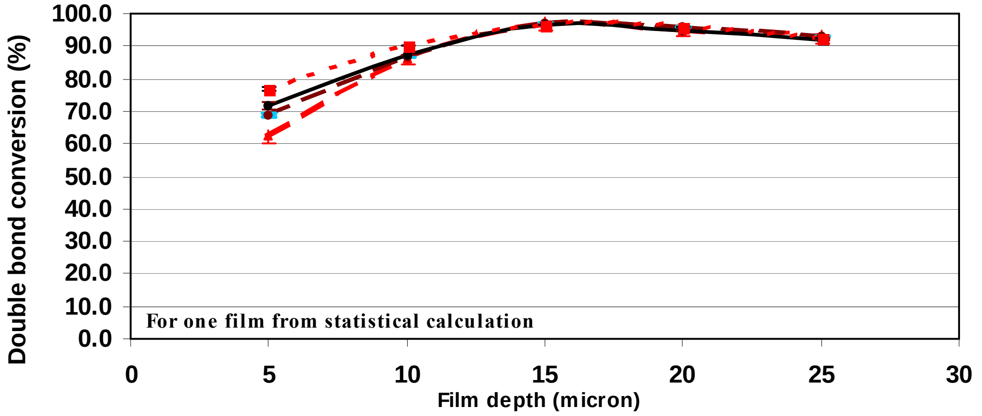

Fig. 10 Double bond conversion as a function of film depth and I_0 (mW/cm^2), with equal UV Dose (mJ/cm^2), CF1 OPV in air

A gradient of conversion curve in Fig. 10 is sharper than the corresponding one shown in Fig. 9. This is due to the fact that because the Fig. 10 really reflects the changing of the conversion depth profile as a function of film depth in the 25μm film. The sharp conversion curve also proves that the oxygen inhibition can be minimized in a deeper part of a film. The conversion of the top 5μm is cured faster than that of the bottom 5μm when the UV intensity is increased. The conversion at 15μm depth (third 5μm) is highest (peak conversion) in 5 different depths of the cured film, which means that there is a minimum of oxygen inhibition and filter effect in this depth of the cured film. A more uniformed cured film can be achieved by using a combination of a high I_0 (mW / cm^2) lamp and short exposure time.

With this "new" approach, it is possible to show much more influence of using a High I_0 (mW / cm^2) lamp /short exposure time on reducing the oxygen inhibition, compared with using a Low I_0 (mW / cm^2) lamp / long exposure time. A difference of analytical results between the traditional FTIR and the new approach is summarized bellow:

Conversion difference between FTIR and FTIR / Statistical calculation for a 25µm film of CF1 in air

	High I_0 / t exposure short	**Low I_0 / t exposure long**	**Difference**
Average conv.	**90.27%**	**86.65%**	**3.62%**
Bottom 5 conv.	**92%**	**92%**	**0%**
Top 5 conv.	**76.79%**	**62.36%**	**14%**
Ratio of conversion (top / bottom)	**0.84**	**0.68**	**0.16**

By using the new approach, more detailed information of conversion can be obtained!

Using the traditional FTIR, under a high I_0 (mW / cm^2) / short exposure time condition, an average conversion for a 25µm film is 90.27% while under a Low UV Intensity / longer exposure time condition, an average conversion is 86.65%. The difference of the average conversion between these two different setting up is 3.62%.

Using this new approach with the identical formulation, under a high I_0 (mW / cm^2) / short exposure time, a 76.79% conversion for the top 5µm in the 25µm film can be obtained while under a Low I_0 (mW / cm^2) / longer exposure time, a 62.36% conversion for the top 5µm is obtained. The conversion difference between the two different top 5µm is now 14% for the 25µm film. Using the new approach, 3.62% average conversion difference from the two different experimental setting up is re-analyzed along with the depth of the cured film. An effect of a high UV light intensity lamp on the depth profile of conversion has been confirmed.

By using the new approach, a ratio of double bond conversion between top layer and bottom layer can be easily obtained, which is an important information for formulators as well as for PhI designers with respect to balance surface cure and through cure. Using a combination of a high UV intensity with short exposure time, the ratio is 0.84. Using a combination of a low UV intensity with long exposure time, the ratio is 0.68. A more uniformed cured film is gained with a curing condition of a high I_0 / short exposure time.

In Fig.11 is displayed the double bond conversion of the top 5µm and the bottom 5µm in a 25µm thickness film as a function of I_0 (mW / cm^2). Without the oxygen inhibition and less filter effect from this clear formulation, a 92% conversion of the bottom 5µm is reached and is higher than that of the top 5µm under an influence of the oxygen inhibition. Surface curing (Top 5µm) is mainly improved from 62% to 77% by increasing I_0 (mW / cm^2).

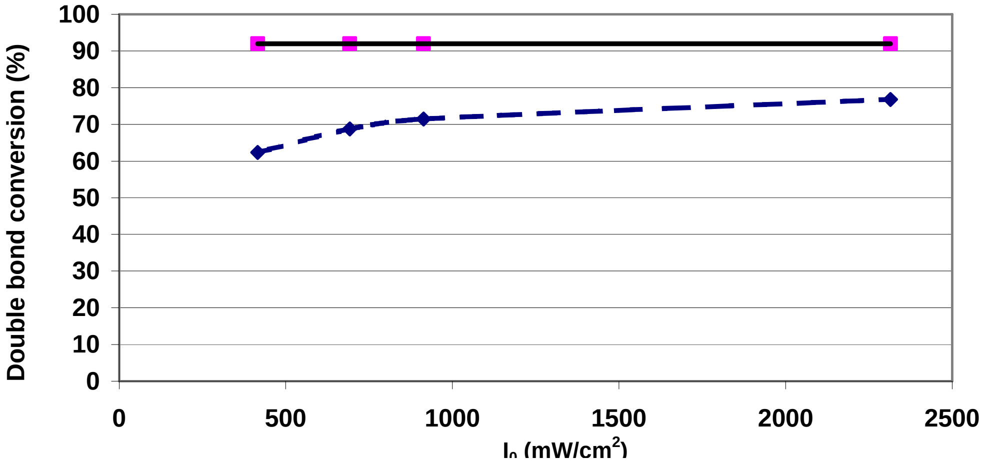

Fig. 11 Double bond conversion of top 5 microns and bottom 5 microns in a 25 micron film as a function of I_0 (mW/cm^2) with equal UV Dose (mJ/cm^2). CF1 OPV in air

4. CONCLUSIONS

This new approach has been used to analyze the double bond conversion using a “layer by layer” characterization of the photo polymerization for model formulations and commercial formulation. Using the statistical calculation and the traditional FTIR together, a gradient of depth profile of double bond conversion for model formulations and a commercial formulation can clearly be demonstrated.

For formulations using non-photo bleaching Irg. 184 as a PhI and commercial formulation in presence of air, there is a peak conversion (highest conversion) at middle 5 microns in this depth profile curve of conversion due to the least oxygen inhibition and filter effect in this depth. By increasing the UV Dose (mJ / cm^2), the peak conversion (highest conversion) can be shifted from 15µm depth to 20µm depth for the same formulation. A benefit of high UV intensity / short exposure time is at the outermost part (top 5µm) of a cured film. Increasing the UV Dose (mJ/cm^2) cannot reduce the oxygen inhibition for the top 5µm. The efficiency of reducing oxygen inhibition at the top 5µm by using a high I_0 has been clearly demonstrated by using this new approach. With a high I_0, a more uniformed cured film was obtained in a 25µm film for evaluated formulations.

6. REFERENCES

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