A New Approach In Analyzing The Double Bond Conversion Using A "Layer By Layer" Conversion In UV Cured Films.

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ABSTRACT OF PAPER

In this paper, a new approach to analyze double bond conversion using a "layer by layer" technique in the characterization of photo polymerization has been developed. In this study, the double bond conversion (X_1) of 5 micron thickness film was analyzed. Subsequently, it was supposed that the double bond conversion (X_1) of this 5 micron film is equal to the conversion of a top 5 micron film of 10 micron thickness film (2 X 5 micron). By utilizing the formula **$(X_1 + X_2) / 2$ = Average conversion**, the conversion (X_2) of the bottom 5 micron film can be calculated. By using the same formula in the **n:th** extension, **$(X_1 + X_2 + X_3 + \ldots\ldots + X_n) / n$ = Average conv**., it is possible to analyze the double bond conversion by each 5 micron thickness layer for a film of any thickness. The final and total double bond conversion was obtained by FTIR using this approach. This investigation was accomplished by a variation of film thickness, exposure time, viscosity of formulation and concentration of PhI as well as UV light intensity (I_0) in presence of air and in the absence of air. A more detailed information, such as a distribution profile of double bond conversion by each 5 microns for any film at any different thickness, will be presented. The difference in conversion between the top 5 microns and the bottom 5 microns in a photopolymerized film, the depth of oxygen diffusion into the film and how to balance the double bond conversion between top layer (5 microns) and bottom layer (5 microns) in a 25 micron film will be discussed.

1. INTRODUCTION

For most photo induced free radical based polymerizations, a depth profile of double bond conversion as a function of coating thickness as well as a high total degree of conversion are crucial for the performance characterization of photopolymerized coatings. FTIR and RTIR are very important methods for monitoring the UV curing processes.

However, it is a limitation that an IR beam signal has to pass through the entire film thickness in order to collect the total spectral information, according to the principles for FTIR and RTIR. Due to the limitation of FTIR and RTIR analytical instrumental equipments used generally, there have been a few research papers reported related to the depth profile of double bond conversion by using FTIR and RTIR (1,2,3,4). Recently, Tom Scherzer reported depth profiling of degree of cure during the photopolymerization of acrylate studied by real-time FTIR-ATR spectroscopy (5). Due to the finite depth of penetration of the infrared probe signal into the sample, conversion was analyzed only in a narrow layer at the bottom of the coating, which does not give the total profile of conversion across the cured film. To study a depth profile of double bond conversion in a UV curable film enables the formulators to further understand the photochemistry of UV curing and to improve the cured film properties. In this paper, by using a combination of a statistical calculation and FTIR, a new approach to analyze double bond conversion "layer by layer" in the characterization of photo polymerization has been developed.

In our previous papers (1,2,3), 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. With this experimental model, we can clearly demonstrate a benefit of high I_0 in reducing the filter effect and the oxygen inhibition. Using the double or single laminated model, a film needs to be separated physically to different layers by using PP films. In this report, a new approach to analyze double bond conversion "layer by layer" is presented.

By the characterization of photo polymerization by using a verity of instruments, such as FTIR, RTIR and photo DSC, one usually study an average double bond conversion through the entire film. A conversion curve obtained by using these analytical methods cannot show a kinetic depth profile of double bond conversion as a function of film thickness through a given thickness film. A real benefit of I_0 on reducing oxygen inhibition at outermost top layer of the coating and filter effect at the bottom part of the coating may not be fully demonstrated by an average double bond conversion, when a relatively thicker film is cured. So, a method of analyzing double bond conversion "layer by layer" (in a controllable film thickness) is needed in order to fully characterize the UV curing process.

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.

Photoinitiators:

Irgacure 819 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. 819, 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 5 μm, 10 μm, 15 μm, 20 μm and 25 μm, respectively. A series of drawdown bar was used to control the film thickness.

In this study, the double bond conversion (X_1) of 5 micron thickness film was analyzed. Supposing that the double bond conversion (X_1) of this 5 micron film is equal to the conversion of top 5 micron film of a 10 micron thickness film. By utilizing a formula such as **$(X_1 + X_2) / 2$ = Average conversion**, we could calculate a conversion (X_2) of bottom 5 micron film.

By using a formula of **$(X_1 + X_2 + X_3 + \ldots\ldots X_n) / n$ = Average conv**., the double bond conversion by each 5 micron thickness for any thickness films can be analyzed.

2.3. Analysis

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

3. RESULTS AND DISCUSSION

3.1. Depth of oxygen diffusion

The depth of oxygen diffusion into a UV cured film is a function of functionality of oligomers / monomers, viscosity of formulations, film thickness and I_0 (mW/cm^2). In order to study the depth of oxygen diffusion into the film and the gradient of oxygen inhibition, 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 5 microns increments. The formulation is EB8402/SR506 (3:7) with Irg. 819 0.1%. Curing speed is 67 mpm. UV lamp is LH6H.

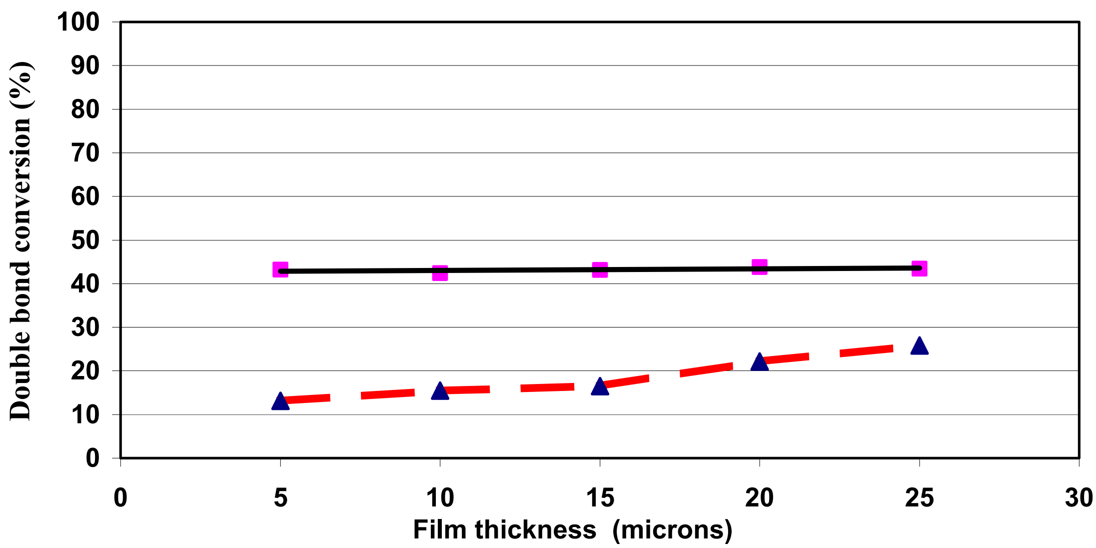

Fig. 1 Double bond conversion as a function of film thickness, 67 mpm, EB8402/SR506 (3:7), Irg. 819 0.1%

◻ UV curing in absence of air ▲ UV curing in presence of air

From Fig. 1, we can see that the profile of double bond conversion in a laminated film (in absence of oxygen) as a function of film thickness is virtually unchanged, when the film thickness is changed from 5 microns to 25 microns. We cannot see filter effect on a conversion of double bond when a film thickness is increased gradually because Irg. 819 is a photo bleaching PhI and in addition the maximum film thickness is 25 microns.

By curing in presence of air, the average double bond conversion can be increased from 13% to 26%. Even for this case (a total 25 micron film), a 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 without or with much less oxygen inhibition. All results in Fig. 1 are average conversion through the films. By analyzing the depth profile of conversion by each 5 micron for a 25 micron film, some interesting results can be demonstrated.

When the film is 5 microns, the conversion in presence of air is 13.15%. X_1 = 13.15%. Subsequently, it was supposed that the double bond conversion (X_1 = 13.15%) of this 5 micron film is equal to the conversion of a top 5 micron film of 10 micron thickness film (2 X 5 micron). By utilizing the formula **$(X_1 + X_2) / 2$ = Average conversion**, the conversion (X_2) of the bottom 5 micron film can be calculated. X_2 = 17.75%.

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 (5 microns), the average conversion of any 5 micron section can be calculated from prior and total average conversion. Following table 1 is a calculation result of each 5 micron thickness for a 25 micron film.

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

Film Thickness	Ave. Conv.	Top 5	Second 5	Third 5	Forth 5	Fifth 5
5 microns	13.15%	13.15%				
10 microns	15.45%	13.15%	17.75%			
15 microns	16.49%	13.15%	17.75%	18.57%		
20 microns	22.15%	13.15%	17.75%	18.57%	39.13%	
25 microns	25.80%	13.15%	17.75%	18.57%	39.13%	40.47%

From Table 1, one can find that the double bond conversion (40.47%) of bottom 5 micron (Fifth 5) section in a 25 micron film is close to the conversion (43%) of laminated film at the same cure speed, which means that for this formulation, there is almost no oxygen inhibition from 20 micron depth of this film (Compare 39.13% to 40.47% from Table 1). The film from 1 to 20 micron depth thickness is under influence of oxygen diffusion.

In Fig. 2 is plotted the depth profile of double bond conversion of a 25 micron film in absence and presence of air, which is a more "visible" result than the Table 1 comparison. For the film in presence of air, UV curing from 5 to 15 microns is under strong influence of oxygen inhibition. UV curing from 15 to 20 microns is still under oxygen inhibition. There is almost no oxygen inhibition from 20 microns. When a film is cured in absence of air, a uniform conversion can be obtained, since there is no oxygen inhibition and filter effect (limited film thickness). By comparing the difference of an average double bond conversion for a 25 micron film in Fig.1, the average conversion in absence of air is 43% and the average of conversion in presence of air is 26%. For the bottom 5 micron film (Fifth 5) in Fig. 2, the conversion in absence of air is 43% and conversion in presence of air is 40.47% because for this part of the film (Fifth5), neither of them had oxygen inhibition and inner filter effect. Using FTIR or RTIR, one cannot see this phenomenon. Obviously, a major difference of an average conversion for a 25 micron film results from oxygen inhibition at the top part of the cured film.

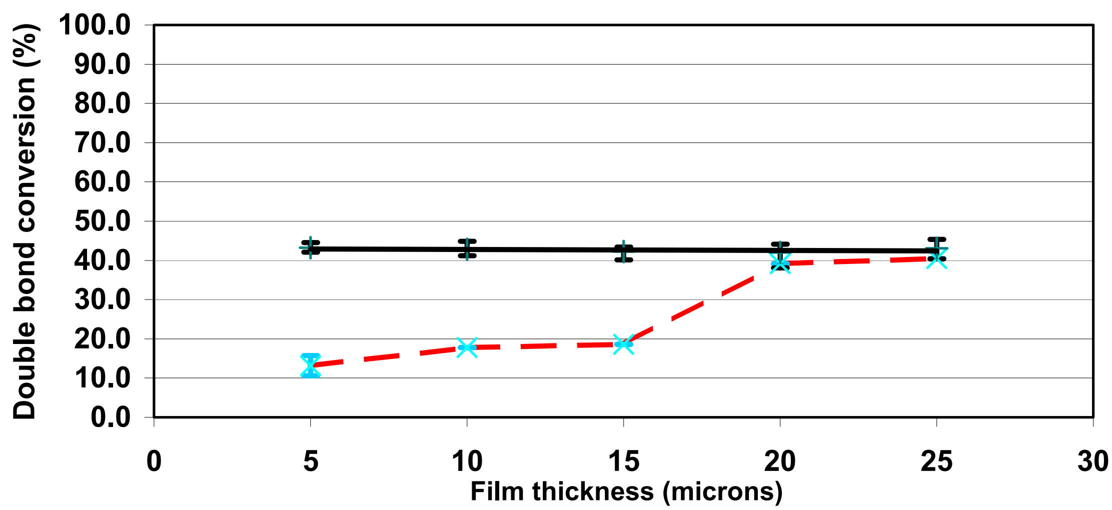

Fig. 2 Double bond conversion as a function of film thickness in a 25 micron film, EB8402/SR506 (3:7), Irg. 819 0.1%

In presence of air   In absence of air

3.2. Oxygen inhibition as a function of curing speed and film thickness:

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 double bond conversion of top 5 micron film due to oxygen inhibition. Meanwhile, the average conversion of 25 micron film is increased from 26% to 32%. Increasing UV dose cannot reduce oxygen inhibition at the outermost surface (top 5 microns) of the cured film and, but it improves the conversion of the underlying layers without or with much less oxygen inhibition. The conversion of bottom 5 micron was changed from 40.47% to 61.82% (see table 2), which is a 50% increase (40.47% vs 61.82%). This can be clearly shown by using this new approach to analyze double bond conversion "layer by layer". If one analyzes an average conversion using FTIR method, only 6% changing (from 26% to32%) in Fig. 3 can be shown. Using $\mathbf{(X_1 + X_2 + \ldots\ldots X_n) / n}$ **= Average conversion**, the conversion of Forth 5 micron section film equals to 42.98%, which means that for this formulation at 33 m/min, there is no oxygen inhibition from 15 microns in this film. The film from 1 to 15 micron thickness is still under influence of oxygen diffusion or inhibition.

Table 2 Depth profile of double bond conversion as a function of film thickness in air at 33 mpm

Film Thickness	Ave. Conv.	Top 5	Second 5	Third 5	Forth 5	Fifth 5
5 microns	13.00%	13.00%				
10 microns	15.58%	13.00%	18.16%			
15 microns	16.42%	13.00%	18.16%	24.34%		
20 microns	24.62%	13.00%	18.16%	24.34%	42.98%	
25 microns	32.06%	13.00%	18.16%	24.34%	42.89%	61.82%

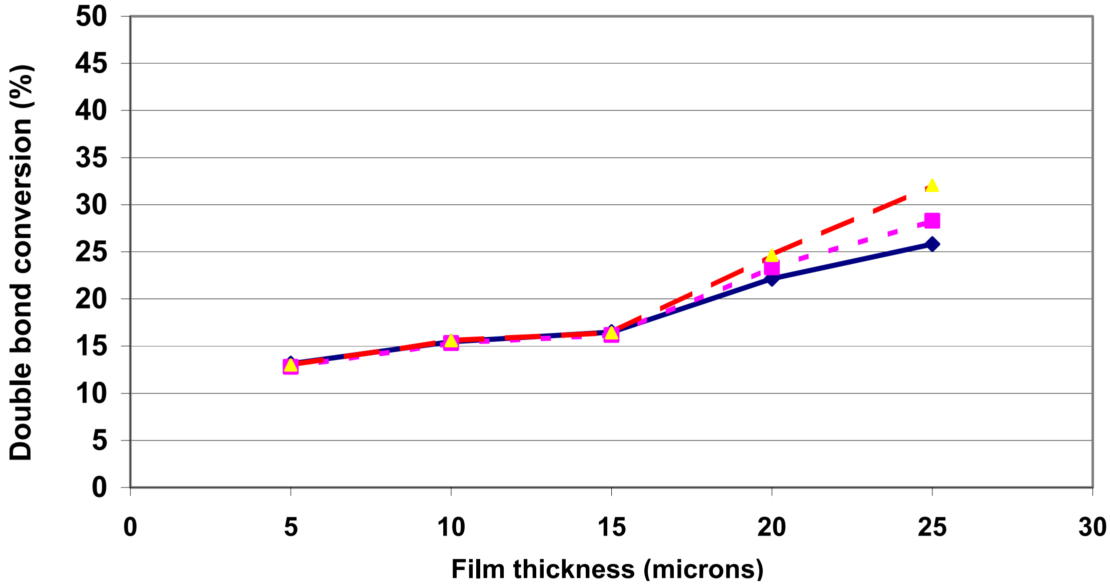

Fig. 3 Double bond conversion as a function of film thickness and curing speed, EB8402/SR506 (3:7), Irg. 819 0.1% in air

3.3. Conversion of top 5 and bottom 5 microns films as a function of [PhI] and film thickness:

In general, there are two factors needed to take into consideration in conducting UV curing, the top layer as well as the bottom layer. Conversion in top layer will control the "surface tacky" and "scratch resistance ability", and conversion of bottom layer will determine "solvent resistance ability and film hardness". For a conversion in the top layer, oxygen inhibition is a major "enemy" and for a conversion of the bottom layer inner filter effect is a major concern. So, it is important to look into a depth profile of double bond conversion in order to fully understand UV curing. In Fig. 4 is shown that the influence of [PhI] and film thickness on the depth profile of average double bond conversion. By increasing film thickness and [PhI], an increase in average double bond conversion can be detected. With the new method, one can study a distribution of double bond conversion as a function of each 5 microns individually.

For a relatively low [PhI], increasing [PhI] from 0.1% to 0.4% improves the average conversion from 13% to 20% for a top 5 micron thickness film, and gain average conversion from 26% to 59% for a 25 micron film. For a total 25 micron film of formulation of EB8402 /SR506 (3:7) with Irg. 819 0.4%, using the formula: (**$X_1 + X_2 + X_3 + X_4 + X_5 =$ 59%**), the conversion (75%) at the bottom 5 micron is 4 times higher than the conversion (20%) of the top 5 micron film due to oxygen inhibition as shown in Fig. 5.

For a relatively high [PhI], increasing [PhI] from 0.6% to 3.5% an increase in average conversion from 38% to 90% for a top 5 micron film is found, and gain average conversion from 75% to 96% for a 25 micron film in Fig. 4. For a total 25 micron film of the same formulation with Irg. 819 3.5%, the conversion is 100% (from calculation) of bottom 5 micron, which is 1.1 times of the conversion (90%) of top 5 micron film as shown in Fig. 5.

By increasing the film thickness one can see an increase in the average conversion, which results from a major contribution of underneath part of the films, but not from top 5 microns exposed to air directly. One cannot see an inner filter effect for this formulation because Irg. 819 is a photo-bleaching PhI.

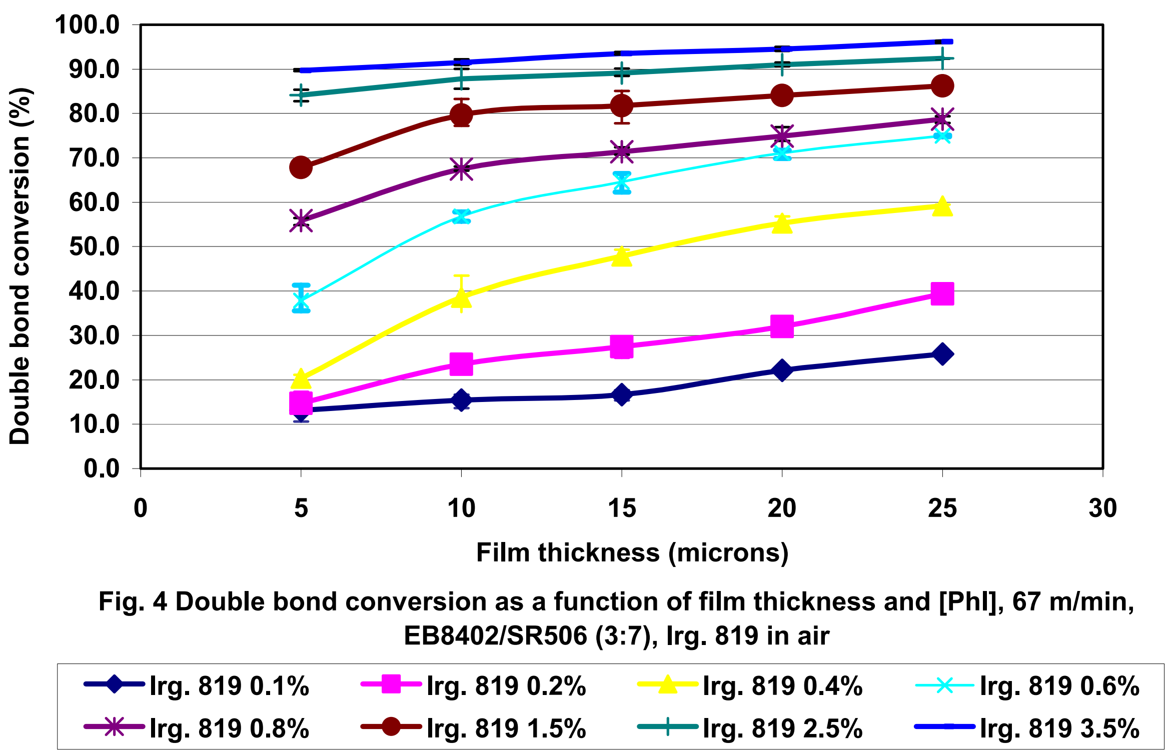

Fig. 4 Double bond conversion as a function of film thickness and [PhI], 67 m/min, EB8402/SR506 (3:7), Irg. 819 in air

In Fig. 5 is displayed the double bond conversion of the top 5 microns and bottom 5 microns in a 25 micron thickness film as a function of [PhI]. Without oxygen inhibition and inner filter effect (photo bleaching PhI), a conversion of bottom 5 microns is increased quickly and is higher than that of top 5 microns under an influence of oxygen. When [PhI] equals to 0.6%, the conversion of the bottom 5 microns is 90% and the conversion of top 5 microns is 39%. In order to obtain the same conversion for the top 5 microns, a 5 times higher [PhI] is needed. It is clear that one needs to add reasonable [PhI] in order to reduce the oxygen inhibition at the surface of the film. A ratio of double bond conversion between top layer and bottom layer is an important information for formulators as well as for PhIs designers with respect to balance surface cure and through cure.

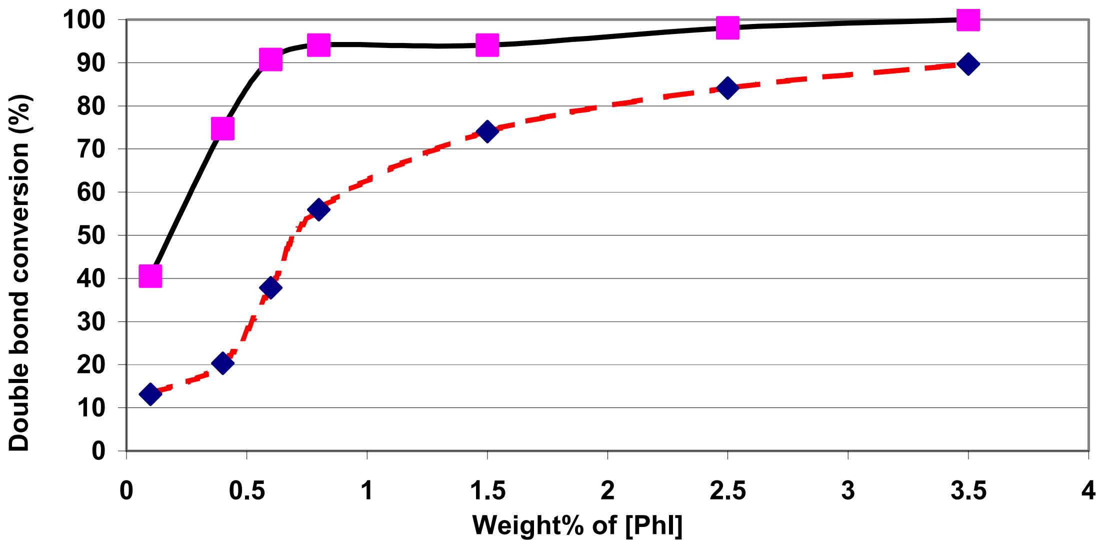

Fig. 5 Double bond conversion of top 5 microns and bottom 5 microns in a 25 micron film as a function of [PhI], 67 m/min, EB8402/SR506 (3:7), in air

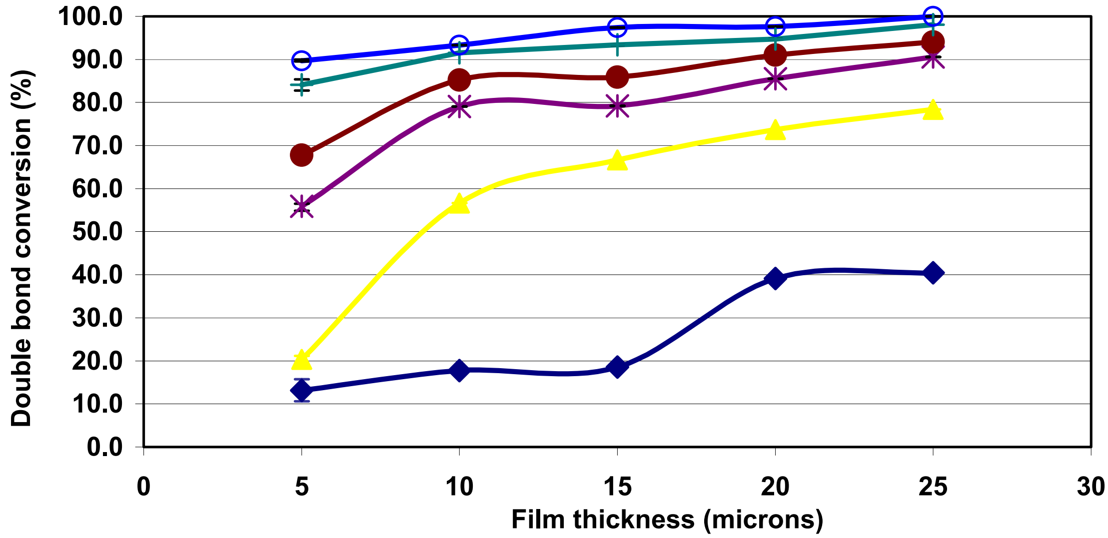

Fig. 6 Double bond conversion as a function of film thickness and [PhI], 67 m/min, EB8402/SR506 (3:7), Irg. 819 in air

In Fig. 6 is displayed a depth profile of double bond conversion for a 25 micron film in the presence of air. Compared with Fig. 4, a gradient of conversion curve as shown in Fig. 6 is higher than that shown in Fig. 4, which really reflects the changing of conversion as a function of film thickness in a 25 micron film. From 10 micron to 25 micron thickness, the conversion in Fig.6 is higher than the corresponding conversion in Fig. 4, because the conversion in Fig. 4 is an average conversion through a film and conversion in Fig. 6 is a conversion at a given thickness for the film. Obviously, this approach of analyzing double bond conversion can provide a more detailed information for a depth profile of double bond conversion.

For the two formulations with Irg. 819 1.5% and Irg. 819 2.5%, their average conversion difference of a 25 micron film is 5% (87% vs 92%) in Fig. 4. But their conversion difference of the top 5 micron part (First 5) is 15% (69% vs 84%) in Fig. 6.

3.4. Oxygen inhibition as a function of film thickness and I_0 (mW/cm^2):

In Fig. 3, it is proven that increasing UV Dose (mJ/cm^2) cannot reduce the oxygen inhibition at the outermost part of the film.

One can reduce oxygen inhibition at the surface of the film by adding more PhI in a reasonable range of concentration or add a Benzophenone / organic tertiary amine mixture. However, a more efficient method for reducing oxygen inhibition is the use of a high UV intensity (I_0) lamp. The effect of film thickness and I_0 (mW/cm^2) on average double bond conversion is outlined in Fig. 7. In this test, we use exactly the same UV spectral distribution (LH6H) but four different power settings (I_0) and the same UV dose (mJ/cm^2). Increasing film thickness cannot reduce the oxygen inhibition at the top 5 micron of a 25 micron film. A double bond conversion of a thin film (5 microns) can be increased more efficiently than the double bond of conversion of a 25 microns, simply by increasing I_0 (mW/cm^2). This is of curse due to minimizing the oxygen inhibition. For this case, the conversion of bottom layer (5 microns) can be changed from 97%, using a UV intensity of 1222 mW/cm^2, to 98%, using a UV intensity of 4399 mW/cm^2. At relatively low I_0 (mW/cm^2), the conversion of bottom 5 microns almost reaches a limit of conversion, so there is no further increase of double bond conversion. Surface curing (top 5 microns) is mainly improved from 61% to 84% when I_0 is increased from 1222 mW/cm^2 to 4399 mW/cm^2. Once again, an influence of I_0 (mW/cm^2) on reducing oxygen inhibition can be clearly demonstrated. With a major drawback of the presence of oxygen in this formulation, the photo polymerization stars from the bottom part of the film initially (Fig. 8).

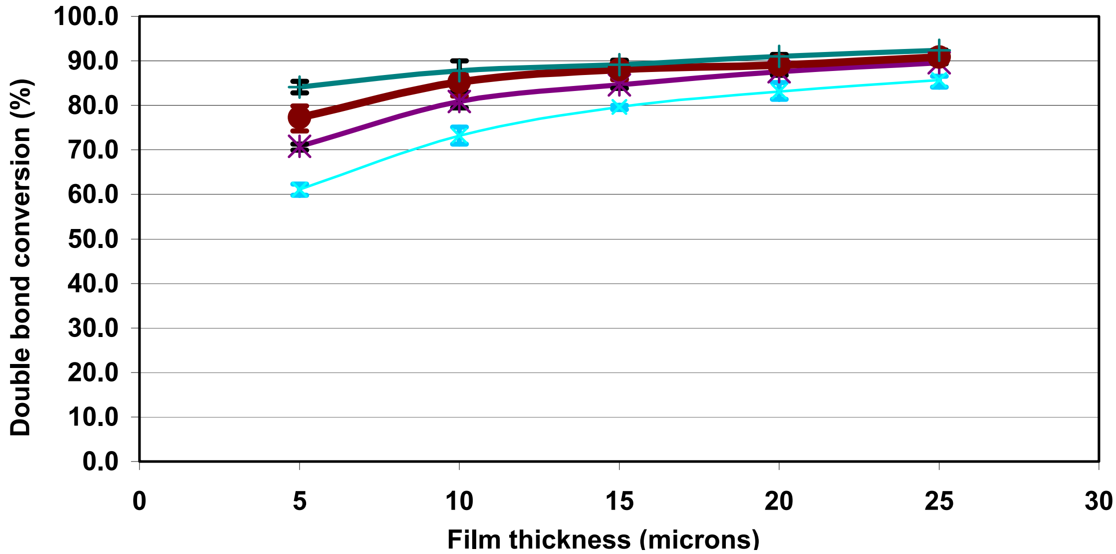

Fig. 7 Double bond conversion as a function of film thickness and I_0(mW/cm^2), EB8402/SR506 (3:7), Irg. 819 2.5% in air with the same total UV dose and at different cure speeds

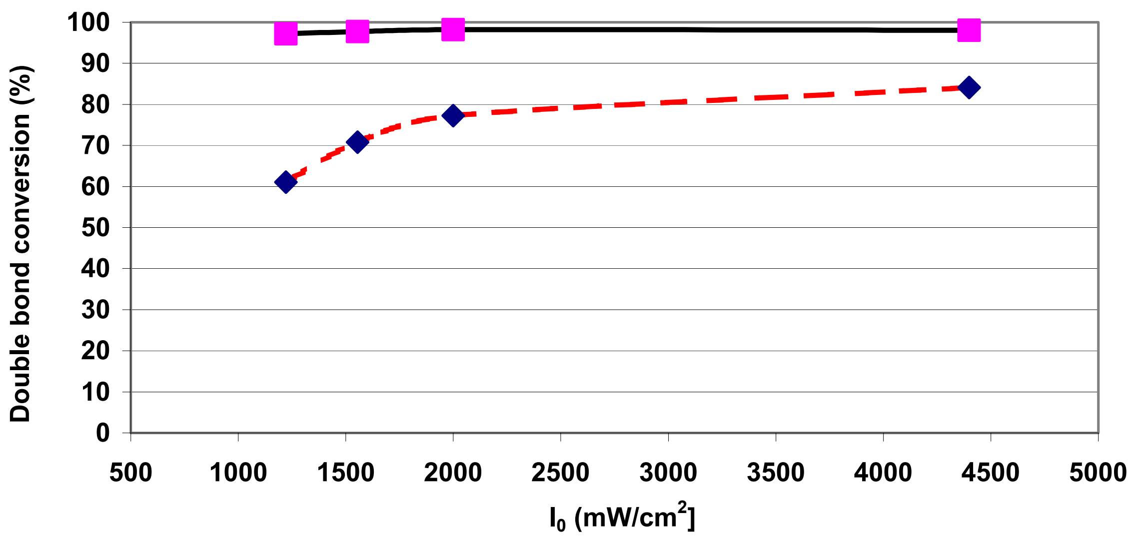

Fig. 8 Double bond conversion of top 5 and bottom 5 microns in a 25 micron film as a function of UV light intensity, with the same UV Dose and at different cure speeds, EB8402/SR506 (3:7) with 2.5% Irg. 819, in air

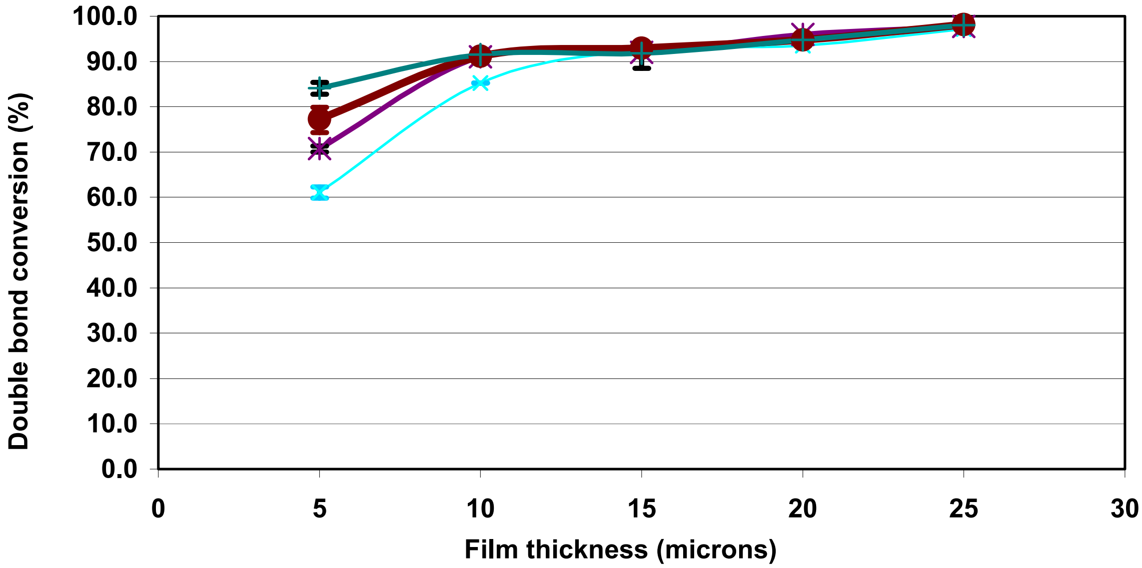

Fig. 9 Double bond conversion as a function of film thickness in a 25 microns and I_0 (mW/cm^2), EB8402/SR506 (3:7), Irg. 819 2.5% in air with the same total UV dose and at different cure speeds

In Fig. 9 is shown that the different profiles of double bond conversion using four different I_0 (mW/cm^2) conditions are similar due to a relatively high [PhI]. In a depth profile of double bond conversion as a function of film thickness for the entire 25 micron film, the closer to the surface, the more benefit could be seen when a higher UV I_0 (mW/cm^2) lamp is used. For both UV curing condition with 1222 mW/cm^2 and a condition with 4339 mW/cm^2, they have about 5% average conversion difference for a 25 micron film as shown in Fig. 7. In Fig. 9, the double bond conversion of the top 5 microns from a low I_0 (1222 mW/cm^2) is 61% and the conversion of the top 5 microns from a high I_0 (4339 mW.cm^2) is 84%. So, for a 25 micron film cured by two different I_0 (mW/cm^2), the average double bond conversion difference is 5% while the conversion difference of top 5 micron is 23%. Once again, an efficiency of reducing oxygen inhibition by using a high I_0 can clearly be demonstrated by using the new approach method. With a high I_0 (mW/cm^2), a more uniformed cured film can be obtained in a 25 micron film.

3.5. Double bond conversion as a function of film thickness and viscosity:

In Fig. 10 is shown the double bond conversion as a function of film thickness and formulation viscosity. Increasing the content of oligomer will increase the viscosity of the formulation, which will reduce the diffusion of oxygen into the cured film. Changing the ration between oligomer and monomer from 3:7 to 7:3 with Irg. 819 = 0.6%, the conversion of a 5 micron film can be increased from 39% to 87%, which is close to the conversion of the formulation consisting EB8402/SR506 with Irg. 819 = 2.5% as shown in Fig. 7. The oxygen inhibition at the outermost top layer of the films can be reduced by increasing the formulation viscosity. The oxygen inhibition underneath the outermost top layer of the film can be reduced by increasing the film thickness.

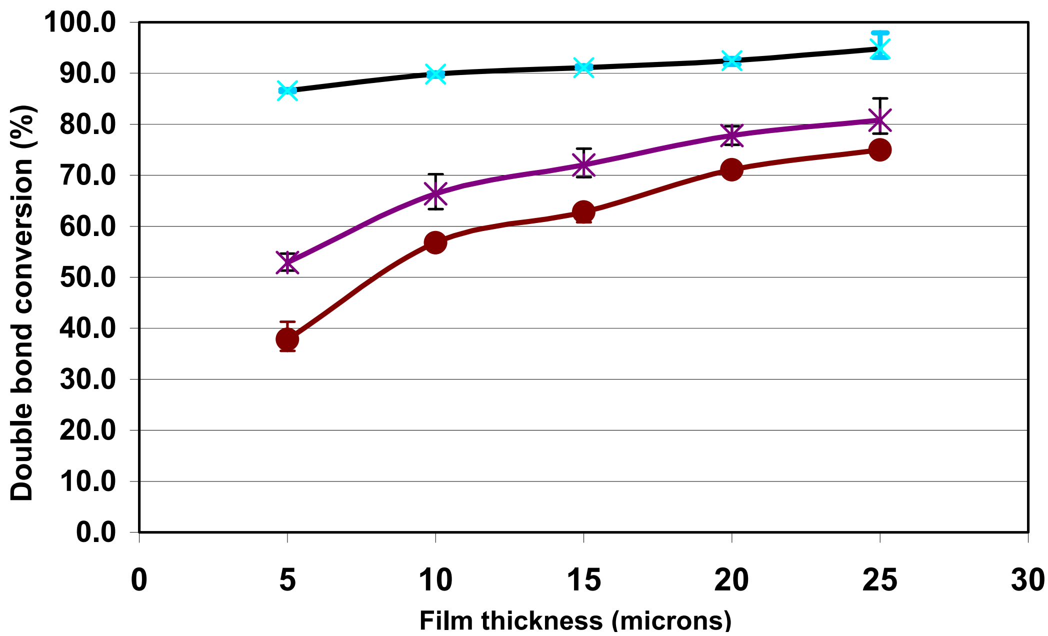

Fig. 10 Double bond conversion as a function of film thickness and viscosity, 67 m/min, EB8402/SR506 (3:7), Irg. 819 0.6% in air

EB8402/SR506 (7:3) EB8402/SR506 (1:1) EB8402/SR506 (3:7)

4. CONCLUSIONS

A new combination method of a statistical calculation and FTIR technology has been developed. This new approach enables the analysis of double bond conversion using a "layer by layer" characterization of the photo polymerization. Using this statistical model as an analytical method, a gradient of depth profile of double bond conversion can clearly be demonstrated.

In a 25 micron film, the double bond conversion is continually increased from the outermost part of the film to the bottom part of the film due to oxygen inhibition and no or very small inner filter effect on I_a (mW/cm^2) can be detected in a limited film thickness and in combination with photo bleaching PhI. Increasing the UV Dose (mJ/cm^2) cannot reduce the oxygen inhibition for the top 5 microns. Using this approach, a ratio of double bond conversion between different given depth of a 25 micron film was obtained, which is important for formulators to balance surface cure and through cure. The efficiency of reducing oxygen inhibition at the top 5 microns by using a high I_0 has been clearly demonstrated by using this new approach method. With a high I_0, a more uniformed cured film was obtained in a 25 micron film.

5. REFERENCES

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