Analyzing Depth Profile of C=C Conversion as a Function of Film Depth and [BPh]

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Abstract

Influence of different concentration of Benzophenone (BPh) on double bond conversion at different depths of UV cured films was studied using a new approach that is a combination of traditional FTIR and statistical calculation[1,2,3,4]. A combination of BPh and organic tertiary amines is frequently used to overcome oxygen inhibition at the outmost part of UV curable films in UV curing applications. Self-contradiction of BPh in reducing oxygen inhibition at the surface of cured films and increasing inner filter effect on UV light intensity (I_0) at the bottom of cured films was digitally demonstrated by using the new approach. It is very important to correctly utilize [BPh] and other [PhI] to balance surface cure and through cure for a UV cured film. By studying the depth profile of a conversion as a function of different BPh / N-Methyldiethanolamine (MDEA) mixtures, the optimum ratio of BPh and MDEA was found for a formulation of EB8402 / SR506 (3:7) containing Irg. 184 1.94% or Darocur 1173 1.94%. This investigation was performed with a variety of film depth, different PhI mixtures, different ratios of BPh / MDEA in a PhI mixture in the presence of air and different I_0 (mW/cm^2) with equal UV Dose. The efficiency of BPh / MDEA in different UV curable formulations was analyzed using the new approach. A depth profile of C=C conversion for a commercial "off the shelf" LCD trim coating was analyzed also. The purpose of this paper is to help formulators and end-users learn how to correctly use BPh and correctly choose UV lamps that improve and balance the surface curing and the through curing in their UV curing applications.

1. Introduction

A lot of time and energy have been spent on reducing oxygen inhibition (surface tackiness) in the UV curing industry. Following methods have been widely used in UV curable applications in order to overcome the oxygen inhibition:

To add more photoinitiators (PhIs)
To use BPh and organic tertiary amines or their mixture
To make UV curing in inert atmosphere or between laminate film
To increase UV exposure time
To increase UV light intensity

In this paper, an effect of BPh / organic tertiary amine as well as I_0 (mW/cm^2) on minimizing the oxygen inhibition was explored by analyzing the depth profile of double bond conversion. Both BPh and organic tertiary amine are used to reduce the oxygen inhibition during the UV curing, with different mechanisms. Organic tertiary amines act as "chain transfer" agents in that peroxy radicals ($R\text{-}OO^{\cdot}$) from oxygen inhibition easily abstract α-hydrogen to Nitrogen producing an α-aminoalky free radical ($\text{-}N\text{-}CH^{\cdot}$) that is new initiating species for free radical polymerization of acrylate. BPh acts as a photo sensitizer for the decomposition of peroxy compounds (R-OOH) of acrylate from

oxygen inhibition to produce oxygen free radicals (R-O· and HO·) that enable to re-initiate the free radical polymerization. After absorbing UV light, BPh, at its exciting state, also abstracts an α-hydrogen to Nitrogen in organic tertiary amines to generate a new efficient α-aminoalkyl free radical (-N-CH·) to re-start the new polymerization [5,6].

Both BPh and organic tertiary amines also have their disadvantages in the UV curing. While increasing [BPh] prevents a UV curable film from oxygen inhibition, there is an upper limit of the amount of BPh that can be used due to the inner filter effect of BPh. Amines, on other side, often have a "softener" effect or may include some yellowing. Use of high amount of organic tertiary amines may also be limited[5].

A combination of BPh and organic tertiary amines has shown all their advantages and disadvantages in the UV curing applications. A mixture of BPh / amines shows to be more efficient than single BPh or amine in minimizing the oxygen inhibition, because of a synergism effect of BPh / amines. In order to reduce surface tackiness at the outmost layer of a coating due to oxygen inhibition and wet approach at an interface between a coating and a substrate due to an inner filter effect, a mixture of BPh / organic tertiary amines and other PhIs is a common choice in the UV curing applications. It is very important to look into the effect of the BPh / amines mixture with their different ratios on the C=C conversion at different depths of a cured film, in order to fully understand photopolymerization and to improve the physical properties of a cured film. In this paper, by studying the depth profile of a conversion as a function of different BPh / MDEA mixtures, the optimum ratio of BPh and MDEA was found for a formulation of EB8402 / SR506 (3:7) containing Irg. 184 1.94% or Darocur 1173 1.94%. These PhI mixtures have been frequently used in commercially available UV formulations, such as clear coatings. A depth profile of the conversion is controlled by changing a ratio between Benzophenone and MDEA. The influence of the I_0 (mW/cm^2) on increasing the conversion at the surface of the cured film and at the bottom of the cured film with a mixture of BPh / MDEA for model formulations and commercial formulation was also studied. To the author's best knowledge, there is no such research work reported on an influence of different BPh / MDEA ratios on the depth profile of double bond conversion as a function of a film depth and [BPh].

2. Experimental

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 184 and Darocur 1173 from CIBA. BPh and MDEA from Sigma-Aldrich.

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) containg Irg. 184 or Darocur 1173 with a mixture of BPh / MDEA, was used as model formulation in the 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 bars were used to control the film thickness. Following formulations were used in this research:

Formulation A: EB8402 / SR506 (3:7) containing Irg. 184 4%.
Formulation B: EB8402 / SR506 (3:7) containing BPh 4% and MDEA 4%.
Formulation C: EB8402 / SR506 (3:7) containing Irg. 184 1.94% and MDEA 1.5%.
Formulation D: EB8402 / SR506 (3:7) containing Darocur 1173 1.94% and MDEA 1.5%.

2.3. Analysis

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

3. Results and discussion:

3.1 Oxygen inhibition and inner filter effect of model formulation A, B and C

3.1.1 Depth profile of C=C conversion as a function of film depth of formulation A and formulation B

Fig. 1 shows the double bond conversion in the presence of air as a function of film thickness with Irg. 184 4% or BPh 4% and MDEA 4%. Under UV irradiation, Irg. 814 in the model formulation A undergoes homogenous cleavage between a carbonyl group and an adjacent α-carbon to produce free radicals, which is Narrish type one reaction; BPh in the model formulation B goes to an exciting state and abstracts α-hydrogen from a co-initiator, MDEA, to generate α-aminoalkyl radicals **(-N-CH·)**, which is Narrish type two reaction. Narrish one reaction obtains a higher double bond conversion than Narrish two reaction in UV curing processes.

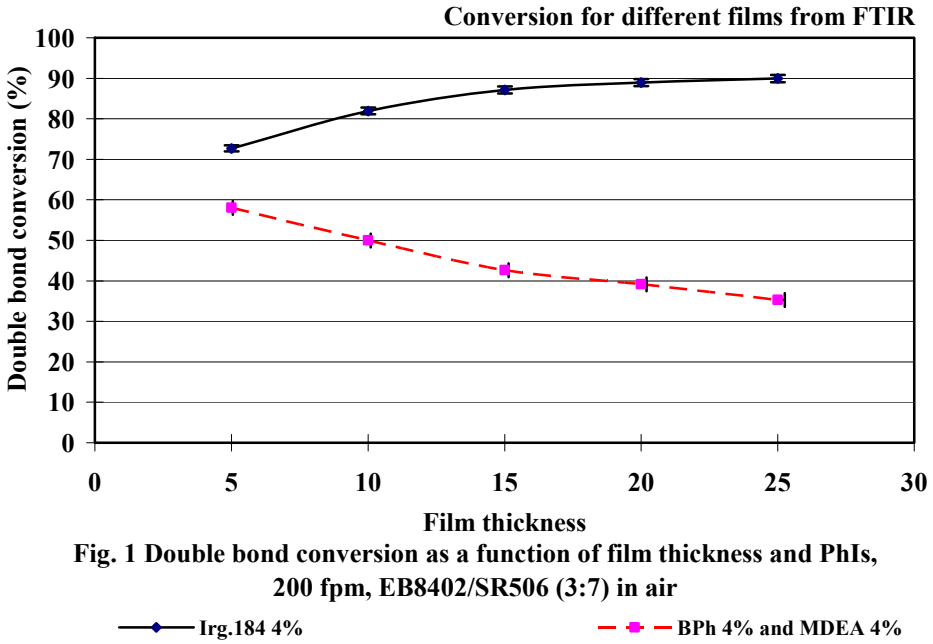

Fig. 1 Double bond conversion as a function of film thickness and PhIs, 200 fpm, EB8402/SR506 (3:7) in air

For a thin film (5 µm), the formulation A gives a higher conversion (72% vs 59%) than formulation B. For thick film (25 µm), Irg. 184 has even more benefits in terms of double bond conversion than a mixture of BPh / MDEA (90% vs 45%). All results in Fig. 1 are the average

conversion for different films. Overall, the average conversions of the formulation A with Irg. 184 4% are always higher than those of the formulation B with a mixture of BPh / MDEA. By analyzing a depth profile of the conversion using the new approach, some interesting results are demonstrated. By using a formula such as: **$(X_1 + X_2 + \ldots\ldots X_n) / n$ = Average conv**. Where n = 1, 2, 3……n is the number of layers (5 μm), then every conversion of 5 μm section can be calculated from the prior and average conversions. Table 1 is calculation result of each 5 μm depth for a 25 μm film from Fig. 1.

Table 1 Depth profile of double bond conversion as a function of film depth in air at 200 fpm

Film Thickness	Ave. Conv.	Top 5	Second 5	Third 5	Fourth 5	Fifth 5
5 μm	72.71%	72.71%				
10 μm	81.97%	72.71%	91.15%			
15 μm	87.14%	72.71%	91.15%	97.56%		
20 μm	88.93%	72.71%	91.15%	97.56%	94.30%	
25 μm	89.394%	72.71%	91.15%	97.56%	94.30%	93.98%

In Fig. 2, the depth profile of C=C conversion of a 25 μm film in the presence of air is plotted using data from Table 1 and similar data.

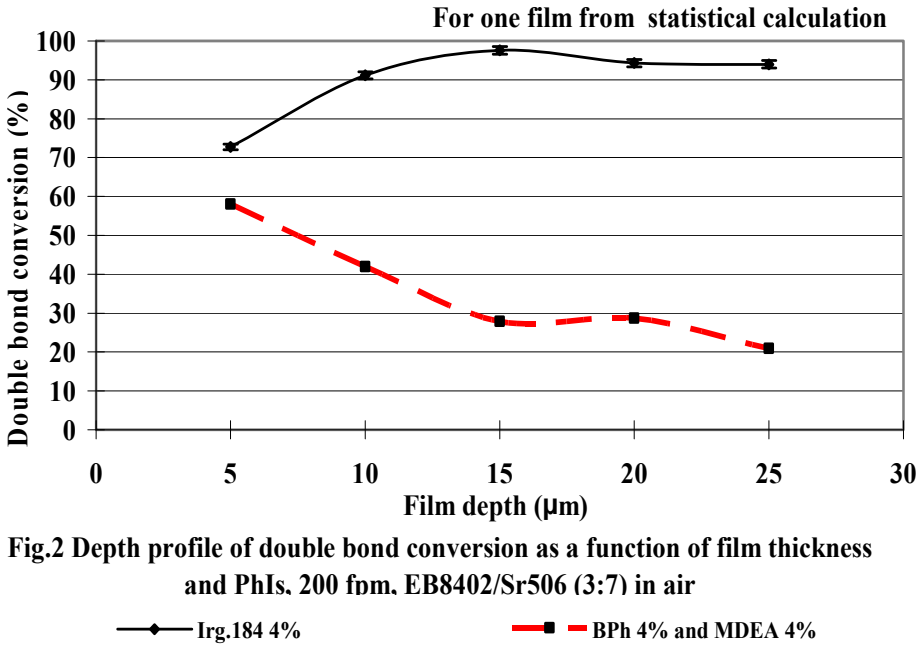

Fig.2 Depth profile of double bond conversion as a function of film thickness and PhIs, 200 fpm, EB8402/Sr506 (3:7) in air

By analyzing the depth profile of the conversion in Fig. 2, people find that for a 25 μm film, formulation A has a higher C=C conversion in the top 5 μm and the bottom 5 μm than formulation B. At the interface between the coating and the PP film, BPh / MDEA in formulation B shows a much higher inner filter effect than Irg. 184 in the formulation A. The major inner filter effect results from Benzophenone. For a distribution of the conversion of the formulation A across the film depth (from top to bottom), there is a peak conversion at the 15 μm depth of the film. For a distribution of the conversion of the formulation B across the film depth, the conversion continually goes down from

60% (top 5 μm) to 20% (bottom 5 μm). The depth profile of the C=C conversion of EB8402 / SR506 (3:7) as a function of the film depth is totally changed with different PhIs (Irg. 184 or BPh / MDEA).

3.1.2 Depth profile of C=C conversion as a function of film depth for model formulation C with [BPh]

In the formulation C, EB8402 / SR506 (3:7) containing Irg. 184 4% and MDEA 4% was held constant and the concentration of BPh was changed in order to study the influence of [BPh] on the double bond conversion of different thickness films. Fig. 3 shows an average double bond conversion as a function of film thickness for five different thickness films. The C=C conversion of the thin film (5 μm) is increased by adding more [BPh] to the formulation C because a mixture of BPh / MDEA reduce the oxygen inhibition for the thin film. The C=C conversion of the thick film (25 μm) is reduced by adding more [BPh] to the formulation C due to the inner filter effect of BPh in the near bottom part of the cured film.

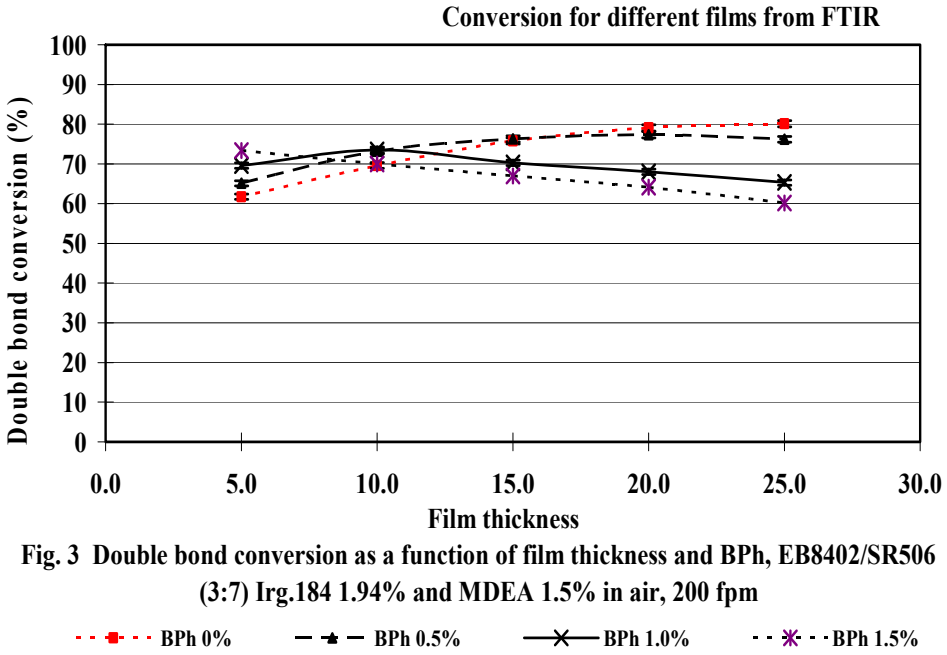

Fig. 3 Double bond conversion as a function of film thickness and BPh, EB8402/SR506 (3:7) Irg.184 1.94% and MDEA 1.5% in air, 200 fpm

A combination of BPh and organic amines is a common choice in reducing the oxygen inhibition in UV curing. However, self-contradiction of BPh in reducing oxygen inhibition at the surface of cured films and increasing inner filter effect at the bottom of cured films has been a big challenge for formulators to balance surface cure and through cure. It is very important to investigate the distribution of C=C conversion across the film depth (from top to bottom). By using the new approach, the depth profile of C=C conversion as a function of film depth and [BPh] is plotted in Fig. 4. Conversion change of each 5 μm across the film depth of the cured film, with different [BPh], has been studied.

By adding more BPh to the formulation C from 0% to 1.5%, minimzing the oxygen inhibition at the top 5 μm is found because of an effect of BPh on a decomposition of Peroxide and abstraction of α-hydrogen from MDEA as discussed above. The conversion at the top 5 μm is changed from 61% to 73%. The more BPh, the more conversion at the top 5 μm. On the other hand, increasing [BPh] or [Irg. 184] will also enhance the inner filter effect of the formulation at the interface between UV the coating and the PP film. In the formulation C, the major inner filter effect results from Benzophenone. The more BPh, the more inner filter effect. As a result, the conversion at the bottom

5 µm declined from 84% to 45%, due to the inner filter effect with increasing [BPh]. For the formulation C, a mixture of MDEA 1.5% with BPh 0.5% is the optimum combination of BPh and MDEA for balancing surface cure and through cure at current curing condition. In this PhI package (Irg, 184 1.94%, MDEA 1.5% and BPh 0.5), the model formulation C gives more uniform C=C conversion distribution at the depth from 10 µm to 20 µm. There is no clear peak conversion in this depth profile of the conversion at 15 µm depth of the film. Obviously, formulations with different PhI package give total different depth profile of double bond conversion as a function of the film depth.

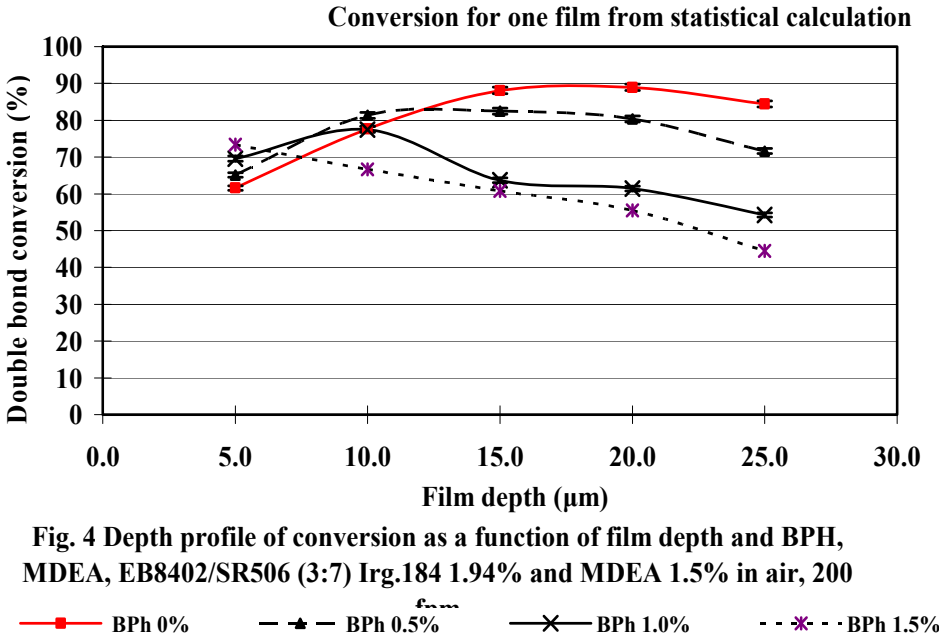

Fig. 4 Depth profile of conversion as a function of film depth and BPH, MDEA, EB8402/SR506 (3:7) Irg.184 1.94% and MDEA 1.5% in air, 200 fpm

Fig. 5 shows a trend of the C=C conversion changing at the top 5 µm and at the bottom 5 µm versus different concentration of Benzophone in the formulation C. A clear reversed trend of double bond conversion was observed for this 25 µm film. A conversion changing rate (moving down) of bottom 5 µm is faster than that (moving up) of top 5 µm, which explains why adding more BPh provides a negative effect on the total average conversion for a 25 µm film in Fig. 3.

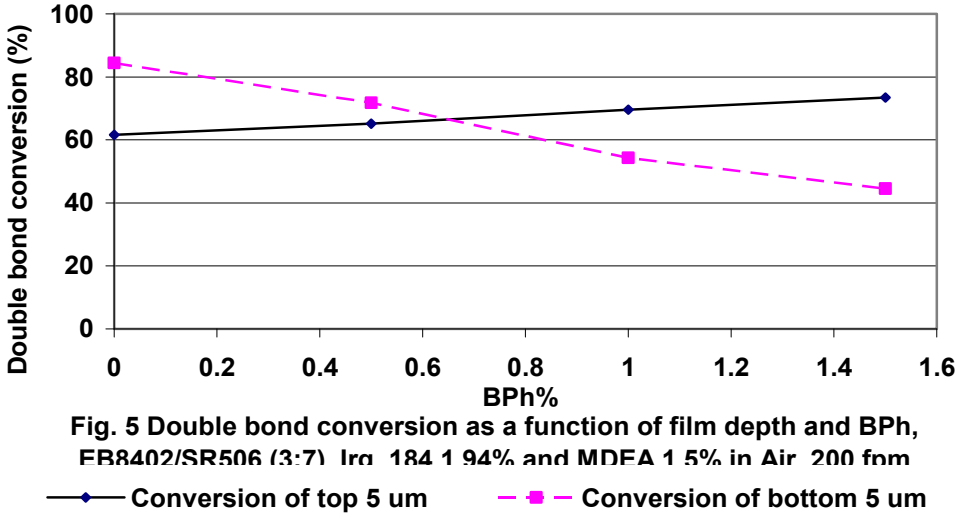

Fig. 5 Double bond conversion as a function of film depth and BPh, EB8402/SR506 (3:7) Irg. 184 1.94% and MDEA 1.5% in Air, 200 fpm

3.1.3 Oxygen inhibition and inner filter effect as a function of film depth and UV light intensity for model formulation C with BPh 1.5%

By adding more BPh to the formulation C, a reduction of oxygen inhibition at the surface of a cured film is observed. However, the inner filter effect at the bottom of the cured film can also be enhanced by adding more BPh. A more efficient method of reducing the oxygen inhibition and the inner filter effect at the same time is to use a high I_0 (mW/cm^2) lamp. An effect of film thickness and I_0 (mW/cm^2) on the average double bond conversion for the formulation C with BPh 1.5% is outlined in Fig. 6. In this group test, exactly the same UV spectra distribution (LH6H) but two different power settings (UV light intensity) and the same UVC dose were used. From Fig. 6, a high I_0 (mW/cm^2) with a short UV exposure time always can gives a high conversion for the thin film (5 μm) and the thick film (25 μm), compared with a low I_0 (mW/cm^2) with long exposure time.

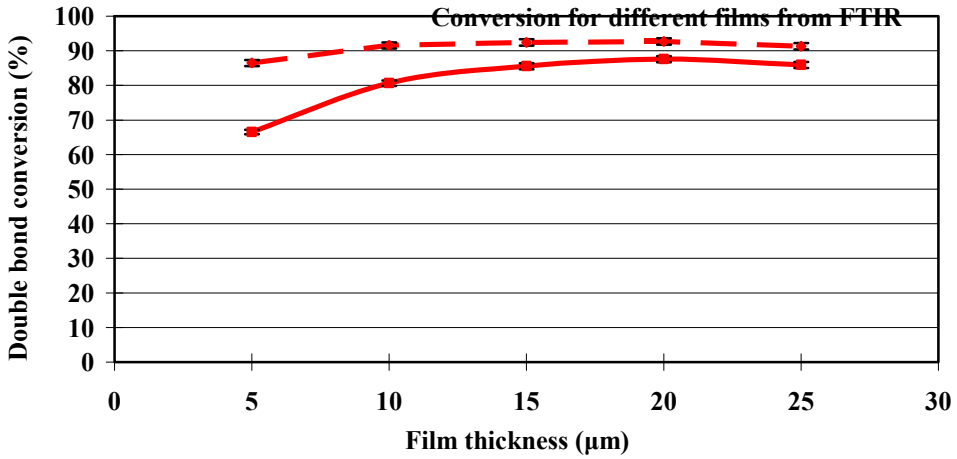

Fig. 6 Conversion as a function of film thickness and UV intensity with equal UVC Dose, EB8402/SR506 (3:7) Irg. 184 1.94%, MDEA 1.5 and BPh 1.5% in air

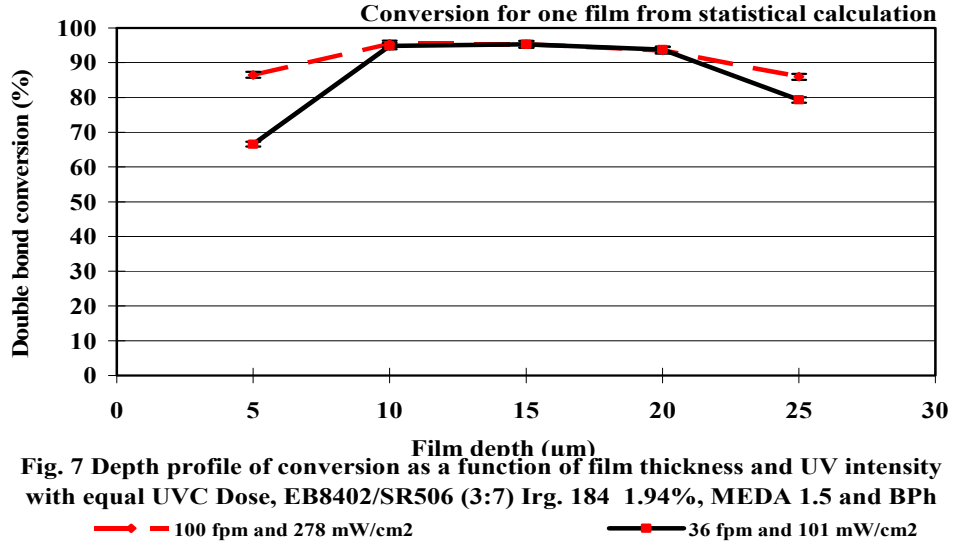

Fig. 7 Depth profile of conversion as a function of film thickness and UV intensity with equal UVC Dose, EB8402/SR506 (3:7) Irg. 184 1.94%, MEDA 1.5 and BPh

By using the new approach, Fig. 7 is obtained, that shows a depth profile of the C=C conversion as a function of the film depth and I_0 (mW/cm^2) for the formulation C. Increasing the film

thickness does not reduce the oxygen inhibition at the top 5 μm of a 25 μm film but enhances the inner filter effect in the bottom part of a 25 μm film. The inner filter effect is observed in a small decline of the average conversion from 20 μm thick film to 25 μm thick film in Fig. 6. From the depth profile of the conversion in Fig. 7, a decline of the C=C conversion from 20 μm depth to 25 μm depth in a 25 μm film is observed for two curing conditions (from 93% to 87% for high I_0 / short exposure time; from 93% to 79% for low UV intensity / long exposure time). However, due to the high penetration ability of a high I_0 (mW/cm^2) for the cured film, a combination of high I_0 (mW/cm^2) / short exposure time obtaines a higher conversion at the bottom 5 μm than a combination of low I_0 (mW/cm^2) / long exposure time (87% vs 79%) with equal UVC Dose. On the other hand, the oxygen inhibition at the top 5 μm of the 25 μm film is observed using a low I_0 (101 mW / cm^2). The surface curing is mainly improved from 67% to 87% by increasing UV intensity lamp from101 mW/cm^2 to 278 mW/cm^2 with equal UVC Dose. Ability of the high I_0 (mW/cm^2) lamp in obtainting a higher surface curing and through curing has been clearly demonstrated in Fig. 7.

3.2 Oxygen inhibition and inner filter effect of model formulation D

3.2.1 Depth profile of C=C conversion as a function of film depth for formulation D with [BPh]

A package of Darocur 1173 with BPh and MDEA is another popular combination of PhIs in UV curable clear coatings. By adjusting a ratio of BPh vs Darocur 1173 and MDEA in the formulation D, formulators can reach certain degree of conversion and improve physical property at a given depth of the cured film. Fig. 8 shows that the average double bond conversion in the presence of air as a function of film thickness and the concentration of Benzophone. Overall, the formulation C with BPh in Fig. 3 has a higher conversion than formulation D with BPh in Fig. 8 for both thin film (5 μm) and thick film (25 μm), in the same curing condition. Once again, adding more BPh for the formulation D provides less oxygen inhibition for the thin film average conversion and more inner filter effect for the thick film average conversion.

A depth profile of the conversion of the formulation D is demonstrated in Fig. 9, by using the new approach. For a 25 μm film of the formulation D (BPh 0%), there is a peak conversion (97%) in the 15 μm depth of the film, which means that there is a minimum oxygen inhibition and inner filter effect for this depth, similar to the formulation C in Fig. 4. The depth profile of the formulation D is changed by adding different [BPh]. Formulation D with BPh 0.5% is the optimum ratio (1:3) between BPh and MDEA, which can give a uniform conversion from 10 μm depth to 20 μm depth of 25 μm film under a high UV I_0 (mW/cm^2). For below 20 μm, the inner filter effect is observed again.

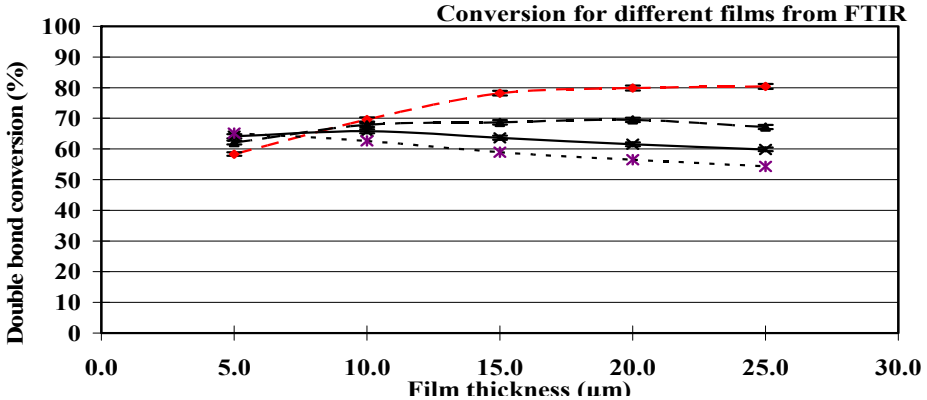

Fig. 8 Double bond conversion as a function of film thickness and BPh, EB8402/SR506 (3:7) 1173 1.94% and MDEA 1.5 in air, 200 fpm

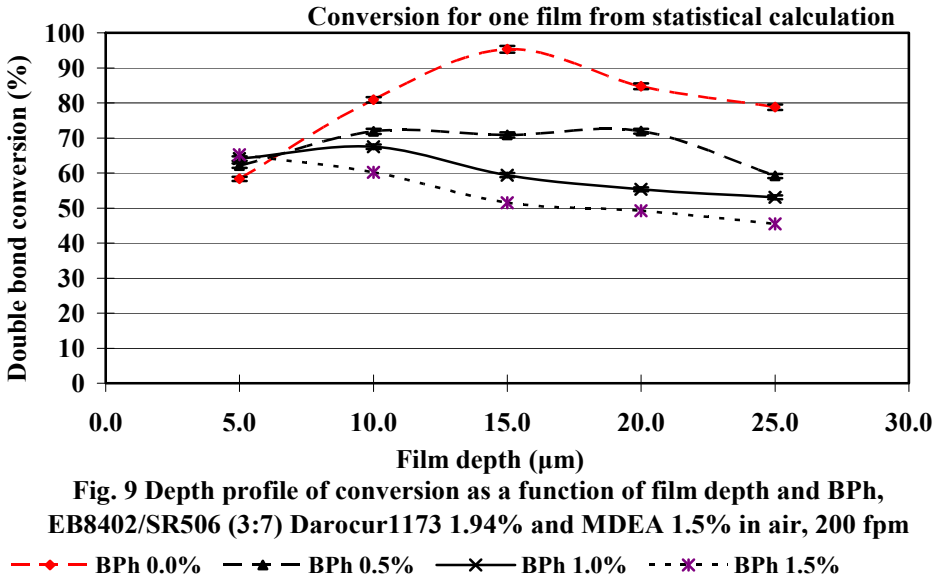

Fig. 9 Depth profile of conversion as a function of film depth and BPh, EB8402/SR506 (3:7) Darocur1173 1.94% and MDEA 1.5% in air, 200 fpm

Fig. 10 shows a trend of C=C conversion changing at the top 5 μm and at the bottom 5 μm against different [BPh] in the formulation D. A clear reversed trend of C=C conversion was observed for the top 5 μm and the bottom 5 μm of this 25 μm film. The formulation D in Fig. 10 has a smaller effect of reducing the oxygen inhibition at the top 5 film and increasing the inner filter effect at the bottom 5 μm with increasing [BPh], compared with the formulation C in Fig. 5. Once again, BPh reducing oxygen inhibition at the top 5 μm is not as fast as its increasing inner filter effect at the bottom 5 μm.

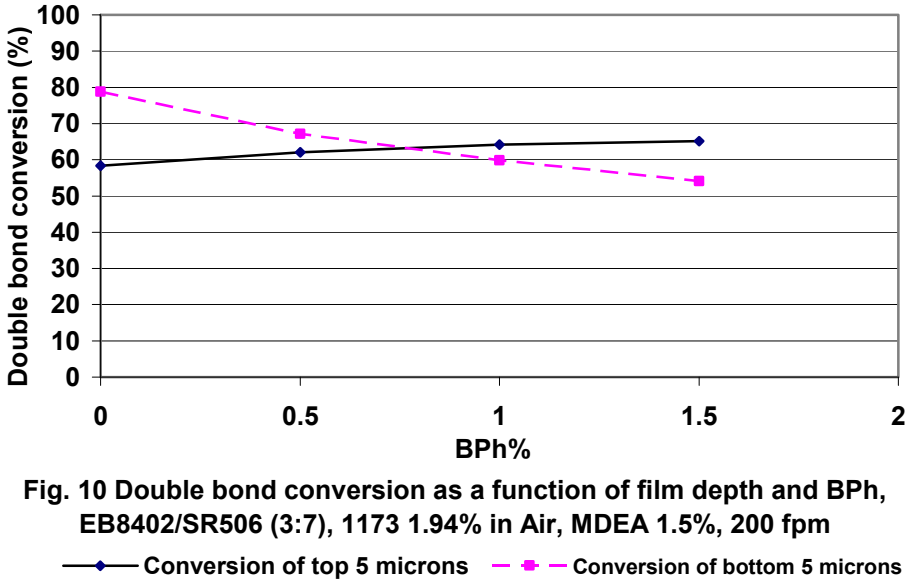

Fig. 10 Double bond conversion as a function of film depth and BPh, EB8402/SR506 (3:7), 1173 1.94% in Air, MDEA 1.5%, 200 fpm

3.2.2 Oxygen inhibition and inner filter effect as a function of film depth and UV light intensity for model formulation D with BPh 0.5%

An effect of film thickness and I_0 (mW/cm^2) with equal UVC Dose on average double bond conversion for the formulation D with BPh 0.5% is outlined in Fig. 11.

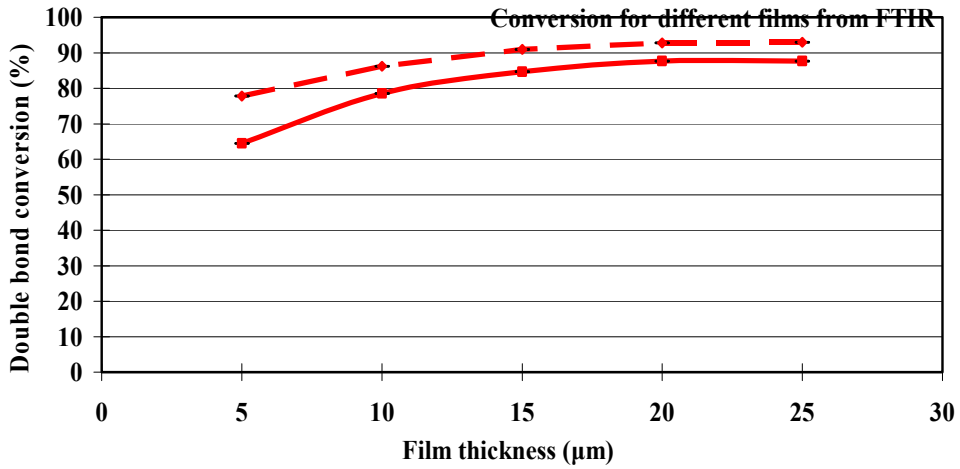

Fig. 11 Conversion as a function of film thickness and UV intensity with equal UVC Dose, EB8402/SR506 (3:7) 1173 1.94%, MDEA 1.5 and BPh 0.5% in air

A depth profile of double bond conversion as a function of the film depth and I_0 (mW/cm^2) for this formulation is outlined in Fig. 12. Even if there is only BPh 0.5% in the formulation D, a clear inner filter effect was observed from 20 µm depth to 25 µm depth in the 25 film for two curing conditions, high I_0 (mW/cm^2) / short exposure time or low I_0 (mW/cm^2) / long exposure time. However, due to the high penetration ability of a high UV intensity light for the cured film, a combination of high I_0 (mW/cm^2) / short exposure time obtains a higher conversion at the bottom 5 µm than a combination of low I_0 (mW/cm^2) / long exposure time (94% vs 87%) with equal UVC Dose. On the other hand, a clear oxygen inhibition at the top 5 µm of the 25 µm film is detected using a low I_0 (130 mW / cm^2). The surface curing is improved from 64% to 79% by increasing UV I_0 from 130 mW/cm^2 to 278 mW/cm^2 with equal UVC Dose. Ability of the high I_0 (mW/cm^2) lamp to gain a higher surface curing and through curing has been clearly demonstrated in Fig. 12.

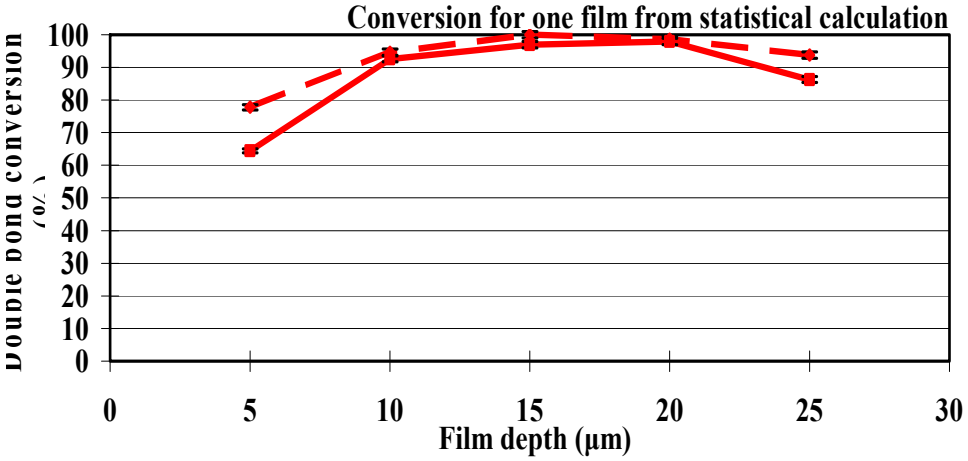

Fig. 12 Depth profile of conversion as a function of film thickness and UV intensity with equal UVC Dose, EB8402/SR506 (3:7) 1173 1.94%, MEDA 1.5

4. Depth profile of C=C conversion for a LCD trim coating as a function of film depth and I_0 (mW / cm^2):

A commercial LCD trim UV coating was analyzed using the new approach. The concentration of PhI and what PhI were used in this formulation is unknown. From this "off-the-shelf" commercially available formulation, a benefit of a high UV intensity lamp in reducing the oxygen inhibition and the inner filter effect was demonstrated, even with equal UVA Dose. An effect of the film thickness and I_0 (mW / cm^2) on total average double bond conversion for the UV gloss formulation is outlined in Fig. 13. Fig. 13 shows two different group tests for five different thickness films. Overall, a combination of high UV I_0 (mW / cm^2) with short exposure time gains a high double bond conversion in thin film (5 μm) and thick film (25 μm). The depth profile of conversion for this commercial formulation is demonstrated in Fig. 14. A peak conversion (97%) of the commercial formulation is located in 10 μm depth for two different UV curing conditions (high UV / short exposure time or low UV intensity long exposure time), which is different from the model formulations. From Fig. 13, using the traditional FTIR method, it can be seen that a high I_0 (2200 mW / cm^2) / short exposure time obtains 3% more average conversion for a 25 μm film than a Low I_0 (821 mW/cm^2) / long exposure time condition (85% vs 82%). In Fig. 14, using the new approach, 3% average conversion difference from the two different experimental setups is re-analyzed along with the depth of the cured film (from top to bottom). The real conversion difference at two different bottom 5 μm is 9%. A benefit of a high UV light intensity lamp to obtain a higher surface curing and through curing for this commercial available formulation has been confirmed. For this commercial formulation, using the low I_0 (821 mW/cm^2) with equal UVA Dose, more inner filter effect at the bottom 5 μm (80% vs 87%) and more oxygen inhibition at the top 5 μm (72% vs 81%) are displayed.

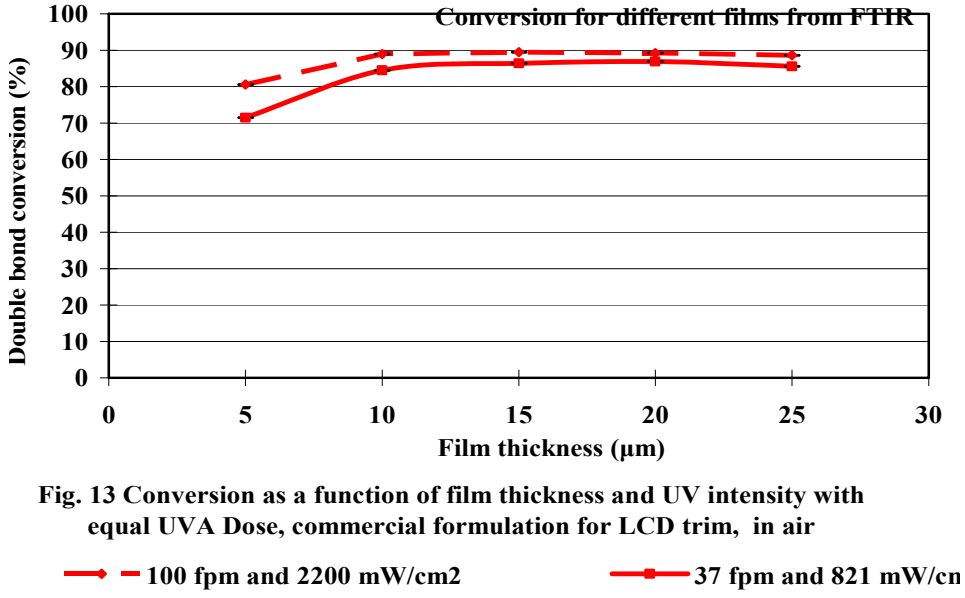

Fig. 13 Conversion as a function of film thickness and UV intensity with equal UVA Dose, commercial formulation for LCD trim, in air

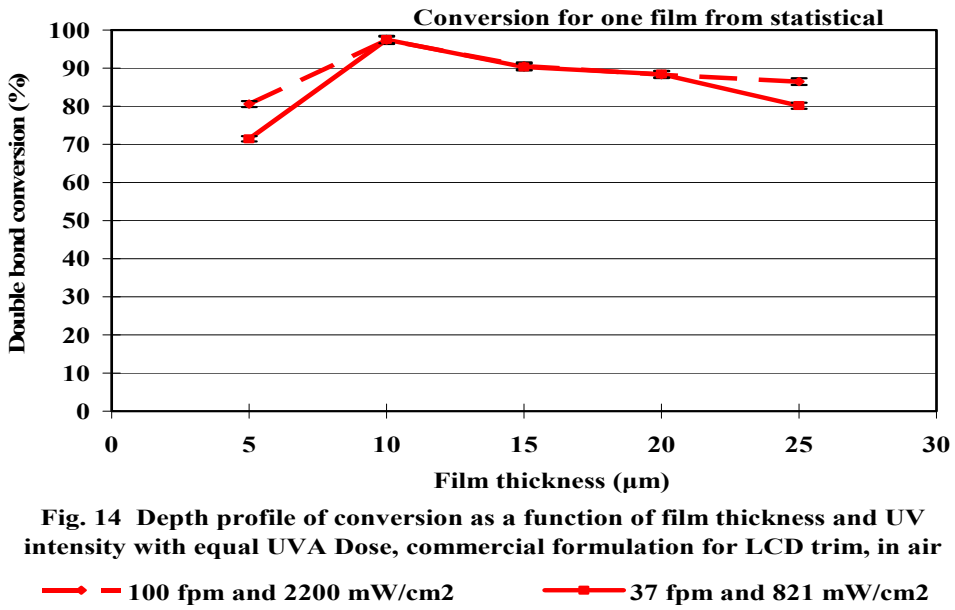

Fig. 14 Depth profile of conversion as a function of film thickness and UV intensity with equal UVA Dose, commercial formulation for LCD trim, in air

5. Conclusions

A depth profile of C=C conversion of the model formulations with different ratios of BPh / MDEA in PhI mixtures and a commercial UV gloss formulation were analyzed. Using high UV intensity / short exposure time, with equal UVA Dose, to reduce the oxygen inhibition at the outmost part of a cured film and the inner filter effect at the bottom part of a cured film has been confirmed. By changing the ratio between BPh and MDEA, double bond conversion at certain depths of the cured film and the depth profile of conversion is controlled. The optimum ratio of BPh / MDEA (1:3) is found for a formulation of EB8402 / SR506 (3:7) with Irg. 184 or Darocur 1171 in order to balance a surface cure and through cure. A depth profile of double bond conversion is changed by using different PhI mixtures, or different ratio of BPh / MDEA in a PhI mixture and I_0 (mW / cm^2). By applying the new approach to investigate the above model and commercial formulation examples, formulators and end-users will learn how to correctly use BPh and choose UV lamps to improve their film physical properties.

6. References

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