

Electron Beam Dose Rate Effects

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Electron beam (EB)-curing is a technique used in different industrial applications such as curing of adhesives, lacquers, floor vanishes and printing inks. EB irradiation is also used for sterilization of food and packaging materials.

Most common EB-curing processes utilize a free-radical polymerization

reaction. The reaction mechanism occurs in four steps as shown in Figure 2. In the first step, EB irradiation causes the cleavage of an organic chemical bond to form two radicals. The “start” reaction occurs when a radical reacts with the first monomer unit to form a new radical species. In the propagation reaction, the new radical reacts with additional monomer units in a chain reaction to form the polymer. If two radicals meet each other, they recombine and the polymerization is terminated.

Industrial curing processes are designed to operate at a desired speed. Web processes are characterized by the speed at which the web travels. It is desirable to maintain the speed of the radical polymerization process corresponding to the operating line speed. The electron beam dose determines the number of radicals that are formed. As the process speed increases, the dose must be delivered in a shorter period of time. The speed at which the dose is delivered is defined as the “dose rate.” The effect

FIGURE 1

Electron beam curing applications

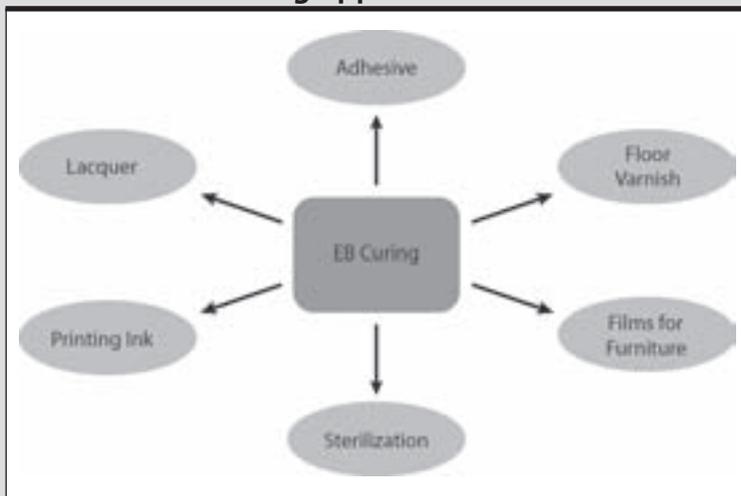


FIGURE 2

Reaction mechanism of the radical polymerization

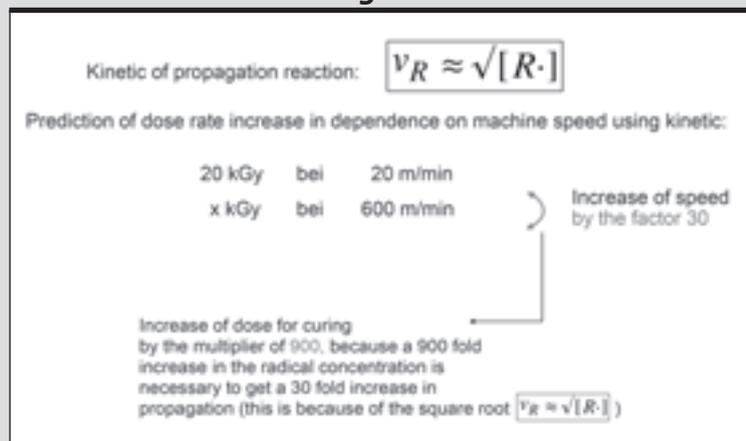
- | | | | |
|-------------------------|-----------------------|---------------------------|---------------------|
| 1. Initiation | R-R | $\xrightarrow{\text{EB}}$ | 2R· |
| 2. Start reaction | R· + M | \longrightarrow | RM· |
| 3. Propagation reaction | RM _n · + M | \longrightarrow | RM _{n+1} · |
| 4. Termination reaction | R· + R· | \longrightarrow | R-R |



$$v_R \approx \sqrt{[R\cdot]}$$

FIGURE 3

Dose rate effect on curing



of increasing the dose rate is to increase the concentration of radicals that are formed. The concentration of radicals influences the rate of the polymer formation; however, the propagation steps leading to the formation of the desired polymer are only proportional to the square root of the radical concentration. This square root in relationship is due to the termination reaction that competes with propagation.

Consider a process with an applied cure dose of 20 kGy running at a line speed of 20 m/min. An increase in line speed to 600 m/min will require a 30-fold increase in the propagation reaction. The simple kinetic model predicts that the 30-fold increase in propagation would need a 900-fold increase in dose rate (Figure 3).

It is common for commercial EB-curing processes to run at high speeds; however, there have been few studies that examined the effect of dose rate on the curing process. In order to examine the effect of dose rate, pilot trials were conducted at Polytype Converting in Freiburg, Switzerland. Polytype is a manufacturer of converting machines and also operates

a pilot facility that includes EB-curing capability. A schematic drawing of the Polytype Techma 2 pilot line is shown in Figure 4.

The operating parameters of the EB unit were very important for the trials. The EB unit has an acceleration voltage range of 125 to 250 kV. The unit is capable of delivering a maximum dose rate of 12,000 kGy-m/min. The dose is controlled by a combination of line speed and beam current settings from 30 to 600 mA. The EB unit includes nitrogen inerting that can produce oxygen levels of less than 50 ppm in the reaction chamber.

The pilot trials included experiments with different speed and dosage profiles. For example,

FIGURE 4

Techma 2, polytype converting, Freiburg, Switzerland

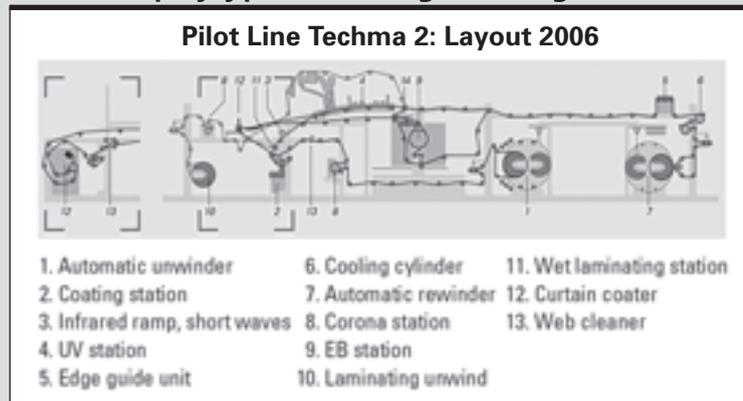


FIGURE 5

Electron beam of the Techma 2

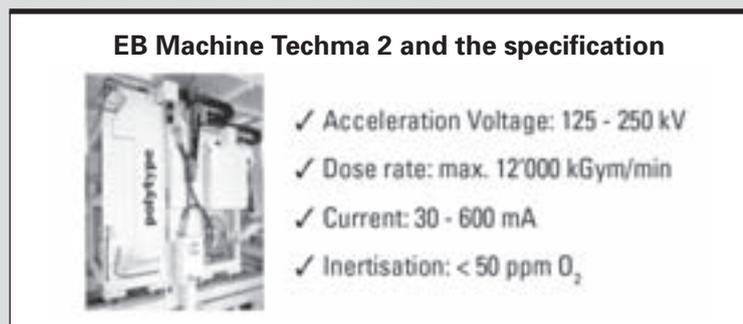


FIGURE 6

Speed and dosage profiles used in the pilot trials

Speed [m/min]	Dose [kGy]	Dose [kGy]	Machine Speed [m/min]
100	5,8	Low dosage	100
	7,8		200
	10,0		400
	12,0		600
	14,0		
	16,1		
	18,1		
	19,9		
	22,1		
	24,1		
	26,1		

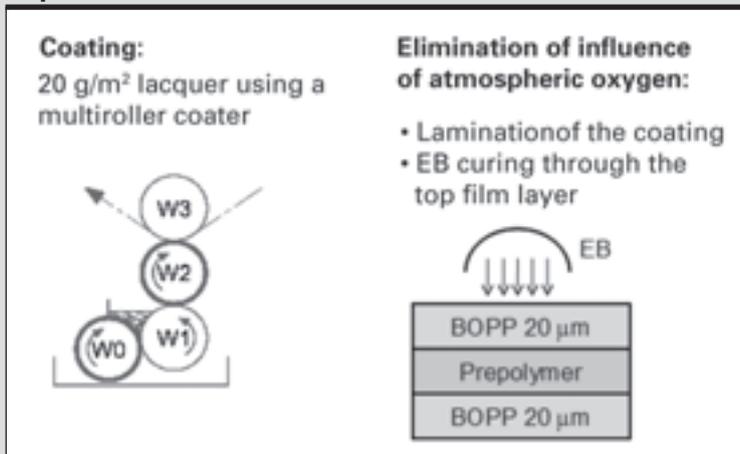
the coating was cured at a constant line speed of 100 m/min with varying dosages from 6 to 26 kGy. In a second trial, dosage was kept constant at a relatively low level of 6, 8 or 10 kGy while varying line speed from 100 to 600 m/min. These curing profiles are shown in Figure 6.

A multiroller coater was used to apply an EB-curable clear coating. A constant coating weight of 20 g/m² was maintained for all testing.

A second very important experimental detail was the elimination of the influence of atmospheric oxygen. This is very important as oxygen has a large impact on the radical polymerization reaction. Even though the pilot was equipped to provide nitrogen inerting, it would be difficult to assure the oxygen level at the surface of the coating would remain constant at all line speeds. This variable was eliminated by curing the coating between two layers of film. After applying the coating on the first film, it was laminated with a second film. The coating was then cured by EB irradiation through the top film layer (Figure 7). After the trials, the top film layer was removed to allow analysis of the cured coating.

FIGURE 7

Experimental details



Five different methods were used to characterize the cured coating. These methods are listed in Figure 8.

FIGURE 8

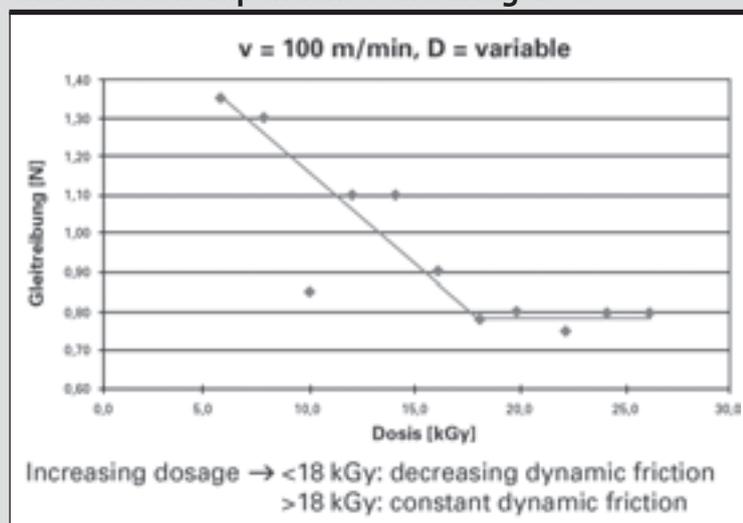
Analytical methods

- Measurement of the curing**
- dynamic friction
 - potassium permanganate staining method
 - UV spectroscopy
 - Gas chromatography
 - IR spectroscopy

The first analytical method used to characterize the coating was dynamic slide friction measurement. After removing the top laminate film, the slip properties of the cured coating were examined. The slip properties were quantified by dynamic slide friction force measurements. The results for coatings cured at a constant line speed and varying dose levels are plotted in Figure 9. The friction force decreased with increasing dose from 6 to 18 kGy. The slide friction force was nearly constant at dosages above about 18 to 20 kGy. At higher doses, more

FIGURE 9

Slide friction dependence on curing dose



complete cure is expected. This should produce a harder coating which results in reduced friction forces.

In the next series of tests, the coating was cured at a constant dose of 6 kGy while varying line speed. At a speed of 100 m/min, the slide friction was significantly lower compared to

curing at a line speed of 400 and 500 m/min (Figure 10). These results indicate that the curing at the higher line speeds was not as effective as curing at lower line speeds.

The second method used to characterize the coating was a potassium permanganate staining test.

This test method was based on the potassium permanganate reaction with the double bond of uncured acrylate groups in the coating. If the coating is well cured, then the double bonds are polymerized and are not available for staining. If the curing is not complete, however, remaining double bonds react with potassium permanganate producing a characteristic brownish color. Samples were immersed in the potassium permanganate solution. After two minutes they were removed, cleaned and the brightness was measured using a spectrophotometer. This test procedure is outlined in Figure 11.

Figure 12 shows that the brightness of the sample measured after curing changes significantly depending on the dose used for curing. At 6 kGy, the brightness is quite low. At 26 kGy, the brightness of the lacquer after the staining test is high. This is expected because at 6 kGy there are significant double bonds remaining due to incomplete curing. This produces significant staining. At 26 kGy, no staining was observed due to high conversion of double bonds.

The next series used a constant dose of 6 or 8 kGy while varying line speed from 100 to 600 m/min. Very little difference in potassium permanganate staining was observed. The brightness at 200 m/min was higher at 600 m/min. This means that at higher line speeds the curing is reduced. However, at 100 m/min low brightness was also observed which is not easily explained.

The next method involved a new curing test method based on UV-spectroscopy. The method is based on the theory that, after good curing, the coating forms a dense cross-linked polymer network; but, if the curing is not complete, the density of the network is reduced. If there is a compound such as a photoinitiator in the network, the

FIGURE 10

Slide friction at 6 kGy depending on machine speed

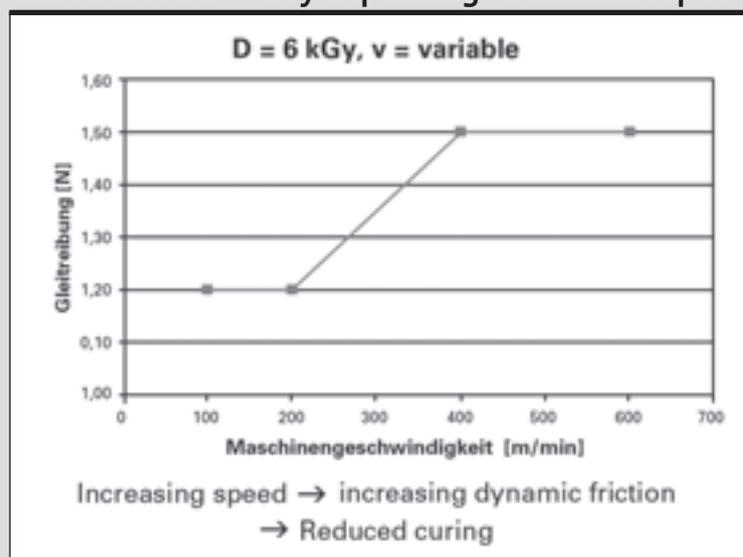


FIGURE 11

Potassium permanganate stain test

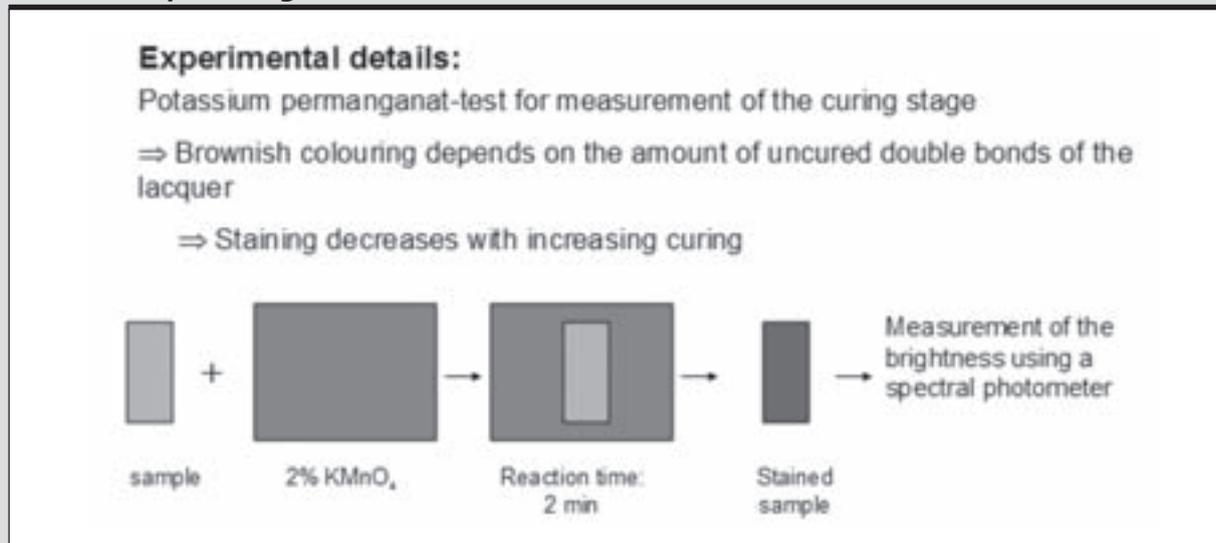
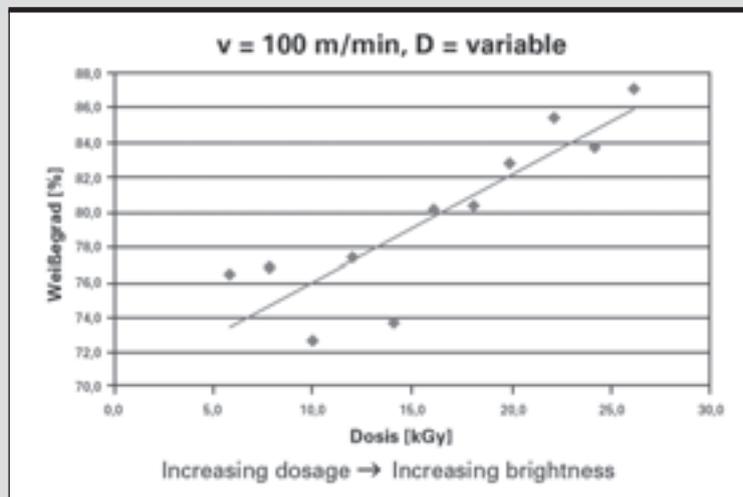


FIGURE 12

Stain brightness of coating stain after curing at different dose levels



speed at which this compound can migrate will depend on the density of the polymer network. The migration may be characterized by the speed of solvent extraction of the compound from the cured coating. If there is an open network, the extraction should be fast. If there is a dense network, extraction

should be much slower. Therefore, the extraction speed is expected to vary inversely with the curing of the coating. The extraction can be measured quite easily by UV spectroscopy which can be monitored continuously during the extraction process. This test method is illustrated in Figure 14.

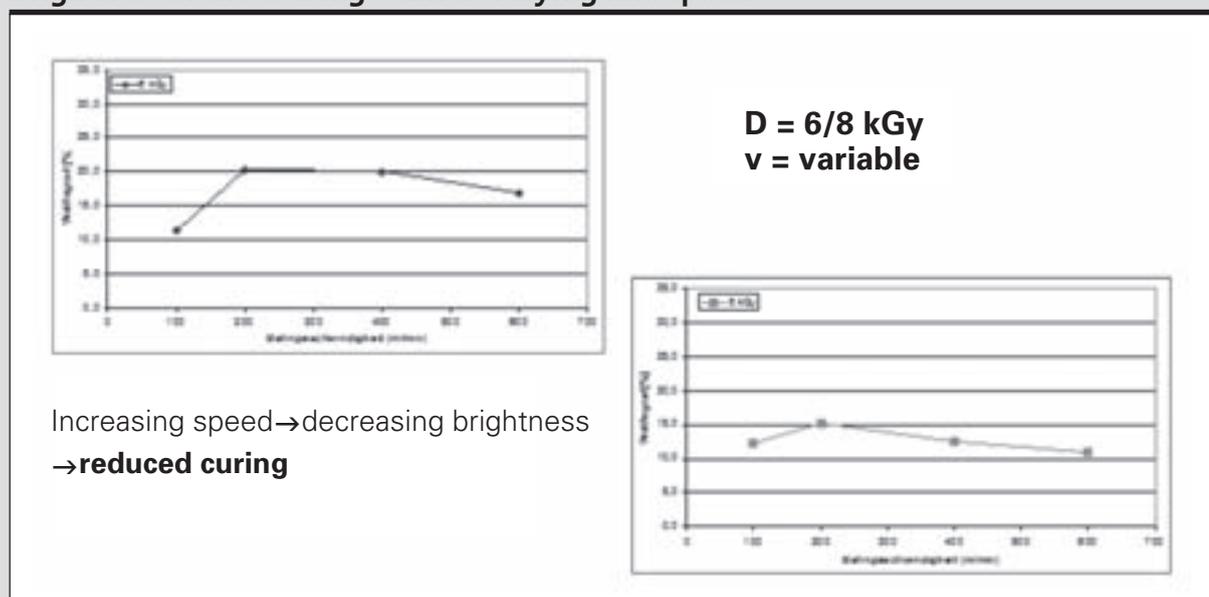
A photoinitiator was added to the coating to facilitate this test method; however, it is not needed for the curing reaction because EB will form radicals without an added initiator. Figure 15 shows the extraction of the photoinitiator from coatings cured at 8 to 26 kGy using a constant line speed of 100 m/min.

The migration of the photoinitiator compound out of the coating cured at 20 to 26 kGy is much slower compared to lower dose levels. This result demonstrates the effect of the curing process on the extraction.

The next series used a constant cure dose of 8 kGy at different line speeds ranging from 100 to 600 m/min. The results show significantly slower extraction after curing at 100 to 200 m/min compared to 400 and 600 m/min. Again it was somewhat surprising that the coating cured at 100 m/min extracted faster than the 200 m/min sample; however, both showed significantly lower migration compared to the 600 m/min sample. In general, the extraction of the photoinitiator increases with increasing

FIGURE 13

Brightness of the coating stain at varying line speeds



line speed that indicates reduced curing properties of the coating.

The last analytical method was based on gas chromatography. Gas chromatography provides a measure of volatile compounds remaining in the coating. A higher degree of cure provides higher conversion of volatile

monomer components of the coating. This results in lower peak areas in the chromatogram.

A representative peak in the chromatogram is shown in Figure 17. In this case, cure dose was constant at 6 kGy while increasing line speed from 100 to 600 m/min. A similar trend was

also observed for the series samples cured at a constant dose of 8 and 10 kGy. The results indicate that more effective curing was achieved at slow speeds compared to higher speeds.

Discussion

In general, all the test methods show there is an influence of the line

speed on the curing. The higher the line speed, the greater the reduction in the resulting coating properties. The dose rate must increase in order maintain a constant dose as line speed is increased; therefore, the observed effects may be attributed to changes in the dose rate. In most cases, these dose rate effects were relatively small. To explain the magnitude of the dose

FIGURE 14

Curing test based on extraction measured by UV spectroscopy

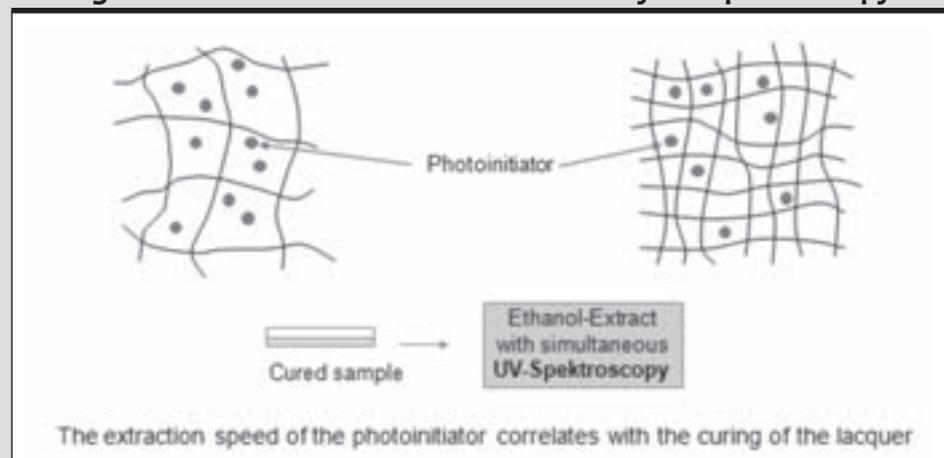


FIGURE 15

UV extraction at different EB-cure doses

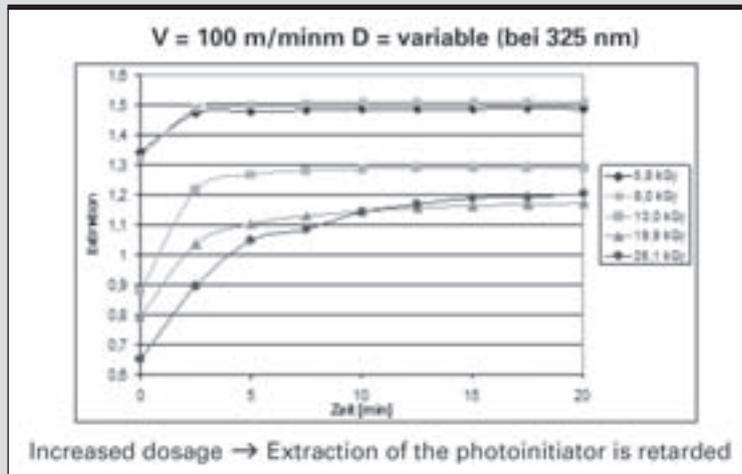
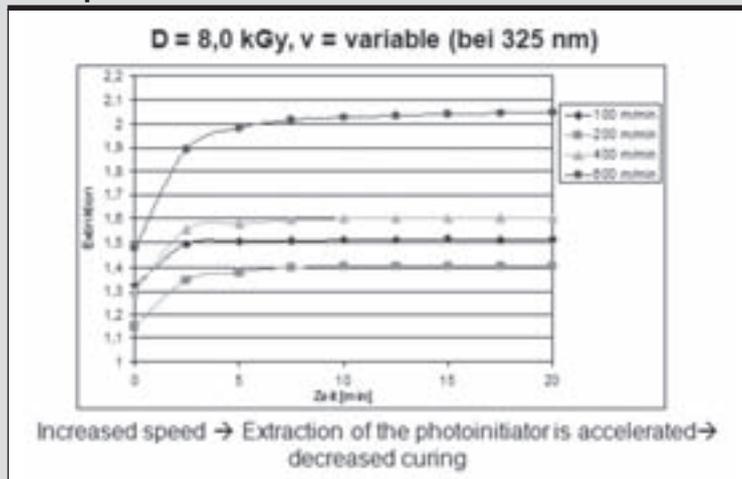


FIGURE 16

UV extraction of samples cured at different line speeds



rate effects, the whole curing process of a coating must be considered. Figure 18 shows a typical change in the elastic modulus (stiffness) of a UV/EB coating as the curing progresses. It is helpful to separate the curing process into different sections. In section I, inhibition occurs; in section II, the reaction starts; and in section III and IV, the curing advances to its endpoint. It is interesting to consider the kinetics of the different sections. In section I, III and IV, the rate of curing is proportional to the radical concentration. The square root relationship was the main reason why a large influence of the dose rate on the curing properties could be expected. Section II is the only region in which the rate is expected to be proportional to the square root of the radical concentration. Section II is relatively small compared to section I, III and IV and, therefore, the effect of section II is relatively small compared to the whole process. This means that the influence of the dose rate does not have the large impact predicted by a simple kinetic analysis.

Summary

The influence of dose rate on the electron curing process was investigated. The analysis of coatings cured at different dosages and line speeds demonstrates that there was a small effect of the dose rate on the polymer network which was formed.

This information was originally presented at the RadTech Europe Conference in Nice France, in October 2009. ▀

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FIGURE 17

Change in gas chromatogram peak with variations in line speed

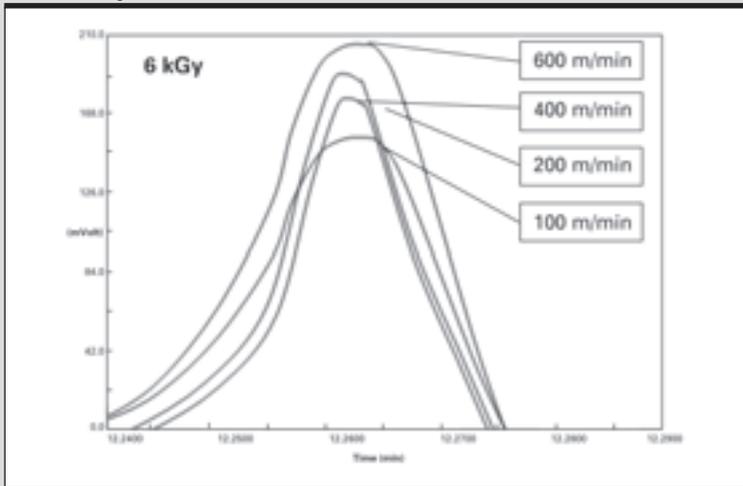
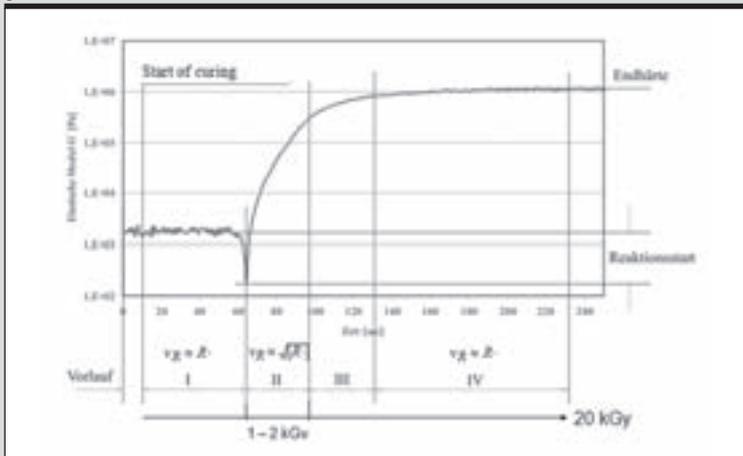


FIGURE 18

Dynamic modulus during a typical UV/EB-curing process



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