Plasma technology: a solution for UV curing on 3-dimensional substrates

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ABSTRACT

On 2-dimensional substrates, UV-curing is state-of-the-art coating technology. If UV-mono-cure coatings are applied on 3-dimensional substrates using conventional lamps for exposure, shadow areas might not be cured. Dual-cure systems involving a UV-curing and a thermal curing step have been recommended to overcome this problem. UV plasma curing is an effective method of achieving good crosslinking in shadow areas using acrylate based UV-coatings. Recent results on mechanical properties and durability will be discussed.

INTRODUCTION

Highly crosslinked polymer networks can be produced quasi instantly at ambient temperature by photoinitiated polymerization of multifunctional monomers and oligomers[1-2]. These UV-cured coatings are usually made of acrylate-based resins, known for their high reactivity, which undergo a radical-type polymerization on UV exposure in the presence of small amounts of photoinitiator, as shown in Scheme 1. This UV-curing technology is now widely accepted because of its distinct advantages, namely, solvent-free formulations cured within a fraction of a second on illumination at ambient temperature. Hence, UV-radiation curing has experienced steady growth for the past 20 years and found its major applications in fast-drying varnishes for surface protection of various materials (plastics, metals, wood, paper) by fast drying varnishes[3].
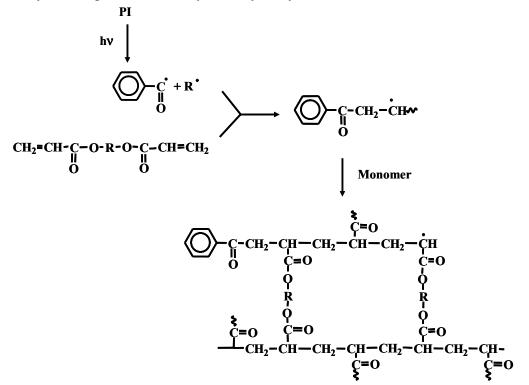
However, UV technology has encountered two critical obstacles to its further development:
- the growing demand to cure coatings protecting three-dimensional objects, such as car bodies
- strong oxygen inhibition (Scheme 2), which remains an important issue that must be overcome in any successful free-radical photocuring application to give high performance materials.
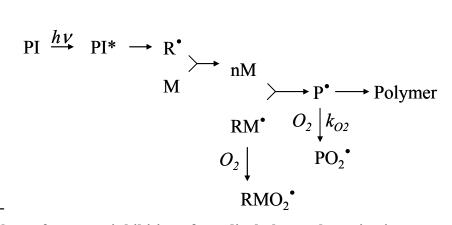
Although the practical design aspects of UV equipment used for achieving uniform illumination of large 3D objects have already been successfully addressed[4-6], one of the recurrent issues in photopolymerizable systems is the cure of films coated onto items of complex shape, such reactions being induced by UV light. UV radiation will not reach the whole surface of a 3D object and the formulation will therefore remain liquid in shadow areas.

A number of investigations have resulted in the development of "dual-cure" systems, which comprise two types of curing mechanisms[7-9]: a UV-curable functional group and a thermally curable functional system (usually an isocyanate in conjunction with a polyol), thus ensuring the hardening of the resin in these non-irradiated areas. After heating and exposure to UV light, they lead to a crosslinked

polyurethane polyacrylate network exhibiting high mechanical properties, even in the non-irradiated zones. A major concern with these 2-pack systems is to find a compromise between the potlife of the formulation in the presence of catalysts and their poor reactivity at relatively low temperature in the absence of catalysts. Photolatent catalysts now allow a satisfactory balance between the two parameters[10], but they cannot prevent the isocyanate/hydroxyl addition.

Scheme 1: crosslinking of a diacrylate by photoinitiated polymerization

Scheme 2: oxygen inhibition of a radical photopolymerization

Similar attempts were made to eliminate oxygen inhibition: a new process was introduced to replace nitrogen, usually used as inert gas, by carbon dioxide[11-13]. This technique has the following advantages:

- CO_2 is readily available
- CO_2 is heavier than air and can therefore easily be contained, hence minimizing gas losses.

This process, however, does not provide a better solution to curing in shadow areas than lamps specially built for UV-curing on 3D substrates.

A recently developed technology addresses the problems of shadow areas and oxygen inhibition in UV polymerization simultaneously. UV-plasma curing consists in placing the coated substrate in a closed chamber filled with a specific gas, usually a mixture made of nitrogen and helium, followed by microwave excitation, inducing a plasma from this gas. Excited species of the plasma revert to their fundamental state by emitting UV light, and hence generating UV radiation throughout the chamber under oxygen-free conditions. Some kinetic investigations performed in shadow areas and an assessment of the properties of coatings cured in this way show the benefits of plasma technology.

BASICS OF UV-PLASMA CURING TECHNOLOGY

What is a plasma?

Interest in plasma technology, especially surface treatments, has grown over the past few years. Plasma is popularly known as the fourth state of matter, after liquids, solids and gases: it is usually generated by the ionization of gases by means of electrical energy. The resulting plasma is a gas that is composed of neutral molecules, fragments of molecules, free electrons and cations, which make the gas electrically conductive (Figure 1). This partially ionized gas, however, remains macroscopically neutral. Hence, this electrical discharge converts the gas into an excited state, which subsequently emits electromagnetic radiation when reverting to its ground state. This electromagnetic energy is characterized by the emission of light in both the UV and visible spectral region. Neon lamps are the most well-known application of using plasma discharge to emit light.
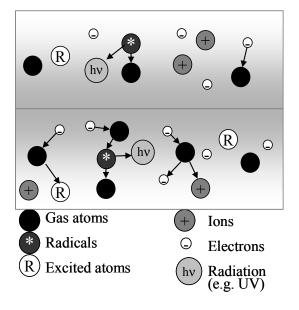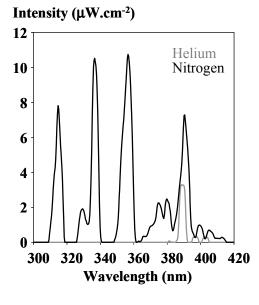

Figure 1: composition of a plasma

Figure 2: emission spectra of plasma generated by nitrogen and helium

What is the link between UV curing and plasma?

By adapting process parameters such as the nature of the gas, it is possible to emit UV light between 200 and 380 nm. The idea is to use these radiations to induce photoinitiated polymerization. Arc-lamps used for UV-curing applications, also called plasma arc lamps, are not much different from the plasma process described above, as long as they are filled with the same gas. However, in this latter case, the light is directed radiation, which can be reflected by mirrors to reduce shadow areas. During the plasma process, the light is emitted throughout the chamber. In other words, UV-plasma curing consists in placing the coated substrate in the light source.

As previously mentioned, the light emission spectrum of the plasma can be controlled by adapting the gas composition: Figure 2 shows that the UV emission induced by a nitrogen and a helium plasma are different. Depending on the spectral photosensitivity of the UV-curable formulation, it is therefore necessary to check whether the UV emission of the plasma overlaps the absorption of the photoinitiator in the coating system. Other properties of plasmas can be customized by modifying the process parameters and thus adapted to specific technical application requirements.

The benefits of UV-plasma curing

The fundamentals of UV-plasma curing are that as long as gas occupies the entire volume around the car body, UV radiation will reach all areas of the substrate to be cured, even on objects of complex shape. This efficiency cannot be achieved using conventional UV process, where the shape of the object acts as a screen between the light source and the coating. This effect is clearly illustrated in Figures 3 and 4.

A further benefit lies in the actual plasma process: an oxygen-free environment is required to create an optimum UV-light-emitting plasma as shown in Figure 2, which means that no oxygen inhibition takes place during UV-plasma curing, and a better surface cure is therefore achieved, providing high-performance coatings with outstanding scratch resistance.
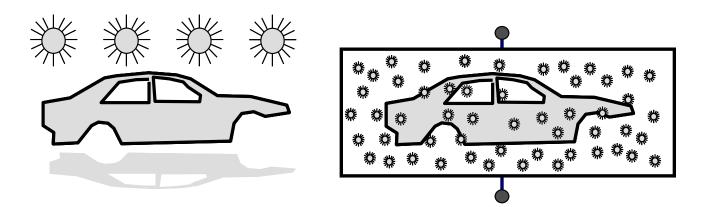

Figure 3: UV-curing of a car body using a conventional UV system

Figure 4: UV-curing of a car body using UV-plasma curing process

EXPERIMENTAL

Formulation

Most of the experiments described in this article were carried out with a formulation based on a polyurethane acrylate, containing a combination of α-hydroxyacetophenone and bisacylphosphine oxide at a ratio of 9:1 (total concentration of photoinitiator was 3% on solids). Additionally a combination of 1.5% hydroxyphenyltriazine as UV-absorber and 1% hindered amine light stabilizer as radical scavenger was incorporated to give the coating satisfactory weather stability. Some experiments were performed using a formulation containing 3% of a bisacylphosphine oxide BAPO. The UV-curable formulation was applied on a white pre-coated aluminum panel by means of a 100 μm thick calibrated wirewound bar coater, to give a dry film thickness of about 40 μm.

Plasma process

The pressure in the plasma chamber was first reduced to 0.02 mbar, and the cavity was further filled by a mixture of nitrogen (gas flow=65 sccm) and helium (gas flow=35 sccm) to reach a pressure of 0.05 mbar. A microwave power of 800 W was applied to induce the plasma. The total processing time (i.e. irradiation time) was 90 s. The experimental setup is illustrated in Scheme 3.

To provide a comparison with conventional UV-cured materials, UV irradiation was performed on an IST UV line equipped with two medium-pressure mercury lamps (electric power of 80 $W.cm^{-1}$). At the belt speed used, 5 m/min, the UV dose received by the sample at each pass under the lamp was estimated to be approximately 0.9 $J.cm^{-2}$.

Assessment

The chemical modifications resulting from the crosslinking were monitored by Attenuated Total Reflectance spectroscopy (ATR, Magna-IR spectrometer 750 from Nicolet): this equipment (Figure 5) records the IR spectrum of the top 2 μm thick layer on both sides of the coating. The film was therefore removed from the substrate, and both faces were analyzed to assess through cure after irradiation, as shown in Figure 6. The reaction of the acrylate double bonds was followed quantitatively by monitoring the disappearance of the IR band at 1410 cm^{-1} of the acrylate double bond. The degree of conversion (x) is directly related to the decay of the IR absorbance, and was calculated from the equation:

$$Conversion(\%)x = \frac{A_0 - A_t}{A_0}.100,$$

where A_0 and A_t represent the area of the IR band centered at 1410 cm^{-1}, before and after curing respectively.

The hardness of the cured polymer was evaluated by monitoring the damping of the oscillations of a pendulum placed on a glass plate coated with a 50 μm thick film. König values, expressed in seconds, typically range from 10 s for soft elastomeric materials to up to 250 s for very hard and glassy polymers.

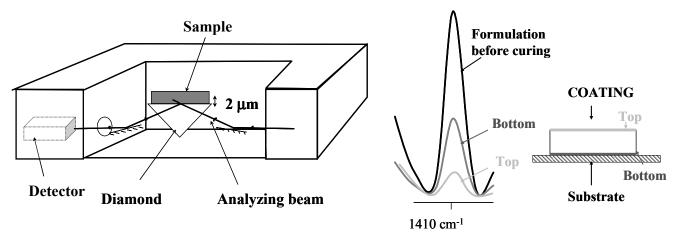Accelerated weathering tests were performed using the Xenon Wom Cam 180 procedure (5000 hours exposure).

Figure 5: ATR equipment

Figure 6: ATR spectra of both sides of the film (top and bottom) after curing and of the formulation before curing as reference

RESULTS

Cure efficiency

Our major concern was first to evaluate the benefit of UV-plasma curing compared to conventional UV curing. To this end, two coated plates were introduced in the plasma chamber as shown in Scheme 4. The first, film A, was directly exposed to the microwave generator: the light intensity received by sample A is supposed to be the highest from the whole chamber volume, as the absorbed light is emitted close to the excitation source. The second plate, film B, was placed opposite, i.e. the light released by the plasma was emitted far away from the microwave generator: the UV dose absorbed by the film should be the lowest in the chamber.
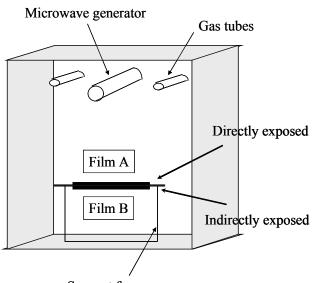
If a UV-lamp had replaced the microwave generator, film A would have been fully cured within a few seconds, while film B, being placed in a shadow area, would remain liquid.

Promising results were obtained, as shown in Figure 7: 80% of the acrylates were converted after 20 s of plasma process for film A, while 55% had polymerized in film B. Since the tack-free conversion limit is about 50% for this urethane acrylate, a tack-free surface was obtained after at most 20 s plasma process. As expected, longer exposure results in improved crosslinking as a higher UV dose is absorbed by the film.
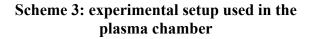
Since the through-cure depends on the light spectrum and the photoinitiator, it was also essential to assess polymerization in the deepest coating layer in contact with the substrate. Figure 8 shows that outstanding through-cure is obtained with film A (65% conversion after 40 s, film thickness 40 μm). Even in the worst case (film B), it was possible to achieve an overall conversion of more than 70% after 90 s irradiation (Figure 9). This efficient through-cure can be explained by the excellent spectral overlap between the nitrogen plasma emission spectrum to the absorption spectrum of BAPO photoinitiator, as
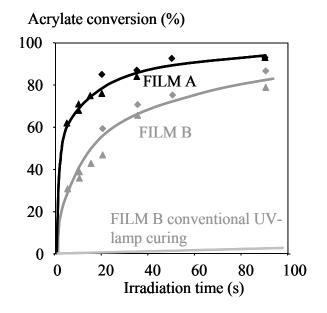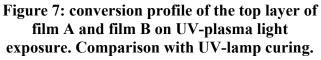
shown in Figure 10. The addition of α-hydroxyacetophenones should further provide an excellent surface cure, thus improving the surface properties of the coating.
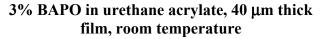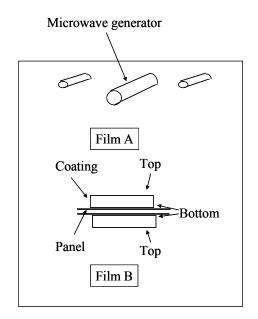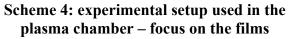

Scheme 3: experimental setup used in the plasma chamber

Scheme 4: experimental setup used in the plasma chamber – focus on the films

Figure 7: conversion profile of the top layer of film A and film B on UV-plasma light exposure. Comparison with UV-lamp curing.

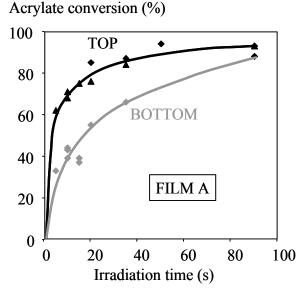**3% BAPO in urethane acrylate, 40 μm thick film, room temperature**

Figure 8: conversion profile of the top and the bottom layer of film A on plasma exposure

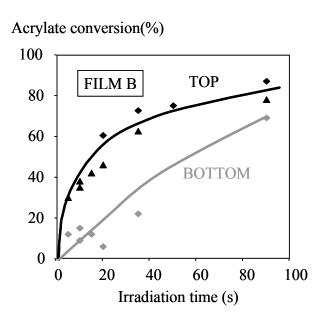**3% BAPO in urethane acrylate, 40 μm thick film, room temperature**

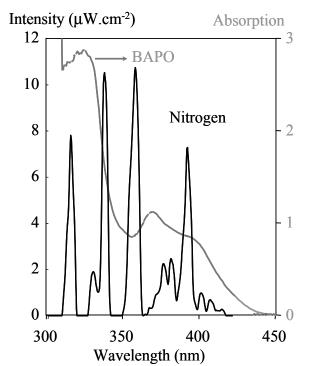**Figure 9: conversion profile of the top and the bottom layer of film B on plasma exposure**

3% BAPO in urethane acrylate, 40 μm thick film, room temperature

Figure 10: emission of nitrogen plasma and typical absorption of BAPO photoinitiator

Comparison of the curing process: UV curing / UV-plasma curing

It might be feared that the high energetic plasma process could adversely affect the chemical structure of the coating surface. ATR measurements were performed on a plasma-cured and a UV-cured material, to determine whether the process damages the chemical composition of the surface exposed to the plasma. Figure 11 clearly shows that similar spectra were measured in both cases, no differences in the chemical composition being observed. Figure 12 further proves that the plasma process does not affect the weathering stability of the final material: yellowing is even slightly reduced with the plasma-cured coating, probably due to the inert process atmosphere. There was no detectable influence of the curing process on pendulum hardness and yellowing immediately after curing, as shown in Figure 13.
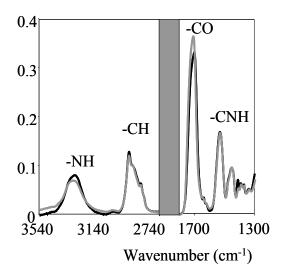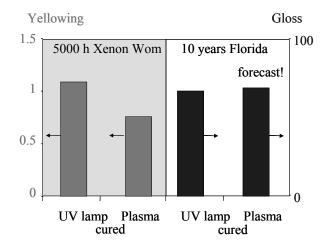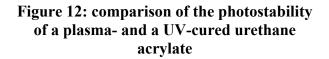
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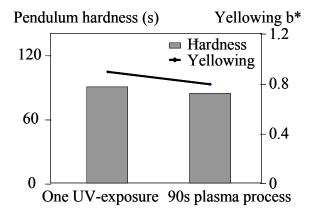**Figure 11: ATR spectra of the surfaces of a UV-cured and a plasma-cured coating**

Figure 12: comparison of the photostability of a plasma- and a UV-cured urethane acrylate

Figure 13: König hardness and yellowing of UV-cured films irradiated either by a Hg lamp or by plasma process

CONCLUSION

The new UV-plasma curing technology allows full hardening of protective coatings on objects of complex shapes. This innovative process also provides a solution to oxygen-sensitive systems, as irradiation is performed under an inert atmosphere. A further advantage is the small space requirements of the plasma system compared to thermal ovens (Figure 14).

Experimental investigations have shown that UV-plasma curing leads to an extensive and fast crosslinking of coatings covering the whole surface of 3D objects. The light emission released by the plasma also corresponds well to the absorption spectra of commercially available BAPO photoinitiators, thus allowing an efficient through curing. It is also crucial to adapt the photoinitiator and its concentration to the expected film properties. Similar to conventional UV-curing, longer irradiation

improves cure efficiency, an optimum process time ranging from 20 to 90 s. Final end performances of UV-cured and plasma-cured materials are similar.

Given all the benefits UV-plasma curing provides, this new technology is expected to enjoy considerable and fast industrial development, as it simultaneously overcomes the two limitations of UV curing. A pilot plant is already in operation, as shown in Figure 15.
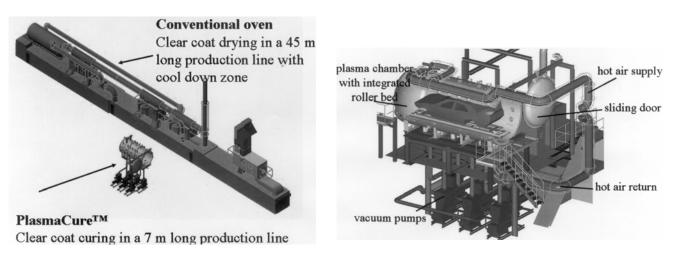

Figure 14: space requirement of a thermal production line and of a UV-plasma curing installation

Figure 15: pilot curing plant

Acknowledgments

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