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Infrared Spectroscopy as a Tool to Monitor Radiation Curing

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1. Introduction

Photoinitiated polymerization of multifunctional monomers and oligomers is one of the most efficient methods to produce quasi-instantly highly cross-linked polymer networks. It has found a large number of commercial applications, mainly in the coating and printing industry. Among the advantages of this technology the high cure speed, the reduced energy consumption, and the absence of VOC emissions are the most remarkable. It is well known that the UV curing can be performed either by a radical or a cationic mechanism. The cationic photoinduced process presents some advantages compared to the radical one; in particular lack of inhibition by oxygen, lower shrinkage, good mechanical properties of the UV cured materials, and good adhesion properties to various substrates [Fouassier & Rabek, 1993]. The properties of a UV-cured material depend not only on the photocurable composition but also on its photopolymerization kinetics, it is very important to have access to an analytical technique that will facilitate this purpose.

One of the common features of all UV-curable systems is the rapidity at which the polymerization takes place under intense illumination, usually less than one second. Therefore it is difficult to accurately follow the kinetics of such ultrafast reactions, which is a prerequisite for a better understanding and control of the curing process. Moreover, evaluation of the kinetic parameters (rate of polymerization, kinetic chain length, propagation and termination rate constant) is essential in order to compare the reactivity of different photosensitive resins and assess the performance of novel photoinitiators and monomers.

Two types of analytical methods are currently used to study the kinetics of radiation curing:

1. Those based on discrete measurements of the physical or chemical modifications induced after a short exposure to UV light.
2. Those based on the continuous monitoring in real time of some physical or chemical modifications induced by light.

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The first method, which provides quantitative and reliable information on the extent of cure, is a time-consuming technique. In addition, there is certain error included in the measurement owing to the post-polymerization reaction, which occurs during the lapse of time between the end of exposure and the measurements

Among the real-time (RT) techniques RT-FTIR spectroscopy is one of the most powerful analytical methods for monitoring UV-initiated curing processes, which proceed rather rapidly. RT-FTIR has several advantages over other real-time methods such as photo-DSC. The most important limitation of photo-DSC is its long response time, which makes it inadequate for the monitoring of fast polymerization reactions. In addition, using photo-DSC requires the knowledge on the theoretical enthalpy of reaction for the conversion of functional groups to be calculated using the heat release measured. Finally, the sample thickness is much higher than that in most practical applications (coatings, printing, etc), moreover, the thickness of the layer in the sample pan is poorly controlled.

In contrast, RT-FTIR spectroscopy allows a rapid and quantitative measurement of the conversion of specific reactive functional groups under variable conditions as light intensity, photoinitiator concentration, coating thickness, etc., which are closer matched to those in technical coating and printing processes. In the past, RT-FTIR spectroscopy has been successfully used to study the kinetics of photopolymerization reactions in dependence on the irradiation conditions and other experimental parameters, the reactivity of monomers and oligomers and the efficiency of newly developed photoinitiator systems.

One of the unique advantages of the IR technique is to permit an instant and precise evaluation of the amount of un-reacted groups (residual bonds or monomer groups), which remain trapped in the glassy polymer network. Its value is highly dependent on the monomer functionality as well as on the glass transition temperature, T_g , of the network. It should be emphasized that RT-FTIR spectroscopy has been proven to be very valuable for the precise determination both of the rate of polymerization and the amount of residual un-reacted groups where the knowledge of the initial group content is not required.

2. Real time FTIR spectroscopy

Real Time (RT-) FTIR spectroscopy permits not only to follow quantitatively the polymerization by monitoring the disappearance of the IR absorption characteristic of the polymerizable reactive groups (acrylates, methacrylates, epoxy rings, vinyl ether double bonds, thiol groups etc.) but also to determine at any moment the actual degree of conversion and hence the residual unreacted groups content. This analytical method has proved extremely valuable for measuring the polymerization rates and quantum yields of reactions that develop in the millisecond time scale.

The polymerization rate, R_p , being the rate of monomer conversion, can be determined by measuring the decrease of the infrared absorption of the reactive group:

$$R_p = \frac{-d[M]}{dt} = \left(\frac{A_1 - A_2}{A_0} \right) \cdot \left(\frac{[M_0]}{t_1 - t_2} \right) \quad (1)$$

where A_1 and A_2 are IR absorption values of the reactant A after exposure to UV-light during time t_1 and t_2 , respectively; A_0 and $[M_0]$ are the absorption and the molar initial concentration values of the monomer, A, before irradiation.

In the RT-FTIR technique, the sample is simultaneously exposed to the polymerizing UV-irradiation beam and to the analyzing IR beam (Fig. 1), which monitors the resulting drop of absorbance. In all the reported data the UV light was a medium pressure mercury lamp, with a broad UV spectra emission.

As an example the RT-FTIR spectra for a methacrylic resin at different irradiation time are shown in Figure 2 [Amerio et al. 2008]. It is evident that the band at 1630 cm^{-1} ($\text{C}=\text{C}$), attributed to the methacrylic functional group, decreases during irradiation of the sample with the UV beam. The decrease in intensity of the band at 1630 cm^{-1} is accompanied by an increase and shift to higher wavenumbers of the $\text{C}=\text{O}$ oscillation mode related to the change in mobility of the $\text{C}=\text{O}$ bonds with the gradual opening of the $\text{C}=\text{C}$ bonds.



Fig. 1. Set up for RT-FTIR monitoring of UV irradiation curing

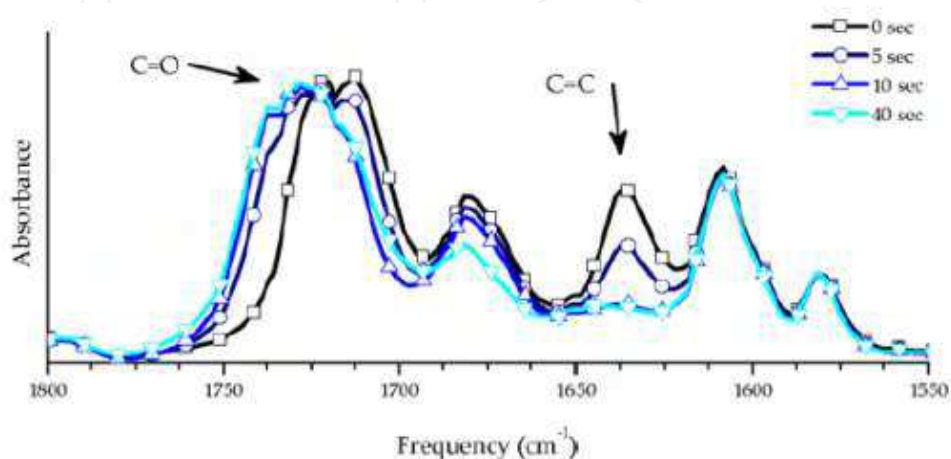


Fig. 2. RT-FTIR spectroscopy during UV curing of a methacrylated system [Amerio et al. 2008]

The reactivity and the kinetics of a UV curable system is affected by numerous parameters i.e. nature and amount of photoinitiator and functionalized monomers and oligomers, thickness, light intensity, concentration of O_2 , the presence of fillers or additives etc. RT-FTIR has been extensively used for the rapid and quantitative assessment of the effect of such parameters on the UV curing kinetics. Further down characteristic examples of the use of this powerful analytical technique are listed.

2.1 Irradiation time

The reaction kinetics curve follows a characteristic sigmoid, S-shaped profile (Fig. 3) due to two major factors: (i) the initial induction period is resulting from the well-known inhibition effect of O_2 on the radical-induced polymerization, which disappears completely for experiments carried out in vacuum or in N_2 ; (ii) the progressive slowing down observed at degrees of conversion above 30-40% is the direct consequence of the network formation and the subsequent gelification, which reduces the segmental mobility of the growing polymer chains and of the un-reacted double bonds [Fouassier & Rabek, 1993].

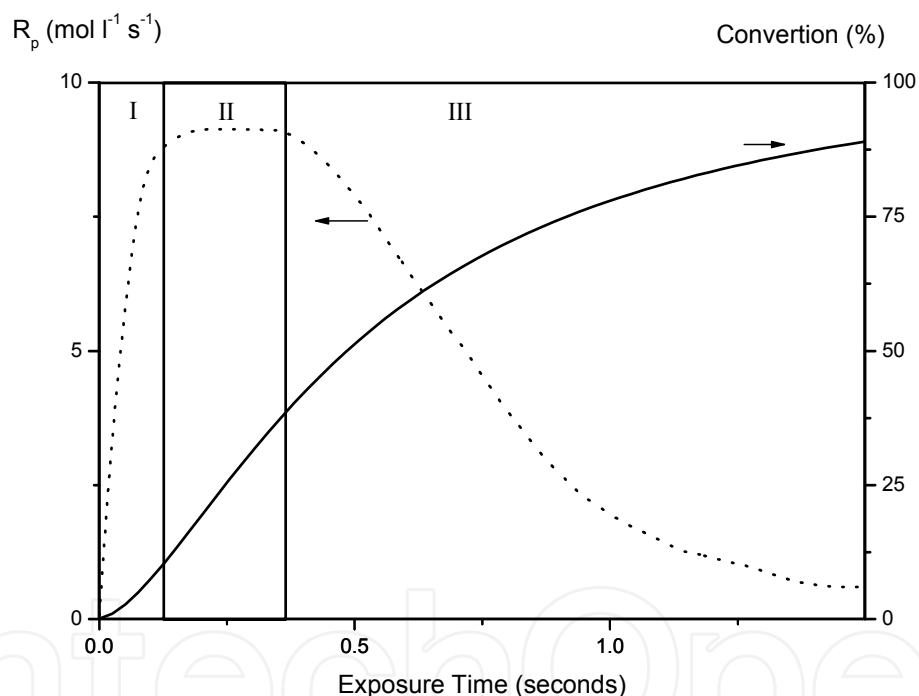


Fig. 3. Conversion curve and R_p curve as a function of irradiation time for a radical induced polymerization [Fouassier & Rabek, 1993].

2.2 Presence of O_2

The free radicals formed by the photolysis of the initiator are rapidly scavenged by O_2 molecules to yield peroxy radicals. These species are not reactive towards the acrylate double bonds and can therefore not initiate or participate in any polymerization reaction. An additional amount of photoinitiator (and of UV energy) is therefore needed to consume/compensate the oxygen dissolved in the resin, as well as the atmospheric O_2 diffusing into the sample during the UV exposure, in order to obtain coatings with the desired mechanical properties and tack-free surfaces.

Overcoming this unwanted reaction has turned into a major challenge. Different methods have been considered: A clear, illustrative example is reported in Figure 4 in which the effect of air and inert atmosphere (CO_2 and N_2) was investigated [Studer et al., 2003]. In the presence of air, the polymerization starts after an induction period of 0.2 s, at a speed four times lower than that in an inert atmosphere (Fig. 4). After 0.35 s, once 15% of the acrylate double bonds have polymerized, the reaction begins already to slow down because of the continuous diffusion of air into the sample. To prevent the diffusion of oxygen into the sample, a UV-transparent polypropylene (PP) film was placed on top of the liquid coating (laminated sample). The induction period is then slightly shorter than in air (oxygen is still dissolved in the film) and the polymerization proceeds three times faster than in air to reach an 85% conversion by the end of the UV-irradiation (35 s).

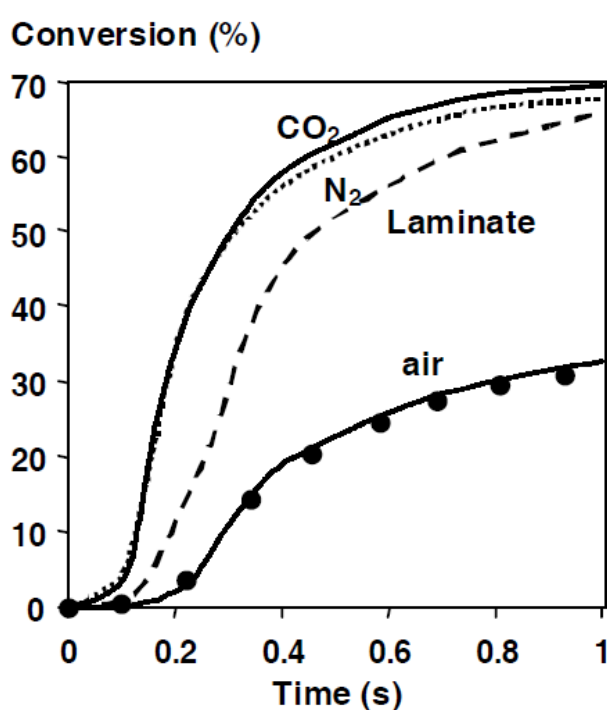


Fig. 4. Conversion curves as a function of irradiation time. Profiles recorded by RT-FTIR spectroscopy for a PUA (Polyurethane) resin exposed to UV light under different atmospheres and with a PP-film as oxygen barrier ("lamine"). [Studer et al., 2003]

2.3 Photoinitiator

The efficiency of the radical photo-initiator can be described by two quantum yields: The *quantum yields of initiation*, which represents the number of starting polymer chains per photons absorbed, and the *quantum yields of polymerization*, which is the number of monomer units polymerized per photons absorbed. Therefore, it is clear that if the monomers are absorbing in the same UV range as the photoinitiator the competition will limit the photons absorbed by the latter. This can lead to a decrease of quantum yields and therefore to a lower degree of conversion as well as polymerization rate. In such cases special care needs to be taken when selecting the proper photoinitiator. This issue becomes particularly important when dealing with formulations containing fillers which absorb light in the same spectral range as the photoinitiator.

In Figure 5 the UV-Vis spectra of a radical photoinitiator and the BaTiO₃ (BT) filler that was used in an acrylic formulation are presented. It is evident that there is a competitive absorption between the photo-initiator and the ceramic powder in the UV region between 200 and 400 nm. That leads to a linear decrease of acrylic double bond during UV irradiation by increasing the filler content in the photocurable formulation [Lombardi et al., 2011].

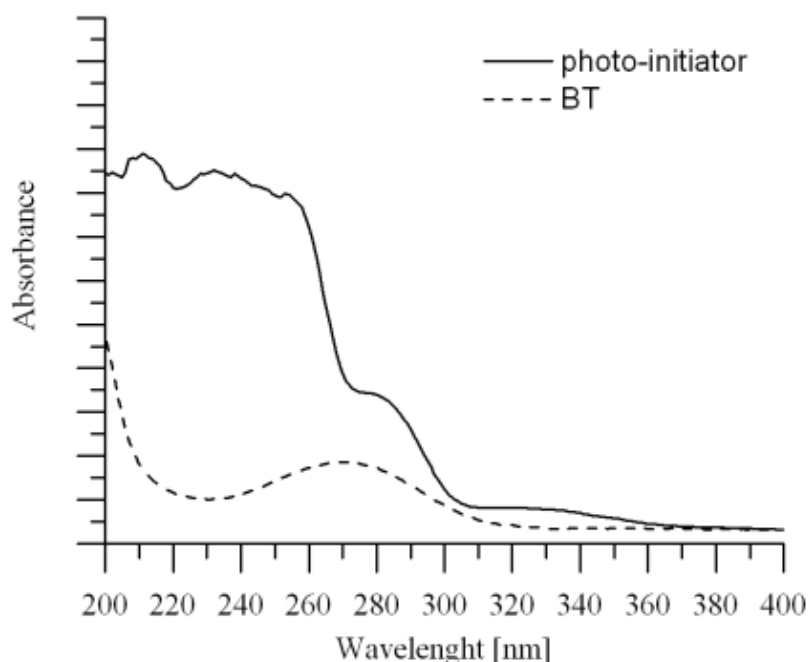


Fig. 5. UV-VIS spectra of the 2-hydroxy-2-methyl-1-phenyl-propan-1-one (DAROCUR® 1173, Ciba®) photo-initiator and the BaTiO₃ (BT) filler. [Lombardi et al., 2011]

2.4 Monomers

From the slope of the RT-FTIR kinetic curves it is easy to evaluate the rate of polymerization (R_p) which can be calculated at any moment of the reaction. It is therefore possible to plot the R_p values as a function of the conversion rate. The overall polymerization quantum yield, ϕ_p , can be calculated from the ratio of polymerization, R_p , over the absorbed light intensity.

In a pioneer study from Christian Decker the photopolymerization of polyurethane-diacrylates was investigated by using the RT-FTIR technique [Decker & Moussa, 1988]. The RT-FTIR conversion curves as a function of irradiation time were examined for different systems (Fig. 6).

The polymerization rate, R_p , values as a function of the percentage of conversion are presented in figure 7. R_p reaches its maximum value ($= 8 \text{ mole l}^{-1}\text{s}^{-1}$ for the most reactive system) at a degree of conversion of 25% for the 3 systems investigated. This peak corresponds to the phase at which the O₂ inhibition has been overcome and gelification has not yet slowed down the polymerization rate. Higher R_p values up to $10^3 \text{ mole l}^{-1} \text{ s}^{-1}$, were obtained with such multiacrylic monomers by merely increasing the intensity of the UV source [Decker & Bendaika, 1984].

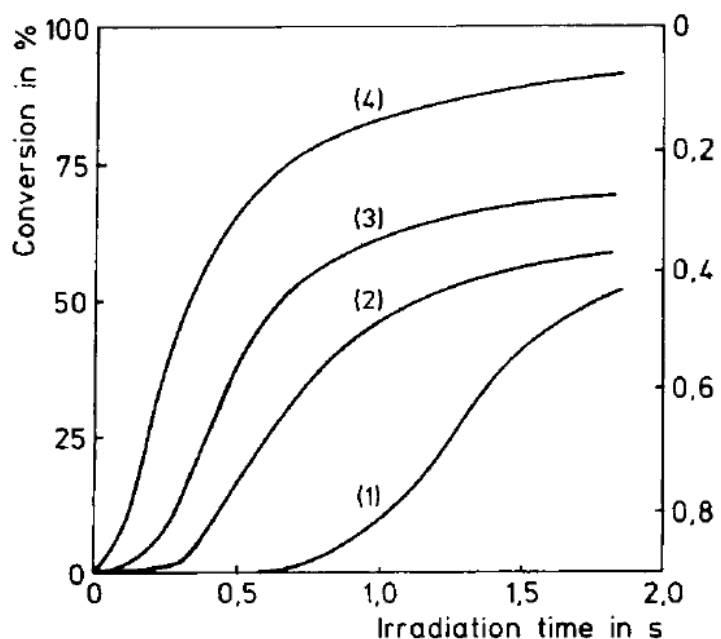


Fig. 6. Photopolymerization profiles (left) and variation of the rate of photopolymerization, R_p , (right) recorded by RT-FTIR spectroscopy for: (1) ethyldiethylenglycol monoacrylate, (EDGA) (2) EDGA + TPGDA, (3) tripropyleneglycol diacrylate (TPGDA), (4) Oxazolidone monoacrylate. [Decker & Moussa, 1988]

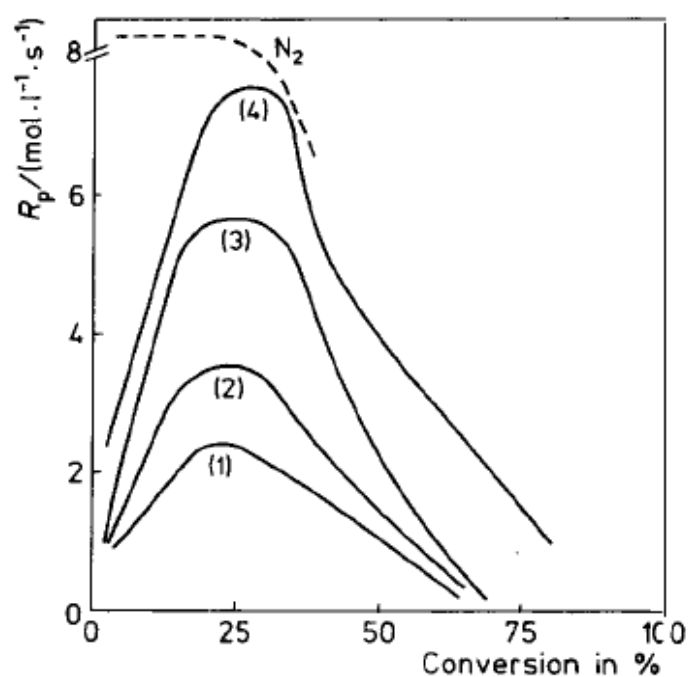


Fig. 7. Variation of the rate of photopolymerization, R_p , recorded by RT-FTIR spectroscopy for: (1) ethyldiethylenglycol monoacrylate, (EDGA) (2) EDGA + TPGDA, (3) tripropyleneglycol diacrylate (TPGDA), (4) Oxazolidone monoacrylate. [Decker & Moussa, 1988]

2.5 Additives: Photosensitizers

In a recent paper [Beyazit et al., 2011] long wavelength free radical photopolymerization of (meth)acrylic monomers (TMPTA) is described. The polymerization was carried out using a conjugated thiophene derivative (3,2-diphenyldithieno[3,2-b-2,3-d]thiophene, DDT) as photosensitizer and a diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) as photoinitiator. The progress of conversion versus time as well as the final conversion level (Fig. 8) shows that the presence of DDT affects significantly the polymerisation of TMPTA. In general the extension of spectral sensitivity by adding a photosensitizer consists of an energy transfer processes as schematized in the following:



The photosensitizer is excited by light and it is able to transfer the energy, through orbital overlap, to the photoinitiator that is indirectly activated. In the cited work, the photosensitizer DDT that is photoexcited by a UV source in the range of 350–450 nm is rapidly quenched by the onium salt, which is transparent in that range.

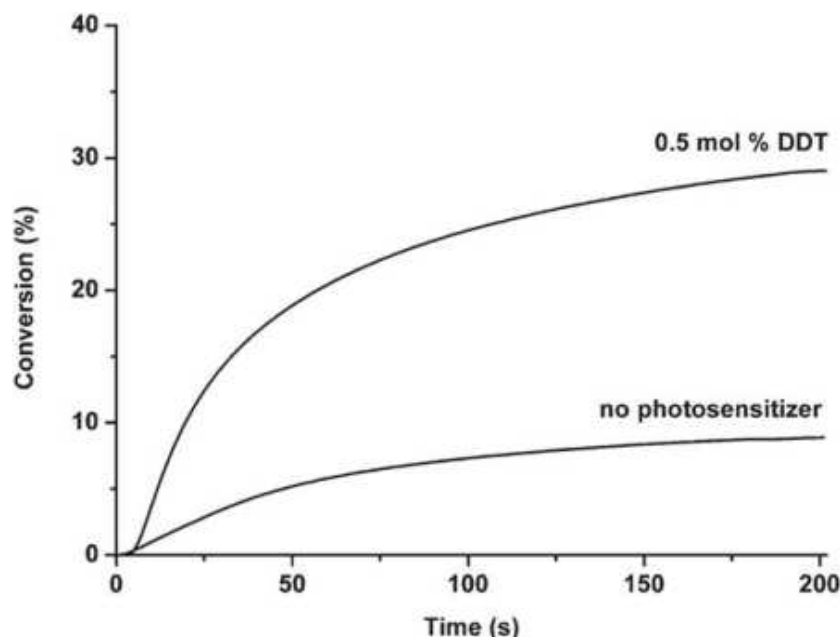


Fig. 8. Real-time FT-IR conversion curves as a function of irradiation time for TMPTA w/wo a photosensitizer, DDT. [Beyazit et al., 2011]

2.6 Fillers

Recently [Sangermano et al., 2008] reported for the first time the preparation of antistatic epoxy coatings via cationic UV curing of an epoxy resin in the presence of a very low content of carbon nanotubes (CNT). After dispersing the CNT into the epoxy resin, in the range between 0.025–0.1 wt.-%, the formulations were cured by means of UV light in the presence of a sulfonium salt as cationic photoinitiator.

The effect of the presence of CNT on the photopolymerization process was investigated by means of real-time FT-IR. The conversion curves as a function of irradiation time for the epoxy resin with and without CNT are presented in Figure 9.

The high reactivity of the epoxy groups results to a quite high initial rate of polymerization (slope of the curve). The epoxy groups' conversion levels off, after 2 minutes of irradiation, to a value of about 60%. This is due to the formation of a glassy polymer network, which hinders the mobility of the reactive species so that a large number of un-reacted epoxy groups remained trapped. Introduction of CNT leads to a slight decrease if the epoxy group photocuring rate compared to the neat epoxy system. In addition, the final conversion (after 120 seconds of irradiation) decreases from about 60% to 50%.

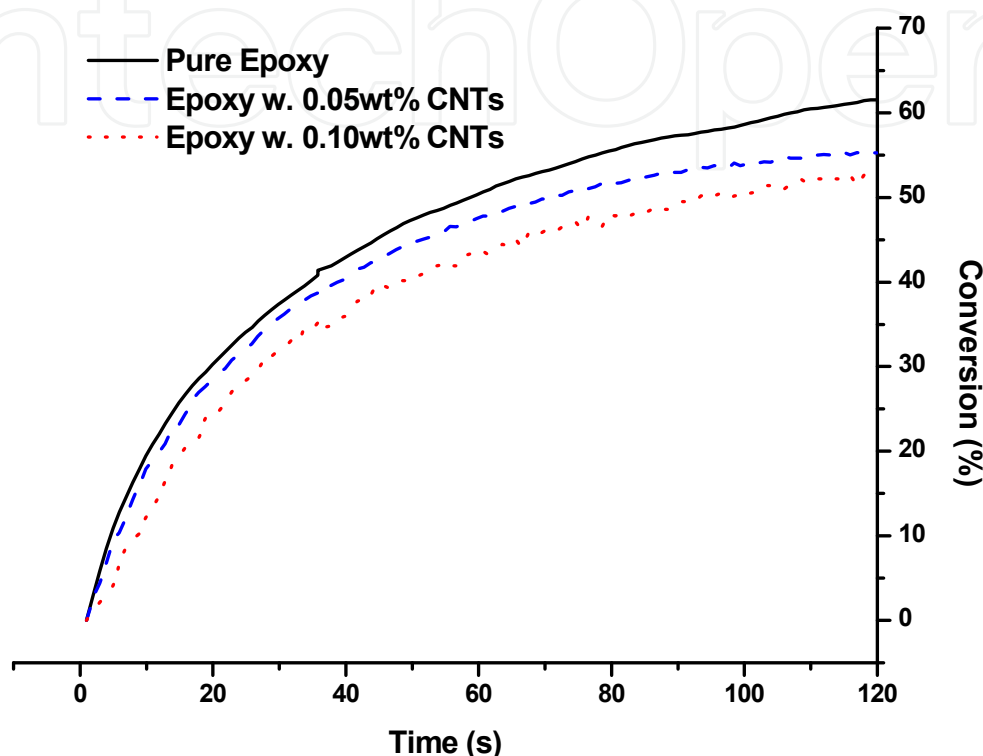


Fig. 9. RT-FTIR conversion curves as a function of irradiation time for dicycloaliphatic epoxy resin and in the presence of increasing amount of CNT. [Sangermano et al., 2008]

2.7 Thickness and photoinitiator concentration

In a clear formulation, UV radiation is absorbed mainly by the photoinitiator, so that the curing depth is directly controlled by its concentration. For each specific application, the best compromise must be found between curing speed and depth. Ideally, the initiation wavelength should be selected so that the initiator is the only absorbing specie.

By selecting an initiation wavelength where the monomer does not absorb, one can significantly increase the maximum photoinitiation rate and the rate of spatial propagation of the polymerization front. It is advantageous to use photobleaching initiators whose light absorption is higher than the one of the initiator products, thereby allowing more light to pass through the system.

Simulation results have confirmed that, at any given time, the initiation rate profile resembles a wave front, and the breadth of this front is determined by factors such as:

- Initial initiator concentration;
- Molar extension coefficient

Fouassier & Rabek, 1993, show that there is an optimum initiator concentration for the efficient photopolymerization of thick samples (Fig. 10). As the initiator concentration is increased, the initiation rate at the surface is increased, but the rate of propagation of the front through the sample is decreased.

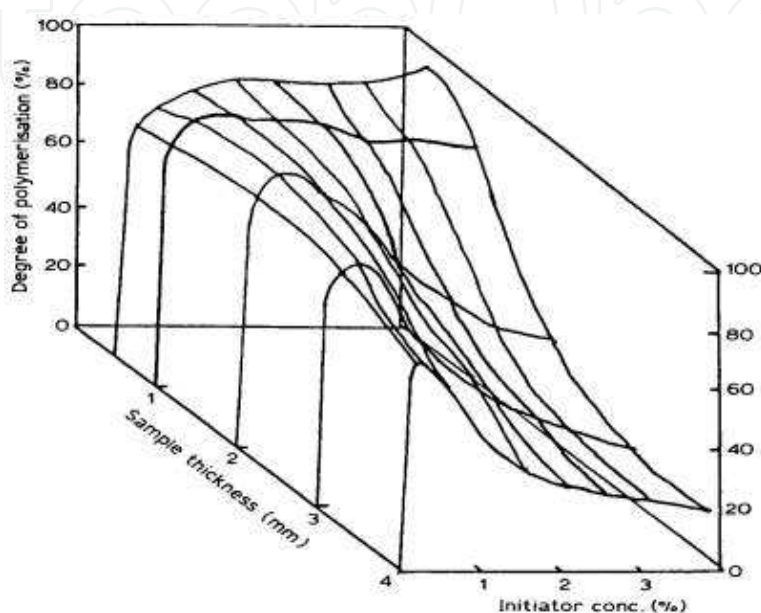


Fig. 10. RT-FTIR conversion curves as a function of sample thickness and concentration of the initiator [Fouassier & Rabek, 1993].

Low initiator concentration and/or photoinitiator of low extinction coefficient is required for the photocuring of thin films:

- A low molar absorptivity allows more efficient penetration of light into the sample; however, a higher molar absorptivity leads to higher rates of photon absorption and higher rates of bleaching.
- As the initiator molar absorptivity increases, so does the maximum initiation rate, the breadth of the propagating front decreases, and the rate of spatial propagation through the sample decreases.

2.8 Light Intensity

Lovelh et al., 1999 investigated the photo-copolymerization of 50/50 BisGMA/TEGDMA at various light intensities (0.4, 1.5, and 2.9 mW/cm²). The effect of light intensity on the polymerization rate of the comonomer mixture at 25°C is depicted in Figure 11. The maximum rate of polymerization and the final conversion are both significantly affected by the differences in light intensity. Increasing the intensity of the UV light from 0.4 to 2.9 mW/cm² leads to an increase of the maximum rate to more than double. This is a clear investigation/result evidencing the effect of light intensity to photocuring reaction.

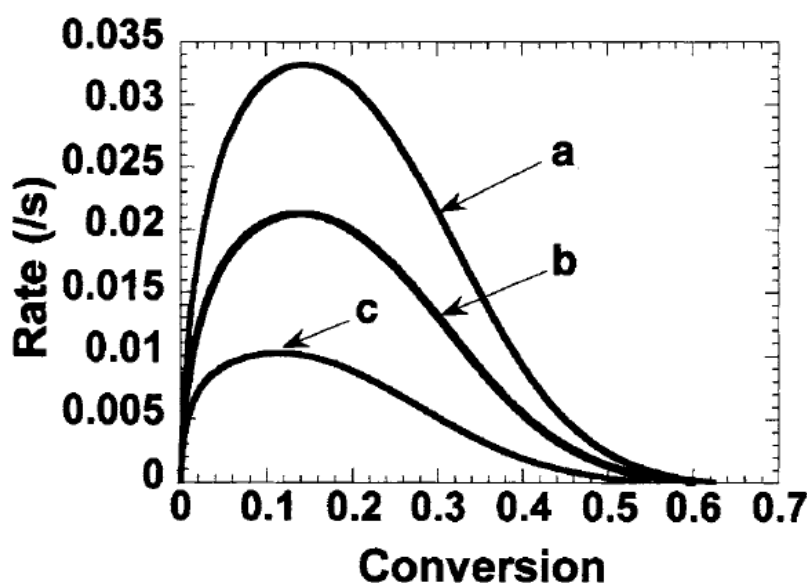


Fig. 11. Rate of polymerization of 50/50 BisGMA/TEGDMA (25°C) as a function of double-bond conversion for various light intensities of (a) 2.9 mW/cm², (b) 1.5 mW/cm², and (c) 0.4 mW/cm². [Lovelh et al., 1999]

3. Conclusion

Real-Time FTIR spectroscopy has been used extensively for the monitoring of UV-induced polymerization reactions. As shown in the present chapter starting from the pioneer work of Prof. Decker in the late 80s RT-FTIR has been proven to be a powerful technique, which allows following such reactions quantitatively, even if they occur in fraction of a second. Using this technique it is possible to calculate the conversion as a function of irradiation time during the progress of a reaction. From this data the polymerization rate can be calculated at any time, obtaining the true rate of photopolymerization and the amount of the residual reactive groups in the cured polymers. The efficiency of new photoinitiators as well as the reactivity of the different monomers can be studied in detail. Furthermore, the effect of experimental parameters on the photopolymerization rate and on the final conversion can be investigated in depth.

The RT-FTIR spectroscopy has a number of advantages over other existing methods:

- Real-Time monitoring, providing a species analysis of the quasi-instant liquid-solid phase change in a fraction of a second.
- The great sensitivity of IR spectroscopy allows very small changes in the monomer concentration to be detected.
- The kinetics of cure reactions can be studied over a very broad range of light intensity.

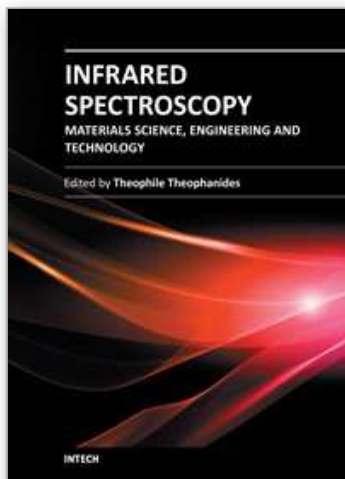
In spite of a number of advantages the RT-FTIR spectroscopy has also several limitations, such as:

- The sample thickness is limited to the range 1-100 μm .
- It is not possible to investigate samples containing black pigments and high concentration of other coloured pigments.
- The coatings support must be transparent to IR radiation.

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The present book is a definitive review in the field of Infrared (IR) and Near Infrared (NIR) Spectroscopies, which are powerful, non invasive imaging techniques. This book brings together multidisciplinary chapters written by leading authorities in the area. The book provides a thorough overview of progress in the field of applications of IR and NIR spectroscopy in Materials Science, Engineering and Technology. Through a presentation of diverse applications, this book aims at bridging various disciplines and provides a platform for collaborations among scientists.

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