# Cure Monitoring of UV-Curable Free Radical And Cationic Systems by Using In-situ Dielectric Analysis and Real-Time FT-Infrared Spectroscopy

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**Abstract**

In the present work, the photopolymerization kinetics has been studied by real-time infrared spectroscopy (RT-FTIR) and in situ dielectric analysis (DEA) . We were able directly correlate the dielectric properties of resins studied and the monomer conversion during the irradiation time. By monitoring changes in the electrical properties of the UV curable formulation, the polymerization rate and cure extent can than be determined in real-time. Dielectric analysis has become an effective instrumental method for monitoring a variety of polymer resin processing properties. This is because the dielectric properties are sensitive to the changes of resins properties linked to the mobility of the polymer molecules. A linear correlation was found between the dielectric loss factor and acrylate or epoxy monomer conversion for radical or cationic photopolymerization reactions. By this technique, for the same sample, others properties can also be monitored in on-line processing, such as  the diffusion properties in  coating films and the effect of moisture, the temperature, the viscosity, the Tg and the shrinkage. DEA measurements are especially attractive because information they have the potential of providing fundamental information on the curing processes and can be performed on-line in UV-curing industrial applications.

**Introduction**

The cure monitoring of the UV-curable formulation is usually carried out using a combination of techniques; differential scanning calorimetry [1], rheology, real-Time FTIR [2] spectroscopy analysis of the degree of reaction, fluorescence[3] spectroscopy for the monitoring of cationic photopolymerizations and recently dielectric analysis[4-6]. This article will only consider dielectric analysis. In this contribution, the kinetics of cationic and radical  photopolymerizations were investigated by using both *in situ* real-time FTIR spectroscopy and *in situ* Dielectric Analysis (DEA). For the first time, for a given UV curable formulation, we have established a correlation between the extent of monomer conversion during the photopolymerization and the dielectric properties of the polymer obtained.

Electrical conductivity measurements have been used for many years to follow the cure process in thermoset materials. The electrical conductivity of the material is usually a consequence of ionic impurities, (chloride ions in the case of epoxy resins) which are introduced during synthesis. As resin changes from a liquid to a solid, the electrical effects due to these conducting species will be reduced. Recently, dielectric analysis and frequency dependent electromagnetic sensing, has been extensively used for cure analysis [7,8].

This technique consists in applying a sinusoidal voltage between two electrodes placed in intimate contact with the material sample and the resulting sinusoidal current is measured. Dipoles in the material will attempt to orient with the electric field, while charged ions, present in the materials as ions, electrons, charged atoms or charged molecular complexes, will tend to move toward the electrode of opposite charge. As long as the frequency of excitation, the exact area of the electrodes and exact  distance

between the electrodes are know, the changes in amplitude and phase of the response may be converted into the fundamental dielectric properties, dielectric constant (permittivity) and dielectric loss factor[9].
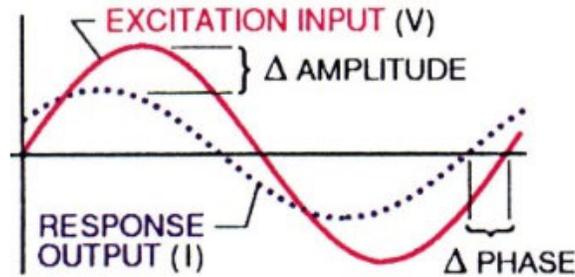


Figure 1 : Excitation and response between two electrodes

Prior work has shown that a strong correlation exists between the ionic mobility component of the loss factor and the mechanical viscosity during curing[5] . The ion viscosity (electrical resistivity), which specifically describes the ionic behavior in the loss factor, has similarly been shown to be more sensitive to change taking place at the cure monitoring. The relation between ion viscosity and resin viscosity can also be derived from theory [10]:

ion viscosity = bulk resistivity =  1/ (μ [C] q)
where μ = Ion mobility, [C] = Mobile ion concentration  and q = Charge of an Ion

All of the approaches used involve examination of the frequency dependence of the real ($\varepsilon^{'}$ ) and imaginary ($\varepsilon^{''}$ ) parts of the complex permittivity ($\varepsilon^{*}$ ). The permittivity and loss factor can be obtained as follows :

$$\varepsilon'(\omega) = \frac{C(\omega)}{C^0}, \qquad \varepsilon''(\omega) = \frac{G(\omega)}{\omega C^0}$$

where ($C(\omega)$) is the capacitance measured at frequency $\omega$, $C^0$ is the equivalent air capacitance of the capacitor, ($G(\omega)$) is the conductance at frequency $\omega$. Both the real and imaginary parts of ($\varepsilon^{*}$ ) can have an ionic and a dipolar component.

$$\varepsilon' = \varepsilon'_d + \varepsilon'_i, \qquad \varepsilon'' = \varepsilon''_d + \varepsilon''_i$$

The dipolar component ($\varepsilon_d^{'}$ )  arises from rotational motion of molar dipoles associated with the resin system. The ionic component ($\varepsilon_i$ ) arises from the constrained translational diffusion of charge, which is either trapped at the electrode surfaces or within the microstructure of the curing resin. In addition, the loss component ( $\varepsilon^{''}$ ) contains a contribution from the ionic conductivity which can be expressed by:

$$\sigma = \varepsilon_0 \omega \varepsilon(\omega)$$

where ( $\varepsilon_0$ )  is the permittivity of free space. The ionic component of the loss at higher frequencies can be subtracted to reveal the nature of the molecular dipolar contribution.
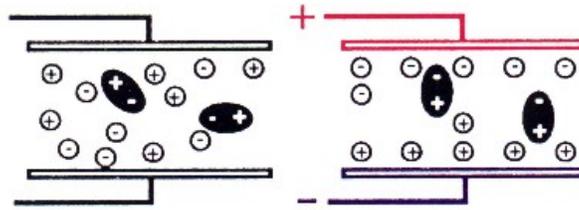
Figure 2 :  Dipolar and ionic behavior between two electrodes

**Experimental**

*Dielectric Measurement*

The instrument used in this study was a Micromet Instruments Inc DEA –231 single Channel mode.  The DEA 231/1 Cure Analyzer is a low cost dielectric cure monitoring system designed for applications where high measurement speed at only a single sensor location is required. The DEA 231/1 can measure at frequencies of 10, 100, 1000, and 10000 Hz at a maximum sampling rate of 55 milliseconds and can also accept inputs from a thermocouple, pressure sensor, and LVDT.
For all measurement the frequency 1000Hz was selected. The sensor used in this study is the MS-25 sensor, which has line widths and electrode spacing of 25 microns.
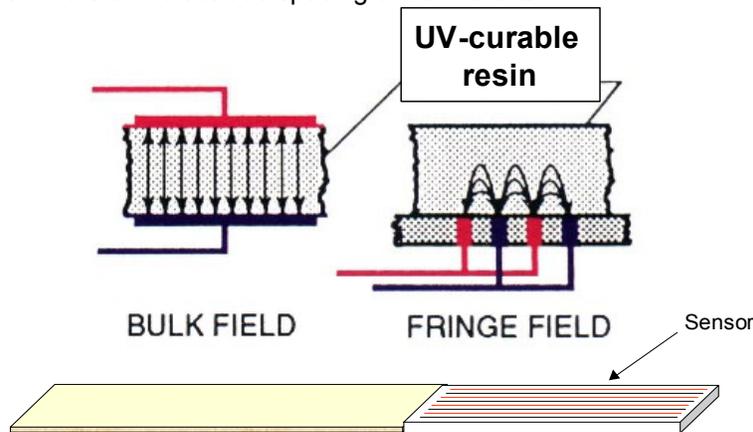


Figure 3 : Implantable Dielectric Sensors  Micromet MS-25

Dielectric sensors require intimate contact with the material under test. Sensors can be located on the surface or within the material. The sensors are operated by applying a voltage across the electrodes at a chosen frequency(s) and measuring the resultant change in amplitude and phase. From these properties the permittivity ($\varepsilon'$) and Loss Factor ($\varepsilon''$) are calculated. Ion Viscosity, or electrical resistivity, is extracted from the Loss Factor and is directly related to the mobility of ions in the material. For most polymers, ion viscosity follows closely the changes in mechanical viscosity and cure state. It is for these reasons that we have monitored in situ variation of Log (ion viscosity) upon Uv curing.

Surface, or fringe, measurement sensors are comprised of two planar interdigitated comb electrodes on an inert substrate and are available in a variety of electrode spacing configurations. The electrode line width and the spacing between the electrodes determines approximately how far into the material the fringe field will be measured. The MS-25 sensor used in this study has line widths and electrode spacing of 25-micron will measure approximately 25-micron depth into the material.

### *UV-curable formulation*

The photopolymerizable urethane acrylate formulation (Table 1) consisted of a mixture of acrylic monomers, such as hexanediol diacrylate (HDDA from UCB) and an aliphatic polyurethane acrylate ( Ebecryl-284 or Ebecryl-8402 from UCB). The following radical type photoinitiators were used in this study : Irgacure 819, Darocur 1173 and Irgacure 651 from Ciba SC at photoinitiators at typical concentrations of 1 wt% ,2 wt% and 2% , respectively.
The cationic UV curable formulation consisted of a mixture of a cycloaliphatic epoxy resin a Cyracure (UVR-6105) and aryl sulfonium salt photoinitiator (UVI-6976), both from Dow Chemical. The cationic photoinitiator was used at typical concentration of 2%.

| Formulation | W% |
|---|---|
| Ebecryl 8402 | 80 |
| HDDA | 20-X |
| Photoinitiator | X |

Table 1: UV-curable radical type formulation

### *Irradiation.*

The UV-curable formulation was applied onto a sensor or a $BaF_2$ crystal with a calibrated coater bar to obtain a layer with a typical thickness of 30µm. It was exposed for a short time to the radiation of a minicure lamp from EFOS, the UV light intensity at the sample position being set at 300mW $cm^{-2}$. The light intensity at the sample position was measured by radiometry (international light-IL –390),. All the experiments have been performed at ambient temperature in the presence of air.

The extent of the polymerization reaction upon UV exposure was evaluated quantitatively by Real-Time FTIR infrared spectroscopy [2,11] by following the decrease of the IR band at 810 $cm^{-1}$ characteristic of the acrylate double bond, or at 790 $cm^{-1}$ characteristic of epoxy for the cationic formulation. This analytical method permits one to determine the final conversion, and thus the amount of residual unsaturation in the UV-cured resin
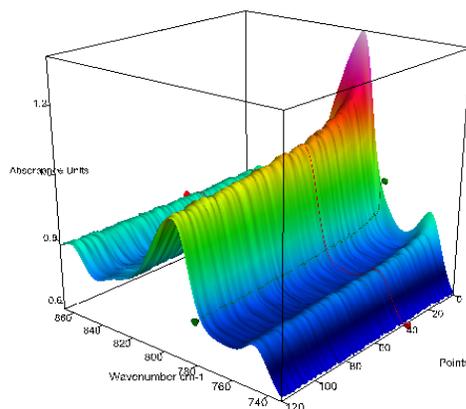


Figure 4. Polymerization 3D profiles recorded by RTIR spectroscopy for the cationic formulation resins exposed to UV radiation I = 300 mW $cm^{-2}$.

**Results and discussion**

Figure 5  shows as example a typical decrease of the permittivity $\varepsilon$' ($\omega$) at 1000 Hz upon UV irradiation of the UV-cationic formulation film [thickness 24µm]. AS polymerization proceeds the resin viscosity increases and which affect ionic motion; dielectric measurements retain sensitivity past the time when ion and physical viscosity deviate. Consequently, with proper interpretation, dielectric measurements are useful throughout the entire cure for determining changes in viscosity and rigidity, and are extremely sensitive in determining the end of cure. This example, shows that we can follow the reaction of photopolymerization reaction with high-resolution data collection evry 50 milisecondes.

Permitivitty ($\varepsilon$ ' )
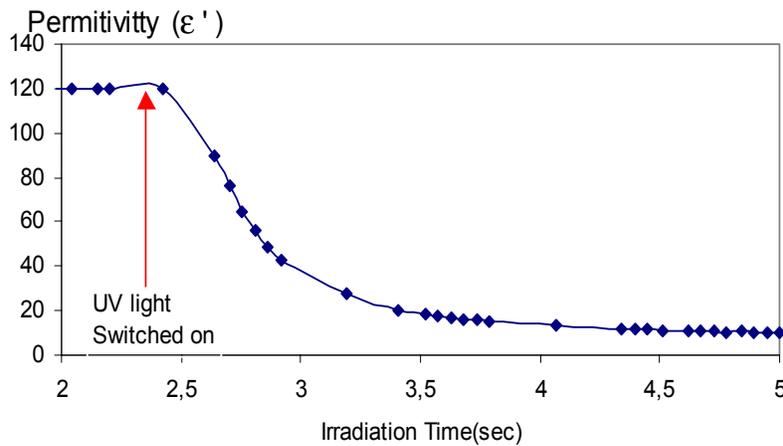


Figure 5 : Permittivity *vs.* irradiation time for the UV-curable cationic formulation (Cycloaliphatic epoxide)

Afterward we will focus our study only in the Log (ion viscosity), which describes in a complete way all dielectric properties of our obtained UV curable polymer materials.

The figure 6 shows the  Log (ion viscosity) data during the cure of an UV-curable sample. As the irradiation time increases, the  photochemical reaction is initiated (causing decreased ion mobility due to crosslinking) and reaction competes with the exothermic temperature effect.  This results in Ion Viscosity followed by a rapid increase in viscosity as reaction begins to dominate. Gradually, as the reaction slows down, the rate of increase in ion viscosity also slows; showing the cure is near completion. As cure proceeds, the physical nature of the UV curable mixture changes from a Newtonian fluid to a gel and finally a glassy solid [12]. Gelation corresponds to the point at which an infinite network is formed. While the vitrification is the point at which the chains become closely packed and there is insufficient volume for co-operative motion to occur. At vitrification, the material changes from a rubber to a glass and reaction is effectively quenched for those reactions where intramolecular reactions are not important.
We notice the same tendency between both curves representing respectively the Log (Ion viscosity) and epoxy conversion (Figures 6 & 7 ).

**1.  Correlation between Log (ion viscosity) and monomers conversion**

Log(Ion Visc)



Epoxy Conversion%          6105  2%
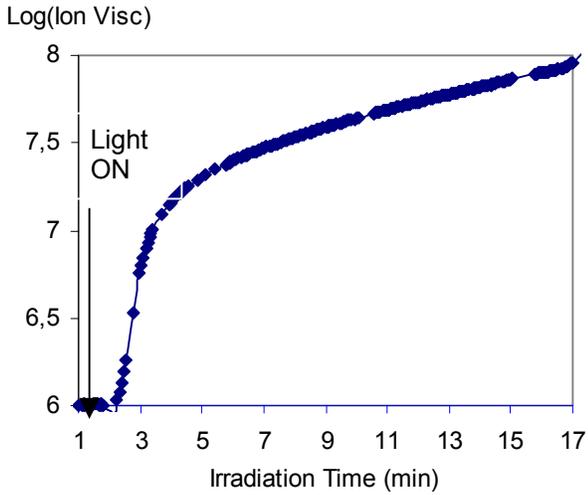


**Figure 6**. Plot of  the Log (ion viscosity) vs. irradiation time, for cationic formulation based on cycloaliphatic epoxide
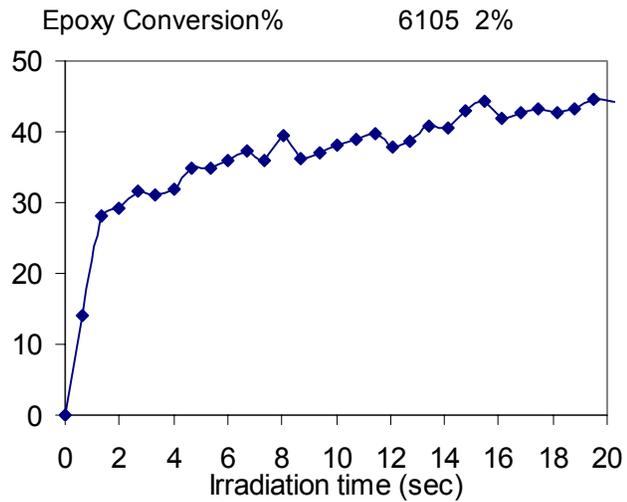
**Figure 7**. Polymerization profiles recorded by RT-FTIR spectroscopy for cationic formulation

**Log (Ion Visc )**



$y = 0,0583x + 5,7405$

$R^2 = 0,9743$
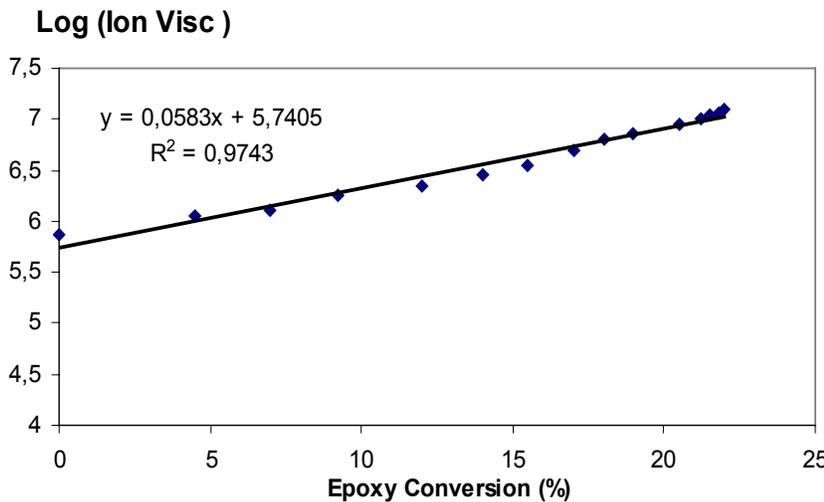
Figure 8 : Linear correlation between the Log (ion viscosity) and the monomer conversion ; for the UV curable cationic formulation

ith the epoxy conversion.  With these

This technique could supply to the manufacturers and industries that use the UV-curing  technology a reliable and fast method for the control in online process the curing of the UV curable coatings and materials

The same trend was observed for the UV curable radical type acrylate resin. A linear correlation was found again between the Log (ion viscosity) and the cure extent of the acrylate monomer monitored by real time by IR spectroscopy (Figures 9 and 10).
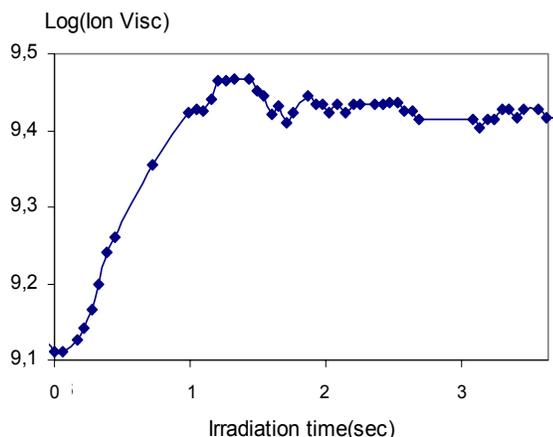
**Figure 9**. Log(ion viscosity) vs. irradiation time, for Uv curable radical formulation
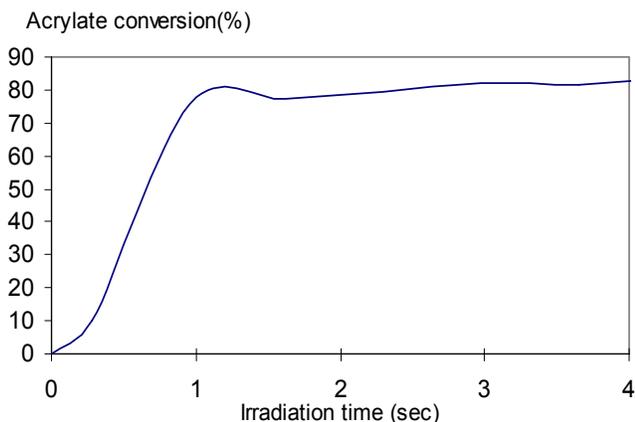


**Figure 10**. Polymerization profiles recorded by RT-FTIR spectroscopy. [Irgacure 651] = 2 wt%.  I = 300 mW cm$^{-2}$.



$$y = 0{,}0038x + 9{,}1491$$
$$R^2 = 0{,}9818$$
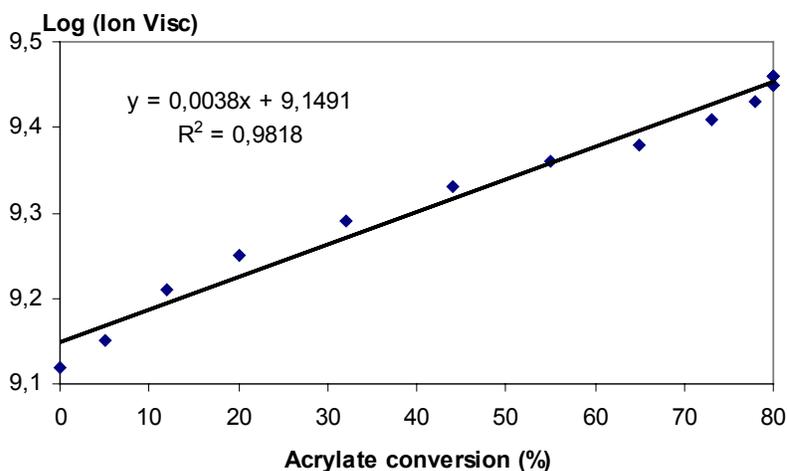
Figure 11                          :Linear correlation between the Log (Ion Viscosity) and the monomer conversion ; for the UV curable acrylate resin

## Conclusion

This study has outlined some of the applications that have benefit from the ability to perform real-time dielectric measurements. For the first time we have established the linear correlation between the two very efficient analytical method: the real-Time FTIR and *In situ* Dielectric analysis (DEA). It clearly appears that the DEA analysis shows a very fast and easily manageable on-line process control of the UV curing process and should be useful in monitoring such UV ultrafast reaction commonly used in coatings, composites, adhesives and others industrial applications.

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