Analysis of UV-Curable Resins by FT-IR

Introduction

There are on the market an increasing number of special adhesives, coatings and sealants that allow curing in just few seconds upon exposure of the resin to the appropriate radiation. Those adhesives are gaining great interest in specialized applications (medical, glass and lighting repairs, rapid prototyping, etc.) because they allow accurate and immediate bonding and avoid some of the more problematic aspects like toxicity, polluting and organic solvent formulations of conventional adhesives.

Typically these resins cure by using UV and, more recently, visible radiation to initiate a photochemical reaction that proceeds to the curing of the resin. Many parameters may affect the speed and depth of the curing, including the intensity of the illumination, the spectral range used during the curing (single wavelength or range of wavelengths), thickness of the curing area, distance to the light source, transparency of the substrate the light must pass through, and many other environmental parameters, such as nature of the material to bond and presence of external oxidizing materials, that affect the time of hardening the adhesive.

It is important to have a good understanding not just of the speed of cure but also of the mechanism of the curing process. One way to investigate and quantify the curing process is to measure spectroscopic changes of the functional groups involved in curing. The formation and destruction of functional groups is easily followed by rapid scan FT-IR. Determining relative peak areas can help to understand the kinetics process and identifying the presence of reaction intermediates can help to understand how changing conditions affect the curing process.
Many photo-curable adhesives, coatings and sealants are based on acrylates. The curing process involves a photo-initiator that forms free radicals when exposed to UV radiation. The radicals react with acrylate monomers, opening the double bonds to form further radicals. These react with further acrylate molecules, building up bands with cross-linking to provide a network that gives mechanical strength to the cured product. The kinetics of the curing process depends on the generation of the reaction intermediates, so their detection, characterization and quantification are fundamental to understanding the properties of a resin.

Monitoring the reaction

Numerous techniques have been used to study the curing process. Differential scanning calorimetry (DSC) measures the heat produced by the reaction and so can determine the degree of cure as the reaction proceeds. Dynamic mechanical analysis ( DMA) measures the modulus of the resin so that the properties of the cured material can be related to the degree of cure. FT-IR spectroscopy provides more chemical information than DSC because many absorption bands are measured. For example in an acrylic resin the curing process involves the disappearance of C=CH₂ groups in the monomer. The progress of this can be followed by measuring the intensity of absorption bands that are specifically associated with these groups, such as the C=CH₂ twisting at 812 cm⁻¹ or the =CH₂ deformation near 1400 cm⁻¹. No bands are completely free from overlap which hinders kinetic analysis but qualitative measurements are straightforward. Figure 4 shows the decay in absorbance of the 812 cm⁻¹ band for two different UV intensities. However disruption of the double bond is only the first step in the reaction as radicals produced by photoinitiation react with acrylate groups and cross-linking proceeds.

An overview of the reaction is obtained by applying principal components analysis (PCA) to the data. For a simple reaction there should be a single principal component representing the difference in spectra between the starting material and the product. For the resin studied here we consistently find two principal components. The first PC accounts for about 99% of the variance while the second PC accounts for the remaining variance except noise. The scores for the first PC correspond to the overall reaction, changing monotonically, but the scores for the second PC reach a peak during the most rapid phase of the reaction Figure 5. Thus the second PC can provide information about the intermediate stage of the reaction that is not available from DSC measurements.

Experimental

Spectra were measured with a Frontier™ FT-IR spectrometer, a research grade instrument with fast scanning, collecting up to 16 scans/second which is more than sufficient to follow reactions with half-lives of a few seconds. Data collection was controlled using PerkinElmer® TimeBase™ software. The same software can generate profiles of specific band intensities or intensity ratios as a function of time. Data were also analyzed with Principal Components Analysis (PCA) using the QUANT+ program.

The most convenient approach to making these measurements is to use a diamond ATR accessory. The liquid resin is placed on the diamond crystal and illuminated from above. We used a UATR accessory with a single-bounce diamond crystal (Figure 1). The UV source was an Omnicure® S2000 and fiber-optic light guide with variable output, providing radiation from 320 to 500 nm.

The resin was Loctite® 3494, a clear light cure adhesive used for bonding glass and plastics.³ It contains a mixture of acrylic and methacrylate monomers with a benzoyl phosphine oxide initiator. We verified that curing was extremely slow under the background laboratory illumination.

A drop of resin was placed on the crystal and the UV illumination was switched on a few seconds after starting data collection. Spectra were recorded with 16 scans/second. Two illumination levels were used, 10 and 50% of the maximum, corresponding to outputs of 75 and 430 mW at 365 nm.
Results
Spectra of the initial and fully cured resins are seen in Figure 3. Typical intensity profiles derived from the \( =\text{CH}_2 \) twisting vibration at 812 cm\(^{-1} \) are shown in Figure 4. The profiles are taken from 800 scans obtained in 50 seconds. The reaction is much faster with the higher illumination level, being nearly complete after 10 seconds.

The results from PCA for the two illumination levels are seen in Figure 5. Clearly they show the same pattern, the scores on PC2 peaking in both cases at the time that scores on PC1 are changing most rapidly.

Discussion
These data clearly show the suitability of the Frontier spectrometer with TimeBase software for studying the UV curing process. PCA demonstrates that the data contain more information than can be obtained from UV-DSC measurements as an intermediate process is revealed. The complexity of this commercial formulation makes interpretation difficult but investigation of simpler systems would be feasible.

Using ATR is very convenient and allows UV illumination without an intervening window. One limitation is that curing is being measured only for the layer in contact with the crystal. In this case the amount of the resin as uncontrolled but curing at different depths can be studied by varying the thickness of the resin layer.

Reference

Figure 3. ATR spectra of Loctite® 3494 resin before and after curing.

Figure 4. Intensity profiles of the \( =\text{CH}_2 \) twisting band at 812 cm\(^{-1} \) for different illumination levels.

Figure 5. Principal component scores for resin curing at different illumination levels.