PHOTOACOUSTIC FT-IR SPECTROSCOPY AND CROSSLINKING OF ORGANIC COATINGS

Marek W. Urban
Department of Polymers and Coatings
NORTH DAKOTA STATE UNIVERSITY
Fargo, ND 58105
USA

ABSTRACT

The primary objective of this paper is to explore several new avenues for monitoring crosslinking processes in organic coatings using photoacoustic Fourier transform infrared spectroscopy (PA FT-IR). This paper highlights a few novel approaches to the in-situ analysis of crosslinking reactions and the processes associated with it. It is shown that PA FT-IR can be employed not only for the studies of crosslinking reactions, but also for a quantitative analysis of volatile organic content in coatings. Furthermore, adhesion of organic coatings to thermoplastics as well as the possibility of re-crystallization processes occurring on polymeric substrates will be discussed in view of the newly developed rheo-photoacoustic FT-IR technique. The principles of photoacoustic FT-IR detection will be also presented.

KEYWORDS

Photoacoustic Fourier transform infrared spectroscopy, time-temperature-transformation, crosslinking on thermoplastics, rheo-photoacoustics.

INTRODUCTION

Although crosslinking reactions have been known and utilized for a long time, relatively little is known about molecular processes governing chemical reactions leading to crosslinking. Although theoretical approaches might have shed some light on the principles of crosslinking, in practice, there is a need for experimental methodology that would allow monitoring not only molecular level processes occurring during crosslinking, but also other processes associated with this process. After all, during crosslinking, small chemical changes lead to apparently significant physical changes. Furthermore, thermodynamic principles teach us that during crosslinking, entropy of the system decreases, as oligomer or usually small crosslinker molecules react with each other forming polymer network. As these molecules react, they undergo a transition from highly disordered liquid state to somewhat more ordered "network" with restricted mobility of freedom. This process can be compared to freezing of gaseous molecules during which very mobile gas molecules loose their translational and rotational motions. For such ideal gas, it would imply that gaseous molecules move freely within the boundaries of occupied volume. Following the ideal gas behavior and thermodynamics, the heat capacity of such species will be 3/2RT, where each 1/2RT comes from translational, vibrational and rotational degrees of freedom. As the molecules freeze, they loose their translational and rotational motions and the heat capacity will be reduced to 1/2RT. In view of the above considerations, the crosslinking of amorphous polymers is a similar process, and the measurements of heat capacity changes would require a technique that is sensitive to the thermal property changes during crosslinking. As we will see later on, such opportunity may offer photoacoustic FT-IR spectroscopy which should be considered not only as a spectroscopic method of recording an infrared spectrum, but as a calorimetric method monitoring the amount of electromagnetic radiation converted to heat.[1,2]
Figure 1 schematically depicts the generation of photoacoustic signal. The modulated infrared light with intensity $I_0$ enters the sample with refractive index $n$ and absorption coefficient $\beta$. The intensity of the infrared radiation diminishes exponentially as it penetrates the sample, giving rise to the intensity at depth $x$:

$$ I(x) = I_0 (1-n) \exp(-\beta x) $$

Figure 1. Schematic diagram of the photoacoustic detection.

The amount of light absorbed within the thickness $x$ is equal to:

$$ E(x) = \beta l(x) = \beta I_0 (1-n) \exp(-\beta x) $$

The depth of optical penetration is defined as optical absorption length, $L_p$, and is inversely proportional to $\beta$:

$$ L_p = 1/\beta $$

In other words, this is the distance from the surface at which the initial intensity, $I_p$, attenuates to $(1/e)I_p$. The absorbed energy is released in a form of heat which is transferred to the sample surface. The efficiency of the heat transfer is determined by the thermal diffusion coefficient of the sample, $\mu_T$, and the modulation frequency of the incident radiation, $\omega$:

$$ \mu_T = [\omega/2\alpha]^{1/2} $$

where $\alpha$ is the thermal diffusivity ($\alpha = k/\rho c$; thermal conductivity/(density x specific heat)). The thermal diffusion length, $L_{\mu_T}$, is related to the thermal diffusion coefficient, $\mu_T$:

$$ L_{\mu_T} = 1/\mu_T = [2\alpha/\omega]^{1/2} $$

The amount of heat periodically transferred to the surface through the sample is then equal to:

$$ H(x) = E(x) \exp(-\mu_T x) = \beta I_0 (1-n) / [\exp(-\beta x) + \mu_T x] $$
As was indicated in the introductory part, the amount of heat periodically transferred to the surface depends upon the thermal properties of the sample [5,4] and, if thermal properties change during crosslinking, the photoacoustic intensity will also change. The thermal property changes may be reflected in either the changes of gaseous content above the coating or in changes of thermal properties during crosslinking.

**CROSSLINKING AND PHOTOACOUSTIC EFFECT**

A protective action of coatings on various substrates greatly depends upon the crosslinking reactions on the surface. These, in turn, dictate a lifetime of adhesion and corrosion protection. With this in mind, let us focus on the crosslinking processes of amorphous polymers. This process, regarded as a formation of the crosslinked polymer network, involves transition from liquid to solid via chemical reactions which result in the increased molecular weight. During the molecular weight build-up, thermal properties also change. As we recall eqs. 5 and 6, photoacoustic detection is a two-stage process, and the second stage involves heat propagation to the surface. Therefore, in an effort to establish how thermal property changes during polymer network formation may affect photoacoustic intensity, let us compare the crosslinking processes of hydroxyl-terminated poly(dimethyl siloxane) detected by transmission and photoacoustic FT-IR modes of detection.[5] Figure 2 illustrates a log plot of the intensity changes observed in transmission and photoacoustic measurements as a function of log viscosity during crosslinking. It is quite apparent that photoacoustic measurements are sensitive to the viscosity changes, and parallel transmission measurements appear to show no changes resulting from crosslinking. The latter is associated with the fact that during crosslinking reactions only small number of crosslinks is present compared to the number of other bonds in the system.

![Figure 2: Log-log relationship between PA and transmission intensities plotted as function of viscosity of poly(dimethyl siloxane) (PDMS) and tetrathioxysilane (TES).](image)

Furthermore, during crosslinking of this particular system, the Si-OH bonds of PDMS and H2C2-O-Si of TES break to form the Si-O-Si network and ethanol. Thus, the simultaneous cleavage and formation of energetically similar bonds results in a heavy spectral overlap of strongly absorbing bands, making transmission measurements alone not sensitive to the crosslinking process.

Other example of PA FT-IR sensitivity in monitoring crosslinking reactions is polyester-styrene system. This system crosslinks by a free radical mechanism, such as shown below.[6]
Let us focus on the intensity changes of the C-H bending mode of styrene as a function of time. Figure 3 illustrates two crosslinking reactions conducted at 15 and 30°C. While in the case of crosslinking process at 15°C, a steady, linear decrease of intensity is initially observed, after 6 hrs., the slope of the line changes. In contrast, the same process conducted at 30°C indicates two breakpoints. In an effort to further understand this temperature dependence, isothermal experiments covering the temperature range from 15 to 40°C were conducted and the temperatures of the breakpoints were plotted as a function of log time. This is illustrated in Figure 4 and indicates that two curves are observed. They are attributed to gelation and vitrification processes of the system. At the initial stages of crosslinking, the process is kinetically controlled until molecular weight builds up, leading to gelation. Then the process becomes diffusion controlled. Depending upon the cure temperature and T_g of the system, one or two transitions are observed. The second transition occurs at higher temperatures and is attributed to the vitrification process during which a sol/gel glassy state is generated. To our knowledge, this is the first spectroscopic evidence showing a time-temperature-transformation dependence.

Figure 3. Integrated intensity of the C-H bending mode at 775 cm⁻¹ plotted as a function of time.

Figure 4. Time-temperature-transformation diagram for the polyester-styrene system.
In the previous paragraphs it was shown that photoacoustic FT-IR spectroscopy may be used in the analysis of crosslinking reactions. Although such measurements are relatively simple, their interpretation often involves the analysis of gaseous and liquid components of the crosslinking system. The presence of gaseous phase comes from volatile species, such as low molecular weight solvent or crosslinker molecules, which may significantly contribute to the photoacoustic signal intensity. Detection and quantitative analysis of volatile species is particularly important because it may further enhance the understanding of crosslinking reactions by considering the equilibrium thermodynamics between species in a vapor and the same species reacting in a resin. Furthermore, the amount of solvent molecules escaping a crosslinking mixture is important because of various environmental concerns; in particular, volatile organic content (VOC). As we recall Figure 1, infrared light "sees" both gaseous and liquid/solid components of the sample, and in order to determine only gaseous phase, IR beam needs to be blocked so, the modulated infrared light will not "see" liquid/solid phase. For that reason, we developed so-called "photoacoustic umbrella" which, is essence, is a cover for a liquid/solid fraction of the sample, but allows gaseous phase to be seen by infrared light.[7] Figure 5 illustrates this modification, which allows isolation of the photoacoustic signal attributed to the gaseous and solid/liquid components of the sample. Such configuration allows not only a detection of vapors in the concentration range of parts per billion, but also isolation of the species present in a vapor phase. The latter is attributed to the fact that each species exhibit characteristic IR bands which can be identified and subsequently quantified.

![Diagram](image)

Figure 5. Photoacoustic "umbrella" utilized for the analysis of gaseous species in equilibrium with a resin.

In many practical applications, mixed solvents are often used for improved control of film formation and others. In general, photoacoustic vapor intensities of two solvents are two-variable functions of both concentrations. The VOC measurement would be simplified if the photoacoustic vapor intensity of each solvent was determined by its weight per unit volume of the solutions. In such cases, the VOC value of each solvent can be calculated simply from the calibration curves established in the absence of other solvents. The validity of such assumptions can be quickly determined by comparing the sum of VOC values for individual components with a total VOC calculated from the results of non-volatile content measurements. Normalized PA vapor intensity of a paint thinner, added to an alkyl solution that contains 65 w/v% of other solvent can be plotted as a function of the VOC values. The coefficients of the best fit second-order polynomial function is given by:

$$PA_i = PA_i^0 + A \times VOC_i + C \times VOC_i^2$$

where $PA_i$ is the PA vapor intensity of the added thinner and $PA_i^0$ is the PA saturated vapor intensity.

The vapor phase alone above a polymer mixture that undergoes crosslinking reaction can be used as a probe for monitoring crosslinking reactions. This is particularly useful in the cases where volatiles are involved in the crosslinking process. Figure 6 illustrates an example of styrene/polyester resin in a ratio of 35/65 w/v % cured at 40°C. Although in order to provide a detailed analysis of this data it is necessary to know diffusion and activity coefficients, this Figure illustrates again that there are two transitions during crosslinking, indicating that for this particular system either vapor analysis in equilibrium with the resin alone or the analysis of both vapor and resin leads to similar results.
CROSSLINKING ON POLYMERIC SUBSTRATES

It is well known that adhesion of organic coatings to thermoplastics may be difficult and in many cases is simply impossible. It is also known that the low surface tension of thermoplastic substrates results in poor wetting and therefore, problems associated with interfacial stability are of significant concern. What is not adequately understood are the molecular level processes occurring between two substances. The importance of these processes comes from the fact that they ultimately govern the interfacial reactions and stability which, in turn, governs adhesion. In response to these difficulties, we have recently developed rheo-photoacoustic FT-IR (RP-PA FT-IR) technique which allows monitoring interfacial stresses developed at the polymer-polymer interfaces.[8,9] In essence, it is a "chemical Instron" which induces stresses at the interface by stretching plastic substrate only. Figure 7 schematically illustrates this elongational process.

Figure 6. Photoacoustic intensity of the styrene vapor for a 65/35 w/w% styrene/polyester ratio.

Figure 7. A schematic representation of inducing shear interfacial forces (only external forces are imposed on a substrate).
Such approach results in the generation of shear forces at the interface which, in turn, cause distortion of the thermal waves propagating through the interface, thus allowing detection of the molecular processes responsible for failure.

Although during the course of this study, various polymeric substrates were examined, here, we will focus on one example illustrating the effect of pendant methyl groups in polypropylene (PP) on the crosslinking of vinyl-terminated polydimethylsiloxane. For this reason, isotactic polypropylene containing approximately 10% of syndiotactic stereoisomer was used as a substrate, and vinyl-terminated PDMS was crosslinked on its surface. Figure 8. A illustrates RPA FT-IR spectra in the C-H stretching region of a double layer sample at various elongations. For comparison, Figure 8. B illustrates the same measurements, but on PP film only. The X axis is the wavenumber axis, whereas the Y and Z directions are the extent of elongation and RPA FT-IR intensity.

Figure 8. A - Normalized RPA FT-IR spectra of vinyl-terminated PDMS/PP double layer samples in the 3025-2750 cm$^{-1}$ region; B - RPA FT-IR spectra of PP alone. All spectra were recorded as a function of elongation.

The intensity changes observed in Figure 8, A are similar to that previously observed for polyethylene [8] and are observed only when PDMS coating is deposited on PP. Similarly to the previous studies, these data again indicate that microvoids are being formed at the interface, such as depicted in Figure 7. This is manifested by the band increase at about 3 % elongation, attributed to a signal leakage at the interface [7]. As shown in Figure 8, B, no intensity changes are observed for the PDMS coating and PP substrate alone. However, external forces imposed on the PP substrate may cause crystallinity changes within the substrate. In an effort to identify this possibility, X-ray diffraction (XRD) experiments were performed. As illustrated in Figure 9, traces A, the presence of crystaline structures in PP is clearly observed and elongation up to 20 % (trace B) does not generate new XRD peaks. This observation is in agreement with the previous studies, which indicated that the elongations of an order of 50 % and above cause crystallinity changes.[10]
Figure 9. XRD patterns of: A - Polypropylene (PP) (no elongation); B - Polypropylene (20% elongated); C - vinyl-terminated PDMS/PP (no elongation); D - vinyl-terminated PDMS/PP (5% elongation); E - Vinyl-terminated PDMS coating alone; F - aluminum backing alone.

The situation, however, changes drastically when vinyl-PDMS film is deposited on the same PP substrate. In this case, which is illustrated in Figure 9, trace C, a new X-ray band corresponding to a d-spacing of 5.67 Å is detected, along with the splitting of a broad amorphous band to two bands corresponding to d-spacings of 4.29 and 4.17 Å. Apparently, elongation does not affect these results (trace D) and these changes are not observed for the individual components (traces A, B, E). While XRD peaks illustrated in Figure 9, trace A, are attributed to isotactic PP, the new XRD peaks are due to a syndiotactic counterpart. Since isotactic PP cannot be converted to syndiotactic polymer without breaking C-C bonds of the polymer backbone, our hypothesis is that a fraction of the syndiotactic form recrystallizes at the interface as a result of the following mechanism: initially liquid vinyl-terminated PDMS partially dissolves PP surface, and as PDMS crosslinks, it immobilizes PP macromolecules, causing their recrystallization. If, however, the above assessments are correct, a preferential solubilization of the syndiotactic form should occur. Indeed, the solubility data indicates that the isotactic form dissolves in common solvents, but only at elevated temperatures, whereas syndiotactic stereoisomer can be solubilized in the same solvents even at room temperature. Therefore, based on the solubility experiments and associated differences between each stereoisomer, it is believed that the higher solubility of the syndiotactic form leads to higher concentrations of this form at the interface. Figure 10 schematically illustrates the processes occurring as PDMS and PP surfaces are being brought to contact. The above assessments were also supported by the presence of syndiotactic bands in ATR FT-IR spectrum of PP surface after removal of the PDMS coating.
Figure 10. A schematic representation of processes leading to the enhanced concentration of syndiotactic PP at the interface.

CONCLUSIONS

These studies illustrate that photoacoustic FT-IR spectroscopy exhibits a useful sensitivity to the in-situ monitoring of crosslinking reactions and it can be used to quantify a low level VOC in coatings. Furthermore, rheo-photoacoustic FT-IR is sensitive to the polymer/polymer interfacial interactions and adhesion. In the case of PDMS/PP, it is found that interfacial recrystallization of polypropylene occurs.

REFERENCES