

Time-Based FT-IR Analysis of Curing of Polyurethanes

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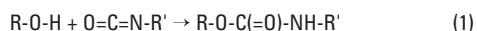
Introduction

The construction and automotive industries make use of a huge number of vendors, supplying anything from raw materials to complete assemblies. Among the critical components for both industries are adhesives and sealants. Each application requires specific characteristics, including curing conditions (temperature, moisture and speed of cure) and long term material properties, such as flexibility, UV resistance and bond strength.

The curing and working properties of adhesives generally result from polymerization reactions, which form a lattice of chemical bonds. Basic chemical kinetics identifies four steps in these polymerizations – initiation, propagation, termination and branching. The relative rates of these determine the properties of the final polymer. For instance, the termination step can control overall polymer chain length, branching impacts the cross-linking, and propagation rate determines curing times.

The initiation step is critical. Early initiation may result in ruined product, while sluggish initiation can lead to poor or slow curing. The initiation can be stimulated chemically, as in most two-part epoxies (the hardener stimulates a reaction in the resin), via UV-irradiation (many modern dental sealants) or using temperature. Storage needs require that the initiation reaction be halted until the proper moment. Urethanes provide an excellent example, where the initiation step can be blocked until heat is applied. Failing to do this can result in railroad cars filled with solid, useless, product.

The polyurethane reaction starts with a diisocyanate (or a poly-isocyanate) reacting with a comonomer like an alcohol (frequently a diol):



Thiols and amines can also be used (instead of the alcohol) – it is the reactivity of the acidic hydrogen which drives the reaction. This reaction can be very rapid, even at room temperature, so the liquid mixture rapidly becomes a solid. This rapidity can be used to produce unique products. For instance, during manufacturing,



Figure 1: Examples of items produced from polyurethanes. Photo of parts provided by Plastics International.

a little water can be added to the reaction mixture. The water reacts with the diisocyanate to produce a diamine and CO₂. The CO₂ forms bubbles in the reaction mixture which are trapped within the rapidly forming polymer matrix, yielding polyurethane foam.

Shipping and storage of the liquid urethanes requires preventing the reaction (1) from occurring. This can be done by reacting the isocyanate with a “blocker”:



where BH is the blocking agent. The blocking group can be eliminated at elevated temperatures, yielding the reactive isocyanate and initiating the cross-linking reaction. Different blocking agents will eliminate at different temperatures, so research into the best adapted blockers (least toxic, lowest deblocking temperature, etc.) is underway.

A key part of investigating blocking agents requires studying the temperature dependence of the initiation and the time-evolution of the reaction mixture. Infrared is ideally suited to this, as the spectrum gives specific information regarding the progressing reaction. In the study highlighted here, FT-IR was able to elucidate both the progression and the mechanism for a crosslinking reaction.

Experimental

A Thermo Scientific Nicolet™ FT-IR spectrometer was used to collect infrared spectra at 15 second intervals, using 8 scans at 2 cm⁻¹ resolution. The spectrometer was equipped with a KBr beam splitter and a DTGS detector. Our OMNIC™ spectroscopy software with the time-based Series™ software module was used to collect, process and present the data.

A perfluoropolyether diol (PFPE, Solvay Solexis) was mixed with ketoxime blocked isophorone diisocyanate (K-IPDI or IPDI once unblocked, Hüls-Degussa) in butyl acetate. This mixture was placed into a variable temperature cell, which was purged with dry air to remove volatiles during the reaction. The data reported here were obtained with an operating temperature of 150 °C.

Key Words

- Adhesives
- Curing
- OMNIC Software
- Sealants
- Series Software
- Urethanes

Discussion

Table 1 gives the assignments for some of the observed infrared peaks.

Peak Location (cm ⁻¹)	Chemical Structure	Motion
3420-3200	N-H	Stretching
3000-2800	CH ₂ and CH ₃	Stretching
2260	NCO	Stretching
1740	C=O	Non-bonded urethane stretching
1690	C=O	Associated urethane and isocyanurate ring stretch
1510	H-N-C=O Amide II	Combined motion

Table 1: Assignment of major peaks, from references 1 and 2

Figure 2 shows individual spectra taken at a series of time slices, and Figure 3 shows a large region of the dataset in the 3-D presentation of Series software. The 2260 cm⁻¹ NCO peak can be seen to grow after initiation (as the blocker is removed), then disappear as the polymerization proceeds. The N-H blocking agent peak at 3420 cm⁻¹ disappears rapidly. This is more clearly shown in the functional group time profiles in Figure 4.

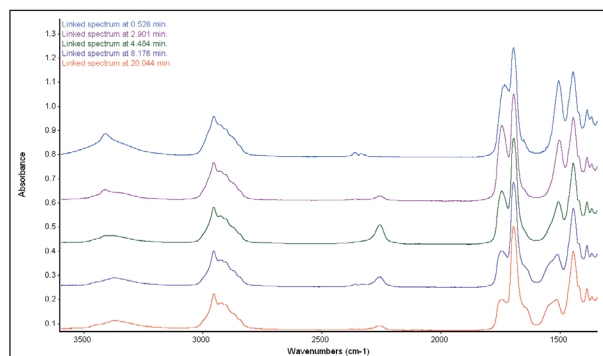


Figure 2: Time slices of spectra for the blocked urethane

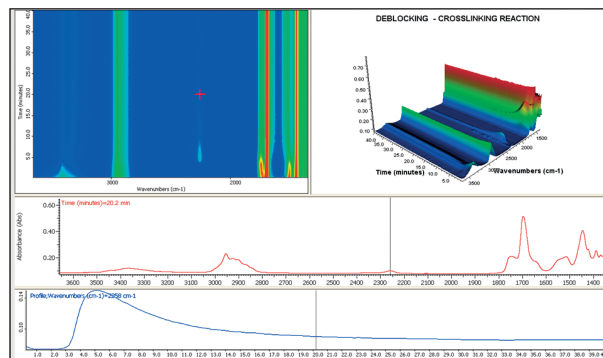


Figure 3: 3-D presentation of entire Series data set for the curing of the blocked urethane

The intriguing aspect of this analysis is the insight into the reaction mechanism obtained from the profiles. Reactions (1) and (2) can occur sequentially (elimination (2) followed by addition(1)) or in a concerted manner (addition of the alcohol to the blocked isocyanate followed by elimination of the blocker). In the first case, the isocyanate

intermediate would form immediately after the removal of the blocker, in the latter, the isocyanate would not form, or would form only later as thermally induced reversions

of the urethane to the isocyanate. The data shown in Figures 3 and 4 supports the latter mechanism. The isocyanate does not form immediately upon unblocking, but shows a time delay consistent with thermal reversion of the urethane.

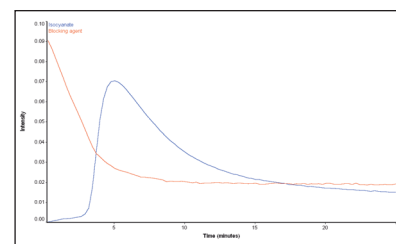


Figure 4: Time profiles of the intensity of the NCO and NH (blocking agent) during reaction

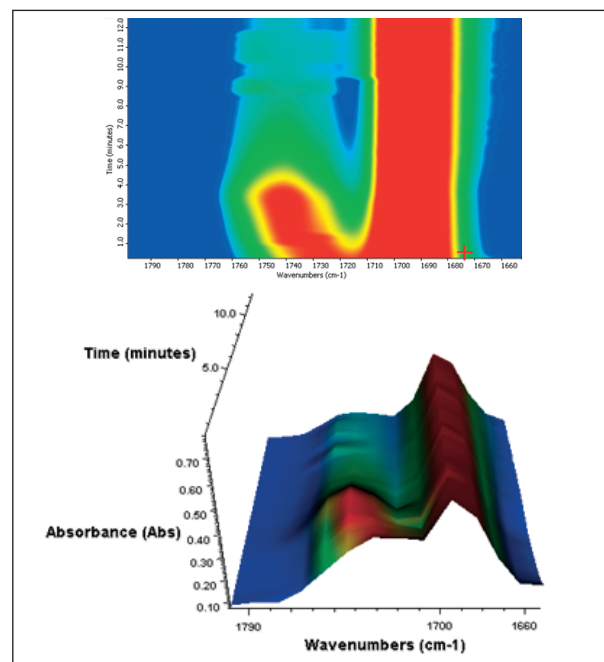


Figure 5: Contour and 3-D plot showing the shifting of the C=O peak as discussed in text

Additional support for this mechanism is provided by the shift of the C=O band from 1734 to 1744 cm⁻¹. This is seen clearly in the contour and 3-D plots of a narrow region shown in Figure 5. The shift in the carbonyl peak is typical for urethanes close to fluorine.

Conclusion

The study of polymerization reactions requires the ability to take spectra against a time base under a wide range of conditions. The OMNIC Series software allows complete control over the experimental conditions, data collection parameters and starting trigger point. Further, the presentation capabilities provide excellent insights into subtle changes within the spectra.

Acknowledgement

The data was kindly provided by Solvay Solexis (<http://www.solvaysolexis.com/>). The analysis is largely based upon the discussion in the first reference.

References

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2. Turri, S.; Scicchitano, M.; Marchetti, M.; Sanguineti, A.; Radice, S. in *Fluoropolymers 2: Properties*, (New York, Kluwer, 1999), p. 145.

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