Specac

Application Note

Multi-day Batch Reaction Monitoring of Packaging Adhesives with the Arrow™ consumable ATR

Specac Quest and Arrow ATR

INSIDE: Find out how Arrow opens the door to routine batch ATR in multiple day experiments and handle difficult to clean samples.

Introduction

Conventional lamination adhesives used in multi-layered flexible packaging are commonly a product of solvent-based or solvent-free two-pot systems that undergo the following reaction:

Polyol (-OH)	+	Isocyanate (-N=C=O)	→	Polyurethane (-(H)NC(=O)O-)

FTIR is often used in industry to test the decay rate of isocyanate (NCO) in a freshly applied adhesive because unreacted aromatic NCO molecules can migrate through laminated packaging into food to react with water molecules, generating carcinogenic primary aromatic amines that are harmful to humans and pets alike.

Transmission spectroscopy is routinely used in industry; however, the coating weight must be carefully controlled to ensure consistent pathlength. This requires preparation techniques such as screen printing that adds complexity and requires user know-how. ATR spectroscopy would eliminate this sample preparation owing to its fixed pathlength [1]; however, this ties up the expensive ATR accessory for the duration of the experiment and can be difficult or impossible to clean once the glue is set. Arrow eliminates these difficulties and opens the door to the use of ATR spectroscopy in more applications than ever before.

Silicon ATR consumable technology helps you zero in on your analysis. Designed for the Quest™ ATR accessory, Arrow™ allows rapid assessment of a range of liquid analytes.

- Long duration ATR experiments.
- Batch sample preparation.
- Archive samples.
- Prevent sample cross contamination.
- Remote sample preperation.

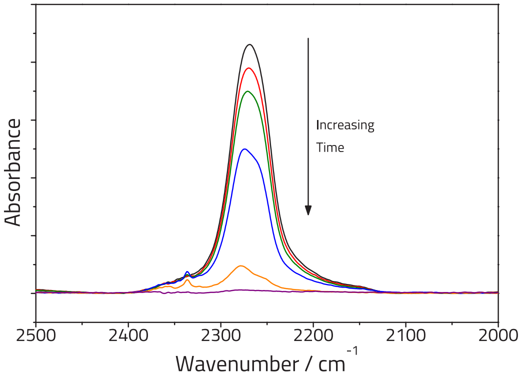

Figure 1: *Time-Resolved FTIR spectra showing the decay of the N=C=O band.*

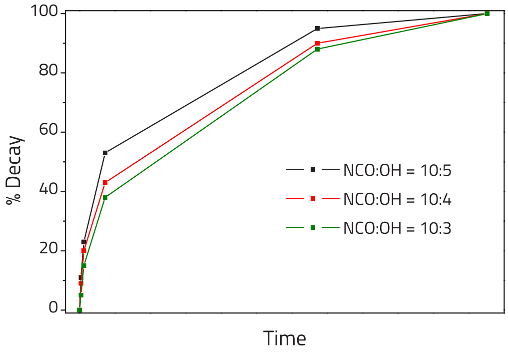

Figure 2: *Curing speed of adhesives at different mix ratios.*

Figure 3: *Images showing the lamination adhesives before (left) and after (right) curing.*

Experimental

Three different samples were prepared with different starting ratios of NCO:OH, and then placed onto individual Arrow slides. Time-resolved spectra were obtained on a commercially available spectrometer as the adhesive set. A new background spectrum was obtained before each time set from an unused reference Arrow slide. The percent decay of the isocyanate peak was then calculated by applying the Beer Lambert law (i.e. that Absorbance is proportional to the concentration) using the formula:

$$\%Decay = 100-A_t/A_0*100$$

where A_t is the absorbance at time t (minus the absorbance value of the residual after curing) and A_0 is the absorbance at time zero (minus the absorbance value of the residual after curing).

Results and Discussion

Figure 1 shows the time-resolved decay of the N=C=O stretching vibration at *ca.* 2270 cm^{-1} recorded for a single sample. At time zero (black spectrum) the peak is at its maximum and as the adhesive cures the peak decreases in intensity over time, until the glue has fully cured (purple spectrum). The curing speed is dependent on many variables such as NCO to OH mix ratio, curing temperature, relative humidity, the crosslinkability of starting components and the reactivity of the aromatic NCO component. Sometimes the curing process can take days or even weeks and it would be unfeasible to conduct multiple experiments varying different parameters using conventional ATR.

With the Arrow, batch experiments can be conducted in parallel, eliminating this constraint. **Figure 2** shows the decay of the NCO band over time for 3 experiments conducted in parallel comparing the decay as a function of varying ratios of NCO:OH.

As can be observed, increasing the proportion of polyol in the mix results in an increase in the curing speed. This is desirable to prevent migration of aromatic-NCO free monomers through the packaging; too fast, however, and the working time of the adhesive will be too short. Studying these reactions with FTIR allows the optimal conditions to be selected for the application.

Figure 3 shows the lamination adhesive before and after curing. The reaction is irreversible and bonds to the ATR crystal element. Since Arrow is a consumable ATR platform, the delicate process of chipping the cured resin from an expensive ATR crystal is avoided.

Conclusion

The decay of the NCO band has been successfully used to monitor the curing of the lamination adhesive using ATR spectroscopy without the need for screen printing preparation techniques required for a transmission measurement. Three separate experiments were run simultaneously, however tens or even, hundreds of experiments could be run by a single analyst at once. At the end of the experiment no cleaning was required freeing up the analyst to immediately begin the next round of testing.

References

[1] Specac Technical Note TN21-02: ATR Penetration Depth

AN20-02

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