A Diamond ATR Study of Adhesives Curing

INTRODUCTION

Adhesive manufacturers need to frequently examine their formulations to perform quality control as well as optimize their formulations. Diamond ATR can be useful in studying and monitoring the dynamic changes in the adhesive curing process. Numerous types of adhesives, epoxies, autobody paints, and other durable and difficult to remove liquid to solid transformations can repeatedly be tested on the Diamond ATR easily and safely.

This application note examines two adhesives, an isocyanate based adhesive and a thiocyanate based adhesive, using the Harrick DiaMaxATR™ single-reflection high throughput diamond ATR accessory.

Figure 1. The DiaMaxATR.

EXPERIMENTAL

Infrared spectra were collected on an FT-IR spectrometer equipped with the Harrick DiaMaxATR™ single-reflection high throughput diamond ATR accessory. The system was purged to remove water vapor and CO_2. Spectra were collected at 8 cm^{-1} resolution and signal averaged over 32 scans. The spectra were referenced to the clean ATR crystal. A spectrum was collected every minute for a total of 40 minutes to observe the changes over time.

Two samples were examined: White Gorilla Glue (The Gorilla Glue Company, Cincinnati, OH) and TiteBond Genuine Hide Glue (Franklin International, Columbus, OH). The curing process for the white gorilla glue requires that the surface is damp before applying the glue. A cotton swab moistened with water was used to dampen the diamond ATR, and then a small drop of white gorilla glue was placed on the surface of the diamond ATR. To study the Titebond Genuine Glue, a small drop was placed on the diamond ATR. The curing time took a total of 40 minutes for each adhesive.

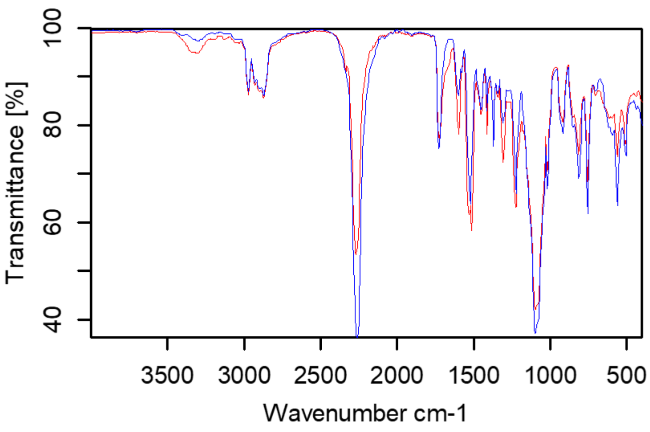

Figure 2. Spectra of Gorilla Glue after 0 minutes (blue) and after 40 minutes (red).

RESULTS AND DISCUSSION

Figure 2 shows the spectra of White Gorilla Glue before and after it dries for 40 minutes. The broad band in the 3200-3400 cm^{-1} region indicates either O-H stretches or N-H stretches from secondary amines.

The peak increased in intensity and shifted to a higher frequency as the adhesive solidified. Since water was used to moisten the surface of the diamond before applying the Gorilla Glue, it is likely the presence of secondary amines formed by the reaction of hydroxyl groups from the water and isocyanates from the adhesive. The bands in the 2840-3000 cm^{-1} region are attributed to C-H stretches. The isocyanate functional group (N=C=O), the active ingredient in Gorilla Glue, presented a prominent characteristic peak at 2250 cm^{-1} at the initial reaction stage but then it exhibited two peaks as the reaction progressed: the prominent

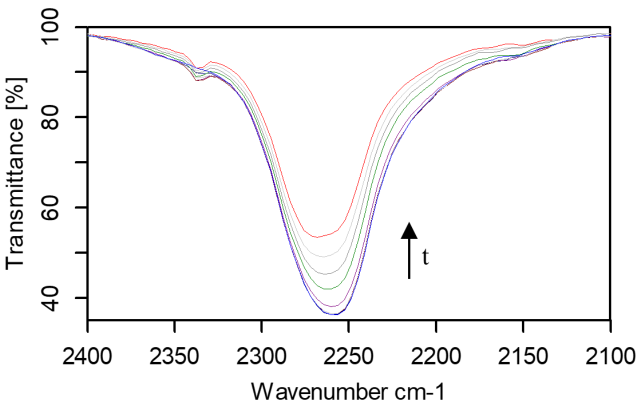

Figure 3. White Gorilla Glue Spectra of the isocyanate functional group over time for a total of 40 minutes at 5 minute intervals, where 0 minutes is blue and 40 minutes is red.

peak decreased gradually and shifted to 2267 cm^{-1} and a weaker peak appeared at 2335 cm^{-1}. Figure 3 illustrates the changes of the isocyanate functional group over time, which could be used to determine its reaction rate. The peak at 1597 cm^{-1} may indicate the presence of C=C cyclic alkenes, which increased in intensity and shifted to 1599 cm^{-1} after 40 minutes. Interestingly, the peak at 1309 cm^{-1} shifted to a lower frequency 1307 cm^{-1} and increased in intensity, indicating either C-N stretching due to aromatic amines or C-O stretching due to aromatic esters.

These variations imply the isocyanate functional group and the hydroxyl group participated in the reaction to form strong bonds in the structure of the adhesive at the final stage of the reaction.

The other adhesive, Titebond Genuine Hide Glue, is shown in Figure 4 before drying and after 40 minutes. The broad characteristic peak at 3300 cm^{-1} is associated with O-H stretches. Over time this peak progressively changes shape, decreasing in intensity and shifting to a lower frequency with two new peaks emerging around 2950 cm^{-1} and 3000 cm^{-1}. The new peaks possibly indicate N-H stretches as the solvent in the adhesive evaporated. There are three peaks in the 2000-2200 cm^{-1} region: 2195 cm^{-1}, 2154 cm^{-1}, and 2060 cm^{-1}. They enhance gradually in intensity and shift to lower frequencies. The 2195 cm^{-1} band may indicate C≡C stretching, the 2153 cm^{-1} band are ascribed to the thiocyanate functional group (S-C≡N stretches), and the 2058 cm^{-1} band could possibly be (N=C=S stretching) isothiocyanates.

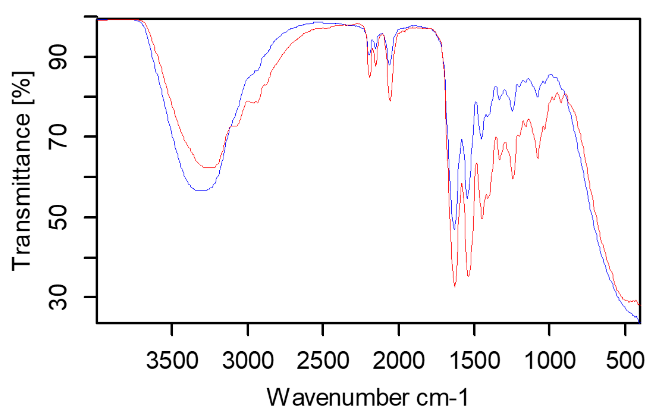

Figure 4. Spectra of Titebond Glue after 0 minutes (blue) and after 40 minutes (red).

CONCLUSION

The Harrick DiaMaxATR™, high throughput, single reflection diamond ATR is effective at examining the chemical changes of the functional groups present in adhesives. Additional studies will continue the investigation of adhesive reactions and extracting their kinetic data from the ATR measurement.