

INFRARED SPECTROMETER ACCESSORIES

Measurement of 2 Part Epoxy Glue (Araldite) Curing Using the Specac Quest ATR Accessory

Introduction

An alternative method for spectral collection is to use the Attenuated Total Reflectance (ATR) technique, whereby a liquid or solid sample is brought into direct contact with an ATR crystal material and internally reflected and measurable light from the sample crystal interface results in a spectrum being collected for the sample from a specific penetration depth into the sample material itself.

To achieve a similar spectral range of collection for the transmission range of 4000cm^{-1} to 400cm^{-1} from the ATR technique a monocrystalline type IIIa diamond ATR crystal element can be used. The Specac Quest™ ATR accessory offers the choice of a diamond, ZnSe or germanium ATR crystal pucks to be used on a dedicated optical unit with mirrored reflectance optical components only. This optical combination allows for the full transmission spectral range capability of the ATR crystal chosen to be achieved.

Application

ATR measurement of the “curing” reaction of a 2 part epoxy glue from combination of the epoxy resin and the polyamine (hardener) component materials.

Equipment and Method

For the ATR measurement of the epoxy resin curing reaction, to obtain a full spectral range for the sample between 4000cm^{-1} and 400cm^{-1} , the Quest ATR Accessory P/N GS10801-B was used with the single reflection diamond extended range ATR crystal puck option on the black surface coloured optical unit.

The spectra were collected on a Thermo Nicolet iS5 instrument using the standard room temperature



Specac's Quest ATR Accessory

detector system set at a resolution of 4cm^{-1} for 16 scans.

The sample chosen was Araldite “Rapid” 2 part epoxy glue.

Epoxy resin part is 1 4-butanediol diglycidyl ether.
Polyamine (hardener) part is
n(3-dimethylaminopropyl)-1 3- propylene diamine.

To start, individual spectra were taken for both the epoxy resin and polyamine (hardener) component materials of the 2 part reaction mixture. Then a 50:50 mixture of resin to hardener was mixed thoroughly together and placed over the diamond crystal of the puck assembly. Spectra were collected for this sample mixture from the start of mixing when initially placed on the diamond crystal and at 5 minute time intervals thereafter to monitor the reaction to completion of hardening of the epoxy resin.

Spectral Data

The Infra red spectra collected for the epoxy resin and polyamine hardener materials are shown as Figures 1 and 2 respectively. The spectra collected for the curing reaction mixture are shown as Figures 3 and 4. Figure 3 shows the full spectral range from 4000cm^{-1} to 400cm^{-1} comparison overlays for the reaction mixture after 1, 3, 6, 10 and 20 minutes after mixing and Figure 4 is a “detailed” comparison for the same spectra shown over the spectral range from 900cm^{-1} to 760cm^{-1} .

Discussion

The individual resin and hardener samples are both relatively mobile fluids. For spectral acquisition they were simply spotted into place onto the diamond crystal of the puck and no force for contact was required by employment of the flat or pellet anvil from the arm assembly of the Quest ATR optical unit. After spectral acquisition the sample was simply wiped away from the crystal puck by use of tissues moistened with methanol and acetone solvents.

For testing of the reaction mixture approximately equal amounts of resin and hardener were combined as a 50:50 mixture. When these compounds

Fig. 1. Araldite Rapid Resin on diamond puck of Quest ATR Accessory

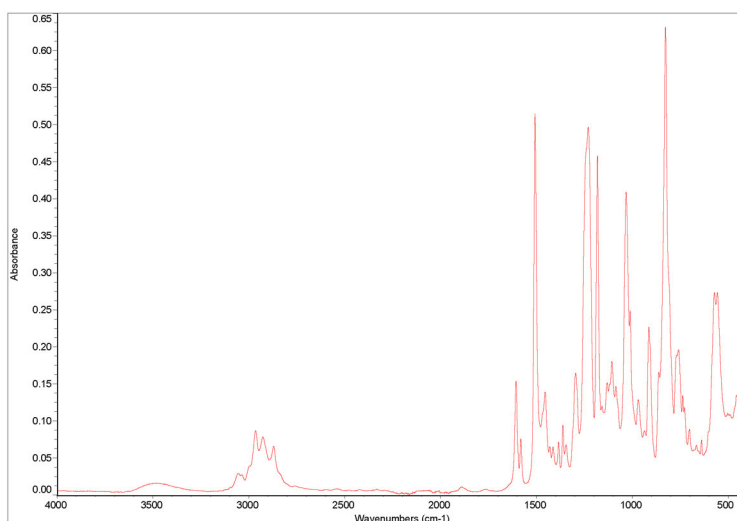
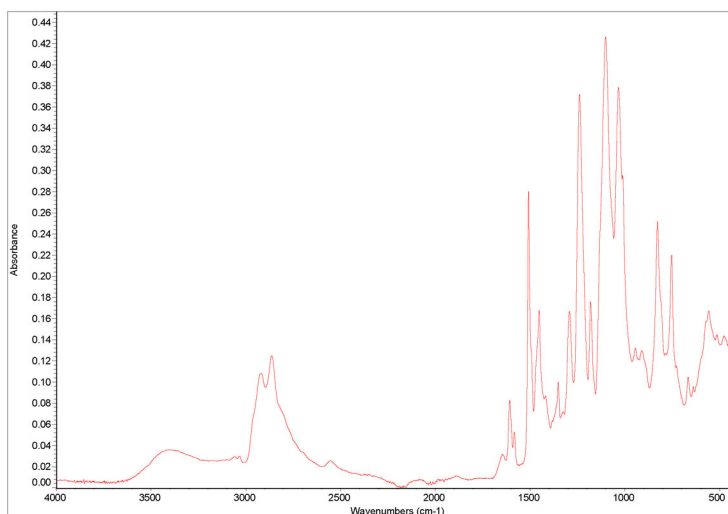


Fig. 2. Araldite Rapid Hardener on Diamond puck of Quest ATR Accessory



are mixed, the amine groups from the hardener react with the epoxide groups of the resin to form a covalent bond. Mixing of the two components took about one minute and then this mixture was transferred to cover the diamond and a small amount of the surrounding area to the diamond crystal of the puck. Similar for the spectral acquisition of the start constituents (resin and hardener), the initial reaction mixture was in a relatively mobile liquid like state and of a clear, pale yellow colouration, so neither the flat or pellet anvil option for the anvil arm assembly were used for the sample to make good contact with diamond ATR crystal.

As soon as the mixture was spotted into place, an

IR spectrum was collected which has been shown as the spectrum collected in Figures 3 and 4 for the blue coloured trace labelled as 1 minute after mixing. The reaction curing process was then allowed to continue whilst in situ on the diamond crystal and regular spectral acquisitions were taken to monitor any changes occurring during the curing time. In the meantime the sample mixture was also observed by eye and tested by probing with a small metal rod to check that the sample was beginning to harden. From visual observation, after 10 minutes or so the clear, pale yellow colouration was turning to a milky, creamy opaqueness and with this change the sample was beginning to set hard as it was becoming increasingly difficult to penetrate the

Fig. 3. Araldite Rapid Mixture on diamond puck of Quest ATR Accessory

Spectral overlay at 1, 3, 6, 10 & 20 minutes after mixing

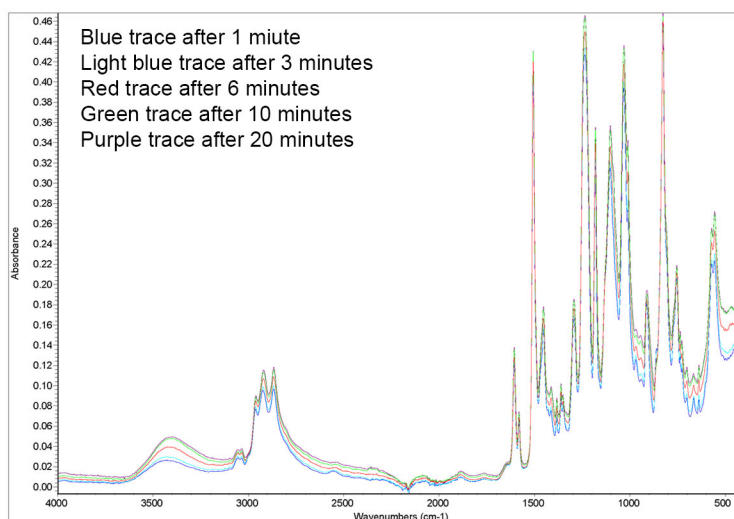
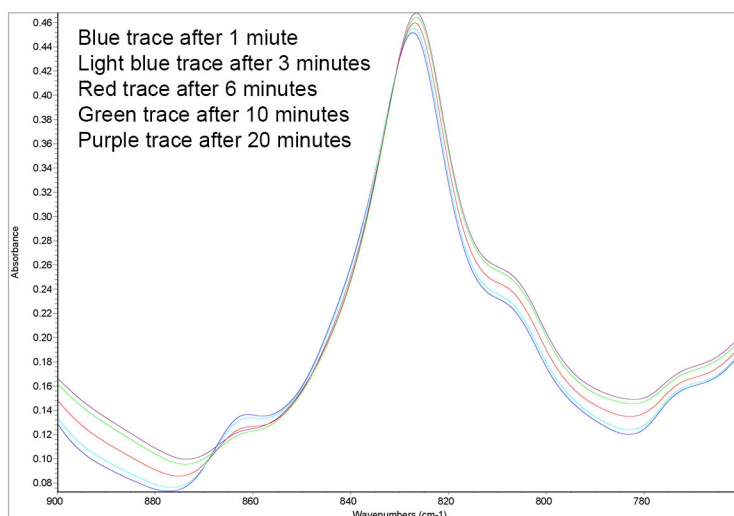


Fig. 4. Araldite Rapid Mixture on diamond puck of Quest ATR Accessory

Spectral overlay at 1, 3, 6, 10 & 20 minutes after mixing



samples outer form with the metal rod.

From observations of the IR spectra similarly collected over this time period after 3, 6, 10 and 20 minute intervals from the start of the reaction mixing, this physical change of opacity and hardening manifests itself in a very gradual change to the spectral profile, as shown by the examples of the full wavenumber scale spectra overlaid in Figure 3. From comparison of these spectra over time there appears to be an overall rise in the background profile, with a consistency of the spectral profile which may suggest that as the sample is beginning to harden it is attaining closer contact to the diamond crystal surface, for heightened spectral peak absorption throughout the entire range. This observation by itself may be an indication that there is a change occurring in the sample state, but on closer examination of the spectra, and over the spectral range between 900cm^{-1} to 760cm^{-1} , an absorbance feature at circa 860cm^{-1} is diminishing in peak intensity as the reaction time continues. From Figure 4, this feature diminishes within the first 10 minutes of the reaction time, whereby after 20 minutes for this particular combination/proportion of mixed reactants at the ambient temperature and pressure conditions given during testing, this spectral peak diminishment in intensity has stabilised. For subsequent spectral acquisitions at a later time, although there is a continuation in the general rise in overall background profile of the spectra being collected, which supports the fact for continued hardening of the sample and ever improving binding of closer contact to the diamond surface, the spectral peak feature at circa 860cm^{-1} has disappeared. The presence or absence of this spectral peak feature could be considered a marker for the state of the reaction curing process.

It can also be seen that with the diminishment of the 860cm^{-1} peak there is a corresponding slight increase of the peak intensity and shift to a lower wavenumber at circa 830cm^{-1} with an increase in the time measurement of the curing reaction. A slight spectral peak shift for ATR spectra is a phenomenon that can occur with polymeric materials if there is a change in the refractive index of the material and from the contact to the ATR crystal at a specific incident angle of light. In many materials the refractive index can change significantly across an

absorption peak region. This causes a variation in the penetration depth across the peak region and will “skew” it to longer wavelengths compared to a transmission spectrum peak position. The amount of shift will depend on the refractive index change across the band and this will be different for different bands in the spectrum. This band shift, once again, can be indicative of the sample material changing its phase from a liquid like to a solid like, hardened state from the curing reaction.

After 20 minutes, subsequent IR spectra collected showed no changes (no presence of the 860cm^{-1} peak), other than an overall increase to the background profile. After 60 minutes, the sample had become very hard and it was difficult to make an indentation into its outer shell using the metal rod. Therefore from the spectral data taken and the physical observations it may be perceived that within a 20 minute time period from the start, the sample mixture had converted to most of its structural change by the chemical reaction of the resin and hardener that can be observed directly by an IR spectral measurement and that the sample continues after this reaction period to set harder and harder.

After the reaction process could be considered complete (24 hours or so for no further hardening of the sample), this type of cured hardened sample was relatively easily removable from the diamond crystal puck. Ordinarily this type of sample reaction monitoring could not be carried out using an ATR accessory with a ZnSe crystal as in the process of hardening and adherence of the sample to the ATR crystal, it would be impossible to remove the sample without damage and permanent destruction to the ZnSe crystal. However, because of the hardness of the diamond crystal, the hardened cured resin sample was “shocked” from the puck by placing the sharp edge of a screwdriver blade to the side of the sample and knocked with a hammer. The resin sample came away from the diamond crystal completely cleanly, but there were some residual parts of the resin material stuck to the stainless steel puck around the diamond area. With subsequent cleaning and a partial abrasion action using tissue materials with acetone and dichloroethane solvents, the puck was effectively cleared of remaining sample and was ready for use with a new

sample.

Conclusion

It has been demonstrated that the Quest ATR accessory with a diamond puck is suitable for use in applications whereby a sample such as a two part epoxy resin adhesive can be studied for its reaction of bonding and co-polymerisation.

Use of a diamond crystal as the ATR top plate allows for a wide spectral range in the IR from 4000cm^{-1} to 400cm^{-1} to be studied and recorded for the sample material, but most importantly the hardness, structural and chemical integrity of a diamond crystal allows for such samples to be studied using the ATR technique, as the sample can be easily removed from the crystal puck after a reaction curing process, with minimal, if no risk of damage to the ATR top plate itself.

Acknowledgement

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