

# X-RAY FLUORESCENCE SOLVENT DETECTION AT THE SUBSTRATE-ADHESIVE INTERFACE

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## Introduction

With environmental regulations limiting the use of volatile organic compounds, low-vapor pressure solvents have replaced traditional degreasing solvents for bond substrate preparation. When used to clean and prepare porous bond substrates such as phenolic composites, low vapor pressure solvents can penetrate deep into substrate pore networks and remain there for extended periods. Trapped solvents can interact with applied adhesives either prior to or during cure, potentially compromising bond properties. Currently, methods for characterizing solvent time-depth profiles in bond substrates are limited to bulk gravimetric or sectioning techniques. While sectioning techniques such as microtome allow construction of solvent depth profiles, their depth resolution and reliability are limited by substrate type. Sectioning techniques are particularly limited near the adhesive-substrate interface where depth resolution is further limited by adhesive-substrate hardness and, in the case of a partially cured adhesive, mechanical properties differences. Additionally, sectioning techniques cannot provide information about lateral solvent diffusion.

Cross-section component mapping is an alternative method for measuring solvent migration in porous substrates that eliminates the issues associated with sectioning techniques. With cross-section mapping, the solvent-wiped substrate is sectioned perpendicular rather than parallel to the wiped surface, and the sectioned surface is analyzed for the solvent or solvent components of interest using a two-dimensional mapping or imaging technique. Solvent mapping can be performed using either direct or indirect methods. With a direct method, one or more solvent components are mapped using infra-red or Raman spectroscopy together with a moveable sample stage and/or focal plane array detector. With an indirect method, an elemental "tag" not present in the substrate is added to the solvent before the substrate is wiped. Following cross sectioning, the tag element can then be mapped by its characteristic x-ray emission using either x-ray fluorescence, or electron-beam energy- and wavelength-dispersive x-ray spectrometry. The direct mapping techniques avoid issues of different diffusion or migration rates of solvents and elemental tags, while the indirect techniques avoid spectral resolution issues in cases where solvents and substrates have adjacent or overlapping peaks.

In this study, cross-section component indirect mapping is being evaluated as a method for measuring migration of d-limonene based solvents in glass-cloth phenolic composite

(GCP) prior to and during subsequent bonding and epoxy adhesive cure.

## Experimental Approach

Development of an accurate, reliable solvent mapping technique involves three parts. First, the solvent laden phenolic substrate must be cross-sectioned without altering the solvent position at the sectioned surface or introducing new species that could interfere with solvent analysis. Second, a tag element must be selected which matches the diffusion and surface absorption characteristics of d-limonene while optimizing x-ray analysis sensitivity. Third, acceptability of both cross-sectioning method and elemental tag must be verified.

Cross-section methods: In order to avoid altering the distribution of d-limonene within the phenolic pore network, it was necessary to use a cross-sectioning technique that did not generate significant heat or require the use of lubricants. The two most promising methods include slow speed wafering blade without lubricant, and interlaminar cleaving. The interlaminar cleaving method involves fracturing a notched sample along the resin-to-glass cloth interface. This method will only result in a true cross-section when the GCP's with plies are oriented at 90° to the solvent-wiped surface, however, due to the position of GCP pores at the resin-fiber interface, the 90° ply orientation is ideal for solvent migration studies. The slow speed wafering method has the advantage of providing a cross-section for GCP samples with ply orientations other than 90° relative to the wiped surface, but also presents a significant risk of smearing liquid solvent or non-volatile residues across the cut surface. Prior to using a wafering method, it's potential for smearing absorbed solvent will be evaluated by sectioning phenolic samples impregnated with a colored solvent then examining the cut surfaces using optical microscopy to see if the solvent has been spread across the cut surface. In the event that a wafering method must be used for cross sectioning, solvent smearing might be reduced by freezing samples prior to sectioning.

Elemental Tag Selection: In order for an elemental tag to provide accurate data about solvent migration in a porous substrate, that tag must have the same diffusion and surface absorption characteristics as the solvent to which it has been added. In order to be detectable with x-ray fluorescence or emission techniques, the elemental tag must also contain elements that permit a fairly low minimum detection limit. In the case of d-limonene solvent, these two requirements oppose one another. Limonene diffusion

and absorption characteristics are most likely to be matched by using low tag concentrations and selecting small non-polar tag molecules. X-ray sensitivity will be increased by using high tag concentrations and including metallic or high atomic number elements, both of which will tend to make the tag molecule either too large or too polar. For this study, several tag compounds are being evaluated including brominated limonene, various bromoalkanes, and n-butylferrocene. The brominated limonene, avoids the solubility issues, but being more polar than non-brominated limonene, could have a much lower diffusion rate. The butylferrocene is a liquid at room temperature, and is very non-polar due to shielding of the iron by the two cyclopentadiene groups, but could present solubility issues under solvent drying conditions.

**Acceptability Verification:** In order to ensure that the selected tag molecule migrates at the same rate as the limonene, side-by-side control depth profiles were run using "tagged" vs. "untagged" limonene in silica-filled ethylene-propylene-diene-terpolymer (SF-EPDM). The depth profiles were constructed by microtome sectioning followed by gas chromatography-mass spectroscopy headspace analysis (GC-MS/headspace). The SF-EPDM provides a verification of "tagged" diffusion in GCP as the GCP and SF-EPDM have comparable pore sizes, and are both relatively non-polar. Unlike GCP, however, the SF-EPDM can be sectioned by microtome easily and reliably. Microtome sectioning was conducted by applying known quantities of solvent to the surface of a small SF-EPDM coupon and allowing it to diffuse in and/or evaporate at room temperature. Coupon sides were masked to prevent solvent intrusion. Following solvent drying, the coupons were microtomed sectioned in 0.010-inch slices with the first slice containing the wiped surface. Slices were weighed and then placed immediately in sealed vials. Sealed vials were heated at 110°C for approximately 30 minutes to permit equilibration of limonene in the headspace gas prior to injection into the GC/MS instrument.

## Results and Discussion

Depth profiling has currently only been performed for the brominated limonene tag molecule. Results for butylferrocene solutions and other brominated compounds will be available in the poster presentation. The brominated limonene tag was primarily monobrominated with a small fraction of multibrominated limonene compounds. Acceptability depth profiling was performed using a 20% solution of brominated limonene in non-brominated limonene. Figure 1 shows a GC/MS direct injection chromatogram with the brominated limonene compounds identified as "bromonene". SF-EPDM depth profiles for limonene in the brominated solution vs. the non-brominated control at 15, 30, and 60 minute dry times are shown in Figures 2 through 4, respectively. From these profiles it is clear that the brominated solution does not migrate into the SF-EPDM to nearly the same extent as unaltered limonene.

This lack of in-migration could be due to increased viscosity that was observed for the 20% brominated solution. SF-EPDM depth profiles for limonene vs. "bromonene" in the brominated solution at 15 and 60 minute dry times are shown in Figures 5 and 6, respectively. From these profiles it is clear that the rate of in-migration into SF-EPDM of the brominated molecules is significantly lower than the non-brominated limonene molecules in the same solution. The lower migration rate of the brominated limonene is possibly due to their larger size and/or more polar character as compared to the non-brominated limonene.

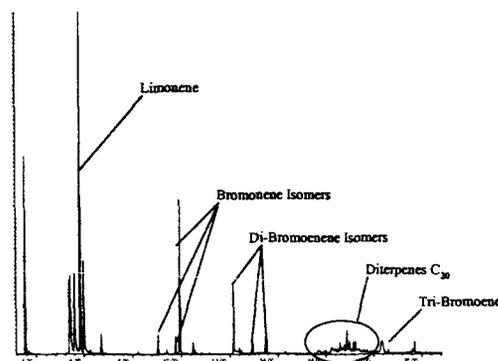


Figure 1. GC/MS chromatogram of 20% brominated limonene solution

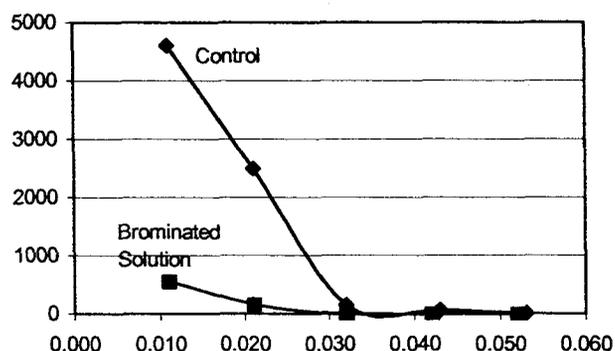


Figure 2. Limonene depth profile after 15 minute dry time. Concentration in ppm, depth in inches.

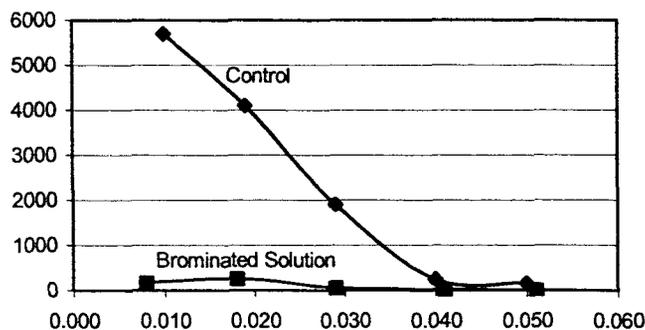


Figure 3. Limonene depth profile after 30 minute dry time. Concentration in ppm, depth in inches.

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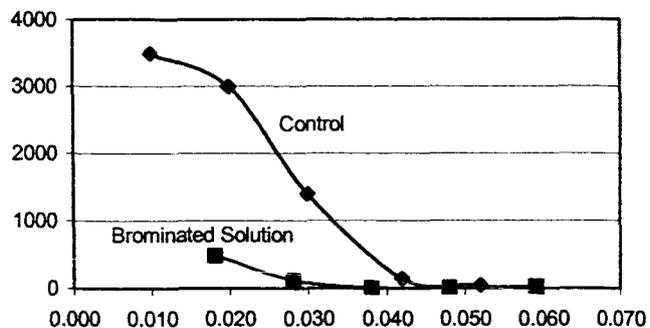


Figure 4. Limonene depth profile after 60 minute dry time. Concentration in ppm, depth in inches.

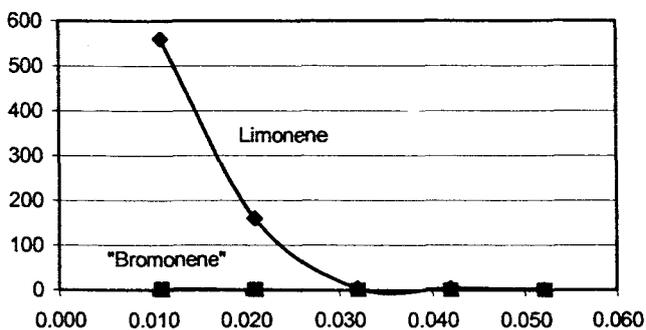


Figure 5. "Bromonene" vs. limonene depth profile at 15 minute dry time. Concentrations in ppm, depth in inches.

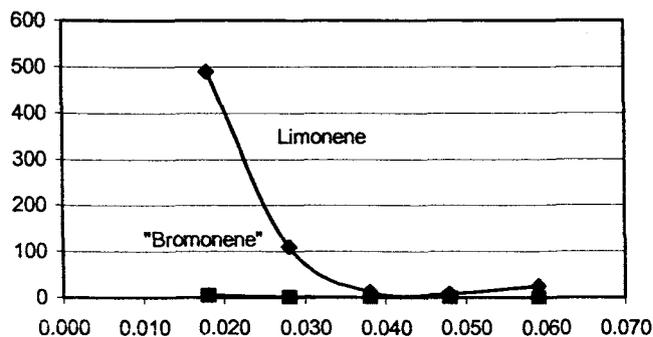


Figure 6. "Bromonene" vs. limonene depth profile at 60 minute dry time. Concentrations in ppm, depth in inches.

## Conclusions

Brominated limonene is unsuitable as a tag molecule for limonene based on its significantly slower migration rate. Additionally, the increased intermolecular interactions permitted by the larger and more polar brominated limonene reduces the migration rate of the non-brominated limonene in solution, thereby changing the overall characteristics of the solvent. Use of smaller, more non-polar tags such as butylferrocene should reduce these issues and provide a suitable tag for limonene migration in phenolic substrates.