

# MEASURING ADHESIVE CURE USING PYROLYSIS GC-MS

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## Abstract

The primary pyrolysis products of the poly(isoprene) in natural rubber are well defined: the isoprene monomer and the two dimers 1,4-dimethyl-4-vinylcyclohexene and d-limonene. When natural rubber is cross-linked, it affects the pyrolysis pattern resulting in an increase in the isoprene monomer relative to the dimers. An experiment was run using pyrolysis GC-MS to measure the degree of cure in a natural rubber adhesive. In theory, the higher the cure of the adhesive, the higher the amount of monomer and the lower amount of dimer that should form. Samples with different amounts of cure were analyzed using Pyrolysis GC-MS, Gel Content and Solvent Cure to determine the degree of cure. The results of all three tests were comparable. Using pyrolysis GC-MS has some advantages since, as it is based on peak height ratios, it is more sensitive to small variations in cure. A second experiment was run to show how this methodology is also applicable to cured acrylic adhesives as well.

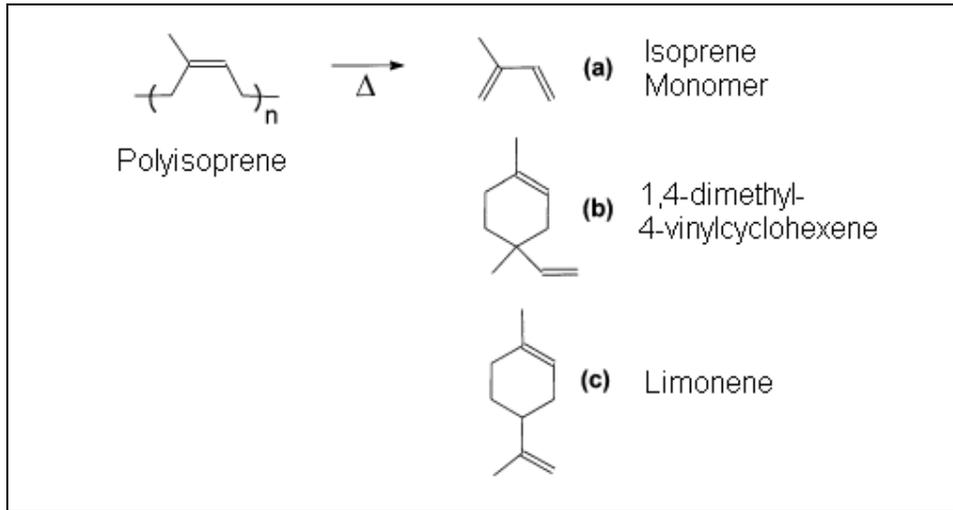
## Introduction

Numerous methods have been developed to determine the degree of crosslinking in natural rubber vulcanates. Some methods mentioned in literature include measuring changes in specific volume, thermal expansion coefficient, glass-transition temperature ( $T_g$ ) and viscoelasticity of the rubber. Other common methods measure the solubility of the cured rubber in solvents such as toluene and benzene. Researchers [1, 2] have also developed methods for measuring crosslink density of sulfur-cured natural rubber using Pyrolysis Gas Chromatography-Mass Spectrometry. Pyrolysis GC-MS is a well established method for teasing out structural information about polymers [3, 4]. In this experiment, pyrolysis GC-MS was used to measure the degree of phenolic cure in a natural rubber adhesive.

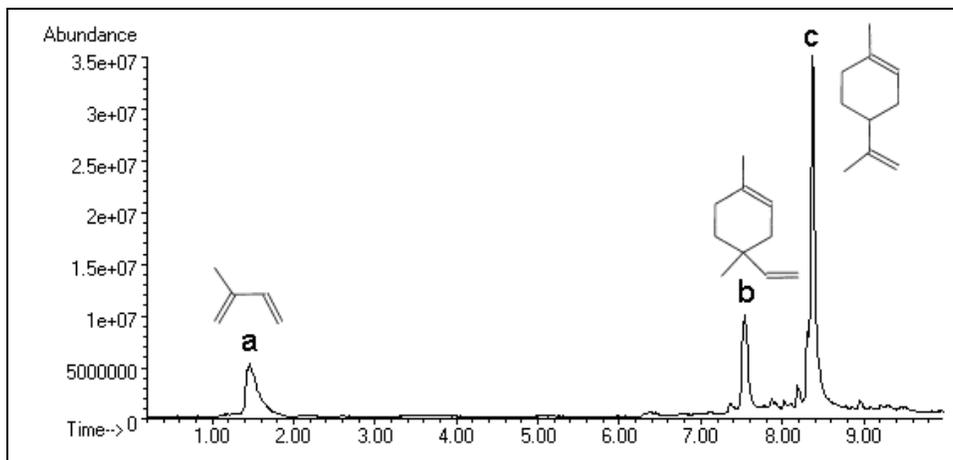
## Theory

Typically, polymers undergo scission when pyrolyzed resulting in the formation of large amounts of monomer. This is not the case with the polyisoprene linkages found in natural rubber. In addition to monomer, the pyrolysis of natural rubber yields large amounts of dimer. There are head-to-head and head-to-tail linkage between 1,4-isoprene units in polyisoprene. The products (b) and (c) shown in *Figure 1&2* are isoprene dimer species and are formed by cyclization from the head-to-head and head-to-tail sequences. 1,4-dimethyl-4-vinylcyclohexene is formed from the head-to-head sequence (*Figure 3*) and 1-methyl-4-(1-methylethenyl)-cyclohexene (d-Limonene) is formed from the head-to-tail sequence (*Figure 4*).

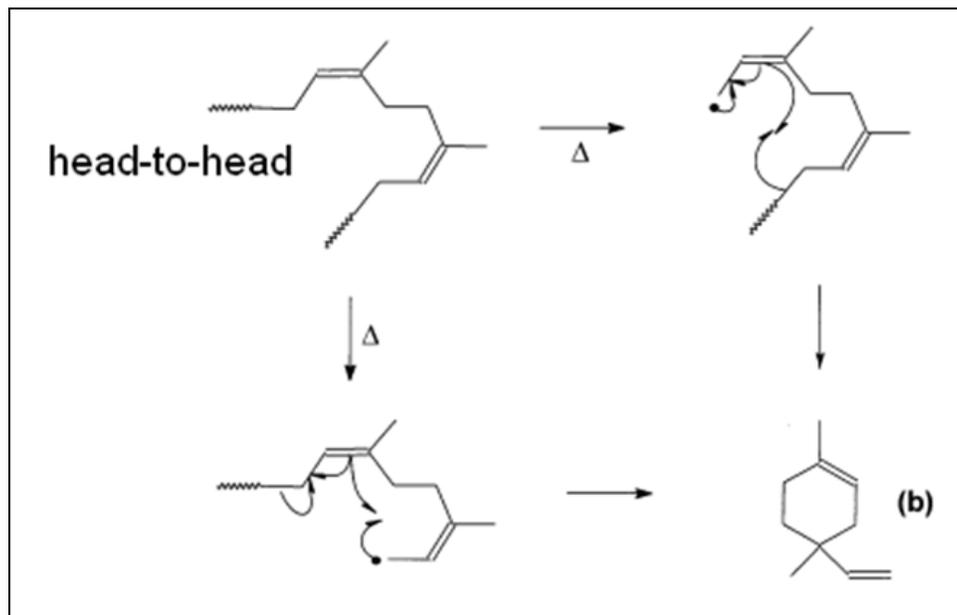
According to Choi [1] the peak area of d-Limonene (product c) is more than six times larger than that of 1,4-Dimethyl-4-Vinylcyclohexene (product b). This means that natural rubber is mainly composed of the head-to-tail configuration.



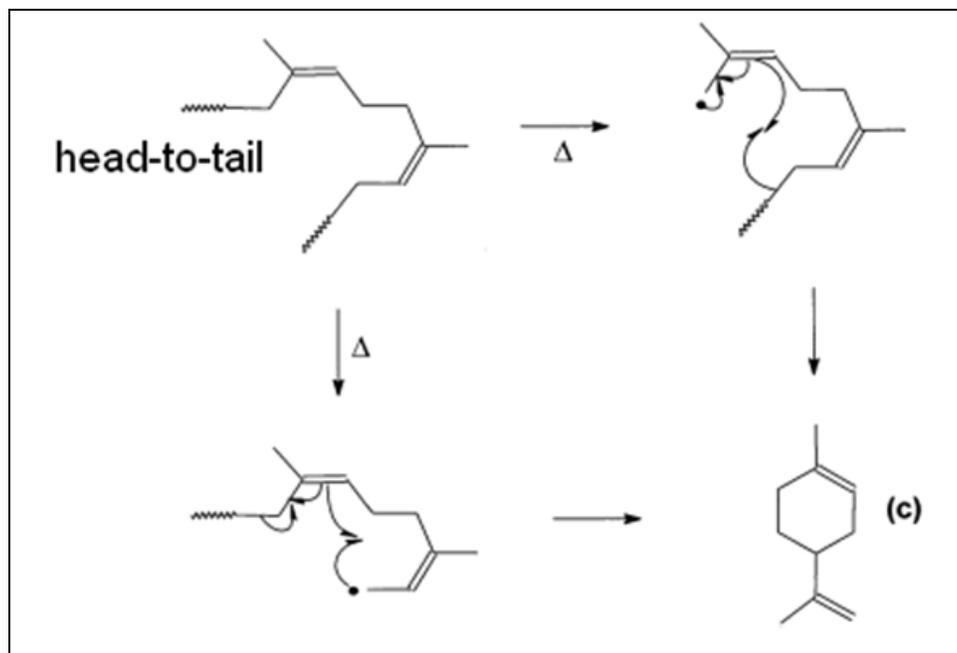
**Figure 1.** Pyrolysates of Polyisoprene (Image Source: Choi [1])



**Figure 2.** Pyrolysis GC-MS of Natural Rubber Adhesive



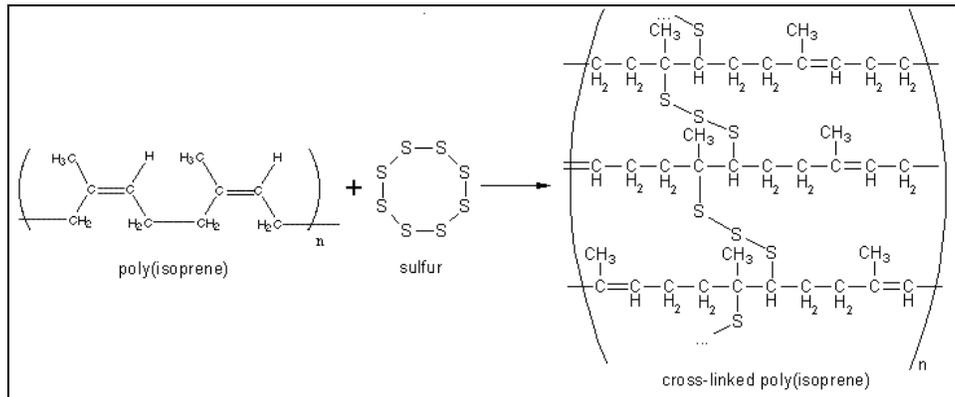
**Figure 3.** Production of 1,4-Dimethyl-4-Vinylcyclohexene during the Pyrolysis of Natural Rubber (Image Source: Choi [1])



**Figure 4.** Production of 1-methyl-4-(1-methylethenyl)-cyclohexene (d-Limonene) during Pyrolysis of Natural Rubber (Image Source: Choi [1])

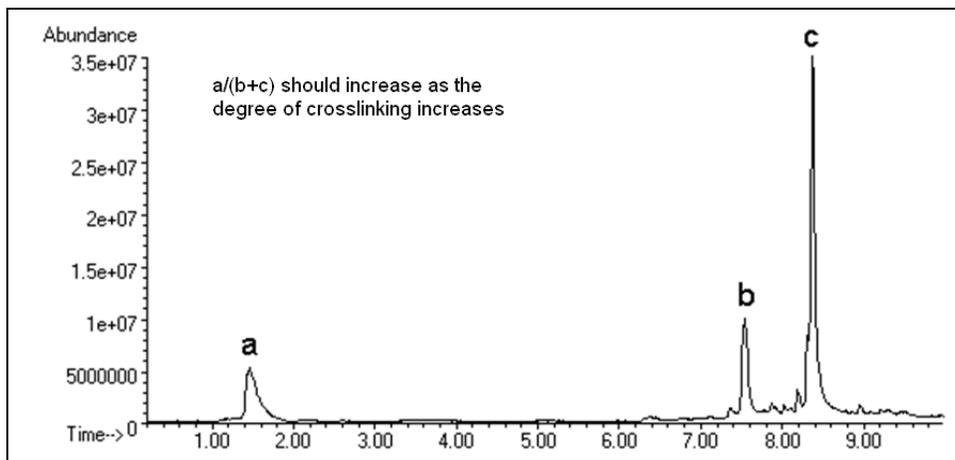
### Effect of Crosslinking

Studies of the effect of sulfur cures on natural rubber vulcanates [1,2,and 3] have shown that the isoprene dimer species formed during the pyrolysis of natural rubber decrease with increasing crosslink density. This can be explained by the free chain length of NR between crosslink points. The free chain length of NR between crosslinks in the vulcanizates becomes shorter as the crosslink density becomes higher. Since production of the isoprene dimer species is inhibited by the crosslink points, the ratio is reduced with an increase of the crosslink density (Figure 5).



**Figure 5.** Sulfur Crosslinking of Polyisoprene (Image Source: Wikipedia)

Choi [1] proposed the following formula to determine the degree of crosslink density  $a/(b+c)$  where  $a$  is the monomer concentration produced by pyrolysis and  $b+c$  is the sum of the dimer concentration (Figure 6).



**Figure 6.** Proposed Method for Determining Degree of Crosslinking of NR

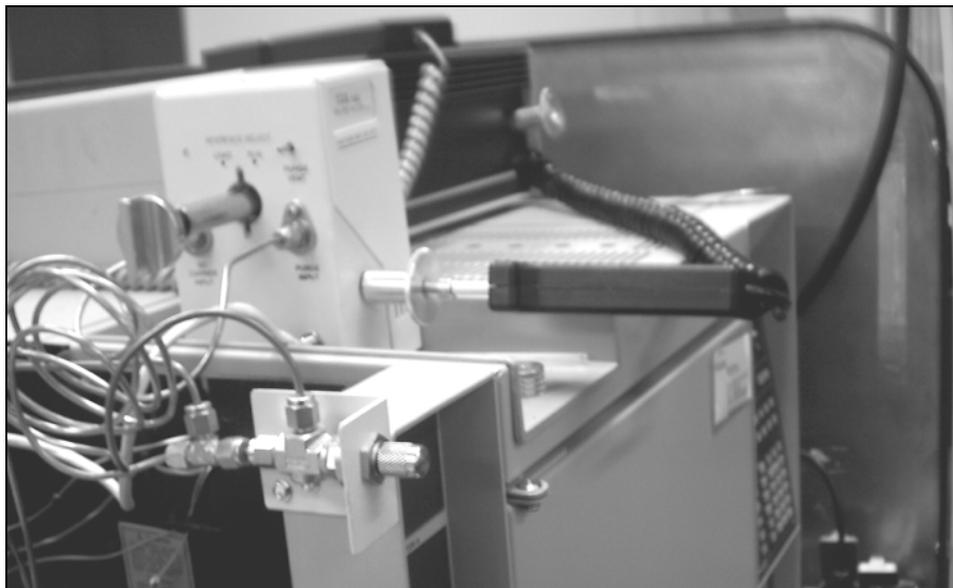
## Experiment

For this experiment, an uncured natural rubber adhesive with an added phenolic cure agent was used. This was to test to see if the same method that worked for sulfur-cured rubber would work for a phenolic cured adhesive. The adhesive was rolled out onto release liner and exposed to 300°F for 15, 30, 45, and 60 seconds. Three different methods of analyzing for cure were run and compared.

1. Analyze by Pyrolysis GC/MS
2. Test for Solvent Cure
3. Test for 'Gel' Content

For the Pyrolysis GC/MS experiments, a small ball of adhesive was placed inside of a glass tube and placed within the coil of a CDS Pyroprobe 2000 pyrolyzer (*Figure 7*). Based on the work of Choi [5] the maximum pyrolysis temperature was 550°C. The pyrolyzer was interfaced with an HP 5890 Gas Chromatograph. The separation of the pyrolysates was done on a 30 meter RtV-5MS 5% phenyl capillary column at a flow rate of 1 ml/min.

The temperature program for the GC was as follows: initial temperature 50°C held for 5.0 min; a 25°C/min ramp up to 225°C; hold at 225°C for 33min. The total run time was 45 min. The mass spectrometer was a HP 5970 MSD single quadropole MS scanning between 40 and 550 amu.

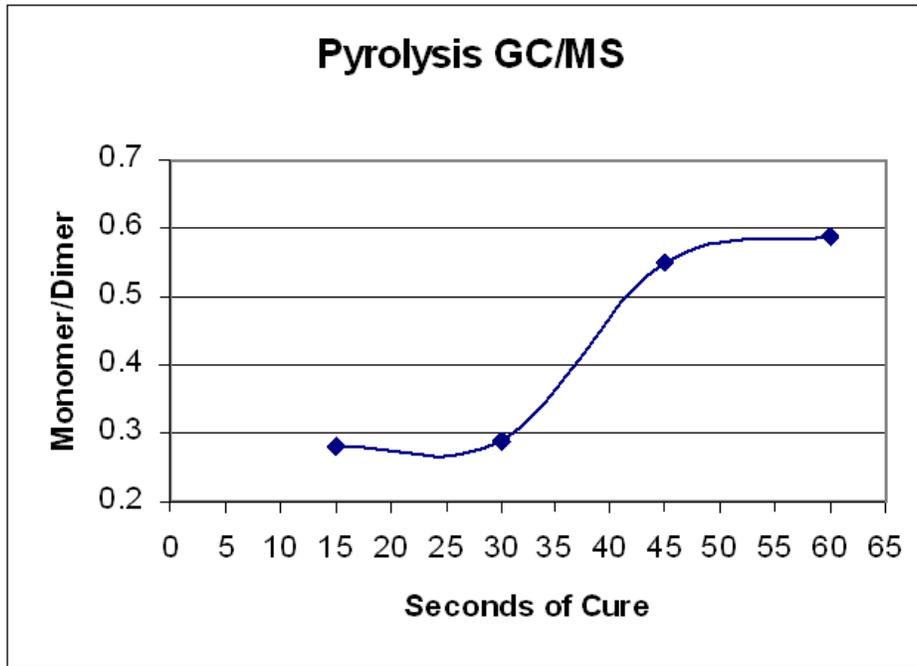


**Figure 7.** CDS Pyroprobe 2000 interfaced with HP 5890 Gas Chromatograph

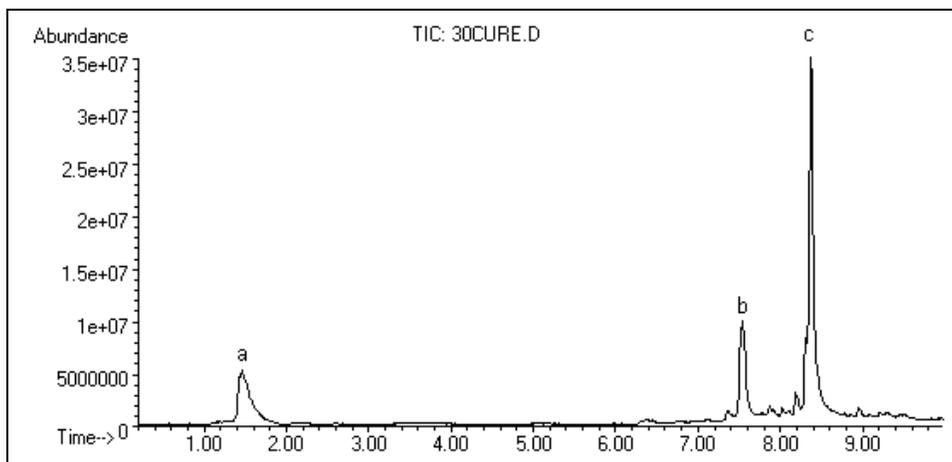
## Results

### Pyrolysis GC/MS

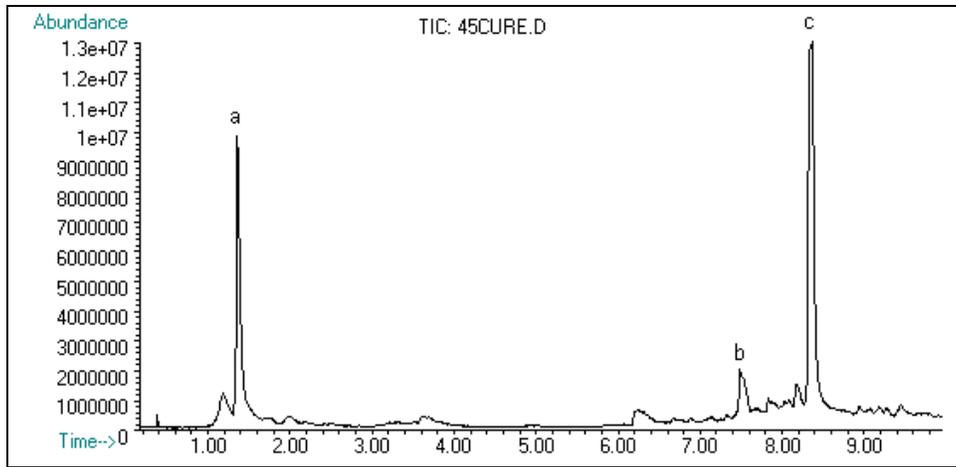
As expected the ratio of  $a/(b+c)$  increased as the amount of cure increased. The greatest change occurred between 30 and 45 seconds of cure (*Figures 8, 9 and 10*).



**Figure 8.** Ratio of  $a/(b+c)$  vs. Seconds of Cure



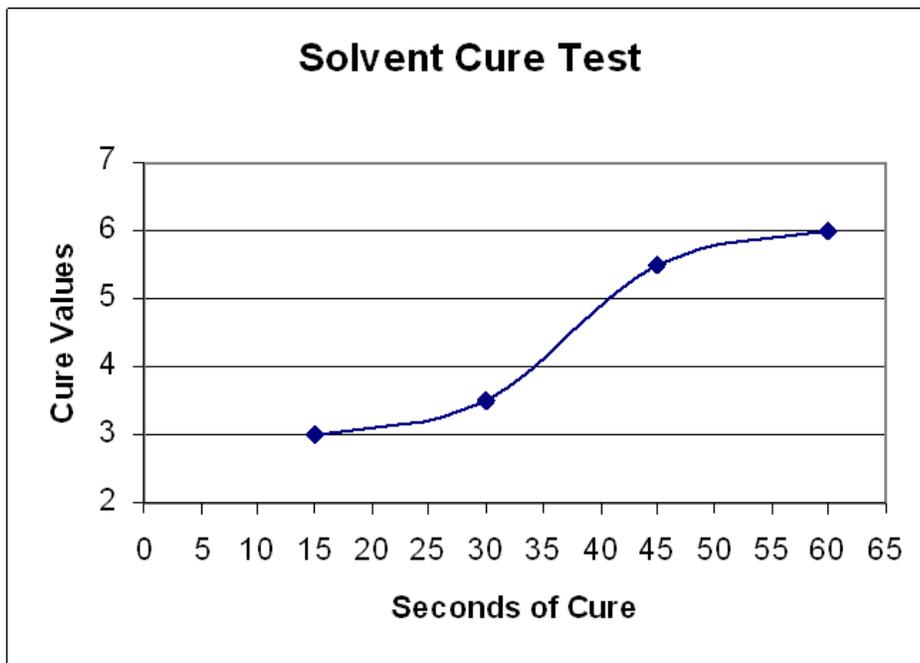
**Figure 9.** Gas Chromatogram of 30 Second Cure



**Figure 10.** Gas Chromatogram of 45 Second Cure

### Solvent Cure Test

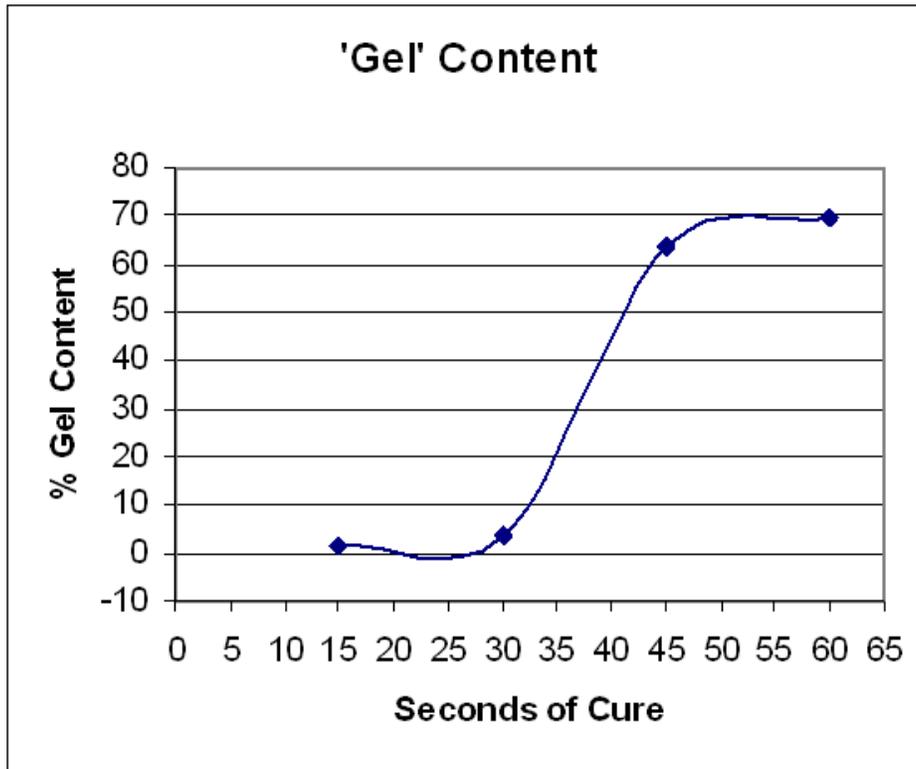
In this test, samples of the cured adhesive were immersed in toluene for 3 minutes, placed on absorbent paper and then rated for degree of cure. Because this 'solvent cure' rating is somewhat dependent on personal experience, three people rated the cure and the results were averaged. The degree of cure is ranked between 1 and 8. 1 being the least amount of cure, and 8 being a very strong cure. The results are shown in *Figure 11*.



**Figure 11.** Result of Solvent Cure Test

## 'Gel' Content

'Gel' content was defined as that portion of the adhesive that remains insolvent in THF after curing. 'Gel' content of the cured adhesives was determined by drying and weighing the amount of gel remaining when 0.25 grams of adhesive was allowed to sit overnight in 8ml of tetrahydrofuran (THF). The results are shown in *Figure 12*.

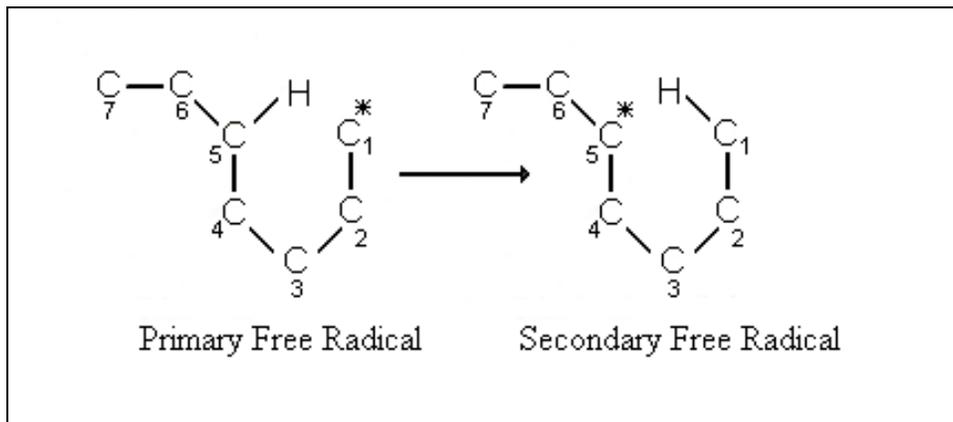


**Figure 12.** Result of 'Gel' Content Test

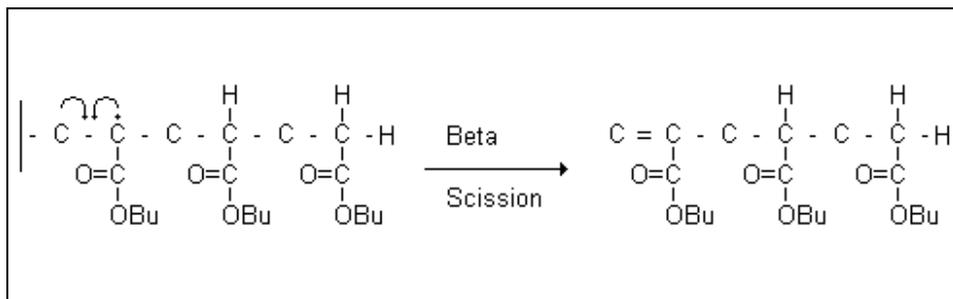
All three experiments showed similar results, with the greatest change of cure occurring between 30 and 45 seconds.

## Second Experiment

As a second experiment, the effectiveness of pyrolysis GC-MS to measure cure in an acrylic homopolymer was tested. As mentioned in the introduction, most polymers undergo scission to monomer when pyrolyzed. Poly(n-butyl acrylate) is another exception. Poly(n-butyl acrylate) undergoes a 1-5 H shift during scission (*Figure 13*). This weakens the bonding between the 6<sup>th</sup> and 7<sup>th</sup> carbon molecules leading to higher than normal levels of butyl acrylate trimer in the pyrolysates (*Figure 14*). In the same way curing rubber lowers the amount of dimer produced, curing poly(n-butyl acrylate) should lower the amount of trimer.



**Figure 13.** 1-5 H Shift

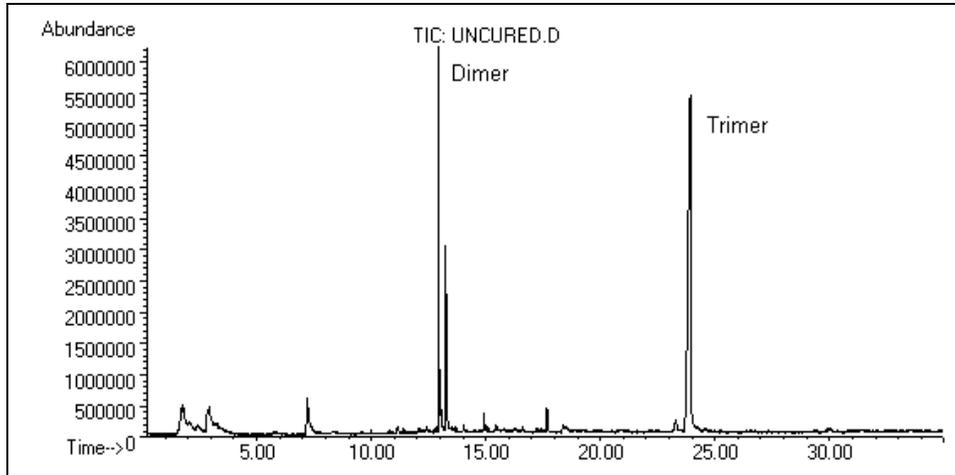


**Figure 14:** Trimer Formation in Butyl Acrylate

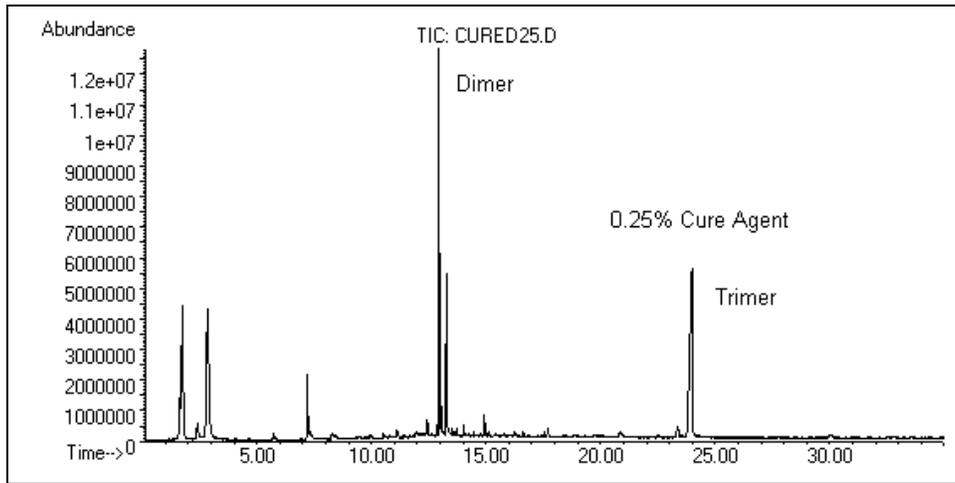
## Experiment

A sample of uncured poly(n-butyl acrylate) was analyzed using pyrolysis GC-MS under the same conditions described previously. Next, 0.25% of a curing agent was added and the sample was exposed to an electron beam to trigger the cure.

As can be seen in *Figures 15&16*, the amount of trimer formed during pyrolysis was reduced after the poly(n-butyl acrylate) was cured.



**Figure 15.** Pyrolysis Gas Chromatogram of Poly(n-Butyl Acrylate) Before Cure



**Figure 16.** Pyrolysis Gas Chromatogram of Poly(n-Butyl Acrylate) After Cure

## Conclusions

The use of pyrolysis GC/MS as an analytical tool to measure degree of cure was successful. Because the formula  $a/(b+c)$  is based on measuring peak areas it is less subjective than some other methods. The peaks were large and readily quantifiable which would allow the method to distinguish small variations in cure. The method is slower than the 3 minute 'solvent cure' test, but on a par with tests such as DMA analysis of changes of glass transition ( $T_g$ ) as a measure of cure. Preliminary tests with an acrylic polymer have shown that the methodology may also be applicable to non-rubber based adhesives as well.

## Acknowledgements

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