

## Changes in the C≡N Group Infrared Absorption of Dicyandiamide in the Presence of Moisture

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### Synopsis

A correlation between lap shear bond strength and an infrared absorbance ratio of reactive groups in a commercial dicyandiamide (dicy.)-cured epoxy adhesive was explained by the presence of a hidden factor in the nitrile absorbance measurement of the dicyandiamide. The absorbance at  $2210\text{ cm}^{-1}$  due to the C≡N of the dicy. was the denominator of the absorbance ratio in the correlation. Water present in the adhesive changed the two infrared absorptions in the  $2200\text{ cm}^{-1}$  region of the spectrum resulting in a lower  $2210\text{ cm}^{-1}$  absorbance than expected stoichiometrically for high (0.4%) water concentrations in the adhesive.

### INTRODUCTION

Dicyandiamide (dicy.) is used as a latent curing agent for epoxy polymers in the form of adhesives or composites. In previous characterization work with such a system,<sup>1</sup> a correlation was obtained between the mechanical properties of the cured epoxy adhesive and a measure of its oxirane and dicy. concentrations before cure. Many batches of the adhesive were monitored in the uncured state by infrared spectroscopy. The oxirane group (epoxy) at  $910\text{ cm}^{-1}$  was proportioned to the C≡N nitrile stretching absorption at  $2210\text{ cm}^{-1}$  in terms of an absorbance ratio. These measurements were graphed against the single lap shear strengths of the cured adhesive. The lap shear specimens were aged at  $365^{\circ}\text{F}$  and  $420^{\circ}\text{F}$  for 18 and 3 hr, respectively, prior to testing at those temperatures. The resulting correlation is shown in Figure 1. Based upon past work with other cured epoxy systems,<sup>2</sup> one would have expected no minimum in the curves provided the infrared absorbance ratio was related to the stoichiometry of the epoxy and dicy. constituents. A higher crosslink density increases the lap shear strength of the adhesive although other properties such as peel are reduced.<sup>3,4</sup>

This communication offers a possible explanation for the shape of the curves in Figure 1. In addition, the information on the infrared spectrum of dicy. should serve as a warning to institutions using infrared spectroscopy to characterize and monitor batches of dicy./epoxy materials for adhesive and composite structural applications.

### RESULTS AND DISCUSSION

Commercial dicyandiamide contains about 7% water as determined by proton magnetic resonance spectroscopy (PMR).<sup>1</sup> Since 3-5% dicy. is usual in an

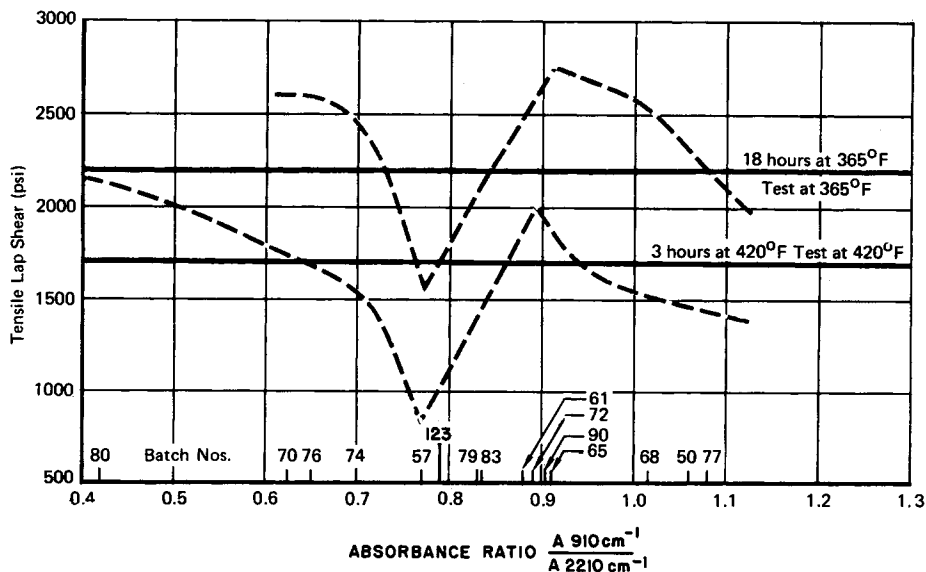


Fig. 1. Lap shear vs. IR ratio correlation.

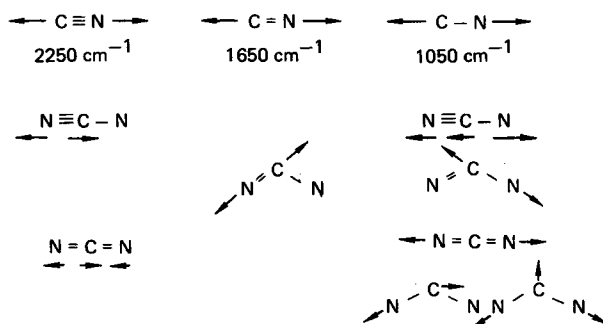


Fig. 2. Stretching-stretching interactions of carbon-nitrogen bonds in the infrared spectrum.

adhesive or composite resin formulation, 0.21–0.35% water would be the minimum amount contained in any formulation consisting of only resin and dicy. The destructive effect of water upon adhesion in the form of single lap shear strength is well known.<sup>1,5</sup> The water content contained by the adhesive after 30–40 days of humidity exposure was shown to be 0.8% by vapor-phase chromatography. Thus, the effect of small amounts of water on the  $C\equiv N$  absorbance was examined to establish any relationship between water content of the adhesive and the infrared spectrum absorption of the  $C\equiv N$  stretch in the  $2200\text{ cm}^{-1}$  region. This absorption consists of mainly two peaks for dicy. in the solid state. The structure of dicy. as determined by PMR<sup>6</sup> is shown as

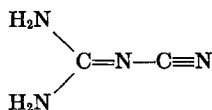


Figure 2 shows the infrared absorption frequencies of various types of carbon/nitrogen bonded groups. The double peak of the dicy. in the  $2200\text{ cm}^{-1}$  region

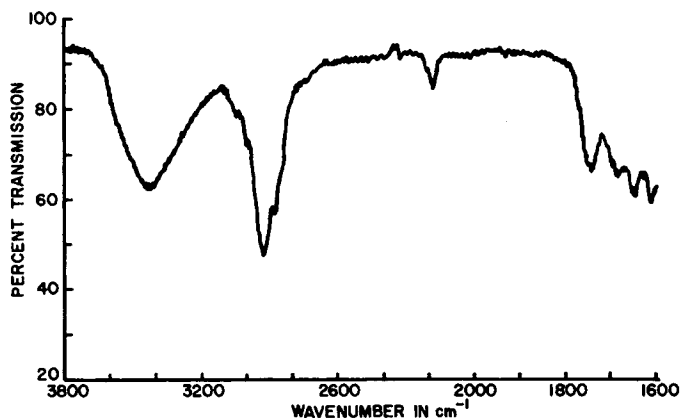
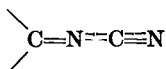
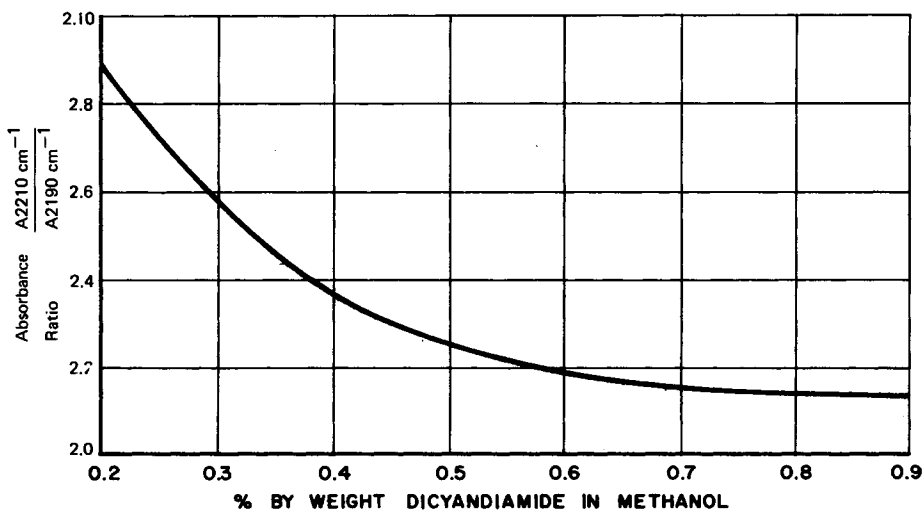


Fig. 3. Part of infrared spectrum for boron/epoxy prepreg, cured at 350°F for 90 min on KBr plate.

may be due to localized  $p\pi$  bonding in addition to the  $C\equiv N$  stretch. Thus, the  $N-C\equiv N$  may exhibit some  $N=C=N$  character due to delocalization, i.e.,

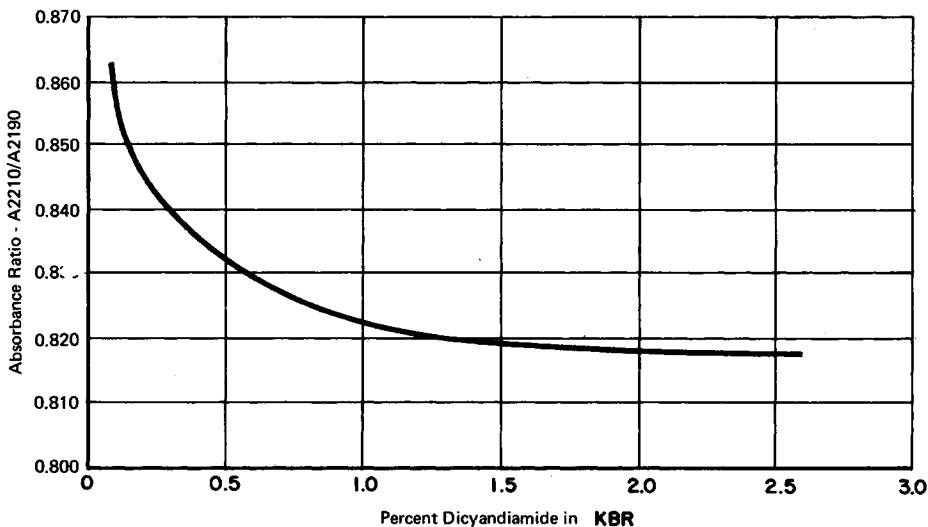


On dissolving the dicy. in acetone or heating the dicy. to curing temperatures in the epoxy matrix, a single absorption of the  $C\equiv N$  is observed at  $2200\text{ cm}^{-1}$  (Fig. 3). Once a single peak is obtained, the dicy. obeys Beer's law, the absorbance being directly proportional to dicy. concentration. However, when dissolved in an alcohol, or water, or as a solid in a KBr matrix, the dicy.  $C\equiv N$  absorption does not obey Beer's law, even though in the solvent case, the two  $2200\text{ cm}^{-1}$  region peaks are nearly merged into one. Thus, in the Figure 1 correlation, the  $2210\text{ cm}^{-1}$  absorbance denominator does not reflect proportional de-



(a)

Fig. 4 (continued)



(b)

Fig. 4. Effect of dicyandiamide concentration on the splitting in the  $2200\text{ cm}^{-1}$  region.

pendence upon the dicy. curing agent concentration in the adhesive. However, the absorbance ratio of the two absorptions was a constant independent of dicy. concentration after a certain dicy. concentration was reached. This applied for both the media of KBr and methanol (Fig. 4). The  $2210\text{ cm}^{-1}$  absorbance decreased relative to the  $2190\text{ cm}^{-1}$  absorbance until concentrations by weight of 0.7% (in methanol) and 0.2% in KBr had been reached. Thus, in the 3–5% by weight concentrations in the adhesive, the absorbance ratio of the two peaks at  $2200\text{ cm}^{-1}$  was considered independent of dicy. concentration. Therefore, the split peak absorbance ratio should have been used as the denominator in the Figure 1 correlation since, in the absence of moisture, the ratio of epoxy/curing agent as measured by infrared spectroscopy would have related to the stoichiometry of the two reactive constituents.

Upon addition of water to dry solid dicy., this split spectrum changes appreciably both in the intensity of each peak and the total absorption. The  $2210\text{ cm}^{-1}$  absorption increases in intensity as water is mixed into the dicy. This feature was observed independent of the presence of resin and fillers. Figure 5 shows this effect when the dicy. was mixed with an epoxy matrix from a boron/epoxy composite prepreg tape.

To investigate further the effect of moisture upon this dicy. absorbance ratio of the  $2200\text{ cm}^{-1}$  region, a commercial epoxy resin (Union Carbide ERL510) was mixed with known amounts of dicy. and water. The resin was similar chemically to the commercial adhesive previously defined.<sup>1</sup> Figure 6 shows the results, the absorbance ratio of the two bands occurring in the  $2200\text{ cm}^{-1}$  region being plotted against the weight per cent water added to the epoxy/dicy. mixture. Data from the commercial adhesive are also given. The water contents of the commercial adhesive batches were determined by vapor-phase chromatography.<sup>1,5</sup> These data indicate that with higher moisture contents the  $2210\text{ cm}^{-1}$  absorbance decreases and thus the  $A_{910\text{ cm}^{-1}}/A_{2210\text{ cm}^{-1}}$  ratio of

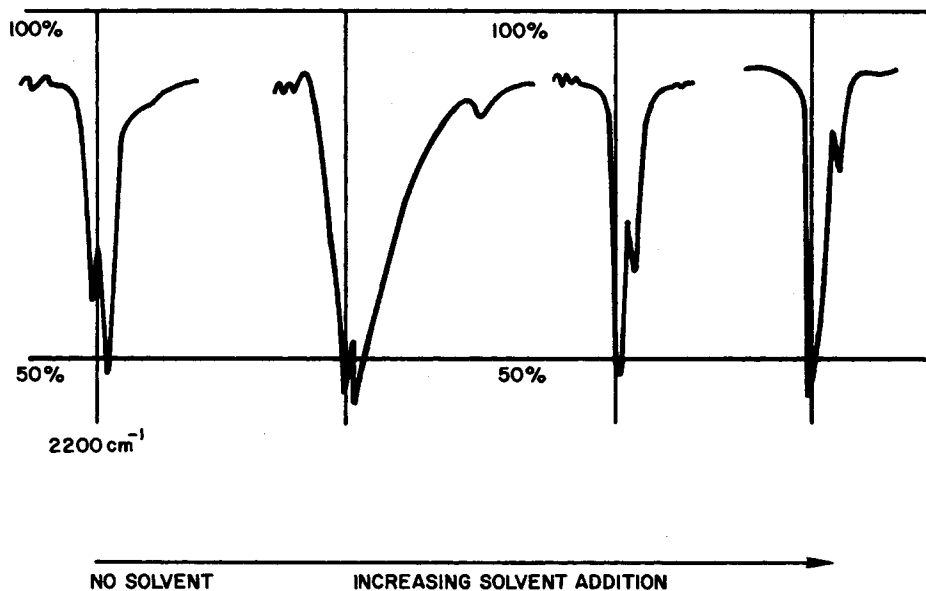


Fig. 5. Boron/epoxy prepreg; effect of absorbed solvent on the curing agent  $C\equiv N$  absorption at  $2200\text{ cm}^{-1}$ .

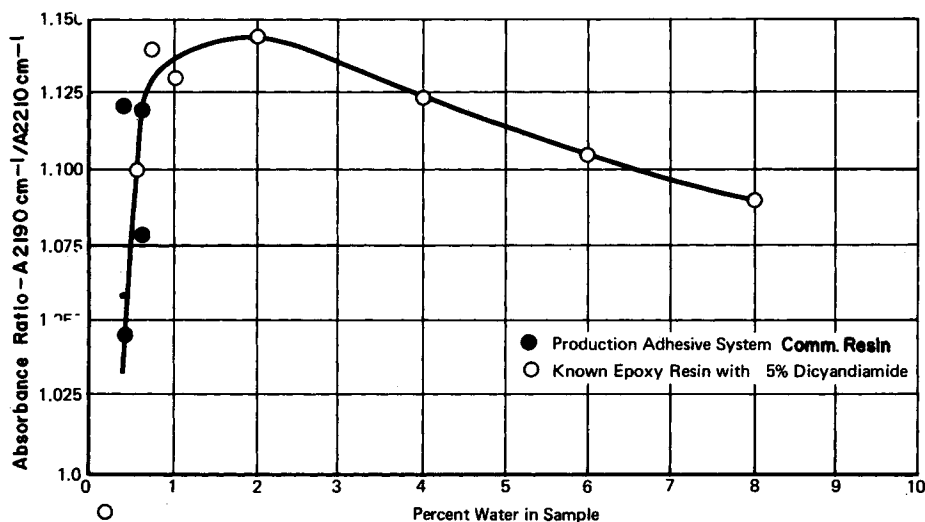


Fig. 6. Effect of water on the dicyandiamide splitting.

Figure 1 could be higher than for a stoichiometric one. This could cause some superposition of the Figure 1 curve.

McCarvill and Bell<sup>7,8</sup> obtained similar shaped curves when they examined the effect of adherend water treatment on the bond strength of epoxy-aluminum joints. The force required to break the joint increased for short adherend immersion times in water. They attributed the increase in bond strength to thin-layer bayerite formation on the adherend surface prior to bonding. In our case, the moisture content of the adhesive may also perform similarly on the adherend during cure and thus promote adhesion. High moisture content (e.g., 0.4%)

effectively gives a high  $A_{910\text{ cm}^{-1}}/A_{2210\text{ cm}^{-1}}$  ratio, which according to Figure 1 also yield high bond strengths.

### CONCLUSIONS

The peculiarities of the Figure 1 correlation in which the lap shear strength of a commercial adhesive is correlated to the uncured adhesive's absorbance ratio of its oxirane and dicy. functionality may be explained by the dependence of the  $2210\text{ cm}^{-1}$  absorption upon the water content of the adhesive. This yields two possible explanations. The first suggests that in order to obtain stoichiometry in the infrared absorbance ratio shifting of parts of the curve is required to eliminate the water factor in the absorbance ratio. The second suggests that, since a higher water content (0.4%) may enhance bond strength, the high absorbance ratios of Figure 1 contain more of a water factor which causes the  $A_{2210\text{ cm}^{-1}}$  to be lower than true stoichiometry. This relates to the higher bond strengths shown in Figure 1 for these high absorbance ratios.

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