AEROSPACE RECOMMENDED PRACTICE

ARP1610™ REV. A

Issued 1981-10
Revised 1985-04
Reaffirmed 2022-06

Superseding ARP1610

Physical-Chemical Characterization Techniques, Epoxy Adhesive and Prepreg Resin Systems

RATIONALE

ARP1610A has been reaffirmed to comply with the SAE Five-Year Review policy.

1. SCOPE:

1.1 This recommended practice describes the physical and chemical characterization techniques for identification of epoxy adhesive and prepreg resin systems in order to verify the chemical formulation, resin B-staging (See 8.1), cure reaction rates, adhesive moisture content, and resin component mix ratios, as necessary to achieve manufacturing and quality producibility and engineering performance.

1.2 Application: While these techniques have been developed and validated for epoxy adhesive and prepreg resin systems, they are expected to be applicable to other thermoset materials, such as phenolics, polyimides, or polyesters. It is the responsibility of the user of the materials to establish limits on the acceptable variations of compositional parameters from the standard or baseline values of the original formulations qualified for use. When established, these variations should be included in applicable material specifications.

1.3 Limitations: These techniques have been developed to detect chemical formulation variations in epoxy systems. Chemical formulation variations have not been quantitatively related to changes in mechanical properties, long-term durabilities, or moisture sensitivities of the material. These techniques should not be considered all-inclusive. The equipment used herein is generally applicable to the quantitative and qualitative analysis of epoxy resins; however, specific materials, other than those discussed herein, may require modified techniques.

1.4 Justification: The procedures described herein are the result of extensive evaluations of structural epoxy adhesive and resin formulations applicable to aerospace applications.

TO PLACE A DOCUMENT ORDER: Tel: 877-606-7323 (inside USA and Canada)
Tel: +1 724-776-4970 (outside USA)
Fax: 724-776-0790
Email: CustomerService@sae.org
SAE WEB ADDRESS: http://www.sae.org

For more information on this standard, visit
https://www.sae.org/standards/content/ARP1610A/

2. DESCRIPTION OF THE METHOD:

2.1 Objective: The use of structural adhesives and epoxy composite materials requires that the composition of these materials be reproducible within prescribed limits established by the user of the materials through applicable procurement specifications. This document describes physical and chemical techniques to identify the constituents in the formulations and to aid in detection of qualitative and quantitative changes or variations of the constituents.

2.2 Summary: This document outlines a standard method to chemically and physically analyze and control epoxy adhesive and composite matrix formulations.

2.3 Processing Steps: In order to achieve the high reliability and consistency necessary in structural applications using epoxy adhesives and composite materials, the following primary steps must be followed:

Chemically characterize selected epoxy formulations,
Establish minimum and maximum formulation standards,
Provide quality control methods for purchased formulations,
Develop manufacturing cure cycles and controls.

3. ANALYTICAL METHODS:

3.1 Chemical Analysis and Quality Control Methods: Quality control for aerospace structural applications requires that epoxy adhesive or prepreg materials selected for a specific design be controlled. This control can only be achieved by knowing the chemical composition of the particular adhesive or composite matrix formulation. The use of the methods described herein, spectroscopy, elemental and wet chemical analysis, chromatography, differential scanning calorimetry and dynamic dielectric analysis, serve not only to identify and confirm the chemical constituents of a formulation but also to establish the basis for ensuring that the purchased products are chemically identical and have been processed to the proper degree of B-staging. A schematic on how the analytical techniques can be used to identify the formulations is given in Fig. 1. The techniques required to use these methods to characterize and ensure the consistency and quality of material are described in the individual methods. Selection of which procedures are required for quality assurance testing is based on the components of a given formulation.

3.2 Spectroscopy: Spectroscopy is a valuable tool for the identification of specific components of a prepreg or adhesive resin. It is used primarily in the qualitative identification of formulative components. It can be used in special cases for quantitative estimation of formulation constituents as demonstrated herein. The primary areas of spectroscopy useful for epoxy materials are infrared, ultraviolet, and emission spectroscopy.

3.2.1 Infrared Spectroscopy: Infrared absorption spectroscopy (IR) is extremely useful for ascertaining the absence or presence of a variety of organofunctional groups.

3.2.1.1 General Infrared Spectroscopy Methods:

(1) Extract the prepreg or adhesive resin in acetone, tetrahydrofuran (THF), or chloroform.

(2) Filter the solution, saving the filtrate.

(3) Apply the filtrate to an infrared plate (KBr or NaCl) and allow solvent to evaporate.

(4) Place the plate in the spectrometer.

(5) Run the spectrum from 4000 cm^{-1} to 400 cm^{-1} using a slow scan and transmission mode.

(6) Compare epoxy spectra to known epoxy reference standards.

3.2.1.2 Quantitative Estimation of the Sulfone Group, Diaminodiphenyl Sulfone (DDS) by Infrared Spectroscopy:

Step 1. Weigh (to the nearest 0.1 mg) 30, 40, 50, 60, 75, and 200-mg (if the IR absorbs in this range) samples of DDS plus resin component into 50-mL volumetric flasks. Dilute to volume with acetonitrile.

Step 2. Place two 1.0 mm KBr precision path length, matched liquid cells filled with acetonitrile in both the sample and reference beams of the spectrophotometer. Scan the region from 1200 to 1100 cm^{-1} to ensure a clean baseline free of extraneous absorptions.

Step 3. Replace the acetonitrile in the sample cell with a standard sample solution. Flush 2 - 3 times with the solution to be analyzed. Record the spectrum from 1200 to 1100 cm^{-1} for each standard solution.

Step 4. Construct a calibration curve on linear graph paper for percent DDS by plotting the negative logarithms of the percent transmittance (T) values for the standard solutions divided by the baseline transmittance (100% T) versus their concentrations in g/L of DDS.

Step 5. Weigh between 0.5 - 0.6 g (to the nearest 0.1 mg) of prepreg; dissolve in 20 mL of acetonitrile. Filter on a tared glass crucible, decant liquid into a 50-mL volumetric flask, dilute to volume.

3.2.1.2 (Continued):

Step 6. Dry the reinforcement to constant weight at 100°C (212°F). Determine the amount of resin by subtracting the dry reinforcement weight from the prepreg weight and divide by 50 to give the sample concentration in g/litre.

Step 7. Analyze the sample in accordance with steps 3 and 4 above.

Step 8. Take the negative log (%T/100%T) of the sample from the IR spectra and determine the amount DDS from the calibration curve.

Step 9. Record the DDS value (mg/mL).

Step 10. Calculate percent DDS (by weight) as follows:

$$\% \text{ DDS} = \frac{\text{DDS concentration g/L}}{\text{Sample concentration g/L}} \times 100$$

3.2.1.3 Quantitative Estimation of Dicyandiamide (DICY) by Infrared Spectroscopy:

Step 1. Weigh (to the nearest 0.1 mg) 10, 25, 37.5, and 50-mg samples of DICY into 50-mL volumetric flasks. Dilute to volume with a mixture of 80/20 tetrahydrofuran/methanol. DICY is extremely sensitive to moisture; it should be stored with a desiccant and weighed in a dry atmosphere.

Step 2. Place two 1.0-mm KBr precision path length matched liquid cells filled with 80/20 tetrahydrofuran/methanol in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 2300 to 2100 cm^{-1} to verify a clean baseline.

Step 3. Replace the 80/20 THF/CH_3OH in the sample cell with a standard sample solution. The cell should be flushed 2 - 3 times with the solution to be analyzed. Record the spectrum from 2300 to 2100 cm^{-1}. DICY exhibits a transmittance minimum at 2190 cm^{-1}. A calibration curve for determining DICY, percent, in resin samples is constructed by plotting the negative logarithm of the percent transmission (%T) values for the standard solutions divided by the baseline transmittance (100%T) versus their concentration in g/L on linear graph paper.

Step 4. Weigh between 0.8 and 0.9 g (to the nearest 0.1 mg) of prepreg and transfer to a 50-mL beaker. Add 20 mL of 80/20 tetrahydrofuran/methanol. Thoroughly agitate the solution to ensure resin dissolution.

3.2.1.3 (Continued):

Step 5. Decant solvent into a 50-mL volumetric flask and collect reinforcement in a preweighed fritted glass crucible. Wash fibers with 80/20 tetrahydrofuran/methanol to ensure complete solution of resin and combine the wash solvent with the 20 mL in the volumetric flask. Dilute to volume and shake until adequately mixed.

Step 6. Dry the glass crucible containing the reinforcement to constant weight at 100°C (212°F). Determine the amount of resin by subtracting the reinforcement weight from the prepreg weight and divide this value by 50 to give the sample concentration in g/litre.

Step 7. Analyze the liquid portion of the sample as described in step 3.

Step 8. Take the %T value of the sample and calculate -log/100%. Determine the amount of DICY by constructing a parallel line to the X-axis from this value to the calibration curve and dropping a perpendicular line to the X-axis. Record the value of DICY in mg/mL.

Step 9. Calculate the percent of DICY (by weight) in the resin as follows:

$$\frac{\text{DICY Concentration, g/L}}{\text{Sample Concentration, g/L}} \times 100$$

3.2.2 Ultraviolet Spectroscopy: Ultraviolet spectroscopy (UV) is similar to infrared spectroscopy except that wavelength is in the 190 - 400 nm range and is rarely used by itself for chemical characterization. UV is useful in conjunction with liquid chromatography where the separated solution is passed through a UV beam, absorbs the UV light and a spectrophotometer detects and quantifies the change in transmittance. An analysis can be based on a fixed wavelength or a scan of the entire spectrum.

3.2.2.1 Ultraviolet Spectroscopy Methods: Ultraviolet spectroscopy chemical characterization techniques are explained under chromatography (See 3.3).

3.2.3 Emission Spectroscopy: Emission spectroscopy is useful to determine the elements and the relative percentages present in the filler materials, resins, or accelerators. The emission method makes use of prisms and diffraction gratings to disperse the radiant energy emitted by excited atoms, ions, or molecules when a sample is excited by an electric arc or spark discharge across electrodes. The energy is recorded photographically and measured for wavelength and intensity.

3.2.3.1 Emission Spectroscopy Method:

Step 1. Prepare a suitable size sample of the material by ashing at not lower than 425°C (800°F) or by extraction with solvent.

Step 2. Place sample on holder in spectrometer.

Step 3. Spark the sample.

Step 4. Determine the elements present from the wavelengths on the photographic plate.

Step 5. Record the elements.

3.3 Chromatography:

3.3.1 Chromatography Parameters:

3.3.1.1 Chromatography is a technique that can be used for separating epoxy formulations based on either the polarity or molecular size of the particular constituents. The adhesive or prepreg formulation is extracted with a solvent. Tetrahydrofuran (THF), acetonitrile, acetone, or chloroform are commonly used. The extracts are passed through various columns which separate the formulative components depending on the molecular size or polarity of the particular constituent. High molecular weight (large) and low polarity compounds pass through the column in question more rapidly, thus effecting the separation. The presence of a particular compound in the effluent stream is detected by either refractive index or ultraviolet light. The component is identified by the time required to elute from the column. The area under the IR- or UV-peak is used to obtain a quantitative measure of the concentration. Resin/curing agent reaction product peaks are also separated in the process giving a measure of the degree of B-stage.

3.3.1.2 The eluent fractions can also be collected separately for IR scans to determine the structure for chemical identification.

3.3.1.3 Three commonly used chromatographic techniques are described herein: Thin layer chromatography (TLC), reverse phase liquid chromatography (RPLC) and gel permeation chromatography (GPC). The RPLC method separates the components by polarity. GPC analysis is based on the use of molecular sieves. TLC makes use of an adsorbent on a glass plate for its separation.

3.3.2 Thin Layer Chromatography (TLC): Thin layer chromatography is a simple, low cost, qualitative tool for separating an epoxy formulation into its components, i.e., resin, diluent, additives, and curing agents. The separation is achieved by applying a solution of the mixture near the lower edge of a glass plate coated with an adsorbent, normally a silica. The plate is placed vertically in a closed container containing a small amount of the elution solvent on the bottom. The solvent migrates up the plate by capillary action carrying the components of the formulation which separate out at specific distances depending on the adsorption coefficients of the compound from the base. The components are located and scraped off the plate for solvent extraction and subsequent IR analysis to identify the chemical structure (See Fig. 2).

3.3.2.1 Thin Layer Chromatography Procedure:

Step 1. Use silica gel coated glass plates (50 x 200 mm) which contain a fluorescent dye (See 8.2).

Step 2. Extract the resin with acetone and filter as necessary.

Step 3. Spot the plate 20 mm from the bottom with extract to form a continuous line of sample using a streaking pipette.

Step 4. Evaporate the acetone.

Step 5. Develop the plate 40 - 60 min. in a vertical position by immersing the lower edge approximately 10 mm in the selected solvent.

Step 6. Locate components using UV light.

Step 7. Scrape gel containing components from plate.

Step 8. Extract samples with acetone and filter the solutions.

Step 9. Obtain IR spectra of the components.

Step 10. Match with spectra of known compounds.

Step 11. Report IR results.

3.3.3 Gel Permeation Chromatography (GPC): Gel permeation chromatography is a form of liquid chromatography in which molecules in solution are separated by permeating through a porous packing gel (molecular sieve). The rate of elution is directly proportional to the speed at which the molecule travels through the column. Small molecules move more slowly since they permeate into the pores of the gel. Thus, the smaller the molecule the longer the elution time. GPC is a valuable tool for epoxy formulations as separations of the resin mixture can be performed quickly and quantitatively. Identification of the peak for each constituent is made

3.3.3 (Continued):

by running each of the components through the column(s) and noting the time at which it is eluted. The fractions can also be collected for further analysis by IR spectroscopy although TLC is the preferred method for IR analysis.

3.3.3.1 Gel Permeation Chromatography Procedures Using Waters Model 244 Chromatograph, or equivalent:

3.3.3.1.1 Chloroform Method:

Step 1. Prepare a stock solution of benzoic acid by weighing 0.250 g ± 0.001 in a 50-mL volumetric flask; dilute to volume in chloroform.

Step 2. Prepare several standards containing 20 - 40% hardener in base resin; the weight should be about 0.350 grams. Dissolve in 100 mL of acetonitrile.

Step 3. Weight 0.350 g of unknown to the nearest 0.1 mg into a 100-mL volumetric flask; dilute to volume in acetonitrile.

Step 4. Pipet 1.0 mL of these solutions into separate 50-mL flasks containing 10 mg of benzoic acid stock solution. Dilute to volume with chloroform (See 8.3).

Step 5. Inject a 100 µL sample onto the GPC column (See 8.4) and elute using chloroform at a flow rate of 2.0 mL per minute.

Step 6. Set the UV detector at a wavelength of 230 nm, if possible. Wavelengths of 270 or 280 nm may also be used.

Step 7. Measure the peak areas of the base resin as well as the advancement peak, the hardener peak and the internal standard peak (See Fig. 4). Normalize the peak areas to a constant sample weight of 0.350 gram. Plot the ratios of base resin plus advancement and the hardener peaks to the internal standard peak against the percent of each component in the weighed standards.

Step 8. Calculate the percent of base resin plus advancement as base resin and percent free hardener in the sample using standard curves.

Step 9. Fractions can be collected for further infrared analysis if necessary.

3.3.3.1.2 Tetrahydrofurane (THF) Method; Standardized Procedure Using Waters Model 244 Chromatograph, or equivalent:

Step 1. Prepare a stock solution of 30 g/L diethylene glycol in tetrahydrofuran (THF).

Step 2. Prepare several standards containing 20 - 40% hardener, the remainder being base resin. Weigh 1.0 g of each resin standard to the nearest 0.1 mg into separate 50-mL volumetric flasks. Dissolve in THF and dilute to volume.

Step 3. Pipet 3.0 mL of the resin solution into a 25-mL volumetric flask containing 120 mg ± 1 of the diethylene glycol stock solution. Dilute to volume with THF.

Step 4. Inject a 100-μL sample onto the GPC columns and elute the sample using a flow rate of 2.5 mL/minute.

Step 5. Set the refractive index detector sensitivity.

Step 6. Measure the peak heights of the hardener, the internal standard, and the base resin from the base line at the start of the chromatogram. Multiply the peak heights of the hardener peak and the base resin peak by the factor $\frac{1.0000\ g}{\text{sample wt}}$ to normalize the data.

Step 7. Plot the ratios of the normalized peak heights against the added hardener concentration.

3.3.3.1.3 Sample Analysis:

Step 1. Prepare samples and obtain chromatograms as in 3.3.3.1.2.

Step 2. Measure the peak heights of the hardener, the base resin, and the internal standard. Normalize the peak heights to a 1.000 g sample weight. Determine the percent free hardener in the sample from the plot of the ratio of the normalized peak heights to the hardener peak.

Step 3. Determine the mix ratio of hardener to base resin from the plot of peak ratio against percent hardener added.

Step 4. Report hardener/base resin percentages.

3.3.4 Reverse Phase Liquid Chromatography: Reverse phase liquid chromatography is a form of chromatography in which molecules in solution are separated based on the relative solubility and distribution of solutes between the mobile phase (solvent) and stationary phase (polar column packing) (See Fig. 3). Molecules of highest polarity tend to elute last because of

3.3.4 (Continued):

their attraction to the column packing. The reverse phase technique is currently preferred for epoxy formulations. This method separates each component including advancement peaks, thus guaranteeing the integrity of the formulations.

3.3.4.1 Reverse Phase Procedure Using Waters Model 244 Chromatograph, or equivalent:

Step 1. Set up the chromatograph with the appropriate reverse phase column (See 8.5).

Step 2. Weigh 0.150 g ± 0.01 (highly absorbing epoxies) or 0.30 g ± 0.01 (normal absorbing epoxies, i.e., most adhesives) neat resin into a 100-mL volumetric flask.

Step 3. Add 1 mL of internal standard solution, 0.02 g benzaldehyde/mL THF (HPLC grade), or equivalent (See 8.6).

Step 4. Dilute to volume (~1.5 g/L) with THF, or equivalent).

Step 5. Shake the mixture.

Step 6. Filter solution through a 0.45-micron (0.45-μm) fluoromembrane filter.

Step 7. Inject 50 - 100 μg of solution onto columns.

Step 8. Set flow rate at 1.5 - 2.0 mL/minute.

Step 9. Set the untraviolet detector at 230 nm, if possible. Wavelengths of 270 or 280 nm may also be used.

Step 10. Gradient: 20 - 95% solvent

Opposing solvent: H_2O

Step 11. Set linear program 25 min. and hold 5 min. at 95% solvent.

Step 12. Compute peak areas for a minimum of the main curing agent, resin peak, and reaction product peak with reference to the internal standard. The peak area can be calculated with a planimeter, by cutting out the peaks and weighing them or by an electronic integrator. Compute percent area of peaks.

Step 13. Compare the peak areas to the standards established for the curing agent, resin, and reaction products.

3.4 Moisture Analysis by Karl Fischer Technique: The moisture content of prepregs and adhesives is a function of storage environment prior to analysis. The Karl Fischer method of moisture analysis employs an electro-chemical measurement (aquameter) of an attracted sample in a methanol-pyridine solution and titration with the Karl Fischer solution until neutralized.

3.4.1 Moisture Analysis Method by the Karl Fischer Technique (ASTM E203):

Step 1. Place 50 - 75 mL of a 4/1 ratio (methanol (absolute)/pyridine) solvent mixture in a 250-mL titration beaker.

Step 2. Place the beaker in the rubber holder and insert the rubber stoppers.

Step 3. Titrate with the Karl Fischer reagent while stirring with a magnetic stirrer, until a neutral value of 4 is obtained on the aquameter. This reagent can be adversely affected by basic amine curing agents giving erroneous results.

Step 4. Add 20.000 g $\pm$ 0.001 of the test sample (w).

Step 5. Dissolve the sample in the methanol/pyridine solution.

Step 6. Back titrate to the neutral value of 4.

Step 7. Record the millilitres of reagent used; (V_L).

Step 8. Standardize the Karl Fischer Reagent by titrating a known weight of water (W); approximately 0.1 g weighed to the nearest 0.1 milligram.

Step 9. Record the amount of Karl Fischer Reagent required to neutralize the water (V_w).

Step 10. Calculate the standardization factor (F) for the Fischer Reagent. $F = 1000W/V_w$.

Step 11. Report the percent water in the sample and sample weight.

$$\text{Water, \%} = \frac{V_L F}{1.0\ w}$$

3.4.2 Gas Phase Chromatography: Moisture analysis by gas phase chromatography is an acceptable alternate to the Karl Fischer technique.

3.5 Other Analytical Techniques: There are a number of analytical procedures which have been available to the chemical industry for a long time that also are useful in the characterization of prepreg and adhesive materials. The methods which follow include percentage of reinforcement, hydrolyzable chlorine, percentage of sulfur, and atomic absorption for boron analysis, an element present in the accelerators commonly used in epoxy formulations.

3.5.1 Percent Reinforcement: The percent reinforcement, either fiber, cloth, scrim, or filler, can be determined quantitatively by extracting the reinforcement with solvents. An optional visual or chemical analysis of the reinforcement can be performed as required.

3.5.1.1 Percent Reinforcement Methods:

Step 1. Weigh a 25 - 50 g sample of the resin or prepreg to the nearest 0.1 milligram.

Step 2. Extract the resin from the reinforcement with acetone or methyl ethyl ketone or other suitable solvent.

Step 3. Dry the scrim for adhesives, or fiber for prepregs, and reweigh.

Step 4. Resins with fillers can also be filtered and washed with solvents to determine the percent filler.

Step 5. Calculate the percent fiber, scrim, or filler by:

$$\%\ \text{Reinforcement (or Filler)} = \frac{\text{wt of resin free reinforcement (or filler)}}{\text{wt of resin or prepreg}} \times 100$$

3.5.2 Hydrolyzable Chlorine: Chemically bound chlorine is usually found in liquid epoxy resins. It can be quantitatively estimated in concentrations substantially less than 1% by using ASTM D1726. The chlorine residues result from the fact that most epoxy resins are manufactured using epichlorhydrin as one of the reactants. The net use of the processes involved leaves chlorine-containing residues in the base resin. This analysis is normally used as a quality assurance procedure by the resin formulator prior to making an adhesive or prepreg material.

3.5.3 Atomic Absorption: Atomic absorption (AA) is used to measure the concentration of boron contained in epoxy catalyzed formulations. The AA method operates by flaming a sample which volatilizes the element. Light from a hollow cathode lamp is passed through the volatiles and the absorbed energy is quantified by a photomultiplier detection system.

3.5.3.1 Atomic Absorption Method:

Step 1. Prepare a calibration curve measuring the absorbance of boron for at least four standards of accelerator. Weigh each standard to the nearest 0.1 mg accuracy. Dissolve each standard in methyl isobutyl ketone (MIBK) to an accurately known volume. The amounts of accelerator should be less than, approximately equal to, and greater than the amount contained in the sample. Construct the calibration curve by plotting accelerator in kg/L versus absolute absorbance units. Flame conditions in the AA unit should comply with the manufacturer's recommendations.

Step 2. Weigh (to the nearest mg) a 2.0-g sample of the resin being analyzed into a 50-mL beaker and dilute with approximately 25 mL MIBK. Thoroughly agitate for not less than 10 minutes. Transfer to a 50-mL volumetric flask. Rinse the beaker twice with approximately 10 mL of MIBK into the flask, then dilute to volume with MIBK.

Step 3. Withdraw a weighed sample, insert in the AA unit, and record the absorbance units.

Step 4. Use the calibration curve to obtain the weight of accelerator per millilitre. Calculate the weight percent as follows:

$$\text{Accelerator, weight percent} = \frac{\text{accelerator weight, kg/L (from calibration curve)}}{\text{sample weight, g}} \times 100$$

3.5.4 Sulfur Analysis: Sulfur analysis on the resin/curing agent mixture can be determined by a modification of the ASTM D817 procedure. Sulfur analysis is important since it relates to the percentage curing agent in some formulations. Results from this method have been found to agree well with the sulfone analysis method (See 3.2.1.2).

3.5.4.1 Sulfur Analysis Method: Perform the sulfur analysis in accordance with ASTM D817 using the nitric acid and perchloric acid mixture as the oxidant. The sulfur is determined gravimetrically as barium sulfate.

3.6 Cure Cycle Development and Control Methods:

3.6.1 Differential Scanning Calorimetry (DSC): The differential scanning calorimetry (DSC) technique is a method for measuring the amount of heat evolved due to the chemical reactions of curing, or the amount of heat required to evaporate a solvent or melt a component. DSC is a useful tool for determination of the temperature where curing starts, the reaction exotherm peaks, heat of reaction, and the completion of cure of adhesive or prepreg resins. The method described below is particularly sensitive to B-stage and formulative changes. This technique plots heat evolved, or required, for a particular event, Δq, versus temperature (Fig. 5).

3.6.1.1 Thermal Analysis Method by DSC:

Step 1. Extract the resin-curative materials from the adhesive or prepreg using a mixture of 90% acetone and 10% methyl alcohol by volume (See 8.7).

Step 2. Vacuum evaporate the extract to dryness at room temperature.

Step 3. Weigh out a 5 - 10 mg sample.

Step 4. Place the sample with container in the instrument together with a suitable reference.

Step 5. Set the time base and program rate desired.

Step 6. Start the Thermal Analyzer with the equipment in the DSC mode.

Step 7. Determine the temperature of reaction initiation, T_i, for a series of three DSC runs at three different heating rates.

Step 8. Reduce the data by obtaining the best straight line fit by linear regression of the Arrhenius expression:

$$\text{Log } \emptyset = A/T_i + B$$

where:

$\emptyset$ = Heating rate (°C/min.)

T_i = Temperature (°K) of reaction initiation

A = Constant related to activation energy

B = Constant related to the Arrhenius frequency factor

Step 9. Report the reaction initiation temperature in °C.

Note: Aging or resin advancement increases the T_i value.

3.6.2 Dynamic Dielectric Analysis (DDA): Dynamic dielectric analysis (DDA) is a method to develop cure cycles for prepreg materials or adhesives and has also been used as a fingerprinting technique to monitor the processing characteristics and composition of the matrix. The DDA technique plots dissipation factor (Tan δ) of the prepreg or adhesive as a function of cure temperature (See Fig. 6).

3.6.2.1 Dielectric Analysis Method (See 8.9):

Step 1. Cut not less than two 3-in. (75-mm) diameter circles of the prepreg or adhesive.

Step 2. Remove the parting films or paper.

Step 3. Place the layered samples in an aluminum cup or other suitable container.

Step 4. Cover sample with 1 layer of glass cloth (any fabric style) and 1 layer of polyimide film (See 8.8).

Step 5. Place cup in a Lavite holder and insert press plunger.

Step 6. Turn on temperature-controller power.

Step 7. Turn on dielectrimeter and set at 100 - 1000 Hz.

Step 8. Place Lavite holder in a hydraulic press, close, and set desired pressure on sample.

Step 9. Check capacitance and dissipation meter for signal level.

Step 10. Insert sample thermocouple in a sample cup port.

Step 11. Turn on recorder and set chart speed, temperature level, capacitance, and dissipation.

Step 12. Zero capacitance and dissipation with sample disconnected.

Step 13. Reconnect leads, lower chart pens and run 2 min. to establish baseline.

Step 14. Turn on heater and temperature controller.

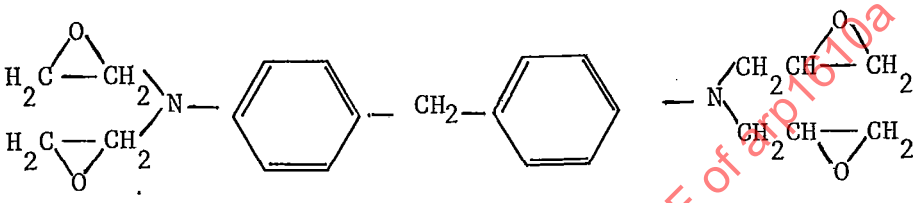
Step 15. Allow run to continue to cure completion.

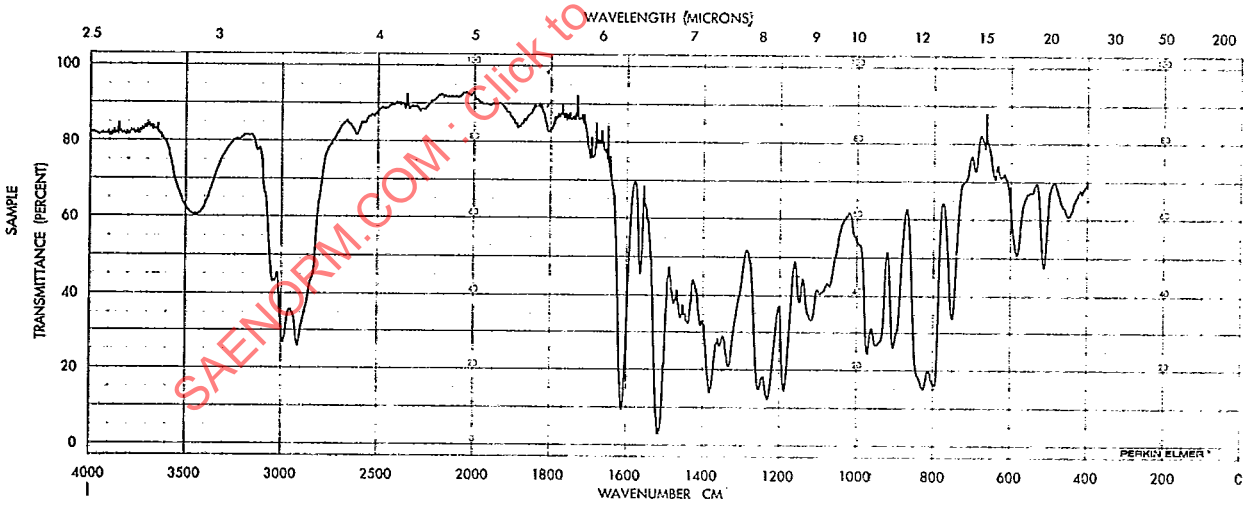
Step 16. Report time to reach each peak, heating rate, and top temperature. These data will essentially reproduce the Tan δ curve. The first peak is the softening of the resin. The gel is associated with the second or "reaction" peak, but does not necessarily occur at the apex.

4. GENERAL MATERIAL REFERENCES ON FORMULATIVE COMPONENTS:

4.1 Epoxy Resins:

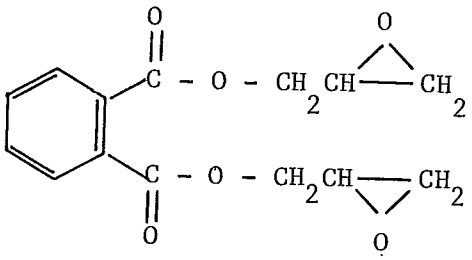
4.1.1 Tetraglycidylmethylenedianiline (TGMDA):

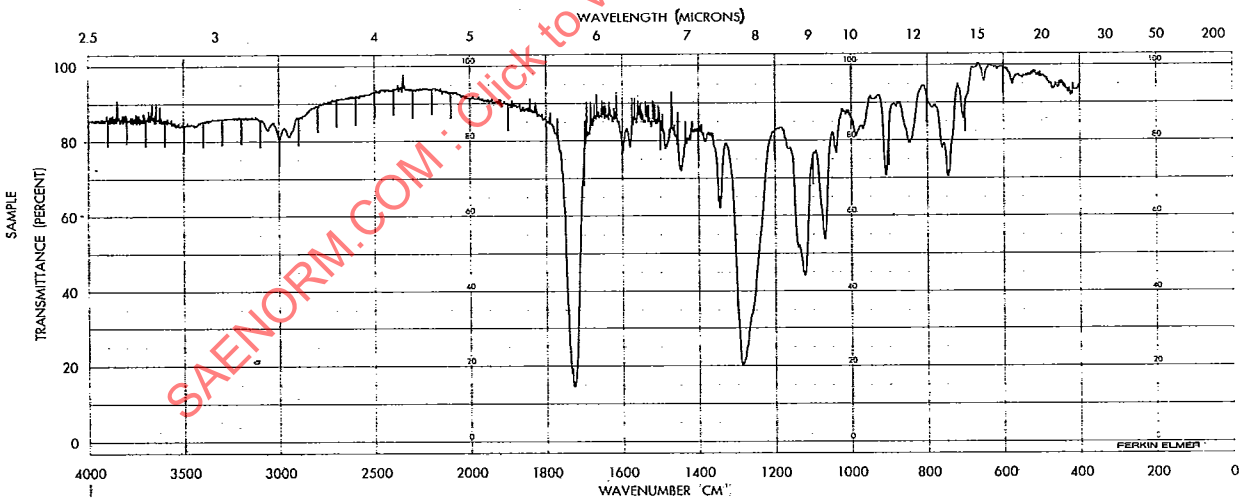




IR SPECTRA TGMDA

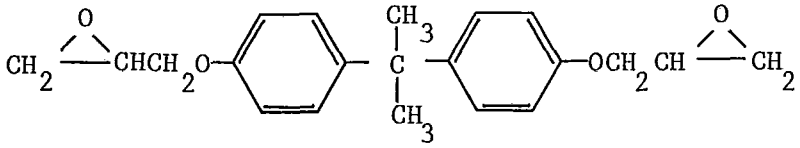
4.1.2 Diglycidylorthophthalate (DGOP):

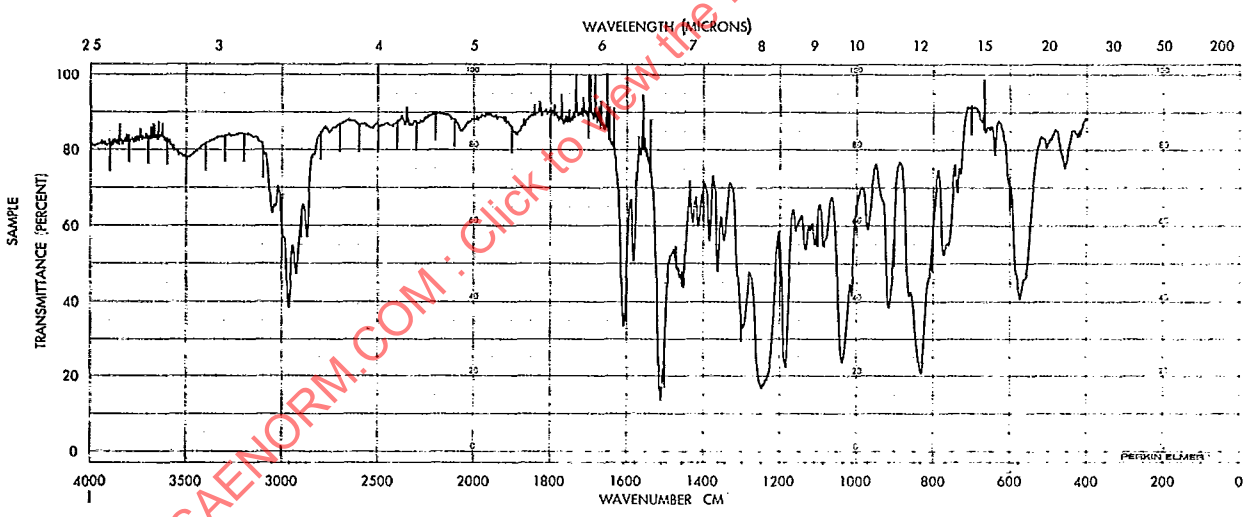




IR SPECTRA DGOP and TGMDA

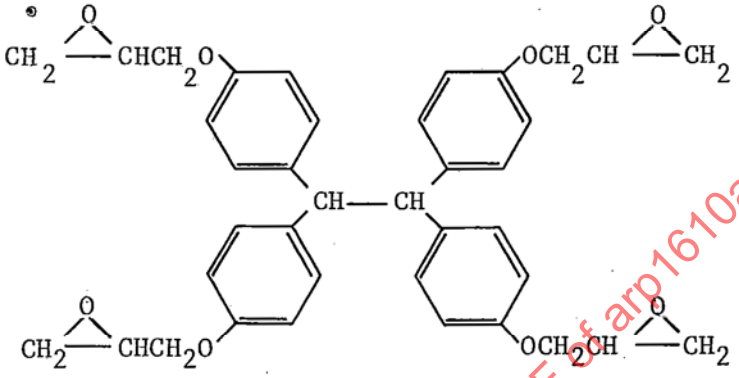
4.1.3 Diglycidyl Ether of Bisphenol A, (DGEBA):

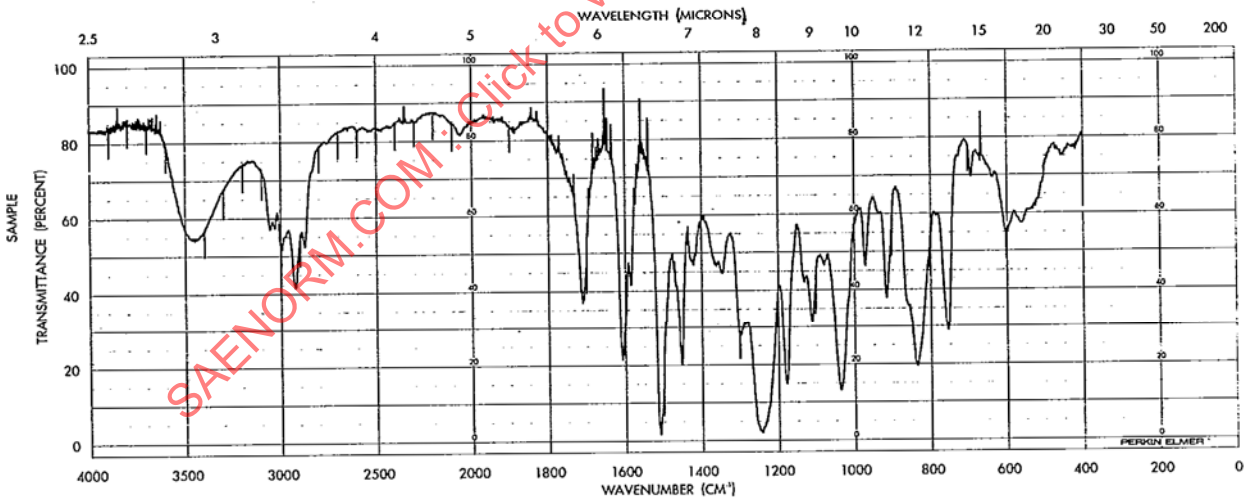




IR SPECTRA DGEBA

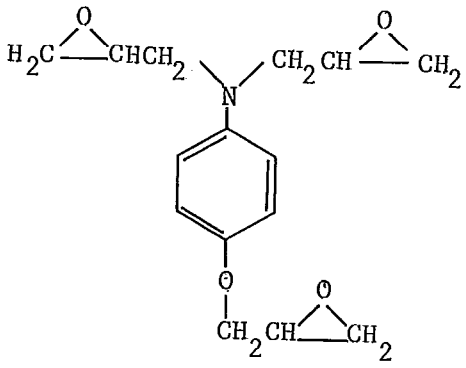
4.1.4 Tetraglycidyl Ether of Tetraphenolethane, (TGETPE):

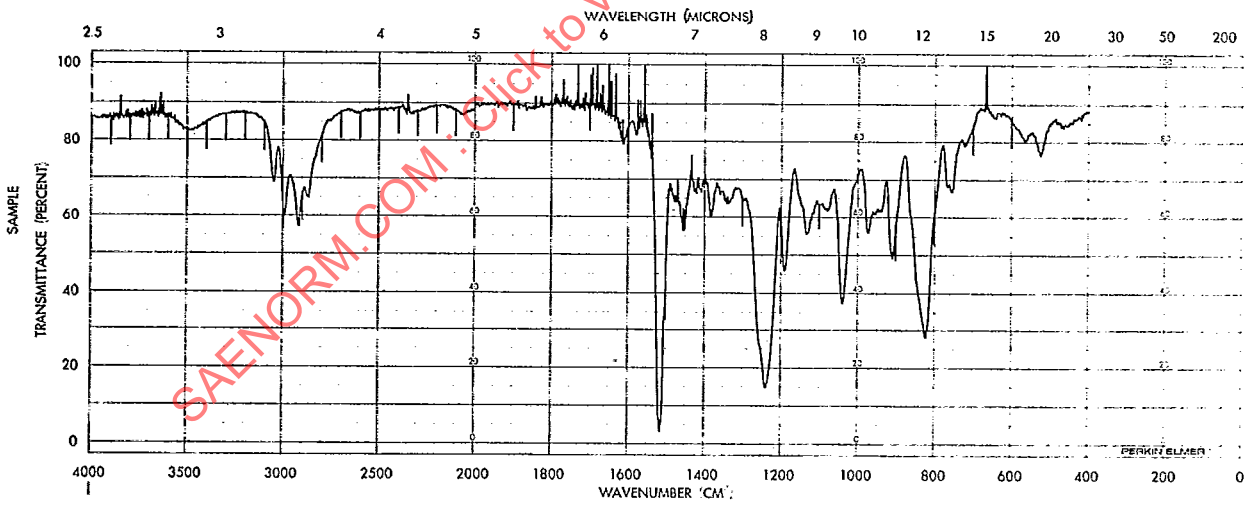




IR SPECTRA TGETPE

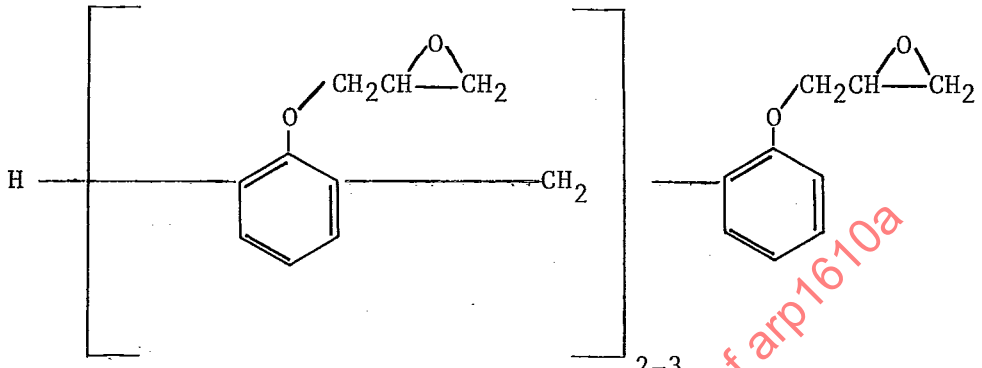
4.1.5 N,N-Diglycidyl-P-Amino Phenyl Glycidyl Ether, (TGPAP):

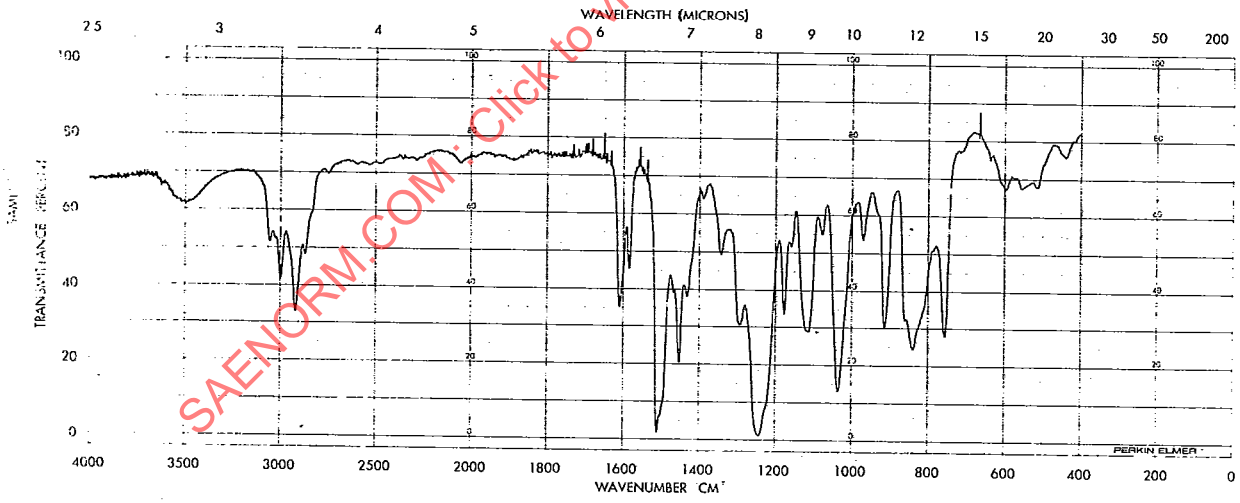




IR SPECTRA TGPAP

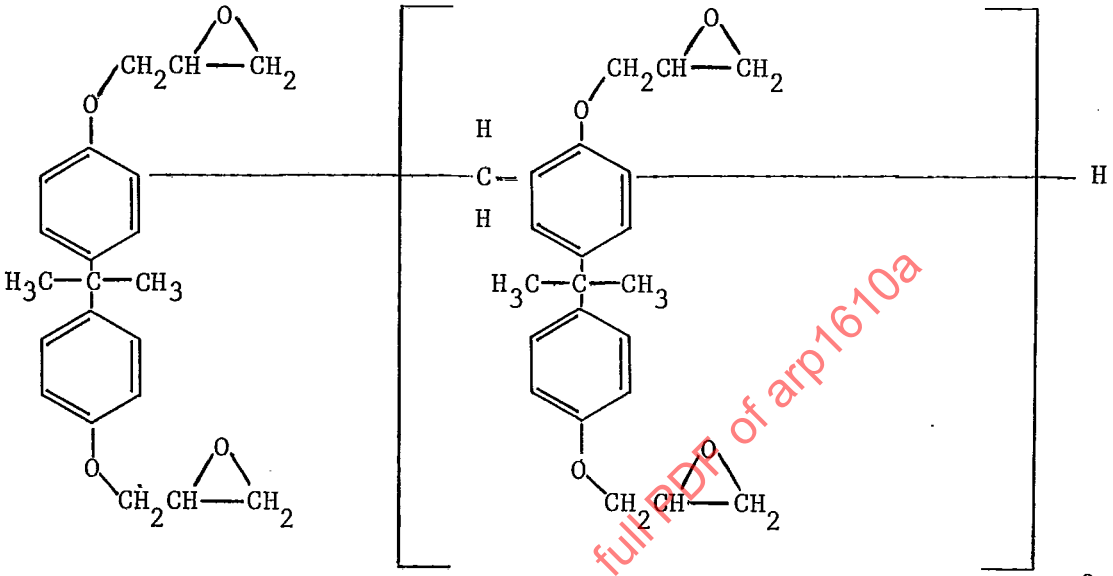
4.1.6 Glycidyl Ether of a Novolac, (E/N):



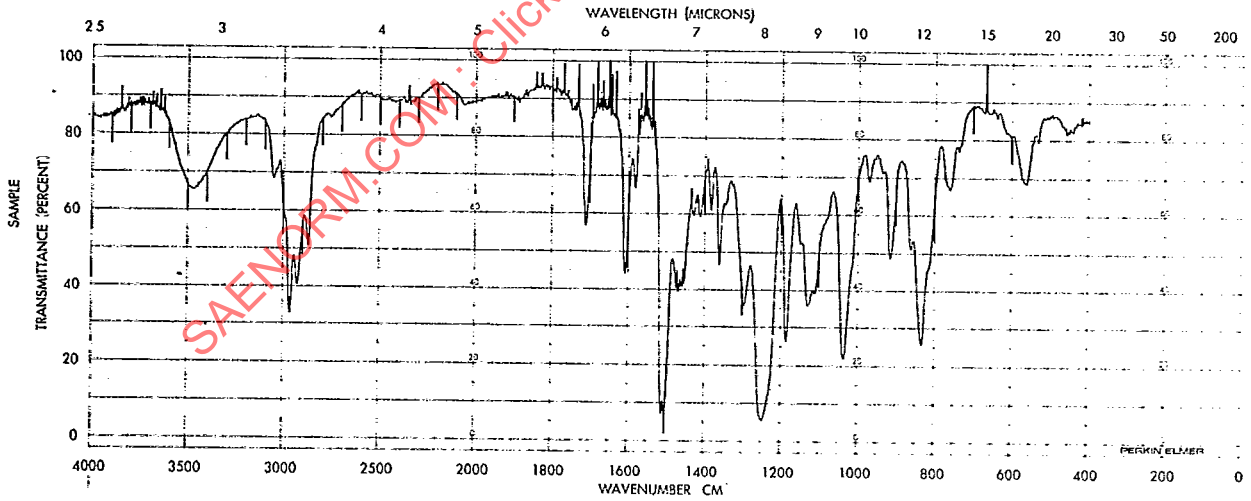


IR SPECTRA E/N

4.1.7 Glycidyl Ether of a BPA Novolac, (E/BPN):



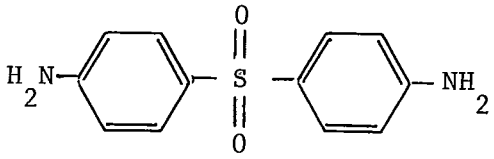
3

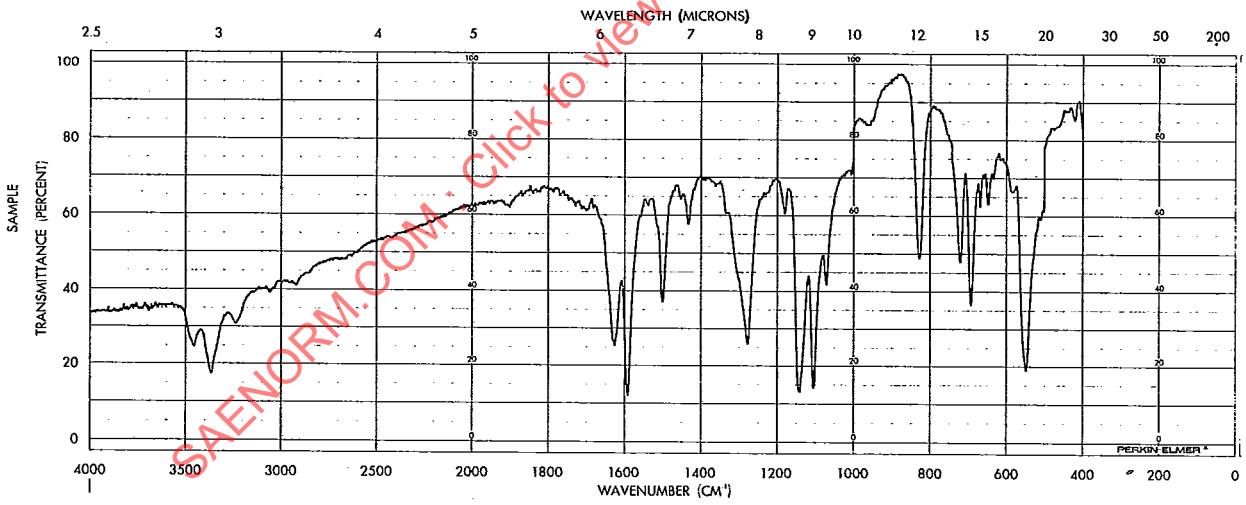


IR SPECTRA E/BPN

4.2 Curing Agents:

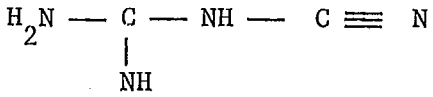
4.2.1 Diaminodiphenylsulfone, (DDS):

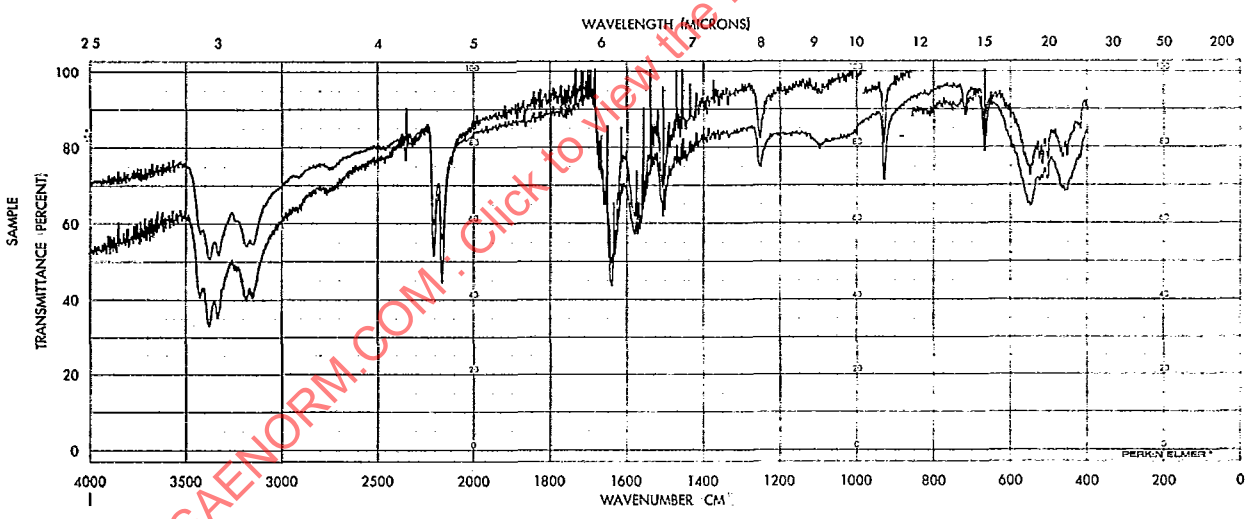




IR SPECTRA DDS
(See Note 8.10)

4.2.2 Dicyandiamide, (DICY):





IR SPECTRA DICY