Quantitative Analysis of PMR-15 Polyimide Resin by HPLC

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Synopsis

PMR-15 resin solutions consist of nadic ester (NE), the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDE), and 4,4′-methylenedianiline (MDA) dissolved in methanol in a 2.000/2.087/3.087 molar ratio. Other chemical species may be present as a result of impurities in the monomers or reaction products which form upon aging of the solution. The effect of these other chemical species on the resin cure chemistry and composite properties is only partially understood. The composition of 50 wt % PMR-15 resin solutions was measured by reverse phase, high performance liquid chromatography (HPLC). The major impurity in the monomers was found to be monoester and tetraacid impurities in the BTDE solution. These impurities could be eliminated by recrystallizing the dianhydride from which the BTDE was made. Triester formation was not a problem because of the high rate of esterification of the anhydride compared to that of the carboxylic acid. When the PMR-15 monomer solution was aged at room temperature, the concentration of BTDE remained constant. The concentration of NE and MDA decreased as their reaction products formed. The amide-acid formed quickly but remained at a small concentration. The monoimide and bisimide concentrations increased monotonically during the entire aging time. When the PMR-15 resin was stored as a dried film, imidization of NE and MDA still occurred, but at a reduced rate.

INTRODUCTION

PMR polyimides are addition type, thermosetting polymers used for applications at high temperature (up to 316°C) in thermooxidative environments.[1] These materials are particularly useful as the matrix resin in carbon fiber composites because their high temperature stability is accompanied by ease of processing and formation of void-free composites. The resin is prepared from the three monomer reactants shown in Figure 1. The abbreviated names (NE, BTDE, and MDA) indicated in Figure 1 will be used throughout the text. The abbreviation BTDA will be used for the dianhydride of 3,3′,4,4′-benzophenonetetracarboxylic acid, and BTTE will be used for the tetraester. An idealized reaction sequence leading to the crosslinked network structure is shown in Fig. 2.[2] If NE, BTDE, and MDA are combined in a 2.000/2.087/3.087 molar ratio, the formulated number average molecular weight of the oligomers after imidization but before crosslinking is 1500. Resin of this composition is designated PMR-15. In practice, the monomers are generally dissolved in methanol, and the solution is used to impregnate the reinforcing fibers. The impregnated fibers with solvent removed is called prepreg. Ideally, no chemical reaction occurs during prepreg formation. Imidization and crosslinking occur during the cure process at high temperature. However, the reactions in the first step of Figure 2 occur at some low (but finite) rate even at room temperature.[3] In addition, BTDE and NE may react with methanol or water

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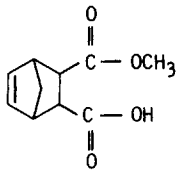
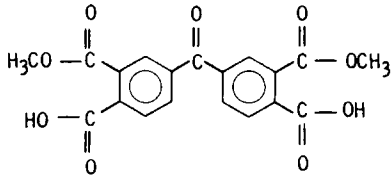
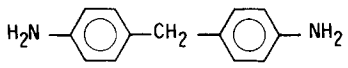
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3,3'4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

Fig. 1. PMR-15 monomers.

to form the other acid-esters indicated in Figures 3 and 4. Therefore, the PMR monomer solution consists of MDA, NE, and BTDE as the main ingredients plus reaction products of the monomers, acid-esters of benzophenonetetracarboxylic acid, and acid-esters of nadic diacid as impurities. The concentration of the impurities depends on the purity of the starting materials, the age of the solution, and the extent of exposure to heat and humidity. It has already been demonstrated that the presence of the trimethyl ester of benzophenonetetracarboxylic acid may result in poor laminate quality because of void formation in the resin during cure.[4,5] The effect of other impurities on laminate quality is not fully known. The purpose of the present work was to develop a technique for quantitatively determining the composition of the monomer solutions and to use this technique to observe the changes in composition of PMR-15 resin solution and prepreg with aging time. An effort was made to keep the procedure as simple as possible so that the technique could be used as a tool in future studies relating the monomer solution composition to composite performance. All of the components in the PMR-15 monomer solution could be separated by high performance liquid chromatography (HPLC) with a reverse phase column. The composition of solutions could be determined with $\pm 8\%$ accuracy for most components.

EXPERIMENTAL

Starting Materials

The materials used in this work are described in Table I. The purity of the materials was checked by HPLC and melting point. The BTDA purity could not be checked directly by HPLC because it reacts with water in the solvent during the HPLC experiment. However, since esterification is much faster for

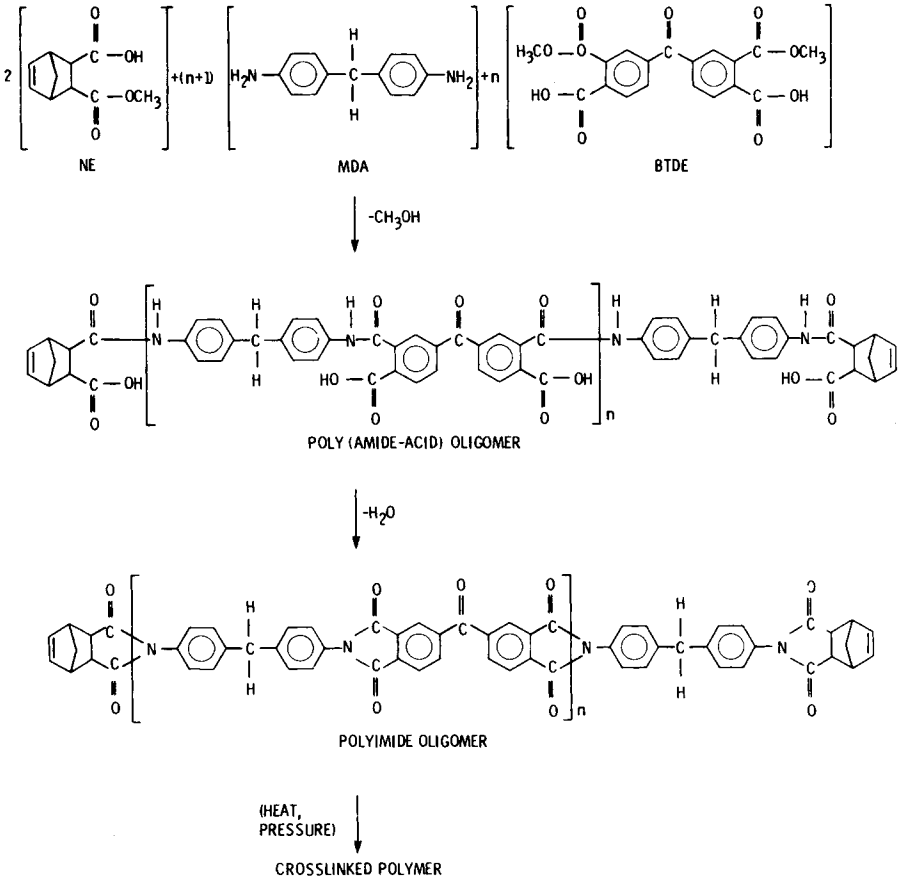


Fig. 2. Idealized reaction sequence for imidization and crosslinking of PMR-15 resin. (n = 2.087 for 1500 molecular weight.)

the anhydride than for the acid, the purity of the BTDA could be inferred from the composition of esterified BTDA. Pure BTDA was prepared by recrystallization from acetic anhydride. NE always appeared as a single peak in the HPLC chromatogram, even when stored as a dilute solution for several weeks. It was therefore assumed that the NE was pure endo isomer and that no isomerization to the exo isomer occurred. The water was deionized to 1 MΩ cm resistivity and distilled. HPLC grade solvents were used. Polarographic grade tetrabutylammonium perchlorate was used as a PIC (paired ion chromatography) reagent.

Preparation of BTDE

The 50 wt % BTDE solutions were prepared by weighing BTDA and methanol into a flask in a 1.000/1.398 mass ratio. The solution was then stirred and refluxed for 2 h after all solids were in solution. Methanol was then added to make up for solvent lost during reflux. Batch sizes ranged from 25 to 200 mL.

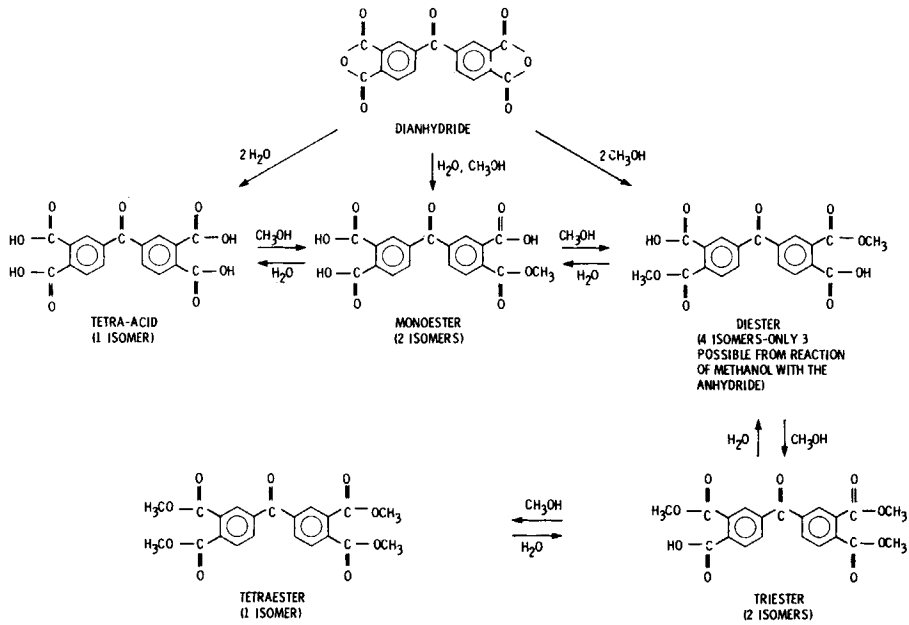


Fig. 3. Reaction products for the dianhydride of benzophenonetetracarboxylic acid in the presence of methanol and water.

Preparation of PMR-15 Monomer Solutions

The cooled 50 wt % solution of BTDE and the monomers MDA and NE were weighed separately in a 1.000/0.379/0.243 mass ratio. A 50 wt % PMR-15 monomer solution was prepared by combining the three components along with an amount of methanol equal to the mass of MDA plus NE. The NE and MDA powders dissolved easily with no apparent heat of solution. HPLC chromatograms of freshly prepared solutions showed that no chemical reactions had occurred during mixing, regardless of the order in which the components were mixed.

HPLC Technique

A 25 cm reverse phase column (PRP-1, part number 79427 from Hamilton Co.) was used for all HPLC data reported in this paper. The column packing is 10 μm beads of styrene-divinylbenzene copolymer. A Spectra Physics Model SP8100 chromatograph with a Model SP8440 variable wavelength UV/visible detector was used. The wavelength of the detector was set to either 200 or 254 nm. All solutes absorbed sufficiently at 200 nm, and all but nadic anhydride, nadic diacid, and its methyl esters absorbed at 254 nm. The solvent system was acetonitrile/PIC solution pumped at 1 mL/min. The 0.005*M* PIC solution was prepared by adding the PIC reagent to boiling water. Solvent compositions of 25/75 and 50/50 acetonitrile/PIC solution were used. Samples to be run were dissolved in 25/75 acetonitrile/PIC solution. The 50 wt % PMR-15 formed a precipitate when added directly to the acetonitrile/PIC solution. In order to avoid this precipitation, the 50 wt % solution was first diluted with methanol to about 5 wt %. The acetonitrile was then added,

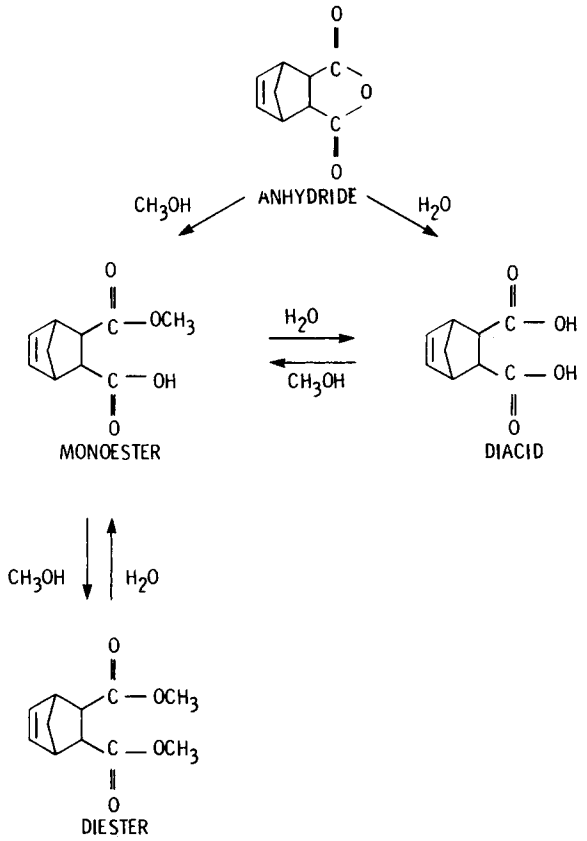


Fig. 4. Reaction products for nadic diacid in the presence of methanol and water.

followed by the slow addition of the PIC solution. Sample concentrations were typically 0.2 g/L and the volume injected was 10 μL. Nonpolar, organic matter from the solvent[6] deposited on the column when the volume fraction of water in the solvent was < 0.5. This caused no problems in reproducibility during repeated isocratic (constant solvent composition) runs. However, when the water fraction of the solvent was reduced, the contamination adsorbed on the column began to elute. This prevented the use of a solvent gradient for quantitative analysis. When the solvent composition was changed between isocratic runs, the solvent was first changed through a gradient to 100% acetonitrile and held for 10 min to clean the column. Then the solvent was changed through a gradient to the desired composition and pumped isocratically for at least 20 min to obtain a stable baseline before injecting the sample. At the end of each day, the column was flushed with 100% acetonitrile for at least 30 min before stopping the solvent flow.

Data were collected and stored on a Hewlett-Packard 3354 minicomputer.

UV Absorbance Spectra

A Varian Model 2390 spectrophotometer was used to measure the UV absorbance of solutions from 190 to 290 nm. Quartz cells with 1 cm path length were used with typical solution concentrations of 0.01 g/L.

TABLE I
Material Sources and Purity

Material	Supplier	Minimum purity
5-norbornene-2,3-dicarboxylic acid	Prepared in-house	-----
-monomethyl ester (endo isomer)	Burdick and Jackson	99
-dimethyl ester	Prepared in-house	-----
-anhydride	Eastman, lot B4X	-----
3,3'4,4'-benzophenonetetracarboxylic acid	Prepared in-house	97
-monomethyl ester	(not isolated)	
-dimethyl ester	Prepared in-house (in methanol)	99
-trimethyl ester	(not isolated)	-----
-tetramethyl ester	Prepared in-house	99
-dianhydride	Aldrich, lot 3915LJ, 96 percent	-----
	-recrystallized in-house	99.5
	-recrystallized and sublimed	99.5
4,4'-methylenedianiline	Eastman, lot A64	99
-mononadamide	(not isolated)	-----
-mononadimide	Prepared in-house	98
-bisnadimide	Prepared in-house	98
Acetonitrile	Fisher	HPLC grade (λc = 190 nm)
Methanol	Burdick and Jackson	HPLC grade (λc = 204 nm)

RESULTS

Retention Times in Reverse Phase HPLC

In the reverse phase HPLC experiment the solvent flows through a porous, nonpolar, stationary medium.[7] Since the solvent is more polar than the stationary phase, solute molecules elute in the order of decreasing polarity. Retention times can be shifted by varying the polarity of the solvent. For the present work, the polarity of the solvent was increased by increasing the volume fraction of water in the solvent. Figure 5 shows the HPLC chromatogram of an aged PMR-15 monomer solution at two different solvent compositions. With a solvent composition of 50/50 all components are eluted within 12 min, but the peaks in region A (0–5 min) overlap. If the solvent composition is changed from 50/50 to 25/75, region A is expanded from about 5 to 30 min. The peaks within region A are then well separated. However, most of region B is shifted to retention times greater than 50 min. Notice that the mononadimide of MDA does not elute within 50 min with a solvent composition of 25/75. It is therefore necessary to perform two separate isocratic experiments with solvent compositions of 50/50 and 25/75 for complete separation of all components.

If the solvent consists of acetonitrile and pure water, the peaks corresponding to the trimethyl ester of benzophenone tetracarboxylic acid become very broad with nonreproducible retention times as the volume fraction of water is increased to 75%. This may be a result of reduced solubility in solvent with a high water content. It was found that addition of 0.005*M* PIC reagent to the water resulted in good peak shapes with reproducible retention times. In addition, the monoester and tetraacid peaks were shifted to longer retention

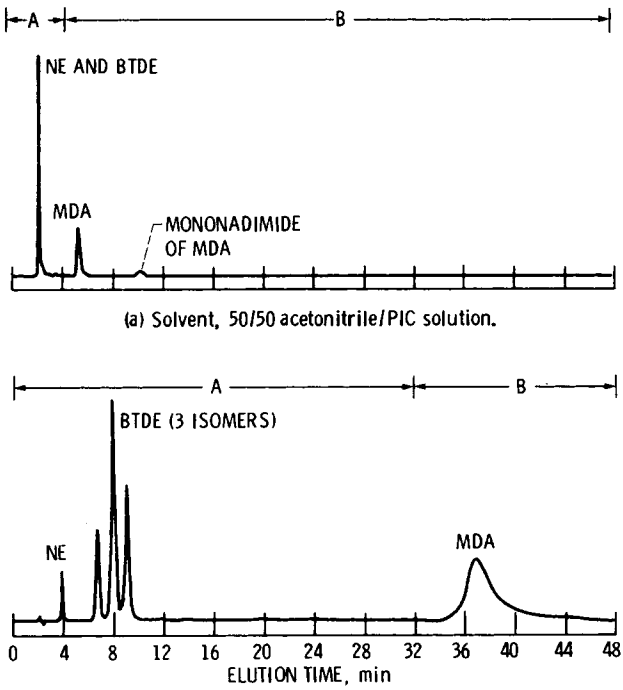
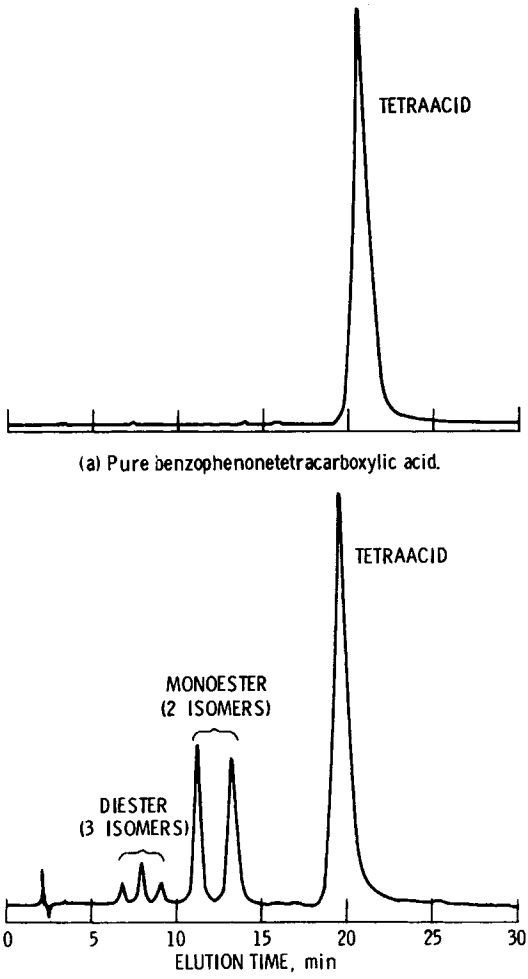


Fig. 5. HPLC chromatograms of PMR-15 resin. (Solvent = 25/75 and 50/50 acetonitrile/PIC solution.)

times. This resulted in good separation of all the acid-esters of benzophenonetetracarboxylic acid. The presence of the PIC reagent had little effect on retention times of other components.

Figure 6 is the chromatogram of pure benzophenonetetracarboxylic acid and of the tetraacid refluxed in methanol for about 24 h with sulfuric acid catalyst. After refluxing, the two isomers of the monoester appear with retention times of 11.34 and 13.13 min, and the three isomers of the diester appear with retention times of 6.59, 7.62, and 8.67 min. Since the acid group is more polar than the ester group, one expects the tetraacid to elute first followed by the monoester isomers and then the diester isomers. If there is no PIC reagent in the water the expected order of elution is observed, but significant overlapping of the peaks occurs. In the presence of PIC reagent, the peaks are well separated, but the diester isomers elute first followed by the monoester isomers and then the tetraacid (as in Fig. 6). A similar effect occurs with nadic diacid and nadic monoester (not shown). It appears that when two carboxylic acid groups are attached to adjacent carbon atoms, the PIC reagent causes a significant increase in retention time. In one experiment the retention time of the tetraacid increased from 1.83 to 21.61 min upon addition of the PIC reagent. The retention times of the monoester isomers, which have paired acid groups on only one end of the molecule, were shifted only about half as far as that of the tetraacid. The retention time of the nadic diacid peak was shifted from 2.04 to 4.59 min.



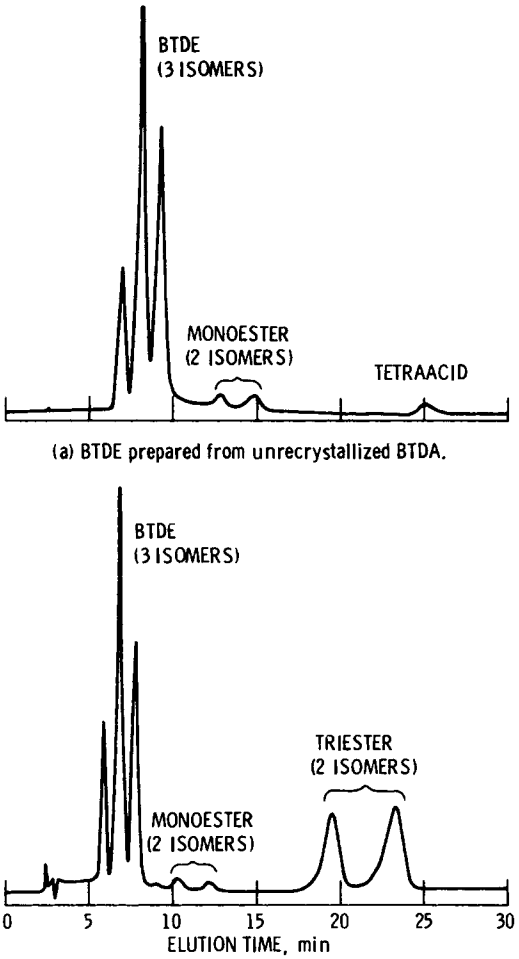
(a) Pure benzophenonetetracarboxylic acid.

(b) Benzophenonetetracarboxylic acid refluxed 24 hr in methanol with sulfuric acid catalyst.

Fig. 6. HPLC chromatograms of pure and partially esterified benzophenonetetracarboxylic acid. (Solvent = 25/75 acetonitrile/PIC solution.)

The chromatogram of BTDE prepared from unrecrystallized BTDA is shown in Figure 7(a). Even in the freshly prepared BTDE solution there is some monoester and tetraacid present. This is a result of acid impurities in the BTDA. After the methanol solution of BTDE is refluxed for 96 h with sulfuric acid catalyst, the tetraacid and the monoester concentration is reduced and the triester forms [Fig. 7(b)]. The two isomers of the triester appear as peaks at 20.33 and 23.56 min.

The retention times of interest in this work are listed in Table II. In most cases the retention times were determined from the HPLC chromatograms of standard samples, or from chromatograms of the esterification products of standard samples (as discussed above). The retention time of the amide-acid of NE and MDA was determined by following the reaction of NE and MDA



(a) BTDE prepared from unrecrystallized BTDA.

(b) BTDE refluxed 96 hr in methanol with sulfuric acid catalyst.

Fig. 7. HPLC chromatograms of pure and partially esterified BTDE prepared from unrecrystallized BTDA. (Solvent = 25/75 acetonitrile/PIC solution.)

in dilute acetonitrile solution. Retention times were generally reproducible within ±4% on any one day. Analysis of retention time data over a period of several months showed reproducibility within ±20% (based on twice the standard deviation). This variation is probably a result of day to day variations of room temperature in the lab. The retention time of the tetraacid was especially sensitive to these variations.

Quantitative HPLC

The HPLC detector measures the amount of light absorbed by the solution passing through the cell. The absorbance of the solvent is negligible or small enough to be balanced out electronically. For dilute solutions the detector output voltage is proportional to the concentration of the solute in the solution passing through the detector. For a specified flow rate the peak area

TABLE II
Retention Times and Relative Response Factors

Material	Abbreviation	Solvent = 25/75		Solvent = 50/50		
		Retention time, min	Relative response factor (λ = 200 nm)	Retention time, min	Relative response factor (λ = 200 nm)	Relative response factor (λ = 254 nm)
5-nonbornene-2,3 dicarboxylic acid		4.5	1.25	2.1	----	0.00
-monomethyl ester	NE	3.8	[a]1.00	2.1	----	↓
-dimethyl ester		25	----	6.9	----	
-anhydride		28	----	5.9	----	
3,3',4,4'-benzophenonetetracarboxylic acid		27-33	5.46	2.4	----	----
-monomethyl ester (2 isomers)		11.9 13.6	4.22	----	----	----
-dimethylester (3 isomers)	BTDE	6.8 8.0 9.1	4.34	2.1	----	----
-trimethyl ester (2 isomers)		20.0 22.5	3.42	2.5	----	----
-tetramethyl ester	BTTE	-----	----	15.9	[a]1.00	[a]1.00
-dianhydride	BTDA	-----	----	----	----	----
4,4'-methylenedianiline	MDA	39	[b]10.3	5.6	2.37	1.12
-mononadamide		19.0	----	2.5	----	----
-mononadimide		-----	----	10.4	1.35	0.40
-bisnadimide		-----	----	20	1.04	0.06

[a]Used as a standard.
[b]Approximate: peak does not return to baseline in less than 50 min.

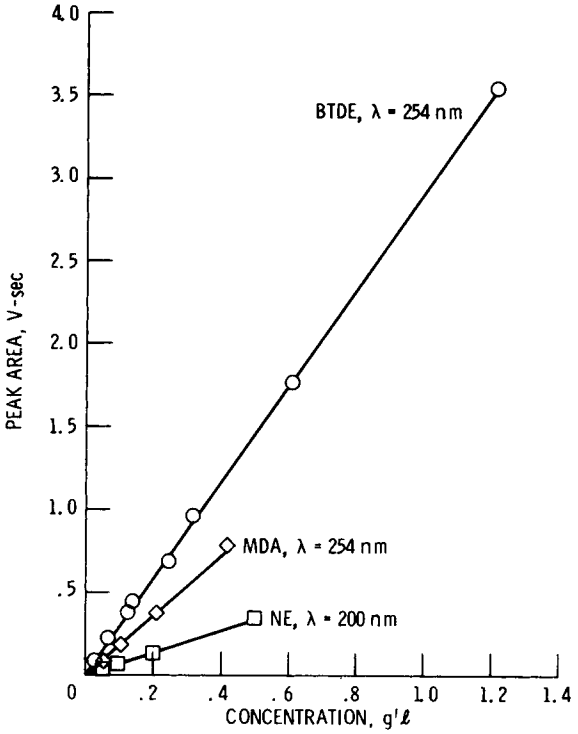


Fig. 8. Peak area vs. solution concentration for PMR-15 monomer solutions.

is proportional to the mass (or concentration) of solute injected:

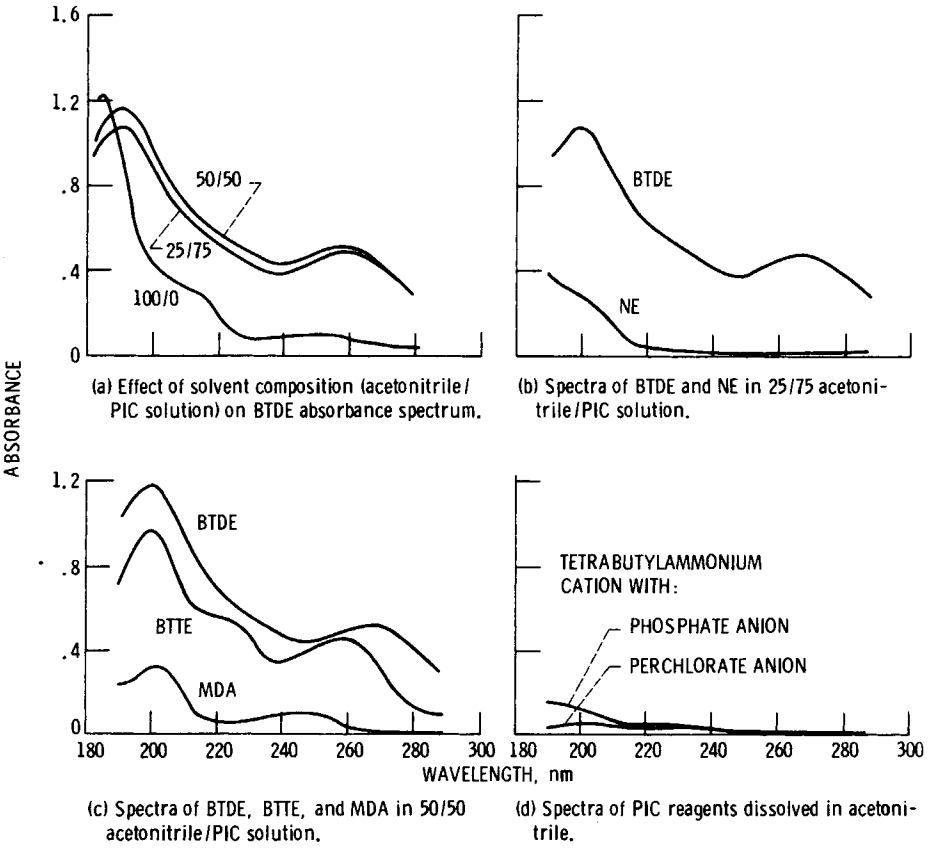
$$A_i = K_i M_i \tag{1}$$

where M_i is the mass of component i injected, A_i the area of peak corresponding to M_i, and K_i the constant for given flow rate, wavelength, and detector.

Figure 8 shows the peak area versus concentration for several materials. The sample concentration used for quantitative analysis of the PMR-15 resin was 0.2 g/L. This is well within the linear response range for each of the materials. The constant K_i is valid only for a specific flow rate, wavelength, and detector cell path length. It is desirable to have a technique which does not depend on these parameters, so that the experiment can be performed on different instruments. This can be accomplished by taking the ratio of the constants K_i to the constant K_s for some standard material:

$$R_i = K_i/K_s \tag{2}$$

where R_i is called the relative response factor for component i. Although K_i and K_s depend on several parameters, their ratio should depend only on the detector wavelength and the absorptivity of the materials at that wavelength. However, the absorptivity of molecules in solution does depend on the particular solvent used. UV absorbance spectra of BTDE solutions at three different solvent compositions are shown in Figure 9(a). The information in



(a) Effect of solvent composition (acetonitrile/PIC solution) on BTDE absorbance spectrum.

(b) Spectra of BTDE and NE in 25/75 acetonitrile/PIC solution.

(c) Spectra of BTDE, BTTE, and MDA in 50/50 acetonitrile/PIC solution.

(d) Spectra of PIC reagents dissolved in acetonitrile.

Fig. 9. UV absorbance spectra of PMR-15 monomers and PIC solutions.

Figure 9(a), along with a first order propagation of errors analysis, indicates that accurate control of solvent composition should not limit the accuracy of the response factors.

The absorbance spectra of BTDE and NE are shown in Figure 9(b). NE does not absorb appreciably at 254 nm, but does absorb at 200 nm. Therefore, if the NE and BTDE peaks overlap, it is possible to observe the BTDE peaks alone by setting the detector to 254 nm. Early in this work an attempt was made to eliminate the need for two separate isocratic experiments by using a detector set at 200 nm in series with a detector set at 254 nm during a single isocratic experiment. This resolved the problem of overlapping BTDE and NE peaks, but two separate isocratic experiments were still needed in order to obtain adequate separation of all the acid-esters of benzophenonetetracarboxylic acid. As a result of this work response factors were determined for wavelengths of both 200 and 254 nm with a solvent composition of 50/50 acetonitrile/PIC solution. Since most of the materials of interest show a maximum absorbance near 200 nm [Figs. 9(b) and (c)], it is preferable to detect at 200 nm. This was done in the more recent work.

The absorbance spectra of BTDE, BTTE, and MDA are shown in Figure 9(c). The data of Figures 9(b) and (c), along with a first order propagation of

errors analysis, indicate that accurate control of the detector wavelength should not limit the accuracy of the response factors. However, the response factors determined with two different UV detectors may differ slightly if there is a significant difference in the wavelength or spectral distribution of the detectors. The method of peak integration may also affect the response factors.

The absorbance spectra for solutions of PIC reagent with the tetrabutylammonium cation but two different anions are shown in Figure 9(d). The perchlorate anion does not absorb appreciably at 200 nm while the phosphate anion does. This is the reason the perchlorate anion was chosen for this work. If absorbance at 200 nm were not consideration, the phosphate or nitrate anion would be acceptable. Once the relative response factors are known, one can determine the amount of any species present by

$$M_i = M_s A_i / R_i A_s \tag{3}$$

In practice, a known amount of standard material M_s may be added to a solution as an internal standard or an external standard solution may be run adjacent to the unknown material. The latter approach was chosen for this work. NE was used as a standard when the solvent composition was 25/75, and BTTE was used when the solvent composition was 50/50. Relative response factors are listed in Table II. When pure standard samples were available, the accuracy of the response factors was $\pm 5\%$ (based on twice the standard deviation). Standard samples of the monoester and triester of benzophenonetetracarboxylic acid are not readily available. The response factors for these materials were determined from the chromatogram of partially esterified benzophenonetetracarboxylic acid or partially esterified BTDE using known response factors and the requirement of mass balance. The accuracy of response factors determined in this manner was estimated to be $\pm 25\%$.

As a check on the reliability of the response factors determined by HPLC, the absorptivity of several of the materials was determined from UV absorption spectra. The relative absorptivity (ratio of the absorptivity of component i to the absorptivity of a standard material) from the UV data was equal to the relative response factors within $\pm 10\%$.

HPLC Analysis of BTDE Solutions

Figure 10 is the chromatogram of BTDE prepared from BTDA of 96% purity [Fig. 10(a)] and from the same BTDA recrystallized from acetic anhydride [Fig 10(b)]. Refluxing of the BTDA solution was done under nitrogen in order to exclude water from the reaction. Since there is no monoester or tetraacid present in BTDE prepared from recrystallized BTDA, these products must come from the tetraacid and the diacid–anhydride impurities in the BTDA. If it is assumed that the rate of esterification of the anhydride is much higher than that of the carboxylic acid, then the amount of acid impurities in the BTDA can be calculated from the amount of tetraacid

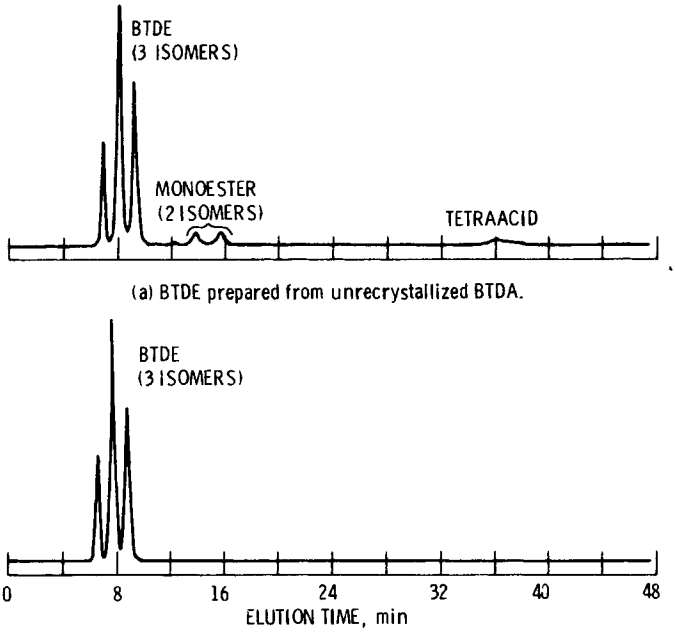


Fig. 10. HPLC chromatograms of BTDE prepared from BTDA before and after recrystallization. (Solvent = 25/75 acetonitrile/PIC solution).

and monoester in the BTDE. Experimental justification for this assumption will be given later. From the peak areas in Figure 10(a) and the response factors of Table II, the composition of the BTDA before recrystallization was determined to be 86.5% BTDA, 8.5% diacid–anhydride, and 5.0% tetraacid on a mass basis. This sample came from an old bottle of BTDA. Samples from newer bottles were > 96% BTDA.

In our laboratory the standard method for preparation of 50 wt % BTDE solutions has been to continue refluxing the BTDA solution for 2 h after all solids have gone into solution. It was observed during this work that unrecrystallized BTDA took about 30 min to completely dissolve, whereas the recrystallized BTDA took about 80 min. Figure 11(a) is the chromatogram of BTDE prepared from recrystallized BTDA by refluxing for 40 min after all solids dissolved. If esterification of the anhydride were incomplete, water inthe HPLC solvent would react rapidly with the remaining anhydride groups to form tetraacid and monoester. The absence of these impurities in Figure 11(a) indicates that complete esterification has occurred. Since it takes about 80 min for the solids to dissolve, it appears that the rate of conversion of BTDA to BTDE is controlled by the limited solubility of BTDA in methanol rather than the rate of esterification of the BTDA in solution. Figure 11(b) indicates that further refluxing from 40 min to 2 h does not result in any significant formation of triester. This confirms the earlier assumption that the rate of esterification of the anhydride is much greater than that of the carboxylic acid.

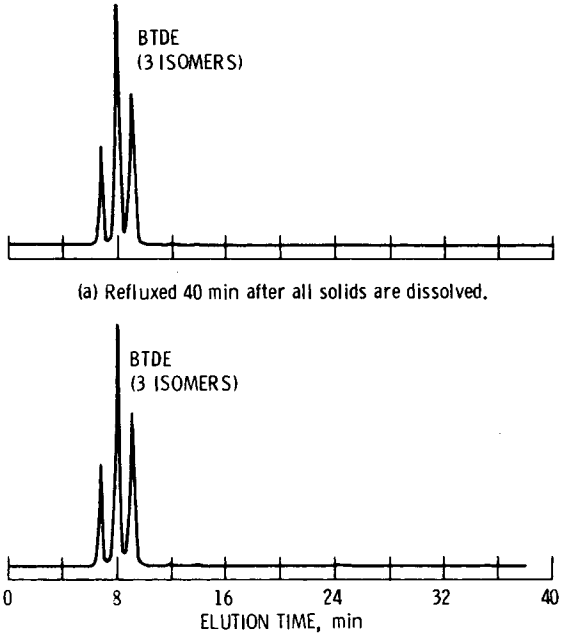
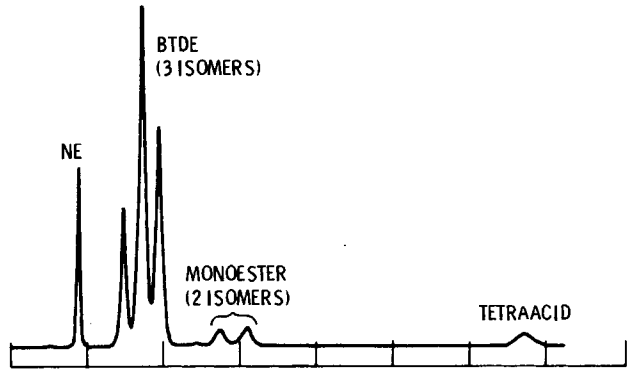


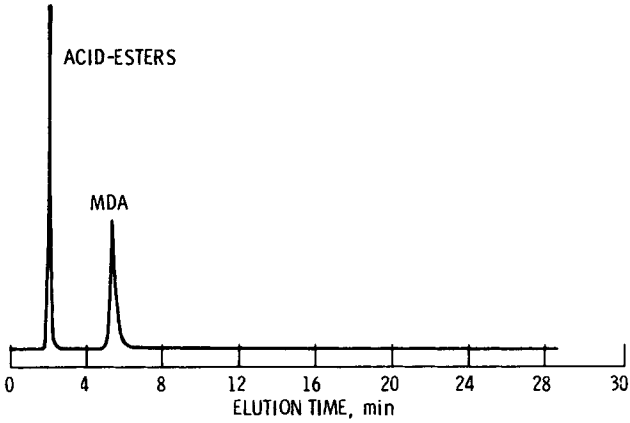
Fig. 11. HPLC chromatograms of a 50 wt % BTDE solution refluxed for 40 min and for 2 h after all BTDA is in solution. (Solvent = 25/75 acetonitrile/PIC solution.)

HPLC Analysis of PMR-15 Monomer Solutions

Figure 12 is the chromatogram of a 50 wt % PMR-15 monomer solution made from NE, MDA, and unrecrystallized BTDA. The only impurities present are the monoester and tetraacid which come from acid impurities in the BTDA. The composition of this solution measured by HPLC is compared to the formulated composition in Table III. The aging of a PMR-15 monomer solution prepared from recrystallized BTDA is shown in Figure 13. The weight percent of each component in Figure 13 is plotted as a function of aging time in Figure 14. Initially the solution consists of only the three monomers (BTDE, MDA, and NE). The amount of BTDE remains nearly constant over the 22-day aging period. The amount of NE and MDA decreases as their reaction products form. The first step in the reaction of MDA and NE is the formation of the mononadamide. It is assumed that this is the amide-acid rather than the amide-ester. Ring closure results in the formation of the mononadimide. Further reaction with NE results in formation of the bisnadimide. The amount of mononadimide and bisnadimide increases monotonically. The amount of mononadamide rises quickly to a small concentration, then drops gradually to zero by the end of the 22-day aging period. This indicates that amide formation is the rate controlling step in the imidization reaction. Since the mononadamide is never present in large amounts, it was not possible to determine its response factor. A relative response factor equal to that of the monoimide was used as an approximation.



(a) Solvent, 25/75 acetonitrile/PIC solution.

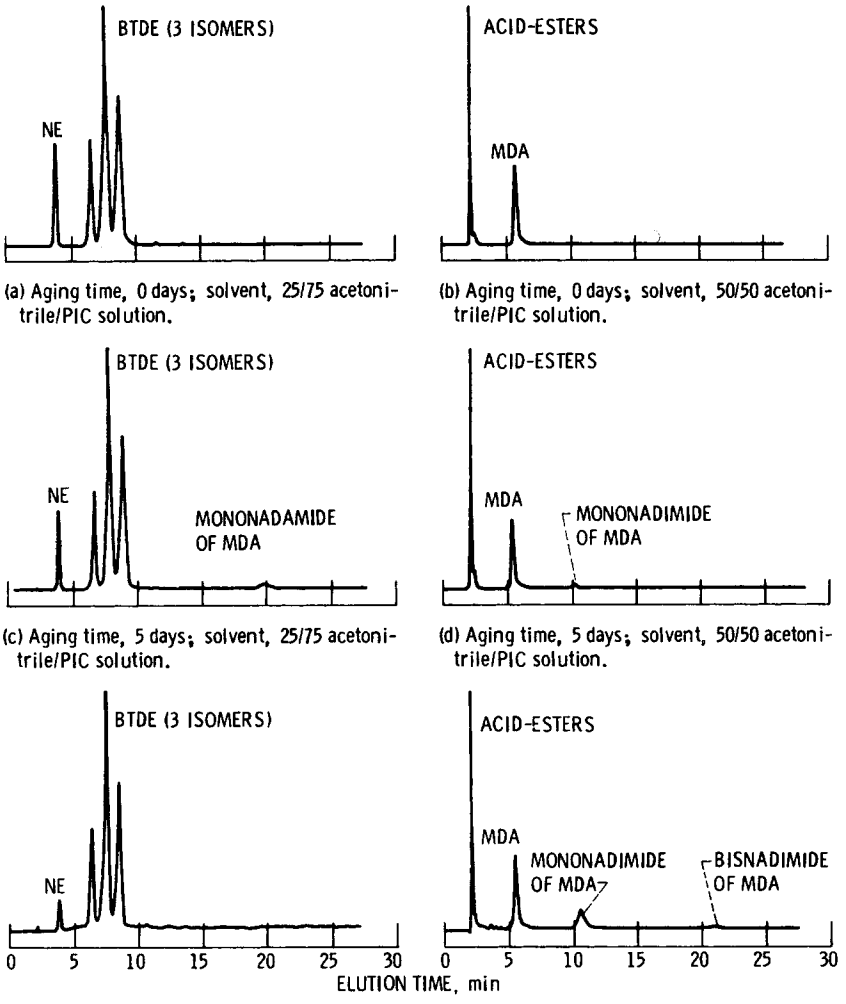


(b) Solvent, 50/50 acetonitrile/PIC solution.

Fig. 12. HPLC chromatograms of a 50 wt % PMR-15 resin solution prepared from unrecrystallized BTDA.

TABLE III
Composition of a PMR-15 Resin Solution

	Formulated weight percent	Weight percent measured by HPLC
BTDE	18.9	20.5
Monoester	1.7	1.8
Tetraacid	0.9	1.0
NE	10.7	10.6
MDA	17.4	17.4
Total solids	49.6	51.3



(a) Aging time, 0 days; solvent, 25/75 acetonitrile/PIC solution.

(b) Aging time, 0 days; solvent, 50/50 acetonitrile/PIC solution.

(c) Aging time, 5 days; solvent, 25/75 acetonitrile/PIC solution.

(d) Aging time, 5 days; solvent, 50/50 acetonitrile/PIC solution.

(e) Aging time, 22 days; solvent, 25/75 acetonitrile/PIC solution.

(f) Aging time, 22 days; solvent, 50/50 acetonitrile solution.

Fig. 13. HPLC chromatograms of a 50 wt % PMR-15 resin solution aged for 0, 5, and 22 days.

After the solution was aged for about 2 weeks, a precipitate began to form. The precipitate was determined to be mostly bisnadimide by HPLC. It was possible to redissolve the precipitate by diluting the monomer solution with a methanol/acetonitrile solvent.

HPLC Analysis of PMR-15 Film and Prepreg

Thin films of PMR-15 resin were prepared by placing a drop of the resin solution on a glass plate and allowing the methanol to evaporate. The HPLC chromatograms of PMR-15 resin stored as a solution and as a dried film are compared in Figure 15. There seems to be sufficient molecular mobility in the dried film for some imidization to occur. The major differences between the

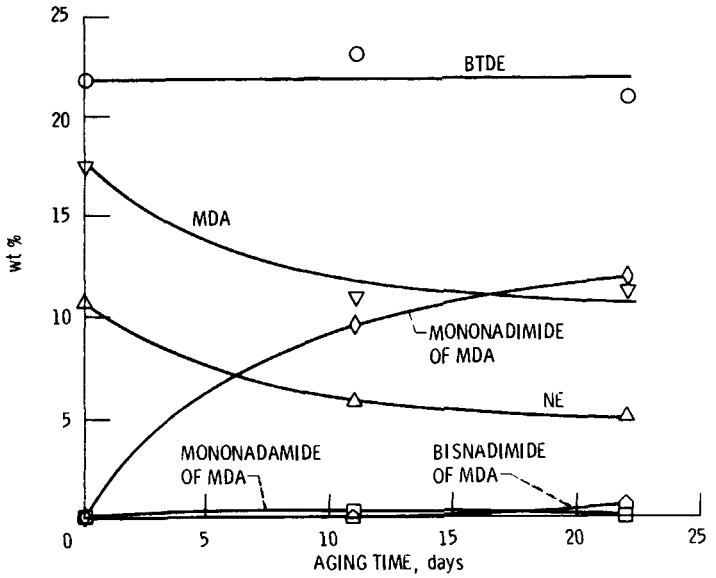


Fig. 14. Composition of a 50 wt % PMR-15 resin solution aged from 0 to 22 days.

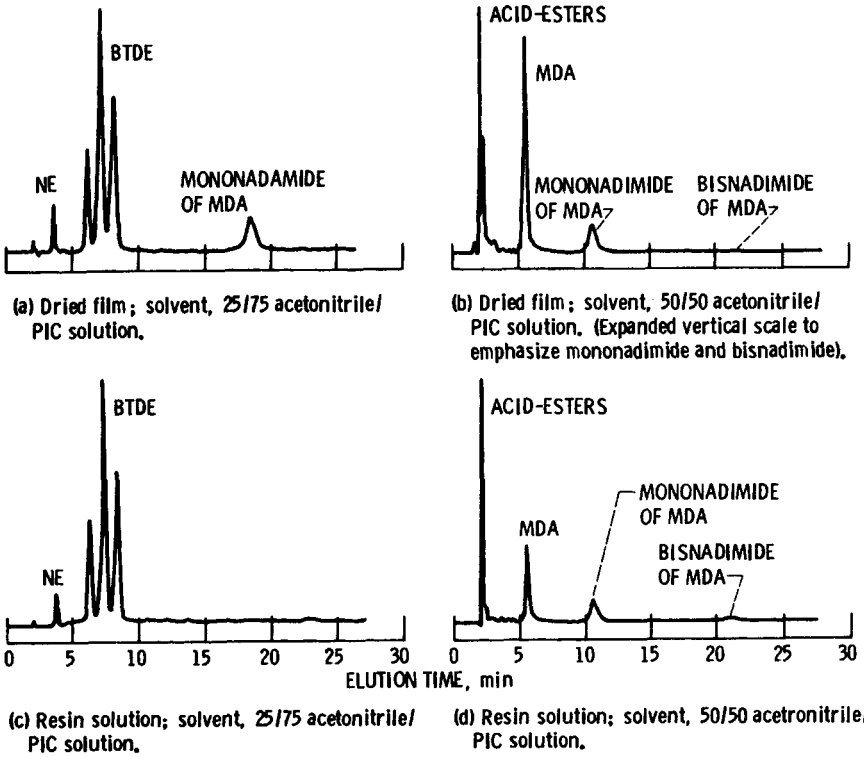


Fig. 15. HPLC chromatograms of PMR-15 resin aged 22 days as a dried film and as a 50 wt % solution.

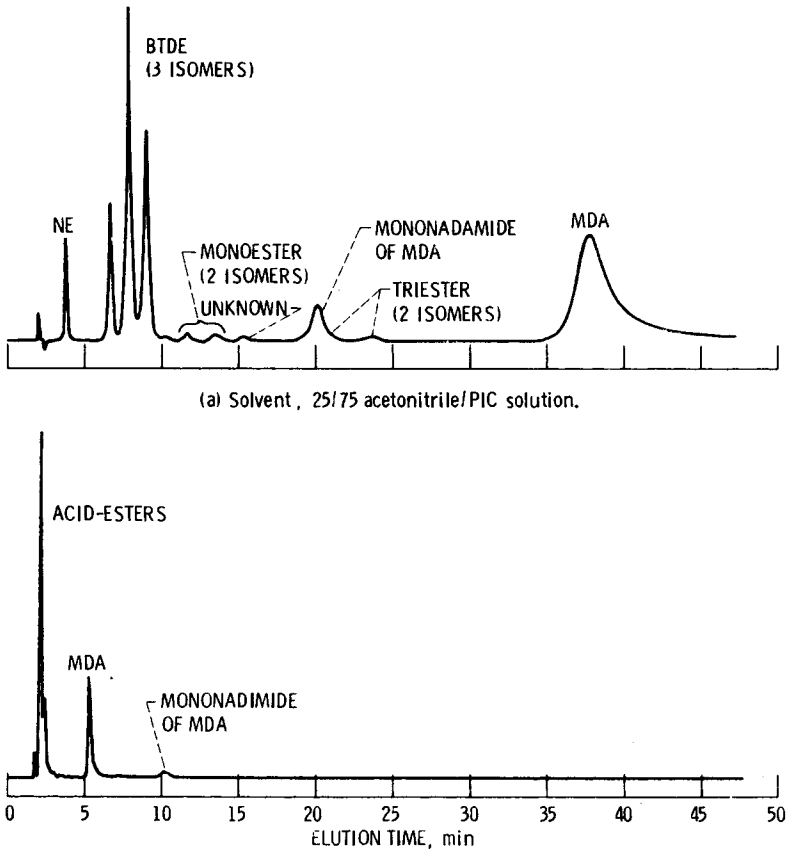


Fig. 16. HPLC chromatograms of a PMR-15 resin extracted from a commercial prepreg.

compositions of the dried film and the solution are the presence of a larger amount of mononadamide and a smaller amount of mononadimide and bisnadimide in the film. Figure 16 is the HPLC chromatogram of resin dissolved from a piece of commercial prepreg. As expected, this chromatogram is very similar to that of the PMR-15 resin which was stored as a dried film.

DISCUSSION

BTDE Solutions

When BTDE is prepared by refluxing BTDA in methanol, it is important that the reflux time be long enough for complete conversion of BTDA to BTDE, but short enough to prevent further esterification of BTDE to the triester. If unreacted BTDA were present in the PMR-15 solution, it would undergo rapid imidization with MDA forming oligomers which would likely be insoluble in the methanol solution. If, in addition, water were present in the solution, hydrolysis of the anhydride would rapidly form monoester and tetraacid. Monoester and tetraacid may also be present as a result of acid impurities in the BTDA. If the presence of acid impurities is not taken into

account in the formulation of the PMR-15 solution, the ratio of monomers will not be stiochiometric because of the molecular weight difference between BTDA (MW = 322) and the tetraacid (MW = 358). A 10% tetraacid content would result in a formulated molecular weight of 1490 plus 0.7% excess MDA. The excess amine is expected to reduce the molecular weight of the oligomers and therefore affect resin properties. However, addition of small amounts of excess amine to PMR-15 resin has been shown to have only a small effect on mechanical properties and thermooxidative stability of unidirectional carbon fiber composites.[8] Reactivity of the carboxylic acid may be different from that of the methyl ester toward MDA. Imidization of the monoester and tetraacid could therefore occur at a different temperature during the cure cycle than imidization of BTDE. The presence of triester may also affect the rate of imidization. In this case, imidization of the ortho amide-ester has been shown to occur at a higher temperature than that of the ortho amide-acid.[4,9]

In laboratory preparation of 50 wt % BTDE solutions, tetraacid and monoester impurities can be easily eliminated by using recrystallized BTDA and reagent grade methanol as starting materials and refluxing under nitrogen to prevent water from entering the system. Triester formation is not a problem because of the high rate of esterification of the anhydride compared to that of the carboxylic acid. On the industrial scale recrystallization of the BTDA may be impractical, and control of exposure to moisture may be more difficult. Therefore, the effect of monoester and tetraacid on processing and composite quality should be examined. In some industrial applications the solids content of the BTDE solutions is much higher than 50 wt %. The higher reflux temperature and increased viscosity of these high solids solutions could promote the formation of triesters. The HPLC technique reported in this paper is ideal for determining the composition of BTDE solutions prepared under various conditions. The full analysis can be done in about 1 h with about 8% accuracy for single injections. The procedure is readily automated so that multiple injections could be used for improved accuracy.

PMR-15 Solutions

If PMR-15 resin solution is prepared by mixing pure NE and MDA with the BTDE solution at room temperature, the only impurities in the freshly prepared solution are those originating in the BTDE solution. Room temperature aging of the resin solution or prepreg results in gradual formation of the mononadamide, mononadimide, and bisnadimide of MDA. The effect of the amide and imides on processing and composite properties has not been systematically studied. It is possible that the loss of prepreg tack is related to the formation of the imides as well as to the loss of residual solvent. The effect of amide and imide formation on resin cure chemistry is not obvious since these reactions occur anyway during the cure cycle. Processing conditions may have to be modified because of changes in resin melt viscosity and the evolution of volatiles at different times in the cure cycle. The number average molecular weight of the imidized oligomers depends only on the molar ratio of NE/BTDE/MDA and not on the particular reaction conditions if full imidization occurs. However, it is likely that full idimization is not attained in a typical cure cycle.

The reverse phase HPLC experiment is capable of determining the concentration of all components in PMR resin which has been aged up to 3 weeks. Accuracy is within ±8% for a single injection and could be improved with multiple injections. Since some of the impurities in aged resin solutions are not available in pure form for model studies, this technique should be quite useful in studies relating resin composition to composite properties. In addition, the technique is simple and fast enough for use as a quality control test in industrial settings.

CONCLUSIONS

The chemical components of BTDE solutions and PMR-15 resins can be fully separated by performing two separate isocratic HPLC experiments. A PIC reagent in the solvent is required for full separation of the various acid-esters. The concentration of individual components and of total solids can be determined within ±8% accuracy. Acid impurities in BTDA are the major source of impurities in freshly prepared BTDE solutions. These impurities are easily eliminated by recrystallizing the BTDA prior to esterification. Trimethyl ester impurities are easily kept to negligible amounts because of the rapid rate of esterification of the anhydride relative to that of the carboxylic acid. Aging of PMR-15 resin solutions results in gradual formation of the mononadimide and the bisnadimide of MDA. The mononadamide appears as an intermediate at a very small concentration. The same chemical reactions occur at a reduced rate in dried films of PMR-15 resin.

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