

A Comparison Study: The New Extended Shelf Life Isopropyl Ester PMR Technology versus the Traditional Methyl Ester PMR Approach

William B. Alston,¹ Daniel A. Scheiman,² Gloria S. Sivko³

¹U.S. Army Research Laboratory (ARL), Vehicle Technology Directorate (VTD), at NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, Ohio 44135

²QSS Group, Inc, at NASA Glenn Research Center, Cleveland Ohio 44135

³Ohio Aerospace Institute, at NASA Glenn Research Center, Cleveland, Ohio 44135

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ABSTRACT: Polymerization of monomeric reactants (PMR) monomer solutions and carbon cloth prepregs of PMR II-50 and VCAP-75 were prepared using both the traditional limited shelf life methanol based PMR approach and a novel extended shelf life isopropanol based PMR approach. The methyl ester and isopropyl ester based PMR monomer solutions and PMR prepregs were aged for up to 4 years at freezer and room temperatures. The aging products formed were monitored using high pressure liquid chromatography (HPLC). The composite processing flow characteristics and volatile contents of the aged prepregs were correlated versus room temperature storage time. Composite processing cycles were developed and six-ply cloth laminates were fabricated with prepregs after various extended room temperature storage times. The composites were then evaluated for glass transition temperature (T_g),

thermal decomposition temperature (T_d), initial flexural strength (FS), and modulus (FM), long term (1000 h at 316°C) thermal oxidative stability (TOS), and retention of FS and FM after 1000 h aging at 316°C. The results for each ester system were comparable. Freezer storage was found to prevent the formation of aging products for both ester systems. Room temperature storage of the novel isopropyl ester system increased PMR monomer solution and PMR prepreg shelf life by at least an order of magnitude, while maintaining composite thermal and mechanical properties. © 2006 Wiley Periodicals, Inc. * J Appl Polym Sci 99: 3549–3564, 2006

Key words: polyimide composites; high performance polymers; composite thermal oxidative properties; PMR II-50 and VCAP-75; solution and prepreg shelf life

INTRODUCTION

Polymerization Monomer Reactants (PMR) type resins^{1–3} are currently employed in a variety of high technology applications. Their high temperature performance makes them excellent candidates for weight-saving applications in aircraft engines. VCAP-75² (vinyl endcap of 7874 formulated molecular weight (FMW), $n = 14$) and PMR II-50³ (second generation PMR at 5047 FMW, $n = 9$) are two such promising polyimides undergoing commercialization. Both required the development of optimal processing parameters and quality control techniques. An important factor affecting the quality of the polymer precursor solutions is their finite shelf life for both first and second generation type PMR resin systems.^{4,5} PMR

monomer solutions and PMR prepregs (monomer impregnated fiber or fabric) storage stability depends on temperature, monomer reaction rates, concentrations, and reagent purity.

One of the primary concerns about solution and prepreg storage is reactions between the monomers, resulting in undesirable aging products. The polyimides in this study are thermoset polymers formed through thermally driven condensation reactions between aromatic diamines, aromatic dicarboxylic acids diesters, and endcaps. The monomers can combine at much lower temperatures, even room temperature, to produce a variety of adducts or aging products. The most detrimental aging products are the chain extending combinations between both monomers, causing a significant increase in melt viscosity. However, the reactions between some PMR endcaps and one or both ends of a monomer, while not chain extending reactions, can occur at a much faster rate, which significantly increases melt viscosity. Both of these product types will undesirably affect the composite processing and ultimately the finished laminate properties. Thus, a study using aged prepregs and examining the resultant laminate properties should

Correspondence to: W. B. Alston and D. A. Scheiman (william.b.alston@grc.nasa.gov and daniel.a.scheiman@grc.nasa.gov).

reveal any inherent undesired effects from the prepreg storage.

The overall objective of this study was to identify the PMR monomer solution and prepreg aging processes and to characterize their effects in traditional methyl ester PMR monomer solutions, prepregs and composites, followed by demonstrating the lack of these aging effects when using extended shelf life isopropyl ester PMR monomer solutions, prepregs, and composites.

The approach used for this study involved the monitoring of methyl ester second generation type PMR monomer solutions and prepregs using high pressure liquid chromatography (HPLC) and rheology at various room temperature storage time intervals (from 0 to 6 months) to track the formation of aging products and subsequent viscosity changes.^{6,7} The prepreg volatile contents and flow characteristics were correlated versus prepreg room temperature storage time. These PMR prepreg materials were then processed into laminates at these same time intervals.⁸⁻¹⁰ The quality of the laminates was evaluated using ultrasonic C-scans, thermal analysis, and mechanical testing. Long term oven aging to monitor the high temperature stability (via isothermal weight loss) was also done followed by mechanical testing of these oven aged laminates to determine their retention of composite mechanical strength. Differences noted in the aged prepregs and monomer solutions were then correlated with the changes in the laminate properties.

The alternative novel extended shelf life technology was applied to the second generation type PMR polyimides. A similar characterization scheme was performed for their solutions, prepregs, and composites after up to 50 months of room temperature prepreg storage times.¹¹ Solution solubility and stability studies of first generation type polyimides and their composite fabrication have also been previously reported.¹²⁻¹⁴ Those studies compared methyl ester and isopropyl ester solution shelf life¹² and also the use of various cosolvents,^{13,14} both of which were reported to extend PMR shelf life.

The reason the extended shelf life technology provides longer shelf life is because it is based on the larger isopropyl ester groups compared to the methyl ester group. The isopropyl group is a bulkier and poorer leaving group and consequently should significantly slow the reactions between the PMR monomers in solutions and prepregs by slowing the rate determining step in the aging process. The mechanistic rate determining step in the aging process has been identified¹⁵ as anhydride reformation from the ester acid, even at room temperature. The anhydride reformation rate determining step is always followed by rapid reaction of the anhydrides with amines to form amide acids. Amide acids may react further by rapidly dehydrating to form imides, even at room tempera-

ture. These imides are traditionally identified as the products of the PMR aging process. The increasing amount of imide oligomers narrows the traditional methyl ester PMR composite processing window. The lack of aging in the isopropyl ester PMR approach could lead to more consistent composite processability and composite properties, promoting a longer working "out life" time during composite processing. The lack of aging also provides a bonus of increased prepreg storage time and temperature compared with that methyl ester shelf life conditions.

EXPERIMENTAL

PMR monomer synthesis

The monomers and endcaps for VCAP-75 and PMR II-50 used to prepare the standards for the HPLC analysis and to prepare the PMR solutions and the prepregs are shown in Figure 1. A 50 wt % solution of 6F diphthalic acid ester (HFDE) was prepared using 1,1,1,3,3,3-hexafluoroisopropylidene diphthalic anhydride (HFDA, Hoechst Chemical) by heating at reflux temperature with the appropriate alcohol for an additional 1–2 h in methanol or isopropanol after dissolution of the HFDA (which took 1–2 h in methanol or 5–6 h in isopropanol). The *para*-aminostyrene (PAS, Polyscience), *para*-phenylenediamine (PPDA, DuPont), and methyl nadic acid ester (NE, Pharm-Eco Laboratories) were used as received. Nadic anhydride (NA, Hitco Lab) was heated at reflux temperature in isopropanol for 24 h to generate the isopropyl nadic acid ester, according to the patented procedure.¹⁶ Isopropyl nadic acid ester was then isolated by filtration and recrystallized from *n*-hexane in 98% yield, melting point 89–90°C. A 1% impurity, the nadic diacid, was shown by HPLC. All compounds were run in the HPLC individually to check retention times and purity. Some of the aging products (mono and bisnadimides of PPDA, and mono, tri, and tetraesters of HFDA) were synthesized in house using the appropriate monomers or purified for use as HPLC standards to identify their retention times.

PMR monomer solution and prepreg preparation

The PMR solutions were prepared in the traditional manner by mixing the three monomers together in methanol or isopropanol and diluting to 50 wt % solids content in the solvent. Two lots each of methyl ester VCAP-75 and methyl ester PMR II-50 and one lot each of isopropyl ester VCAP-75 and isopropyl ester PMR II-50 were prepared. PMR II-50 was mixed in a molar ratio of 9 HFDE, 10 PPDA, and 2 NE (formulated at *n* value of 9, thus providing a numeric FMW of 5047, hence called PMR II-50). The VCAP-75 was mixed in a molar ratio of 15 HFDE, 14 PPDA, and 2

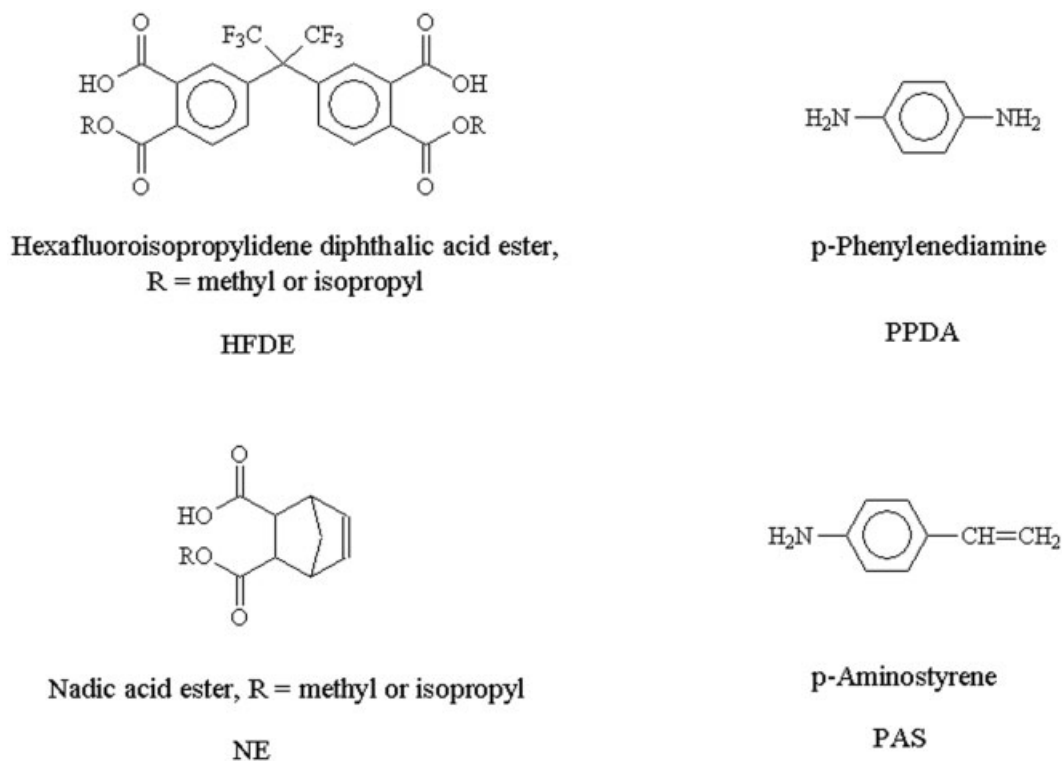


Figure 1 VCAP-75 and PMR II-50 monomers used in PMR solution preparation.

PAS (formulated at n value of 14, thus providing a numeric FMW of 7874, hence called VCAP-75). Samples of the monomer solutions were aged for up to 4 years at freezer (-15°C) and room temperatures for HPLC analysis.

Prepregs were made from these same 50 wt % PMR monomer solutions. Unsized T650-35 graphite fabric was hand impregnated (hand painted with a paintbrush) with the amount of 50 wt % PMR monomer solutions calculated to generate a 37 wt % resin laminate after curing. The methanol wet prepreg was allowed to dry overnight to form a pliable prepreg, while the isopropanol wet prepreg was allowed to dry up to five days to only still give a wet and tacky prepreg. Both prepregs were then cut into $10.16 \times 10.16 \text{ cm}^2$ plies, with some prepregs aged for up to 4 years at room temperature and some at freezer temperature.

HPLC samples and analysis

The initial (unaged) and aged 50 wt % solutions were diluted to a 0.5% weight to volume (wt/v) solution in acetonitrile (AcN) for HPLC analysis. The resin was also analyzed after being leached from the aged prepreg by allowing it to sit in methanol for 1 h (a simple study determined 1 h was sufficient to dissolve the resin) at a 1 : 100 wt/v dilution. This was further diluted 1 : 10 with AcN for HPLC analysis.

HPLC analysis was performed using a Beckman 167 System Gold LC pump connected to a Beckman 167 System Gold variable ultraviolet (UV) detector interfaced with a standard IBM compatible computer. The data processing software is the Maxima package from Waters. HPLC grade AcN from Fisher and Milli-Q filtered distilled water with 0.005M tetrabutyl ammonium perchlorate (PIC reagent, Fisher) added were used in the mobile phase. A gradient solvent flow of 25–100% AcN at 1.0 mL/min over 40 min, a reverse-phase technique, on a Hamilton PRP-1, 250 mm \times 4.1 mm, column packed with polystyrene divinyl benzene of 10 μm particle size, and 75 \AA pore size was used.

Prepreg volatile contents and prepreg rheology

Prepreg volatile contents for the methyl ester composites were determined in triplicate after storage aging but before composite processing, using $2.54 \times 2.54 \text{ cm}^2$ prepreg pieces, and reported as the weight percent of volatile material lost after heating to 204°C for 1 h (the temperature/time by which most imidization has occurred). Prepreg volatile contents for the isopropyl ester composites were determined as single data points from the actual weight of volatiles lost at 371°C during composite processing, and reported as the weight percent of volatiles lost during the composite processing cycle. Thus, isopropyl volatile content does not include any B staging weight loss when staging

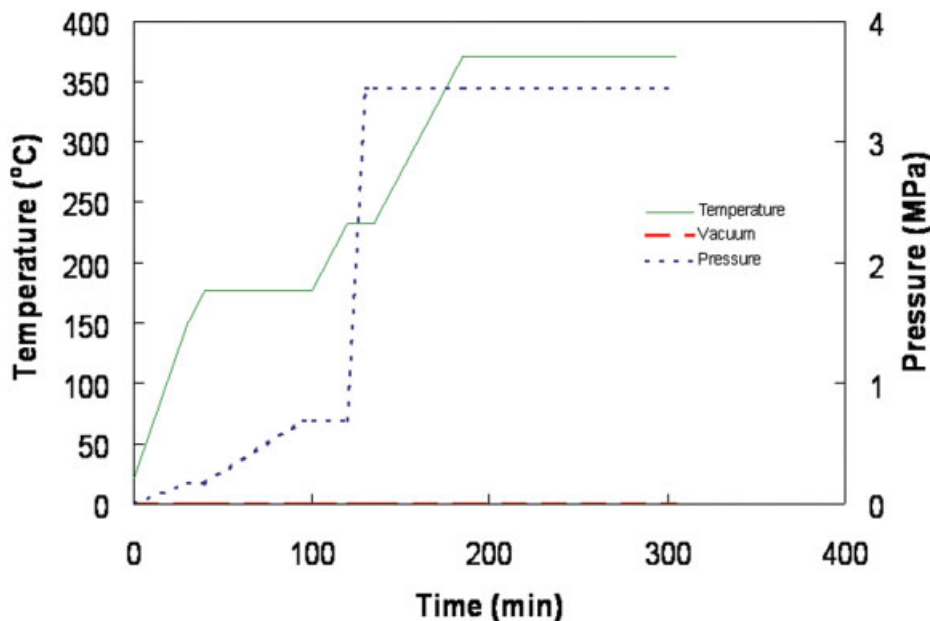


Figure 2 Representative cure cycle for methyl ester VCAP-75 and methyl ester PMR II-50. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was done in an oven before composite processing. Without B staging, the two volatile contents done at widely different temperatures still mean the same thing because all PMR imidization volatiles are evolved within the 1 h at 204°C; the only difference being triplicate prepreg pieces used for methyl esters versus a single data volatile content calculated from the actual isopropyl ester composite processing at a higher temperature.

A relative viscosity for the methanol and isopropanol based PMR prepreps was obtained for comparison using rheology¹⁷ after various room temperature storage times. The methanol rheological data was obtained using a Rheometrics RMS-800 Rheometer while the isopropanol rheological data was obtained using a TA 2980 Dynamic Mechanical Analyzer (DMA). Both sample types were prepared in the warp direction as a four-ply 0° graphite fabric symmetrical lay-up, B staged in a mold at 121°C for 1 h under the weight of the top plate of the mold. The methanol sample size was 1.25 × 6.35 cm², while the isopropanol sample size was 1.25 × 2.5 cm². Torsional rectangular geometry was used for the methanol samples with a temperature ramp from 80 to 450°C at 10°C/min, while a single cantilever fixture was used at the same temperature ramp for the isopropanol samples. Both samples used a strain of 0.5% applied with no auto tension or autostrain options at a frequency of 1 Hz (6.28 rad/s). Duplicate runs were made when possible. The analyzing software was Rhios version 4.2.2 for the Rheometrics instrument, while the DMA used universal analyzer version 2.5H.

Composite preparation

Six-ply, 10.16 × 10.16 cm², 0° graphite fabric symmetrical layup composites were processed from each lot of prepreg after various long-term room temperature storage times. These composites were processed in a 12-ton press, using a simulated autoclave vacuum bagging technique with a final pressure of 3.45 MPa (500 psi) and a final temperature of 371°C. Figure 2 shows the same cycle was used for both of the methyl ester PMR systems. Full water aspirator vacuum was applied throughout the entire processing cycle shown. Before processing, the only difference was in using a lower B staging temperature of 149°C for the methyl VCAP-75 prepreg versus 204°C for the PMR II-50, each for 1 h before processing as per Figure 2.

The isopropyl ester processing cycle required more modifications because of the lower isopropanol volatility and higher prepreg volatile content of the isopropanol based prepreps. Figure 3 shows the same final conditions in processing cycles for both isopropyl based systems. Processing differences not seen in the oven staged cycle in Figure 3 result from the staging of the prepreps in an oven at 65°C for 1 h and then 106, 121, 135, 149, or 177°C for an additional hour. After oven staging, processing then starts with a 1 h hold at 204°C, then a half hour temperature hold at 232°C before the final 371°C processing. Additional modifications (also not shown in Fig. 3) were either staging the isopropyl prepreg in a 65°C vacuum oven overnight and using a dry ice trap to capture the isopropanol and water evolved by sweeping air through the

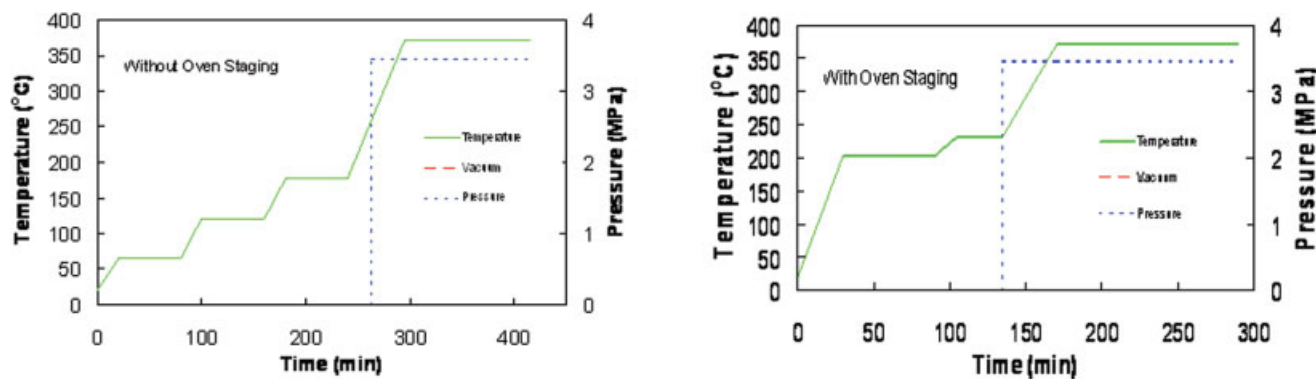


Figure 3 Representative cure cycles for isopropyl ester VCAP-75 and isopropyl ester PMR II-50. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mold during the heat up before full vacuum was applied when 204°C was reached. The latter was used as an attempt to remove the last volatiles rather than entrapping them to create voids when pressure was subsequently applied at 232°C. In contrast, isopropyl prepreps not staged in an oven initially (also shown in Fig. 3) were instead staged in the processing cycle using a series of three 1 h temperature holds at 65, 121, and 177°C, with pressure and vacuum applied at 260°C, thereafter both cycles in Figure 3 increase the temperature up to 371°C to complete the processing. Thus, the staging during processing cycle always consumed more processing time, but without better results as seen later.

Composite evaluation

After processing, the quality of the composites was evaluated by ultrasonic C-scan (through transmission, 5MHz) to qualitatively determine the amount of voids present. The laminates were then postcured in a forced air oven, using a ramp rate of 17.4°C per hour for 8 h starting at 232°C to reach the final postcure temperature of 371°C, where they remained at 371°C for 16 h. Mechanical test specimens ($\sim 6.9 \times 0.5 \text{ cm}^2$) were then cut from each methyl ester laminate and from one half of each isopropyl ester laminate. These were used for zero time (initial, unaged) three point flex tests in triplicate, according to ASTM D-790 at both room temperature and 316°C for each laminate made from each lot of room temperature aged prepreg.

The methyl and isopropyl ester laminate end pieces were then cut into three nominally $2 \times 2 \text{ cm}^2$ pieces. These, along with the cut methyl ester test specimens and the other half of each isopropyl laminate, were aged isothermally at 316°C for 1000 h, to determine the percent weight loss. After thermal aging, the larger aged isopropyl pieces were cut into smaller mechanical flexural test specimens. These were used along

with the previously cut, 316°C aged methyl ester specimens for the same room temperature and 316°C flexural tests after the 1000 h of aging at 316°C. The weight loss after 1000 h of isothermal aging at 316°C and any change in flexural strength (FS) and modulus (FM) at room temperature and 316°C at each storage interval were determined.

Thermogravimetric analysis (TGA, ramp rate = 10°C/min) and thermomechanical analysis (TMA, 5 g expansion probe, ramp rate = 10°C/min) were performed on the unpostcured and postcured laminates, using the smaller end pieces and some of the mechanical tested specimens. Also, acid digestions of the tested specimens and end pieces were performed for quantitative void content determination according to ASTM method D-3171, in addition to the qualitative void content determination by ultrasonic C-scanning of the uncut laminate, done both before and after postcuring.

RESULTS AND DISCUSSION

Methyl ester versus isopropyl ester PMR technology

HPLC comparisons

Evaluation of the HPLC data from the methyl ester approach (shown in Fig. 4) indicates a gradual decrease in the amounts of pure monomers present as the solutions age (their prepreps aged slower so their HPLC data is not shown). There is also a decrease in the rate of disappearance of pure monomers with increasing storage time. The largest drop in this rate occurs within the first 2 weeks, somewhat leveling-off to a steady rate afterward. This is consistent with the concentration changes and subsequent kinetic effects.¹⁸ The growth of aging products is consistent with the decrease in pure monomers present. Table I lists the retention times of the PMR monomers and adducts formed and the appearance times when de-

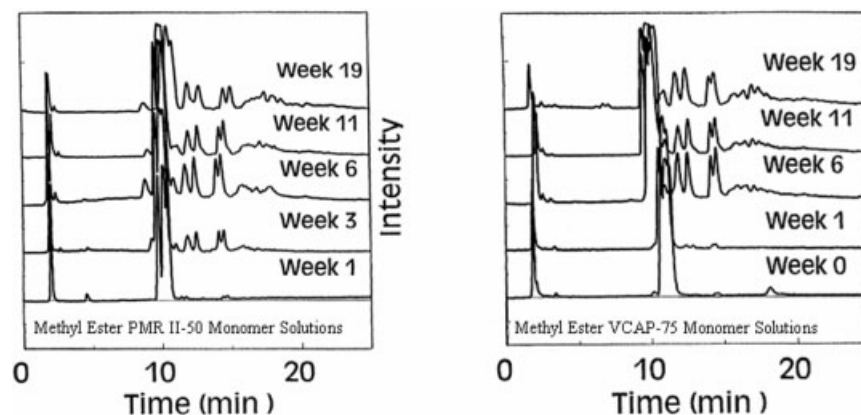


Figure 4 Methanol PMR II-50 and VCAP-75 HPLC retention time versus peak intensity for 50% monomer solutions after designated room temperature storage times, shown offset vertically.

tectable amounts of aging products are found in the room temperature aged solutions.

Some scatter in both the monomer solution and prepreg samples was seen in the HPLC data. This is due in part to week-to-week instrument variability, but also due to concentration changes associated with solvent (methanol or isopropanol) evaporation from the prepreps and sampling variations inherent within a hand layup prepreg preparation. Other complications arise because of the precipitation of some of the aging products formed when preparing the methanol solution HPLC sample in AcN. The methyl ester aging products increase in concentration and molecular weight, which decreases their solubility in methanol and AcN. This became a factor after about 20 weeks for only the room temperature stored methanol based solutions. Consequently, all HPLC evaluations were

discontinued at 20 weeks, as seen in Figure 4. However, precipitation was not found for any of the isopropanol solutions and prepreps as they remain fully soluble because they do not react during room temperature aging.

The room temperature isopropyl ester approach HPLC data indicates a similar trend compared with the methyl ester approach, however, at a significantly reduced rate. HPLC data for the methyl ester and isopropyl ester solutions and prepreps aged at freezer temperature (-15°C) also did not show any significant formation of aging products so both the room temperature stored isopropyl ester and all the freezer stored sample HPLC data are not illustrated. The HPLC data clearly indicates that the isopropyl ester approach significantly reduces the aging reactions for the monomer solutions and prepreps, such that it generally takes at

TABLE I
Retention Times of Components and Times of Peak Appearance for Methyl Ester PMR II-50 and Methyl Ester VCAP-75 solutions

Peak Identity	VCAP-75	PMR II-50	Week first appeared
T_{initial}	0.65 (min.)	0.65 (min.)	Dead volume
PPDA	1.73	1.73	— ^a
HFDE	10.48	10.48	— ^a
NE	— ^a	4.3	— ^a
PAS	18.2	— ^a	— ^a
NE/PPDA adducts	— ^a	9.1	1
NE/PPDA/NE adducts	— ^a	18.1	5
PAS products (2)	26.4	— ^a	— ^b
	32.0	— ^a	— ^b
HFDE/PPDA Adducts (5)	11.2	11.2	3
	12.5	12.5	1
	14.5	14.5	1
	16.1	16.1	3
	38.7	38.7	>6
HF triester	14.5	14.5	— ^b
HF tetraester	26.8	26.8	— ^b

^a Not applicable, either an initial monomer or not used in that monomer mixture.

^b Not detected.

TABLE II
Various Methyl Ester versus Isopropyl Ester PMR Monomer Solution Stabilities as Determined by Days Until Precipitation Time During Room Temperature Storage

PMR Resin Monomer mixture	Methyl Esters & Solvent Systems			Isopropyl Esters and Solvent Systems	
	100% methanol	Refluxed methanol	Methanol and acetone	Methanol and isopropanol	100% isopropanol
PMR-15	17–21	__a	__a	210	700
PMR II-50	7	__a	__a	__a	>60
VCAP-75	7	__a	__a	__a	>60
PMR II	3	__a	__a	__a	>30
COBAX PMR-15	__b	__a	12	3	13
BAX PMR-15	__b	1	2–3	10	42

__a = Not attempted; __b = Not soluble.

least ten times longer to produce the same amounts of aging products as found in the methyl ester aging. Because the aging products tend to be less soluble, they precipitate during room temperature aging to act as a visible indicator of aging with the methyl esters giving precipitates much faster than the isopropyl esters. This is seen in Table II (which was compiled from data in Ref. 5 and 12), as a comparison of precipitation times for various PMR solutions. It is also important to note that the large increases in precipitation times resulting from isopropyl esters is generic, i.e., it is also seen (Table II) in first generation PMR polyimides based on benzophenone dicarboxylic acids diisopropyl esters combined with other aromatic diamines found in PMR-15, COBAX PMR-15, and BAX PMR-15.

In spite of all these HPLC complications, it can be concluded that VCAP-75 resin aging products form as follows: PAS disappears very fast, presumably forming a polystyrene type polymer; next HFDE reacts more slowly with PPDA forming the 1:1 adduct, and later the 2:1 and 1:2 adducts. Similarly, the PMR II-50 resin aging products form as follows: NE reacts with PPDA extremely fast to form mononadimide (which is found as a precipitate within a week,⁵ see Table II) and later some bisnadimide; next HFDE reacts more slowly with PPDA as in VCAP-75. The pathway to these aging products in methanol using methyl esters is shown in Figure 5. The aging pathways using isopropyl esters and isopropanol instead of methyl ester groups and methanol are identical to Figure 5 so they are not illustrated, however, they proceed significantly slower.

Prepreg viscosity comparisons

The rheological analysis (Fig. 6) shows that there is a general shift toward a higher temperature minimum viscosity with increased storage time for both the methanol based PMR II-50 prepreg and the methanol based VCAP-75 prepreg. Both exhibit a broadening and flattening of their minimum melt viscosity with

increasing room temperature prepreg storage time, starting at about 225°C, which shifts higher during six months storage to almost 250°C, indicating that processability is being lost with increasing storage time.

The depth of the decrease to reach the minimum viscosity in the range starting from 175°C is also important. Figure 6 shows the longer the storage time, the less the decrease to reach the minimum viscosity. This also indicates that processability is being lost as storage time increases from 0 to 6 months. These viscosity changes easily qualitatively correlate with the chemical changes seen in the HPLC during the 19 weeks of storage aging of their solutions (Fig. 4) and prepreps. To attribute the loss of processability to evaporation of methanol solvent from the prepreg would be incorrect for two reasons: (1) later data (Fig. 8) shows these prepreps evaporate to a constant solvent level in only 1 month, while processability decreases over 6 months storage time and (2) rheological samples were all prepared as a ply stack by B staging 1 h at 121°C. Both of these negate solvent level differences in the rheology prepreg samples, hence, the viscosity differences are due to advancing oligomer molecular weight as the prepreg ages, previously identified in the HPLC analysis. While the reader considers all this, it is important to note that the measured viscosities shown in the logarithmic scale in Figure 6 are relative, besides being offset vertically. The measured viscosities represent a combination of the graphite fabric and the resin, as such are meant to compare only visually. However, this data provides an indication of the maximum and minimum viscosity ranges and any temperature shifts occurring within these viscosity ranges. It is also good as a comparative tool between samples run under identical conditions.

The isopropyl ester based PMR II-50 and VCAP-75 have different changes with increasing room temperature prepreg storage time compared with that of the methyl ester systems. Figure 7 shows that the minimum viscosity occurs at a significantly lower temperature (about 170°C instead of in the 225–250°C range

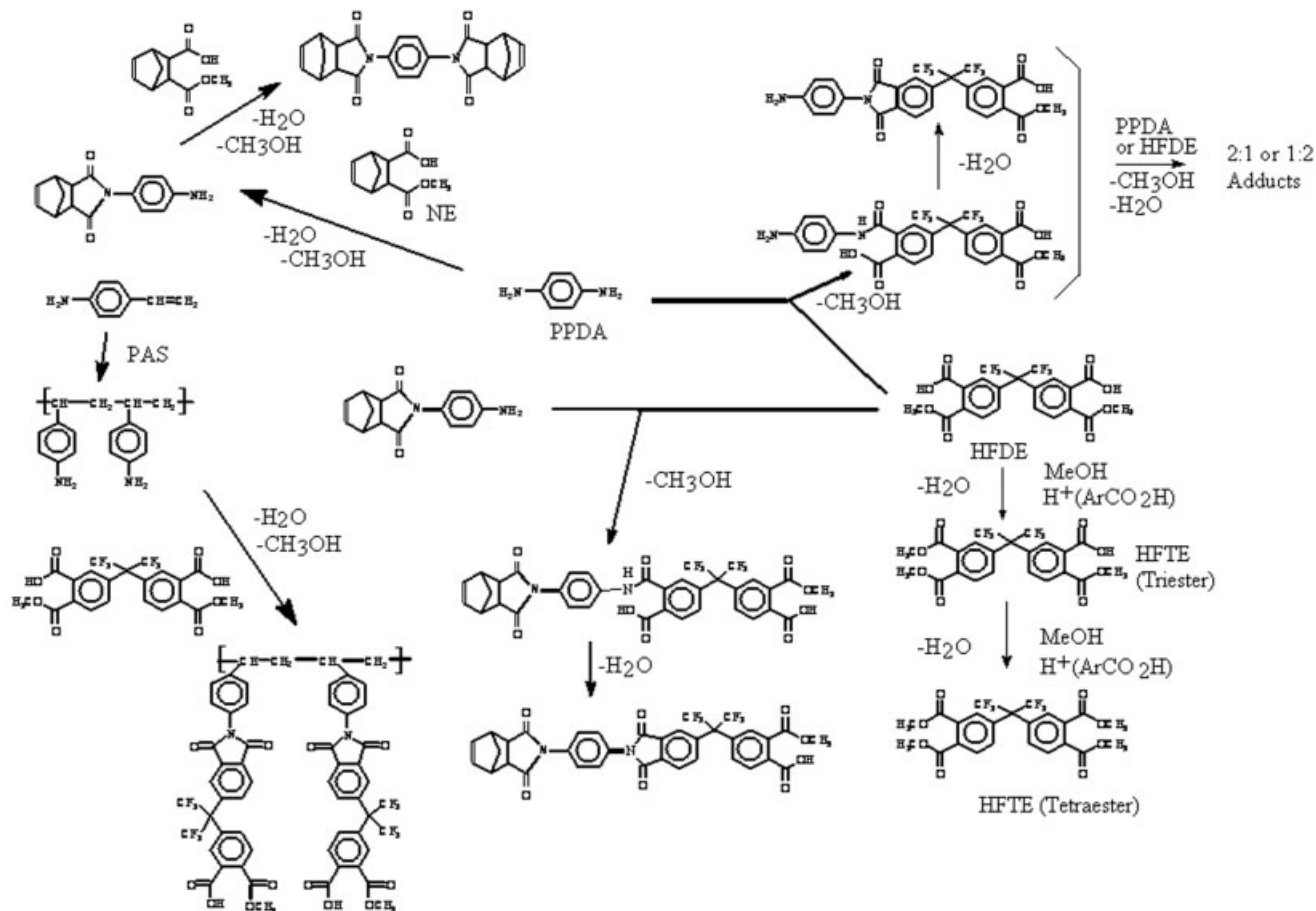


Figure 5 PMR II-50 and VCAP-75 monomers aging pathways and aging products.

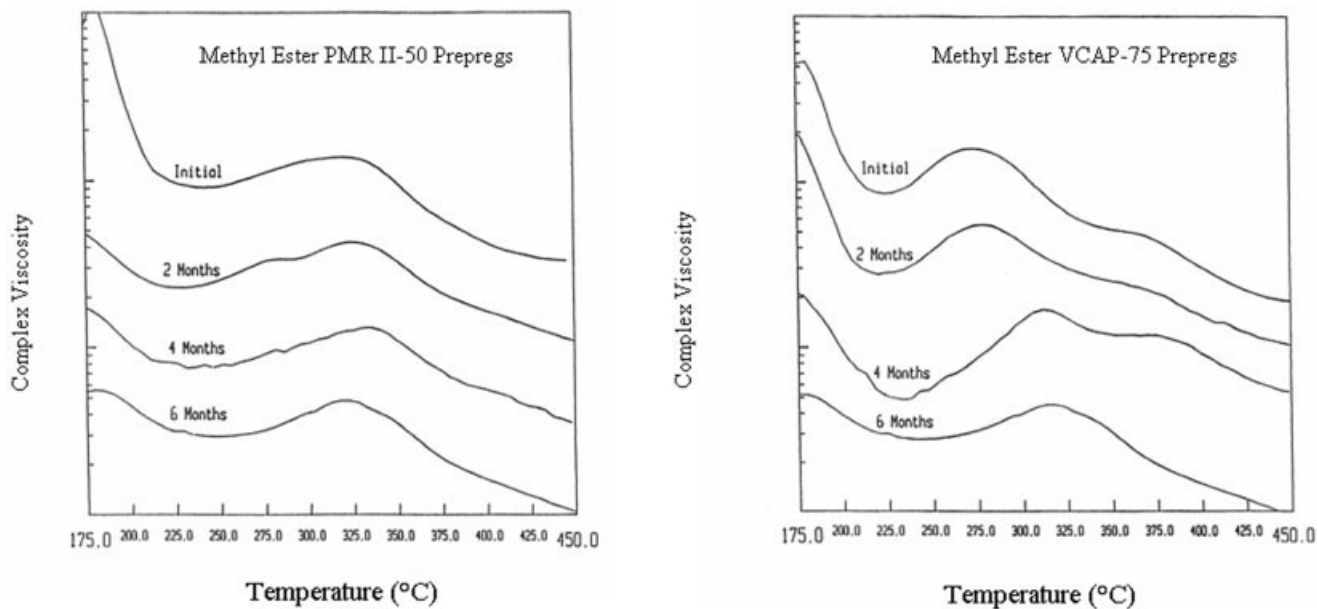


Figure 6 Complex viscosity during heat up of methyl ester PMR II-50 and VCAP-75 prepregs aged at room temperature for 0–6 months, shown offset vertically.

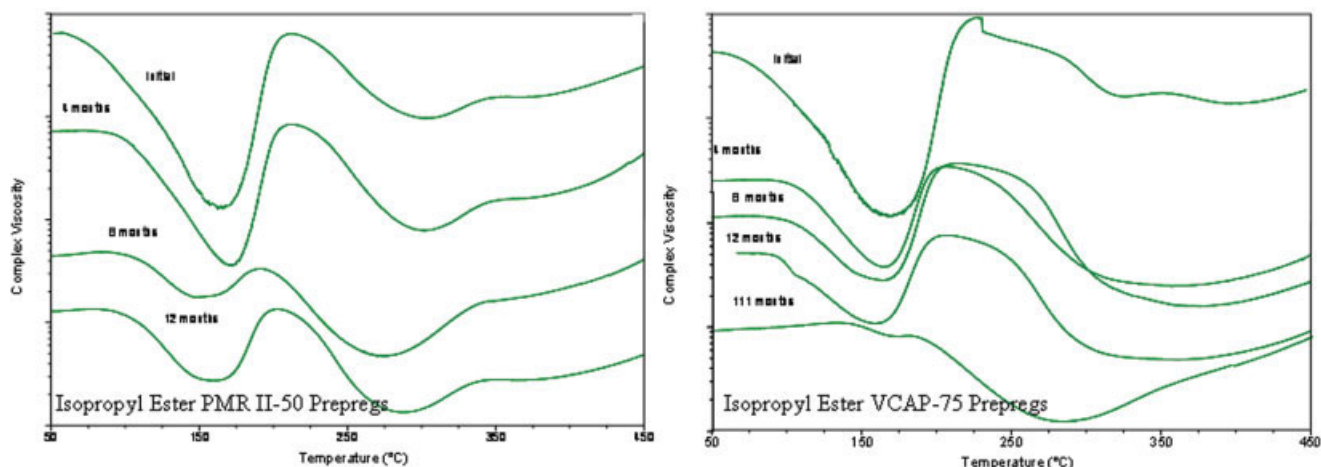


Figure 7 Complex viscosity during heat up of isopropyl ester VCAP-75 and PMR II-50 prepregs aged at room temperature for 0–12 months, shown offset vertically. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for methyl ester), does not shift toward higher temperatures with increasing prepreg storage time, and is much broader and deeper in the unaged isopropyl ester prepreg compared with the 4–12 month aged isopropyl ester prepregs. This correlates well with the much higher processing flow seen in the unaged isopropyl ester prepreg (shown later in Fig. 9 in the processing flow comparison discussion). Thus, unlike the methanol prepregs, the broader and deeper minimum viscosity could be solely due to physical changes, i.e., the retained isopropanol content. Chemical changes are ruled out by the lack of aging in the isopropyl prepreg HPLC data (discussed earlier) while the evaporation of the isopropanol is shown to level off at 4 months storage time (see Fig. 8). Significant isopropanol, about six percent of prepreg weight as retained isopropanol plus nine percent more as imidization volatiles, is yet to be lost. This seems to be a valid explanation of the very deep initial minimum viscosity curves compared with the aged prepreg curves and visually fits Figure 7. However, because rheology sample preparation first included staging 1 h at 121°C, the volatile contents should be approximately equal, about 11–12% instead of 15% without staging at 121°C, as seen later in Figures 8 and 10. Either way, all of the isopropyl ester prepreg processing flows exceeded that of the methyl esters. Additional data from isopropyl VCAP-75 prepreg that had been aged for 111 months at room temperature finally shows almost a total loss of the minimum viscosity well. This would indicate that its storage life has finally been grossly exceeded.

Prepreg volatile content comparison

The initial volatile content of the methyl ester PMR prepreg allowed to dry overnight after the resin solu-

tion is painted onto the fiber is typically around 10–12% (Fig. 8). During room temperature storage aging, there is an initial rapid drop over 1 month that levels off at about 7% volatiles for both of the methyl ester based prepregs. This amount of 7% volatiles represents the remaining volatiles tied up as methyl esters and water, to be lost later during conversion to imides during the condensation polymerization (see Fig. 5) plus any remaining methanol solvent in the prepregs (“free” methanol). The theoretical total volatile content of freshly painted wet prepreg (calculated to contain 37% resin in the finished laminate) is 21.57% for methyl ester PMR II-50 and 21.46% for methyl ester VCAP-75. The theoretical imidization volatiles in these prepregs are only 6.24% and 5.93%, respectively. These remaining <7% volatiles are not lost until imidization occurs during either the 204°C prepreg volatile content determinations, very long term room temperature prepreg aging times (>6 months), or composite processing.

In contrast to the methyl ester systems, the isopropyl ester systems initial theoretical volatile content are 22.7–22.9%, but only nominally dry to the 18–19% range (Fig. 8) after 4 days of room temperature storage (hereafter called zero months storage time). The difference is due to the loss of some of the “free” isopropanol used as solvent for the initial 50% monomer solution. After 4 months of room temperature storage, there is a slow decrease to the 14–15% isopropyl volatile range. It remains at this level for up to 50 months of storage time (but not shown past 12 months in Fig. 8). This is still much higher than the theoretical 8.74% and 8.49% volatile content loss expected from the imidization condensation products of isopropyl PMR II-50 and isopropyl VCAP-75, respectively. Unlike the methyl prepregs, the isopropyl prepregs never totally dry out during room temperature storage. Surpris-

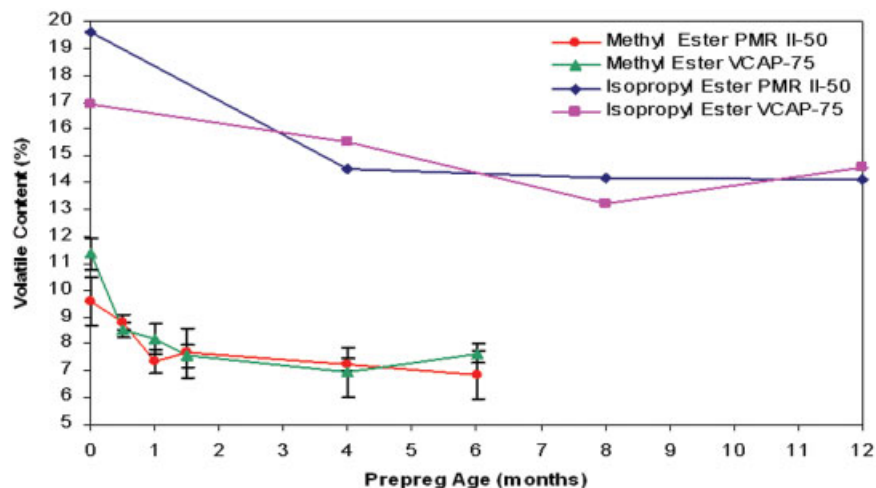


Figure 8 Prepreg volatile contents for methyl and isopropyl ester PMR II-50 and VCAP-75 versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ingly, the isopropyl processing volatiles remain as much as 6% higher than the theoretical imidization volatiles after 4 years of room temperature storage.

Oven staging of the unaged isopropyl prepreps was required before processing to alleviate the excessive initial isopropyl prepreg volatile contents. The oven staging was done by heating the unaged isopropyl prepreps in a forced air oven to 63°C for 1 h, followed by another hour at 121°C. (Another approach to lower the initial high volatile contents using a 65°C vacuum oven overnight still required additional oven staging at 121°C.) The oven staging reduced the unaged prepreg volatile contents during processing to 11–12% (with one as low as 9%), starting from a 19.5 to 21.3% range without prior storage aging, or starting from 13.9 to 15.0% for the 50 to 8 month room temperature storage prepreps, respectively. The volatiles after staging were still at, or above, the theoretical imidization volatiles (8.49–8.74%) and always below the minimum 14–15% volatiles range (Fig. 8) for the unstaged aged isopropyl prepreps. Surprisingly, the 121°C staging of aged prepreps only reduced the processing volatiles down to the same 11–12% level as that obtained for unaged/staged prepreps, i.e., this represents the lower volatile limit after 121°C staging, irrespective of any amount of prior storage aging time. Additional data showed the processing volatile levels after oven staging at 135°C were still 14.88–14.84% (slightly higher than the 11–12% obtained after 121°C staging, but done with a new prepreg batch in a different oven at a different time so the overall data trend still does somewhat agree). More aggressive staging at higher temperatures (in place of the 121°C/1 h hold) drove the volatiles below the 9% theoretical level. At higher staging temperatures (149–177°C) lower imidization volatile contents (3.60–2.10%) were found. A benefit of any oven

staging >106°C was that the unaged prepreps were considerably less tacky.

Composite processing resin flow comparison

Figure 9 shows the amount of resin flow squeezed into the bleeder plies for the methyl and isopropyl resins, determined from the weight gains in the bleeder cloths, versus prepreg storage time. The methyl ester composites were processed as per Figure 2 and the isopropyl ester as per Figure 3, both without prior oven staging. The only exception was the 8 month isopropyl ester composites. They were processed with prior oven staging, causing the lower flow shown by the minimum in the isopropyl resin bleeds at the 8 months point in Figure 9.

The most important thing to note in Figure 9 is methyl VCAP-75 loses almost all its processing flow in the first month of prepreg storage time, while methyl PMR II-50 takes 4 months to lose a comparable amount of flow. It cannot be attributed to solvent drying out since both do so at the same rate (see Fig. 8). This difference is probably due to the PAS endcap found in VCAP-75. PAS is very reactive and disappears within the first day of room temperature storage as seen by HPLC. This endcap reactivity, in combination with subsequent imidization during the first month of methyl ester VCAP-75 storage, would cause higher adduct formation and decreased processing flow compared to the methyl ester PMR II-50.

This same drop in processing flow should be observed for isopropyl VCAP-75, however, the imidization aging reaction is considerably slowed down by the use of isopropyl esters, so the resin flow curves of isopropyl VCAP-75 and isopropyl PMR II-50 are virtually identical for almost the entire extended storage time (Fig. 9). The isopropyl ester flow curves look

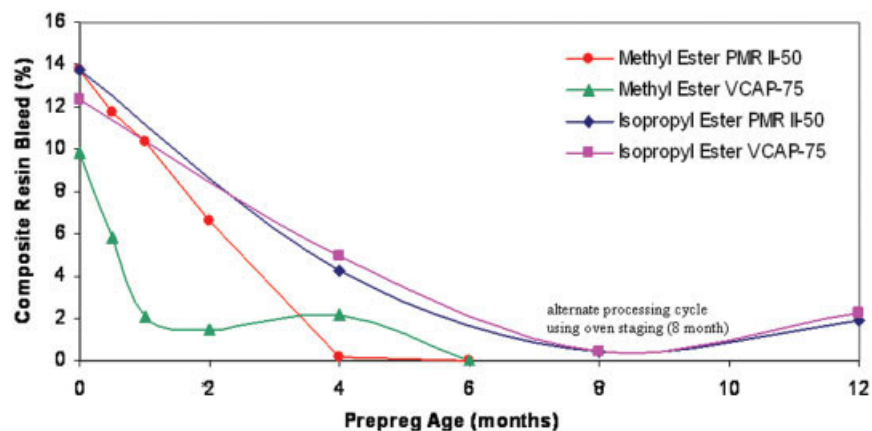


Figure 9 Resin flows calculated from composite bleeder ply weight gain during processing versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

similar to the processing flow curve of the methyl ester PMR II-50 for the first two months of storage. The methyl ester PMR II-50 ages faster (by solvent loss (Fig. 8) and imidization (HPLC, Fig. 4)) causing the flow curve to diverge from the two isopropyl curves after 2 months of storage time (Fig. 9). In contrast, the isopropyl prepregs only lose flow during the first two months of storage because of a slower loss of solvent and additionally, for isopropyl VCAP-75, by the reaction of the PAS endcap. Thus they lose flow slower.

The last interesting point is that while oven staging did lower the volatile contents of unaged and aged isopropyl prepregs, the aging of the isopropyl ester systems did not lower the volatile contents. The aging

of unstaged isopropyl prepregs provided nearly the same volatile contents irrespective of the storage time (see in Fig. 10, the upper four lines where unaged volatile contents versus aged volatile contents were only slightly higher). Similarly, the staging of unaged versus aged isopropyl prepregs also provided nearly the same volatile contents (see in Fig. 10, where the two lower lines of unaged-staged versus aged-staged lines (three data points each) are closely equal volatile contents).

After mild oven staging, the processing flow did not significantly decrease from their respective unaged or aged processing flows without staging (compare the four upper lines above their respective unaged/staged

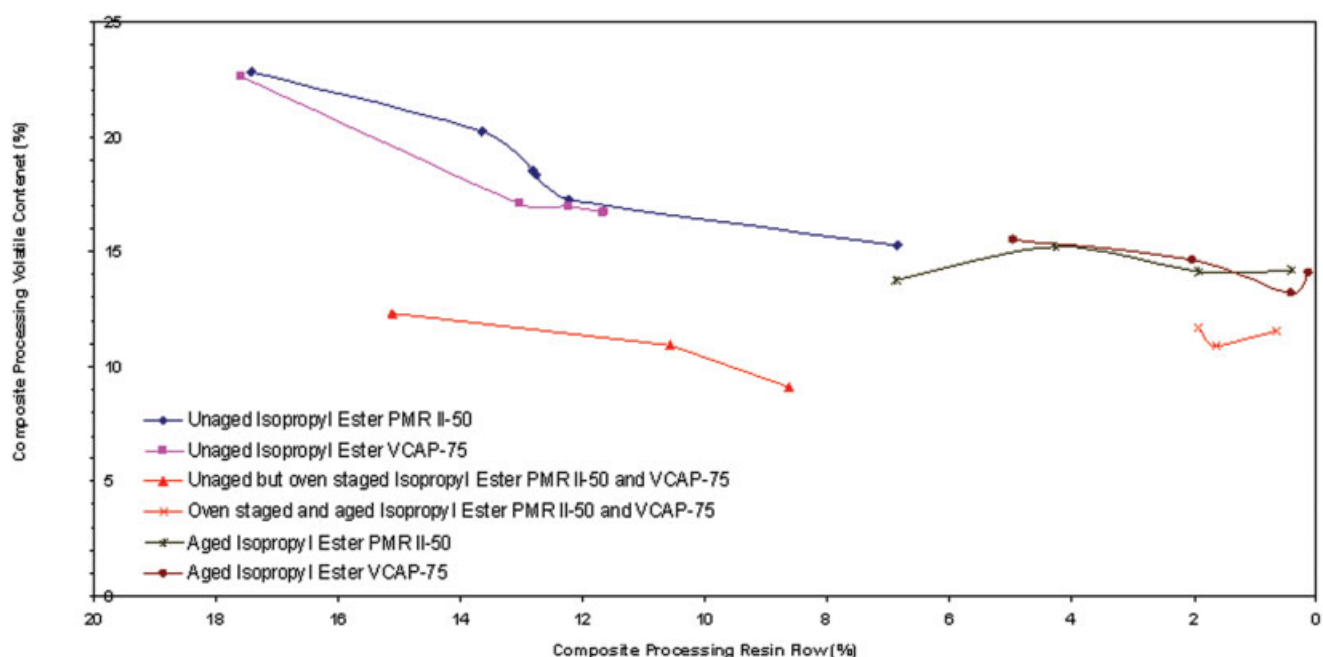


Figure 10 Correlation plot of isopropyl ester composite processing volatiles lost versus composite processing resin flows. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and aged/staged lower lines being at the same resin flow amounts in Fig. 10). The flow was not significantly reduced at mild staging temperatures (up to 121°C) for unaged isopropyl prepreg (8.63–15.11% range for staged prepreps compared to 6.85–17.58% for unstaged prepreps) nor was flow reduced for aged prepreps (0.65–1.92% for staged prepreg compared to 0.41–6.88% for unstaged prepreps). At even higher staging temperatures (not shown in Fig. 10 but staged at 149°C and 177°C), the flow was reduced to 0% regardless of the age of the isopropyl prepreps. Figure 9 showed isopropyl prepreps lose most of their processing flow by 4 to 8 months of aging via the loss of isopropanol in the aging process, thus additional oven staging is not needed.

The reader should note that Figure 10 is set up with volatile content increasing vertically, just as in Figure 8, while processing flow is shown decreasing to the right. This agrees visually with flow decreasing as storage time increases, as seen in Figure 9. Combining Figure 8 and Figure 9 drops out the common denominator of storage time and creates the correlation plot seen in Figure 10. Additionally, the 50 month and staged volatile and flow data, not shown in Figures 8 and 9, were added to Figure 10. The resulting correlation plot (Fig. 10) of isopropyl prepreg volatiles versus isopropyl resin flow clearly shows the utility of the isopropyl ester PMR extended shelf life technology. It indicates the isopropyl ester prepreps are less susceptible to accidental temperature excursions than the methyl ester prepreps because they retain processability, with or without oven staging at up to 121°C and irrespective of whether or not they had additional room temperature aging before the temperature ex-

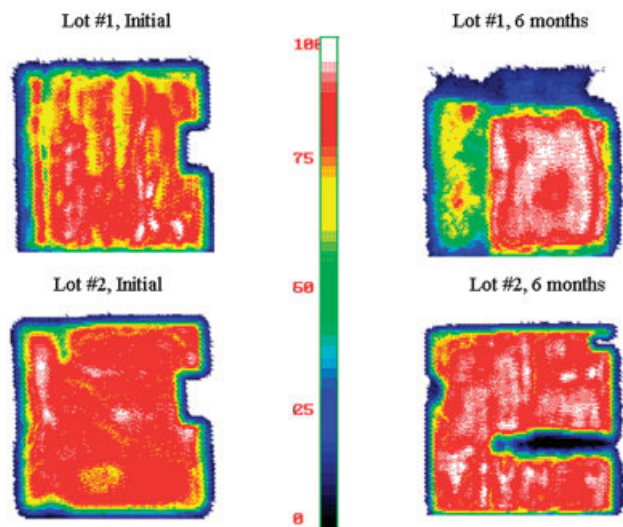


Figure 11 Ultrasonic C-scans for methyl ester PMR II-50 versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

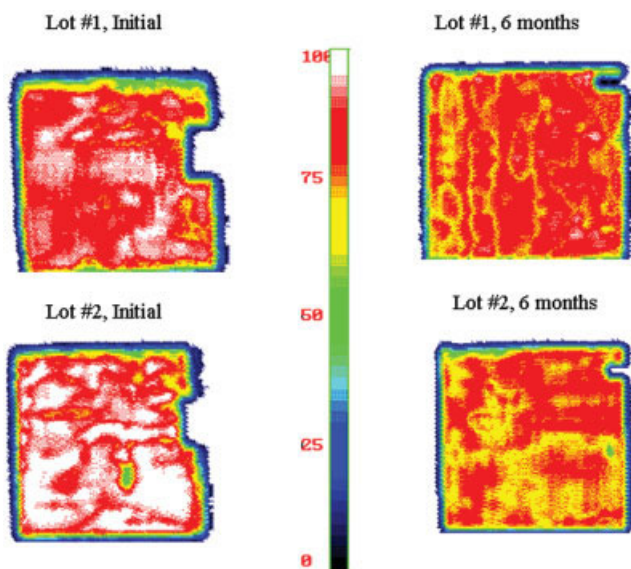


Figure 12 Ultrasonic C-scans for methyl ester VCAP-75 versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cursion. This fact could be useful in hot melt manufacturing processes and in preventing aging accidental damage during manufacturing, shipping, handling, transportation, and storage.

Composite quality comparison

Evaluation of the processed methyl laminates using ultrasonic C-scan results show that all the panels were of acceptable quality with a slight decrease in C-scan quality with increasing prepreg storage time at room temperature (Figs. 11, 12). The lighter colors indicate lower void volumes than do the darker colors. Both lots of each methyl resin went from white–red to red–yellow over 6 months prepreg storage time, indicating slightly higher void contents with increased prepreg storage time. Acid digestion results (Table III) showed a low level of voids (<3%, most < 2%) over the entire 6 months of prepreg storage time. Evidently, the chosen methyl ester processing cycle is capable of accommodating some variability in the starting materials when processing flat laminates. However, shaped or curved composite structures would be expected to be less forgiving.

Similar C-scan results were found for both of the isopropyl systems for the laminates prepared with prepreps stored 4 months or more at room temperature (Fig. 13). However, the acid digestion results (Table IV) of these composites showed a higher level of voids (<4% for isopropyl VCAP-75 and 6–7% for isopropyl PMR II-50) than for the methyl ester composites. Without the 4 months or more room temperature

TABLE III
Methyl Ester PMR II-50 and VCAP-75 Acid Digestion Results for Composites Prepared from Aged Prepregs

Lot no.	Prepreg		Methyl ester PMR 11-50 Composite		Methyl ester VCAP-75 Composite	
	Storage time		Void volume (%)	Fiber volume (%)	Void volume (%)	Fiber (%)
1	Initial (0)		3.48	61.5	1.18	58.5
1	2 Months		2.69	56.4	1.40	57.2
1	4 Months		2.09	59.6	1.75	61.1
1	6 Months		2.14	65.5	1.23	59.4
2	Initial (0)		1.33	59.0	1.01	57.7
2	2 Months		2.08	60.7	1.61	59.6
2	4 Months		1.19	61.9	1.93	61.2
2	6 Months		1.28	64.7	1.30	57.8

aging, the isopropyl VCAP-75 laminates were clearly unacceptable. They showed (Fig. 13) a large no transmission (white) area except for minimal black spots. Acid digestion results in Table IV showed 16–20% voids. The isopropyl PMR II-50 laminates had satisfactory void contents, but excessive resin flow caused higher fiber volumes. Surprisingly, the void volumes for isopropyl PMR II-50 did not change significantly over the 12 months aging period (already being scat-

tered in the 4–7% range during the 12 months) while the void volumes for isopropyl VCAP-75 did lower significantly after 4 months aging to a lower 3–4% void range. Four months of aging was needed for both isopropyl systems before satisfactory composites could be fabricated.

Attempts to improve the processing of both unaged isopropyl prepregs by passing air through the simulated autoclave mold during heatup and using a dry

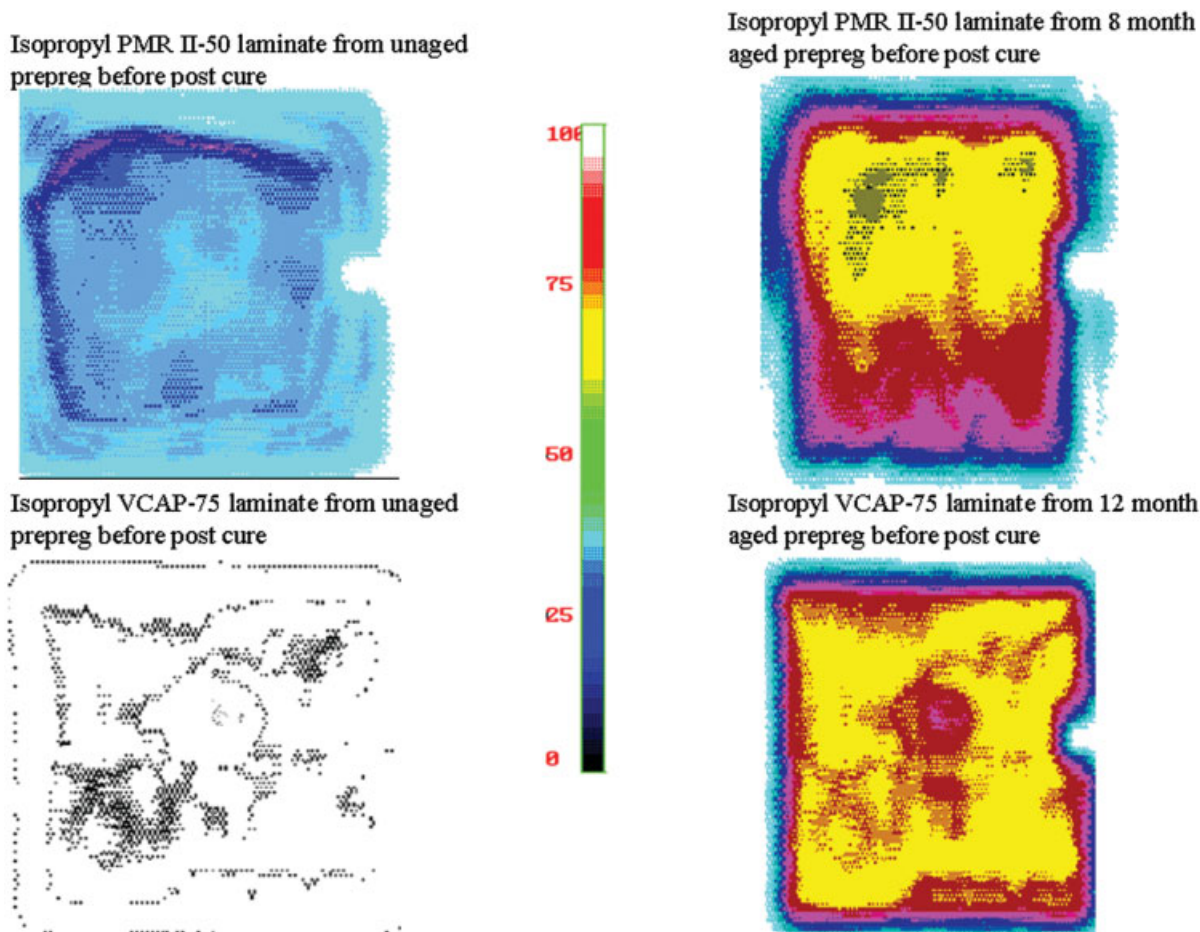


Figure 13 Ultrasonic C scan for isopropyl ester PMR II-50 and isopropyl ester VCAP-75 prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Isopropyl Ester PMR II-50 and VCAP-75 Acid Digestion Results for Composites Prepared From Aged Prepreg

Prepreg Storage time	Isopropyl ester PMR II-50 composite		Isopropyl ester VCAP-75	
	Void volume (%)	Fiber volume (%)	Void volume (%)	Fiber volume (%)
Initial (0)	4.87, 6.36	70.00, 68.12	16.06	55.70
Initial(0)	5.38, 3.73	67.46, 68.95	19.78	53.06
Initial (0)	5.37	65.66	16.62	53.87
4 Months	6.62	57.92	3.57, 3.98	58.66, 57.55
8 Months	6.44, 3.80	56.40, 57.92	3.90	56.37
12 Months	7.57	55.47	2.77	57.23
50 Months	7.94	61.52	3.19	56.42
50 Months	8.97	57.95	5.86, 4.60	55.17, 56.01

ice trap on the vacuum line to reduce the excessive initial resin flow and obtain lower void contents failed to remove the last imidization volatiles. This was surprising because these same processing modifications were successful for fabricating graphite fiber unidirectional and cloth fabric first generation polyimides, i.e., isopropyl PMR-15 and isopropyl BAX PMR-15.¹²⁻¹⁴ It is believed that the wider processing window of these lower FMW first generation PMR materials allowed their isopropyl esters to be successfully processed into composites. In summary, isopropyl ester second generation type PMR laminates were of comparable quality to those obtained using state of the art methyl ester PMR technology only after their prepregs were allowed to dry for at least 4 months at room temperature.

Composite thermal analysis comparison

The TMA and TGA data results did not show a significant change in T_g and T_d with either increased room temperature storage time or the ester approach used. The average T_g of the methyl versus isopropyl PMR II-50 ranged from 348 to 362°C and 354 to 368°C, respectively. The methyl versus isopropyl VCAP-75 ranged from 326 to 344°C and 323 to 384°C, respec-

tively. The average T_d of the methyl versus isopropyl PMR II-50 ranged from 517 to 540°C and 514 to 540°C, respectively. The methyl versus isopropyl VCAP-75 ranged from 528 to 538°C and 526 to 539°C, respectively. When viewing these temperature ranges, without considering storage times and lot numbers, any noticeable trends were not observed, thus, they were not shown in a Table.

The isothermal aging at 316°C for 1000 h (Fig. 14) showed that the methyl PMR II-50 laminates made from prepreg stored 0 to 6 months lost between 1.58 and 2.47% of their initial weight, while the isopropyl PMR II-50 laminates made from prepreg stored 4–12 months lost between 1.96 and 3.36% (larger specimen size) to 4.96% (smaller specimen size in Fig. 14). The unaged isopropyl PMR II-50 prepreg produced inferior laminates that had a higher (5.01%) weight loss. Beyond 12 months of room temperature prepreg storage, i.e., 50 months storage, the isopropyl PMR II-50 composites showed a much higher 6.89% weight loss, presumably also due to a poorer quality laminate. In contrast, the isothermal aging at 316°C for 1000 h (Fig. 15) shows that the methyl VCAP-75 laminates made from prepreg stored 0 to 6 months lost between 1.44 and 2.37% of their initial weight, while the isopropyl VCAP-75 laminates made from prepreg stored 0 to 12

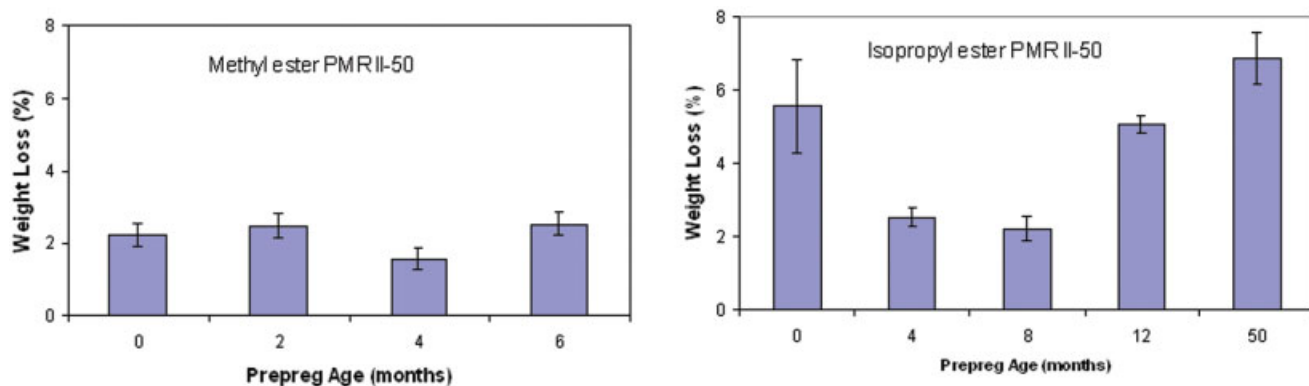


Figure 14 PMR II-50 small specimen composite weight loss data after 1000 h at 316°C versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

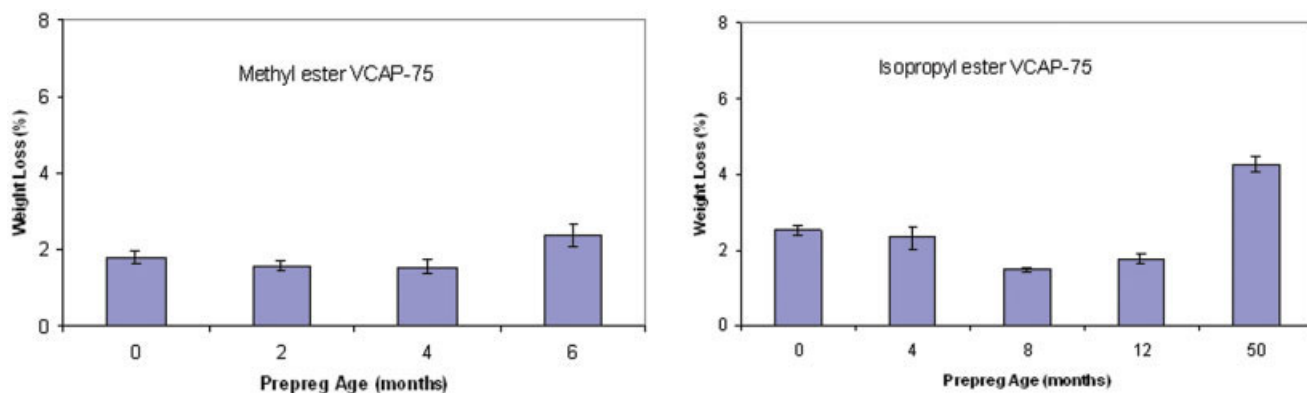


Figure 15 VCAP-75 small specimen composite weight loss data after 1000 h at 316°C versus prepreg room temperature storage time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

months lost between 1.54 and 2.51%. (Note; 2.51 is surprisingly low for zero months considering the poor laminate quality seen via C-scans and acid digestion). Beyond 12 months of room temperature prepreg storage, i.e., 50 months, the isopropyl VCAP-75 composite showed a higher 4.27% weight loss, presumably due to a poorer quality laminate. After 50 months of prepreg storage, the oven aging weight loss of both isopropyl laminates had the highest weight loss. This further suggests the useful shelf life has finally been exceeded.

A trend of increasing composite thermal oxidative weight loss with increasing prepreg storage time was apparent in the oven aging weight loss data (Figs. 14 and 15): 6 months of storage for both methyl prepreps, 12 months for the isopropyl PMR-II 50, and beyond 12 months the isopropyl VCAP-75. At these times, both ester systems are now beyond usual storage times (barring shipping, handling, transportation and storage accidents). The weight loss data infers that the room temperature prepreg storage limit is about 4 months for the methyl ester and over 12 months for the isopropyl ester prepreps.

Composite mechanical property comparison

Mechanical tests showed the usual expected large decrease in initial flexural strength (FS) of 30–50% and initial flexural modulus (FM) of 5–20% between the room temperature tests and the 316°C tests, for both unaged samples and 1000 h 316°C aged samples. That is, initial room temperature FS of 700–900 MPa dropped to 350–450 MPa at 316°C, after which FS remained close to this range after 1000 h of 316°C aging for both room temperature and 316°C tests. Similarly, the initial room temperature FM was around 50 GPa, which dropped to 40 GPa range at 316°C, after which FM remained close to 40 GPa after 1000 h of 316°C aging for both room temperature and 316°C FM tests. Thus, a significant difference in FS and

FM was not detected between the laminates made from methyl prepreps stored for 0–4 months at room temperature until at 6 months when the mechanical properties tended to be slightly lower yet. This qualitatively agrees with the rheological analysis, HPLC data, processing flow data, C-scans, and composite thermal oxidative stability that the end of the shelf life was reached by 6 months of room temperature storage for methanol prepreps.

Similar normal decreases in initial room temperature FS and FM were observed for the corresponding isopropyl systems. The initial room temperature FS of 600–800 MPa dropped to 400–500 MPa at 316°C, after which FS remained close to this range after 1000 h of 316°C aging, for both room temperature and 316°C tests. Similarly, the initial room temperature FM was in the 45–60 GPa range, which dropped to the 40–45 GPa range at 316°C, after which FM remained in this range after 1000 h of 316°C aging for both room temperature and 316°C FM tests. A significant difference in FS and FM was not detected between the laminates made from isopropyl prepreps stored for 0–12 months at room temperature until after 12 months (50 months samples) when the mechanical properties found were even lower. The only unusual mechanical response was for the very low initial FS for isopropyl VCAP-75, which was clearly attributable to the poorer laminate quality, as verified by the acid digestion and C-scan data. This data qualitatively agrees with the rheological analysis, HPLC data, processing flow data, C-scans, and composite thermal oxidative stability that the end of the shelf life is approached after 12 months of room temperature storage of isopropyl prepreps.

Summary of comparisons

Comparing the two ester systems data, the HPLC analysis showed that there is a significant amount of aging product formation in room temperature stored methyl prepreg. The rheological data also showed

methyl ester prepreg aging as a shift toward a higher temperature minimum viscosity (as much as 25°C higher); along with less decrease to reach the minimum viscosity, as the storage time reached 6 months. The isopropyl systems do not show nearly this extent of changes in the HPLC or rheological data, indicating a lack of aging during storage. It also appears from the composite quality analysis of the methyl PMR II-50 and VCAP-75 laminates that there is a serious decrease in the quality of the finished composites after 6 months of room temperature prepreg storage. The methyl ester laminate processing windows appear to be broad enough to only accommodate the changes in the prepregs during the first 6 months of aging.

The isopropyl ester laminates processing window remains constant for up to 12 months of room temperature storage once the prepreg is either partially dried by 4 months of room temperature storage, oven staged before processing, or additionally staged within the process cycle. This greater processing window happens primarily because significant aging is not seen for the isopropyl prepregs when looking at it as two different isopropyl laminate processing techniques: (1) oven staging used primarily for the shorter prepreg storage times to control volatile content and excessive processing flow or (2) autoclave staging in discrete steps and temperature holds used primarily for longer prepreg storage times.

CONCLUSIONS

The results of this study show that after 6 months of room temperature storage, a detrimental effect is seen on the composite quality of the methyl ester system for PMR II-50 and VCAP-75 polyimides. However, this time frame extends to at least a year for isopropyl PMR II-50 and isopropyl VCAP-75 polyimides. Freezer storage is still preferable for both ester systems because it creates an added safety margin against product failure. The methyl and isopropyl ester type solutions or prepregs can be stored in the freezer for an indefinite period of time without noticeable formation of aging products. But, if freezer storage is not possible, the results indicate that finite room temperature storage can be an acceptable option.

The major advantage of the isopropyl ester is the protection afforded if overheating during prepreg manufacturing happens, accidental aging in transit occurs, the freezer fails, or the resin is used in room temperature stored repair kits. However, some processing considerations are required. The major disadvantage of the isopropyl ester is considerable extra effort in processing time at intermediate temperatures is needed to remove the processing volatiles (a mass transport problem) before comparable quality lami-

nates can be obtained. Attempts to do so with B staging in ovens, adding temperature holds during heat up, trapping volatiles with dry ice and other volatile removing techniques, e.g., prepreg aging, always made the composite processing longer and more tedious. In conclusion, comparable results with both ester systems can be obtained, but additionally, the isopropyl ester system provides a more forgiving processing window in the event of mishandling or improper storage of prepregs because the isopropyl esters age significantly slower.

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