Introduction

In choosing a polymer-matrix composite material for a particular application, a number of factors need to be weighed. Among these are mechanical requirements, fabrication method (e.g. press-molding, resin infusion, filament winding, tape layup), and use conditions. Primary among the environmental exposures encountered in aerospace structures are moisture and elevated temperatures, but certain applications may require resistance to other fluids and solvents, alkaline agents, thermal cycling, radiation, or rapid, localized heating (for example, lightning strike). In this chapter, the main classes of polymer resin systems found in aerospace composites will be discussed. Within each class, their responses to environmental factors and the associated degradation mechanisms will be reviewed. Table I lists some common resin systems along with their processing and nominal long-term use temperatures. Exactly what is meant by “long-term” is not always specified. For airframe structure and aircraft engines, it should probably mean tens of thousands of hours (Bowles et al. 1998).

Table I Classes of Matrix Resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Typical Tg, °C</th>
<th>Processing Temperature, °C</th>
<th>MIL-HDBK-17 (composites handbook) test recommendations</th>
<th>Typical use Temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Default elevated temperature</td>
<td>Default range</td>
</tr>
<tr>
<td>Vinyl Ester</td>
<td>130</td>
<td>120</td>
<td>20 – 80</td>
<td>--</td>
</tr>
<tr>
<td>Epoxy</td>
<td>199</td>
<td>140</td>
<td>20 – 180</td>
<td>104</td>
</tr>
<tr>
<td>Cyanate Ester</td>
<td>232</td>
<td></td>
<td>135 – 200</td>
<td>--</td>
</tr>
<tr>
<td>Bis maleimide</td>
<td>296</td>
<td>210</td>
<td>177 - 204</td>
<td>177</td>
</tr>
<tr>
<td>Polymide Ethers</td>
<td>290</td>
<td></td>
<td>250</td>
<td>--</td>
</tr>
<tr>
<td>Polymides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMR</td>
<td>338</td>
<td></td>
<td>316</td>
<td>288</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td>340</td>
<td></td>
<td>350</td>
<td></td>
</tr>
</tbody>
</table>

General statements about aging behavior of particular backbone structures (e.g. “Structure A is more stable than Structure B”) must be tempered with the knowledge that degradation is affected by 1) polymer molecular weight and endgroups 2) purity and defects 3) physical form (e.g. bulk, composite, or powder) and 4) property examined (e.g. weight loss, microcracking, strength or toughness loss) (Hergenrother 2003). In addition, there is a potential gap between academic studies on purified systems and performance metrics on composites from commercial prepreg.

General effects of thermo-oxidative exposure.

In the following sections, detailed information on chemical changes for various resin chemistries will be presented where it is available. It is possible to make some generalized observations even in the absence of detailed mechanisms, however.
The first distinction to be made is between physical and chemical aging. A glassy polymer (thermoplastic or thermoset) or the glassy phase of a semicrystalline polymer is typically in a kinetically-frozen non-equilibrium state. If the material is annealed below its glass transition temperature, \(T_g\) it evolves toward equilibrium. This evolution is characterized by decreases in volume, enthalpy, and creep rate and the material generally becomes stiffer and more brittle (Truong and Ennis 1991). These changes can be reversed by heating the polymer above \(T_g\) and quenching. Because no chemical changes are taking place, the material can be “rejuvenated” multiple times in the laboratory by repeatedly cycling above \(T_g\) (Nicholson and Gates, 2001). Of course, it is not practical to do this on an article in service.

In addition to physical aging, thermal exposure can cause chemical aging. The curing reactions of thermoset resins may continue, leading to increased crosslink density, evidenced by rises in \(T_g\) and often embrittlement. On the other hand, the strength of an initially under-cured resin may actually increase during this stage due to post-curing. It may be worth mentioning that some elastomers, although they are not usually matrix resins may undergo reversion, where a decrease in crosslink density brought about by heat causes them to soften or even liquefy (Datta et al. 2007). Aging of composites at higher temperatures and longer times may lead to weight loss in the resin due to chain fragmentation and volatilization of the resulting small molecules. In the presence of oxygen, it is not unusual to see an initial small weight gain due to the formation of oxidation products (Akay and Spratt 2008) followed by faster weight loss. Oxidative weight loss is usually indicative of extensive chemical changes in the resin, leading to embrittlement, shrinkage and cracking. When cracking occurs, weight loss commonly accelerates due to the increased surface area in contact with oxygen (Colin et al. 2005).

General effects of exposure to water and other solvents.

Water and other small molecules in polymers usually cause a decrease in \(T_g\) known as plasticization. The effect has been fitted to equations originally used to predict the \(T_g\)s of copolymers and blends (Brewis et al. 1980). Usually the glassy modulus is not much affected. In some cases where the small molecule interacts strongly with the matrix, there is a density and modulus increase in the glassy phase, a phenomenon called antiplasticization (even though \(T_g\) still decreases).

The amount of water sorbed by polymers varies widely. At low degrees of absorption, the diffusion into the polymer obeys Fick’s law and produces at most a small degree of reversible swelling. Larger degrees of solvent swelling can lead to what is known as Case II sorption, in which a swollen layer with a very sharp boundary moves into the material with time. Even in the absence of that effect, certain materials, especially epoxies, may exhibit irreversible water sorption/desorption/re-sorption. This is usually attributed to cracking arising from swelling stresses (Weitzman and Guo 2002), but the existence of nanoscopic inhomogeneities that can retain water has also been proposed (Zheng and Morgan RJ 1993; Soles et al. 1998).

Chemical changes due to reaction with water are not common in composite matrix resins, but they can occur under certain circumstances. One example is the hydrolysis of polyimides at high pH or in the presence of superheated steam (Shin et al. 2000). Another example is the degradation of the matrix resin or of fiber/matrix interfaces when a graphite composite is galvanically coupled to an active metal, usually in the presence of salt water (Miriyyala et al. 2002).
This degradation may be the result of hydroxyl ions or peroxy-species evolved at the graphite cathode.

**General effects of exposure to radiation.**

Ultraviolet radiation is effectively blocked by carbon fibers, but can still produce severe surface degradation of films, coatings, and composite matrix resins. Weathering by combined UV/air/water exposure removes substantial quantities of composite surfaces (Kumar et al. 2002). Other forms of ionizing radiation (electrons, protons, gamma rays) produce free radicals via homolytic scission of covalent bonds. These in turn lead to simultaneous polymer chain scission (decrease in molecular weight), crosslinking, and evolution of small molecules, chiefly H2. In the presence of oxygen, chain scission tends to dominate and properties such as Tg and toughness decrease dramatically. In general, all-aromatic polymers are more radiation-resistant than those containing aliphatic structures (Sasuga and Hagiwara, 1987).

**General effects of mechanical loads.**

Although creep and fatigue damage will be considered in more detail in Chapter 4, it is worth mentioning that time-dependent behavior in carbon-fiber and glass-fiber composites is controlled by the matrix. In particular, matrix cracking (in response to thermal stresses) and interply delamination depend on matrix toughness. Interestingly, while static strength and toughness are directly related to matrix ductility, fatigue thresholds vary less (O'Brien 1988).

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Datta RN, Huntink NM, Datta S, Talma AG 2007 Rubber vulcanizates degradation and stabilization Rubber Chemistry And Technology Volume: 80 Issue: 3 JUL-AUG Pages: 436-480


Sasuga T; Hagiwara M 1987 ‘Radiation Deterioration Of Several Aromatic Polymers Under Oxidative Conditions’ Polymer, v 28, n 11, p 1915-1921


**Epoxies**

Because they cure readily from liquid or tacky oligomers without the release of volatiles, epoxy resins are very popular starting materials for composites. For adhesives and lower-temperature structural resins, a common monomer is the diglycidyl ether of bisphenol A, DGEBA, shown in Figure 1. In aerospace and other high-temperature applications, it is helpful to use a resin with higher functionality such as the tetrafunctional TGMDA (tetruglycidyl methylene dianiline, Figure 2), the tri-functional triphenyl methane derivative (Figure 3) or a multifunctional novolac epoxy (Figure 4). All these various epoxy components tend to be miscible, and the mixture can be formulated to give the desired film-forming ability, prepreg tack and drape, and cured Tg. Additional components may be incorporated in order to modify toughness, moisture resistance, and other properties.
While commodity epoxy adhesives and coatings may be cured with a variety of catalysts and curing agents, (e.g. anhydrides, aliphatic polyamines) most high-performance matrix resins are cured with aromatic diamines such as MDA (methylene dianiline, Figure 5) or DDS (diamino diphenyl sulfone, Figure 6). The reaction of epoxy groups with primary and secondary aromatic amine produces crosslinks of the types shown in Figure 7. At higher temperatures and when epoxy is present in stoichiometric excess, homopolymerization to ether structures (Figure 8) may occur (Pyun and Sung 1991). This latter reaction is catalyzed by hydroxyl groups, so it tends to occur in the later stages of reaction. Thus, even in the simplest case, a cured epoxy-amine system will contain multiple crosslink chemistries, some of them cyclic.

Early aerospace prepregs were based on the TGMDA/DDS chemistry (Morgan and Mones 1987). The combination of a tetrafunctional epoxy and a tetrafunctional amine crosslinker led to a network of very short chains, giving a desirable high Tg and high modulus. These resins, however, were very brittle. Furthermore, the addition of functionalized liquid rubber additives (such as ATBN, amine-terminated butadiene/acrylonitrile) -- a strategy that was very successful for toughening of epoxy adhesives -- was not an effective approach for these resins with high cure temperatures and limited inherent ductility (Chen and Jan, 1995). A much more successful approach has been to incorporate thermoplastics, preferably with amine end groups that can react directly into the curing resin (Hodgkin et al. 1998). The properties of the resulting matrix material depend on the solubility of the thermoplastic and on the reaction conditions, but in general, toughness can be improved by at least a factor of two over that of the base epoxy without a loss in room temperature modulus or hot/wet properties. It should be noted that, in contrast to rubber toughening, which usually involves no more than 15% rubber, thermoplastic toughening can use large amounts of the additive. In fact, a “phase-inverted” morphology, where the thermoplastic becomes the continuous phase, may give optimum toughness (Kinloch et al. 1994). In an additional toughening approach, a current state-of-the-art graphite/epoxy contains spherical particles of an amorphous polyamide at the ply-ply interface; in the finished composite laminate, the particle-toughened interlayer is about 30 um thick, or perhaps 15% by volume (Odagiri et al. 1991). Modern resins are thus designed to be inhomogeneous on several length scales in order to capture the desired combination of properties (chiefly good laminate compression strength along with interlaminar toughness for damage resistance and damage tolerance).

It may be mentioned that there have been efforts to modify epoxy-matrix composites with various nanoscale additives, although they do not seem to be commercial (e.g. Siddiqui et al. 2007). Some modifiers might be expected to slow water permeation (Kim et al. 2005) but strength improvements have been generally modest so far (Zhou et al. 2008) and long-term data are lacking.

**Thermal Aging**

A typical aerospace epoxy, Hxcel 8552, is a 180º C curing system “designed to operate in environments up to 121ºC.” With a dry Tg of 200ºC and a wet Tg of 154ºC, it is usually evaluated for aircraft service at 82ºC. Data for a range of epoxy systems, shown in Table II, indicate that resin moduli fall off by about 25-30% at this temperature under moisture-saturated conditions (Coquill and Adams 1989). This softening adversely affects composite compression strength, so a temperature of 120ºC probably already represents an accelerated exposure relative to a practical use temperature. The composites handbook (MIL-HDBK-17) recommends an
aircraft service environment for testing purposes of 85% R.H. The corresponding test temperature or Material Operating Limit is not specified, but is often 28°C below the Tg.

Table II  Temperature/Moisture Effects on Epoxy Modulus

<table>
<thead>
<tr>
<th>System</th>
<th>Neat resin Tensile Modulus, GPa</th>
<th>Room temperature, RT</th>
<th>82°C</th>
<th>121°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3502</td>
<td>dry</td>
<td>3.8</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>3.5</td>
<td>2.6</td>
<td>1.9</td>
</tr>
<tr>
<td>2220-3</td>
<td>dry</td>
<td>3.0</td>
<td>2.5</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>3.1</td>
<td>2.1</td>
<td>0.9</td>
</tr>
<tr>
<td>8551-7</td>
<td>dry</td>
<td>3.1</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>2.8</td>
<td>2.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Wolfrum and co-workers (2009) attempted to rapidly evaluate thermooxidative effects in graphite/epoxy laminates using exposures at up to 200°C for 450 days. Under these conditions, oxidation is much more severe at the composite surface, although changes in the infrared spectrum were observed even 500 μm below the surface. These were interpreted as oxidative destruction of the epoxy resin. Specifically, the absorption bond at 1510 cm⁻¹ assigned to an aromatic CH vibration, but sensitive to attached aliphatic structures (Dao et al. 2006) decreased almost to zero. Simultaneously, peaks assigned to carbonyl (1710) and amide (1668 cm⁻¹) groups increased. Though not shown by Wolfrum, the –OH and -CH₂- peaks correspondingly drop sharply. This is consistent with the mass spectroscopy results indicating release of 2-propanol, acetic acid, etc. At 200°C, aromatic groups are being eliminated by oxidation (Dao et al. 2006) or volatilization of aniline, N,N-dimethylaniline, etc. The weight loss of a 16-ply composite under these conditions is over 3%, but is concentrated at the surface. Still, it is probable that elevated temperature exposure, even in the absence of oxygen, will lead to chain-breaking (Stutz, 2004; Bellenger, 1985).

It is important to reiterate that the detailed structure of an epoxy network is dependent upon the stoichiometry, impurities in the monomers, and cure temperature (Gupta 1983).

Radiation effects

Ultraviolet (UV) radiation, including sunlight at sea level, is very injurious to epoxy-matrix composites. UV does not penetrate beyond the near-surface layer so paints or other coatings can provide adequate protection. Unprotected laminates erode rather quickly. Kumar et al. (2002) showed that a 177°C-cured laminate lost the equivalent of over half a ply’s thickness and underwent severe microcracking when exposed to only 500 h of alternating UV/condensation exposure. Giori et al. (1983), in a simulation of space exposure, detected fairly high yields of CO, CO₂ and H₂ from TGMDA-based composites that were exposed to 200-400 nm UV in vacuum. The CO₂ was attributed to oxidized species formed during fabrication; the H₂ is considered indicative of generalized free radical processes. In this study compressive or flexural strengths of the composites were not greatly affected. In the same study, electron radiation in
vacuo at $10^9$ rads produced a measureable increase in Tg for one of the resins (Narmco 5208) but a decrease for the other (Fiberite 934). Fox et al. (1987) exposed 934 resin and composite to $10^{10}$ rads of 1MeV electrons, corresponding to a “worst case” 30-year exposure in geosynchronous earth orbit. The decline in Tg and production of low-molecular-weight products were attributed to polymer chain scission. This had the effect of making the resin more brittle, especially at cryogenic temperature, and led to decreases in composite transverse strength. Comparison of neat resin to composite properties was complicated by the significant finding that the neat resin cured differently, at least in this study. The report mentions in passing that 934 contained a minor amount of BF$_3$ complex (a homopolymerization catalyst). Noting that the flexural strength as a function of absorbed dose is the same for either electron or gamma radiation, Egusa (1988) concluded that their effects are equivalent. Ultimate strain of TGMDA/DDS resin fell by over a factor of two at 150 MGy dose. Takeda et al. (1995) studied a TGMDA/DDS system with either carbon or glass cloth reinforcement. The decreases in composite Mode I interlaminar fracture toughness that they observed upon irradiation are consistent with resin embrittlement.

Bellenger and Verdu (1985) proposed the interesting idea that internal stresses (valence distortions) caused by the curing reaction and by cool down from the cure temperature may promote bond-breaking under oxidative conditions. This idea explained the larger degree of network degradation (decrease in Tg) when photo oxidation was conducted deep in the glassy region, where thermal residual stresses would be highest.

**Moisture and solvent effects**

In cured epoxy resins, there are a variety of polar groups (hydroxyls, amines, sulfone) that would be expected to have an affinity for water. In fact, it is difficult to desorb the last traces of absorbed moisture by heating at moderate temperatures ($60^\circ$C). Zhou and Lucas (1999) suggest that this water is doubly hydrogen-bonded to hydroxyls, whereas Zinck and Gerard (2008) infer (by studying different crosslinkers) that tertiary amines are responsible. How much water is strongly bound seems to be a function of the sample history.

Many investigators have posited therefore that water may exist in two states in epoxies, e.g. bound/free; dissolved/clustered; in nanovoids/microvoids (Popineau 2005). The existence of more than one kind of water absorption site is not of merely academic interest, since hysteresis in the absorption/desorption curves will affect the nature of the steady-state distribution (and hence the internal stresses) when a composite part undergoes cyclic temperature/humidity exposure (Tenney 1978). Although details differ, these models call attention to the fact that at least for some resins at some temperature/moisture conditions, plateau moisture uptake values may depend on sample history (Suh, 2001) even in the absence of gross cracking, cavitation, or failure at fiber/matrix interfaces (Weitsman and Guo 2002). Moisture hysteresis may be less prominent in high-Tg tetrafunctional resins than in the commodity DGEBA materials. Lee and Peppas (1993) found no evidence of cracking or irreversible changes in TGMDA/DDS exposed to water at $70^\circ$C, even though that system absorbs almost 7% by weight (Zhou and Lucas, 1999). Nogueira (2001) studied the effect of cure schedule on water uptake in a DDS-cured tetrafunctional blend containing excess epoxy. Even with 0.3 mm thin resin plaques, moisture uptake did not reach equilibrium in several cases, suggesting that ongoing damage processes may be occurring beyond 1000 hours. Reversibility was not examined in that study. In amine-cured epoxies there does not seem to be any evidence for actual hydrolysis of chemical bonds.
contrast, epoxy adhesives cured with dicyandiamide or anhydride may hydrolyze (Xiao 1998, Deneve 1995, Antoon 1981), causing permanent damage to the network.

Effects of moisture exposure on mechanical properties are illustrated in some early work by Augl (1977). He studied composite properties of Narmco 5208 on two different carbon fibers. Thin (2.0 mm) unidirectional specimens were exposed to 80% relative humidity (RH) at 75°C for 21 days, absorbing 0.64% moisture. This is not long enough to reach moisture saturation or to achieve a uniform through-thickness water concentration profile, but Augl pointed out that in his flexural testing, the outer surfaces were the most highly stressed. Although the hot/wet rigidity of the neat resin at 175°C was half the dry value after the 80% RH exposure, the room-temperature resin modulus was practically unaffected. Still, the room temperature composite flex strength dropped about 12% after the humid exposure and the failure mode changed. Interestingly, a composite made with a higher-modulus, but unsized, fiber seemed to retain more strength, implying that the undercured epoxy sizing may have been more moisture-sensitive than the bulk matrix. In Augl's experiments, all moisture effects were completely reversed upon re-drying the specimens.

Humidity decreases resin modulus and strength (at least at elevated temperatures), but the increased ductility in water-plasticized epoxies might be expected to improve toughness. This is in fact the case: some neat resin castings of a bisphenol-A epoxy cured with an aromatic diamine doubled in toughness when stored in laboratory air (50% humidity, 25°C) relative to the as-prepared state (Clarke, 1984). Ordinarily, higher resin toughness would be expected to translate to higher composite (e.g. interlaminar) toughness. The situation is not quite so simple, though, given the large role played by fiber/matrix adhesion in both the initiation and propagation of delaminations (Davies et al. 1996; Kim 2004). Russell and Street (1989) found for 3501-6/AS1 that wet composite $G_{IIc}$ was only about 10% higher than dry. Wet $G_{IIIc}$, on the other hand, was marginally lower. The toughness trends with temperature were opposite for the neat resin and composite, a discrepancy that the authors attributed to the roles of residual stresses and constraint effects.

$G_{IIIc}$ of a composite that is toughened with thermoplastic particles in the interply regions decreased about 20% when the laminate was wet (Matsuda et al. 1999). Fatigue thresholds for Mode II interlaminar crack growth were also about 25% lower in wet specimens. This was attributed to a change in crack path toward failure at the particle/epoxy interface. The matrix itself did become more ductile, and creep tests on [±45]$_2$s specimens of this same graphite/epoxy system with about 1% water showed about a 20% increase in creep compliance at 26°C and much more at higher temperatures (Woo, 1994) The creep rate was directly related to the proximity of the wet Tg.

Sala (2000) studied carbon fabric/epoxy laminates that absorbed 4.8% moisture, whereupon static moduli of matrix-dominated (±45) specimens decreased by nearly 50%. When loaded in fatigue, wet (±45) specimens underwent a much slower stiffness degradation than dry ones, although fatigue failure stresses were similar. Wet (0/90) specimens had about 30% higher fatigue failure stress.

There is not a lot of information available on effects on matrix resins of other fluids besides water. In general, it would be expected that solvent sensitivity would depend strongly on the detailed chemistry of the network (Kaplan 1991) as well as on its crosslink density. Curliss and
Carlin (1990) found decreases in modulus and strength when both AS4/3501-6 and toughened epoxy systems were exposed to hot JP-4. Although they attributed the loss in strength to degradation of the fiber/matrix interface, there was also a measurable decrease in Tg due to preferential sorption of certain fuel components. The degradation in 0° flex strength amounted to 25%. Hooper et al. (1991) and Hooper and Subramanian, (1993) showed that absorption of jet fuel tended to toughen AS4/3501-6. Almen et al. (1989) show only minor effects on 977-2 and 3501-6 composites due to immersion in methyl ethyl ketone, although the specimen thickness was not reported.

Effects of stress and time

Like other polymers, composite matrix resins exhibit time-dependent behavior. This applies to stiffness, strength, and toughness properties. For example, Ashcroft et al. (2003) modeled cracking in an epoxy using a viscoelastic fracture model. The implication of this is that subcritical crack growth could occur over very long times. Absorbed moisture would affect the time-dependent (e.g. creep) behavior of a resin, but there is also a more subtle effect: applied stress also increases both the diffusion constant and the ultimate water pickup (Fahmy and Hurt 1980, Derrien and Gilormini 2007). Residual stresses due to cure and cooldown may cause similar effects; this may explain why ±45 coupons absorbed more fuel than did unidirectional coupons under the same conditions (Curliss et al. 1990).

An interesting new approach to damage tolerant composites has been demonstrated: a “self-healing” epoxy matrix (O’Brien and White 2008). At this point mostly a laboratory curiosity, such a material system when damaged would release an encapsulated adhesive into small cracks to seal them or slow their growth (Pang and Bond 2005). The more general research area of remendable polymers (which includes thermoplastics and certain epoxy-like materials designed with thermally-reversible crosslinks) has been reviewed by Bergman (2008).

Fig. 1 DGEBA
Fig. 2 TGMDA

Fig. 3 Trifunctional epoxy
Fig. 4  Novolac epoxy. Typically 3-4 epoxy groups per molecule; meta and para links

Fig. 5 MDA

Fig. 6 DDS
Fig. 7 Epoxy-amine reactions

Fig. 8 Polyether formation via homopolymerization


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Bismaleimides

Bismaleimide (BMI) resins get their name from monomeric structures that are synthesized by condensing maleic anhydride with an aromatic diamine, followed by cyclodehydration to the bis-imide (Stenzenberger 1990). A common component is built on 4, 4’-diaminodiphenyl methane, Figure 1. Maleimides can undergo free-radical polymerization with a catalyst or thermally without a catalyst, but the highly-crosslinked product arising from homopolymerization of this low-molecular-weight monomer is extremely brittle and therefore not very useful. Commercial BMI matrix resins are formulated with other components: chain extenders, reactive diluents, catalysts and tougheners; their cured structures thus may vary widely and are probably very complicated.

One method of chain extension for monomers like that in Fig. 1 employs the Michael addition with aromatic diamines (Fig 2). Another uses Diels-Alder chemistry (Fig 3) to copolymerize either divinyl benzene (Street 1980) or a monomeric or oligomeric bis-propenyl compound (Stenzenberger et al. 1987) with the maleimide. Recent generations of BMI prepregs contain substantial percentages (~30%) of propenylphenoxy or allylphenyl or allylphenol comonomers that improve toughness; a typical example is diallyl bisphenol A (Fig 4). The latter becomes incorporated via an “ene”-type reaction (Fig 5). The ene reaction is complete early in the cure cycle, and further reaction of maleimide and allyl double bonds occurs in the 200-250°C range (Morgan et al. 1997). At higher temperatures and longer times, there is spectroscopic evidence...
of etherification via the hydroxyl functionality. Morgan et al. call this continued crosslinking, but the observed increase in Tg could also be caused by intramolecular reactions that increase the structures’ rigidities.

Because they offer epoxy-like processing with a some improvement in thermal stability, BMI’s are also blended and co-reacted with other thermosets, such as epoxies and/or cyanate esters (Dinakaran et al. 2003). BMIs have also been toughened by the addition of thermoplastics, including maleimide-capped sulfone polymers, although at a sacrifice of prepreg tack and drape (Stenzenberger 1989). An RTM version of the commercial 52504 is said to contain, in addition to the diaminodiphenylmethane-derived monomer, the BMI of toluene diamine (Li 2004), probably as a viscosity modifier.

**Thermooxidative degradation**

Working with cross-plied laminates of BASF X5260, Pederson et al. (1995) showed that isothermal aging in air at 177°C produced a weight loss of 1.5% and increased Tg from 250 to 300°C, which suggests significant chemical changes at this temperature during the 2232-hour aging period. At the same time, the resistance to interlaminar cracking decreased by 50%. Sixteen-ply quasi-isotropic specimens formed microcracks (up to 50/cm) under the influence of thermal degradation and residual stress. The data for crack density as a function of time and ply depth fit the assumption that the reaction was diffusion-controlled. Similarly, Ohno et al. (2000) reported that the surface layers of BMI composites blacken as cracking proceeds. It is difficult to do much detailed chemical analysis on a crosslinked resin, but XPS seemed to indicate that oxidation of carbon to carbonyl (occurring initially at phenol and isopropylidene groups) produced colored species and eventually loss of small molecules (e.g. benzoquinone). Dao et al. (2007) interpreted their FTIR data as showing that even the initial cure conditions (at 170°C or higher) contributed to surface oxidation. –C–OH groups arising from oxidation of –CH as well as the vinyl groups left by incomplete cure are thought to provide sites for continued oxidative attack. These oxidation processes lead to easily-measureable weight gains in the early stages of aging (Colin 2001). After that, the surface composition stabilizes as material is lost. At accelerated aging temperatures, resin from entire surface plies may be vaporized while the interior of a 2 mm-thick laminate is little affected. In spite of this, DMA measurements could detect increases in Tg. Increases in Tg in a few thousand hours at more typical use temperatures have also been seen (Loechet and Rothschild 1992). Morgan et al. (1997) associated this postcuring with “a more brittle mechanical response” but no mechanical data were shown. Boyd and Chang (1993), however, did show that aging at 205°C in nitrogen produced both an increase in Tg and a decrease in composite compression after impact strength, which certainly suggests chemical changes unrelated to oxidation.

**Moisture and solvent effects**

Like epoxies, commercial BMI resins absorb several percent of water (Bao and Yee 2002). A manufacturer’s data sheet quotes a dry Tg of 300°C and a wet Tg of 200°C (Cycom 5250-4). Room temperature properties (modulus, strength) are not greatly affected by moisture (Costa 2005). When tested wet at 82°C, however, about a 15% lower interlaminar shear strength and a 20% lower composite in-plane shear modulus were recorded (Falcone 1995).
Unlike epoxies, BMI’s contain hydrolysable links. Upon water aging a 90°C, Bao and Yee (2002) saw changes in the infrared spectrum that they ascribed to hydrolysis of imides to amides and carboxylic acids. This change was coupled to continuing long-term water uptake as the network relaxed.

A related degradation mechanism is the hydrolysis that occurs when BMI composites are galvanically coupled to metals. Woo (1993) showed that BMI was more susceptible to galvanic degradation than epoxies, and with Rommel et al. (1993) blamed hydroxyl ion produced at the cathode. Taylor (1996), however, compared galvanic results to added caustic and blamed peroxide and superoxide radicals.

Another difference from epoxies is that BMI’s have use temperatures above 100°C. Rapid heating of moisture-saturated coupons (‘‘thermal spiking’’) can cause blistering and other permanent damage.

In addition to water, Falcone and Dow (1995) soaked BMI coupons in JP-4, hydraulic fluid, deicing fluid, methylene chloride, and MEK. At room temperature, only methylene chloride (paint stripper) produced obvious damage in four days. Jet fuel did affect the 82°C properties substantially (producing over 20% decrease in shear modulus and strength).

**Mechanical and time-dependent effects**

A principal mechanism observed upon long-term thermal cycling is the formation of microcracks and their eventual propagation as delaminations. Ju and Morgan (2004) showed that cycling from room temperature to 250°C produced 45% more cracks than room temperature to 200°C. They attribute this to continued postcuring. It is interesting that 0.8% prestrain leads to measureable cracking after only two cycles to -196°C; the mechanical prestrain had little effect on the extent of cracking in 25°C-250°C cycling. The most severe condition included both elevated and cryogenic excursions, especially when combined with humidity. Since moisture-induced swelling should ameliorate ply-level cooldown stresses, a more localized effect of water at the fiber-matrix interface is implicated. Alternatively, the resin itself may be degraded by 100% humidity at 100°C.
Fig. 1 BMI monomer

\[
\text{Ar} - \text{N} - \text{C} = \text{O} + \text{NH}_2 - \text{C} = \text{C} - \text{C} \xrightarrow{\text{Michael addition}} \text{Ar} - \text{N} - \text{C} = \text{O} - \text{NH} - \text{C} = \text{C} - \text{C}
\]

Fig. 2 Michael addition
Fig. 3 Diels-Alder-type extension
Figure 4 Diallyl bisphenol A
Fig. 5 Chain extension and crosslinking via “ene” reactions
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Thermoplastics

A wide variety of thermoplastics such as nylons, polypropylene, and polycarbonate are common matrix materials for chopped-fiber, injection-moldable composites. For high-performance applications in transportation and aerospace, continuous-fiber unidirectional tape and fabric are chosen, and the matrix choices quickly narrow to aromatic polymers (McGrail 1996) containing ether, ketone, and sulfone groups (and sometimes thioether). Figure 1 shows a generic structure. Also in this class are thermoplastic imides, shown in Fig. 2. Table I gives some well-known examples. Melt viscosities of all of these materials tend to be high, so successful composite processing relies on keeping molecular weights low. In semicrystalline materials, crystallites can function as crosslinks to improve toughness and solvent resistance and raise the use temperature. In linear amorphous materials, the molecular weight range that can be used in composite fabrication may be quite small (Hou et al. 1995) so chain extension/crosslinking via reactive end groups or pendant groups is helpful. The chemistries and degradation of these materials are taken up in other sections of this chapter. Another approach to processing a linear polyimide is illustrated by DuPont’s Avimid N, (Tg = 352°C) which is prepregged from a mixture of monomers, probably the fluorinated anhydride 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and the diamines p-phenylenediamine and m-phenylenediamine.

Thermooxidative aging
Because both the use temperatures and the processing temperatures of the thermoplastics tend to be higher than those of epoxies, oxidation tends to play a significant role in loss of properties during aging. Even relatively brief exposures to processing in air at Tg+100°C (Brauman and Chow 1993) produced measureable changes in Tg and melt rheology (Phillips et al. 1997).

Many studies of the pyrolysis of thermoplastics exist (e.g. Perng 1999, Ehlers et al. 1969) but the degradation mechanisms in air and at more-realistic use temperatures are different from those that occur during rapid heating in vacuo. In general, exposure of thermoplastics to high temperatures and oxidation will lead to simultaneous backbone rearrangements, crosslinking or branching and chain scissions. The latter would eventually lead to the volatilization of small fragments. To give an example, Kuroda et al. (1989) heated a soluble polyimide powder in air or in vacuum and were able to quantify scission and crosslinking reactions by employing both gel permeation chromatography and measurements of the elongation of small films in the rubbery state. They also tracked changes in Tg. Although mechanical properties of the glassy polymer were not measured, it is known (Gardner 1979) that reductions in molecular weight lead eventually to a ductile-brittle transition and it is also known that the concentration of crosslinks affects toughness directly (Hinkley and Campbell 1983).

Weight loss, on the other hand, while it is certainly easy to measure, especially for resin films and powders, might not correlate with changes in mechanical properties (Hinkley and Yue 1995). This is because neither crosslinking nor changes in backbone chemistry are necessarily closely tied to reactions that produce small molecules, especially under accelerating conditions. By the time a linear polyimide has experienced a weight loss of 2-3% at 400°C, the remaining polymer is chemically very different from the starting material (Dine-Hart 1971).

When used to study long-term aging, weight loss is also not very sensitive. For example, Abate et al. (2002) could not detect “appreciable” weight loss in their polyarylene ether ketones during 25,000 hours at 270°C, an aging temperature that was above Tg, and thus far above any reasonable use temperature for that material. Parvatareddy et al. (1995) aged IM8/ITX (a semicrystalline thermoplastic matrix with a Tg of ~185°C) for 6-9 months at 150°C leading to a 48% drop in composite 90° flex strength. Comparison of N2 and air aging suggested that a combination of physical and chemical effects caused the simultaneous rises in resin Tg and modulus. The concomitant 1.7% weight loss in the composite is good evidence that some chemical events were occurring.

Physical aging is a known problem for amorphous thermoplastics, but it also occurs in semicrystalline materials like PPS (Krishnaswamy 2003). Physical aging of PEI below Tg increased the yield stress and modulus (Robertson 1999) but produced no discernable embrittlement; composite specimens were stronger after aging.

Moisture and solvent effects
Because of the high processing and use temperatures of most thermoplastic composites, effects of water have not received a lot of attention. Zhang and Piggott (2000) showed that graphite/PEEK absorbed about 0.5% water based on the matrix weight fraction; failure strain decreased by ~25%, which they attribute to the matrix and not to the interface. Bismarck et al. (2007) also saw a decrease in transverse strength. The change was irreversible on drying, so may relate to crystallinity (Boinard et al. 2000). Polyphenylene sulfide (Tg=90°C) undergoes additional crystallization during hot/wet aging (Ma et al. 1992). Wang and Springer (1989) found a small (probably insignificant) increase in the interlaminar fracture toughness of graphite/PEEK with moisture. On the other hand, GIIc decreased about 20% upon moisture saturation (Selzer and Friedrich 1995). While salt water had little effect on polysulfone, steam at 123°C did degrade it (McKenna et al. 1979), causing a change in tensile failure mode from ductile to brittle. A thick graphite composite degraded after 23 hours in the pressure cooker.

Shin et al. (2000) detected the hydrolysis of a thermoplastic polyimide, Avimid KIIIIB, when it was exposed to thermal spiking or pressurized steam. Burcham et al. (1996) concluded that water immersion was unrealistically severe for K3B and they also assumed that degradation of the fiber matrix interface was responsible for the loss in interlaminar toughness that they observed. Han and Nairn (2003), however, found that even humid exposures at 80°C decreased the toughness of K3B enough to cause spontaneous microcracking of the composite under the influence of residual stress.

As was the case for BMI’s, aromatic polyimides may be degraded by aqueous base. A structure-property study by Croall and StClair (1992) concluded that films containing the pyromellitic diimide residue were more susceptible to attack than polymers made from dianhydrides that contain bridging groups.

Because of interest in ICI’s APC composite for aircraft, there were a number of studies of immersion of PEEK in aircraft fluids (e.g. Curliss and Carlin 1990). Although PEEK absorbs measureable amounts of JP-4 and hydraulic fluid, the Tg and mechanical properties are not greatly affected. Stronger solvents such as MEK and paint stripper plasticize the matrix and weaken the composite. There is some evidence that aromatic compounds such as phenol are extracted from jet fuel (Curliss 1990).

So-called environmental stress cracking (crazing of stressed polymers in the presence of weak solvents or of surface-active agents) requires careful attention in applications of commodity polymers. Aromatic polyimides seem to be susceptible to stress cracking (Yang and Brown 1988, Dillard et al. 1994) although it has not received a lot of study.

Radiation effects

All-aromatic thermoplastics are considered to be inherently radiation-resistant. Bonin et al. (2008), for example, found little change in the properties of graphite-PEEK exposed to 1 MGy nuclear radiation. Exposures to UV (Rivaton and Gardette 1999) or electron radiation (Giori
1984) can cause polymer chain cleavage as evidenced by the production of benzene and other aromatics in addition to H₂ and CH₄. At 10⁹ rads, Giori saw over 20% decrease in flex strength in a polysulfone composite. The layup was not reported, but one expects that the change in matrix-dominated properties might be even larger. The linear polysulfone seemed more radiation-sensitive in terms of mechanical properties than were highly crosslinked (tetrafunctional) epoxies.

**Stress and time**

It is known that stress can enhance the transport and net uptake of solvent in neat PEEK (Wolf and Fu 1996). Pritchard and Randles (1995) found that diffusion and sorption of aircraft fluids in a composite were strongly dependent on layup and specimen thickness, “probably because of the effect of residual stress”. The reversibility of moisture/temperature cycling in a graphite thermoplastic was highly dependent on internal stress (Gates and Grayson 1999).

Studying the effects of water immersion on KIIIb, Kim et al. (1995) found decreases in the fracture toughness of the neat resin and spontaneous microcracking in composites. No significant changes in Tg occurred, and the authors suggested that plasticization by water may have increased the rate of physical aging; stress gradients due to non-uniform water absorption could possibly initiate damage.

The interlaminar toughness of thermoplastics can be quite high compared to that of typical epoxies. Under fatigue loading, however, the Mode-II toughness is degraded: the threshold strain-energy release rate is much smaller than the static value (O’Brien et al. 1987).

![Generic aromatic polymer](image)

Fig. 1 Generic aromatic polymer
Table I Representative Thermoplastics

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Tg [Tm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyphenylene sulfide (PPS)</td>
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<td>90 [285]</td>
</tr>
<tr>
<td>Poly(ether ether ketone) (PEEK)</td>
<td><img src="image2" alt="structure" /></td>
<td>145 [343]</td>
</tr>
<tr>
<td>Polysulfone (PSF)</td>
<td><img src="image3" alt="structure" /></td>
<td>190</td>
</tr>
<tr>
<td>Ultem polyimide</td>
<td><img src="image4" alt="structure" /></td>
<td>215</td>
</tr>
<tr>
<td>Polyethersulfone (PES)</td>
<td><img src="image5" alt="structure" /></td>
<td>230</td>
</tr>
<tr>
<td>K3B</td>
<td>Proprietary</td>
<td>245</td>
</tr>
</tbody>
</table>
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**PMR and related thermosets**

The PMR (Polymerization of Monomeric Reactants) approach to addition polyimides was first proposed in 1972. By using monomers in a low-boiling solvent such as methanol, it is relatively easy to make a flexible prepreg. The original composition, PMR-15, incorporated monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (nadic ester or NE), 4,4’-methylene dianiline (MDA), and dimethylester of 3,3’,4,4’-benzophenone tetracarboxylic acid (BTDE), formulated to give a polyimide molecular weight of about 1500 (Serafini 1972). The nominal structure is shown in Fig. 1. Since the original publication, modifications have been proposed to the diamin (e.g. RP-46 (Pater 1991)), to the dianhydride (e.g. “PMR-II” (Serafini 1976)) and even to the endcap (Chuang 2003), but PMR-15 is still a commercial product and has received a great deal of study.

**Cure and thermooxidative aging**

During the manufacture of a PMR part, loss of solvent, imidization, and some crosslinking may occur simultaneously, depending on the cure schedule. Imidization is fairly straightforward, and according to IR measurements, can be completed at temperatures as low as 165°C (Jordan 1996). Model compound studies (Johnston 1987) suggest that the initial reaction between monomers proceeds via base-catalyzed anhydride formation rather than by direct displacement from the ester-acid. The bisnadimide of MDA (i.e., Fig. 1 with n = 0) constitutes 35-50% of the oligomers (Milhourat-Hammadi et al. 1994). It might be expected that the product of the thermal reaction of such short oligomers would be very highly crosslinked. The nadimide-terminated polyimide oligomer undergoes an endo- to exo- isomerization at temperatures above 160°C (Mison 1999) to give a mixture of isomers. The model compound N-phenyl nadimide polymerizes at 285°C to give a product with degree of polymerization n = 6-7 (Panigot 1992). The kinetics depend on pressure, suggesting a role of cyclopentadiene (CP). Maleimides produced in the reverse Diels-Alder reaction may play a role in initiating the addition polymerization. Although some authors draw structures with CP copolymerized into the backbone via a double bond, few olefinic carbons are actually detected in the cured resin (Wong 1981). Cyclopentadiene may instead be reacting with the nadic groups yielding end groups with multiple bridges. The crosslink that might result is shown schematically in Fig. 2.

One factor that distinguishes much of the literature on this class of materials is a focus on applications at 316°C (600°F) even though the original paper (Serafini 1972) showed that a composite made from a similar composition lost 18% of its weight in 600 hours at this temperature. The curing conditions were not reported in that paper, but the constant push for higher-temperature performance (Bowles 1988) has led to aggressive postcure conditions: conventionally 16-96 h at 316°C, but in one case up to 100 h at 371°C (Baugher 1997). Scola (1991), in spite of measureable surface erosion and weight loss, found no evidence of pyrolysis in the interior of unidirectional composites. In fact, the elevated-temperature flex strength increased, perhaps due to a 25°C increase of the resin Tg during aging. Thus, in contrast to epoxies, where (wet) Tg limits the use temperature and chemical aging is rarely a major concern, the high use temperatures expected of these addition polyimides produce simultaneous curing and degradation, with the result that e.g. short beam shear strength increases for the first ~2000
hours, then falls rather precipitously (Pater 1991). Weight loss accelerates at about the same point.

In thermosets in general, a high degree of crosslinking is associated with thermooxidative stability. Comparisons among PMR-15, 30, 50, and 75, however, showed that the higher the molecular weight was between endcaps, the less weight was lost during 188°C aging (Vanucci 1987). This improved thermooxidative performance came at a very minor sacrifice in cured Tg. Leung et al. (1997) also varied PMR prepolymer molecular weight. They interpreted their data in terms of crosslink density only, but it could equally well be inferred that the (aliphatic) crosslink structure itself was less stable than the imide backbone with respect to weight loss. Meador et al. (1997) propose a scheme whereby oxidation of the nadic methylene bridge leads to aromatized structures (quinones and hydroquinones) although these were not detected directly. Their scheme maintains the links formed during the initial polymerization, so it does not account for volatilization of small fragments. It is clear though, that early in the aging or oxidation process, the nadimides are transformed, and that this chemical change is accompanied by weight loss, even in nitrogen (Bowles, 1988).

**Moisture and solvent effects**

Due to the emphasis on high-temperature applications, there are relatively few papers on moisture effects in PMR-type resins. Moisture can however be expected to have three kinds of effects: 1) matrix plasticization 2) retention of water after hygrothermal cycling, leading to delamination, blistering or void growth upon thermal spiking and 3) hydrolysis of imide linkages.

As an example of the first effect, moisture saturation had no effect on compression strength of Celion/PMR laminates at room temperature, but at elevated temperatures, the moisture effect was substantial (Poveromo 1985). Strength was down about 50% at 300°C. This may be an under-estimate, since some drying out may have occurred as the test temperature was reached; the heat-up rate is not reported. Shimokawa (1999) saw a similar 50% strength drop at 260°C in wet specimens. Post-impact compression failure strain is apparently improved by moisture, perhaps due to better matrix ductility (Postlewaite 1985).

The second mechanism, void growth, is illustrated by data of Morgan et al. (1998) on AFR700B (Fig. 3). Moisture contents above 0.4 wt % lead to blistering at around 400°C (wet Tg ~340°C).

Finally, although no difference was seen between PMR oxidation in dry air and ambient air (Putthanarat et al. 2008), hydrolysis of imides occurs above a threshold water content and leads to significant losses in toughness at rather moderate temperatures, e.g. 80°C immersed (Han 2003).

**Radiation**

Bowles et al. (1986) exposed both graphite/epoxy and C6000/PMR-15 to 6x10⁹ rads of electron radiation in high vacuum near room temperature. DMA showed a decrease in the Tg of the epoxy (attributed to chemical degradation) whereas Tg of the PMR-15 composite increased about 11°C. Vyhnal (1993) reported on LDEF-exposed composites and concluded that the mechanical properties were unchanged. The latter results may have been compromised somewhat by differences in the quality of the exposed and control panels.
Time and stress effects

Aging (air, 288°C, 1000 hours) degrades the tensile strength of the resin “dramatically” (Ruggles-Wrenn 2009). Matrix embrittlement can cause cracking, and cracks, in turn, provide additional paths for air ingress (Bowles 1999). Thus even though oxidative degradation is largely a surface phenomenon, stresses due to the layup, fiber architecture (Rupnowski et al. 2004) and mechanical loads (Ju et al. 2007) can interact with thermooxidative exposure to affect composite lifetimes.

In contrast to the behavior of thermoplastics, interlaminar fracture toughness of PMR is not greatly affected by the fatigue waveform (Uematsu 1995) in spite of the fact that the matrix does show nonlinear creep at 250°C (Marais 1991).

Fig. 1. Nominal PMR-15 oligomer (n=2.09)


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Phenylethynyl-terminated imides (PETI)

Aromatic polymers containing phenylethynyl (PE) groups were first reported in the mid 1970’s (Hedberg and Arnold 1976); a review was published in 2000 (Connell et al. 2000). Reaction of the PE group leads to both chain extension and crosslinking, and does not evolve significant volatiles when conducted under pressure. With the proper choices of monomers and molecular weight, oligomers can therefore have low melt viscosity – low enough to be suitable for transfer molding -- but high Tg and reasonable toughness when cured. NASA holds many patents on PE aromatic polyimides; these include the composition of matter for PETI-5, AFR-PE-4, and PETI-330 (Hergenrother and Smith, 1996; Connell et al. 2002). They have emerged as versatile matrix resins for high temperature composites on aerospace vehicles. NASA invested significant resources during the 1990’s on the development of PETI-5 for the High Speed Civil Transport. More recently the US Air Force has invested in the development of the AFR-PE-4 matrix resin (Gray et al. 2006) and generated a composites design-allowable database (McConnell 2009).

The resin transfer molding (RTM) resins come as powders in the imide form and are free of unreacted monomers or solvent. Prepreg materials can be obtained in two forms: as a mixture of monomers in alcohol (referred to as the PMR approach), or as an amide acid oligomer in a polar aprotic solvent such as N-methyl-2-pyrrolidinone (NMP). The mixture-of-monomers prepreg contains unreacted aromatic diamine that can be hazardous to handle since most aromatic diamines have varying degrees of toxicity (Sands et al. 2001). The US Environmental Protection Agency has ruled that exposure to at least one diamine, methylene dianiline, presents a significant risk to humans as a carcinogen. The amide acid oligomer form does not contain unreacted aromatic diamine but it does contain NMP, which also must be handled carefully.

The phenylethynyl endcap (Figure 1) reacts appreciably only above 300 °C, providing a substantial processing window. Cure occurs in 1-2 hours at 350-371 °C; a free-standing post cure is typically used to optimize thermal stability and requires several hours in air or an inert atmosphere in the 325 to 400 °C range.

The nature of the crosslinking chemistry is not known in detail, but there may be an analogy to the ethynyl (acetylene)-terminated resins described by Lee et al. (1983). Gel permeation chromatography, electron spin resonance, kinetic and mass spectroscopic results on ethynyl model compounds are consistent with radical polymerization to give polyene structures. Li and
Morgan (2007), citing Fang et al. (2000), show a similar structure arising from the phenylethynyl endcap (Fig 2). Using NMR on labeled oligomers, Roberts et al. (2000) detected some polyenes as well as aromatic groups including substituted benzenes, especially after postcuring. Interestingly, the product distribution seemed to depend on the oligomer molecular weight, perhaps due to concentration and viscosity effects. The average degree of polymerization of the end groups in the usual range of oligomers may be as low as 2.5 (Hinkley and Jensen 1996), due to steric restrictions and radical chain termination. Thus a substantial amount of the curing actually amounts to chain extension. This explains the high elongations and fracture toughness of the cured neat resins and the damage tolerance (compression strength after impact) of composites. It was thought that the phenylethynyl group reacted without volatile evolution, but recent TGA-mass spectroscopy studies have indicated that under ambient pressure small amounts of volatiles are released during cure (Ghose et al. 2009). The volatiles appear to emanate from degradation of the phenylethynyl groups; benzene and substituted benzenes and vinyl compounds evolve near the cure temperature (300 °C). The amount of weight lost is small (1%), but it can lead to significant void formation in composite laminates. Volatilization of the decomposition products is suppressed by pressure so that void-free composites are routinely fabricated at pressures of 0.7 to 1.4 MPa.

Thermooxidative aging

In addition to changes in backbone chemistry (Hale 1967), reactive oligomers can undergo postcuring reactions. These reactions may occur even at temperatures below Tg (Bullions et al. 2003a).

Many features of the degradation of PETI resins are very similar to those of the corresponding linear polymers (Hinkley and Proctor 2000), but the crosslink structure may be more susceptible to oxidation than the backbone is: weight loss of cured PETI oligomers at high temperatures may be slightly greater than in the corresponding linear polymers (Takekoshi and Terry 1994, Hinkley and Jensen 1995, Keifer et al. 1995). In the second of these studies, the difference did not look significant when highly-accelerated aging was extrapolated to probable use temperatures. Takekoshi and Terry assert that resins from phenylethynyl imides perform “substantially better” than, e.g., nadic-terminated ones. Connell et al. (2003) showed that laminates from cured PETI oligomers with a formulated molecular weight of ~750 g/mol (not including the endcap) retained ~75% of room-temperature short-beam shear strength and open-hole compression strength after 1000 hours at 288°C in air. The mechanism of the strength losses was not examined. Accelerated aging at up to 343 °C for 100 hours led to weight losses of less than 2%; cracking was confined to surface plies. Exposure to 371°C, which is close to Tg, produced much larger mass losses (Bain et al. 2006).

Moisture and solvent effects

Composites made from these polyimides pick up measureable amounts of moisture. Amarillas (2009) reported a wet Tg 90°C below that of the dry material for AFR-PE-4 composite. A PETI polyetherimide exposed to 85% relative humidity/90degrees C gained about 1.60 % water based on the matrix (Bullions et al. 2003b). This led to substantial loss of transverse strength. Han and Nairn (2003) showed that PETI-5 composite was considerably more resistant to water-induced microcracking than K3B thermoplastic composite.
Crosslinking should also improve the solvent resistance relative to a thermoplastic. Adhesive bonds employing PETI-5 were virtually unaffected by a hydraulic fluid soak (Cano and Jensen 1997). MEK produced crazing in some cured neat resin films, but the most noticeable effect of various solvents was plasticization evidenced by slight decreases in modulus and consistent increases in elongation at break (Hergenrother and Smith 1994). Interestingly, a one-week water boil seemed to decrease the neat resin failure strain measured at 177 °C.

**Radiation**

Generally, phenylethynyl imides have an aromatic backbone to maximize thermal stability; this also gives them radiation resistance. After thermal curing, ethynyl and phenylethynyl resins contain a significant population of free radicals, and these radicals are stable, most likely due to resonance stabilization (Hill and Connell unpublished ESR results 1994). The exposure to various types of radiation may however cause these radicals to further react inducing crosslinking and/or chain extension. In one experiment, both molded ethynyl-containing neat resin and carbon fiber reinforced composite specimens were exposed to electron radiation at ambient temperature. Modulus and mechanical properties measured at elevated temperature increased, and toughness as determined by elongation decreased (Connell et al. 1989). These mechanical property changes are similar to those observed after isothermal aging in air.

**Time and stress**

Strengths of AFR-PE-4 composites drop about 30-60% between room temperature and 343°C (Whitley and Collins 2002). Composites also undergo microcracking when they are cycled between 177°C and cryogenic temperatures (Bechel and Arnold 2006). Isothermal treatment of IM7/PETI-5 at -184°C for 555 hours produced unexplained strength increases in some cases, despite the appearance of damage that was visible on polished edges in the form of matrix pitting (Whitley and Gates 2002).

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Fig. 1 End group from phenylethynyl phthalic anhydride.

Fig. 2 Putative polyene crosslink formed in early stage of phenylethynyl cure.