Heat-Resistant Organic Matrices Quo Vadis? (Review)

H. Ben Romdhane1, B. Sillón1 and M.F. Grenier-Loustalot2,*


Received: 31 March 2003 Accepted: 8 July 2003

SUMMARY

The introduction is a brief review of the characteristics desired for heat-resistant composite matrices, and the two possible approaches based on linear polymers and telechelic oligomers that can be cross-linked during use. Special attention is paid to cross-linkable oligomers, whose use currently poses few problems. The different structures in question, i.e. bisamideimides, bismaleimides (modified by cyanates or oxazines), bisamidimides, acetylene and propargylic compounds, are discussed in terms of chemistry (stability of oligomers, mode of polymerization, aging) and mechanical properties (ductility). Several solutions little used at the present time (semi-interpenetrated networks, molecular composites, polymerizable molecular assemblies, hyper branched oligomers and liquid crystal mesomers, etc.) are discussed in terms of the future. These may be technical solutions for use up to 300°C, but industrial development is far from being resolved because of, among other things, the small market for these products.

1. INTRODUCTION

Three principal considerations apply to the development of a heat-stable matrix for fibrous composites. First, a heat-resistant organic composite matrix, as with all other organic binders, has to meet certain requirements in relation to mechanical and physical properties, i.e. tensile and compression strength, modulus, resistance to interlaminar shear, resistance to shock and crack propagation, thermal expansion coefficient suited to reinforcement, etc.

Second, thermal properties can also be added to the list, i.e. high glass transition or crystalline melting-point, resistance to hot chemicals, and thermal degradation (in particular resistance to oxidation when hot). Table 1 summarises several of the properties required for a polymer and of the corresponding composite at room temperature.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Neat resin (unidirectional)</th>
<th>Composite (unidirectional)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Thermal expansion coefficient (°C)</td>
<td>60.10*</td>
<td>1.10*</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>70</td>
<td>2000</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>3.8</td>
<td>160</td>
</tr>
<tr>
<td>Interlaminar shear (MPa)</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>KIC (MPa √m)</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>GIC (J/m²)</td>
<td>-</td>
<td>250</td>
</tr>
</tbody>
</table>

*Author to whom correspondence should be addressed: mf.grenier-loustalot@scs.cnrs.fr.
formation polycondensation reactions (zide, quinoline, benzimidazoles, etc.) as

Finally, the processing question remains. The organic binder must have good storage qualities, preferably at room temperature. Use of a solvent is preferable, with good wetting of the reinforcement, and a large difference between reinforcement impregnation temperature and polymerization temperature is needed. Heat treatments to terminate polymerization and to release stored stresses should be minimized.

2. AROMATIC AND LINEAR HETEROCYCLIC POLYMERS

The structures of aromatic and heterocyclic polymers are rigid. Therefore they have a high glass transition that can be modulated depending on structure. In addition, they exhibit excellent stability towards pyrolysis and oxidizing degradation.

Can they be used as a composite matrix? Table 2 shows several properties of linear polymers. In particular, resistance to crack propagation suggests good behaviour of the composites but they have the disadvantage of requiring high temperatures for their processing.

3. THERMOSETTING OLIGOMERS

Most of these findings had already been known at the end of the 1960s, explaining much of the work since done on thermosetting oligomers. The principle is simple: an aromatic or heterocyclic oligomer is prepared by unbalanced polycondensation. The number-average degree of polycondensation is obtained from the Carothers equation:

<table>
<thead>
<tr>
<th>N°</th>
<th>Commercial name</th>
<th>σ at 5°C (MPa)</th>
<th>Modulus at 20°C (MPa)</th>
<th>G_{b} (J/m²)</th>
<th>IZOD Test (ft-lb)</th>
<th>Tg (°C)</th>
<th>Tst (°C)</th>
<th>Processing temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VITREX® PEK®</td>
<td>100</td>
<td>3.6</td>
<td>-</td>
<td>85.3</td>
<td>143</td>
<td>343</td>
<td>380-400</td>
</tr>
<tr>
<td>2</td>
<td>VICTREX® ITX</td>
<td>-</td>
<td>3.40</td>
<td>-</td>
<td>175</td>
<td>-</td>
<td>353</td>
<td>390-410</td>
</tr>
<tr>
<td>3</td>
<td>PEK®</td>
<td>104</td>
<td>8.00</td>
<td>-</td>
<td>175</td>
<td>375</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PEKK</td>
<td>102</td>
<td>4.48</td>
<td>1000</td>
<td>160-180</td>
<td>330</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>RTON® PPS</td>
<td>90.3</td>
<td>3.79</td>
<td>880</td>
<td>42.7</td>
<td>90</td>
<td>285</td>
<td>315-340</td>
</tr>
<tr>
<td>6</td>
<td>RTON® PAS-2</td>
<td>100</td>
<td>2.76</td>
<td>-</td>
<td>42.7</td>
<td>215</td>
<td>-</td>
<td>329</td>
</tr>
<tr>
<td>7</td>
<td>RTON® PPSS</td>
<td>100</td>
<td>3.17</td>
<td>880</td>
<td>42.7</td>
<td>215</td>
<td>-</td>
<td>309-340</td>
</tr>
<tr>
<td>8</td>
<td>R-ADN®</td>
<td>82.7</td>
<td>2.48</td>
<td>-</td>
<td>101</td>
<td>260</td>
<td>-</td>
<td>350-300</td>
</tr>
<tr>
<td>9</td>
<td>UDEL P 1700®</td>
<td>70</td>
<td>2.48</td>
<td>2500</td>
<td>69.3</td>
<td>190</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>VICTREX® HTA</td>
<td>86.2</td>
<td>2.25</td>
<td>-</td>
<td>123</td>
<td>260</td>
<td>-</td>
<td>340-300</td>
</tr>
<tr>
<td>11</td>
<td>TOLO®N</td>
<td>166</td>
<td>3.65</td>
<td>3400</td>
<td>-</td>
<td>275</td>
<td>-</td>
<td>350-400</td>
</tr>
<tr>
<td>12</td>
<td>J-2®</td>
<td>103</td>
<td>3.1*</td>
<td>2000</td>
<td>80</td>
<td>109</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>13</td>
<td>MATEKME 5218®</td>
<td>86.4</td>
<td>2.90</td>
<td>-</td>
<td>320-330</td>
<td>-</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>AVIMEDE KHI®</td>
<td>102</td>
<td>3.76</td>
<td>1230</td>
<td>-</td>
<td>251</td>
<td>-</td>
<td>360</td>
</tr>
<tr>
<td>15</td>
<td>AVIMEDE N®</td>
<td>119</td>
<td>4.17</td>
<td>2456</td>
<td>42.7</td>
<td>349-370</td>
<td>-</td>
<td>350-400</td>
</tr>
<tr>
<td>16</td>
<td>ULTEM 1000®</td>
<td>105</td>
<td>2.96</td>
<td>3310</td>
<td>53.3</td>
<td>217</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>17</td>
<td>CYPAC 7005®</td>
<td>93.1</td>
<td>1.96</td>
<td>-</td>
<td>53.3</td>
<td>236</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>18</td>
<td>PSURI®</td>
<td>62.7</td>
<td>4.66</td>
<td>1400</td>
<td>-</td>
<td>273</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>19</td>
<td>LARC CPP</td>
<td>134</td>
<td>4.24</td>
<td>6650</td>
<td>-</td>
<td>217-229</td>
<td>315-354</td>
<td>365-400</td>
</tr>
<tr>
<td>20</td>
<td>LARC TTP®</td>
<td>105</td>
<td>4.54</td>
<td>2780</td>
<td>21.2</td>
<td>255</td>
<td>275-305</td>
<td>350-400</td>
</tr>
<tr>
<td>21</td>
<td>NEW LARC TTP®</td>
<td>92.4</td>
<td>2.66</td>
<td>-</td>
<td>85.3</td>
<td>250</td>
<td>388</td>
<td>410</td>
</tr>
</tbody>
</table>

704 Polymers & Polymer Composites, Vol. 11, No. 4, 2003
where $r$ is the molar ratio of the less abundant reactant to the more abundant reactant. The equation is valid in this form only for total conversion.

Two moles of a mono-functional reactant then react with chain ends provided by the more abundant reactant. This reactant, introduced at each end of a chain, will result in cross-linking when heated, without the release of volatile products.

The principal oligomers studied are shown in Figure 1.

At the present time, only nadimides are used industrially for structural applications at temperatures higher than 300°C. Between 200° and 250°, bismaleimides have been the most extensively studied, followed by cyanates and mixtures of maleimides and cyanates, propargyl derivatives and more recently oligomers terminated by phenylacetylene groups.

### 3.1. Bismaleimides (BMI) (Figure 1a)

This family of compounds, developed at the end of the 1960s, has been extensively described and reviewed.[8]

The simplest bismaleimides are obtained by a two-step reaction between maleic anhydride and a diamine (Figure 2). These products melt between 100 and 300°C, depending on the type of amine. They polymerize immediately after melting with a high polymerization rate.
enthalpy (~ 80 kJ/mole) and form highly cross-linked and brittle networks ($G_\tau = 55$ to $30$ J/m$^2$). Several procedures have been attempted to improve the processability window (lowering the melting temperature) and the resulting ductility of the network.

1. The synthesis of anylylether, ester, polynylone ether, polystyrylpyridine and polylethylene sulfide oligomers increases the distance between cross-linking nodes, decreases transitions and thus increases the processability window. The glass transition of the network, on the other hand, is limited to that of the oligomer and if network tenacity increases, the flexural modulus decreases.

2. The addition of a nucleophile to the bisamides, e.g. the amine, causes chain elongation by the Michael reaction before cross-linking (Figure 3). Kerimid 9110 developed by Rhone-Poulenc is a typical example of the type of oligomer prepared by a Michael addition. It has been shown that when the BMI/amine ratio decreases, the toughness increases (increase in the critical strain energy release rate, $G_\tau$) and the glass transition decreases.

3. The processing window can be broadened by the use of BMI mixtures. Compounds 35B from Shell Chemical, developed by Stenzaerberg, is obtained by mixing the following BMM: MDA (methylene diamine) 2.4-toluicodis, and 2.2.4-trimethylhexane 1.6-fluorine (melting at 70°C). The small distance between nodes, however, explains the low $G_\tau$.

4. The copolymerization of bismaleimides or BMI mixtures with diallylthiourethane type reactants improves the processability as well as the mechanical properties, since co-polymerization involves -ene and -diene synthetates that elongate the chain by reducing the extent of cross-linking (Figure 4).

Matrimide 5229B is obtained in the same way but is less sensitive to moisture and its toughness is greatly improved in comparison to that of a simple BMI.

5. The approach of mixing BMMs with elastomers is a hangover from the epoxy modifications. This technique is incompatible with high temperature applications, however, because of the poor thermal resistance of elastomers.

Two reactions limiting the heat stability should be mentioned: nucleophilic additions on the double bond are reversible, and oxidative polymerization itself is reversible, leading to the formation of cyclopentane trimers10. Even though this reaction, observed in model compounds, is more difficult to imagine in a dense network, the instability of a polynylone when hot and under stress should not be neglected.

3.2. Bisacyanates*11 (Figure 1b)

The industrial preparation of cyanates involves the condensation of cyanogen chloride with a bis-phenol in the presence of a base. Mobay Corporation has prepared Tringine A5 (TA KLJ4-4000) by reacting gaseous cyanogen chloride with bisphenol A.

Most pure cyanates are crystalline and commercial products are pre-polymerised to 30% conversion to avoid crystallization. Cyanates are sensitive to the reaction of nucleophiles that cause trimorization (Figure 5).

The control of the lifetime before pre-polymerization, and the polymerization kinetics when used, requires
Figure 3

\[
\begin{align*}
\text{Michaëll addition} & \\
\text{Thermal polymerization} & \\
\text{cross-linked network} & 
\end{align*}
\]

Figure 4
pure starting materials, free of water and phenol. Polymerization is catalyzed by transition metal salts or complexes, with phenol acting as a co-catalyst.

The networks formed after polymerization exhibit Tg values between 260 and 290°C, and slight water uptake (1 to 3%). The materials are slightly more ductile than BMIs (G’max between 140 and 180 MPa).

As far as network stability is concerned resistance to water is good at ordinary temperature, but some metallic compounds such as polymerization catalysts catalyze decomposition. Heat stability is affected by the presence of phenol and water, which lowers the decomposition threshold to 300°C. In addition, unreacted cyanate groups release gas that can deform the network.

Various oligomers have been used as starting materials and resins functional with cyanate groups.

- Condensation products of dicyclopentadiene with phenol, marketed by Dow
- Novolacs resins
- Polymers with phenol terminations, etc.

These products were originally intended for the preparation of composites for printed circuit boards.

The high reactivity of cyanates (comparable to that of isocyanates) was used for reactions with oligomers or reactants with varied functions (epoxies, melamines, etc.). Certain formulations, whose reactions during processing are poorly characterized, are nevertheless proposed commercially.

Increasing the distance between cyanate groups by inserting flexible groups (e.g. phenyl ether) decreases the glass-transition temperature (increasing the number of phenyl ether groups from two to three lowers the Tg from 190 to 110°C) but increases the impact resistance.

3.3 Bisimidazides (BNI)** (Figure 1c)

At the end of the 1960s, an examination of the properties of BMIs (brittle cross-linked materials, rather high water uptake, stability inconsistent with use above 300°C) showed the necessity of having a resin with a higher thermal performance and with improved mechanical properties. Bisimidazides fulfill these criteria.

The first genuine bisimidazole was P13N®, marketed by Ciba Geigy. It was prepared from MDA, benzophenone-tetracarboxylic dihydridate (STDA) and nadic anhydride (NA) (Figure 6a), with a molar mass of 1390 Da. Nevertheless, P13N® has two major disadvantages: the stability of the intermediate acid amide in solution is low and after ring formation of the imide, the resin is insoluble and cannot be melted.

Its successor, P16P® (molar mass ~1,000 Da), was prepared with the same reactants using pyromellitic anhydride (PMDA) (Figure 6b). It exhibits higher thermo-oxidative stability but lower mechanical properties at high temperature.

NASA also used this process to prepare LARC 13® (>1,300 Da), using 3,3’-diaminodiphenylmethane (Figure 6c). The product was used as the acid amide to prepare composites, especially adhesives. After the cyclised oligomer was obtained, melting occurred at 170°C as a result of the 3,3’-cetnation of the diamine.

The formation of acid amides requires the use of solvents that are difficult to eliminate later (o-methyl pyridine (NMP), dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc)). To get around these problems, NASA developed the PMR concept (Polymerization of Monomeric Reactants) that is still used today. This technique involves dissolving a diisyl ester of a tetracarboxylic aromatic acid, an aromatic diamine and an alkyl ester of nadic acid in a low boiling point alcoholsolvent (Figure 7).

The ecochlor solution of reactants is then used to impregnate the reinforcement. The solvent is eliminated at low temperature, followed by the first acid second steps (condensations and ring formations) to imide) between 120 and 230°C. This resultant formation of a low molecular weight imide.
prépolymer, with nadimide group terminations. The network then forms rapidly beyond 250°C.

The synthetic reaction path (Figure 7a) suggests a priori that the cyclization and polymerization steps are without problems, but the reality is more complex.

- The reactant mixture changes at ordinary temperature (there is formation of tri- or tetraesters, with lower reactivity than the diesters but, on the other hand, the reactivity of the nadic ester is not the same as that of the tetra carboxylic acid diester).
Figure 7

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{C}=\text{O} \quad R_{-}\text{N}=\text{N}^\text{+} \\
\text{OH} & \quad \text{H}_2\text{C}=\text{O} \quad R_{-}\text{N}=\text{N}^\text{+} \\
\Delta & \quad \text{H}_2\text{N}^\text{+} \text{Ar}^- \text{NH}_2 \\
\text{OH} & \quad \text{H}_2\text{C}=\text{O} \quad R_{-}\text{N}=\text{N}^\text{+} \\
\text{Network} &
\end{align*}
\]

<table>
<thead>
<tr>
<th>Fig</th>
<th>Ar</th>
<th>Ar'</th>
<th>Mn (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>PMR 13°</td>
<td></td>
<td>1500</td>
</tr>
<tr>
<td>b</td>
<td>PMR 29°</td>
<td>meta or para</td>
<td>1300 to 5000</td>
</tr>
<tr>
<td>c</td>
<td>PMR 11°</td>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>d</td>
<td>LARC 16°</td>
<td></td>
<td>1600</td>
</tr>
</tbody>
</table>

- The diamine is toxic.
- The polymerization cycle is complex with the risk of cyclopentadiene release. It has been shown that below 175°C, the acid amide and imide form at the same rate.

Between 175 and 190°C the acid ester reforms the anhydride, and the latter is responsible for the reaction. This implies that the composition of the mixture before cross-linking can change as a function of the thermal treatment, which evidently affects the properties of the material.

It has been shown that thermal degradation starts with the cycloaliphatic anhydrides created by the cross-linking of amidimide groups. In addition, the methylene of MDA is oxidized to a ketone.

Increasing the distance between cross-linking nodes is thus important for improving stability in an oxidizing atmosphere, but in order to compensate for the lower glass transition resulting from decreased cross-linking density, the group between imidazoles must be more rigid.
The use of the methyl diester of hexafluorocyclopentylidine diphtalic anhydride (HFDE) instead of ITDA increases the heat stability and the resistance to oxidation. The best compromise between ease of processing and stability at high temperature is obtained with mixtures of HFDE and meta- and para-phenylenediamine. This approach results in a new series, called PMR II (Figure 7b) (Tg > 340 °C) that exhibit only moderate weight losses after exposure to 371°C for 300 h (5.5% of PMR II with a mass of 5000 Da).

NASA also developed AFR 700 A and B, oligomers with molecular masses close to 4000 Da. They are also obtained using the same reactants, but with a special feature. They have only one extremity functionalised by a nadimide, the other being either an anhydride (A) or an amine (B) (Figure 8). The glass transition of the network after cross-linking is 380°C [17].

In terms of mechanical properties, PMR 15 forms brittle networks (GII = 90 J/m²).

In 1985, Ciba Geigy introduced allyl nadiimides (Figure 1d) whose special advantage is the ability to undergo polymerization without releasing volatile products. These substances polymerise at 250°C according to complex mechanisms [18]. They can be cross-linked with bis maassides.

The synthesis of the starting materials is based on the alkylation of the sodium salt of cyclopentadiene. This makes these products more costly than nadimides, with uncertain advantages.

2.4 Bisacetylenes and Bisphenylacetylenes
(Figure 1e, f)

End-capped oligomers with acetylene functions polymerise without releasing volatile products. The resulting networks take up water to a relatively small extent and have good thermal resistance [19, 20].

As is the case with all oligomers, the mechanical properties are mainly controlled by the structure of the groups located between the acetylene functions.

Even so, there are some disadvantages when using these oligomers:

- the synthesis of the reactant bearing the acetylene function is a multi-step synthesis and makes the products costly. The most classical process uses a palladium-based catalyst that catalyses an oxidizing degradation even at very low concentrations in the polymerised network.
- the processing window is very narrow, because polymerization starts at low temperatures (120°C), i.e. at the same time as the oligomer is melting.
- the polymerization enthalpy is relatively high (130 kJ per function).

In spite of this, National Starch has marketed Thermid 600®, an oligomide that could be used as a composite or adhesive matrix up to 315°C (Figure 9).

Figure 8

![AFR 700 A](image1)

AFR 700 A

![AFR 700 B](image2)

AFR 700 B

**Polymers & Polymer Composites, Vol. 11, No. 8, 2003**
The search for a broader processing window is the reason behind the study of different types of oligomer, with phenyl acetylene groups within the chain or at the extremities.

The chemistry involved in introducing the groups is the same as that used in the case of acetylene terminations (Sonogashira reaction). Copper phenylacetylide reacts with an aromatic iodine derivative, or phenylacetylene reacts with a bromine derivative, with PdCl$_2$ (C$_5$H$_4$P)$_2$ for Cu as catalysts. The second pathway is generally chosen to create the acetylenic end-capping reactant that will react with an oligomer.

NASA started a considerable development project on oligomides. These are oligomers with masses between 5000 and 10,000 Da, obtained from oxidized alpine and bis-1,3-(3-amino-phenox) benzene, condensed on pyromellitic anhydride and 3-(phenylethylidy) phthalic anhydride. PET/S is an example. The processability window is at least 100°C and the melt viscosity is controlled by the ratio of the two amines.

These oligomers, developed with Cytec Fiberite for the American space program, were used in the construction of composites and adhesive resins as a result of their properties measured at 54, 123 and 177°C.

3.5 Bis Propargyl and/or Chromenes

Propargyl derivatives are obtained by the condensation of a propargyl bromide or chloretane on a bisphenol in a basic medium and in the presence of a phase transfer agent. First studied in the United States, these compounds polymerize at 220°C with a very high polymerization enthalpy of 185 ± 9 kJ per function.

The first transformation during cross-linking involves the formation of a chromone by a rearrangement well known since the 1960s. The chromene is the primary agent responsible for polymerization.

The glass transitions of the networks formed from bisphenol A (BPA) or fluorinated bisphenols (6-FBPA)
are around 370°C, which may appear strange for a thermal post-treatment limited to 260°C for 4 h at 360°C.

3.6 Mixtures of Reactant Oligomers

The idea behind making mixtures of oligomers with different functions is to obtain liquid mixtures, broaden the processing window, and improve ductility by increasing the distance between cross-linking nodes.

- Mixtures of BMI and allylphenol, e.g. Matrimid 5292®, commercialized by Ciba Geigy, fulfill these requirements. Compromise 353™ of Boots Technochimie, mixed with the diallyl ether of bisphenol A (Compkide™) (in 75/25 proportions) yields networks with G of the order of 360 J/m² (compare 30 J/m² for Compkide 353™ alone).
- The chemistry of cyanates provides a large number of possibilities.

They yield iminocarbonates with phenols and isocyanates with amines. Cyanates react with epoxies to form intermolecular aryloxoxazoline. Their condensation with dihydrides yields polyiminocarbonates that decompose above 300°C.

The mixture currently marketed by Mitsubishi is resin BT®, B for Bismaleimides and T for Triazine, a trimerization product of cyanates. It is a mixture of the dicyanate of bisphenol A and the pre-polymerised BMI of diaminodiphenyl methane.

This resin can be used alone (230°C; Tg<330°C, after cross-linking), but is also used for more complex formulations.

Resin 5245C™ of Cytec Fiberte that can be used for the fighter plane Rafale® is in fact a mixture of resin BT®, 8FBPA epoxy, neo-pentylglycol polyester, silica and a catalyst.

3.7 Comparison of the Thermal Stabilities of Different Systems

The comparisons are difficult to obtain consistently from the literature (because the work was done in different laboratories, with different procedures for analyses, etc.), but work by NASA® enabled a comparison between several hexafluorophthalic anhydride-based oligomer systems (Figure 12). Differences can be seen between oligomers prepared with para-phenylenediamine (PMR-II-90®, V-CAP-75®, ACI-II-75®, PEPE-II-75®) (Figure 12a) and those prepared with tetrasubstitutedbenzidine (PMR-MS®, V-CAP-MS®, ACI-MS®, PEPE-MS®) (Figure 12b), that termite with different cross-linkable functions: nadic, styrene, acrylene, phenyl acrylene.

Oligomers containing para-phenylenediamine end-capped with the two types of acetylenes are the most stable during isothermal aging at 310°C in air (3% loss after 600 h) (Figure 13).

4. IMPROVEMENT IN THE PROPERTIES OF THERMALLY STABLE MATRICES

One of the most difficult problems to solve in the context of formulations is the improvement of the ductility of high Tg cross-linked materials. A high degree of cross-linking results in high glass transitions, but the materials are more brittle.

The mixture of two oligomers modifies the cross-linking mechanism by co-reaction, and impact resistance is improved by reducing cross-linking density. The most characteristic examples are those of bismaleimides, discussed in §3.1 and 3.4.
Figure 12
Mixtures of thermally stable linear polymers and cross-linkable oligomers have been investigated in order to optimise their properties by producing semi-interpenetrated networks\(^5\).

The properties of mixtures are governed by miscibility. In the case of totally miscible systems, which are an exception rather than the rule, the property follows a law of mixtures.

In the case of non-miscible systems, three domains have to be considered:

a) the continuous phase is composed of the linear polymer
b) the discontinuous phase is that of the cross-linked network
c) the phases are co-continuous

Properties will depend on the systems in question.

Three types of materials are currently used for aeronautic applications: tri- and tetra-functional epoxies, bismaleimides and nadimides.

The service use temperatures of these materials as a function of service lifetime are indicated in Table 3.

<table>
<thead>
<tr>
<th>Table 3 Maximal service temperature (°C) of organic matrices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration Resins</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Epoxies</td>
</tr>
<tr>
<td>Maleimides</td>
</tr>
<tr>
<td>Nadimides</td>
</tr>
</tbody>
</table>

The mechanical limitations of thermally stable composites are related above all to their impact damage sensitivity, in particular their sensitivity to crack propagation when subjected to the dual constraints of thermal and mechanical fatigue. This is to be related to the low toughness of thermally stable networks.

4.1 Improvement of Bismaleimides Resins

Compositions of bismaleimides (Compamide 796\(^6\)) with 4,4'-bis(ortho-propenyl-phenyly)benzophenone (TM25\(^8\)) have been prepared in solution with a linear polysulfone (Udel 7008 of Union Carbide), a polyetherimide (Ultem 1000\(^9\), General Electric) and a polyhydantoine (PH100\(^6\) of Bayer)\(^7\) (Figure 14). When linear polymers are added at concentrations of 25
30%, threefold or fourfold increases in G' and over the value of the unmodified product have been observed.

The BMI/Ultem mixture was studied in a large concentration range. A phase inversion was observed between 15 and 40% of linear polymer, and the mechanical properties are the highest in this domain.

Mixing by dissolution has the disadvantage of increasing viscosities during the manufacture of composites. With Matrimid 5218 (a BMI system containing 20% spherical particles of a linear polyimide) Ciba Geigy showed that the utilization conditions were unchanged and that all mechanical and thermal properties were improved.

4.2 Improvement of High Temperature Epoxy Resins
The reinforcement of epoxy resins with powders of thermoplastic resin, such as polyamide or polyimide, has been investigated in order to overcome the polymerization-viscosity dependency and to produce materials with controlled diphasic morphology.

In this case, the initial viscosity of the resin-powder combination remains low compared to miscible systems, thereby facilitating utilization. The composition in the interface zone can also be modulated by mixing or by heat treatment before the gel point.

In order to validate this approach, the resin TGMDA/DDS (Figure 15a) was modified by the addition of semi-crystalline polyamide powders PA6 (particle diameter 20 µm), PA12 (diameter 13.7 µm) and a cardo structure polyimide (diameter 28 µm) (Figure 15b). In the latter case, a powder with controlled particles was prepared by successive grinding and sieving.

After dispersion by mechanical agitation that had little effect on the viscosity of the medium (Table 4), mixtures were polymerized with a cycle to generate diphasic systems with a very limited interfacial miscibility. For example, the Tg of the cross-linked polymer increases by 4°C by combination with the polyimide, indicating a dissolved fraction of about 4% by weight.

A clear-cut decrease in the level of polyamide crystallinity was observed after cross-linking the epoxy.
Heat-Resistant Organic Matrices Quo Vadis?

Figures 15a and 15b

Table 4 Blends of epoxy TGMDA/DDS and linear theroplasics

<table>
<thead>
<tr>
<th>Linear polymer</th>
<th>Size of particulates (µm)</th>
<th>% Polymer (w/w)</th>
<th>% TGMDA (w/w)</th>
<th>% DDS (w/w)</th>
<th>% Diuron (w/w)</th>
<th>Viscosity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>0</td>
<td>75.8</td>
<td>19.2</td>
<td>4.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Polyimide (Fig. 1b) solution</td>
<td>-</td>
<td>7.07</td>
<td>64.32</td>
<td>17.60</td>
<td>4.4</td>
<td>0.18</td>
</tr>
<tr>
<td>Polyimide (Fig. 1b) powder</td>
<td>28</td>
<td>7.77</td>
<td>69.91</td>
<td>17.11</td>
<td>4.43</td>
<td>0.18</td>
</tr>
<tr>
<td>PA6 polyamide powder</td>
<td>20</td>
<td>7.77</td>
<td>69.91</td>
<td>15.93</td>
<td>4.04</td>
<td>0.18</td>
</tr>
<tr>
<td>PA12 polyamide powder</td>
<td>13.7</td>
<td>7.77</td>
<td>69.91</td>
<td>15.93</td>
<td>4.04</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 5 Mechanical properties of blends based on epoxy/polyimide linear blends

<table>
<thead>
<tr>
<th>Linear polymer</th>
<th>Size of particulates (µm)</th>
<th>% Polymer (W/W)</th>
<th>K_c (MPa.m^{1/2})</th>
<th>Modulus (GPa)</th>
<th>G_c (J/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>0</td>
<td>0.65</td>
<td>3.7</td>
<td>100</td>
</tr>
<tr>
<td>Polyimide (Fig. 1b) solution</td>
<td>-</td>
<td>7.07</td>
<td>0.69</td>
<td>4.3</td>
<td>97</td>
</tr>
<tr>
<td>Polyimide (Fig. 1b) powder</td>
<td>28</td>
<td>7.77</td>
<td>1</td>
<td>3.85</td>
<td>228</td>
</tr>
<tr>
<td>PA6 polyamide powder</td>
<td>20</td>
<td>7.77</td>
<td>0.85</td>
<td>4</td>
<td>158</td>
</tr>
<tr>
<td>PA12 polyamide powder</td>
<td>13.7</td>
<td>7.77</td>
<td>0.7</td>
<td>3.54</td>
<td>121</td>
</tr>
</tbody>
</table>

At least partial melting of the polymer during thermal polymerization was in fact obtained. The existence of reactions between the epoxy and secondary amine functionalities of the polyamide was not demonstrated, but it remains possible and could explain an incomplete recrystallization when the mixture is chilled.

Fracture energies increased, the most favourable case being the polyimide, since the introduction of 16% (by weight) increased the value of G_c 4-fold (G_c = 388 J/m^2) (Table 5).
4.3 Improvement of Bisnadimides Networks

The general formula of bisnadimide oligomers is shown in Figure 7. Semiflex developed a manufacturing process based on the impregnation of carbon textiles by the mechanico solution of reactants.

Improved toughness by mixing with linear polymer precursors before use has been proposed by Peter.

After cross-linking, a biphasic mixture is obtained with a G \text{el} of 368 J/m² when it contains 20% linear polyimide. This is about four times the value of the nadimide network alone.

By using a totally cyclised but meltble and soluble oligomer, obtained by replacing the ketone group of PMR 15 with a secondary alcohol (benzydrol bisnadimide, Figure 16a) the problems inherent in the PMR system can be circumvented. Mixtures were prepared using this 1500 Da oligomer, with three linear polymers (A, B and C in Figure 16b) having varying degrees of miscibility and glass transitions of 340°C, 350°C and 360°C.

The best mechanical properties after cross-linking were obtained when the nadimide was blended with 20% (weight) insoluble fluorinated polymer.

The analysis of the phenomenon was continued in the case of the fluorinated polyimide. X-ray diffraction studies of the film or powders have shown that the structure has a semi-crystalline organization. This organization is encountered in mixtures of powders containing the oligomer and increasing proportions (5 to 30%) of fluorinated linear polymer.

Fuzzure propagation resistance tests have shown that for a fluorinated linear polymer concentration of 22%, the value of G\text{fr} reaches 1000 J/m², i.e. four times the value obtained with the unfilled resin.

Table 1:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₂OH</td>
</tr>
<tr>
<td>B</td>
<td>O</td>
</tr>
<tr>
<td>C</td>
<td>F₄C₆SF₆</td>
</tr>
</tbody>
</table>

Figures 16a and 16b
times the value of the cross-linked oligomer alone (200 J/m²).

This increase is surprising in the light of the fact that the G\textsubscript{11} of the linear polymer itself is 150 J/m². As a thin film, on the other hand, the fluorinated polymer is very tough. The improved properties of the mixture are undoubtedly related to an organization of the polyimide as a thin region in a matrix for the concentration of 22%. The observed G\textsubscript{11} would thus be the combination of the G\textsubscript{11} of the cross-linked matrix and a "tearing energy" term of the dispersed polyimide.

\[ G_{\text{mix}} = (1 - \varnothing) G_{\text{11}} + \varnothing G \]

\( \varnothing \) is the weight fraction of linear polyimide

### 5. THOUGHTS ON IMPROVED MATRICES

The desirable properties for a heat-stable matrix can be summarised by the following list:

- Stability during storage
- Absence of non-toxic and volatile solvent(s)
- Low viscosity in the molten state
- Large processing window
- Reduced polymerization enthalpy
- Processing avoiding prolonged heat treatment
- High T\textsubscript{g} values
- Good ductility
- Hydrolytic and thermal stability

We are forced to admit that no current product satisfies all these criteria.

What should be avoided and what should be sought?

For stability during storage: mixtures of reactants, e.g. PML, always create problems, as do functions sensitive to water or nucleophiles, e.g. alcohols.

For the processability window, functions are required that react with a high activation energy and an elevated reaction velocity, but with only moderate heat of reaction.

For thermomechanical properties, it is undoubtedly necessary that a high transition should be provided by chain rigidity and not by a high degree of cross-linking. One solution to explore is a blend of thermosetting resins—i.e. linear polyimide powder having a high T\textsubscript{g}, but having little effect on the viscosity of the mixture used for impregnation.

In order to increase heat stability in an oxidizing medium, all aliphatic and cycloaliphatic structures must be eliminated.

A number of research approaches have been explored and are discussed below.

### 5.1 Thermosetting Polymers with a Liquid Crystal Nature\textsuperscript{45}

Epoxies, cyanate, maleimide, acrylene and nadimide oligomers have been examined with the aim of obtaining oriented networks.

The advantages envisaged for these systems are:

- Low viscosity if the molecules are in liquid crystal form before polymerization, facilitating possible RTM (Reaction Transfer Moulding) use
- Low shrinking at the moment of cross-linking of pre-organised systems
- High degree of orientation, which could be a disadvantage because of the anisotropy of the cross-linked network.

#### 5.1.1 Epoxies

The first Japanese patent dates back to 1984\textsuperscript{46}, followed by the entry of Bayer and Dow into this field. It was seen that some epoxies are themselves liquid crystals before cross-linking, while others are isotropes and develop an organization at the moment of polymerization. The resulting structures are nematic or smectic\textsuperscript{47}.

It has been shown that mesomorphic structures form in some cases by elongation of the chain, which becomes organised before cross-linking. Hardeners with two different reactivities have been sought for this purpose\textsuperscript{48}.

In some cases, the chemistry of these thermotropic epoxies yields cross-linked nematic or smectic networks with the same hardener. A time-temperature transformation diagram allows us to determine the corresponding processing conditions. In certain conditions, a nematic network can be obtained from an isotropic phase.
Beyond a given temperature (> 150°C), an isotropic network is obtained\textsuperscript{19}.

### 5.1.2 Cyanates

The first liquid crystal cyanate was discovered in 1992\textsuperscript{20}. This family has a special interest, since certain isotropic bis-cyanates develop a liquid crystal structure during polymerization.

The formation of these anisotropic network is surprising in the light of the 120° angles between the other functions of the triazine group formed by imidization.

It has been shown that the orientation of molecules can be controlled by the frequency of an electric field and that different degrees of orientation can be obtained in this way.

### 5.1.3 Bisateleimides and Bisanodimides

Original work in this area was conducted by Hoyt and Bennewicz\textsuperscript{22,23} in 1990, using BMIs containing aromatic amide groups, and then ester groups. Esters with lower melting points enable the formation of nematic phases in the case of BMIs and BNs. The isothermal heating of an isotropic phase apparently generates a network having a liquid crystal texture, as in the case of cyanates.

These structures can form as a result of a chain extension reaction before cross-linking.

### 5.1.4 Bisacetylene Monomers

In 1984, Celanese patented the preparation of thermostetting networks of this type\textsuperscript{24}. The advantage of the acetylene function is the low polymerization temperature, under 200°C. In addition, the functions are apparently interdigitated, ensuring polymerization in the solid state with no significant movement of the monomers, and thus very low shrinkage during the polymerization\textsuperscript{25,26}.

These families of compounds are interesting and their cross-linked networks have a storage modulus of 4.5 GPa with a very low thermal expansion coefficient, 2.10\textsuperscript{-5} °C\textsuperscript{-1}. They are stable up to 400°C in air.

### 5.2 Hyper Branched Structures

In 1941 Flory\textsuperscript{27} introduced the concept of hyperbranched macromolecules that still remains an area of interest\textsuperscript{58,59}. Hyper-branched macromolecules are obtained by the polymerization of trifunctional AB\textsubscript{2} monomers (Figure 17a).

Perfectly defined structures can be obtained only when polymer condensations are done step-by-step. In other words, at each step, the trifunctional molecule AB\textsubscript{2} reacts selectively via A with only one of the two B functions of another molecule. Because the second B function has been protected. When the B function that could not react is de-protected, the reaction can be continued and a structure without a structural default, a so-called dendrimer, can be obtained\textsuperscript{60}.

Condensation without protecting functions yields structures that are said to be hyperbranched. (Figure 17b).

The degree of branching of these polymers was defined by Frechet et al\textsuperscript{61} by the following relationship:

\[
\text{The degree of branching } DB = \frac{D + T}{D + T + L}
\]

where D, T, and L are the numbers of dendritic, terminal and linear wits in the monomer, respectively. They are determined by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy involving comparison with model structures.

In 1996 Frechet et al\textsuperscript{62} compared linear (Figure 18a), dendritic (Figure 18b) and hyperbranched structures (Figure 18c) obtained with the same reactant, 3,5-dihydroxybenzoic acid.

The thermal properties (glass transitions and heat stability) are unaffected by polymer architecture, but branched structures are more soluble than linear ones.

Behaviour in solution was examined and in the case of hyperbranched aromatic polymers, a low intrinsic viscosity and low coefficient \(\alpha\) in the Mark Houwink-Sakurada equation

\[
\eta = K \cdot M^\alpha
\]

was observed\textsuperscript{63}. Where \(\eta\) is viscosity, \(M\) = Molar mass

The variation of intrinsic viscosity with molar mass for different architectures is shown in Figure 19\textsuperscript{64}.
Heat-Resistant Organic Materials: Who Knows?

Figure 17a and 17b

\[ \text{AP} = \text{A protected} \]
\[ \text{BP} = \text{B protected} \]

Figure 18a, 18b and 18c

\[ \left( \text{NO}_2 \right)_n \]
A review of the properties of hyperbranched polymers enables the following general conclusions to be drawn:

- In the molten state, there is generally Newtonian behaviour resulting from very low entanglement of chains. This is a very interesting point for an application in the area of matrix or matrix composites since at the same molar mass, a hyperbranched polymer is less viscous than the corresponding linear polymer, and will thus flow more easily.
- Viscosity in the molten state is affected by the nature of the chain ends, which will increase viscosity if they are polar.

These observations were confirmed by Mc Hugh et al., who showed that in the case of polyetherimides (PEI) with a molar mass higher than 20,000 Da, the molten polymer behaved as if made up of entangled, viscoelastic chains.

5.2.1 Hyperbranched Polyimides

Publications dealing with hyperbranched polyimides are not very numerous. One-step condensation of AB₈ monomers forza polymers whose degree of branching depends on the degree of polymerization, but this branching is consistently less than 100% because of the formation of linear segments.

The polycondensation of 3,3'-dihydroxyphenyl-4-fluorophthalimide whose phenol functions are alkylated (Fig 20) occurs by heating to 240°C in diphenylsulfone in the presence of cesium fluoride, CsF. The degree of branching in this case is only 65%.

---

Polymers & Polymer Composites, Vol. 11, No. 8, 2003
Another synthesis of a hyperbranched polynamide was recently described by a two-step reaction to first obtain a hyperbranched polynamide ester. This was then cyclised to polynimide (Figure 21). The polymer with 48% branching is soluble in N-methylpyrrolidone\(^\text{67}\).

In a less classical method using a mixture of \(A_2\) monomer (6FDA) and \(B_3\) monomer (tris-(4-aminophenyl)amine), a molar ratio of 1/1 yielded a hyperbranched oligomer terminated by amine functions (Figure 22a), while an anhydride/amine ratio of 2/1 yielded its homologue terminated by anhydride functions\(^\text{69}\) (Figure 22b).

5.2.2 Hyper Branched Polyphenylquinoxalines (PPQ)

Two types of polyphenylquinoxalines have been prepared by aromatic nucleophilic substitutions from \(A_2\)B and \(A_2\)B monomers bearing phenol and fluorine functions (Figure 23)\(^\text{70-73}\).

PPQ obtained from monomer \(A_2\)B, 2,3-bis(4-hydroxyphenyl)-6-fluoroquinoxaline, is insoluble in usual organic solvents. The copolymerization of \(A_2\)B with an \(A\)B monomer yields a hyperbranched PPQ terminated by phenolic functions, having an intrinsic viscosity of 0.27 to 1.11 dl/g (m-cresol at 30°C) and a glass transition varying from 240°C to 274°C (depending on the percentage of \(A_2\)B monomer).

Monomer \(A_3\)B, 2,3-bis(4-fluorophenyl)-6-(4-hydroxyphenyl)quinoline, yields a hyperbranched high molecular weight PPQ by “homopolymerization” in an NMP/volume mixture. The intrinsic viscosity of of hyperbranched polyphenyl quinoxaline (PPQ) terminated by fluorine is 1.12 dl/g (m-cresol at 30°C) and its Tg is 225°C.

5.3 Chain Elongation During Polymerization

A typical example is the copolymerization of benzocyclobutene and malonimide via a Diels-Alder cycloaddition, studied by NASA and Dow Chemicals\(^\text{74-75}\) (Figure 24a). Although the copolymers obtained had relatively high viscous transitions, failure arose because of the insufficient stability of cycloaliphatic functions (15% isothermal weight loss at 177°C after 5000 h)\(^\text{76}\) and the high cost of the bisbenzocyclobutene monomer.

Harris studied an oligomer system terminated by a trifluorovinyl benzene function. The products were polymerised by cycladdition at 220°C and retained 99% of their weight after 100 h at 300°C. Nevertheless, a certain degree of chain flexibility rendered the glass transitions relatively low (Figure 24b).

A more classical pathway of chain elongation based on cycloadditions of functional oligomers deserves further exploration. It involves the addition of oligomers with diphenylamine terminations onto oligomers terminated by phenylacetylene groups (Figure 25)\(^\text{77}\). The advantages of this approach are simple: the reaction must lead to a linear system with a phenanthrene group that ensures a high glass transition.

Both types of reactants are known, however, and can also thermally cross-link to yield very heat stable aromatic systems. As a result, the polymerization reaction can be considered as a chain extension between cross-linking nodes.


6. CONCLUSIONS

Currently available products are relatively inexpensive, but are difficult to process and have rather unsatisfactory properties.

Solutions exist for producing class 300°C heat stable resins, but it is uncertain whether they can ever be widely industrialised.

The main reason that the aerospace industry is a very small market that does not justify the interest of major producers. Industries currently producing resins are generally small companies, often forced to bow out of these low profit margin markets.

Industries requiring these products will undoubtedly have to pay a higher price to benefit from better products (in terms of ease of use and
thermomechanical properties) and also to ensure stable supplies.

If these conditions can be met, research could provide innovations with possibilities for development.

REFERENCES


d) M.F. Grenier-Loustalot and C. Sanglar, High
Heat-Resistant Organic Matrices Quo Vadis?

Performance Polymers, 8 (4) 533 (1996).
Heat-Resistant Organic Matrices Quo Vadis?

Performance Polymers, 8 (4) 533 (1996).
b) N. Sauvage UMR 102, Thèse, Claude Bernard University, Lyon 1, 1992.
36. T. Pascal and B. Sillion, Heat resistant semi IPNs, Advances in Interpenetrating Polymer networks, Vo IV, D. Klemptner and K.C. Frisch, eds. Technomic, 1994, 141


---

Polymers & Polymer Composites, Vol. 11, No. 8, 2003