

26 High Temperature Thermosets

A thermoset or network polymer is an organic material where the molecules are tied together through chemical bonds (crosslinks) and therefore they cannot move past one another. As a result, these materials exhibit a certain degree of dimensional stability. The chemical composition and the degree of crosslink density of the thermoset have a pronounced effect upon the properties.

1. Definition

High temperature thermosets are defined in many ways. One definition is that high temperature thermosets retain useable mechanical properties after long term (e.g. thousands of hours) exposure at temperatures of 177°C. Another definition is high temperature thermosets exhibit high initial properties at 177°C. Still others classify thermosets to be high temperature if they exhibit a polymer decomposition temperature > 450°C as measured by thermogravimetric analysis (e.g. temperature of 5 % weight loss at a heating rate of <10 °C/minute), display a very low weight loss rate as a function of aging at high temperature (e.g. 400°C), or have a $T_g > 250^\circ\text{C}$. All are correct in certain respects but for this article, the first definition will be used. Structural thermosets must have glass transition temperatures in excess of 177°C (e.g. preferably 80-100°C higher) to display respectable mechanical properties at 177°C. A functional material such as a coating need not have a T_g as high as a structural material simply because of the load placed on structural resins.

2. Synthesis

Thermosets are derived from monomers or low molecular weight oligomers containing reactive groups, from high molecular weight polymers containing reactive groups and from combinations of these. Monomers and oligomers can be self-polymerized or polymerized with a co-reactant or curing agent. An example of self polymerization is the trimerization of cyanates ($-OCN$) to form cyanurates (6 membered ring). Examples of polymerization with a co-reactant are reacting a diepoxy with a curing agent such as a diamine or reacting a bismaleimide with a non-stoichiometric amount of an aromatic diamine followed by heating. After the crosslinking reaction, thermosets are generally infusible, insoluble, brittle and stiff. In contrast, thermoplastics are high molecular weight linear or branched polymers that can be reprocessed or dissolved after fabrication (e.g. compression molding under pressure and heat). Thermoplastics are generally moldable, soluble, tough and moderately stiff depending upon the chemical composition and morphology. Thermoset precursors, particularly low molecular weight materials, offer superior processability than thermoplastics for the fabrication of molded parts and better planarization for coating complex parts. After curing, the thermosets also offer distinct advantages over amorphous thermoplastics. Among these are better stressed solvent and chemical resistance, superior dimensional stability (creep resistance), higher modulus, lower coefficient of thermal expansion and higher use temperature (heat distortion temperature). Special epoxies, cyanates and maleimides have been cured to thermosets that have shown good retention of mechanical properties (e.g. adhesive or composite strength retention) after thousands of hours of exposure at 177°C . But as a whole, thermosets derived from epoxies, cyanates and maleimides are generally considered to be moderate temperature and not high temperature materials.

In addition to the synthetic routes to thermosets, they can also be formed by other means such as electron beam curing of appropriate monomers, crosslinking polymers through exposure to other energy sources (high energy electrons, lasers, x-rays and ultraviolet irradiation), by mixing appropriate materials such as inorganic salts with polymers (e.g thermoplastics) that react intermolecularly to form crosslinks and by relatively short term high temperature exposure (e.g. seconds) on thermoplastics to induce crosslinks. These methods have been explored as routes to obtaining higher temperature performance thermosets. Problems arise with crosslinking via some energy sources due to the small depths of penetration (e.g. ultraviolet irradiation) and the total doses required. Some of these methods are traditionally used to modify the surface of polymers or for inducing crosslinking in thin films whereas crosslinking a polymer molding or composite throughout its thickness is a problem. The resulting thermosets exhibit properties similar to the synthetically derived thermosets. They are generally infusible, insoluble, brittle and stiff.

3. Reactive Groups

Many of the reactive groups that have been used in the formation of high temperature thermosets are presented in Table 1. A few less popular groups such as paracyclophane and cyanamide (-NHCN) have not been included in the Table. If desired, more than two of the same reactive groups can be placed on the same molecule. Most of these groups can be placed on the ends of molecules, as side groups on oligomers or polymers and both as side and end groups on molecules. In addition, some of these materials can be

reacted with other compounds containing the same or even different reactive groups. Upon the application of heat, these groups react to form crosslinks. In some cases, a catalyst can be used to increase the rate of reaction and lower the reaction temperature. Care must be exercised however because the presence of the catalyst or its residue in the thermoset can also catalyze thermal and thermooxidative degradation. For example, certain metals (e.g. palladium) and organometallic compounds (e.g. nickel acetate) catalyze the thermal cure of phenylethynyl groups on molecules but often catalyze the degradation of the cured polymer at high temperatures. The thermal polymerization of molecules terminated with phenylethynyl or trifluorovinyl ether groups proceeds predominantly by linear chain extension but the use of multifunctional (> two reactive groups on each molecule) compounds yields high T_g thermosets.

Several of the groups in Table 1 have been copolymerized with other groups in an attempt to form high temperature thermosets. For example, maleimides have been heated with cyanates. Compounds containing benzocyclobutene groups have been heated with compounds containing ethynyl, phenylethynyl and maleimide groups (Eqn. 1). In addition, compounds containing different functional groups such as benzocyclobutene and maleimide on the same molecule have been polymerized. Although the cure chemistry of some of these materials appears to favor the formation of a new ring with linear chain propagation, side reactions occur that yield thermosets. The reaction temperature and rate differs from one group to another such that a quantitatively controlled reaction of two different groups is difficult to achieve. As an extreme example, Table 1 lists the reaction temperature of benzocyclobutene as 220°C and of

phenylethynyl as 350°C. Although the reaction of these two groups to form a new ring can be expressed nicely on paper, in actual reality, this is highly unlikely because of the large difference in reaction temperature.

The exact chemical compositions of thermosets are not known in spite of considerable work that has been devoted to determining them. Model compounds having a single reactive group have been used in initial studies to determine the chemical nature of the thermoset but these model compounds yield products that can be very different from compounds containing two reactive groups and oligomers and polymers containing reactive groups. Problems arise in transferring results of work done with model compounds to oligomers, for example, because of differences in cure temperature, molecular mobility, reactive group density and proximity of reactive groups to one another. The general composition of some thermosets has been deduced from knowledge of organic chemistry and sophisticated analysis (e.g. solid state nuclear magnetic resonance spectroscopy, electron spectroscopic chemical analysis, infrared spectroscopy, etc.). Knowing the precise chemical composition of a thermoset will not improve its performance. It is more of academic interest than of practical significance.

The brief comments in Table 1 describe both the uncured materials containing the reactive group (e.g. high cure temperature) and the cured thermoset (e.g. brittle or tough). Although cure temperatures are cited for the various groups in Table 1, these can vary depending upon factors such as reactive group density, composition of the parent compound, oligomer or polymer, and morphology. High reactive group density generally

favors lower cure temperatures. Amorphous materials cure at lower temperature than semi-crystalline materials because crystalline regions must be melted before adequate molecular mobility occurs to allow reactive groups to collide and react. Other factors such as diffusivity also play a role. The cure temperatures in the table are guidelines. For example, although 350°C has been listed as the temperature to cure phenylethynyl groups, these groups can undergo uncatalyzed cure on amorphous molecules by heating at 288°C for several hours. To achieve proper cure, the cure temperature should be higher than the glass transition temperature (T_g) of the thermoset.

Some reactive groups (e.g., ethynyl, phenylethynyl) cure via free radical processes and therefore are influenced by the cure atmosphere. For example, molecules containing phenylethynyl groups cure faster in air and provide thermosets with higher T_g s than the same materials cured in an inert atmosphere. Mechanical properties are also influenced by the cure atmosphere. Curing in air generally provides thermosets with higher crosslink density and accordingly higher modulus and lower toughness than does curing the same material in an inert atmosphere.

4. Toughening

Since thermosets are generally brittle, various methods have been used to toughen them. These methods include reduction of the crosslink density (by increasing the length between reactive groups, or by using high molecular weight or tough curing agents), the use of non-reactive toughening agents (rubbers, thermoplastics, fibrils, that are incorporated as a second phase), the incorporation of reactive toughening agents (rubbers,

thermoplastics, leading to single or 2-phase morphology) and interlayers [interleafs, primarily for composites where thin layers of tough materials (e.g. thermoplastics) are introduced between plys]. In neat resin form, the best toughened thermosets do not have the toughness offered by most thermoplastics.

5. Use Temperatures

As mentioned previously, the T_g of the thermoset controls its maximum use temperature, especially for structural applications. In regard to use time at elevated temperatures, the thermal stability of organic polymers in general is primarily controlled by bond strength. Carbon to carbon single bonds have dissociation energy of 83 kcalories/mole whereas carbon/carbon double bonds have dissociation energy of 145 kcalories/mole. High temperature thermosets as well as high temperature thermoplastics contain a high concentration of aromatic and heterocyclic rings. Like thermoplastics, thermosets that contain thermally unstable groups such as benzylic do not perform well for thousands of hours at 177°C in air.

In a thermosets, more than one bond must be cleaved to break the chain connections whereas in a thermoplastic, the breakage of a single bond in the polymer chain reduces the molecular weight. The approximate limits of useable strength for high temperature thermosets in air are 10 minutes at 538°C, 200 hours at 371°C, 3000 hours at 316°C, 25000 hours at 260°C, 50000 hours at 232°C and 60000 hours at 177°C. Some of these times are extrapolations based upon Arrhenius plots while others were measured. Specific examples follow. A Dexter Aerospace Company (Hysol) epoxy adhesive (EA

9689) gave lap shear strength of 17.9 MPa at 177°C after 38,000 hours at 177°C. A NASA Langley phenylethynyl terminated imide oligomer adhesive (PETI-1) provided lap shear strength of 27.6 MPa at 177°C after 30,000 hours at 177°C. A Cytec Fiberite bismaleimide (5270) carbon fiber composite showed virtually no mechanical property decline after 6500 hours at 232°C. Carbon fiber composites of a nadimide terminated imide oligomer (PMR-15) gave excellent retention of mechanical properties after 20,000 hours at 232°C. An amorphous boron filled polyquinoxaline adhesive (crosslinked after a high temperature cure) gave lap shear strength of 9.1 MPa at 538°C after 10 minutes at 538°C and 17.5 MPa at 371°C after 50 hours at 371°C.

6. Availability

Thermally stable thermosets are available in a variety of forms such as adhesives, coatings, composite matrices, foams and moldings. Some of these materials are provided in partially reacted or prepolymer forms. Sources for these materials can be obtained from the Internet (Web) or from books such as Chem Sources. Specific information on a thermoset can be obtained by contacting the appropriate material supplier. Commercially available materials leading to moderate and high temperature thermosets include a variety of cyanates and bismaleimides, nadimide terminated imide oligomers such as PMR-15, a benzocyclobutene based material (Cyclotene), phthalonitriles and phenylethynyl terminated imide oligomers such as PETI-5. All of these materials are classified as specialty polymers where the market is small compared to that of epoxies. A material is often available in several forms. For example, bismaleimides are available in various

adhesive forms, glass or carbon fiber prepreg forms that provide composites with different degrees of toughness and resin transfer molding grades.

7. Applications

High temperature thermosets find use or are being considered for use in various applications in industries such as aerospace (adhesive and composite structures), automotive (connecting rods and pistons), electronic/microelectronic (printed circuit boards, thin coatings and moldings), geothermal energy (casings and nozzles), oil (deep downhole drilling parts) and household (decorative exterior coatings on cookware). In selecting a high temperature thermoset for a particular application, various factors must be considered. For the starting material, toxicity, processability (e.g. melt viscosity), cure conditions and shelflife are important. For the cured thermoset, mechanical performance, high temperature durability, coefficient of thermal expansion, dielectric properties, chemical, solvent and microcrack resistance are important. The cost of the final part is generally more important than the cost of the individual items (e.g. starting materials, processing, quality control) that make up the final part. The importance of cost will vary from one industry to another. As an example, the aerospace industry is more performance driven than the automotive industry and therefore will pay a higher price for materials to meet their requirements. Other important factors must also be considered such as reliability and safety.

8. Concluding Remarks

High temperature thermosets offer a favorable combination of properties that makes them attractive for many applications. Their most important features are the excellent processability particularly of the low molecular weight precursor forms, the chemical and solvent resistance and the dimensional stability. Although the market for high temperature thermosets is now relatively small, it will increase as new uses for high temperature thermosets are uncovered and new thermosets with better combinations of properties are developed.

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Some reactive groups (e.g. ethynyl, phenylethynyl) cure via free radical processes and therefore are influenced by the cure atmosphere. For example, molecules containing phenylethynyl groups cure faster in air and provide thermosets with higher T_g s than the same materials cured in an inert atmosphere. Mechanical properties are also influenced by the cure atmosphere. Curing in air generally provides thermosets with higher crosslink density and accordingly higher modulus and lower toughness than does curing the same material in an inert atmosphere.

6. Toughening

Since thermosets are generally brittle, various methods have been used to toughen them. These methods include reduction of the crosslink density (by increasing the length between reactive groups, or by using high molecular weight or tough curing agents), the use of non-reactive toughening agents (rubbers, thermoplastics, fibrils, that are incorporated as a second phase), the incorporation of reactive toughening agents (rubbers, thermoplastics, leading to single or 2-phase morphology) and interlayers [interleafs, primarily for composites where thin layers of tough materials (e.g. thermoplastics) are introduced between plys]. In neat resin form, the best toughened thermosets do not have the toughness offered by most thermoplastics.

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In a thermosets, more than one bond must be cleaved to break the chain connections whereas in a thermoplastic, the breakage of a single bond in the polymer chain reduces

the molecular weight. The approximate limits of useable strength for high temperature thermosets in air are 10 minutes at 538°C, 200 hours at 371°C, 3000 hours at 316°C, 25000 hours at 260°C, 50000 hours at 232°C and 60000 hours at 177°C. Some of these times are extrapolations based upon Arrhenius plots while others were measured. Specific examples follow. A Dexter Aerospace Company (Hysol) epoxy adhesive (EA 9689) gave lap shear strength of 17.9 MPa at 177°C after 38,000 hours at 177°C. A NASA Langley phenylethynyl terminated imide oligomer adhesive (PETI-1) provided lap shear strength of 27.6 MPa at 177°C after 30,000 hours at 177°C. A Cytac Fiberite bismaleimide (5270) carbon fiber composite showed virtually no mechanical property decline after 6500 hours at 232°C. Carbon fiber composites of a nadimide terminated imide oligomer (PMR-15) gave excellent retention of mechanical properties after 20,000 hours at 232°C. An amorphous boron filled polyquinoxaline adhesive (crosslinked after a high temperature cure) gave lap shear strength of 9.1 MPa at 538°C after 10 minutes at 538°C and 17.5 MPa at 371°C after 50 hours at 371°C.

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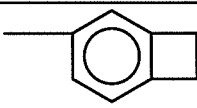
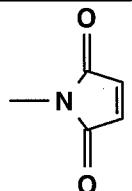

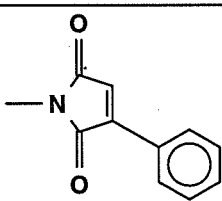
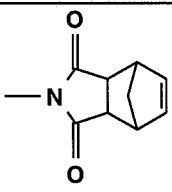
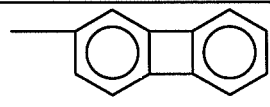
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Table 1. Representative Reactive Groups Used for High Temperature Thermosets

| Chemical Structure | Name | Approx. Cure Temp., °C | Comments |
|--|---------------------------------------|------------------------|---|
| $\text{—O—C}\equiv\text{N}$ | Cyanate | 200 | Brittle, Moderate Thermal Stability |
|  | Benzocyclobutene | 220 | Brittle, Moderate Thermal Stability |
|  | Maleimide | 230 | Brittle, Moderate Thermal Stability |
| —OCF=CF_2 | Trifluorovinylether | 250 | Small Processing Window, Tough, Unknown Thermal Stability |
| $\text{—C}\equiv\text{C—H}$ | Ethynyl | 250 | Small Processing Window, Low toughness, Good Thermal Stability |
| $\text{—C}\equiv\text{C—}$  | Phenylethynyl | 350 | High Cure Temperature, Tough, Good Thermal Stability |
|  | Phenylmaleimide | 350 | High Cure Temperature, Unknown Thermal Stability |
|  | Nadimide | 350 | High Cure Temperature, Cyclopentadiene Evolution During Cure, Brittle |
|  | Biphenylene | 350 | High Cure Temperature, Low Toughness |
| —CN | Nitrile, particularly phthalonitriles | 350 | High Cure Temperature, Low Toughness |

