

# Flexibility or Toughness ? – The Design of Thermoset Toughening Agents

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In memoriam Professor Piero Pino

Functional toughening agents, incorporated as separate microphases into rigid highly crosslinked polymeric matrices, are the key component of high-performance structural materials which exhibit high impact and fatigue resistance without sacrificing high stiffness, dimensional stability, strength, and heat distortion temperature. The chemistry and the basic structure/property relationships of various polymeric flexibilizers and toughening agents applied in the aerospace, aircraft, and automotive industries are reviewed. Special emphasis is given to the role of polymer compatibility in the design of functional liquid rubbers, reactive thermoplastic oligomers, and functional core/shell microparticles. Some of the major synthetic routes to advanced structural materials based on thermoset resin chemistry and functional supermolecular structures are outlined.

## 1. Toughness and Stiffness

Originally conceived to substitute naturally occurring materials such as rubber, silk or wood, especially during war-time raw material shortages, new generations of high-performance polymeric materials have evolved in recent decades. They provide unique combinations of high stiffness, strength, elasticity, thermal, dimensional and environmental stability at comparatively low bulk densities typical of polymeric materials. Advanced polymeric materials compete successfully with metal alloys in aerospace, aircraft, and automotive structural applications.

The design of temperature-resistant high-strength polymers is based on synthetic principles well established in small-molecule organic syntheses. High bond dissociation energies or strong intermolecular interactions as found in hydrogen bonding, crystallization or crosslinking, favor thermal resistance which is expressed by the softening or heat distortion temper-

ature. Condensed aromatic or heterocyclic ring structures increase both thermal resistance and stiffness. As depicted in Table 1, several linear and crosslinked polymers achieve very high thermal resistance, exceeding 400°C in the case of certain polyimides or 1000°C for fully condensed graphite-type materials. In addition to structural units, composite materials containing fiber reinforcements or self-rein-



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forcing, highly oriented, liquid crystalline phases, exhibit high stiffness and strength, as expressed by high moduli.

Highly rigid polymers which soften at elevated temperatures are frequently difficult to process. Two different philosophies have been adopted to overcome the stiffness/processability limitations: micro-

Table 1. High-temperature-resistant polymers.

Structure Type	Example	Softening Temperature
	$(-\text{CH}_2\text{CH}_2-)_n$	100°C
	$(-\text{C}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{O}-)_n$	260°C
$-A-A-A-$	$(\text{C}_6\text{H}_4)_n$	600°C
	$(\text{N}(\text{O})\text{C}_6\text{H}_4\text{N}(\text{O})\text{C}_6\text{H}_4\text{O}-)_n$	450°C (1000°C)
		3600°C

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structure variations in linear condensation polymers to facilitate melt processing ("engineering plastics") or alternatively, low molecular weight, low viscosity, reactive oligomers which are cured to form highly crosslinked polymers ("thermoset resins"). Melt processable engineering plastics including polyethersulfones, polyetherimides or polyetherketones, and thermoset resins such as epoxy or bismaleinimide resins, are examples of commercially available high-temperature-resistant polymers<sup>(1)</sup>.

In addition to thermal resistance and stiffness, other key features of high-performance structural materials include their capability to bear loads over prolonged periods of time under static and dynamic conditions ("creep and fatigue resistance"), and to absorb impact energy ("toughness"). They can successfully resist crack propagation occurring when the material fails under load. As outlined in Fig. 1, several test methods are used to determine fracture behaviour via impact energy absorption and crack propagation. In the tensile test, the toughness corresponds to the area under the stress-strain curve. As depicted in Fig. 2, metals are outstanding in their toughness/stiffness combination, expressed by high modulus of elasticity (slope of the stress-strain curve at low elongations) and their very high tensile strength and elongation at break. The ultimate goal of high-temperature-resistant polymer development is to match the toughness/stiffness performance of steel. Numerous other test methods have been introduced to measure impact strength, fracture toughness or energy release rates. In structural adhesive applications, the lap shear and peel strength<sup>(2-4)</sup> are especially important. The mechanisms of crack propagation in ductile and brittle polymeric materials are

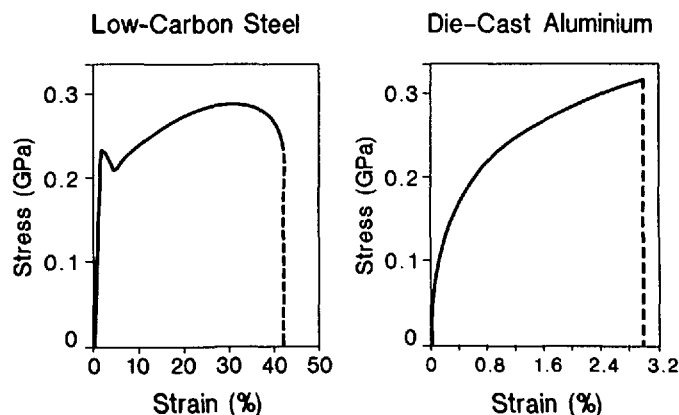


Fig. 2. Stress-strain curves of metals.

quite complex and depend on a variety of parameters such as chemical composition of the polymeric materials, test method and test specimen geometry. These aspects are covered in several review articles and books<sup>(5-8)</sup>.

Comparing various energy release rates of metals and polymeric materials, it is evident that metals outperform polymers in terms of toughness (Table 2). Also as a

rule, crosslinked polymers tend to be brittle in comparison to linear or slightly branched, high-temperature-resistant thermoplastics. As the crosslink density of the rigid polymeric matrix increases, for example, by increasing the functionality of both epoxy resin and hardener, the brittleness of the resulting polymer network rapidly increases, while the fracture toughness approaches that of window glass. In contrast,

Table 2. Toughness of various materials.

Material	Energy Release Rates $G_{Ic}$ [J/m <sup>2</sup> ]
pure metals (Cu, Ni, Ag)	1 000 000
steel	100 000
titanium alloys	53 000
aluminium alloys	30 000
polypropylene	8 000
polyethersulfone	2 500
nitrile-rubber-toughened Bisphenol A-based epoxy	2 000
polycarbonate	800
Bisphenol A-based epoxy cured with diaminodiphenyl-sulfone	250
tetrafunctional epoxy cured with novolacs	30
marble	20
window glass	7

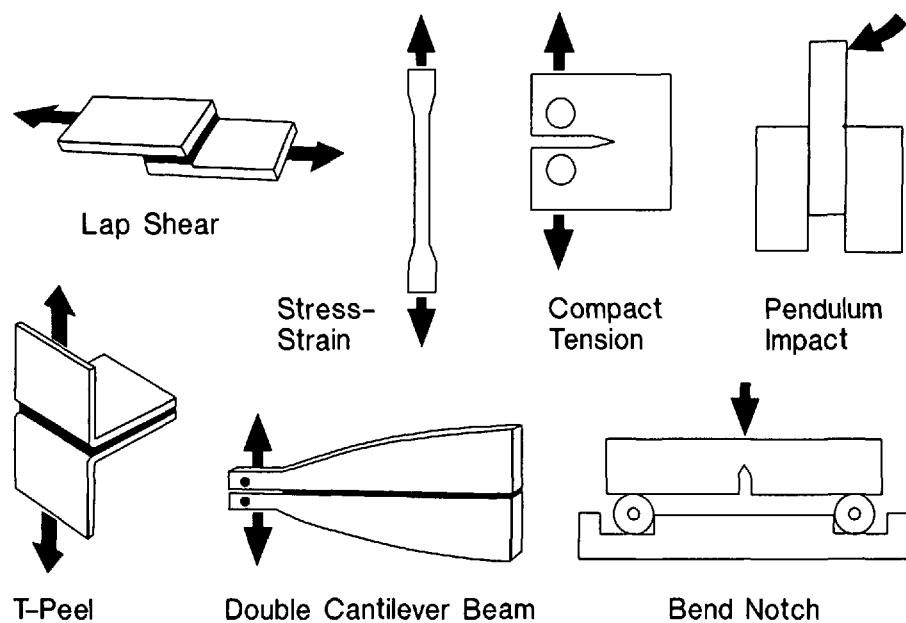


Fig. 1. Test methods to determine fracture behavior and toughness.

when crosslink density is reduced by increasing the molecular weight between crosslinks<sup>(9,10)</sup>, thus approaching non-crosslinked thermoplastic materials, toughness is increased. However, typical thermoset qualities, such as thermal and creep resistance and easy processability are sacrificed. The high-molecular-weight thermoset resins are almost identical to thermoplastics. Highly crosslinked thermoset resins, such as catalytically cured epoxy resins, shown in Fig. 3, can be toughened without sacrificing strength, stiffness, and thermal resistance (see also Section 7).

**2. The Multiphase Approach**

In principle, two fundamentally different concepts have been introduced to enhance the impact energy absorption of highly crosslinked polymeric materials without sacrificing the advantages of ther-

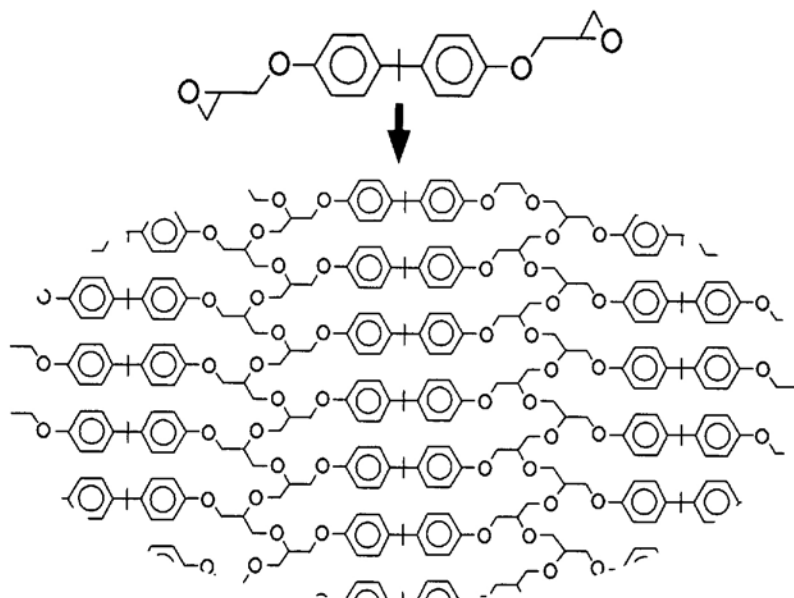


Fig. 3. Thermoset matrix based on catalytically-cured Bisphenol A-diglycidyl ethers.

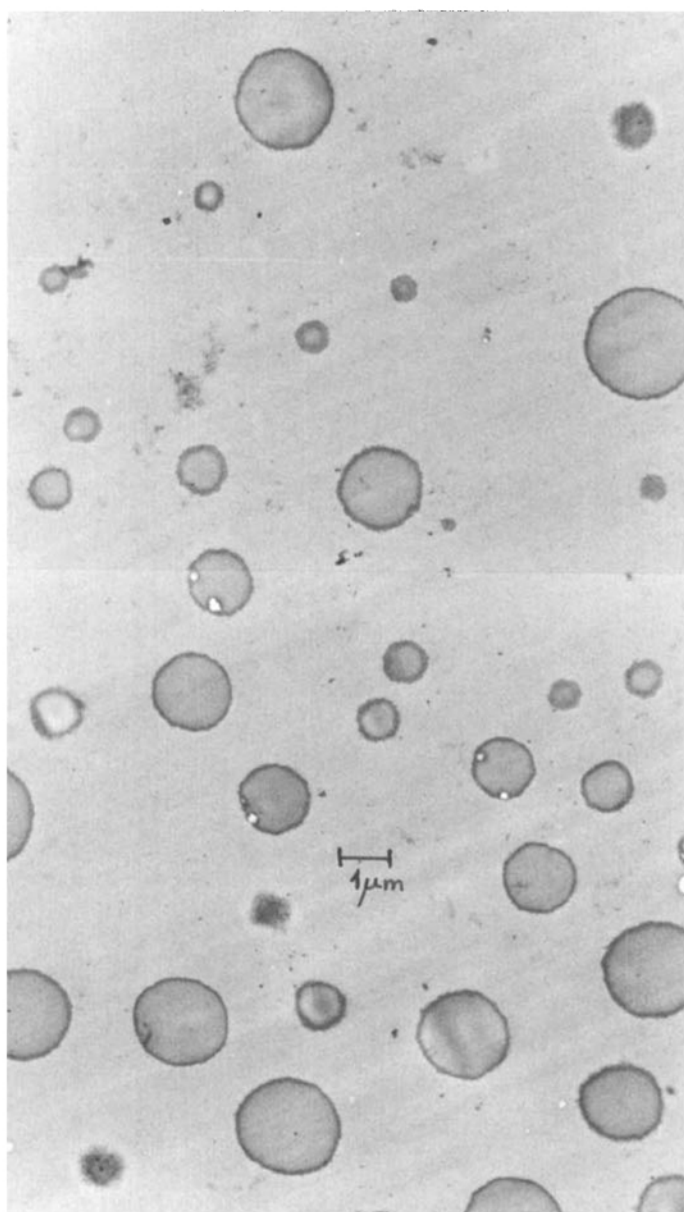


Fig. 4. Morphology of a nitrile-rubber-modified epoxy resin cured with dicyandiamide (transmission electron microscope; sample stained with  $OsO_4$ ).

moset resins over thermoplastic materials. These concepts are matrix flexibilization and the incorporation of crack-stopping microphases.

The matrix flexibilization is accomplished by replacing the very rigid structural units by flexible chain segments. Consequently, stiffness and thermal resistance are sacrificed to enhance toughness. At high flexibilizer content, the materials are rubbery. This concept of flexibilization is widely applied in flexible resin applications such as sealants<sup>[11]</sup> but fails to provide the strength and stiffness levels required in structural applications.

The second concept is to enhance energy dissipation occurring at the crack tip via microphases dispersed in the rigid resin matrix. Among a variety of microphases, e.g., fillers<sup>[12]</sup>, short fibers<sup>[13]</sup>, microvoids<sup>[14]</sup>, glass beads<sup>[15]</sup>, thermoplastics and rubbers<sup>[16]</sup>, elastomeric microphases exhibit outstanding energy absorption. The basic principles of multiphase thermoset rubber toughening and fracture mechanics have been reviewed<sup>[8,16-24]</sup>. In the absence of crazing, the increase of fracture toughness by one order of magnitude in rubber toughened epoxy resins has been attributed to energy absorption due to cavitation of rubber particles in the stress field and shear yielding induced by stress concentrations at the rubber particle phase boundaries<sup>[8,19,25-32]</sup>. Such interfacial stresses are the result of vastly different thermal expansion coefficients of rigid polymers and rubbers. An example of rubber particles dispersed in a cured thermoset resin matrix is given in Fig. 4 for nitrile-rubber modified Bisphenol A-diglycidyl ethers cured at 180°C using dicyandiamide. With separated rubber microphases dispersed in the continuous thermoset matrix, the high stiffness and creep resistance of the polymer network is retained.

To qualify as a toughening agent the following requirements must be met:

- phase separation upon cure to form microphases of 500–5000 nm average diameter;
- no plasticization of the resin matrix, i.e., complete phase separation;
- adhesion of microparticles to the resin matrix;
- no adverse effect on cure cycles;
- no large viscosity build-up of the uncured thermoset resin blend.

According to basic thermodynamics, the compatibility between the thermoset resin matrix, comprising the thermoset resin as well as the curing agent, and the toughening agent is dependent upon the free energy of isothermal mixing,  $\Delta G_m$ . If  $\Delta G_m$  is negative the components are miscible; if  $\Delta G_m$  is positive phase separation occurs (Table 3). Following theoretical approaches by Flory<sup>[33]</sup>, Hildebrand<sup>[34]</sup>, and Small<sup>[35]</sup>, the free energy is expressed as a function of the molar fractions  $n_1$ ,  $n_2$  of the toughening agent and the resin system, the volume fractions  $\Phi_1$ ,  $\Phi_2$ , and the solubility parameters  $\delta_1$ ,  $\delta_2$  which are defined as the

Table 3. Thermodynamics of thermoset/liquid rubber blends.

Thermoset $\delta_1$	Liquid Rubber $\delta_2$
$\Delta G_m = \Delta H_m - T \cdot \Delta S_m$ $\Delta G_m = V(\delta_1 - \delta_2)^2 \cdot \varphi_1 \cdot \varphi_2 + RT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2)$ $0.2 <  \delta_1 - \delta_2  < 0.6$	
incompatibility	adhesion

square roots of the cohesive energy densities. Since the molar entropy of mixing is usually positive due to the increased disorder of the mixture, the phase separation depends primarily on the molar enthalpy of mixing and consequently on the difference of the solubility parameters. Solubility parameters are the key molecular design of toughening agent microstructures. If the solubility parameters of the thermoset resin system and the toughening agents are equal, microphase separation does not occur. This causes severe plasticization of the resin matrix which is highly flexibilized and loses stiffness and strength. If the solubility parameters are markedly different, the thermoset resin matrix as well as the uncured thermoset resin/curing agent mixture are likely to be incompatible, causing macroscopic demixing of the toughening agent before curing occurs. Only if the difference in solubility parameters of the toughening agent and the resin system are carefully matched to fall in the range of 0.2 to 1.0, preferably 0.2 to 0.6, will the functional microphases be formed. This will provide high toughness without affecting stiffness and strength. To select suitable toughening agent candidates, the solubility parameters of the various system components should be mapped using solubility parameter estimates based on structural increment contributions<sup>[36-38]</sup>. As shown for the Bisphenol A-diglycidyl ether in Fig. 5, suitable candidates are identified by choosing polymer systems in the appropriate compatibility range. The following sections demonstrate how this approach is being used to design toughening agents such as functional liquid rubbers, core/shell polymers, and special compatibilized block polymers.

It is important, however, to point out that thermodynamic criteria are not sufficient to predict the morphologies of the multiphase thermoset resins. They also depend upon the cure kinetics and the rubber volume fraction. The fracture toughness increases with the rubber volume fraction. However, at rubber volume fractions exceeding 30%, phase inversions are likely to occur, as evidenced by thermoset resin microparticles dispersed in a rubber matrix as the continuous phase. In ultra-fast or occasionally in ultra-slow curing thermoset systems, in spite of the appropriate solubility

parameter difference, phase separations do not occur for kinetic reasons, thus deactivating the toughening agent<sup>[39,40]</sup>. Furthermore, the rubber microparticle size and size distributions essentially depend on the cure schedule, type and reactivity of the curing agent, and cure chemistry involved<sup>[41-50]</sup>. Therefore universal toughening agents do not exist do date. Individual toughening agents need to be tailored to fit the thermodynamics and kinetics of indi-

vidual multi-component thermoset systems. The toughening agents' microstructures, especially in view of well-balanced interfacial interactions, must be specifically engineered to function and meet the above-listed requirements. In the following sections, selected toughening agent classes and chemistry are reviewed. The focus will be on the synthetic methods applied from polymer science to control polymer compatibility and supermolecular structures.

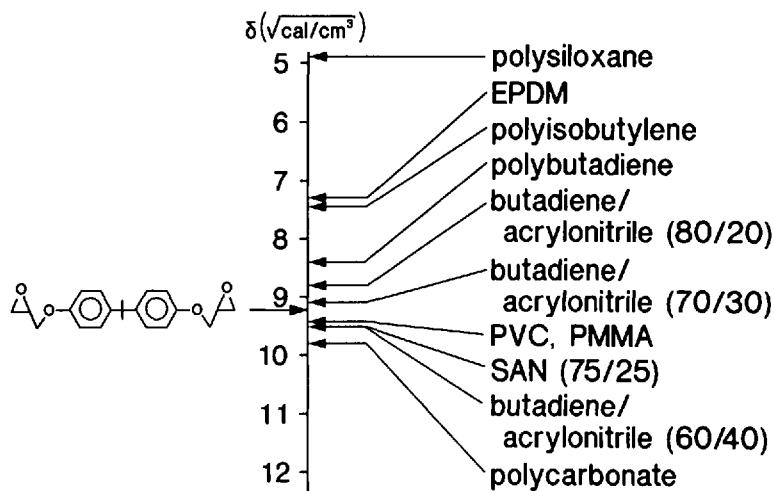


Fig. 5. A solubility parameter map. EPDM: ethylene/propylene/diene-rubber; PVC: poly(vinyl chloride); SAN: styrene/acrylonitrile copolymer; PMMA: poly(methyl methacrylate).

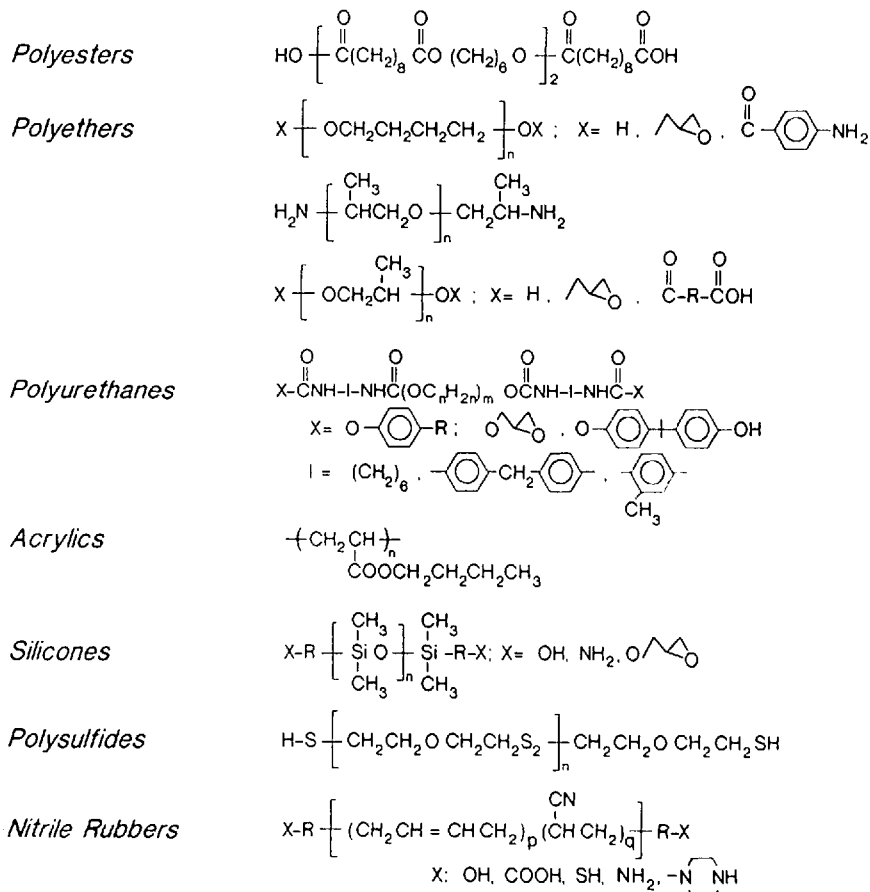


Fig. 6. Functional liquid rubbers.

### 3. Functional Liquid Rubbers

The most important class of toughening agents, widely applied in thermosetting structural materials, are oligomeric elastomers, so-called "liquid rubbers". They are miscible with the thermoset resin systems, have comparatively low viscosities. They also contain functional groups that enhance interfacial adhesion by covalent bonding between the thermoset matrix and rubber microparticles which phase separate during the cure of the thermoset resin system. High molecular weight rubbers, in general, provide better phase separation and higher toughness. However, the low molecular weight of liquid rubbers favors compatibility with liquid thermoset resins without affecting thermoset processing and without undesirable viscosity increases. Preferably, the microphases are rubbery, having glass transition temperatures below  $-20^{\circ}\text{C}$ . This is the prime requirement for acceptable low temperature toughness.

A variety of liquid rubbers, using all available polymerization processes for generating well-defined functionalized elastomer oligomers, have been prepared. Some important classes are depicted in Fig. 6. Numerous low-cost flexibilizers and toughening agents are derived from carboxy-terminated polyesters. They are prepared by non-stoichiometric polycondensations of di- and trifunctional carboxylic acids (e.g., sebacic or adipic acid), and diols or triols (e.g., 1,6-hexanediol, neopentylglycol or 1,2,3-tris(hydroxymethyl)propane). *Lohse et al.*<sup>[9, 10, 51-53]</sup> report the basic structure/property relationships of such systems, including functional polyamides.

Another important class is derived from oligomeric alkylene oxides such as hydroxy-terminated poly(propylene oxide) or poly(tetramethylene oxide), with number average molecular weights varying between 500 and 2500. For instance, the di- or trifunctional hydroxy-terminated poly(alkylene oxides) were added to anhydride-cured epoxy resins<sup>[54]</sup> or converted into glycidyl-ether-terminated poly(alkylene oxides) or various other functional groups<sup>[55, 60]</sup>. Most poly(alkylene oxide)-based thermoset systems have remarkably low viscosities. These flexibilizers are also used as reactive diluents. Polyesters, poly(alkylene oxides), and polysiloxanes, all hydroxy-terminated, are used as soft segments in a variety of urethane prepolymer flexibilizers and toughening agents. Typically, the polyols are end-capped with excess diisocyanate to form isocyanate-terminated prepolymers which can be functionalized at will. For instance, the isocyanate end groups are capped with monophenols or bisphenols, providing aromatic urethane end groups. The phenolic component is released upon heating to deblock the isocyanate end group during thermal or amine cure<sup>[58]</sup>. Amino-terminated poly(propylene oxides) are obtained either by converting hydroxy end groups

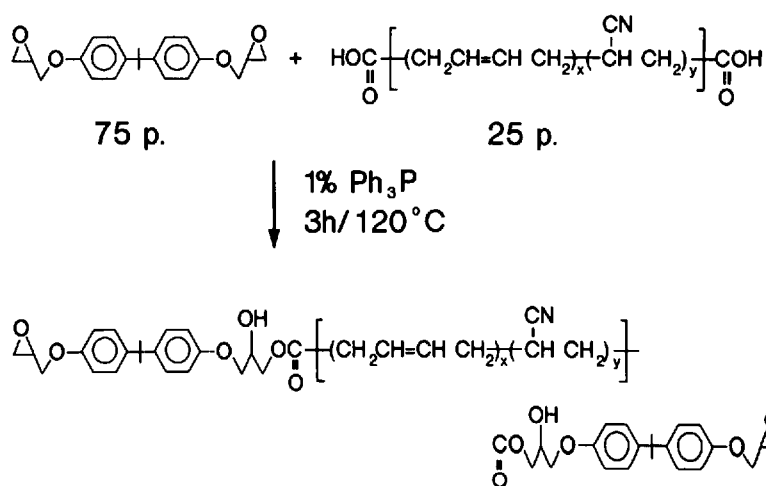


Fig. 7. Adduct formation of carboxy-terminated liquid nitrile rubber.

into amines<sup>[57, 71]</sup> or by esterification of the polyol with aminobenzoic acids<sup>[56]</sup>.

*Gazit and Bell*<sup>[61-63, 70]</sup> and *Lee et al.*<sup>[64]</sup> report acrylic liquid rubbers based upon butyl acrylate homo- and copolymers. *McGrath et al.*<sup>[66, 67, 69]</sup> prepared  $\alpha,\beta$ -difunctional poly(dimethylsiloxanes), for example, by equilibrating difunctional disiloxanes and cyclic tetrasiloxanes. In addition to the well-established polysulfide liquid rubbers<sup>[59, 65]</sup>, the functionalized nitrile rubbers have gained commercial importance. Hydroxy-, carboxy-, vinyl-ester-, and amino-terminated acrylonitrile/butadiene copolymer liquid rubbers are available<sup>[72-87]</sup> containing various amounts of acrylonitrile.

Many liquid rubbers are reacted with the thermoset resin to form adducts that enhance interactions between the liquid rubber and thermoset resin system. An example for liquid nitrile rubber adduct formation is shown in Fig. 7. The adduct formation between carboxylic acid end groups and epoxy resins is carried out thermally at

temperatures around  $160^{\circ}\text{C}$ <sup>[76, 77]</sup> or at lower temperatures, e.g.  $130^{\circ}\text{C}$ , in the presence of catalysts such as triphenylphosphine<sup>[76]</sup>.

Most of the liquid rubbers depicted in Fig. 6 are typical flexibilizers but not toughening agents. They fail to provide high stiffness, strength, and toughness. Toughening agents must match the thermoset resin system compatibility expressed by the solubility parameters in order to form the functional dispersed microphases with an adequate balance of compatibility and interfacial adhesion. As shown in Fig. 8, the conversion of flexibilizers into toughening agents is accomplished by molecular engineering of the liquid rubber microstructure. For the first time, this concept was verified successfully in the case of Bisphenol A-based epoxy resins and functionalized liquid nitrile rubber. In the absence of acrylonitrile, the functionalized butadiene oligomers are not compatible either with the resin or the matrix, giving macroscopic phase separation. As the

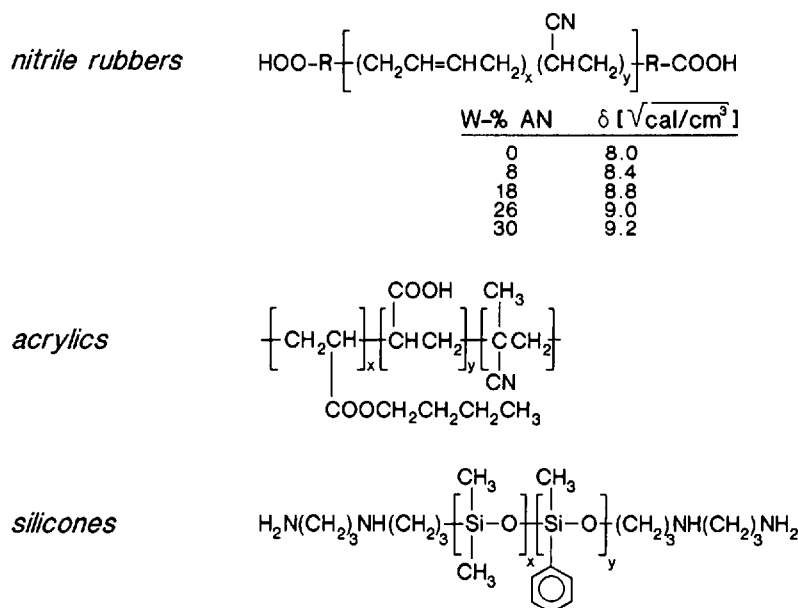


Fig. 8. Converting flexibilizers into toughening agents using copolymerization to vary solubility parameters.

acrylonitrile content increases, the solubility parameter difference between the resin system and liquid rubber decreases. This improvement in toughness reaches a maximum near the optimum solubility parameter difference. At higher nitrile content, the toughness decreases because of increasing miscibility. At high nitrile content, macroscopic demixing occurs. This general trend is depicted in Fig. 9 for nitrile-rubber-modified structural epoxy adhesives, using peel strength as a measure for toughness and reduced crack propagation. According to Drake et al.<sup>[73]</sup>, in the case of Bisphenol A-based epoxy resins, the preferred acrylonitrile content is about 18 to 20 weight-percent to obtain maximum fracture toughness. As mentioned earlier, this optimum depends strongly upon the curing agents and upon the cure chemistry.

In analogy to nitrile rubbers, liquid butyl-acrylate rubbers (Fig. 8) can be improved for epoxy-toughening either by incorporation of functional comonomers which chemically bond with epoxy (e.g., methacrylic acid or glycidyl methacrylate). Alternatively, the solubility parameters can be adjusted through incorporation of methacrylonitrile units into the butyl acrylate chain<sup>[70]</sup>. The thermodynamics-based synthetic route to improved toughening agents was also demonstrated for polysiloxanes. As apparent from Fig. 5, silicone rubbers and epoxy resins are highly incompatible. Many silicone liquid rubber prepolymers, in spite of their low molecular weights, are not miscible with epoxy resin systems. Saito et al.<sup>[68]</sup>, as shown in Fig. 8, demonstrated that the toughening agent efficiency improves drastically when epoxy-compatibilizing structural segments, such as phenyl-methyl-siloxane units, are introduced into the polysiloxane chain.

#### 4. Block Polymer Liquid Rubbers

The molecular design of polymeric liquid rubber toughening agents to balance polymer compatibilities, is accomplished in two ways. Compatible comonomer units can be randomly incorporated along the less compatible chain (Fig. 8), or alternatively, block polymer synthesis can be used to couple polymer segments of varied compatibility (Fig. 10). Block copolymer toughening agent technology was pioneered by Hoeschele<sup>[88,89]</sup>. He discovered that stiffness and toughness of epoxy resins are improved markedly by incorporation of polyester thermoplastic elastomer block copolymers that contained poly(tetramethylene oxide) soft segments. While poly(alkylene oxide) flexibilizers soften the thermoset matrix, the combination of poly(alkylene oxide) segments and polyester segments such as poly(butylene terephthalate) provides high toughness and high stiffness.

Highly incompatible liquid rubbers (e.g., dihydroxy- or dicarboxy-terminated polybutadienes<sup>[90,91]</sup> or polysiloxanes<sup>[92,93]</sup>) are compatibilized by attaching polyester,

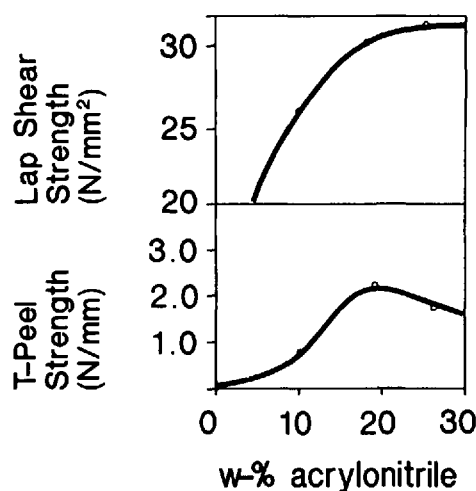


Fig. 9. Lap shear and T-peel strength of an epoxy structural adhesive as function of the acrylonitrile content of the liquid nitrile rubber toughening agent.

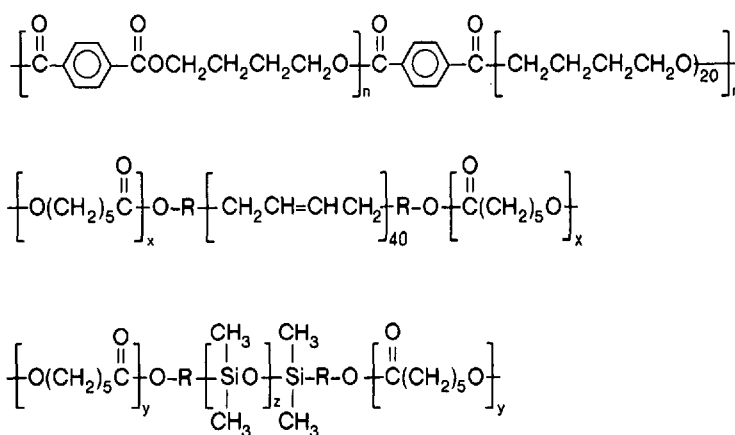


Fig. 10. Block polymer toughening agents containing compatible and incompatible polymer segments.

preferably polycaprolactone, blocks. The polyester gradually improves the compatibility, simply by increasing the block length of the compatible segment. At a certain minimum block length of the compatible segment, the whole polymer becomes fully miscible.

#### 5. Liquid Rubber Blend Systems

Recently, instead of using tailor-made polymers containing segments of different compatibility, functional liquid rubber blends, based on nitrile liquid rubber and urethane prepolymers, were incorporated

into epoxy-based thermoset systems<sup>[94,96]</sup>. Provided the two liquid rubbers are compatible, surprisingly high toughness and markedly increased strength are obtained. They substantially exceed the performance of the corresponding systems containing only the equivalent amount of the individual blend components (Table 4). Morphological and dynamic mechanical studies revealed that the formation of novel rubber blend microphases consisting of interpenetrating elastomer networks account for this outstanding blend synergism. Again it was verified that polymer compatibility is the key to novel classes of high-performance toughening agents.

Table 4. Rubber-blend-toughened epoxy resins.

Toughening Agent Type	Weight-%	Lap Shear Strength [N/mm <sup>2</sup> ]	T-Peel Strength [N/mm]
nitrile rubber/epoxy adduct (25/75)	33	22.7	1.0
phenolic polyurethane	33	8.4	4.5
blend (1:1)	32	26.7	7.9



## 6. Core/Shell Microparticle Toughening Agents

Tailoring linear, or slightly branched, functional liquid rubbers which phase separate during the curing reaction to form rubber microparticles is a process which is rather difficult to control. Instead, rubber microparticles are prepared in a separate step, then dispersed in the resin to be subsequently incorporated into the resin matrix during cure. Particle-forming polymerization processes, such as aqueous emulsion polymerization or non-aqueous dispersion polymerization, allow precise control of the particle sizes and particle size distributions. Furthermore, the interfacial adhesion of non-compatible rubber microparticles is readily modified by grafting compatible polymeric shells onto the rubber microparticle cores. This core/shell polymer technology has proven to provide versatile toughening agents.

In Fig. 11, a highly simplified scheme is presented to illustrate the core/shell particle synthesis in aqueous emulsion polymerization. The rubber, e.g. polybutadiene, is formed in micelles to give a slightly crosslinked polymer latex of well-defined particle sizes which can be varied between 100 and 20 000 nm. It can also be formed in bimodal distributions. Subsequently, a thermoplastic shell, consisting of either styrene/acrylonitrile or styrene/methyl methacrylate, is grafted onto the polybutadiene core<sup>[97,98,116-118]</sup>. Depending on the acrylonitrile or methyl methacrylate content, the compatibility between the shell and the thermoset resin system can be varied over a wide range, thus tailoring the interfacial adhesion between the prefabricated rubber microparticles and the thermoset matrix. It was demonstrated<sup>[97]</sup> that the incorporation of functional groups which interact with the network formation enhances the crosslink density of the thermoset matrix. This provides increased toughness as well as increased strength and thermal resistance.

In a more recent advance, non-aqueous dispersion polymerization has been applied to form toughening agent microdispersions in-situ, e.g., through particle-forming dispersion polymerization in epoxy resins. This eliminates the need for a redispersion step which could depend upon the nature of core/shell primary particle agglomerates formed from the aqueous emulsion. Acrylic<sup>[99]</sup> and silicone<sup>[100,101]</sup> in-situ dispersions have been described. In particular, polysiloxane dispersions in epoxy resins are a very potent class of novel toughening agents. They exhibit remarkably low viscosities, even at high solids content, and increase toughness without affecting stiffness.

As an illustration of the core/shell polymer concept, Fig. 12 shows typical core/shell particles obtained by spray-drying aqueous emulsions which agglomerate to yield large, spherical particles of low porosity. These secondary particles are dispersed in the thermoset resin as reactive

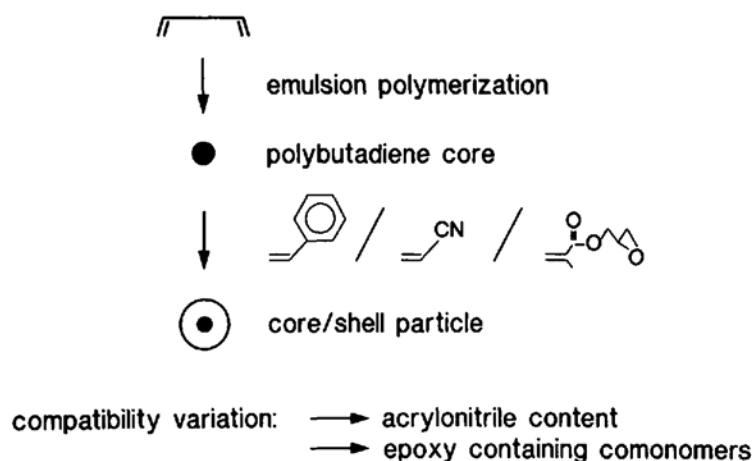


Fig. 11. Simplified scheme for the synthesis of core/shell toughening agents in particle-forming emulsion or dispersion polymerization.

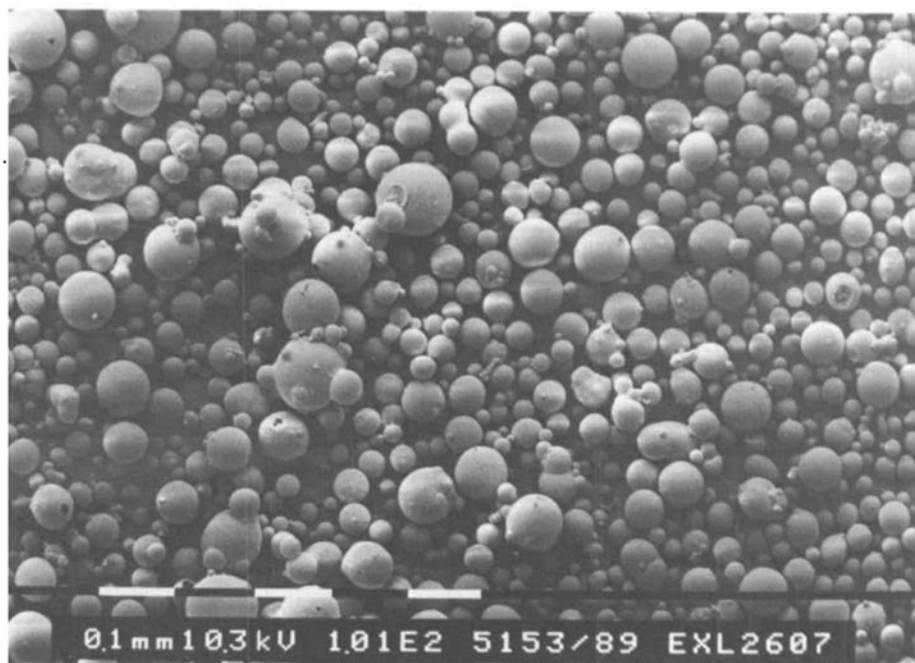


Fig. 12. Morphology of core/shell toughening agents as reactive fillers obtained by spray-drying (scanning electron micrograph).

fillers. Upon cure, the shell dissolves in the resin. The primary microparticles are dispersed to form functional microparticles adhering to the thermoset matrix. This is a result of blend formation between shell polymer and thermoset resin.

Fig. 13 depicts the morphology of an epoxy resin blend with core/shell particles after the curing step. It clearly shows the redispersion of the 1000 nm rubber microparticles in the thermoset matrix<sup>[98]</sup>.

## 7. Functional Thermoplastic Toughening Agents

Highly crosslinked thermoset resins, used in aerospace and aircraft applications, are rather difficult to toughen. In the

case of very low molecular weight chains between crosslinks, the efficiency of rubber-toughening is markedly reduced due to substantially reduced shear yielding in tightly-crosslinked polymers. This prevents rubber particle cavitation known to be the origin of energy dissipation<sup>[113]</sup>. Another type of toughening agent is therefore needed which does not depend upon the deformation of the thermoset resin matrix. In addition, most rubber-toughened thermoset resins suffer modulus losses. This can simply be due to the fact that a small portion of the high-modulus stiff matrix was replaced by a small portion of rubbery, low-modulus, dispersed phase.

As an alternative toughening agent for tightly-crosslinked thermoset resins, ductile high-temperature-resistant thermoplas-

tics or corresponding functionalized oligomers are used. Some of these toughening agents are summarized in Fig. 14.

The basic thermodynamic considerations are very similar to rubber toughening although the phase separation is not necessary in all cases. A high- $T_g$  thermoplastic toughening agent should be miscible with the resin to allow blend formation. Systems based on phenoxy resins<sup>[103]</sup>, polyethersulfones<sup>[101, 102, 107, 109-115]</sup>, polyetherimides<sup>[108]</sup>, and polyimides<sup>[104, 106]</sup> have been proposed for epoxy and bismaleinimide matrix resins. Speciality reactive-oligomer, high- $T_g$ , toughening agents have been tailored, for example, by end-capping polyethersulfones with aminophenols which function in combination with aromatic diamine hardeners<sup>[110]</sup>. Phase separation does not occur in some polysulfone-modified epoxy systems<sup>[105]</sup>. Recent studies by *Bucknall* and *Gilbert*<sup>[113]</sup> on polyetherimide-toughened, multifunctional epoxy resins show that microphase formation of polyetherimide dispersed in tightly-crosslinked tetrafunctional epoxy resins gives substantially better fracture toughness. The source of improved toughness is the dispersed high-temperature-resistant polymer microphase.

## 8. Conclusion and Outlook

The basic understanding of material failure mechanisms and multiphase polymer formation has led to the development of novel advanced structural materials. These materials are based on toughening agents which inhibit crack propagation by dissipating energy at the crack tip. Such multiphase polymers, containing either rubbery or ductile, rigid microphases dispersed in the thermoset matrix as the continuous phase provide unique metal-like property combinations. They include high stiffness, high strength, high thermal, creep and environmental resistance and, in particular, high toughness. While flexibilizers drastically reduce the stiffness by plasticizing the thermoset matrix, a typical toughening agent does not affect stiffness due to the multiphase structure. Depending on crosslink density of the thermoset resin matrix, either rubbery or high-temperature-resistant ductile thermoplastics are being used as the dispersed microphase component. Liquid rubber flexibilizers, developed by incorporating blend technology and the ability to form prefabricated, well-defined microparticles embedded in a compatible shell have boosted the performance of thermoset resin systems. In contrast to the highly brittle resin system, the multiphase thermoset polymers exhibit thermoplastic-like toughness combined with typical advantages of the thermoset systems including easy processability of low molecular weight, low viscosity resins and high creep and fatigue resistance. While the phase separation of functional liquid rubber is dependent upon a multitude of chemical

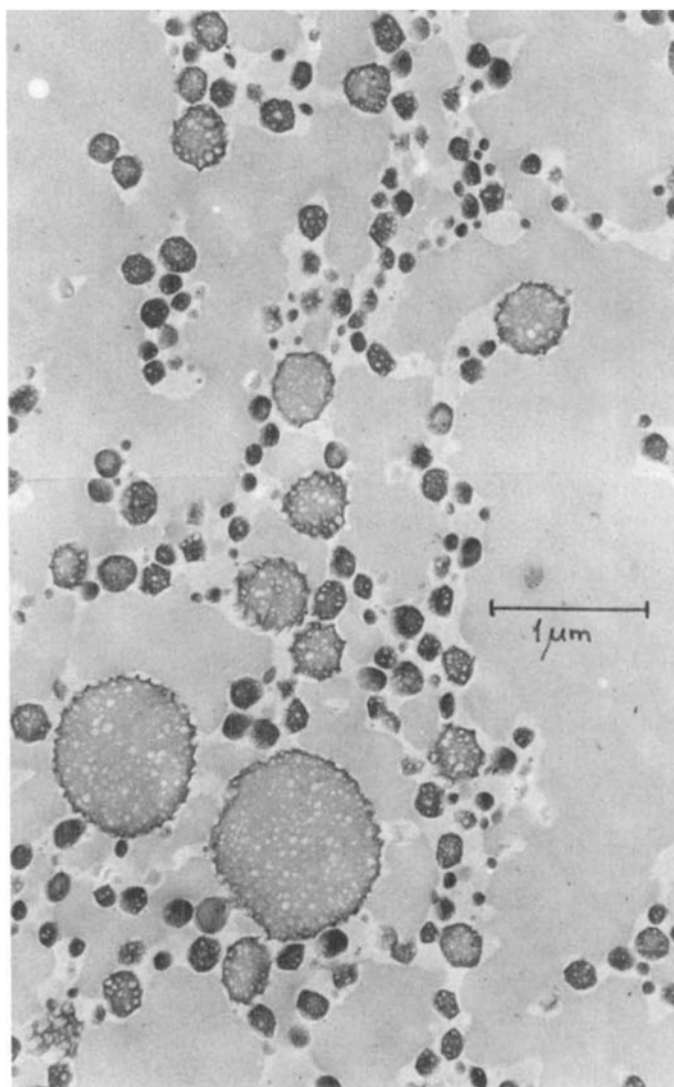
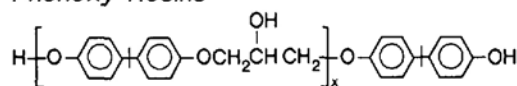
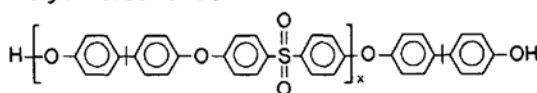


Fig. 13. Morphology of cured epoxy resins containing acrylic core/shell microparticles (transmission electron micrograph, using  $OsO_4$  staining of the butadiene-based rubber cores).

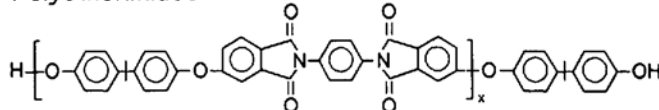
### Phenoxy Resins



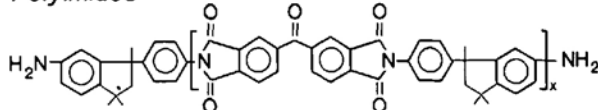
### Polyethersulfones



### Polyetherimides



### Polyimides



### Amino-terminated Polysulfones

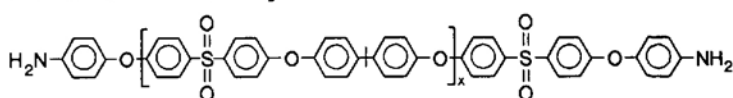


Fig. 14. Ductile thermoplastic high- $T_g$  toughening agents.



and physical parameters and therefore difficult to control, the core/shell approach appears to offer the prospects of well-defined multipurpose toughening agents. These, however, do need to be engineered separately for different thermoset/curing agent systems. This provides new synthetic routes to high-performance, multiphase polymers for advanced structural applications.

In spite of the recent advances in thermoset toughening, the ultimate goal of metal-like toughness has not yet been met. Even at the highest level of toughness achieved in thermoset resin systems, metal alloys still prevail by almost one order of magnitude. As the thermal stability of thermosetting structural materials increases, toughness markedly decreases due to the reduced matrix deformation of the tightly-crosslinked system. Furthermore, toughness is also dependent upon load rate. As the load rate increases, toughness drastically decreases.

Both the materials scientist and the polymer chemist are challenged to overcome the inherent brittleness of thermoset resins and improve crack energy dissipation under static as well as dynamic conditions. Several promising approaches are being explored. For instance, rubber blend microphases containing comparable nitrile and polyurethane rubbers gave surprisingly high dynamic fracture toughness.

In typical thermoset systems, the research has been aimed at the formation of well-defined microphases either through controlled phase separation processes during cure or by dispersing functional tailor-made core/shell polymers. These will continue to provide novel generations of high-performance multiphase toughening agents and better insight into the nature of energy dissipation processes occurring near a crack tip. Furthermore, blend or interpenetrating network formation using combinations of compatibilized thermoset resins and toughening agents is likely to lead to major breakthroughs in thermoset toughening. Already blend systems have appeared which outperform the corresponding systems containing only the individual blend components. Similar approaches in thermoplastic toughening have led to super-tough thermoplastic materials with metal-like toughness.

As an alternative to crosslinked polymer systems with inherent toughness limitations, a new matrix resin has been introduced recently to combine thermoset-like processing and thermoplastic-like toughness. Instead of curable resins, low-viscosity cyclic oligomers of thermoplastics like polycarbonates were used to form high-temperature-resistant linear thermoplastic materials via ring-opening polymerization in the mold. Thus, thermoset-like processing gives linear polymers of high molecular weight which could not be processed in conventional melt extrusion. This approach, in combination with interpenetrating network and multiphase polymer for-

mation, may lead to novel types of high-temperature-resistant, tough, polymeric materials which are likely to match metal-like toughness, strength and stiffness.

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