REVIEW

Toughening of photo-curable polymer networks: a review†

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Photo-curable resins based on multifunctional acrylate monomers are commonly applied as thin films (*e.g.* protective coatings, printing inks, *etc.*) and in recent years are also used for the fabrication of bulk objects such as dental fillings and 3D-printed parts. While rapid curing and good spatial resolution are advantages to these systems, brittleness and poor impact resistance due to inhomogeneous polymer architecture and high crosslink density are serious drawbacks. By comparison, epoxy thermoset resins suffered many years ago from similar problems, but since then are found in ever demanding applications thanks to a variety of approaches to increase polymer toughness. Based on these successes, researchers have tried to translate strategies for toughening epoxy resins to photopolymer networks. Therefore, this review surveys relevant scientific papers and patents on the development of crosslinked epoxy-based polymers and also photo-curable polymers based on multifunctional acrylates with improved toughness. Strategies developed to reduce brittleness include working with monomers, which intrinsically give tougher polymers, particulate additives, and alternate forms of polymerization and polymer architecture (*e.g.*, dual-cure networks, interpenetrating networks, thiol–ene chemistry). All of these strategies have advantages and yet application specific rigours must also be considered before and during formulation development.

Introduction

Epoxy-based thermosetting resins were first developed in the 1940s and are today found in a range of applications such as metal can coatings, printed circuit boards and aerospace composites. While these crosslinked resins have always been renowned for good chemical resistance and electrical passivity, brittleness was historically a problem. In the 1960s and 1970s, however, techniques were developed for toughening these plastics allowing them to be used more and more in structural applications.

By comparison, due to limitations of light penetration, photo-curable multifunctional acrylates have traditionally been applied in thin film applications such as inks and coatings and not as engineering plastics.[1,2] The advancement of photo-curable dental restoratives and additive manufacturing (or 3D-printing) based on layer by layer assembly[3] have changed the role of photopolymers though, and thus mechanical properties, especially toughness, have taken increasing importance.[4] To reduce brittleness, researchers try to translate toughening strategies from epoxy-based systems to acrylate-networks.

Borrowing largely from techniques developed for toughening of industrial epoxy and vinyl ester thermosets (typically but not specifically cured by heat), bending and impact strength of photopolymer networks has improved greatly over the last two decades. This can be attributed to proper selection of monomers and additives as well as layering and curing conditions. To better understand toughening, we first present the commonly used experimental techniques to measure mechanical properties related to toughness. We then introduce some of the fundamental terms used to describe material failure. Next we overview some of the more important toughening techniques as they were first applied to thermosets. Additional toughening techniques developed specifically for photo-curable polymers will be described as well. Focus here is chiefly on acrylate-based monomers, with mention also of photo-curable epoxy and oxetane resins as they are commonly found in 3D-printing resins. It should also be noted that

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the term "acrylate-based monomer" refers here to methacrylates as well. While methacrylates are less reactive and much less common in coatings, they are of significant importance in bulk applications such as dental fillings and 3D-printed parts. The use of chain transfer agents with acrylate resins is explored fairly in depth and is one of the most promising strategies to improve material properties including toughness. In addition, photo-curable interpenetrating polymer networks (IPNs) and photo-induced phase separation (PIPS) are investigated. In closing, application and processing specific concerns shall be considered.

Techniques for measuring toughness

Toughness is a material property related to the resistance against crack growth. Typically, toughness decreases if strength, stiffness or hardness is increased. For many engineering applications, though, high values for strength, stiffness AND toughness are desired. It is therefore essential to develop efficient toughening mechanisms, which keep toughness at reasonably high levels, even in the case of strong and stiff materials. The stiffness of the sample describes its ability to withstand elastic (reversible) deformation and is determined by the geometry of the sample and the elastic modulus of the utilized material. Strength describes the ability of the sample to withstand plastic (irreversible) deformation. Strength and modulus of a material can be determined by applying tensile testing.

Tensile testing

Tensile testing is described as a quasi-static testing method since the experiment is performed with a very slow strain-rate.[5] For example, recommended crosshead speeds for common polymers are 20–100 mm min^{-1} for HDPE, nylon, and PP and 5–20 mm min^{-1} for ABS, PMMA and polyester.[6] With a normal universal testing machine, loading is applied electrically or electro-hydraulically which is essentially shock-free, steadily increasing until ultimate failure of the specimen occurs. The applied tensile load or force induces a uniaxial loading state on the specimen, which results in a homogeneous and evenly distributed axial stress over the sample cross-section. The area of the cross-section is assumed to be constant during the experiment.

$$\sigma = \frac{F}{A_0} \tag{1}$$

σ, tensile stress [MPa]; F, tensile force [N]; A_0, initial cross section [mm^2].

The stress during the measurement is calculated *via* the equation above while the strain can be determined by the following equation.

$$\varepsilon = \frac{\Delta L}{L_0} 100\% \tag{2}$$

ε, tensile strain [%]; ΔL, elongation [mm]; L_0, initial length [mm].
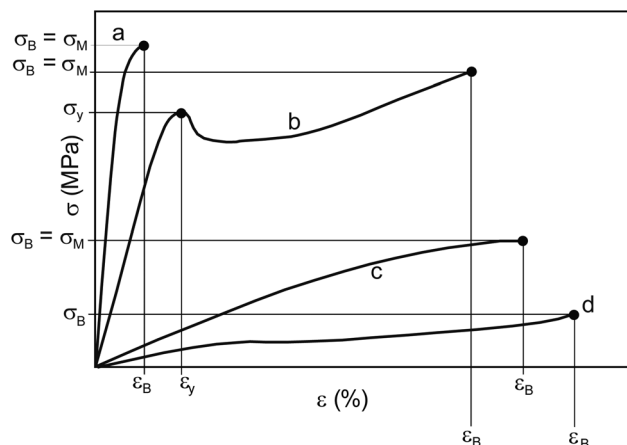

Fig. 1 Exemplary stress–strain curves for various polymers: brittle materials (a), tough materials with yield point (b), tough materials without yield point (c) and elastomers (d).[7]

By monitoring the strain with increasing stress, a stress–strain curve is obtained. A typical curve is depicted in Fig. 1 showing the different stages observed when testing polymers. Independent of the type of polymer, the linear regime at the onset of the stress–strain curve can be used to determine the Young's modulus (E), which corresponds to the slope of the curve. When the stress is increased, the curve becomes non-linear, and depending on the type of tested polymer various behaviours can be observed.

Photo-cured acrylates are typically rather brittle and therefore fall into category (a) in Fig. 1: the strain at break (ε_B) is small, and no yield point with yield strength (σ_y) can be observed. The maximum stress (σ_m) occurs at the point of failure and maximum stress is therefore the stress at break (σ_B). If the cross-link density is sufficiently low, the photo-cured polymer will exhibit elastomeric behaviour, corresponding to curve (d) in Fig. 1. In toughened photo-curable polymers and thermoplastic polymers, behaviour as depicted in (b) and (c) might be observed.

Deformation energy (U_T), which is related to the toughness of a material, is defined as the area under the stress (σ)–strain (ε) curve:

$$U_T = \int_0^\varepsilon \sigma \, d\varepsilon \tag{3}$$

High deformation energy indicates good resistance against crack growth, since crack propagation will require a larger amount of energy in these materials.

Impact testing

Although tensile testing does provide values for strength and for toughness, these values are quasi-static and additional dynamic techniques may be required for polymers intended for real-world applications. For example, resistance to projectiles such as hailstones or gravel is essential for exterior automobile components. To determine if a new material is suitable
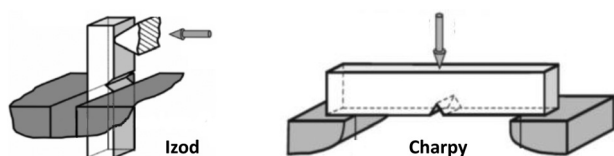
Fig. 2 Schematics of Izod and Charpy impact testing setups.

for such an application, the loading must be applied quickly. High-rate loading or impact can be applied in a number of manners with pendulums being commonly used due to accuracy and reproducibility. For example, two of the most common standardized methods for measuring impact strength (those of Izod and Charpy) are both based on pendulums. While the sample dimensions are different for the Izod and Charpy tests, the basic setup is comparable. In both cases notched as well as unnotched samples can be used. Notches are used in both cases to provide an intentional 'weak point' where the sample should break upon impact. A schematic comparison of Izod and Charpy methods is shown in Fig. 2.

The most obvious difference in the two methods is that the sample is supported on one end for the Izod test and on both ends for the Charpy test. There are also differences in the relation of the point of impact of the pendulum and of the notch. ISO 180 defines the Izod notch impact strength (a_{iN}) as the absorbed impact work of the fractured notched sample divided by the initial cross section area of the sample under the notch tip.[8]

$$a_{iN} = \frac{W_i}{b_N \times h} \quad (4)$$

W_i, impact energy [kJ]; b_N, width at notchbase [m]; h, thickness of specimen [m]; a_{iN}, Izod notch impact resistance [kJ m^{-2}].

Impact energy can be determined as the loss in potential energy (ΔPE) measured from the difference in release height (h_0) and maximum height attained for the pendulum hammer after impact (h_{final}).

$$\Delta PE = W_i = mg(h_0 - h_{final}) \quad (5)$$

This equation assumes an ideal pendulum where force is based on the gravity (g) driven mass (m) alone. Friction can be accounted for by swinging the hammer without a sample. In comparison to the ISO method, ASTM D256 calculates Izod impact strength by dividing impact energy by the thickness of the specimen (eqn (6)). The result in this case has the dimensions of J m^{-1}.

$$a_{iN} = \frac{W_i}{h} \quad (6)$$

Dynamic mechanical analysis (DMA)

Mechanical properties of polymers are dependent on temperature and on the frequency of an applied load. When polymers are subjected to a sufficiently high mechanical load, they tend to yield. The stresses which lead to yielding are usually strain-rate dependent. This strain-rate-dependent behaviour is called viscoelasticity.[9]

Dynamic Mechanical Analysis (DMA) is a powerful technique to study the viscoelastic nature of polymers. The technique applies a periodic force to the sample and measures the response. The applied dynamic stress (σ) can be described as:

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (7)$$

ω, angular frequency [rads^{-1}]; t, time [s]; δ, phase angle [rad].

The resulting dynamic strain (ε) has a similar equation:

$$\varepsilon = \varepsilon_0 \sin(\omega t) \quad (8)$$

Dividing these two terms provides modulus as a complex number where the real (or in-phase portion) describes the storage modulus (E'):

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (9)$$

And the imaginary (or out-of-phase portion) describes the loss modulus:

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (10)$$

The storage modulus describes the elastic response of the material and is related to the Young's modulus, E. The loss modulus relates to the viscous properties of the material and is sensitive to different kinds of molecular motions, phase transitions, and other structural heterogeneities.[10] Both storage and loss modulus are dependent on temperature although this dependence is not always linear. Non-linear or in some cases abrupt changes in modulus will occur at or near the glass transition temperature (T_g) of a material. Specifically the loss factor (or tan δ), which is the ratio of the loss modulus to the storage modulus, will increase and reach a maximum at the T_g.[11] Thus DMA (or DMTA) is a much more sensitive method for measuring T_g than Differential Scanning Calorimetry (DSC). DMA can also be used to investigate the frequency- and time-dependent nature of this transition and is often able to resolve sub-T_g transitions, like beta-, gamma- and delta-transitions that DSC is typically not sensitive enough to measure. Since mechanical properties can change drastically at or near the T_g, this measurement will often partially define the useful temperature range of a polymer. As an example, Young's modulus of crosslinked rubber can increase by a factor of more than 1000 below its T_g, resulting in a hard but also very brittle material. Elastomers with even lower T_g values were developed throughout the twentieth century and have allowed vehicles to operate in extreme arctic or high altitude conditions not possible before. Although photopolymers are not intended for such applications, temperature is an important consideration and the lessons learned in material development are still relevant.

Hardness

Hardness is a material property describing the resistance of a material against penetration. Hardness is usually related to the yield strength of a material, although owing to the differences in measuring techniques it is not possible to give a simple conversion factor applicable for all materials. The two most commonly used methods for measuring the hardness of photo-curable coatings are those of Persoz and of König.[12] Both methods are based on pendulums supported by balls resting on top of the sample material. The pendulum is set into motion and the time required for the angle of the pendulum to decrease from 12° to 4° (Persoz) or from 6° to 3° (König) is recorded in seconds.

Nanoindentation is a slightly newer and yet well-established method for measuring the hardness of coatings and thin films. With nanoindentation, a small pyramidal shaped diamond tip is pressed into the sample, while the load and displacement are recorded.[13] The slope of the load–displacement curve gives the stiffness (S) which can be used with other terms to determine a reduced Young's modulus (E_r) for the material.

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_p(h_c)}} \tag{11}$$

β, geometric constant on the order of unity; A_p, area of the diamond tip at h_c; h_c, contact depth.

Fracture and crack propagation

Polymeric materials intended for use in engineering applications are expected to withstand high levels of stress without failing.[14] Fractures are one of the principal causes of catastrophic material failure, which warrants a description of how cracks arise and how they propagate. Fractures originate from defects (cracks, internal voids, inhomogeneities of the microstructure, *etc.*) within the material or on its surface. The toughness of a material is then defined by its ability to withstand crack growth. Impact strength as well as the area under the stress–strain curve are commonly used metrics for the toughness of a material. Other measurements for material toughness include the critical stress intensity factor (K_{IC}), critical *J*-integral (J_{IC}) and the crack tip opening displacement (CTOD).

Depending on the applied load, a crack can propagate by three principal modes (Fig. 3). In mode I, a tensile force is applied normal to the crack plane. Mode II and mode III propagation are driven by shear forces.

Fractures may be classified as brittle or ductile, where in the first case the principle driving force for crack propagation is the release of elastic energy of the propagating crack which is counteracted by the consumption of surface energy from the two newly created surfaces adjacent to the crack. With ductile materials such as metals and polymers, surface energy plays a lesser role. Instead, a plastic zone develops around the crack tip, and depending on the size of the plastic zone and the level of the yield stress large amounts of energy can be dissipated. In the case of brittle fracture, the energy release rate of the
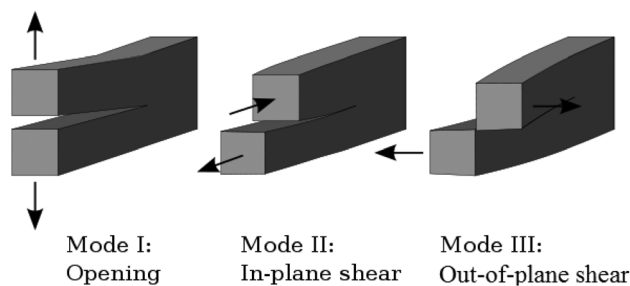

Fig. 3   Modes of crack propagation.

material (G) is related to the Young's modulus (E) by the following equation:

$$G_I = \frac{K_I^2}{E} \tag{12}$$

K_I stress intensity factor for mode I

The critical stress intensity factor (K_{IC}) is the minimal value for propagating a crack under mode I tensile forces, and is commonly referred to as the fracture toughness of the material.

Considerations for the mechanical testing of photopolymers

The geometry of the sample and the nature of the testing apparatus have great bearing on results and generally standardized mechanical testing methods are applied. Some materials, including photopolymers printed by layer by layer assembly, can be anisotropic with strength normal to and axial to the build direction being sometimes different.[15] Photopolymer samples intended for mechanical testing are commonly cured in moulds and then cured a second time on the back side. For additive manufacturing, thermal post curing is also quite common. While sample geometry is normally defined by a standard, curing conditions (intensity, time, wavelength, and O_2 concentration) are not. Such parameters must be considered when comparing mechanical testing results of one polymer sample with those of another.

Polymer architecture

The molecular architecture of a polymer has an obvious influence on the mechanical properties of the bulk material. Two important classes of highly crosslinked thermosets are those based on epoxies and those based on acrylates. Epoxy resins are typically cured in the presence of amines or anhydrides in a step growth manner. Acrylate monomers, on the other hand, undergo radical chain growth polymerization. Fig. 4 illustrates schematically how networks develop from both of these monomer systems. While the epoxy-amine system evolves in a fairly regular manner, the acrylate system will polymerize and crosslink inhomogenously leading to a highly irregular network. As the modes of polymerization are fundamentally different, they are thus treated separately. First we would like
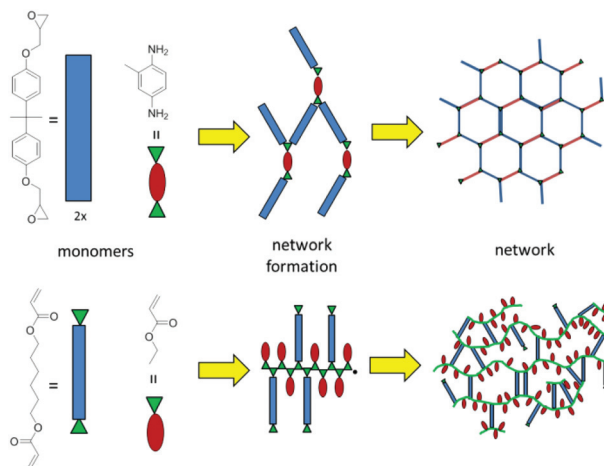
Fig. 4 Network formation *via* step-growth polymerization of epoxy thermosets (above) and radical chain growth of acrylates (below).

Fig. 5 Epoxy structural monomers and reactive diluents for thermoset resins.

Fig. 6 Commonly used amine curing agents for epoxy resins.

to consider typical monomers and hardeners and their impact on the polymer architecture.

Epoxy resins

Epoxy monomers may with appropriate additives be cured by heat or with light. Thermally cured epoxies (also commonly referred to as epoxy thermosets) are by far more commonly used and due to their industrial importance are the subject of hundreds of papers and patents concerning methods to improve polymer toughness.[16] The most popular family of monomers are the digylcidyl ether derivatives of bisphenol A (DGEBA in Fig. 5) with varying molecular weight. Other epoxy monomers of commercial use include epoxides of phenol-formaldehyde Novolac resins, hydrogenated DGEBA (H-DGEBA) and glycidyl imides including triglycidyl isocyanurate (TGIC). The viscosity of resins consisting of these structural monomers can be reduced with reactive diluents including alkyl glycidyl ethers (AGE) and epoxidized plant oils such as soy bean oil (ESBO).

With DGEBA based resins, the distance between crosslinks will be strongly dependent on the average value of *n* (Fig. 5) and on the concentration and degree of substitution of the curing agent. Amines are most commonly used as curing agents in two-component systems (Fig. 6), where primary aliphatic amines are low in viscosity and have the highest reactivity. To reduce odour and premature gelation in such systems, primary amines such as diethylenetriamine (DETA) can be reacted with ethylene oxide and water to give aliphatic secondary amines endcapped with hydroxyethyl moieties. Aromatic amines such as *m*-phenylenediamine (MPD) are commonly used as curing agents due to the good thermal properties of the cured polymer but may be substituted with less toxic cycloaliphatic amines (such as PACM) in applications where the extra cost can be justified. Polyether amines (PEA) are claimed to reduce resin viscosity better than traditional polyalkylamines and to improve cured material toughness.[17] In comparison to two-component systems, one component epoxy
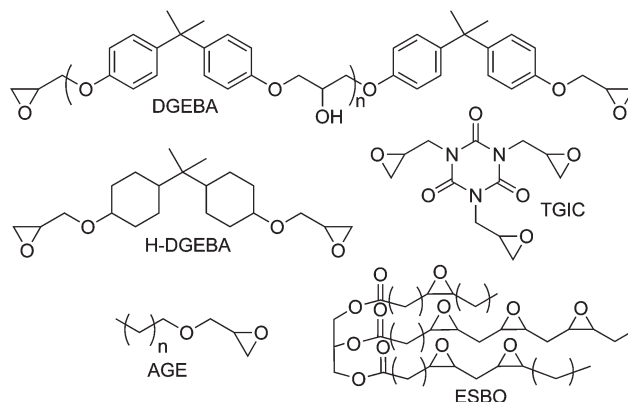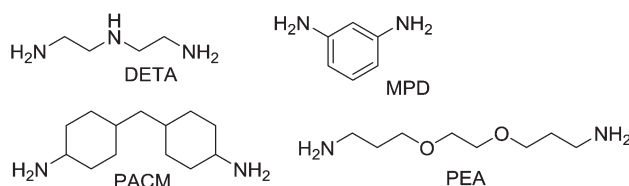
resins are based on less reactive curing agents such as ketamines, which form amines when exposed to air moisture.[18]

In thermosets, a primary amine can react with two epoxy groups (Scheme 1). When both the amine and epoxy monomer are difunctional, a crosslinked network will steadily arise with numerous hydroxy groups. These hydroxy groups can also react at elevated temperature with epoxy rings and will do so if the amine concentration is kept low.[19]

While amines are by far the most commonly used curing agents for epoxy resins, acid anhydrides are the second most utilized class of curing agents and deserve some recognition. Commonly used acid anhydrides for epoxy curing include phthalic anhydride (PA) and methyl tetrahydrophthalic anhydride (MTHPA), the latter of which is used in filament winding composites. Epoxy-acid anhydride resins are much more stable than primary amine based resins and require high temperatures (>200 °C) to crosslink.[20] The mechanism of crosslinking is proposed to commence *via* reaction of the anhydride with secondary alcohols of the epoxy monomer (Scheme 2). The resultant carboxylic acid will then open the epoxy and form new secondary alcohol to propagate the reaction.
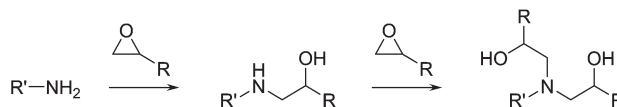
Scheme 1 Crosslinking reaction of epoxides with primary amine.
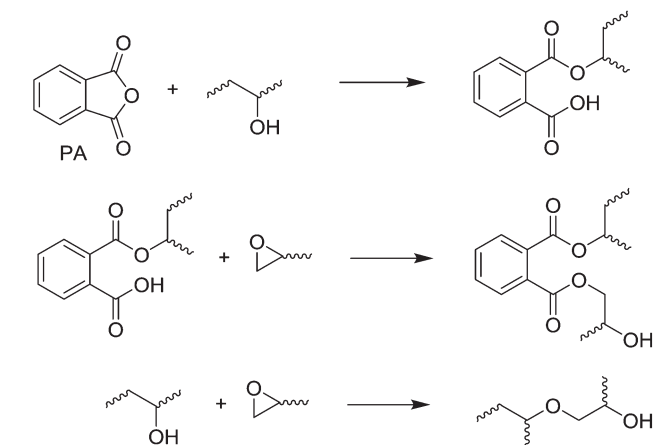
Scheme 2 Crosslinking of epoxy thermosets with acid anhydrides.[20]

Fig. 7 Monomers, initiators and fundamental reactions of photo-curable epoxy resins.

Lewis bases, including tertiary amines and imidazoles, are also used to cure epoxy resins. They can be used alone, where they function as nucleophilic catalytic curing agents for epoxy homopolymerization, or alternately as co-curing agents with primary amines and polyamides and as catalysts for anhydrides. The preferred reaction mechanism of tertiary amines with epoxies will depend on the presence or absence of proton donating moieties.[21] In the absence of protons, the tertiary amine will act as a nucleophile and ring open the epoxide to form a zwitterion (with the positive charge on the nitrogen countering a hydroxyl anion). This hydroxyl anion can then ring open another epoxide to form a new anion and thus propagate polymerization. In the presence of weak proton donators such as alcohols, chain transfer will occur from the zwitterion. In the presence of stronger proton donators (phenols and thiols), a proton is donated already to the amine, and the anion (phenyl or thiyl) serves as the nucleophile to open the epoxide ring. Commonly used tertiary amines include 2-dimethylamino-methylphenol (DMAMP) and 2,4,6-tris(dimethylaminomethyl) phenol (TDMAMP), which both contain phenolic hydroxyl groups and can be used as catalysts and co-curing agents for room temperature curing of epoxies.[20]

Photo-curing epoxy resins

Epoxy monomers can also be cured with light, where a photo-labile cationic initiator (typically an aryl sulfonium or iodonium salt)[22] is used instead of the traditional amine or anhydride coreactant. Polyols are widely used to improve the toughness of photo-curable DGEBA based resins[23,24] and in resins based on more flexible cycloaliphatic epoxides such as 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate (ECC in Fig. 7).[25] The differences between thermal and photo based epoxy resins are actually rather significant. With photo-curable epoxy resins, the photoacid generator or PAG (shown in Fig. 7 as an aryl iodonium salt) decomposes to give reactive intermediates which can abstract hydrogen atoms from solvent or monomer to give a Bronsted-acid. This acid then propagates
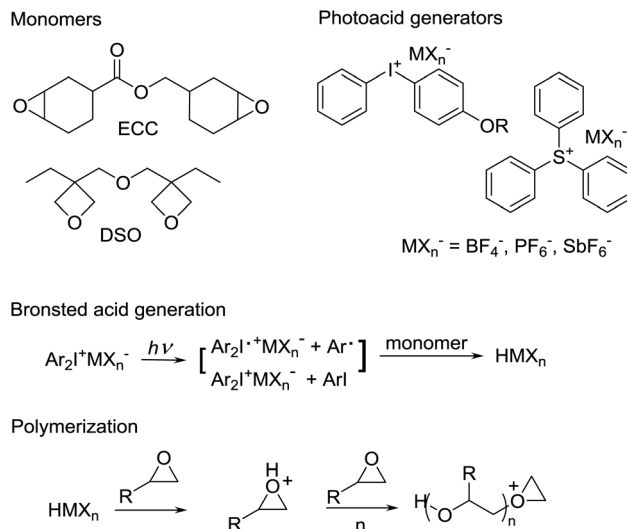
the cationic ring opening polymerization.[26] In addition to epoxide monomers, oxetane monomers (*i.e.* DSO in Fig. 7) may also be polymerized with PAGs. Oxetanes are commonly used in commercial additive manufacturing resins since they react fast and give polymers with low shrinkage and reduced moisture uptake relative to analogous polymers based on epoxies.[27]

Although less commonly used than PAGs, photobase generators (PBGs) can also be used to cure epoxides.[28–31] An early class of PBGs was based on [(benzoinyl)oxy]carbonyl protected amines, which release the free amine when exposed to UV irradiation.[32] The quantum yield of these early PBGs was often low, leading Arimitsu *et al.* to study quarternary ammonium salts of ketoprofen and of xanthone acetic acid.[33] Curing of aliphatic epoxides was conducted with a thiol coreagent, due to sterical hindrance and thus poor nucleophilicity of the generated tertiary amine. Allonas *et al.* used quarternary ammonium salts of phenylglyoxylic acid as PBG in combination with thiols to crosslink DGEBA resins. pK_a of the ammonium counterion was varied from 8.2 (DABCO) to 13.6 (tetramethylguanidine) which tended to increase the rate of cure as witnessed by disappearance of the epoxy signal in RTIR.[34] Addressing the issue of gas formation from decarboxylation of this class of PBG, Arimitsu *et al.* have also investigated *ortho*-hydroxy derivatives of cinammic acid.[35] Network formation with PBGs will depend on the presence of a coreactant such as a thiol but should be primarily step-growth as is the case with the traditional epoxy/amine thermoset (Fig. 4). Depending on stoichiometry and on the presence of latent moisture, a degree of anionic ring opening polymerization can also be expected.

Acrylates

Typical photoresins consist of a combination of structural monomers, photoinitiator, stabilizers and other additives such

as dye or filler all dissolved or dispersed within a reactive diluent.[36,37] Acrylate-based monomers undergo radical chain growth polymerization even at room temperature at a rate much faster than that of epoxy polymerization and are thus more readily applied in photo-curable coatings.[4,38] A typical acrylate-based resin will consist of oligomeric polyester, poly-urethane or DGEBA based diacrylates dissolved in a low viscosity reactive diluent such as dipropylene glycol diacrylate (DPGDA), trimethyloylpropane triacrylate (TMPTA) or pentaerythritol tetraacrylate (PETA).[39] Polymerization is triggered by a photoinitiator (either Norrish Type I or Type II).[40] Type I initiators are single molecules which decompose into radical fragments when exposed to light of an appropriate wavelength. Benzoin esters (such as that portrayed in Scheme 3) are commonly used. Benzyl acyl phosphine oxides, which can absorb above 400 nm, have become increasingly popular in the last twenty years. Type II photoinitiation systems consist of a light absorber or sensitizer (*i.e.* benzophenone as shown in the following figure) along with a coinitiator, which donates a hydrogen atom to the sensitizer and in the process provides the initiating radical. Tertiary amines are the most commonly used coinitiators.

Type I initiators are faster and can be used at a low concentration since both radical fragments are capable of initiating polymerization. Type II systems are still very common since they are typically less expensive and can be less sensitive to oxygen. Oxygen inhibition is a serious problem with acrylate polymerizations,[41,42] and additives such as tertiary amines (such as the Type II coinitiator depicted in the figure above) can be used to at least partially mitigate this.[43] The benefit of using multiple photoinitiators is exploited with broad wavelength light sources, where the lower wavelength absorbing initiator provides good surface cure and the longer wavelength initiator improves through cure.[44]

Methacrylates are less reactive than acrylates but are also much less toxic and are thus preferred in photo-curable dental resins.[45] Di-, tri- and tetramethacrylate monomers are formed
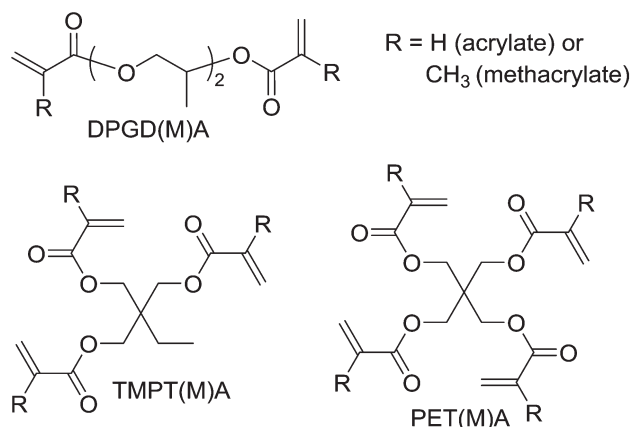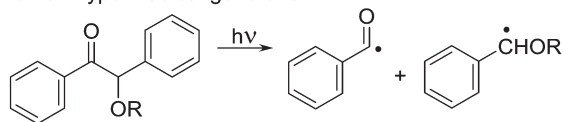

Fig. 8 Common acrylate (R = H) and methacrylate (R = CH₃) reactive diluents.

from the same alcohols used to produce acrylates (*i.e.* pentaerythritol) using methacrylic acid instead of acrylic acid as feed stock. Example monomers are indicated in Fig. 8. Due to high modulus and low shrinkage, the dimethacrylate of DGEBA (Bis GMA) is readily used. Dental restorative resins also contain fairly high loadings of inorganic fillers (typically 70–80 wt%), which has great bearing on resultant optical and mechanical properties.[46]
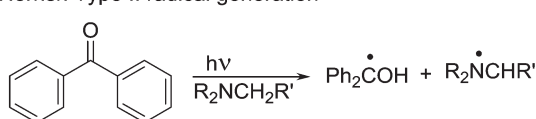
Typical photo-curable acrylate resins consist mainly of multifunctional monomers (*i.e.* diacrylates and triacrylates) where termination reactions are mobility restricted and thus autoacceleration is observed in the early stages of polymerization.[47] Usually, the kinetic chain length in early stages of polymerization is rather high, which contributes greatly to the formation of inhomogeneous polymer networks. Reduced termination causes an increased population of propagating radical chains, which are principally tethered to the polymer network. As the polymerization progresses, the majority of acrylate groups are tethered to the network making propagation diffusion controlled and autodeceleration is observed (Fig. 4).[48] Ultimately due to occlusion of both radicals and unreacted acrylate moieties, the final double bond conversion (DBC) for a "fully cured" acrylate system will always be some fraction of 100%. Formation of macrocycles and polymer backbiting are yet other phenomenon which will have bearing on mechanical properties and are both found to be more prevalent with flexible as opposed to rigid monomers.[49]

The addition of chain transfer agents to a radical curing system (*e.g.*, thiols, addition fragmentation chain transfer AFCT agents) can change the uncontrolled radical chain growth mechanism to a step-growth type polymerization process, enabling good regulation over the final polymer architecture by tuning crosslinking density, average kinetic chain length, and distribution of crosslinks alongside the polymer backbone. Hybrid systems consisting of both epoxy and acrylate monomers are also quite common (*i.e.*, interpenetrating networks; IPNs) and will be discussed in the IPN section.
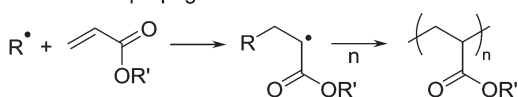

Scheme 3 Photoinduced radical generation, initiation and propagation.

Additives for toughening polymer networks

While photo-curing of thin coatings has been in industrial use since the early 1950s, crosslinking of polymers with heat has been known much longer. For a variety of reasons, organic and inorganic additives have essentially always been used to some extent in these polymer networks. Already in 1907 Baekeland recognized that phenol-formaldehyde resins were much tougher when they were compounded with wood fibres, rubber, or mineral powders.[50] Since then the development of thermosets has run hand in hand with the development of polymer composites. Acrylate-based coatings emerged in the early 1930s and by the mid-1940s lightly crosslinked acrylate polymers were being proposed as synthetic rubbers.[51] Bisphenol-A based epoxy resins were first developed in the 1940s.[52] In the mid-1960s McGarry and coworkers began examining methods to modify epoxy and polyester resins in order to improve the mechanical performance of the materials.[53] The mechanical properties of epoxy and acrylate based networks have improved tremendously over the last 50 years thanks to proper use of additives. Some of the more important classes of additives for thermosets are considered here.

Inorganic nanoparticles

While polymer composites based on macroscopic and microscopic inorganic particles have been in use for more than 100 years, the systematic use of inorganic nanoparticles in polymers is relatively new. In the early 1990s, Usuki and Kojima[54,55] reported a tremendous increase in the tensile strength of nylon 6 (by a factor of 5) with the addition of montmorillonite. It has been recognized since then that nanocomposites can show sometimes significantly altered electrical, optical or mechanical properties from the parent polymer. While this can also be said with most "non-nano" composites, change in properties can often be accomplished with a much lower loading of the inorganic component. Important for photo-curable coatings, particle size is much less than typical layer thicknesses and in some cases below the diffraction limit of the utilized light.

Although not fully understood, it is assumed when there are strong interactions between the nano-sized filler and the matrix that the polymer chains adjacent to the nanoparticles will behave differently from those surrounded by other polymer chains alone. Due to the very high surface area provided by nanoparticles, the portion of polymer in the vicinity of the nanoparticle surface can make up the majority of the matrix polymer already at moderate filler loadings and hence, novel properties can arise.[56] If adhesion between the filler particle and the matrix is high, debonding is restricted when stress is applied which results in increased modulus and strength (Fig. 9).

Another explanation for the sometimes unexpected thermomechanical properties of nanocomposites is chain confinement.[57,58] In this case when little or no interfacial interaction
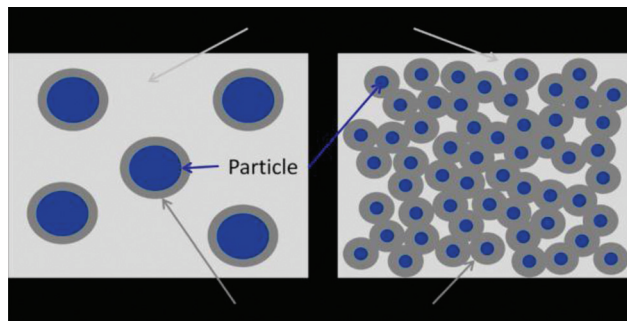

Fig. 9 Schematic comparison of interfacial polymer in conventional composites with micron-sized filler (left) and in nanocomposites (right).

between filler and matrix is present but the interparticle distance is small enough, the polymer chains between two adjacent nanoparticles will be confined in their motion and thus start to act like they would in a thin film.[59] Numerous studies have demonstrated that particle size as well as the morphology and the filler–matrix interaction play crucial roles in this process, but elucidation of the toughening mechanism has yet to be fully realized.[57,60]

Some of the better studied inorganic nanoparticle polymer additives include silica, alumina and $CaCO_3$. Zuiderduin et al. found that sub-micron $CaCO_3$ particles could increase impact strength of polypropylene from 2 to 50 kJ m^{-2} at high loadings.[61] The shift in the brittle-ductile transition temperature was found to shift by up to 50 °C with dependence on both particle size and the presence of surfactant.[62,63] Similar improvements have also been found with polyethylene.

Although the toughening effects of inorganic nanoparticles in thermosetting resins is not as remarkable as the results obtained for thermoplastics, improvements in fracture toughness have at least been made.[64,65] For example, a number of studies have been conducted using inorganic nanoparticles to improve the toughness of epoxy-based thermosets. The usual base material in these works is DGEBA or a related diepoxide.[66] A popular choice of inorganic filler for epoxy resins is surface modified silica nanoparticles, also known as fumed silica. Fumed silica typically has a mean diameter of approximately 20 nm and in some cases has a narrow particle-size distribution. In one study, epoxy formulations cured using different agents (i.e. methylhexahydrophthalic acid anhydride (AD600), polyether-amine (J230) and 4,4′-diaminodiphenyl sulfone (DDS)) were tested with different particle loading. Addition of up to 20 wt% of silica nanoparticles was found to increase the Young's modulus by 50% while maintaining the original T_g of the material. The fracture toughness was increased by a factor between 1.7 and 2.4. Sangermano et al. found that the addition of 4 vol% 150 nm Al_2O_3 NPs improved both toughness and scratch resistance of photocured cycloaliphatic epoxies.[67]

Other thermosetting materials successfully toughened with fumed silica include tetraglycidyl-4,4′-diaminodiphenylmethane[65] (fracture toughness K_{IC} increased by a factor of 2.2),
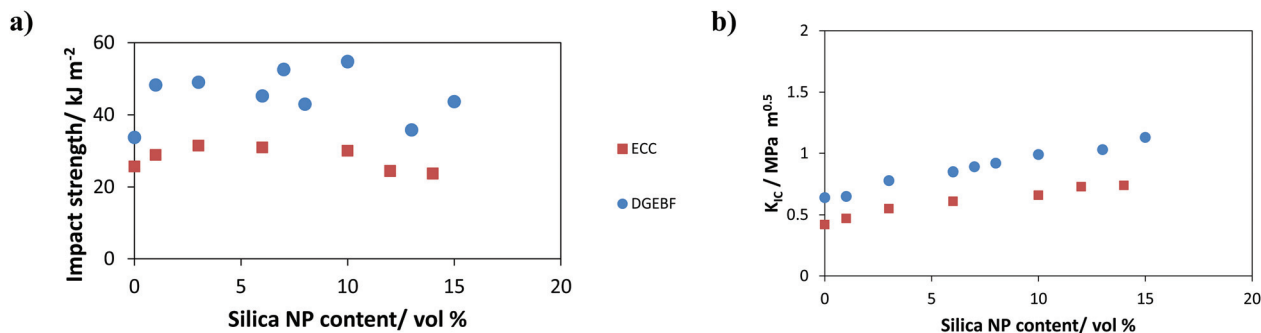
Fig. 10 Toughening effects of SNPs on epoxy thermosets.

3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate (ECC)[68] and diglycidyl ether of bisphenol AF (DGEBF).[69] The results of the latter two works regarding toughness improvements are summarized in Fig. 10. Similar to Zhang, Mahrholz *et al.* also reported an increase by a factor of 1.5 in the DGEBA-SNP system.[70]

Rubber

Natural and synthetic rubbers have long been used to improve the mechanical properties (and particularly the impact strength) of a variety of organic polymers and inorganic materials.[71] An early example is provided by Aylsworth who in 1914 added natural rubber and sulphur to the polymerization of phenol and formaldehyde producing a tougher plastic that was used for early phonographic discs (before vinyl).[72] In the late 1940s Dow introduced high impact strength polystyrene (HIPS) formed by adding polybutadiene to styrene monomer and stirring vigorously during polymerization.[73] Not long afterwards acrylonitrile was added to the mixture which provides ABS plastic. Impact strength of HIPS is 2 to 4 times higher than polystyrene and ABS can be more than 8 times as strong (Izod impact >400 J m^{-1}).[74] The morphology of ABS and HIPS are not homogenous but consist of micron sized butadiene or styrene-butadiene rubber (SBR) particles dispersed within a continuous phase (polystyrene or polystyrene–acrylonitrile).

Not long after this early work with thermoplastics, rubber began to be tested as a toughening additive for epoxy-based thermosets. Epoxy resins, and more specifically those based on DGEBA, find widespread application and one principal reason for this is their high modulus. This modulus arises principally from the rigid and highly crosslinked architecture of the polymer, which is also responsible for its major drawback: poor impact strength.[16] Rubber additives thus tend to be used sparingly since they should increase toughness and at the same time not lower the modulus or effect the T_g. Recognizing proper phase separation as an integral component to rubber toughening in epoxy resins, two strategies have developed both to control particle size and to regulate the rubber–matrix interface. The first strategy is based on low molecular weight "liquid rubbers" and the second is based on preformed core–shell particles.[75]

Liquid rubber

The term "liquid rubbers" is commonly used to refer to elastomeric polymers which have a sufficiently low molecular weight in order to maintain low viscosities to enable homogeneous mixing with the epoxy resin. The most commonly used liquid rubbers are based on polybutadiene or acrylonitrile–polybutadiene copolymers with varying acrylonitrile-content. To improve interfacial adhesion to the polymer matrix, liquid rubbers are usually endcapped with functional groups capable of reacting with it. The most common modification is a carboxyl-endgroup giving carboxyl-terminated butadiene (CTB) or carboxyl-terminated butadiene-acrylonitrile (CTBN), but amino- (ATB/ATBN), epoxy- (ETB/ETBN) or vinyl-modified (VTB/VTBN) compounds are commercially available as well (Fig. 11). The first attempt to utilize this approach in order to improve the toughness of brittle epoxies was made by Sultan and McGarry using butadiene–acrylonitrile rubber.[66]

Russell and Chartoff showed that the fracture toughness of DGEBA-based thermosets could be improved by a factor of 2 by adding CTBN. They also showed that the volume fraction of the phase separated domains were up to twice as large as the amount of utilized liquid rubber.[76] It was then shown that the modulus of the phase separated domains had a greater influence on the toughness of the material than the volume fraction. Bagheri *et al.* also tested CTBN in DGEBA and reported a size-dependence of the phase-separated domains with respect to the rubber loading. The higher the rubber content, the larger the average domain size (from 0.3 μm for 1 wt% to 0.7 μm for 15 μm). Resultantly the fracture toughness could be increased by a factor of 2.3 at 5 wt% CTBN.[77] Kunz

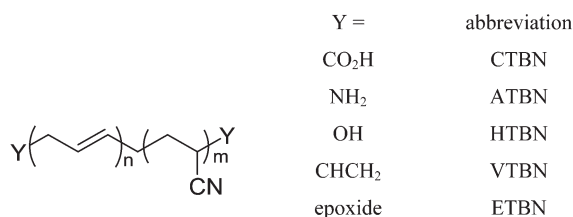| Y =	abbreviation
CO$_2$H	CTBN
NH$_2$	ATBN
OH	HTBN
CHCH$_2$	VTBN
epoxide	ETBN

Fig. 11 End-capped liquid rubbers for toughened thermoset resins.

et al. also tested the CTBN/DGEBA system and showed a 2.5-fold increase of the fracture toughness at 5 wt%. The same increase was obtained at higher rubber loadings while the modulus was linearly decreasing with increasing rubber content (from 2.96 to 2.25 GPa for 15 wt% CTBN). ATBN-rubber additives were also tested and found to provide almost identical results.[78] Chikhi *et al.* obtained different results when using the same ATBN-rubber in DGEBA-resin, when they showed a fracture toughness improvement by a factor of 1.5 with a distinct maximum at 12.5 wt% additive. The impact strength however, could be enhanced by up to 3 times its original value at the same rubber concentration.[79] Thomas *et al.* employed hydroxyl terminated polybutadiene (HTPB) to toughen DGEBA. Addition of 10 wt% of HTPB caused a 1.5-fold increase in impact strength from 9.2 to 13.6 J m^{-2} while fracture toughness was 5 times higher than that of the neat epoxy-resin.[80] Interesting results were published by Kong *et al.*, who synthesized a liquid rubber possessing pendant epoxy groups. This modifier increased the impact strength by a factor of 1.75 at a rubber loading of 5 wt% with only a moderate decrease of the modulus and heat resistance of the toughened material.[81]

Although the application of liquid rubbers has been predominantly studied for epoxy systems, there are a few publications dealing with the usage of these modifiers for other thermosetting materials including unsaturated polyester resins and vinyl ester resins.[82] It should be mentioned that the term vinyl ester in this context actually refers to methacrylic monomers, usually the products of reacting DGEBA with methacrylic acid to yield the respective dimethacrylate. Due to its high viscosity this compound is usually cured with the addition of approximately 50 wt% of styrene to simplify handling. Robinette *et al.* has tested the usage of ETBN and VTBN while Auad *et al.* compared VTBN and CTBN.[83,84] The impact on modulus and fracture toughness (quantified as critical stress intensity factor K_{IC}) is depicted in Fig. 12.

It can be seen that an improvement in fracture toughness was achieved although at the expense of the stiffness of the material. Also, distinct differences in performance are noted for the different end groups of the tested liquid rubbers. CTBN exhibits a distinct maximum in toughness at around 5 wt%

loading while the copolymerizable VTBN has to be incorporated in larger amounts. The difficulties in toughening of these systems can be attributed to the differences in network formation. While traditional epoxy systems cure *via* a step growth mechanism, vinyl esters polymerize by a cationic or free radical chain growth mechanism. Celikbilek *et al.* evaluated the usage of endcapped polydimethylsiloxane (PDMS) in DGEBA resins but were not able to observe any improvement in terms of impact strength or fracture toughness.[85]

Preformed particles

Not long after the first experiments with liquid rubbers, a related technique was introduced, based not on liquid oligomers but on solid, preformed particles of an elastomer.[86] These particles are often termed "core/shell-particles" (CSPs) since the actual toughening part – the elastomeric core – is usually coated with a thin layer of a glassy shell. In the absence of this shell, the elastomeric particles are not stable and stick together. The shell thus prevents agglomeration and allows the particles to hold their size and shape well above the T_g of the rubbery core.[87] While standard CSPs consist of an elastomeric core and a glassy shell, there are other variations mentioned in the literature. One example is a multi-layer CSP with a glassy core as well as a glassy shell with a rubbery interlayer.[88] The toughening mechanism is similar to conventional CSPs.

Marouf *et al.* used CSPs consisting of a styrene/butadiene core with a PMMA-shell to improve the mechanical properties of a DGEBA-based resin. They reported an increase of the fracture toughness by a factor of 2.3 with the addition of 5 wt% CSP.[89] Similar results for this system have been published by other authors.[75,77,90,91] Fig. 13 provides a comparison of a selection of this data. Generally speaking, fracture toughness could be improved significantly, and the effect was noticeable already at comparably low loadings.

Jingqiang *et al.* synthesized CSPs based on a soft polyurethane-core and were able to increase the impact toughness of the DGEBA resin by a factor larger than 3 (from 2.25 to 7.6 kJ mol^{-1} with 8 wt% filler).[92] Subramaniyan *et al.* used commercial CSPs in a vinyl ester/styrene matrix but they were not able to show toughness improvements at loadings of 5 wt%.[93] Lin and Shieh carried out a thorough study
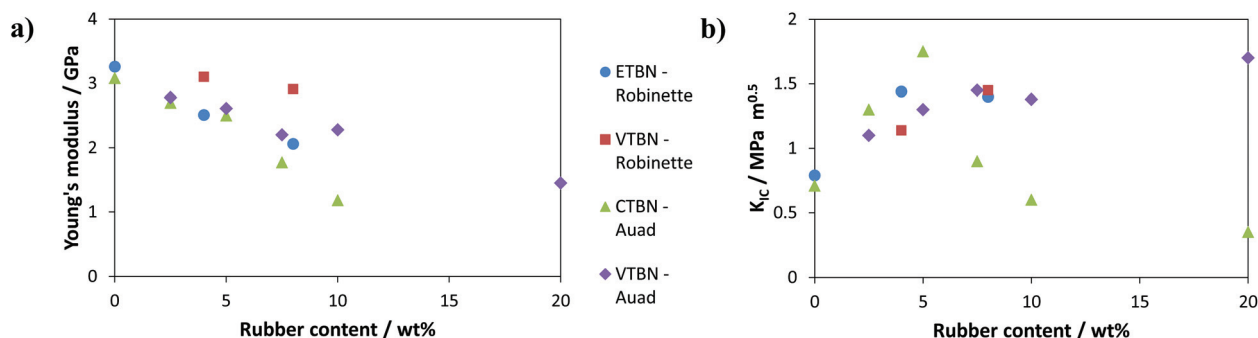

Fig. 12 Effect of LRs on Young's modulus (a) and fracture toughness (b) of vinyl ester resins.
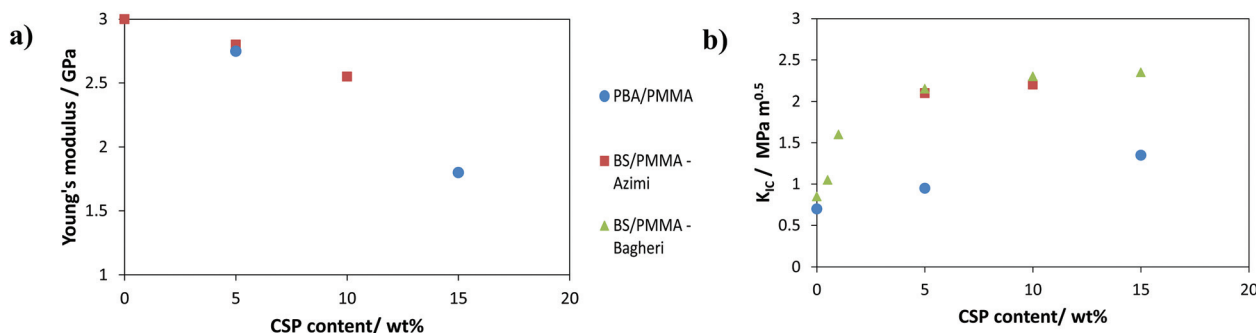
Fig. 13 Effect of CSPs in DGEBA epoxy resins on Young's modulus (a) and fracture toughness (b). Note: Bagheri *et al.* provide values for toughness of BS/PMMA CSPs but do not give values for modulus.[77]

investigating optimum particle size and modifier loading as well as the influence of copolymerizable groups in the shell. The best thermomechanical properties were obtained with average CSP-diameters around 300 nm; the optimum loading for high fracture toughness was around 20 wt%. The presence of reactive groups in the shell was also found to have a positive effect on the toughness of the composite.[94] Naguib *et al.* have more recently confirmed this finding by adding up to 15 wt% PBA/PMMA-PGMA CSPs to cycloaliphatic epoxy resins.[95] Noting reaction of GMA epoxy units with the matrix, impact strength was improved at all tested concentrations and T_g was not affected.

In addition to the previously discussed CSPs, another type of preformed rubber particle has recently been commercialized. Similar to silica nanoparticles, these rubber particles are prepared in the resin monomer. Since the particles are suspended in the resin as a master batch, there is no need for drying and the problem of agglomeration is avoided. He *et al.* and Le *et al.* both employed this type of modifier in DGEBA. Since the type of rubber and the particle sizes were not the same in these 2 publications, the observed behaviour was also slightly different.[96,97] He *et al.* reports a 4-fold increase of the fracture toughness with 500 nm particles at 12.5 wt% loading while Le *et al.* found a 3-fold increase for the 55 nm particles at 5 wt%. In addition to conventional dispersions of rubber-particles, preformed particles based on polydimethylsiloxane (PDMS) are also commercially available. Due to their production process these are, however, only available as master batches in a liquid monomer. PDMS has other advantages for this application since it provides an extremely low T_g and is very hydrophobic. Rey *et al.* used larger 4 μm particles and were able to achieve a moderate increase of the fracture toughness of DGEBA by a factor of 1.5; however, the Young's modulus was also significantly reduced.[98] Bittmann and Ehrenstein used smaller PDMS-particles with an average diameter around 0.5 μm in ECC and reported a slight improvement in toughness. The influence on the stiffness of the material was not disclosed.[99]

Self-assembly of block copolymers

Jordan *et al.* stated in their review on trends in nanocomposite technology that for most toughening agents, the efficiency of

the filler in the composite is inversely proportional to its size but directly proportional to its surface/volume ratio.[59] This concept has been well exploited with the inorganic nano-particles mentioned earlier. By comparison, the application of rubber nanoparticles did not receive its due notice until more recently. The preparation of rubber nanoparticles as toughening agents is rather demanding since conventional techniques require either the subsequent addition of a rigid shell or the preparation of the particles within the resin to prohibit agglomeration of the particles. A very elegant method to circumvent these restrictions is provided by the self-assembly of block copolymers (BCs). In 1997 Hillmyer *et al.* were the first to report the formation of nanostructured aggregates (micelles) upon the addition of BCs into epoxy resin.[100] After this, numerous publications investigating the behaviour of amphi-philic BCs in thermosetting matrices with emphasis on their effect on the mechanical properties of epoxy resins have been released. Ruiz-Pérez *et al.* give a compact summary of some of the endeavours to toughen epoxy resin with the aid of BCs.[101] They suggest a differentiation between three categories of BCs:

• Non-reactive BCs that self-assemble in the uncured state due to the presence of an epoxy-miscible and an epoxy-immiscible block. This order in the uncured state is subsequently fixed during the polymerization.[100,102–105]

• Non-reactive BCs where both blocks are initially miscible and one of them undergoes microphase separation during the crosslinking reaction of the matrix. In this case, the morphology is generated during the curing process.[106–109]

• BCs where the resinophilic block contains reactive groups enabling copolymerization with the surrounding matrix. For this group, the other block is immiscible and thus the final morphology is established prior to cure.

Diblock- or triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) (*i.e.* PEO-*b*-PPO or PEO-*b*-PPO-*b*-PEO) have been investigated by multiple groups since they are commercially available and applied as non-ionic surfactant in detergents.[110,111] These publications primarily focused on the microphase morphologies and polymerization kinetics and not so much on the mechanical properties of the resulting material. Since PEO and PPO both are relatively hydrophilic polymers, phase separation does not occur until
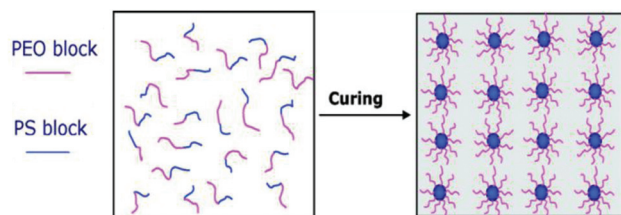
Fig. 14 Reaction-induced microphase separation in BC-toughened thermosets. Reprinted with permission from *Macromolecules*.[109] Copyright 2006 American Chemical Society.

the polymerization stage. This results in microphase-separation similar to that exhibited by the PS-PEO block copolymer system (Fig. 14) where in both cases the resinophilic PEO block maximizes contact with the DGEBA-matrix. Other examples for reaction induced phase separation include poly(ε-caprolactone)-*b*-polybutadiene-*b*-poly(ε-caprolactone) (PCL-PB-PCL) dispersed in DGEBA.[109,112,113]

BCs which undergo self-assembly in the uncured state typically consist of blocks of polymers with a more pronounced difference in polarity. Examples of such block copolymers include PEO-*b*-polyethylene (PE) or PEO-*b*-poly(ethylene-*alt*-propylene) (PEP). PEO-PEP copolymers in DGEBA have been extensively investigated in the work by Dean *et al.* and Liu *et al.*[114,115] With this system, parameters such as block ratio, BC molecular weight and the crosslink density of the matrix are shown to have a strong impact on the self-assembled structures. Not too surprisingly, the morphology itself was found to be a crucial parameter contributing to bulk mechanical properties. An improvement in fracture toughness by a factor of almost 3 was reported by Liu,[116] which is an exceptional result compared to others where toughness was enhanced only to values twice as large as that of the neat resin. With only 5 wt% of the PEO-PEP modifier, Young's modulus and heat deflection temperature remain almost unchanged. Ocando *et al.* used PS-PB with different degrees of epoxidized double bonds in the PB-block also in a DGEBA-based resin. They reported less significant improvements in toughness and also observed significant lowering of stiffness and heat resistance.[102]

Bates and coworkers also used diblock copolymers of PEO with poly(butylene oxide) (PBO)[117] and poly(hexylene oxide) (PHO)[118] in DGEBA. Since the contrast of their small angle X-ray apparatus was too low, no information on the behaviour of these BCs in the uncured state is given. Nevertheless the fracture toughness could be increased by a factor of 4 for PEO-PBO and by a factor of 6 for PEO-PHO where the block ratio used resulted in the formation of cylindrical structures. The Young's modulus was reduced by approximately 20% and, most interestingly, the T_g was significantly increased. Similar observations have been reported elsewhere;[117] however, no explanation for this surprising behaviour is provided.

Another popular type of BC that has been employed for the toughening of thermosetting materials are compounds based on PDMS. PDMS is inherently incompatible with almost every standard resin system, which necessitates other additives or clever synthesis to avoid macrophase separation. Riffle *et al.* were the first to propose the preparation of linear block copolymers to fulfil this requirement.[119] The behaviour of silicone-based BCs of this type in thermosetting matrices was then tested by various researchers.[120,121] The evaluation of their potential as toughening agents for DGEBA was conducted by Könczöl and Mülhaupt while Bittmann and Ehrenstein used a similar silicone BC additive in a cycloaliphatic epoxy resin (ECC).[122–124] Fig. 15 shows the impact of the silicone BCs on fracture toughness (K_{IC}) and glass transition temperature (T_g) of these two epoxy resin systems.

Fig. 15 well illustrates how sensitive the application of BCs can be depending on the compatibility of the modifier and the matrix. For the system investigated by Könczöl, microphase separation of 20 nm silicone domains was observed leading to significant improvements in toughness without inadvertently affecting the thermal stability of the material.[122] By comparison, Bittmann did not report the formation of any nanostructures.[99] It was also noted though that the glass transition temperature decreased with higher BC-loadings while fracture toughness reached a maximum with 5% additive. This indicates that the modifier remains dissolved even after curing.

A very interesting feature of using BC additives is the possibility of simultaneously increasing toughness and heat resistance,[125] a phenomenon which appears somewhat contra-
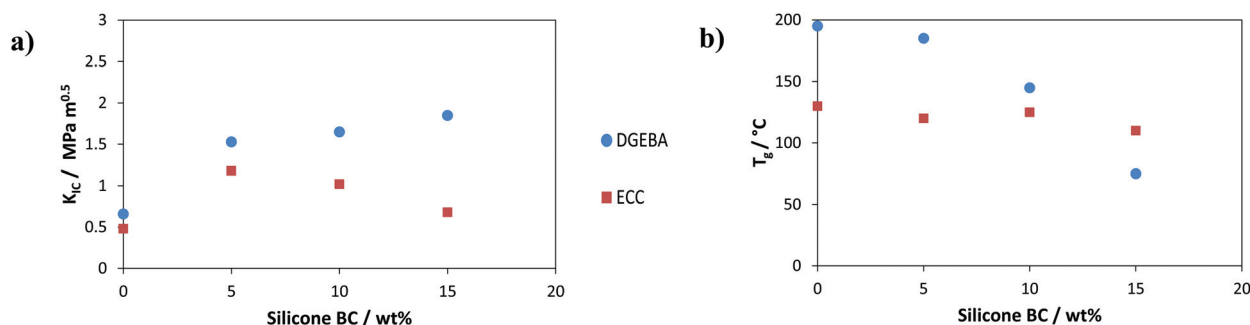

Fig. 15 Effect of CSPs in DGEBA epoxy resins on toughness (a) and glass transition temperature (b).

dictory and is still not well understood. Toughness enhancement is dependent on both domain size and on morphology of the self-assembled BCs (*i.e.* micelles, vesicles or cylinders).[126] Liu *et al.* found that cylindrical micelles of PEP-PEO provide improved toughness in DGEBA-based resins in comparison to resins with spherical micelles.[116] Wu *et al.* synthesized block copolymers of partially sulfonated PS and poly(ethylene-*co*-butylene) and used these to modify DGEBA based resins. Fracture toughness was increased with the addition of the BCs and was found to reach a maximum where degree of sulfonation was equal to 5.8%.[127] TEM show that the particles were flattened, but with higher degree of sulfonation the resinophilic block penetrates into the epoxy matrix making phase separation less apparent.

Special monomers and curing agents for tough epoxy polymers

Epoxy monomers. The mechanical properties of thermosetting, crosslinked polymers are closely related to the underlying molecular architecture. High crosslink densities lead to very stiff and thermally resilient materials, however; these benefits come at the expense of the toughness of the respective polymer. For instance, phenol-formaldehyde epoxy Novolacs (with epoxy functionality between 2.2 and 3.8) are prized for high chemical and thermal stability, but are also notoriously brittle. Other monomers such as tris[4-(2,3-epoxypropoxy)-phenyl] (TEPP in Fig. 16) have been found to provide polymers with high thermal resistance and superior toughness.[128] Monomers such as diglycidyl ether of tetramethyl biphenol (DGETM) have low viscosity and allow high filler loading (up to 90%). Resultant composites have low coefficients of thermal expansion, which manages thermal shock and provides better crack resistance.[129] In the 1980s Dow Chemical developed liquid crystalline epoxy monomers including the diglycidyl ether of α-methyl stilbene (DGEMS), which imparts excellent thermal and mechanical properties.[130] Copolymerization of these specialty epoxy monomers with DGEBA allows polymers with mechanical properties intermediate to the homopolymers. Low molecular weight hyperbranched polyesters with terminal epoxy moieties have also been used to modify DGEBA. With the addition of 30 wt%, impact strength increases from 0.41 J cm^{-2} to 0.73 J cm^{-2} while the T_g is lowered by roughly 20 °C.[131]
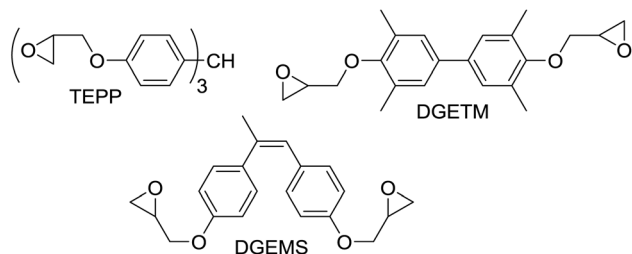

Fig. 16 Alternative epoxy monomers reported to improve polymer toughness.

Amine and anhydride curing agents. The choice of curing agent for an epoxy resin will depend on the application, where pot life, cure conditions and ultimate physical properties are all to be considered. Polyether and polysiloxane amines have long been used in combination with DGEBA to provide polymers with reduced brittleness *versus* those formed with simple alkyl amines.[132] Long chain alkylene diamines such as hexamethylene diamine (HMD) and cycloaliphatic amines such as isophorone diamine (IPDA in Fig. 17) provide resins with longer pot life and polymers with better toughness. Polyamide amine curing agents formed from dimerized and trimerized vegetable oil fatty acids with diamines are commonly used in industry, and provide flexible films with good adhesion to concrete. Amidoamines formed from alkyl amines and monofunctional fatty acids have performance similar to polyamides but with lower viscosity.[133] Huntsman markets Jeffamine® polyetheramines with different molecular weights and degrees of amine functionality.[134] For the curing of epoxides, the carbon adjacent to the terminal amine moieties is secondary, which sterically hinders nucleophilic reactions and provides good shelf life and "moderate" reactivity. Acid anhydride curing agents can also be used to give epoxy polymers with high toughness, where stoichiometric quantities of reagents and high temperature curing are found to give the best results. The monomer methyl tetrahydrophthalic anhydride (MTHPA) is the highest volume anhydride curing agent. The controlled use of less reactive tertiary amines has also been used to regulate the morphology of DGEBA. Hsu *et al.* reacted quantitative amounts of 2- and 1-methyl imidazole with DGEBA prior to addition of 4,4′-methylene dianiline (MDA) curing agent.[135] Thermal curing provides networks with nanostructured domains as seen by AFM. Although the imidazole concentration is never more than 0.6 wt%, tensile and fracture toughness are both significantly increased while T_g is decreased. Interestingly thermal stability was in all cases with imidazole slightly higher.

Hydroxyl curing agents. Amines and anhydrides are not the only reagents for curing epoxies. Aromatic alcohols (phenols) and poly phenolic Novolacs are used in high temperature curing of epoxy resins, where the cured systems find use in electronic encapsulation applications.[20] Aliphatic alcohols are less reactive towards epoxides and are not likely to be used alone as curing agents. They are however commonly used to lower viscosity of resins and to modify the reactivity of the amine curing agent. With hindered amines, or with primary amines at higher conversion, alcohols can act as accelerators. Lower molecular weight alcohols such as benzyl alcohol are commonly used as epoxy plasticizers, where they can be cured into the network at higher temperatures.

In photo-curable DGEBA based resins, aliphatic polyols are commonly used. In combination with cationic initiators, aliphatic polyols are found to react significantly faster than phenolic additives.[136] Lützen *et al.* examined polycaprolactone (PCL) diols of different molecular weights in copolymerization with ECC.[137] In comparison to the neat epoxy, the ECC-PCL copolymers have greater fracture toughness and lowers T_g
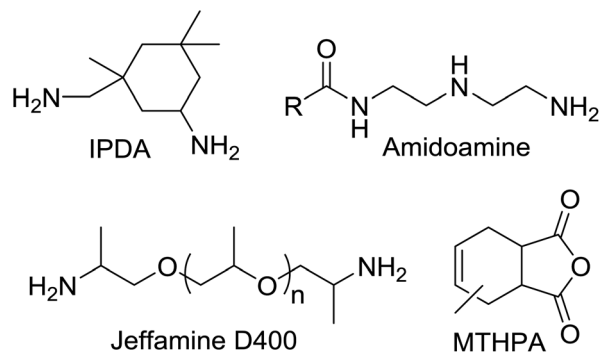
Fig. 17 Amine and anhydride curing agents claimed to give tougher epoxy polymers.

values. The shift in both values is dependent on wt% of PCL and on molecular weight, where lower molecular weight PCL has a more dramatic effect.

In comparison to linear polyols, dendritic and hyper-branched polyols are found also to improve toughness without significant reduction in modulus.[138] Manjula Dhevi et al. used hexamethylene di-isocyanate to couple hyperbranched polyesters into DGEBA-based resins.[139] The resultant IPN polymers were tougher than the neat DGEBA polymer tough-ened with a comparable weight of linear polyurethane diol. Thermal stability and T_g were however lowered. Foix et al. have studied hydroxy terminal hyperbranched polyesters as additives for epoxy resins and seen an accelerating effect during cure followed by phase separation.[140,141] Improvement in mechanical properties was however most promising when the hyperbranched additives are epoxy terminal.[131]

Considerations for radical chain growth

Interestingly, several attempts by the authors of this review using different particle toughening strategies suitable for epoxy thermoset resins have not been forthcoming when applied to acrylate networks.[142] Differences in the manner in which the epoxy and acrylate networks form provide clarification.

The absence of a significant change of polarity during network formation in radical photopolymerization seriously hinders the efficient use of polymerization-induced phase separation, which has been extensively used in thermosetting epoxy systems.[21,32,35,143] This means a system comprising of two or more phases must already be present in the uncured polymerization mixture.

Liquid rubbers above a certain concentration improve the toughness of the rigid photopolymers both under low and high strain rates. However, especially at higher contents of LR, one has to sacrifice the stiffness of the material to a certain extent. Moreover, high concentrations of LRs tend to signifi-cantly increase the viscosity of the respective formulations,

which can become a limiting factor for many applications since highly viscous resins often cannot be processed properly.

Block copolymers also exhibit the potential to modify the mechanical properties of photopolymers (in particular flexibility and impact toughness). While improvements in terms of toughness can be made, this is generally accompanied by a reduction in polymer modulus.[142] This indi-cates that the BCs at least partially remain dissolved in the matrix and in this manner act as plasticizers similar to LRs.

For CSPs to act as toughening agents in thermosetting materials, good adhesion between the dispersed particles and the polymer matrix is required. However, due to high shrink-age, which is typically associated with the photopolymerization of acrylates, good adhesion is difficult to obtain with conven-tional CSPs. Sandmann et al. used particles with EGDMA/PBA cores and PMMA shells to improve the mechanical properties of urethane dimethacrylate/TEGDMA based dental composites.[144] Best results were found with a core–shell ratio of 30/70, which showed a fracture toughness of 1.21 MPa m$^{1/2}$ (an improvement of 65%), a flexural modulus of 1.90 GPa (an increase of 18%) and a flexural strength of 79 MPa (also an increase of 18%). Success in this case is likely due to good compatibility and thus adhesion of the PMMA shell with the TEGDMA matrix and reduced polymerization shrinkage of the urethane based monomer.

Silica nanoparticles on their own provide no significant improvement in the toughening of the tested acrylate-based polymer networks.[142] However, they have the potential to improve other mechanical properties such as stiffness or hard-ness without affecting any of the other material properties. This behaviour would make SNPs an interesting candidate for a "co-modifier" since they obviously have the ability to coun-terbalance reduced stiffness caused by other additives.

In general the proven concepts for toughening of epoxy thermosets could not be directly transferred to photopolymer-ized acrylate-networks. Consequently, in order to fabricate tough photopolymers, the simple use of an additive seems not to be sufficient. Instead, alternative monomers or monomer systems may be required to change the underlying network structure. An optimized architecture of the photopolymer can not only exhibit a better toughness but can also support the 'toughenability' of the resulting material, which would allow conventional additives to have a more pronounced effect.[16,32,134]

The photoinduced polymerization of multi-functional acrylates is a complex process where the ultimate polymer architecture will be dependent on monomer composition, photoinitiator concentration and curing conditions. Generally Type I photoinitiators have higher quantum yields than Type II systems and will thus be used in a lower concentration.[30] Kinetic chain length is proportional to the rate of propagation and inversely proportional to rates of initiation and termin-ation.[145] Values calculated for photo-cured acrylates at low conversions were from 2000 to 10 000 monomer units per radical depending on whether the reaction was performed in air or in nitrogen. Formation of inactive peroxy radicals is the

principal culprit for the lower value.[42] In a multifunctional acrylate system, the average kinetic chain length will decrease dramatically as gelation occurs and ultimately at high conversions approaches zero. The implications on polymer architecture are that the distance between crosslinks will be highly irregular. Resulting inhomogeneously crosslinked photopolymer networks tend to be very brittle and show low toughness.

Where photo-curing of even a single difunctional monomer leads to complex architecture, the situation does not get simpler with a more typical formulation consisting of 3 or 4 different monomers with different structures, molecular weights, and number of pendant photopolymerizable moieties. Touching on the first of these subjects, Jansen *et al.* found that acrylate monomers that form hydrogen bonds or that are more polar tend to polymerize at higher rates. This can be ascribed to monomer preorganization and possible cage effects with the propagating radical.[146] Hydrogen bonding also has a strong effect on the mechanical properties of the crosslinked polymer. Torres-Filho and Neckers added different diacrylate monomers to a resin consisting of tri- and pentaacrylates and found that with butanediol and short PEG diacrylates, Young's modulus and tensile strength both tended to decrease.[15] By comparison, addition of 10 wt% of a hydrogen bond forming polyurethane diacrylate increased both values. Polyurethane diacrylates are cited in a number of patents for improving mechanical properties.[147,148] The polyurethane can vary in molecular weight and composition, where one popular class is based on "soft" polyether diols copolymerized with "hard" aromatic diisocyanates. Crystalline "hard" domains tend to phase separate from the "soft" domains which helps to improve toughness and in some cases provide materials with unusually long elongation at break.[149]

Photo-curing conditions and photoinitiator concentration also contribute to toughness.[150] For practical reasons, it can be difficult to find tensile or impact testing results for incompletely cured polymer samples. Real time FTIR (RTIR) and photorheology, however, provide equally useful insight into the process of network formation.[151] With the first technique, the integral of the acrylate $C=CH_2$ stretch is followed and referenced to its starting value to provide double bond conversion (DBC).[41] Generally the hardness of a material will increase with DBC, but is also heavily influenced by monomer structure. For example, TMPTA cured with a medium pressure Hg lamp for 60 seconds will have a DBC of approximately 60% and a Persoz hardness of 280 s while DPGDA under the same conditions will have a DBC of 90% and a Persoz hardness of only 120 s.[152] Irradiance conditions are also important and particularly in the presence of oxygen. Decker *et al.* cured DGEBA diacrylate resins and found DBC after 10 seconds to be only 26% when cured with a 20 mW cm^{-2} source *versus* 50% with a 55 mW cm^{-2} source. For laminated samples, the difference is much less: 93% with 20 mW cm^{-2} *versus* 95% with 55 mW cm^{-2} irradiance.[153]

While high intensity light and adequate concentration of photoinitiator are both needed to provide polymer hardness, too much of either of these can be detrimental. Using a resin consisting of MMA with TMPTA (Fig. 8), Cunico and Carvalho found that photoinitiator (PI) concentration had a tremendous effect on both modulus and tensile strength.[154] Thus polymers cured for 20 minutes with 5 wt% PI (Omnirad 2500 from IGM) were on average 40% stiffer and half as strong as those cured with 2 wt% PI. Interestingly DBC for the polymer with 2 wt% PI was 90% after 60 seconds while the value was only 65% for the same polymer with 5 wt% PI.
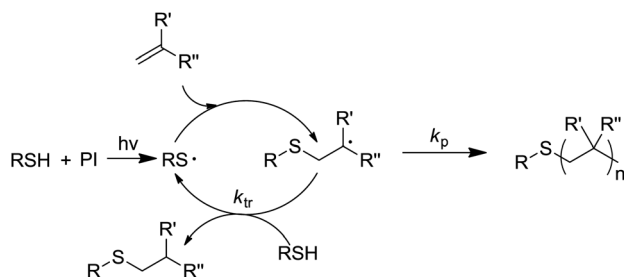
Chain transfer

With recognition that rapid gelation (frequently as low as 20% double bond conversion) and high crosslinking density are prime factors contributing to the brittleness of photo-cured systems, coreactants that can regulate network formation have been investigated. Chain transfer agents, which have been used for many decades to regulate the molecular weight of linear polymers, began to be tested for regulating photocurable resins as well.[155] Amines are commonly used as coinitiators in Type II systems and to reduce the effects of oxygen inhibition.[156] In both roles they act as hydrogen donors, which in the latter case is also an example of chain transfer. Thiol based chain transfer agents readily react with acrylates and other vinyl compounds and provide a versatile platform for regulating cure kinetics as well as mechanical properties of the final polymer.[157]

A number of other methods for regulating a free radical polymerization are described in literature (*e.g.*, reversible addition fragmentation chain transfer (RAFT)[158] and atom-transfer radical polymerization (ATRP)[159] but almost exclusively for linear polymers. Irreversible addition fragmentation chain transfer (AFCT)[158] reagents also have the potential to regulate radical polymerization reactions. AFCT proceeds similarly to the polyreaction of thiol–ene/yne[160–162] systems in a mixed chain growth/step growth-like mechanism. For photopolymerizable crosslinking systems, the thiol–ene and AFCT approaches seem to be more promising today, since RAFT and ATRP reagents tend to have strong UV/vis absorbance and more importantly have strong retardation.

A good measure for the ability of a chain transfer agent to regulate a radical photopolymerization is the chain transfer constant ($C_{tr} = k_{tr}/k_p$) which is described by the ratio of the reaction constant for chain transfer (k_{tr}) to the reaction constant for monomer propagation (k_p). However, this value is greatly influenced by a number of different factors such as monomer reactivity, functionality of the chain transfer agent, reaction temperature, radical initiation, solvent, and conversion.[163]

Thiol–ene/–yne chemistry

The history of photo-induced thiol–ene chemistry is as old as that of acrylates,[164] but has flourished much less primarily due to problems with odour and storage stability.[165] Thiols act as potent hydrogen donors in the presence of appropriate sensitization. A photoinitiator (PI) is not essential but allows the radical formation to proceed at a greater rate. The resultant

Scheme 4 Radical reactions of double bond in the presence of thiol chain transfer agent.

Table 1 Chain transfer constants (C_{tr}) for typical ene-compounds with alkyl thiols

Ene-compound	C_{tr}
Norbornene[167]	1
Vinyl ether[167]	0.83
Methacrylate[168]	0.26
Acrylate[167]	0.08

thiyl radical reacts in an anti-Markovnikov manner with an unsaturated carbon–carbon bond (Scheme 4).

The rate of addition is highest with electron rich double bonds (norbornenes and vinyl ethers) and much slower with styrene or (meth)acrylates (see Table 1).[166] Reactivity with acrylates is intermediate which means that the resulting radical will undergo chain transfer with thiol (k_{tr}) but at a rate significantly less than acrylate propagation (k_p). In the presence of oxygen, chain transfer will however become more important since peroxy radicals react several orders of magnitude faster with thiols than with acrylate double bonds. Consequently thiol–ene chemistry is much less sensitive to oxygen inhibition, which is a major topic for the coatings industry.[41]

Scheme 4 presents chain transfer with a monofunctional thiol. The same cycle of reactions (addition to ene and hydrogen donation) will build polymer networks when the functionality of the thiol and the ene are both more than two. Polymers based on tri- or tetra-thiols with electron rich alkenes such as norbornenes or allyl monomers follow step-growth kinetics to give architectures different from those formed via radical chain growth. In this manner, gelation is delayed allowing a more uniform crosslink density and a higher final double bond conversion. Thiol–ene polymers tend to exhibit much sharper glass transitions at lower temperatures compared to acrylate networks. Thiol–ene polymers also tend to have lower hardness but better impact properties.[169] The limited hardness is due in large part to the flexible thioether linkages. With the help of thiol–ene chemistry, high energy absorbing materials can be formed. Due to their homogeneous network structure and very sharp glass transitions, energy absorption values of >90%[170,171] and high fracture toughness of 0.6–0.9 MPa m$^{1/2}$ can be reached.[172]

Thiols may also undergo photo-induced addition to carbon–carbon triple bonds, allowing thiol–yne chemistry.[173] The product of a thiol–yne addition is a vinyl sulphide which can undergo a second reaction with available thiol to give a dithioether. With a terminal alkyne and an excess of thiol under UV irradiation conditions, the preferred product is almost exclusively the 1,2 dithioether.[174] The reaction is regiospecific and high yielding, which provide a good platform for building high molecular weight polymers. Thiols and yne monomers should ideally be reacted with a ratio of 2 to 1, where the arising network structure will be more crosslinked and tend to have a higher glass transition and higher modulus compared to a thiol–ene system with comparable degree of functionality.[175] Curable formulations containing urethane oligomers with alkyne groups and polythiols can be photocured into hard, heat-resistant and tough films, which are promising for coatings and adhesives.[176]

Thiol–ene/–yne chemistry is described as a "click" process, with advantages of high conversion, fast reaction rates, low oxygen inhibition, and good tunability of the resulting polymer networks formed via both radical step-growth polymerization as well as base-catalysed Michael-addition reactions.[161,162,177]

Thiols are often used with monomers like (meth)acrylates that prefer to undergo homopolymerization. In this case, polymer will grow via a mixed chain growth/step growth-like manner (Scheme 4), where the induced chain transfer (CT) reaction moves the gel point to a higher conversion (e.g. from 25 to 50%). With less double bonds remaining after gelation, a subsequent reduction in shrinkage stress is observed. In addition, the more homogeneous polymer networks exhibit sharper and more defined thermal glass transitions. The less stiff networks with flexible thioether bridges tend to have improved impact resistance. Bowman et al. have studied the use of thiols including pentaerythritol tetra(3-mercaptopropionate) (PETMP) in composites for dentistry,[178,179] claiming methacrylate conversion of >90% which is rare for highly crosslinked photopolymerized networks and should lead to improved long-term biocompatibility. Moreover, the thiol–ene-based networks exhibited better flexural strength, increased depth of cure, and reduced shrinkage stress compared to standard composite formulations for dental applications. Another trending application for regulated photopolymerization using thiol–ene chemistry is the field of tissue engineering (e.g.: shape memory polymers,[180] hydrogels[181–183]). Depending on the thiol used (e.g. trimethylolpropane tris(3-mercaptopropionate) (TMPMP) or an isophorone diurethane based hexathiol (IPDUT)), the thermomechanical and mechanical properties can be tailored over a wide range suitable for biomedical applications. Moreover, the shape memory response and shape recovery of thiol-based networks is more rapid and more pronounced compared to standard acrylic-based shape memory systems. This is due to sharper thermal phase transitions, which arise from the more homogeneous network structures. For biocompatible hydrogels, PETMP[184] or dithiolthreitol (DTT)[185–187] are commonly used as water compatible

thiols. Alternatively the thiol functionality can be incorporated into a water soluble biomacromolecule (e.g., reduced bovine serum albumin BSA,[188] hemicellulose,[189] cyclodextrin[190]). These thiol–ene systems are amenable to lithographic processing[188,191] and may also be of interest as smart coatings.[192]

The most commonly referenced thiols are esters derived from 3-mercaptopropanoic acid. Depending on the required network properties, thiols with different functionalities (e.g., di-, tri-, tetra-, hexafunctional) and functional groups (e.g., urea, ester, ether) can be used (Fig. 18). The company Bruno Bock is a reliable source for many of the commercially available thiols.

The approach of using multifunctional thiols as CT reagents in diacrylate systems is very promising, but unpleasant odour,[193] tendency to colorize the materials, and storage stability issues[194] have hindered development. While toughness of photo-cured thiol–ene/yne based materials can be quite high, other mechanical properties such as hardness and storage modulus are compromised due to the flexibility of the thioether bridges, reduced crosslink density and shorter kinetic chain lengths.[195,196] Moreover, for thiol-acrylate systems the acrylate homo-polymerization is greatly preferred to reaction with thiol (C_{tr} is significantly <1) thus a fraction of thiol groups will remain following polymerization.[167,168,197]

Thiols have also been used in photopolymerization with vinyl ether monomers. In the presence of a photoacid generator, the vinyl ether can undergo both radical thiol–ene reactions as well as cationic homopolymerization. In a 50:50 trithiol/trivinyl ether system, polymerization is almost exclusively thiol–ene, but in a 25:75 trithiol/trivinyl ether system homopolymerization will predominate after the thiol is exhausted. The resultant mechanical properties (tensile strength and deformation energy) of this polymer are higher than the 50:50 polymer and much higher than the trivinyl ether homopolymer (0:100). Young's modulus of the 25:75 polymer was intermediate to the two other polymers.[198]

AFCT

Addition fragmentation chain transfer (AFCT) reagents were first reported to modify radical polymerization in the late 1980s[199,200] and since then more potent reagents have been developed with reactivity dependent on the monomer undergoing polymerization.[201,202] In comparison to thiols which cause chain transfer via hydrogen transfer, AFCT reagents add to propagating radicals in a manner similar to that of the utilized monomer. Research on AFCT reagents has over the years mainly focused on molecular weight control of linear polymers (e.g., styrene[203] and methyl methacrylate[204]), for the synthesis of hyperbranched polymers,[205] or end-group functionalization.[203,205–208] Only recently AFCT reagents including ethylenically unsaturated acrylates[209] and β-allyl sulfides[205,210] have been mentioned for the modification of photo-crosslinked functional materials (Fig. 19). In comparison to radical thiol–ene polymerization (Scheme 4), the AFCT mechanism can also regulate the radical polymerization reaction in a mixed chain growth/step growth-like manner (Scheme 5).[125,126]

Where thiols donate hydrogen atoms to propagating radicals, addition–fragmentation chain transfer (AFCT) reagents allow a slightly different method for modifying the growth of the polymer network.[211] An AFCT reagent[158,159] (Scheme 5) consists usually of a reactive double bond that allows radical

ethylenically unsaturated AFCT reagent   β-allyl sulfide
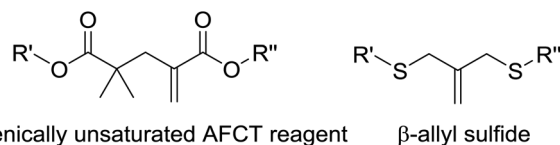
Fig. 19 AFCT reagents used in photopolymerized crosslinked networks.

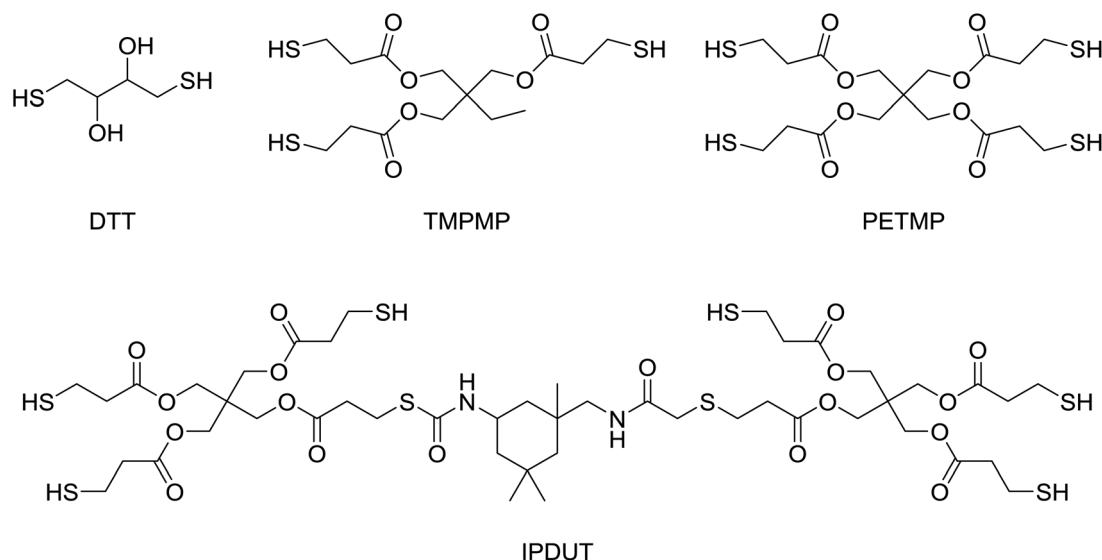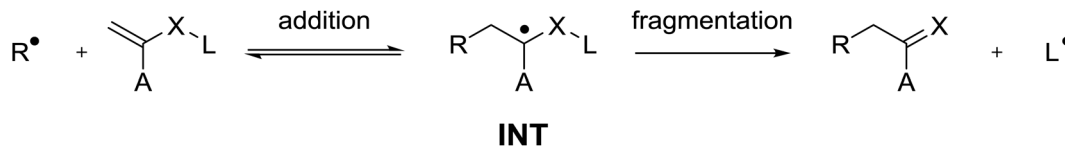DTT   TMPMP   PETMP

IPDUT

Fig. 18 Examples of thiols typically used as additives in photopolymerizable formulations.

Scheme 5 General mechanism for addition−fragmentation chain transfer (AFCT).

attack and a leaving group L that forms a reactive radical after fragmentation. In between the double bond and the leaving group can be usually either a CH_2–group or an oxygen (X). The reactivity of the double bond depends on the activating group A. Commonly used A groups include C_6H_5, CN and CO_2R'. After radical attack of the double bond, an intermediate radical (INT) is formed which can either undergo further propagation, reaction back to the starting components (both not beneficial) or the desired fragmentation *via* β-scission to form the radical of the leaving group, which should have high reactivity to initiate a new radical chain.[201] The stability of INT is influenced by the activating group A and usually propagation of INT is precluded due to steric hindrance. The more stable the radical INT, the longer it takes for the fragmentation step. This could ultimately lead to retardation of the radical reaction which is an undesired side effect of the AFCT approach.

Scheme 5 is drawn in a very general manner. In the case where the propagating radical is carbon centred and X = O, the reaction will be irreversible, where in the case of X = CH_2 a terminal vinyl group is formed that can form additional cross-links by subsequent radical addition. The reaction mechanism proceeds similarly to thiol–ene chemistry and this could potentially lead to materials with comparable properties.[158,159] By adding AFCT reagents to a radical polymerizable cross-linking monomer mixture, the uncontrolled radical chain growth mechanism can be altered to provide materials with a more defined and homogeneous network structure and, consequently, tunable mechanical properties (Fig. 20).

To determine the ideal AFCT reagent for (meth)acrylate monomers, the kinetic rate constants need to be taken into consideration. Most importantly, the rate constant of fragmentation for the AFCT reagent needs to be significantly higher than the rate for self-propagation. For comparison of different AFCT reagents, the chain transfer constant C_{tr} can be seen as a measure for the compatibility of an AFCT reagent with a certain monomer.

• When $C_{tr} < 1$: chain growth is the dominating reaction step yielding inhomogeneous polymers with broad molecular weight distribution.

• When $C_{tr} > 1$: the chain transfer reaction dominates and the molecular weight of the polymer is lower at the beginning of the reaction, until the AFCT reagent is exhausted. After consumption of the AFCT reagent, the radical reaction proceeds in a chain growth manner leading to high and broad distributed molecular weights.

• When $C_{tr} \sim 1$: chain transfer and propagation happen with the same probability indicating a homogeneous consumption of AFCT reagent and monomer. The resulting polymers are more homogeneous and can have well defined thermal-mechanical properties.

Generally, C_{tr} for AFCT reagents with acrylates, styrenes or vinyl esters can range from 0.5–2, sometimes even higher (up to >80), depending on the reagent.[158] Finding an AFCT reagent with a C_{tr} close to 1 allows a more homogeneous copolymerization reaction by comparison to the thiol–acrylate system. In general, highly crosslinked polymers with AFCT reagents have more homogeneous polymer architectures, which paves the way to potential applications such as shape memory polymers[180,212] and covalent adaptable networks.[213]

Bowman *et al.* have reported the first use of AFCT with allyl sulfides for acrylate[214] and methacrylate[205] photopolymerization. In the case of acrylate systems, the photopolymerization induced shrinkage stress could be greatly reduced by tuning the base formulations. For methacrylate systems, the allyl sulfide AFCT reagent is not ideal and stress reduction could only be achieved in combination with thiol–ene chemistry (Fig. 21). Nevertheless, the approach with methacrylic monomers has great potential for in the field of dentistry.[215] In both systems the network architecture of the polymer is regulated, which indicates that the resulting materials could exhibit improved toughness. Unfortunately, some significant delay in curing has to be accepted.

A similar study of methacrylate network regulation with AFCT reagents has recently been published by Liska *et al.* Here β-allyl sulfones were used in methacrylate photopolymerization to regulate final properties such as thermal polymer phase
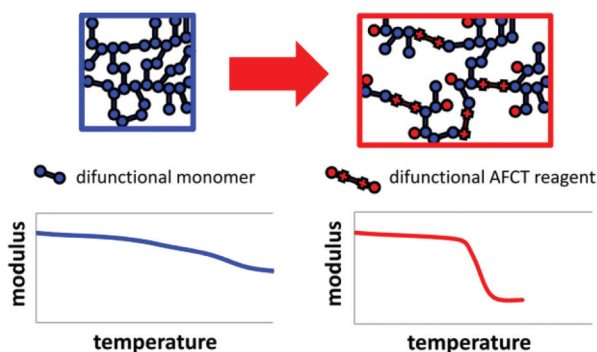

Fig. 20 AFCT regulated radical network modification giving access to tunable thermo-mechanical properties.
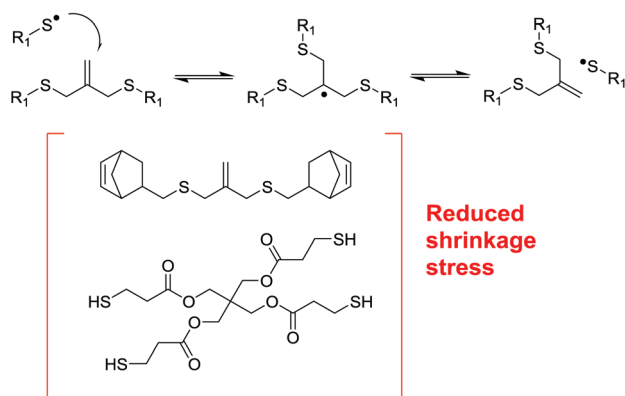
AFCT with allyl sulfides:

Fig. 21 Stress relaxation *via* β-allyl sulfides in thiol-norbornene-based systems.[216]

transition, network density, and network homogeneity.[215] By providing regulation over the radical photopolymerization process, the resulting networks exhibit reduced shrinkage stress, improved conversion and higher toughness (Fig. 22).[217]

Mono- and difunctional β-allyl sulfones (MAS and DAS in Fig. 23) regulate the photopolymerization of dimethacrylates and exhibit significant advantages over thiols. In addition to the notable issues of storage stability and odour, alkyl thiol chain transfer agents do not homogeneously react with methacrylates as methacrylate homopolymerization is greatly
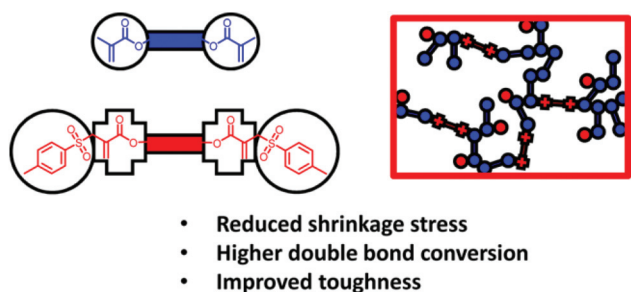

- **Reduced shrinkage stress**
- **Higher double bond conversion**
- **Improved toughness**

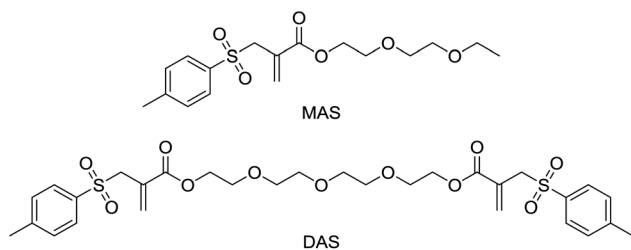Fig. 22 β-Allyl sulfones as AFCT reagents in methacrylate-based networks.

Fig. 23 Mono-(MAS) and difunctional β-allyl sulfones (DAS) as AFCT reagents.

preferred with a $C_{tr} < 1$. By comparison, β-allyl sulfones react homogeneously with methacrylates ($C_{tr} \sim 1$)[218] which allows gelation times at higher double bond conversions compared to the thiol/methacrylate system. This corresponds with a reduction of shrinkage stress, which is significantly lowered for β-allyl sulfone systems. Moreover, materials with increased toughness (factor ~5) are obtained while keeping the storage modulus and indentation hardness unaffected or even improved.

More recently, additional AFCT reagents for regulation of methacrylate network formation have been developed. Generally substitution of the vinyl activating group allows for modification of material properties with lower concentration of additive. AFCT reagents with appropriate substitution of the leaving group, on the other hand, provide higher conversion at gelation with no delay in polymerization speed.[219] All in all, the effectiveness of an AFCT reagent is dependent on the utilized monomer system, and solubility and side reactions such as H-transfer must be considered as well.[220]

Photo-induced living radical polymerization

One of the more exciting recent developments in the field of photopolymer chemistry has been the introduction of photo mediated living radical polymerization techniques.[221] Reversible-addition fragmentation chain transfer (RAFT) is a special case of AFCT where either R˙ or X is not carbon. Two of the more commonly utilized classes of RAFT agents are the dithioesters (where X and A = S) and the trithiocarbonates (where X, A and Z = S).[222] Recently Boyer *et al.* have established photoinduced electron transfer (PET) RAFT, which uses an Ir or Ru catalyst to regulate propagation by reducing the thiocarbonylthio group on the growing polymer chain.[223] Photochemical atom transfer radical polymerization (ATRP)[224] and photoinduced iodine-transfer polymerization (ITP)[224] methods have also been developed. The principal benefit of these living radical polymerization techniques is the linear relation of conversion and molecular weight which lends to polydispersity values approaching 1.[225] A practical disadvantage is that the rate of reaction is orders of magnitude lower than typical photopolymerizations. Living radical techniques are readily used to provide well defined block copolymers. Although it is hard to draw a general trend between mechanical properties and polydispersity, Morales *et al.* found that PS/PB BC additives with PS blocks with higher PDI values (1.6) were 50% more effective in improving the impact resistance of HIPS *versus* additives with PS PDI values of 1.1.[226]

Interpenetrating networks (IPNs)

Mixed modes of polymerization

Acrylate and epoxide monomers do not readily copolymerize either under radical or cationic conditions. Mixtures containing both acrylates (with radical photoinitiators) and epoxides (with cationic photoinitiators) can however undergo polymerization simultaneously (although with different rate constants)

to form an interpenetrating network (IPN).[153] In a system of miscible monomers, where the functionality of both acrylate and epoxide systems is greater than 2, crosslinking will lock the acrylate and epoxide polymers together non-covalently but also irreversibly. Practically co-continuous phases can be observed with different degrees of interpenetration between the two networks.[227] Decker et al. found that with the hybrid system consisting of DGEBA diacrylate with ECC, the acrylate component polymerized much faster than the epoxide under laminated conditions but that the order was reversed in air. The Persoz hardness of the hybrid polymer was higher (360 s) than that of the neat epoxide (340 s) and the acrylate polymer (250 s). Dean and Cook used a mixture of methacrylate monomer with radical photoinitiator and epoxy with thermally labile anhydride to test the influence of curing order.[228] When the mixture was exposed first to UV irradiation and then heated, the methacrylate portion reached a higher conversion and when the order of cure was reversed the epoxide reached a higher conversion. In the first case, two T_g's are observed (105 °C and 196 °C) and in the second case just the lower transition is seen (and sharpened). Jansen et al. prepared IPNs of PPO-based epoxides with MMA.[229] In the presence of a dimethacrylate crosslinker a full-IPN was formed and without it a semi-IPN. A third system containing the epoxy methacrylate monomer GMA to provide a covalently linked copolymer was also prepared. Of the three epoxy/methacrylate systems, the semi-IPN was found to have the highest toughness, reaching a maximum with an epoxy ratio of 30% for tensile toughness and 70% for the impact test.

While mixed epoxide/acrylate polymers are more common, other mixed mode photo-curable polymer systems have also been investigated. Ortiz et al. investigated the effect of thiol–ene monomers (a di-tertiary amine tetra allyl ene and a trithiol) added to DGEBA based resins.[230] With this system, the tertiary amine served the dual purpose of curing the epoxide. Using RTIR, conversion of thiol was found to increase even after the allyl had been consumed which the authors clarify as evidence that the thiol is also acting as an epoxy curing agent. DMTA of these hybrid copolymers shows a sharpening and decrease of the T_g from 93 °C for the epoxy cured with diethylenetriamine to 64 °C for the polymer with 40% thiol–ene monomers. Interestingly low-temperature storage modulus was about the same for those two polymers and the highest for the polymer with 20% thiol–ene additive.

Polymerization induced phase separation

It was earlier explained in the section on rubber additives, that a degree of heterogeneity between the rubber and bulk polymer phases is required to efficiently dissipate potential crack propagating forces and thus increase toughness. Heterogeneous materials consisting of two distinct phases can be prepared by blending of partially compatible polymers at high temperature,[231] via self-assembly of block copolymers,[101] or by polymerization induced phase separation (PIPS).[232] Photo-PIPS with acrylate monomers has been used to lock liquid crystalline domains within a bulk matrix for electro-optic appli-

cations[233] and more recently to reduce shrinkage stress and improve mechanical properties of crosslinked polymers.[234] Crawford et al. determined that a sufficiently low irradiance is needed to limit the rate of polymerization to ensure the desired spinodal decomposition mode of phase separation. Szczepanski and Stansbury have studied the phase separation behaviour of different methacrylate prepolymers (PMMA, PEMA, PBMA) dissolved in TEGDMA monomer and subjected to UV irradiation.[234] Phase separation was efficient with both PMMA and PEMA but not with PBMA presumably due to its sub-ambient T_g, meaning that the polymer was in the rubbery stage throughout polymerization. Phase separation generally slightly precedes gelation and allows ultimate monomer conversions higher than in homogenous monomer systems due to extended auto-acceleration. Using PMMA prepolymers of different molecular weight, it was found that 120 kDa PMMA could induce spinodal decomposition already at 5 wt% loading, while PMMA of 11 kDa did so at 20 wt% loading and that of 1 kDa remained homogenous at all tested concentrations.[235] The resin with 20 wt% 120 kDa PMMA exhibited half the shrinkage stress of the neat TEGDMA system with no significant reduction in modulus. The best results were obtained when the polymer was cured to 50% conversion with low irradiance (300 µW cm²) followed by higher intensity (20 mW cm²) curing.

Self-healing

Although not specifically defined as toughening, recent developments of self-healing polymeric materials do relate to the prevention of crack propagation and thus may be worth mentioning. Self-healing methods can be broadly classified as either intrinsic of extrinsic.[236] Intrinsic self-healing is based on thermally or photolytic bond formation of moieties within the polymer network. Chen et al. introduced self-healing thermosets using reversible Diels–Alder cycloaddition of furans and maleimides.[237] The material can be cracked into two separate pieces and then mended by heating to 120–150 °C. While strength of the mended piece was first reported to be compromised by close to 50%, further system refinements have been introduced allowing full fracture toughness recovery even after multiple cycles.[238] Among the more commonly used photolytic self-healing methods are the reversible 2 + 2 cycloaddition of coumarin and cinammic acid based derivatives (Scheme 6).[239]

Extrinsic self-healing is based on additives such as hollow fibres, microcapsules, or vascular systems containing a self-healing agent which should release during crack propagation.[236] Self-healing agents include mixtures of dicyclopentadiene with Grubb's catalyst, siloxanes with tin catalysts, eopoxy/amine systems and organic solvents. Yao et al. added microcapsules containing GMA monomer to PS grown via RAFT polymerization.[240] Upon fracture, the GMA released and continued to propagate chain growth from the trithiocarbonate end groups. Impact strength of specimens with 15 wt% microcapsules was actually higher after fracture and healing. An example of extrinsic self-healing particularly pertinent to the photopolymer chemist is provided by Leigh et al. where
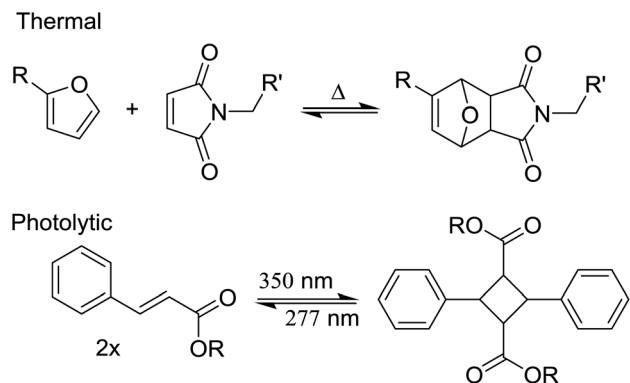
Scheme 6   Thermal and photolytic methods of intrinsic self-healing.

Fig. 24   Silicone acrylate[249] and epoxy[248] monomers for optical fibre coatings.

they use a photoresin with a high concentration of dye as the hydraulic fluid for a micro-actuated forcep.[241] Due to the high concentration of dye, the resin remains liquid. Puncture to the housing membrane, however, secretes a small volume of resin to the upper surface where it then cures in ambient light. The cured resin seals the hole while the bulk remains liquid as desired for the application.

Applications

Coatings

Coatings have always been one of the principal applications for photo-curable polymers. Protective coatings for metal, wood,[242] plastics and concrete[243] are intended to be durable and resist scratches, tears, punctures or other disturbances which may expose the underlying material surface. Typical thicknesses for photo-curable coatings are largely application dependent. As an example, wood is commonly coated with waterborne acrylate coatings which photocure to a thickness from 50–100 μm and generally the thicker the coating the better the impact resistance.[244]

Photo-curable coatings are also used for optical fibres, where one of the principal purposes is to improve flexural strength. The coating can be applied in two layers, where the bottom layer in contact with the glass should be soft and adhere well.[245] The top layer, which is commonly based on urethane or epoxy acrylates is comparatively harder (ideally >400 MPa)[246] and provides the desired resistance. Both layers are applied and cured during fibre drawing, which is one of the appeals of photo-curing over slower thermal curing. Static charge on the surface of the glass fibre during the coating process can be a problem and has been addressed with additives such as nonionic amines.[247] To lower the coefficient of friction of the outer layer and prevent snagging of adjacent fibres, a silicone based acrylate may be added to the formulation.[246] Silicone epoxy monomers are also used as optical cladding material, where high UV transparency of the cured clad allows direct laser patterning of Braggs gratings within the core. In this special case, concentration of iodonium
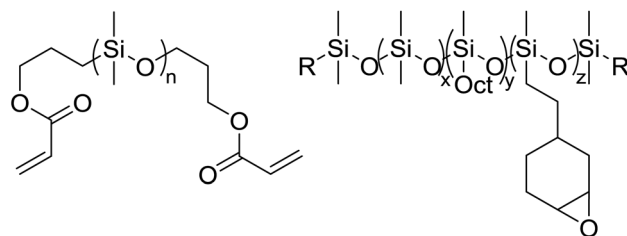
photoacid is very low (>0.001 wt%) allowing transparency at 254 nm of more than 85% (Fig. 24).[248]

Adhesives

Photo-curable adhesives are used to bind glass or plastics to another surface (glass, plastic, metal, or wood). Transparency of the top layer is generally a prerequisite, and the UV cutoff of the material is also to be considered: roughly 320 nm for glass depending on type and 385 nm for polycarbonate.[250] Plastic additives, in particular UV stabilizers, will also affect light penetration.[251] For these reasons, photoinitiators that absorb at or above 400 nm may be needed. To ensure adhesion in shadow regions, a second slower mode of curing (based for instance on heat or moisture) may be used. Tensile adhesion strength can be assessed by using a Universal tester to pull two adhered pieces apart. Recognizing that adhesion can be reduced by moisture, Kim *et al.* used fluorinated silanes and colloidal silica to improve the adhesion strength by 40% of an epoxy acrylate between two glass plates submerged in boiling water.[251] On polycarbonate surfaces, polycarbonate based acrylates (0.92 kgf m^{-1}) adhere better than urethane acrylates (0.46 kgf m^{-1}) or epoxy acrylates (0.0576 kgf m^{-1}).[252]

Additive manufacturing

The term "additive manufacturing" (AM) is that preferred by the ASTM to collectively refer to automated "additive" techniques such as stereolithography (SLA) and fused deposition modelling (FDM) used for building well-defined 3D structures.[253] "Additive" is thus used to contrast traditional "subtractive" techniques such as milling[254] and stamping.[255] AM tends to be more precise, less energy intensive,[256] and produces no waste from residual unused build material.[257] AM has long been considered "rapid" in the prototyping stage of product development, and yet more recently as new and specialized applications have arisen "rapid manufacturing" is now a viable option. AM methods are available for building objects with metals, plastics and other materials. Of these methods, FDM with acrylonitrile butadiene styrene (ABS) is one of the best established AM techniques and stands as a good benchmark. ABS is a reasonably tough polymer (Izod impact strength of 340 J m^{-1}),[258] but it does have its shortfalls. Most notably, ABS is optically opaque and its surface properties are inappropriate for most biomedical applications.[259]

Table 2 Mechanical properties of selected commercial photocurable resins for AM[260–262]

Material	Manufacturer	Tensile modulus/MPa	Tensile strength/MPa	Izod impact/J m^{-1}	Elongation/%
Visijet SL Impact	3D Systems	2626	48	65	14
Visijet SL Tough	3D Systems	1890	41	44	18
Somos 8110	DSM	317	26	87	27
Somos 8120	DSM	690	26	59	26
Somos 14120	DSM	2460	46	24	7.9
Endur RGD450	Stratasys	1700	20	30	20
Digital ABS	Stratasys	2600	55	65	25
TangoPlus FLX930	Stratasys	<100	0.8	—	170

The high temperature of the FDM extruder head is also a limiting factor. By comparison, photo-based AM techniques such as SLA operate at lower temperature and allow feature resolution at least one to two orders smaller than that allowed by FDM. Commercially available resins for photo-based AM allow finished objects with mechanical properties varying from soft and flexible to stiff. Table 2 demonstrates the range of mechanical properties from the three major resin manufacturers. 3D Systems and Stratasys both package their resins in cartridges for material jetting AM devices.[260,261] A major advantage of jetting *versus* vat photopolymerization (*i.e.* traditional SLA) is that multiple materials can be printed during the same build. Stratasys describes their "Digital Materials" as composites of two or more photoresins with optical and mechanical properties controlled by the ratio of the different resins. While the composition of commercial AM photoresins is proprietary, patents and MSDS sheets indicate that both acrylate and epoxy monomers are used. The advantage of a mixed monomer system in AM is that the acrylate component will cure quickly and define the 3D structure, while the epoxy component can be thermally post cured and limit shrinkage. It is also worth noting that photo-based AM is a layer by layer process, which has consequences on spatial resolution and can impart anisotropic mechanical properties. Particulate additives which settle during the build or which increase viscosity may not be appropriate for AM and particularly with jetting processes.

Dental/medical

Photo-curable polymers have been in use in dentistry for more than 40 years. With direct dental restoratives, the prepared tooth surface consisting of enamel and dentin is first etched (commonly with 30–40% phosphoric acid) to remove the dentin smear layer.[263] Next a thin primer layer is added to serve as an intermediary between hydrophilic dentin and the hydrophobic composite. These two-steps can alternately be combined into one step by using self-etching primers containing acidic methacrylate monomers.[46] After curing the primer, the bulk restorative is applied and cured. Photo-curable restoratives are composites consisting of typically 70–90 wt% (30–55 vol%) inorganic filler within a dimethacrylate resin.[264] The high filler content is necessary for aesthetics, to increase modulus and strength, and to reduce polymerization shrinkage and associated stress.[265] Enamel is indeed the hardest material in the human body but is also notoriously brittle and

can crack from shrinkage forces which develop during and after photo-curing. Light scattering in dental composites limits depth of cure meaning that deep carries will require multiple coat-and-cure cycles. Commonly used methacrylate monomers for dentistry include 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (Bis-GMA), urethane dimethacrylate (UDMA) and decanediol dimethacrylate (D_3MA).[266] The filler consists principally of micro- and nanoparticulate silicates with heavier elements such as barium, zirconium and strontium added to improve radio-opacity.[267] Filler particles are treated with silane coupling agents (such as 3-(methacryloyloxypropyltrimethoxysilane), which links the particles within the polymer matrix and helps in the transfer of stress. In addition to substantial masticatory cyclic stresses (chewing), dental composites are exposed to an aqueous environment with regular temperature variations. Dental restoratives must not only be tough they must also stay tough quite literally a lifetime.

The addition of chain transfer agents to dental formulations has been established as such reagents not only increase the toughness but also limit shrinkage stress while increasing conversion and adhesion. Stansbury and Bowman have published a number of patents on the use of thiol–ene formulations for dental applications.[193,268,269] Cramer and Bowman have added to this work,[270,271] using allyl sulfides[272,273] and trithiocarbonates[274] as chain transfer agents. The company 3M has also claimed patents that focus on the benefits of chain transfer agents for self-adhesive compositions,[275] high refractive index formulations (for increased curing depth),[276] or dental formulations in general,[277–279] using monomeric[209] or oligomeric[280] AFCT reagents based on crosslinkers with cleavable ethylenically unsaturated polymerizable groups.

In addition to dentistry, photo-curable polymers are finding use in a variety of other biomedical applications. Using tomographic images (from MRI or X-ray) to create an STL file, photo-based AMT is more and more regularly used for the production of patient specific surgical guides, which saves operational time and reduces associated trauma.[281] While the mechanical demands for plastic guides are low, this is by no means the case for many other AM medical applications. Notably CAD-CAM can also be used to produce anatomically correct implants to serve as replacements for damaged human tissue.[282,283] The demands for materials used in tissue engineering are high. Notably a very high degree of biocompatibility

is required for a long-term implant, which warrants the study of low toxic alternatives to acrylates.[284,285] Among these alternative monomers, vinyl esters have been successfully used to 3D print a porous bone graft. Six months after implanting the graft into a rabbit femur, histology indicated growth of new bone tissue with good osteoconductivity. Vinyl esters have good photoreactivity, which can be increased by addition of thiol comonomers.[195] Thiol-vinyl ester based networks also have substantially improved impact strength, with modulus adjusted by choice of thiol functionality. Thiols have also been used to improve the tear strength (as assessed with a PLA surgical thread) of photo-cured urethane-acrylate networks intended for use as vascular grafts.[286] For vascular grafts, the material compliance (the inverse modulus) should match that of the native vessel to avoid causing disturbances in blood flow which can lead to stenosis.[287] While biodegradability was traditionally considered a weakness for a long term implant, more recently biodegradable polymers have been shown to help in the harbouring of native cells and in the regeneration of new tissue.[288] In this case, surface degradation is essential to maintain the structure and mechanical properties of the graft.[289] As more fresh tissue grows around and into the graft, the mechanical properties of the tissue develop.[290] The initial stages of tissue growth within the graft can be performed within or outside of the patient's body by culturing native cells in a laboratory.[291] Nutrients and growth factors are in this case provided until the tissue graft can be transplanted. The intention is that native tissue gradually becomes the principal component while the graft degrades. At the same time, the collective mechanical properties of tissue and the artificial graft should remain fairly constant. These principals have indeed been demonstrated in animal models, and clinical tests in human are within the foreseeable future.

Hydrogels

Hydrogels are swollen polymer networks where the principal component by weight is water.[292] Crosslinking can be based on covalent or non-covalent bonding or even a combination of the two. Due to rapid cure and to the relatively benign nature of light, photocrosslinking of water soluble acrylate monomers based on PEG,[293] PVA, or natural polymers such as gelatine[294] provides a versatile platform for forming hydrogels. The resultant mechanical properties of such hydrogels, however, are in often poor with typical fracture energy values only 0.1–1 J m^{-2}.[295] The Young's modulus and stress–strain curve of a hydrogel will be largely dependent on molecular structure, crosslink density and water concentration. The copolymer system based on polyglycerol sebacate and PEG shows a decreasing elastic modulus from 2.2 MPa to 13 kPa and a 6 fold increase in elongation with increasing PEG content.[296]

In 2005 Tanaka *et al.* classified classes of hydrogels with distinctly improved mechanical properties.[297] First among these are topological gels where crosslinks are based on non-covalent rotaxane linkages which provide hydrogels capable of being stretched by 20 times their original length. The second category of mechanically improved gels is the nanocomposite (NC) gel. The addition of clay to hydrogels is here found to increase modulus and tensile toughness. The final class of improved hydrogel is the double network (DN) gel.[298] DN gels are formed in two steps, where first a highly crosslinked rigid gel is formed and second a loosely cross-linked gel is formed within the first network.[299] The mechanical properties of DN gels are tuneable and can vastly exceed those of traditional hydrogels: elastic modulus from 0.1–1 MPa, compressive fracture stress of 20–60 MPa, elongation to 2000% and fracture energy values up to 1000 J m^{-2}.[300]

Spearheaded principally by the groups of Bowman, Anseth and Hoyle, great advances have been made in toughening of hydrogels *via* thiol–ene and thiol–yne chemistry.[301,302] Linear and 4-arm PEG oligomers end capped with norbornene or allyl ethers can be copolymerized with hydrophilic multifunctional thiols to give hydrogels with significantly higher strength and elongation *versus* traditional PEG acrylate based hydrogels.[303,304] The more regular networks formed *via* step-growth polymerization of complimentary monomers are apparently more efficient at dissipating fracture stresses than the more random networks formed *via* radical chain growth of acrylates.[305] Thiol-norbornene photo-crosslinking has also been used to build PEG-PDMS hydrogels where critical strain energy under compression (G_c) could be increased from 7 J m^{-2} for the pure PEG hydrogel to 100 J m^{-2} where the volume fraction of PDMS was 3.6 times greater than PEG.[306] Photoinduced thiol–yne crosslinking has also been applied to the synthesis of hydrogels with the benefit that higher modulus gels are also possible.[174] More recently tetrazole-alkene photo click chemistry has been used to give low modulus (0.65–25 kPa) hydrogels.[307]

Conclusions and outlook

Photo-curable polymers provide unique solutions to a broad range of industrial problems. Fast cure kinetics has always been a driving force and yet, with the expansion in applications from mostly coatings to bulk materials as well, mechanical properties have grown in importance. Heavily crosslinked networks based on acrylates and epoxides can often be quite brittle but fortunately strategies have been developed to counter these effects. Some monomers such as those based on urethanes and other moieties which form interchain hydrogen bonds give networks with intrinsically higher tensile strength. Since photocurable epoxy resins intrinsically form more highly crosslinked networks than conventional epoxy thermosets, polyol CTAs are imperative for materials with good mechanical properties. Inorganic and organic particulate additives, which have long been used to improve toughness in thermoplastics and thermosets, prove advantageous in photocurable networks as well. To prevent light scattering which can occur with larger (>1 μm) particles, block copolymers and nanoparticles are perhaps more appropriate. Resins based on oligomeric and hyperbranched acrylates exhibit less polymerization shrinkage *versus* those based on smaller molecule mono-

mers and concurrently provide materials with better impact strength. Also alternate styles of polymerization and particularly those based on thiol–ene/yne and other CTAs tend to provide networks with higher toughness and provide a versatile platform for modifying mechanical properties. AFCT agents have been shown to regulate photo-crosslinking of (meth)acrylates very well due to their near unity chain transfer constants. This allows more homogenous network formation and materials with high impact strength and high modulus. IPNs based on monomers or monomer systems that react simultaneously and separately allow mechanical properties often times superior to those of the individual components.

While many different strategies for toughening of photocurable materials have been developed and improvements have been made, there is still great potential in the combination of successful strategies. In particular, chain transfer and other methods for better regulating network ought to be tested in combination with traditional particle and nanoparticle additives. Combined strategy approaches seem well-suited in cases where not just toughness, but strength and hardness should be high. Ultimately the intended application of the polymer network will dictate the choice of the monomer system and additives. While fast cure and good mechanical properties alone may suffice in rapid prototyping, medical implants garner additional requirements including excellent biocompatibility and other properties specific to the effected tissue. In the case of biodegradable tissue grafts, toughness of the polymer alone may be transcendental although that of the graft and tissue collectively should be maintained for a lifetime.

Acknowledgements

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