Society for Adhesion and Adhesives

CURRENT ASPECTS OF EPOXY RESINS

One-day Symposium 3rd December, 2003
Society of Chemical Industry, Belgrave Square, London
Programme

10.00 Registration and coffee

10.30 A review of the chemistries associated with epoxy adhesives
     Jerry Powell, Huntsman Advanced Materials, Duxford, UK

11.00 Water and epoxides
     John Comyn, Loughborough University, UK

11.30 Development of epoxies with enhanced high temperature and water resistant properties
     S Millington, QinetiQ, Farnborough, UK

12.00 Lunch

14.00 New paste adhesives for aerospace applications
     Dean Bugg, Hexcel Composites, Duxford, UK

14.30 Epoxy adhesive technology: Going from strength to strength
     Terry Gordon, Bondmaster, Eastleigh, UK

15.00 Two-part epoxy adhesives: Synergism between CTBN and nanoparticles
     Stephan Sprenger, Hanse Chemie, Geesthacht, Germany

15.30 Influence of toughening agent incorporation on the hydrophobic characteristics of epoxies
     S Millington, QinetiQ, Farnborough, UK

16.00 Discussion

16.15 Tea
This one-day symposium is one of an ongoing series organised by the Society for Adhesion and Adhesives.

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S G Abbott
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W Broughton
E J C Kellar
A J Kinloch
J D Palmer
S J Shaw
D A Tod

The next symposium is due to be held at the SCI on Thursday 29th April 2004, entitled “Packaging Adhesives”.

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A REVIEW OF CHEMISTRIES ASSOCIATED WITH EPOXY ADHESIVES.

J.H.Powell. C.Chem.MRSC.
Huntsman Advanced Materials.

ABSTRACT

This review paper summarises the significant materials and chemistries associated with the formulation of epoxy adhesives. Since the scope of materials used in formulating epoxy adhesives is considerable, no attempt has been made to be all encompassing, rather examples of significant ingredients are discussed.
These principal materials are categorised, and the reasons for their inclusion in formulations, together with their limitations, are noted.
The applications of epoxy adhesives have expanded considerably in the last 50 years, and the technology with it, however the majority of adhesives – in tonnes sold, rely primarily on simple compositions and unsophisticated ingredients. The accent of this review is on the available chemistries and therefore includes materials used in adhesives for which relatively minor sales volumes are established, but which have significance in the benefit they confer.
One area which has assumed great significance, particularly in academic circles, is the subject of toughening, therefore the materials which influence this characteristic are shown a corresponding level of attention.
Finally, a brief Author’s view on the future direction of epoxy formulation is given, based on 30+ years of experience in the field.
WATER AND EPOXIDES

John Cornyn, IPTME, Loughborough University

Basics

The basic factors which control the interaction between cured epoxides and water, are that the amine cured material contains hydroxyl groups which are hydrophilic and will form hydrogen bonds with water, and water has extreme properties in being a very polar liquid. This gives it an extreme surface tension and dielectric permittivity.

However all polymers are permeable to all fluids. The cause is the high level of molecular motion compared with glasses and metals. Polymers creep (deformation with time at constant load) much more than other materials for the same reason. If metals creep then polymers gallop.

No polymer can therefore be a complete barrier to water. Epoxide adhesives will therefore transmit water to interfaces, which is where its effect is most damaging.

Weight increases in water.

If a thin film of an epoxide polymer is immersed in water or wet air, in most cases it shows Fickian sorption. This means that if $M_t$ is plotted against the square root of time, the plot is linear to $M_t / M_e = 0.6$, it then curves over to equilibrium which is represented by a horizontal line. The fractional uptake $M_t / M_e$ is given by equation 1. Here $D$ is the diffusion coefficient, $l$ the film thickness and $t$ time.

$$M_t / M_e = 1 - \sum_{n=0}^{\infty} 8 \exp\left[-D(2n+1)^2\pi^2 / l^2 \right] / (2n+1)^2\pi^2$$

(1)

$M_t$ is the mass absorbed at time $t$ and $M_e$ is the mass absorbed at equilibrium. At short times equation 1 takes the simpler form of equation 2.

$$M_t / M_e = (4/l)(Dt/\pi)^{1/2}$$

(2)
Table 1. Water uptake properties of epoxide adhesives (Brewis, Comyn & Tegg).

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>t</th>
<th>D</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(10^{-12} m^2 s^{-1})</td>
<td>(%)</td>
</tr>
<tr>
<td>DGEBA WITH THE FOLLOWING HARDENERS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di(1-aminopropylethoxyether), DAPEE</td>
<td>25</td>
<td>0.13</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.46</td>
<td>4.7</td>
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<tr>
<td>triethylene tetramine, TETA</td>
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<td>0.16</td>
<td>3.8</td>
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<tr>
<td></td>
<td>45</td>
<td>0.32</td>
<td>3.4</td>
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<td></td>
<td>45</td>
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<td>3.1</td>
</tr>
<tr>
<td>diaminodiphenylmethane, DDM</td>
<td>25</td>
<td>0.0099</td>
<td>4.1</td>
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<td></td>
<td>45</td>
<td>0.006</td>
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<td>FM1000 epoxide- polyamide</td>
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<td>0.075</td>
<td>(20.4)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.1</td>
<td>(15.8)</td>
</tr>
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</table>

Microcavitation

In many cases the water uptake properties of epoxides depend on previous water exposures. The amount of water absorbed at equilibrium increasing with previous exposure. The interpretation is that water forms microcavities which later fill up with water.

Osmotic effects

Epoxide adhesives contain sodium chloride as a by-product from synthesis. Epoxides are expected to be totally impermeable to electrolytes because of their low permittivities, and hence water will permeate through the resin to dissolve the salt and increasingly dilute the solution. Osmotic pressures can be high, and osmosis has the capacity to form cracks in an epoxide. The osmotic pressure of a 1M solution of an ideal 1:1 electrolyte is 5.0 MPa (750 psi).
Plasticisation

Water plasticizes polymers, and some data for epoxide adhesives are shown in Table 2.

Table 2 Glass transition temperatures (°C) of wet and dry epoxide adhesives formed with DGEB and various hardeners, (Brewis, Comyn & Tegg)

<table>
<thead>
<tr>
<th>Hardener</th>
<th>$T_g$</th>
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<tr>
<td></td>
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<tr>
<td>DAPEE</td>
<td>67</td>
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<tr>
<td>TETA</td>
<td>99</td>
</tr>
<tr>
<td>DAB</td>
<td>161</td>
</tr>
<tr>
<td>DDM</td>
<td>119</td>
</tr>
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</table>

Hydrolysis

The good news is that epoxides do not chemically react with water under normal conditions. An acid anhydride cured epoxide was shown to react with water only under extreme conditions of high pH, high temperature and high stress. The reaction was followed by IR spectroscopy which showed the removal of ester groups.

Interfacial effects

Water lowers the thermodynamic work of adhesion for epoxide-metal interfaces. The basic underlying causes are the very high surface energies of metals and the high surface energy of water. Some values are shown in Table 3; a negative value indicates that the joint is unstable in water.
Table 3. Values of work of adhesion in for various interfaces in dry air and in water.

(Kinloch).

<table>
<thead>
<tr>
<th>Interface</th>
<th>Work of adhesion / mJm⁻²</th>
<th>Interfacial debonding in water?</th>
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<tr>
<td></td>
<td>Air</td>
<td>water</td>
</tr>
<tr>
<td>Epoxide/steel</td>
<td>291</td>
<td>-255</td>
</tr>
<tr>
<td>Epoxide/aluminium</td>
<td>232</td>
<td>-137</td>
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<tr>
<td>Epoxide/carbon fibre composite</td>
<td>88-90</td>
<td>22-44</td>
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Bibliography


Development of epoxies with enhanced high temperature and water resistant properties

D A Jones¹, S Millington¹, S J Shaw², G F Tudgey¹

¹Future Systems Technology Division, QinetiQ, Farnborough, UK
²Physical Sciences Department, Dstl, Porton Down, UK

A large variety of epoxy resins have been developed exhibiting extremes of properties and characteristics. Two characteristics in particular i.e. the ability to withstand temperature extremes, together with the ways in which they respond to environmental moisture, have been highlighted as being of major importance to numerous applications.

The ability to operate at elevated temperatures is dependent upon the chemical structure of the epoxy, formulation variables and cure conditions. Although virtually all epoxy based systems have chemical structures which exhibit weaknesses resulting in scope for thermal instability (at least in comparison to recognised high temperature polymers such as polyimides) the ability to tailor chemical structures and crosslink densities for higher glass transition temperatures (Tg) are available. For example, a common aerospace epoxy resin, based upon a tetrafunctional epoxy, can exhibit Tg's substantially in excess of 200°C. Although this can result in a short-term elevated temperature capability, research has revealed cure reaction anomalies which can lead to Tg's substantially less than what would be expected for a highly crosslinked system. Several molecular modifications have been highlighted as offering scope for both enhancements in polymer Tg and hence improved high temperature adhesive performance. Two approaches to enhanced crosslink density and, thus, improve Tg, have been considered in the authors' laboratories and will be discussed. Results from both approaches have revealed the extent to which significant increases in Tg can enhance a range of important polymer (and ultimately adhesive joint) properties.

Environments exhibiting high levels of moisture combined with elevated temperature can be extremely damaging to bonded joints. Several means of enhancing environmental performance have been considered; the most notable relating to improved interfacial resistance via surface treatment regimes. In addition, several research groups have considered the extent to which enhanced hydrophobic character within the adhesive layer can improve environmental resistance. In particular, the influence of halogen incorporation on hydrophobic character has been extensively studied, with much of this work being conducted within the authors' laboratories.

Overall the results from this work have revealed the extent to which halogen incorporation can substantially inhibit the degree to which water is absorbed by various types of epoxy resins. Some of the molecular approaches considered, together with examples of the beneficial effects obtained, will be discussed in the presentation.
NEW PASTE ADHESIVES FOR AEROSPACE APPLICATIONS
IAN ASPIN, ANDREW BROWNHILL AND DEAN BUGG
Hexcel Composites Ltd., Duxford, Cambridge, CB2 4QD.

SUMMARY
Hexcel Composites has developed a range of paste adhesives to complement its existing range of Redux\textsuperscript{®} aerospace film adhesives. These new products were designed to meet specific challenges and represent an improved range of paste adhesives for aerospace applications.

1. INTRODUCTION
Structural adhesive bonding has traditionally been accomplished using film adhesives. The key characteristics exhibited are high strength, high temperature resistance, toughness and long-term durability. Although handling is simple, they do not very easily lend themselves to automation. Additionally, high cure temperatures, pressures, and expensive tools for component manufacture are commonly required. Generally, paste adhesives incur fewer end use complications and can be utilised in cheaper, automated processes.

Stimulated by such advantages, extensive work has been carried out in order to produce room temperature (RT) curing paste adhesives that match many of the strengths of films. However, such products still suffer from application restrictions where they are required to be hand-mixed prior to use. Hexcel Composites has developed paste adhesives that are cartridge compatible and therefore more readily usable in a variety of applications. This has required a careful balance between the thixotropy characteristics of the two components used, and the subsequent stability requirements for such systems to meet cartridge compatibility. This paper serves to highlight some of the technical challenges overcome in developing new paste adhesives for aerospace applications.

2. REDUX\textsuperscript{®} 810
The development of Redux 810 involved a number of challenges. Amongst the more obvious were high single lap shear strength (SLSS), high bell peel strength (BPS), corrosion inhibition and relatively low viscosity for cartridge application. Other considerations were: long working life, yet high enough reactivity to give good 'green strength' after only 12 hours RT cure; long-term storage stability of the formulated components (especially the hardener); and the ability to give excellent and consistent performance after a wide variety of curing regimes (from ambient up to 120°C).

2.1 Mechanical Performance.
The mechanical performance of a resin system is highly dependent upon the resin and curative. The most common base resins for many adhesives are the diglycidyl ethers of bisphenol A and bisphenol F (DGEBA, DGEBF respectively) or combinations of these.

In addition, solid DGEBA resins are sometimes dissolved in low molecular weight materials but this can lead to highly viscous systems. Multifunctional resins such as tetraglycidyl dianinodiphenyl methane (TGDDM) and epoxy novolacs can also be employed, but in this case were found to impart high viscosity in the uncured material or brittleness after curing and consequently large reductions in peel strength.

A huge number of curatives are available and many alkyd, alkoxy, aliphatic and cycloaliphatic amines were tried either as neat liquids or commercially available blends (some containing accelerators), examples being the Jeffamine, Ancamine and Ancamide series. One of the more widespread and useful curatives is trioxadecane diamine (TTD), an oily, low viscosity liquid that gives good RT lap
shear and peel properties with low molecular weight resins. However, materials cured at RT with this, and similar amines, have glass transition temperatures (Tg's) typically around 40° - 50°C and poor performance above 60°C. To combat this, accelerators are added to catalyse the reactions and produce higher performance products.

One worked example is in the use of bis(aminopropyl)piperazine (BAPP). With a basic low molecular weight epoxy resin, lap shear strengths on chromic acid etched aluminium were quite poor, 3MPa and 7MPa at RT and 60°C respectively. When the curative contained 10% phenol these values were increased dramatically to 34MPa and 18MPa respectively. However, as phenol is toxic, a substituted phenol catalyst with a lower toxicity can be used to similar effect. A great deal of work was conducted to establish the optimum level of this catalyst. Above the critical level and too much acceleration occurs, producing a brittle matrix with poor peel characteristics. Below this critical level and there is too little acceleration resulting in poor lap shear performance at elevated temperatures.

2.2 Toughening.

In many adhesive systems an increase in lap shear performance is accompanied by a decrease in peel strength and vice versa. To obtain a high SLSS by catalytic curing and still obtain a material that is not brittle but flexible and tough enough to give high peel strength (above 225N/25mm) is very challenging. This problem is compounded by the necessity to maintain a suitable viscosity for cartridge application.

The traditional methods of toughening include additions of flexibilisers such as rubber, thermoplastics (TP) and core-shell (CS) particles. The use of ABS rubber at very low levels gave increases in peel strength but this was accompanied by a huge increase in viscosity such that cartridge dispensing became impossible. Other CTBN based rubber adducts were found to cause the same problem or be ineffective tougheners. Incorporation of CS additives at high loadings gave tremendous peel strength but also increased the viscosity and decreased the SLSS values. After many trials a blend of tougheners was eventually found that would impart sufficient flexibility to allow excellent peel characteristics, measured by BPS and climbing drum peel strength (CDPS: - 600-650N/75mm after either 22°C or 70°C cure), without loss of shear strength or large increase in viscosity. A comparison of BPS with that of the leading competition products can be made in Figure 1.

![Graph showing BPS at RT and 60°C for Paste Adhesive A, B, C, D, and Redux 810](image)

**Figure 1.** A comparison of BPS (EN2243-2) of Redux 810 with competition on chromic acid etched aluminium (DTD915B(ii)).

2.3 Corrosion Inhibition.

Redux 810's excellent corrosion resistance results not only from the inclusion of corrosion inhibitor, but also due to its good wetting of the aluminium surface. The latter results in an intimately bonded surface, which helps to prevent the ingress of fluids and foreign material. This is manifested by the fact that a bonded lap shear joint retains 80%-90% of its initial lap shear strength after 2000 hours in a salt spray environment (ASTM B117) regardless of cure temperature. Similar joints retain 75%-85% of their initial values after 30 days at 60°C and 95%R.H.
2.4 Curing.

The careful choice of resin and curative blends allow great versatility in curing characteristics. Effective cure can be achieved at practically any temperature above ambient. However, the balance of catalytic activity to normal epoxy-amine cure allows generous pot life and open time for ease of use when bonding difficult components.

2.5 Stability.

Although the combination of curative and substituted phenol catalyst gave excellent lap shear results, they are intrinsically incompatible and readily separated into two phases over short time periods. Of the vast number of fillers that are available, none are more common than fumed silica. This material can generally be classed as either hydrophilic or hydrophobic. The large number of different grades result from the difference in surface area and organic end groups. The number and availability of H-bonding sites and “solvent-like” end groups can have a major influence on the stability of the formulation. Many experiments were performed before the correct class, grade and level of incorporation could be found. Once this was achieved the subtle balance between low viscosity for cartridge filling and dispensing, and the non-slump behaviour, could be realised.

2.6 Overall Performance.

The work outlined above has led to the careful choice of both type and amount of resin, curative, accelerator, toughener, filler and inhibitor. The result is a product that can be used to bond many materials and cure over an array of temperatures ranging from RT to 120°C. After only approximately seven hours at RT, bonded parts have sufficient strength to be handled, enabling the support tooling or pressure used during cure to be removed. A post cure may then be applied to enhance the level of cure and final strength. Although there are many applications where a film adhesive is used when a paste adhesive is unsuitable, it is nonetheless useful to demonstrate the quality of Redux 810 bonding from either a 70°C or RT cure, by comparing with conventional 120°C curing Redux film adhesives, Figures 2 and 3. Even after a room temperature cure, high shear and peel strengths are achieved when hot curing would usually be required.

Figure 2. Single lap shear strength (EN2243-1) of various Redux adhesives on chromic acid etched aluminium (DTD915B(ii)). Film adhesives at 150gsm, except Redux 609 at 300gsm.
Figure 3. Bell peel strength (EN2243-2) of various Redux adhesives at RT on chromic acid etched aluminium (DTD915B(ii)). Film adhesives at 150gsm, except Redux 609 at 300gsm.

Redux 810 is designed to give good performance from sub-ambient temperatures to approximately 80°-100°C regardless of the cure cycle. This versatility is displayed in Figure 4, which demonstrates the lap shear and bell peel strengths from -55°C for both RT and 70°C cures.

Figure 4. Variation of lap shear (EN2243-1) and bell peel (EN2243-2) strength of Redux 810 with temperature on chromic acid etched aluminium (DTD915B(ii)).

In summary, Redux 810 is a multi-purpose, two-component, corrosion-inhibiting epoxy structural paste adhesive with high shear and peel properties, operating up to 100°C. It is designed for a variety of metal-to-metal, honeycomb and fibre-reinforced composite (FRC) bonding, and structural repair applications. It can also be used to bond inserts and ferrules in the fabrication of sandwich panels. The mix ratio and rheology are such that this material is suitable for use with standard side-by-side cartridge applicators, static mixers and meter mix equipment. At the same time, it has good non-slump and gap filling properties.

3. OTHER REDUX PASTE ADHESIVES.

Other products in the Redux Paste Adhesive range include Redux® 820, a two-component epoxy for cell-edge bonding and the manufacture of honeycomb sandwich structures. Redux 830 is a low density, high strength syntactic paste for potting and edge filling. Redux® 840 is a one part, foaming, epoxy paste that can be used to provide a shear-carrying connection across discontinuities in bonded sandwich panels. Applications of Redux® 850, a two-component epoxy include bonding FRC’s and/or metals with excellent SLSS up to 80°C. It can be applied using automatic equipment via its low viscosity, yet has low slump – making it suitable as a shim material and for filling up to 3.6mm bond lines. It may be cured via any number of regimes from ambient to 120°C, cured parts being sufficiently bonded after only 12 hours at RT.

Redux® is a registered trademark of Hexcel Corporation, Stamford, Connecticut.
Epoxy Adhesive Technology: Going from Strength to Strength

Terry Gordon* & Martin Fakley
Bondmaster Division of National Starch & Chemical

ABSTRACT

The aim of this presentation is to show that new toughening technologies are leading to ever “stronger” epoxy adhesives and that control of a broad range of properties is required to achieve optimal and durable adhesive performance in increasingly diverse applications.

We have shown previously that low modulus substrates such as polypropylene can be successfully bonded with low strength flexible epoxy based adhesives and maintain a durable assembly with minimal surface pre-treatment. By increasing the surface energy by plasma treatment, the bond strength on plastic and metal substrates can be dramatically increased, even allowing polypropylene to be bonded with high strength rigid epoxy adhesives.

With the increased use of thermoplastics and composites in consumer or industrial products, transportation (especially automotive, aerospace and rail), medical, and other fabrications, the need for adhesives to join effectively similar and dissimilar substrates has never been greater. Examples shown include ABS to glass for mirror bonding, melamine to stainless steel for ashtray construction and bonding to steel for valve manufacture. All of these applications have been successful with the use of low strength adhesives.

It is evident therefore that the successful bonding of plastics and metals is not solely reliant upon the inherent strength of the adhesive bond but also the intrinsic properties of the cured material such as energy absorption and thermal expansion and environmental stability.

Where the need arises for an adhesive to perform at maximum strength a family of high performance adhesives is now on offer with a choice of rheology characteristics designed to suit a wide range of applications such as industrial laminate production, where low viscosity is desirable, and composite bonding and repair where good gap filling is required.

The exceptional performance is achieved by incorporation of novel toughening agents into the epoxy system and by careful selection of these ingredients; two part systems with the strength characteristics of heat cure single part epoxy adhesives can now be formulated.
Data will be presented that show how extremely high performance can be achieved with these two-part epoxy adhesives. The influence on strength of the curing conditions and the exposure time at each condition will also be shown. Whilst high performance is possible after ambient temperature cure, slightly increasing the cure temperature produces a significant increase in the performance of the cured material.

Finally the excellent resistance of the cured adhesives to both warm, moist conditions and salt spray will be illustrated. Examples of applications of these new, patented high shear and peel strength adhesives are currently being used will be shown.
Two-part epoxy adhesives: Synergism between CTBN and nanoparticles


Epoxy adhesives, both heat curing and ambient-temperature curing, have been improved considerably by research and development efforts in recent years. Improving toughness is a major development target for structural adhesives with regard to crash-resistant performance\(^1\), \(^2\). This is especially true at low temperatures, where unmodified epoxy adhesives tend to become brittle.

Modifying heat curing, single-component epoxy adhesives with HYCAR® CTBN adducts and ambient-temperature curing, two-component adhesives with HYCAR® ATBN in the hardener component is a well-known and widespread technology.

A rather new class of materials are the so-called nanocomposites: a resin matrix, usually thermosetting, is reinforced with nanoparticles, having average particle sizes of 20 nm. Compared to conventional fillers, totally different effects and much better physical properties can be achieved.

The question is whether combining these two completely different approaches of toughening will further optimise epoxy adhesives.

Toughening using CTBN-adducts

Carboxy functional butadiene acrylonitrile copolymers (CTBNs) have been used for some years to toughen epoxy resins\(^3\), \(^4\). The properties can be controlled by the ratio of acrylonitrile / butadiene. An additional benefit from using these copolymers is the improved adhesion to oily substrates. The copolymers themselves are only partially miscible with epoxy resins.

To use them in one part epoxy adhesives, so-called adducts or prepolymer are prepared first by reaction with an excess of epoxy resin. These adducts can be blended with all common resins in any ratio. During cure, phase separation occurs and rubber domains are formed, which are chemically linked to the resin matrix by their epoxy end groups. The typical appearance of HYCAR®-modified systems develops. The phase separation is crucial for the performance of the adhesive\(^9\) and depends on the hardener used, the adhesive formulation and curing conditions, as well as on the structure of the adduct itself.

Besides the standard grades for typical epoxy applications like adhesives, composites, coatings etc., new adducts especially suitable for metal bonding have been developed in recent years. These adducts can be used by the adhesive formulator as building blocks in a modular system\(^9\).

Reacting carboxy functional butadiene acrylonitrile copolymers with amines yields amine functional products (so-called ATBNs). Combined with conventional amines they are used to formulate tough hardeners for ambient temperature curing epoxy adhesives\(^7\), \(^8\).

During the cure, phase separation occurs as with adducts used in one part heat curing adhesives. However, quite a few RLP molecules do not undergo phase separation but are crosslinked directly into the epoxy network. Hence lower modulus and lower glass transition temperature are found.
NANOPOX® - a new class of materials

In recent years nanotechnology has become an area of very intensive research. In chemical nanotechnology methods have been developed to synthesize nanosized filler particles. Unlike conventional fillers, even surface-modified ones, nanoparticles exhibit many advantages: with the same addition level of filler the number of particles added (and their surface area) is orders of magnitude larger. Accordingly the interactions with the matrix resin are more intensive. The resin viscosity is not increased significantly, even with high loading levels (40%) because there is no formation of agglomerates. In addition, due to the small particle size, resins modified with nanoparticles are still clear, an especially important property for coatings applications. Further, they can penetrate close-meshed fabrics easily, which makes them very suitable for the reinforcement of composites, especially if injection methods (RIM, RTM etc.) are used.

Using a unique manufacturing process\textsuperscript{9} modified SiO₂-nanoparticles can be incorporated in a variety of matrix resins like epoxies or acrylates. The nanoparticles are surface-modified with regard to the chemical nature of the matrix resin, therefore they can be crosslinked into the resin during cure. Furthermore the surface modification prevents agglomeration later on. The particle size of approximately 20 nm created during the sol-gel process remains unchanged during further mixing / blending and processing steps.

Using the products of the NANOPOX\textsuperscript{6} range in a formulation permits many improvements\textsuperscript{10, 11, 12}; for example significantly higher fracture toughness, impact resistance, hardness and modulus. In addition, there is lower shrinkage, unchanged thermal properties and same chemical resistances, plus improved scratch and wear resistance and nearly unchanged viscosity.

It is very important to note that in contrast to "classical" toughening the modulus is not lowered, but increased. Similar results have been found in other investigations\textsuperscript{13}.

Adhesives with µm and nm phases

Recent investigations\textsuperscript{14} have shown that the modification of rubber-toughened one part epoxy adhesives with silica nanoparticles improves the adhesive performance considerably.

The rubber domains formed by the CTBN-adduct were in the range of 1 - 2 µm; 25 - 50 times bigger than the filler particles.

Very surprising was that the best adhesive performance was found at low addition levels of nanoparticles\textsuperscript{14, 15}. Investigations regarding epoxies without rubber-toughening resulted in linear improvements in performance with increasing addition levels of nanosilica.

As two-component structural adhesives have received a lot of interest regarding automotive applications recently, the next step was to investigate the nanomaterials in a suitable ambient-temperature curing adhesive\textsuperscript{15}.

The model adhesive formulations investigated are shown in Table 1. All adhesive formulations are toughened using an amine reactive butadiene acrylonitrile copolymer (ATBN) in the polyaminoamide hardener. The amount of ATBN was chosen regarding best adhesive performance. The nano-SiO₂ was incorporated at different concentrations in the resin using a standard epoxy resin containing 40 % nanoparticles.
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</tbody>
</table>

| % mass SiO₂ (on total) | 1.05 | 2.1 | 4.1 | 8.0 | 21.8 |

Table 1: Model formulations for two-component epoxy adhesive

Lap shear testing was performed on untreated aluminium (automotive grade) as well as on chromic acid etched T3 aluminium as well as on oil treated electrogalvanized steel. Gic was determined using tapered double cantilever beam testing with untreated aluminium as substrate. Roller peel was tested on chromic acid etched T3 aluminium.

Curing conditions were 24 hours at room temperature followed by a postcure of 2 hours at 60 °C. Note that curing for one week at ambient temperature, without the 60 °C postcure, achieves approximately 90 – 95 % of the lap shear strength. Therefore postcuring at elevated temperatures is not a "must" with these formulations.

The tests had been repeated for formulations with a lower content of elastomeric modifier (less Hycar ATBN was used in the hardener) with similar loading levels of nanoparticles. Same substrates and curing conditions. Again, the best adhesive performance was found for low addition levels of nanosilica. Improvements compared to the "Hycar-only" toughened adhesive range from less than 10 % to more than 100 % depending on test method/temperature and substrate.
Figure 1: Best performance versus addition level nanoparticles

In Figure 1 the formulation with the best performance in the respective test (and with the respective substrate) is plotted versus the amount of nanosilica in the formulation.

The Hycar addition level in series 1 was approx. 19 %, in series 2 13 % and in series 3 10 %. It is evident, that regardless of the rubber concentration in the adhesive formulation at an addition level of 2 – 4 mass % nanoparticles best adhesive performance is found.

The rule of a low addition level of nanoparticles in the resin yielding the best adhesive properties seems to be confirmed for one part and two part adhesives.

Still the mechanism of the obvious synergism between microsized rubber domains, nanosized filler particles and long flexible rubber molecules build into the epoxy matrix has to be explored in much more detail. This is an area of further intensive research.

Summary

Tougheners like CTBN-adducts or ATBNs are used in many structural adhesive applications with an excellent price/performance ratio. Combining them with the new nanomaterials showed that the performance of both single- and two-component epoxy adhesives could be further improved. Hence these building blocks are powerful tools for the adhesives formulator.

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Influence of toughening agent incorporation on the hydrophobic characteristics of epoxies

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The absorption of water into adhesive joints can result in the serious degradation of joint performance. In particular, water can influence both the bulk mechanical and thermal characteristics of the adhesive and, as a result of diffusion through to the interfacial regions of the joint, cause serious weakening of the joint.

Many polymer types have been employed in structural adhesive formulations, the most notable being epoxies. Due to tendencies towards brittle behaviour, structural adhesives based on epoxies are generally toughened via the incorporation of additives such as rubbers or thermoplastics. The incorporation of such materials can result in very substantial increases in fracture toughness, with this generally being achieved without significant reductions in other important mechanical or thermal properties.

One particular aspect of adhesive toughening which appears not to have been studied in any detail concerns water absorption. Consequently studies have been conducted within QinetiQ to assess the influence of both rubber and thermoplastic modification on water uptake behaviour in epoxies. In the case of rubber modification, work has been conducted to assess the influence of various formulation and cure parameters on water uptake. In particular the influence of rubber concentration (based on CTBN) and cure temperature on a DGEBA based epoxy has been studied. Results have revealed the extent to which both parameters can influence both the extent to which water is absorbed and the rate of the absorption process. Intriguingly, the morphological characteristics obtained via this form of toughening has been shown to influence the nature of the uptake process.

Further work designed to assess the influence of thermoplastic modification on the water uptake characterises of a tetrafunctional epoxy has also been conducted. Variables considered have included thermoplastic concentration, molecular weight and molecular structure. Results have revealed the extent to which thermoplastic modification can enhance hydrophobic character in addition to, of course, significantly increasing toughness.