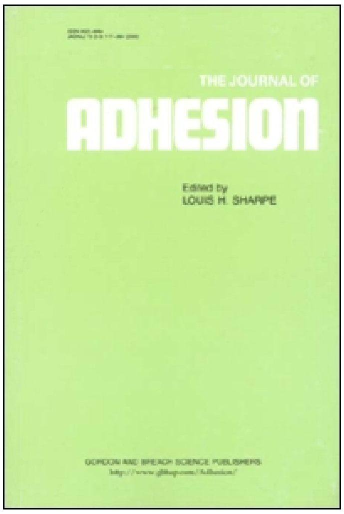

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Modified Epoxides; Practical Aspects of Toughening

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Modified Epoxides; Practical Aspects of Toughening

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It is now almost ten years since the first toughened adhesives were introduced, with restraint, to the UK market with the object of determining the relative merits and shortcomings of the various options. During a prolonged period of controlled evaluation the toughened epoxides have proved to be more versatile than the corresponding acrylics—though the latter are not without virtue. Extremely high levels of performance have been observed particularly from the single-part, heat cured epoxides. Here peel, impact and fatigue resistance have reached remarkable values without sacrificing conventional performance characteristics.

INTRODUCTION

The attention given to the introduction of the polyamide fortified epoxides in the '60s was a reflection of the increasing dissatisfaction with the structural adhesives of the time. For, there was an increasing awareness that shear strength alone was not enough—peel and impact strength being vital if bonded joints were to withstand even occasional abuse. Unhappily, like so many other chemical structures abounding in highly polar groups the nylon-fortified epoxides displayed poor environmental resistance and they thus failed to live up to their early promise. Concurrent with the evaluation of the nylon types Goodrich were developing a range of butadiene based rubbers containing a variety of groups which they showed could have a marked effect on the performance of polyvinyl and polyepoxide based resins. The first of the two part, cold-set epoxies were introduced in 1973, "toughened acrylics" in 1974 and single part heat-cured epoxides (ESP) in 1975. The results and experiences gained with these, the first commercially available toughened

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adhesives in Europe, serve as the basis of this paper which is dedicated to the practical problems and benefits associated with their production and use.

TOUGHENED ADHESIVES

Plastics in general and adhesives in particular are "toughened" by the introduction of a "rubbery" distortable phase within the load-bearing glassy matrix of the body of the adhesive. It is this physically separate—but chemically linked zone—which absorbs fracture energy and prevents crack propagation. In this manner the resistance of the adhesive to catastrophic failure is considerably enhanced and such compositions show a marked resistance to peel, cleavage and impact forces. It must also be borne in mind that extremely destructive loads and stresses are also imposed by vibration, moisture permeation and the differential expansion of dissimilar adherends. Experience has shown that the toughened adhesives also resist these forces much better than conventional materials.

The techniques used to effect this phased structure vary considerably depending on the basic chemistry of the resin system in question. Within epoxy compositions the variations investigated have involved adducting the epoxide, adducting the hardener, using the rubbery curing agent both with and without a conventional hardener and, in single-part heat cured systems, using a rubber both as an adduct and a separate though reactive medium. In the latter case, chemical incorporation only takes place as the epoxide polymerises.

Each of these techniques has its individual advantages. If the optimum particle size distribution of the precipitated phase is not achieved on each and every occasion the effects may be disastrous. In the case of the two part, room temperature curing systems the problem of phase-reliability is not too severe. But, it will be readily appreciated that when heat curing is involved different stoving cycles can profoundly affect the phase separation.

Viscosity control is obviously an important feature of all adhesives. However, thixotropy is of particular significance in toughened systems because the addition of finely divided material can affect the development of the second dispersed phase. Instead of forming discreet homogeneous secondary zones on polymerisation the dispersed areas may take the form of woolly ragged structures which may contain other discontinuities within them. These features will obviously affect the load bearing characteristics compared with the unadulterated resin.

Contamination can also affect the bond strength as can the nature of the adherend itself. This sort of problem is particularly relevant to the acrylic types which will not function correctly on some surfaces. Perverse yet consistent losses of up to 90% of normal performance have been observed with adhesives

TABLE I

Shear strength: comparison of several toughened materials with polyurethane based structural adhesives (manufacturer's figures for suitably prepared aluminium: MNm^{-2})

	Temperature of testing, °C							
Adhesive	−60	−40	−20	+25	+70	+80	+90	+120
ESP105 (Permabond Adhesives Ltd.) (Single-part epoxy)	31.7	35.9	—	41.4	—	33.1	—	20.7
MMA based acrylic	11.0	—	—	29.7	—	—	13.9	12.4
THFMA based acrylic	—	—	11.2	11.2	4.6	2.5	—	—
Polyurethane structural adhesive	—	20.9		17.6	—	5.5	—	3.7

drawn from a number of sources. By contrast, the epoxides behave well and so do not appear to be so subject to catalytic intervention by the surface chemistry of the adherend.

Tables I and II throw an interesting side-light on these comments, and while the figures are not strictly comparable, being drawn from several sources, they are none the less revealing. Single-part epoxies are clearly superior to the other three types. The poor shear performance of the tetrahydrofurfuryl methacrylate (THFMA) based adhesive indicates that its rather more successful peel strength (given as 3.0 kgf per cm width) has been obtained by using elastomeric techniques rather than those of true toughening. A view supported by the manufacturer's statement that the adhesive creeps if loaded. This is an effect of the cross-link density, phase size and its distribution. It is worth noting that even at −50°C the peel strength of the single part epoxide is still given as high as 1.78 kgf per cm width. The performance of the polyurethane based adhesive is much poorer than that based on methyl methacrylate (MMA) and better than that of the variant based on tetrahydrofurfuryl methacrylate.

Again, the figures given in Table II, while not strictly comparable clearly indicate the superior gap-filling properties of single-part epoxies. Particularly

TABLE II

Shear strength: comparison of toughened adhesives at several bond-line thicknesses. (25°C: MNm^{-2} manufacturer's figures)

	Thickness of bond-line (mm)				
Adhesive	0.1	0.25	0.5	1.0	1.5
Epoxy—single part	44.2	38.6	32.8	31.1	—
MMA based acrylic	22.8		13.8	13.7	5.8
THFMA based acrylic	17.6	14.1	7.0	1.8	—

revealing is the inability of THFMA based systems to cope with the gaps which are frequently found in the assembly of metal press-work. This arises from the failure of the surface-activated polymerisation to proceed satisfactorily across a large gap.

SINGLE-PART TOUGHENED EPOXIDE ADHESIVES

It can be readily seen from Tables III and IV that the shear strength of the single part epoxide ESP105 has not been sacrificed during the elevation of its peel and impact strength. Nor has the environmental performance suffered, particularly good figures being recorded in tests in which the toughened acrylics begin to show degradation and polyurethane adhesives fail completely.

Table IV also includes results comparing the durability of unprepared samples with test coupons which have been abraded, degreased and treated with a silane coupling agent. The environmental test for the results involved exposure to 95% RH at 40°C for six months. As expected, the exterior faces of the mild steel coupons show severe corrosion but the bonded areas are entirely free from it. This is interesting for the performance of the adhesive on the oily surfaces was affected by volatilisation of the oil which contaminated them and the sundered joint displayed a somewhat pock-marked and cratered surface not observed elsewhere.

Use of heat-cured, single-part, toughened epoxy as organic solder

In the mechanical engineering industries ESP adhesives can be used as organic solder as they are capable of bonding surfaces as diverse as aluminium, stainless steel or glass reinforced plastics accommodating themselves to a

TABLE III

Typical bond strengths obtained with a heat-cured, single-part toughened epoxy (ESP105, Permabond Adhesives Ltd.)

Lap-shear, MNm^{-2}	Aluminium, 41.4; Steel, 41.4; Copper, 27.6; SMC, (sheet moulding compound) 12.4 (adherend failure)
T-peel (ASTM D1876) $kgf.cm^{-1}$	At −50°C, 1.79; 25°C, 6.43; 80°C, 5.53
Impact (ASTM D950/72)	Pendulum brought to stop without fracture
Climbing Drum Peel (ASTM D1781) $kgf.cm^{-1}$	At 25°C, 8.93

TABLE IV

Environmental resistance of a heat-cured, single-part, toughened epoxy (ESP105, Permabond Adhesives Ltd.)

	Lap-shear strength retention, percent							
Duration of exposure	2 hr	24 hr	1 wk	2	4	8	12 wks	6 mnth
Chrome-etched A1.95% RH, 40°C	—	—	92	90	90	83	80	—
Same, salt spray, RT	—	—	92	92	90	90	90	—
Same, boiling water	90	80	—	—	—	—	—	—
Oily steel, 95% RH, 40°C	—	—	—	—	—	—	—	53
Steel, degreased, phosphated, conditions as before	—	—	—	—	—	—	—	79
Abraded, degreased, silane coupling agent applied, conditions as before	—	—	—	—	—	—	—	77

range of curing cycles or adventitious curing such as may occur in paint stoving ovens. Their tolerance of different curing cycles is illustrated by Figure 1.

Strength of adhesively bonded box beams

Dramatic improvements in the flexural stiffness and ultimate flexural strength of box beams may be obtained if these are fabricated by bonding instead of either riveting or welding. Table V illustrates the comparative performance of

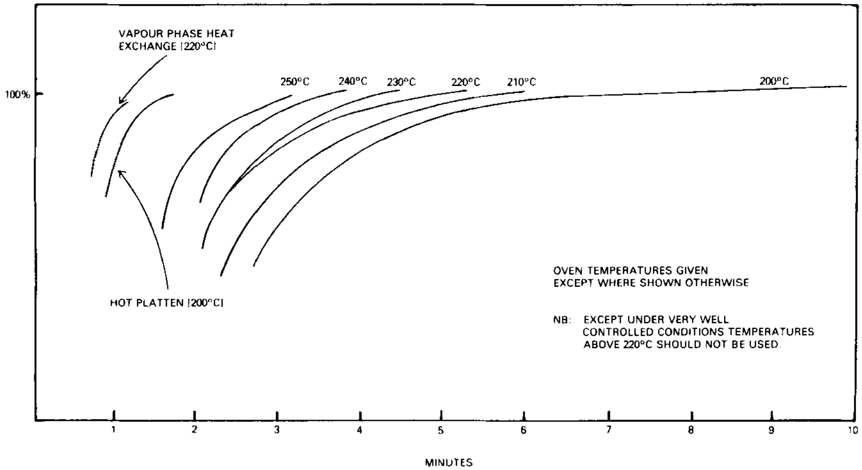
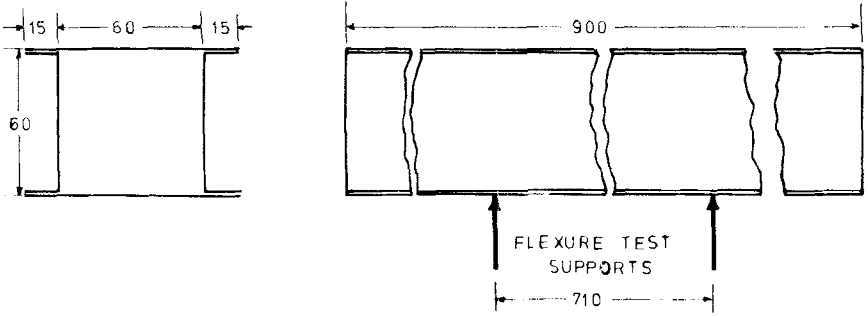


FIGURE 1 Effect of cure schedule on rate of shear strength development (ESP 105).

TABLE V

Mechanical properties of thin sheet fabricated box section beams

Beam dimensions (mm)



Beam material	Joining method	Flexural stiffness kN/mm	Torsional stiffness kNm/rad	Ult. load in flexure kN
1.2 mm Al alloy Beam weight 1.1 kg	Rivet	1.6	2.6	7.0
	Spot weld	1.9	5.3	6.4
	2 part cold cured epoxy adhesive (Permabond E 15)	2.8	6.7	8.2
	One component heat cured epoxy adhesive (Permabond ESP105)	3.9	11.6	8.8
	Toughened acrylic adhesive (Permabond F 241)	4.8	5.4	8.7
0.9 mm mild steel Beam weight 2.3 kg	Rivet	1.8	2.5	3.4
	Spot weld	1.9	9.5	3.6
	2 part cold cured epoxy adhesive (Permabond E 15)	4.0	9.9	7.7
	One component heat cured epoxy adhesive (Permabond ESP105)	4.8	7.9	7.2
	Toughened acrylic adhesive (Permabond F 241)	2.9	11.0	5.0

Notes

1. Spot welds and rivets spaced at 25 mm pitch along each seam.
2. Initial failure at the ultimate load in flexure resulted in buckling of the vertical inner webs. The crippling loads in struts depends on eccentricity of applied load and in the beam webs the loading eccentricity is affected by the bend radius of the flanges. The lower ultimate strengths in mild steel may be due to large bend radii.

TABLE VI

General properties of a cold-cured two-part toughed epoxide formulated for the assembly of FRP (SMC) components and panels

Shear strength Material	GRP*	SMC* (Sheet moulding compound)	PVC	Aluminium	Steel
MNm^{-2}	9.7	12.4	16.6	15.9	16.6

*Adherend failure.

aluminium and steel box beams assembled by riveting, spot-welding, and bonding with a variety of adhesive types.

Potential as laminating resins and use with GRP

Toughened epoxides have now seen several years use in the form of adhesives though, by comparison, another potentially useful role as laminating resins has had scant attention.

While there are several major difficulties to be overcome it is felt that they could make a considerable contribution to the performance of laminates by reducing the incidence of inter-laminar fracture at high strain rates; *e.g.*, splitting on impact.

The difficulties with materials at present available are caused by high viscosity (even when low molecular weight rubber is used), the necessity of employing particulate catalysts for optimum performance and the liability of uncontrollable exotherms. Micronised catalysts have been developed and these should allow the ready penetration of heated resins whose reduced viscosity should give acceptable rates of flow. Encouraging results have already been achieved by several vinyl variants and the toughened two-part cold cure epoxides. However, it is felt that the ESP types offer much more, enough to make their development worthwhile. However, although true laminating resins based on these compositions are not yet available, the adhesives themselves have been modified by formulation with thixotropic fillers into two-part, room-temperature curing materials for the assembly of panels of sheet materials. The normal gel times are about 10 min but if used with heated moulds, de-jigging can be kept to within 10 min. Lap-shear strengths with these adherends are given in Table VI. The T-peel (ASTM D1876) is 2.14 kgf cm^{-1} independent of substrate as the failure is invariably cohesive not adhesive.

CONCLUSION

Although they are newcomers to the field, the toughened epoxides, though still limited in number, have clearly shown that they are at least the equal of the best of the earlier generations. Their influence will be widely felt particularly in the transport industries where their ability to join dissimilar metals and other materials will have great significance. In more mundane applications, they will be seen more often replacing solder and brazing on small part assembly where even the most advanced acrylic systems cannot cope with the small areas, loads and environments which are often imposed.