

IOM Adhesives Section

Cure of Adhesives
Surface Coatings and Sealants

December 12th 1996

The Institute of Materials Adhesives Section has the following committee members

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The next one day meeting will be held on Wednesday 7th May 1997.

Details of the event can be obtained by contacting

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Programme

- 10.30 Coffee and Registration
- 11.00 THE BASICS AND STATUS OF CURING PROCESSES
J Comyn (De Montford and Loughborough)
- 11.45 THE RADCURE ALTERNATIVE FOR VARNISHES
R Kennedy (Paint Research Association)
- 12.15 NON-THERMAL CURING METHODS FOR RESINS
D Attwood (British Aerospace)
- 12.45 Lunch
- 14.15 ADHESIVE DENTAL MATERIALS
J Nicholson (Kings College School of Medicine and Dentistry)
- 14.45 CURE STUDIES ON ADHESIVES USING DMA
D A Tod (DRA Fort Halstead)
- 15.15 Tea
- 15.30 CURE OF POLYSULFIDES
G B Lowe (Morton International)
- 16.00 THE EFFECT OF CURE ON SHRINKAGE IN EPOXY RESINS
R D Adams and H Yu (University of Bristol)
- 16.30 Close

THE BASICS AND STATUS OF CURING PROCESSES

J COMYN

De Montfort and Loughborough Universities

There are two things which a bonding material (adhesive, surface coating, sealant etc.) must do; the first is to wet the substrates and make intimate molecular contact, and the second is to then harden. Hardening can be by loss of solvent or water, cooling in the case of hot melt adhesives, or by chemical reaction. The term *curing* is kept for hardening by chemical reaction.

History of curing

Drying oils are the oldest substances which cure, and the best known of these is linseed oil. Their use was recorded by the Greek physician Galen in the 2nd century, and were used in paints by the Flemish masters. Linseed oil is a mixture of the glycerides of linolenic, linoleic, oleic, stearic, palmitic and myristic acids; the last 3 of these are unsaturated but the first 3 contain C₁₈ chains with respectively 3, 2 and 1 C=C double bonds. Oxygen from the atmosphere initiates free radical addition polymerisation of the double bonds, leading to a crosslinked product.

Uses of linseed oil include varnishes, paints, putty and linoleum. The rubbery layer which forms on chip-pans with polyunsaturated cooking oils is a manifestation of the same curing processes.

In 1839 Charles Goodyear discovered that natural rubber can be vulcanised by heating with sulfur. This involves reaction of C=C bonds with sulfur, to produce crosslinks which are short chains of sulfur atoms. The process is still used; cure temperatures are in the range 140-180°C and accelerators are added.

Things that cause cure

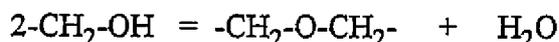
Curing can be brought about by heat, where an example is the cure of epoxide adhesives. Here two components are mixed together and they react thermally either at room temperature when aliphatic amines are used as curing agents, or at temperatures well above 100°C when aromatic amines or acid anhydrides are used. The cure of structural acrylic adhesives is also a thermal process; a redox initiator system reacts to give free radicals at ambient temperature, and the radicals then cause the polymerisation of acrylic monomers. Heat can be supplied by conduction or by microwaves.

Water from the atmosphere causes the cure of cyanoacrylate adhesives (superglues). Such adhesives are cyanoacrylate monomers stabilised with a small amount of acid (e.g. sulfur dioxide). Both substituent groups are strongly electron withdrawing making the monomer very susceptible to anionic polymerisation. The initiating species is the hydroxide anion which is naturally present in water, which conveniently coats all substrates in the atmosphere. Other systems which are water cured are silicone sealants and some isocyanate adhesives, which are examined in more detail later on.

Ionising radiation in the form of UV or electron beam (EB) basically generate free radicals which then initiate polymerisation. Adhesives must be transparent to permit UV cure and a well known example is non-amalgam tooth fillings, where the dentist uses a light-pipe to direct UV to an acrylic material in the cavity. With UV cure there is a substance contained within the material which generates free radicals when UV is absorbed. Electron beam radiation is very energetic and may generate free radicals simply by generally breaking covalent bonds. A significant problem with EB is the capital cost of equipment.

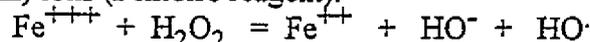
Basic mechanisms of cure

The basic mechanisms are condensation polymerization and addition polymerisation. In condensation polymerization, molecules react with one another because they contain chemical groups which are mutually reactive. Examples are amine and epoxide groups, acid anhydride and epoxide groups, -SH groups in polysulfides, isocyanate and hydroxyl groups, and -CH₂-OH (methylol) groups in phenolic adhesives, which condense as follows.



Here cure takes place at a temperature above 100°C, so pressure must be applied to prevent the unwanted formation of steam-filled voids.

Compounds containing double bonds or rings can be polymerised by addition polymerization, which at its most basic involves opening of the rings or double bonds, and joining them together to make a chain. Addition polymerization is a chain reaction involving the sequential steps of initiation, propagation and termination, and with adhesives the active centre is mostly a free radical, although it is an anion with cyanoacrylates. Radicals can be generated by the thermal or UV decomposition of an initiator, or by a redox reaction, of which a simple example is the reaction of hydrogen peroxide with iron (II) ions (Fenton's reagent).



In reactive acrylic adhesives organic peroxides and transition metal salts that are soluble in organic compounds may be used, but the principle is the same. As direct mixing of the reactants can cause explosions, at least one component must be diluted into the adhesive

Crosslinking

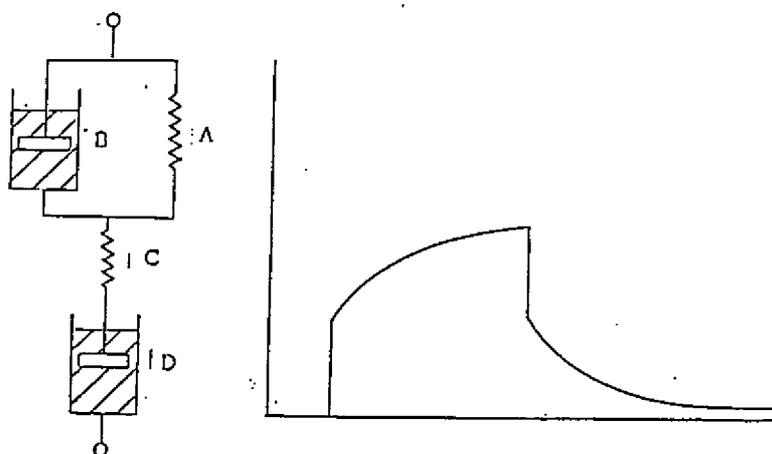
Linear polymers are formed from difunctional monomers (i.e. two functional groups in the case of condensation polymerisation, one ring or polymerisable double bond with addition polymerisation). The addition of a monomer with 3 or more functional groups causes crosslinking.

Viscosity rises with cures, but at the gel-point when there is, on average one crosslink per molecule, the viscosity rises sharply. The whole polymer now becomes a single crosslinked molecule. Further crosslinking will occur beyond the gel-point.

Effect of crosslinking

Crosslinking renders polymers insoluble, infusible and considerably reduces creep, and it is the last of these factors which is of most importance in adhesives. The properties of linear thermoplastics can be represented qualitatively by the four element model which contains two springs and two dashpots, and it is the irrecoverable flow in

dashpot D which represents creep. The cause of this is linear polymer molecules sliding against their neighbours, and the prevention is knot them together by crosslinking. The plot of strain against time shows the effect of loading and then unloading on the model.



4 ELEMENT MODEL

Emulsion adhesives

The ingredients for an emulsion polymerization are water, monomer(s), stabiliser and initiator. The stabiliser can be a surfactant or water-soluble polymer, use of these being referred to as surfactant and colloid stabilisation. Amounts used are 0.2-3.0% wt based on water for ionic surfactants and 2-10% for water soluble polymers. The product of emulsion polymerization is a latex of polymer particles with adsorbed stabiliser. The particle diameters are of the order of 1 μm and the amount of water is normally 50-55%.

Polymer latices are best known as emulsion paints which are based on PVA. Whether used as surface coatings or adhesives, they are spread on surfaces and a continuous film is formed as the water evaporates. The lowest temperature at which a continuous film can be formed is the *minimum film-forming temperature MFT*, which is close to the glass transition temperature. The dried materials contain much hydrophilic material, making them water-sensitive.

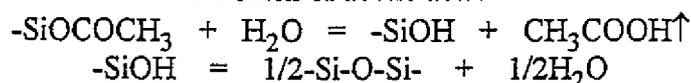
The simplest crosslinking agent that can be added to PVA latices is glyoxal ($\text{CHO}\cdot\text{CHO}$). This is stable below pH 8 and only reacts in the dried film, presumably with hydroxyl groups. With acrylic adhesives up to 5% N-methylolacrylamide ($\text{CH}_2=\text{CH}-\text{CONH}-\text{CH}_2\text{OH}$) can be added as a crosslinking agent, which acts by condensation of methylol groups.

Zirconium compounds can crosslink polymers with certain functional groups (e.g. -COOH and -OH), and have been used to reduce the water-sensitivity of emulsion adhesives by crosslinking water-soluble polymers used as stabilisers.

Cure by water

As already mentioned cyanoacrylates are cured by adsorbed water, but a well known example of water-cure is silicone bath-sealant. One part silicone sealants are often

termed (RTV) room temperature vulcanising, and consist of polydimethylsiloxane (PDMS) with molar masses in the range 300-1600, with acetate, ketoxime or ether end groups. These are hydrolysed by moisture from the atmosphere to form hydroxyl groups, which subsequently condense with the elimination of water. When the acetate terminated PDMS cures there is a smell of acetic acid.



The rate of cure is controlled by water diffusion, which is slow in comparison with the chemical. There is a sharp advancing front of cured sealant, and the cured material acts as a barrier for water permeation. Any water which passes through this barrier quickly reacts with uncured sealant, and thus the barrier is thickened.

The amount of water permeating unit cross section of the cured layer is given by

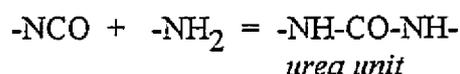
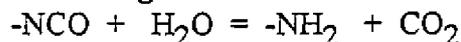
$$dn/dt = Pp/z$$

At time t the thickness of cured adhesive is z ; n is the number of moles of water, p the vapour pressure of water in the surroundings and P is the permeability coefficient of water in cured sealant. V is the volume of sealant which reacts with 1 mole of water. This leads to the following equation for the depth of cure.

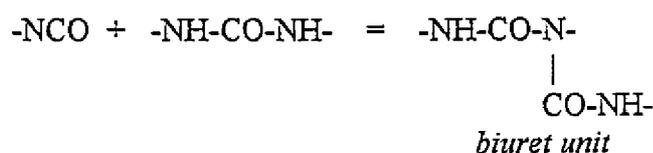
$$z = (2VPpt)^{1/2}$$

The depth of cure is proportional to the square roots of time, relative humidity and permeability coefficient.

One part adhesives consist of low molecular weight, linear polymer molecules, which have isocyanate (-NCO) end groups. Water vapour from the atmosphere diffuses into the adhesive and causes the following reactions which cause chain-extension.



However a further reaction, is that of isocyanate with urea units to form crosslinks.



Cure of hot melts

Isocyanate adhesives of the above type can be applied as hot melt adhesives. Hot melt adhesives have considerable advantages in that they are one part, can readily be applied by machine, and the initial bond is formed rapidly. The fact that they flow means they must be linear at the time of application, but subsequent crosslinking could be a most useful.

One development is the use of EVA/synthetic rubber blends as hemflange adhesives for automobiles. These are thermoplastic up to 130°C, but above this temperature peroxide initiators decompose and cause crosslinking of double bonds in the rubber.

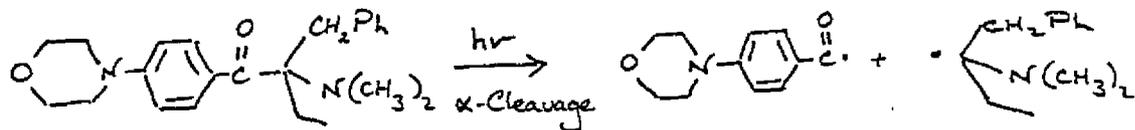
The Radcure Alternative for Varnishes

Dr Richard Kennedy, PRA

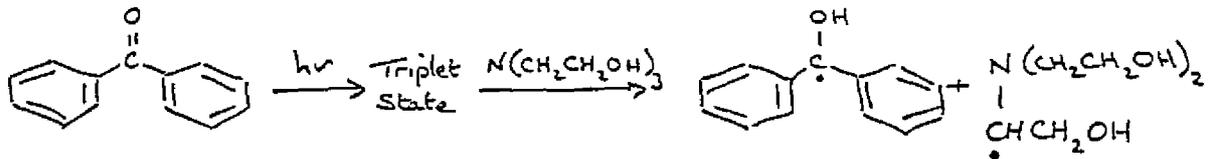
UV Curable coatings are becoming popular because they are environmentally friendly, effectively 100% solids coatings, and give finishing benefits such as very fast and energy efficient curing. Clearcoat UV curable coatings are used largely as wood varnishes (tending to replace nitrocellulose and, to a lesser extent, acid catalysed coatings on flat wood products) and overprint varnishes (which have replaced spirit varnishes eg polyamide/NC in methylated spirits). The principal pigmented UV coatings are inks.

The chemistry of UV curing is a typical free radical polymerisation with initiation, propagation and termination steps. The initiation step involves the absorption of UV light from a UV lamp source by a photoinitiator to form polymerisation initiating radicals, eg

Type I Photoinitiator



Type II Photoinitiator



A very fast free radical reaction proceeds with most commonly a combination of multifunctional acrylates, depending on the coating end-properties required.

As the polymerisation proceeds, the Tg of the developing network increases until a point is reached where the Tg of the network approaches the temperature of the coating and mobility decreases significantly. As a consequence the degree of cure, the percentage of reacted acrylate double bonds is rarely 100% and can be significantly less but still produce a viable, robust film. As expected there is a strong temperature dependence of the "final" extent of reaction.

Conversion is also dependent on light intensity, which can be explained in terms of volume shrinkage during polymerisation. In a linear polymerisation the rate of shrinkage is proportional to the rate of reaction but in cross-linking reactions shrinkage can not keep up with conversion, particularly if vitrification occurs simultaneously.

If a high UV dose rate is applied, most of the reaction will take place in the unrelaxed state, where there is a temporary excess of free volume in the system. At a low dose rate shrinkage occurs during the reaction, a large part of the reaction takes place in the relaxed state, characterised by a much lower free volume.

There are few techniques available for measuring the rate of shrinkage. The most sophisticated measures the decrease in thickness of a thin film confined between a thick glass plate with a machined recess and a thin microscope cover glass, by monitoring the bending of the cover glass. A less sophisticated technique relies on the application of Archimedes Principle. A formulation is placed in a polyethylene sachet and irradiated whilst immersed in water. The change in displacement of water is recorded via a strain gauge.

One of the most important problems with UV cured coatings is their short and long term adhesion to a variety of substrates. It has been suggested that shrinkage may influence the adhesion to plastics and metals. With a higher degree of cure at the surface of the coating than at the base, due to absorption of UV light by the photoinitiator according to the Beer Lambert law, stresses built up during cure might pull the coating away from the substrate.

It is reported that for formulations with similar intermolecular interactions with a substrate, decreasing shrinkage by increasing the molecular weight of oligomer improves adherence properties. It is possible to improve adherence with high shrinkage if a higher content of a swelling monomer is used on plastic substrates. It is clear that the role of shrinkage in adhesion is quite complex.

Loss of adhesion is a concern for the use of UV cured coatings for exterior use. The water permeability of a material is dependent on the solubility of water in the polymer matrix and the diffusion constant D which describes the mobility of water molecules.

The relative order of permeability coefficients for a series of model coatings based on UV monomers was as follows:

Standard stoving acrylic ≈ (EO) Bisphenol A diacrylate ≈ Aliphatic urethane diacrylate < Hexanediol diacrylate < Cationic systems < Diethylene glycol diacrylate ≈ Dipropylene glycol diacrylate ≈ Tripropylene glycol diacrylate < Diethylene glycol dimethacrylate ≈ Triethylene glycol dimethacrylate < Triethylene glycol diacrylate < Aliphatic epoxy diacrylate < Tetraethylene glycol diacrylate

It appears that the water permeability is dominated by the hydrophobicity of the monomer systems and not influenced significantly by the degree of cure. One of the constraints for UV systems is viscosity. Many of the very low molecular weight acrylates are toxic and skin irritants, and they are typically no longer commercially available. The higher molecular weight acrylates used today are safer but higher viscosity. A common strategy is to ethoxylate or propoxylate monomers to reduce toxicity and to lower viscosity, but a consequence is high water permeability and indeed poor outdoor durability.

Other UV curing options are:

- Cationic systems, based on epoxycyclohexane monomers and vinyl ether or polyol diluents.
- Acrylate systems, using vinyl ether diluents.
- Maleate/Vinyl ether systems
- Photoinitiator-free donor-acceptor systems
- UV-curable powder coatings

References

Photopolymerisation of diacrylates: Thermal, mechanical and spectroscopic analysis. J G Kloosterboer. PRA Radcure Coatings and Inks Conference, Aspects of Analysis, Egham 1994, Paper 9

Shrinkage: Its measurement and consequences. N Acham, J Crisp, R Holman, S Kakkar, R Kennedy. RadTech Europe 1995 Conference, Maastricht 1995, p71

Water transport properties of radiation-cured coatings and their effect on adhesion. N Acham, R Holman, R Kennedy, J Crisp. RadTech Europe 95 Conference, Maastricht 1995, p445

How to tackle adherence problems with UV formulations? B Magny, A Askienazy, E Pezron. PRA Radcure Coatings and Inks Conference, Application and Performance, Harrogate 1996, Paper 2

Non-Thermal Curing Methods for resins

David Attwood

British Aerospace

Current methods of processing resins used in adhesives and composites invariably require the input of thermal energy via conduction or convection. These traditional methods have many in-built constraints; the need to use expensive tooling, expensive ancillary materials, long production cycles and imparting thermal stresses into the structure.

Two alternative methods of curing resins to form a crosslinked network are to be reviewed; electron beam and microwave curing. The advantages and disadvantages of these methods as compared with the more traditional methods of resin curing will be summarised. Changes in the resin chemistry will be discussed as well as the practical aspects of manufacturing structures using these techniques. A literature review of the subject will be presented with attention being drawn to existing facilities within the UK, Europe and North America.

Adhesive Dental Materials

J.W. Nicholson

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For about 150 years, amalgam fillings have been used to repair teeth affected by dental caries. Unfortunately, they lack adhesion, necessitating undercut cavities with consequent loss of healthy tooth. They are also obtrusive and increasingly unacceptable to patients.

Modern dental restoratives that match the aesthetics of the tooth have been developed, and these are reviewed in the paper. The most successful, in that they are strong and durable even in load-bearing parts of the mouth, are the so-called *composite resins*. They consist of a polymeric matrix derived from bulky macromonomers such as bisGMA or urethane dimethacrylate, filled with inorganic powders of controlled particle size. They are not adhesive, but may be bonded to the tooth, either by acid-etching to the enamel or by bonding to the dentine. The chemistry of bonding to dentine is complex, and there currently 84 different commercial bonding agents available to the clinician. They generally consist of a conditioner and a primer applied as separate layers. They act partly by forming a *hybrid layer* at the surface of the dentine, which consists of mineralised material from the tooth and monomer from the bonding agent. They may also form so-called *resin tags* by flowing into the dentine tubules before being polymerized, and thus they may also bond partly by mechanical attachment.

Glass-ionomers are an alternative aesthetic material. They consist of an acid-decomposable glass powder which reacts with an aqueous solution of polyacid, of which the most widely used is poly(acrylic acid). They set partly by a neutralization process, involving the acid and ions released from the glass, and partly by a hydration process, involving residual silicate and phosphate structures from the glass powder. Glass-ionomers bond naturally to both dentine and enamel, but they are brittle and unsuitable for load-bearing restorations. Their bonding is quite well understood, and seems to involve local remineralization at the tooth surface and the formation of a tenacious ion-enriched layer at the interface.

To improve mechanical properties of glass-ionomers, in the late 1980s resin-modified versions of these materials were developed. They contain polymerizable monomers, and may also include modified poly(acrylic acid) grafted with unsaturated side-chains. They set by a combination of neutralization/hydration and polymerization, the latter often, but not always, using light-activation. These materials also show natural adhesion to dentine and enamel, though bond strengths are lower than for conventional glass-ionomers, and some manufacturers recommend they be used like composite resins, *ie* with acid-etching for enamel or with bonding agents for dentine in order to achieve bonds of adequate durability.

The most recent development is the polyacid-modified composite resin, a material which is blended to include at least one type of monomeric molecule containing a few carboxylic acid functional groups. These substances are not water-soluble, but take up some water after setting to promote a neutralization reaction. They are reported to bond directly to enamel, and may also bond to dentine, though again it is generally recommended to use special bonding agents. Their overall clinical performance appears promising, but it is too soon to be certain of their long-term durability.

All of these modern restorative materials, together with their mode of bonding, are described in the paper. The paper concludes that, since the use of these materials entails less damage to the restored tooth, the adhesive techniques necessary to use them will continue to grow in importance in clinical dentistry. This will require improved understanding of the interfacial chemistry of tooth-restorative system, and rely increasingly on co-operative research between adhesion scientists, biomaterials scientists and clinicians.

Cure Studies on Adhesives Using Dynamic Mechanical Analysis

David Tod

Defence Research Agency Fort Halstead

Summary

Adhesives are being used extensively in the fabrication of aerospace structures. As the adhesive forms an integral part of the structure it is necessary to fully understand the initial mechanical properties of the materials and how these change with ageing. Testing of materials to satisfy qualification for defence use often involves considerable time. One method of speeding up the process is to study the small strain mechanical properties using the technique of dynamic mechanical spectrometry. This paper identifies the uses of DMA in the assessment of adhesives.

Introduction

To fully characterise an adhesive for all potential uses is obviously too expensive to contemplate if there is no immediate use for the product. It is therefore necessary to establish a cheap reliable methodology to assess these materials.

The technique chosen is that of dynamic mechanical spectrometry which has been widely used for the characterisation of polymeric materials. The main advantages are that it uses only small samples of material and produces very accurate results.

The following is a few examples of the application of this technique.

New adhesives

One area where DMA can provide useful information is in the modification and development of new adhesives. Frequently only small amounts of material are available for test. In figure 1 the dynamic response is shown for three experimental epoxy resins containing differing types of rubber as a toughening agent. These CTBN rubbers have differing acrylonitrile contents (X31 10%, X8 17% and X13 26%). Clearly the mechanical properties of these materials would be very different. Using this technique it is possible to quickly modify the rubber type, concentration etc and re-establish the mechanical response until optimum performance is obtained.

Cure of Adhesives

It is important to correctly cure an adhesive to obtain maximum service life. To

ascertain this by using test coupons would involve extensive trials and the resolution in cure time which could be made would be the order of hours. Samples of a single part epoxy resin were cured at temperatures between 80°C and 140°C in-situ using dynamic mechanical analyzer. The shear modulus results from the four temperatures tested are plotted in figure 2 where the effect of temperature is dramatically shown. The difference in the final moduli seen is due to the fact that the lower modulus are measured at the higher temperatures. Figure 3 shows the relationship between the time to "plateau" cure and the cure temperature. As can be seen there is a reasonable relationship between the cure temperature and the log of the cure time. Obviously compared to lap shear measurements the characterisation by dynamic mechanical analysis is significantly shorter and less labour intensive and will result in more precision in the cure time. In many industrial processes shorter cure times will produce useful cost savings.

This difference in response is again illustrated in figure 4 where the dynamic spectrum of a two part adhesive is compared after curing at ambient and after two hours at 120°C. As would be expected the lower cure temperature equates to a lower operating temperature for the material. Detailed examination of the curves reveal differences in lower temperature transitions and these will result in different mechanical performance.

Durability

In most defence applications of adhesives the aggressive action of moisture on the adhesive joint is the life limiting aspect. In figure 5 the spectrum is shown for an adhesive cured at room temperature and after a similar sample had been immersed in water for 8 weeks at 60°C. The loss in high temperature resistance due to the plasticization of the water is evident. In figure 6 a similar set of results are shown but here the adhesive is cured for two hours at 120°C. Although the exposure time was only six weeks in this case, the relative effect on the upper operating temperature was greater. However the effect over the lower operating temperature is much less significant.

Conclusions

A review has been given of the use of dynamic mechanical analysis to characterise adhesives. This has been illustrated by reference to a number of studies such as the effect of moisture upon adhesive systems, the effect of toughening agents upon adhesive structure and the curing of adhesive systems.

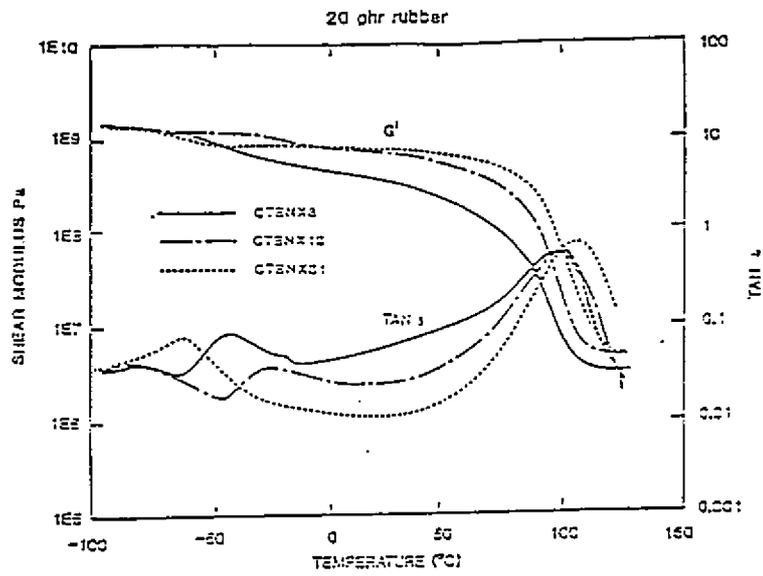


Fig 1 Effect of toughening agent upon the mechanical response

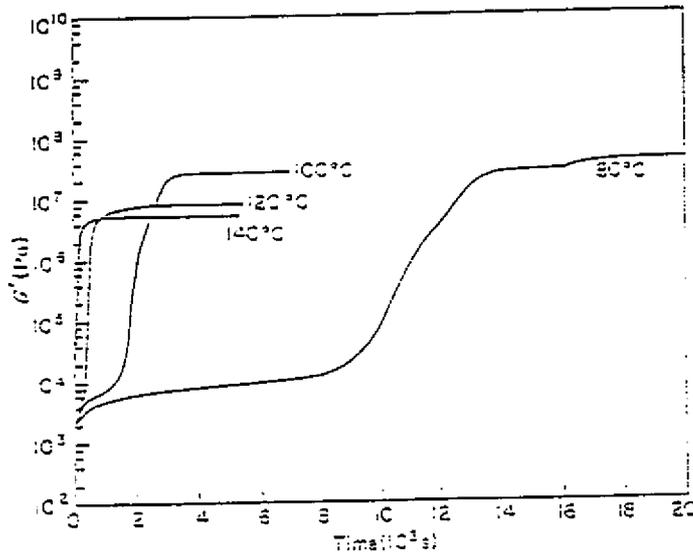


Fig. 2 Effect of cure time on the dynamic modulus of 2007 adhesive at four different temperatures

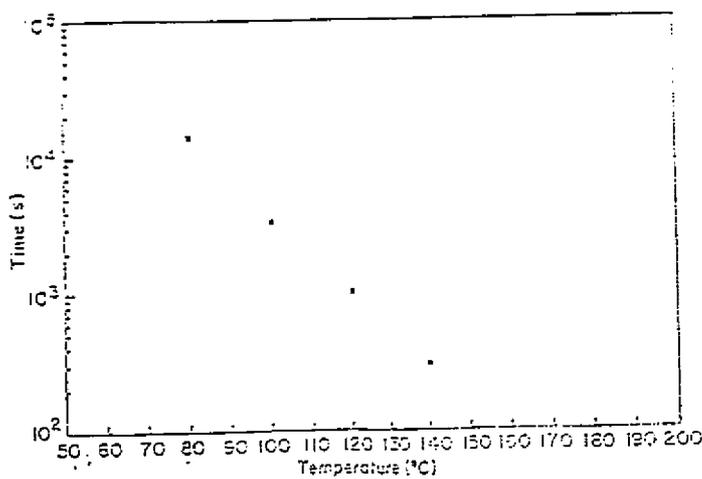


Fig. 3 Relationship between cure time measured by dynamic mechanical analysis and cure temperature

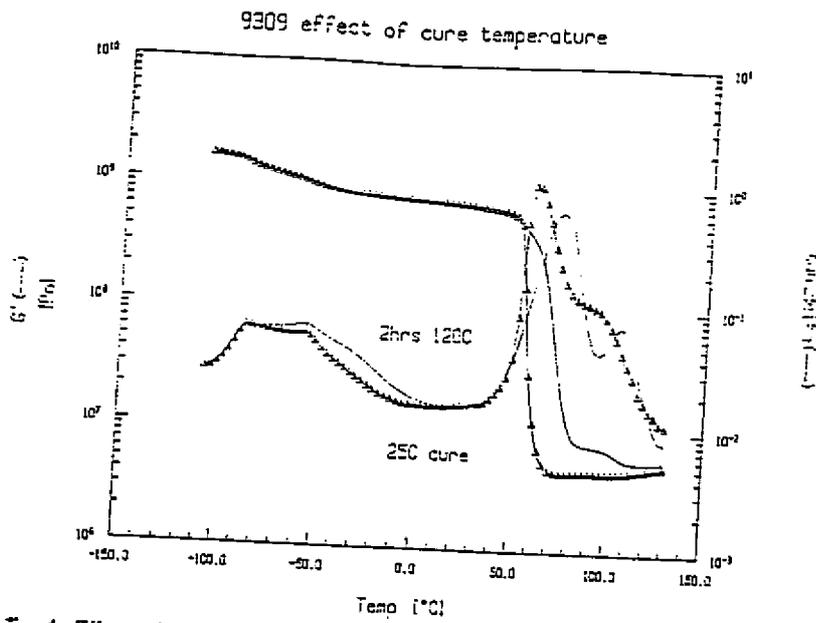


Fig 4 Effect of cure temperature on mechanical response for a two part adhesive.

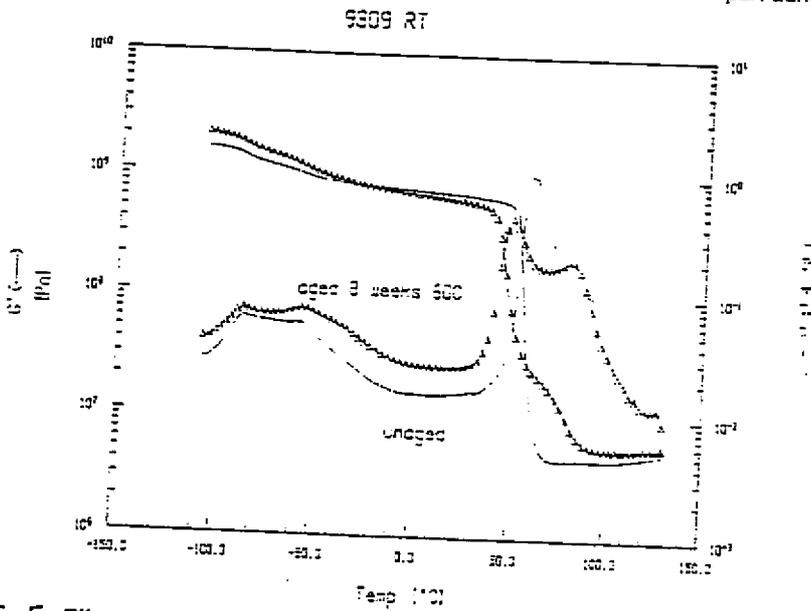


Fig 5 Effect of moisture immersion on mechanical response.

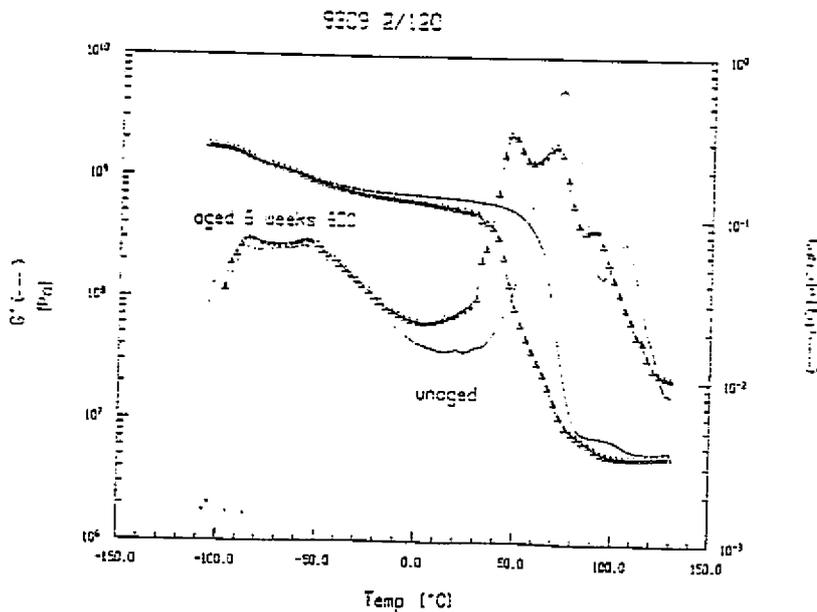


Fig 6 Effect of moisture on the mechanical response for a two part adhesive, cured for two hours at 120°C

The Cure Chemistry of Polysulfides

G B Lowe

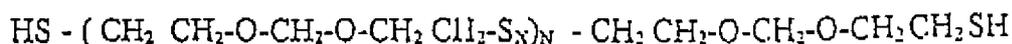
Morton International Limited

Introduction

The original polysulfide (Thiokol) rubbers were solid materials with very high sulfur contents. Early development work treated these compounds as being similar to other rubbers and cure was achieved by addition of sulfur and zinc oxide. It was the introduction of liquid polysulfide polymers (in 1940's) that accelerated the use of alternative curing agents, although it is only recently that the mechanism has been studied in depth. This article deals with the cure of liquid polysulfide polymers only.

The Polymer

Liquid polysulfide polymers are produced by the aqueous polymerisation of short chain dichloro hydrocarbons with sodium polysulfide. The most common polymers are based on Bis(2-chloro ethyl) formal, which following polymerisation and molecular weight reduction yields linear polymers of the type.



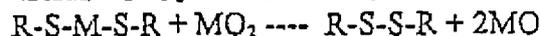
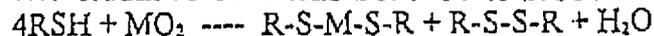
Where X is 1.9 to 2.2 and N can vary from 6 to 42.

Cross linking or branching sites are produced by small addition of 1,2,3 trichloropropane (TCP). The TCP is normally added at levels of 0.5 to 2% by weight on the Bis(2 chloroethyl) formal.

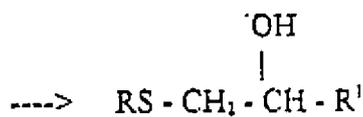
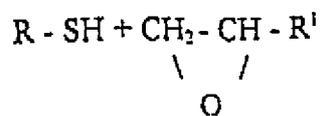
Curing Agents

Over the years it has been found that a wide variety of materials are capable of affecting cure in polysulfide polymers. The main products used for curing agents are metal peroxides and other metal oxy salts which make use of the reducing properties of the thiol group to cause cross linking. Such materials include the dioxides of lead, manganese, calcium, barium, sodium and zinc together with chlorates, dichromates and permanganates. Other curing agents including organic peroxides and hydroperoxides have been used commercially and many other products have been tried experimentally.

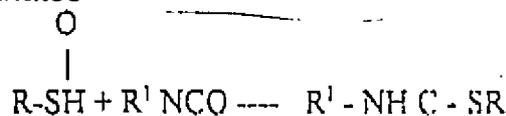
The oxidative cure was believed to proceed via the following path:



The formation of the metal sulfide intermediates will not occur in all cases. Similar reactions can be deduced for the chlorates, dichromates and permanganates. It has also been found that the thiol group can not only undergo oxidation but will also take part in addition and substitution reactions, thus it has been shown possible to react polysulfides with epoxy resins via opening of the oxirane ring.



Or Isocyanates

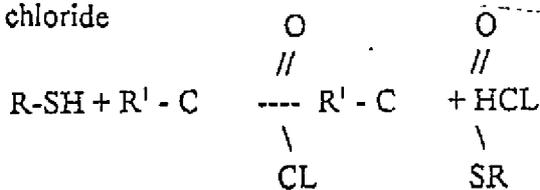


Or across an activated double band

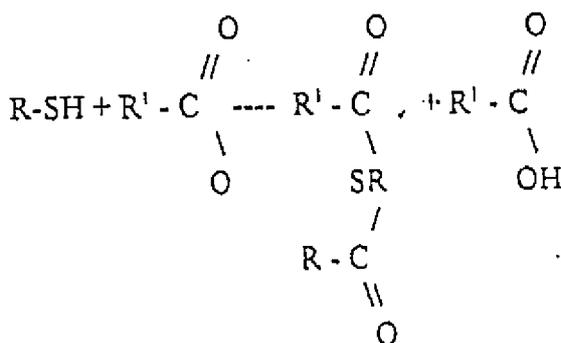


Where substitution is used the following are possible:-

Using acid chloride



And with Anhydrides



Whilst the latter reactions are useful and have been commercially the most important reaction at present is the oxidation of the thiol by metal dioxides.

Influences on Cure

There are a number of problems associated with the simplistic approach. Theoretically the polysulfide converts from 2RSH to R-SS-R regardless of the metal dioxide used. In practice each metal dioxide takes the polymer to different levels of cure and it has been found that lead dioxide yields a lower modulus product than manganese dioxide for example.

Stronger oxidising agents such as the permanganates and dichromates yield a very high modulus material and in the latter case one with improved thermal resistance. Organic peroxides tend to yield high modulus elastomeric cures whilst addition of hydrogen peroxide does not yield a cured material, but under certain conditions can yield elemental sulfur.

Water is known to take part in the cure reaction of polysulfides, and most reactions can be almost permanently delayed or severely retarded by the removal of trace water. Zeolites and Barium oxide have been found useful as water scavengers.

It can be argued that there is a level of water that would be adventitious to the reaction which should be explored.

Other influential additives are acids and bases. All the reactions involving RSH can be catalysed by the addition of a base, and conversely retarded by addition of acid. In practise amines and similar compounds are used as catalysts whilst weak acids such as stearic or oleic are used as retarders.

An interesting point here is that Barium oxide which is used to remove water and delay cure for the production of single pack systems also acts as a catalyst on exposure of the product to the atmosphere. In this case the barium oxide attracts water and creates a basic environment to catalyse the cure once sufficient water is present to allow initiation.

It has been found that mono mercaptans, used as chain stoppers to reduce the amount of cross linking, can have a severe retardation effect on the cure at very low levels of addition.

The early knowledge of the behaviour of polysulfides during cure was sufficient to allow formulators to manufacture a wide variety of products.

These range from large volume usage applications such as -

Insulated Glass Sealants (+70%)
 Construction Sealants
 Aircraft Sealants
 Civil Engineering Sealants

to low volume usage such as -

Dental impression compounds
 Leather impregnation
 Specialist coatings

It was acknowledged however, that a more empirical view of the cure chemistry would be of value in understanding the anomalies often encountered.

Detailed Study of Cure Mechanism

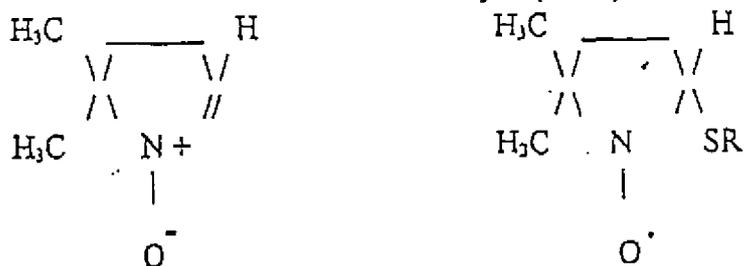
Although the basic outlines of cure were thought to be well understood and, the polysulfides were enjoying good commercial success, the real cure mechanism remained in doubt.

In order to understand the mechanism better a number of fundamental studies were carried out.

A research project, conducted at York University, was initiated to examine the mechanistic details of the chain extension by oxidation in polysulfides.

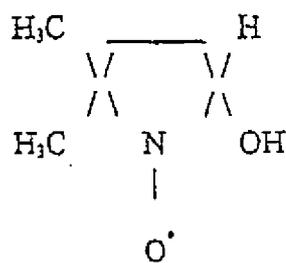
The initial part of the project was to demonstrate the formation of free radicals created by the polysulfide reaction in the presence of an oxidising agent.

Using DMPO (5,5-dimethyl-1-pyrroline-N-oxide) as the spin trap reactions were examined with polysulfide (LP-3) in the presence of manganese dioxide. The thiyl of DMPO was detected when only the two reactants were used, and an additional hydroxyl radical adduct was found when a catalyst (DPG) was used.

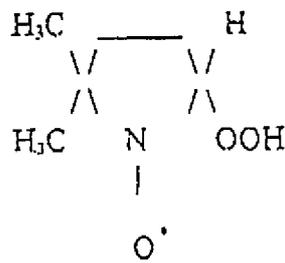


DMPO

THIYL RADICAL



HYDROXYL RADICAL



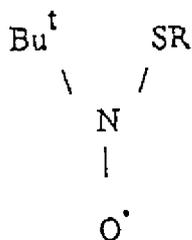
PEROXY RADICAL

The peroxy radical was found when TMG (1,1,3,3 tetramethyl guanidine) was used as a catalyst, this latter catalyst being stronger (more alkaline) than the DPG. It should be noted here that similar no radicals are formed when model di[^]Sulfides are used.

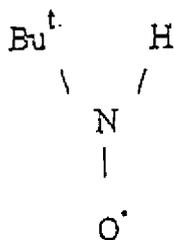
This indicates the radical formation is through the oxidation of the thiol group and not that of the disulfide.

In a separate series of experiments using 2-methyl-2-nitroso propane as the spin trap two important discoveries were made.

Firstly when a less active manganese dioxide was used only the thyl radical



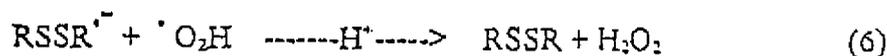
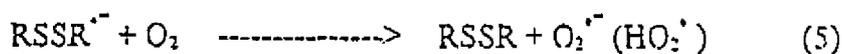
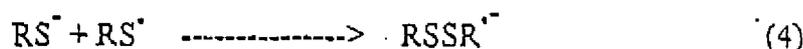
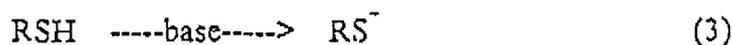
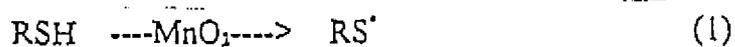
was detected. In the presence of base or with a more active manganese dioxide a hydrogen adduct radical:-



was also detected. This was also true whether oxygen was present or had been

eliminated. From the above and additional work it has been shown that a more complex mechanism takes place when polysulfides are reacted with manganese dioxide in the presence of a base.

A scheme based on the above is:-



As can be seen the reaction mechanism is more complex than initially thought and further work is proceeding to identify more fully the influence of oxygen and water.

CURE SHRINKAGE IN EPOXY ADHESIVES

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Abstract

The build-up of shrinkage over time during curing and on cooling of an epoxy adhesive has been investigated. A new device, designed and built in-house, was used to measure the shrinkage of the epoxy during cure at room and elevated temperatures. In this investigation, the cure of two epoxy resin systems which consists of one part adhesive ESP110 and a two-part adhesive has been successfully monitored using this device and through the way of measurement of shrinkage change with time. By careful monitoring of the shrinkage, we have shown that the cure contraction at room temperature is of the order of 3.75% by volume and 1.24% expansion, 3.45% contraction at 60 °C for the two-part adhesive. It is also shown how the overall volume change caused by expansion and shrinkage is distributed during the cure process. Finally, using a plot of the variation of the shear modulus of the epoxy with time during cure, presented in a previous paper, approximate formulae for estimating the residual stress caused by shrinkage is given.

Introduction

The increasing use of structural adhesives such as epoxy resins to bond composites and metals in the automobile and aircraft industry sectors requires the understanding of shrinkage since it is associated with mechanical strength and fracture characteristics. The rheological changes which occur during the cure of thermosetting resins are very large. Normally, the contractions consist of two parts, one of which is caused by thermal contraction and the other by cure. Many analyses have been performed on the characterisation of thermal expansion to determine the internal stress due to thermal effects(1). It has been shown in the literature that thermal expansion with different materials has an effect on the strength of adhesively-bonded joints. However, knowledge of the characteristics of shrinkage during cure associated with the bond development is limited. The need to analyse the state of stress in joints is becoming increasingly important in order to understand the fracture characteristics and how they correspond to internal stresses and mechanical strength.

It is known that cure shrinkage and internal stresses causing by this shrinkage in the adhesive take place in adhesively-bonded joints during manufacturing(2). Any shrinkage which occurs after the gelation of the adhesive increases the chance of inducing cracks and voids in the adhesive layer within the joints. Therefore, knowing the amount of shrinkage after gelation and the modulus variation with time during cure

plays an essential role in analysing accurately the fracture strength of adhesively-bonded joints.

The research presented in this paper is concerned with determining how the shrinkage during cure at room and elevated temperature changes with time using a new test, and comparing these results. The results obtained in this investigation may be used in the future to calculate the complete stress state of adhesive in the joints.

Test Materials and Procedure

A two-part adhesive, DER 332 resin and HY951 hardener provided by Ciba, and a one part adhesive ESP110, from Permabond Adhesives Limited, UK, were chosen for this investigation. The transparency of the DER 332 resin and HY951 hardener in the liquid and solid state makes the tests simple and observation easy. ESP110 is one of adhesives that are used widely in the automobile industry. For the two-part adhesive, the resin was first warmed in an oven to 60°C and then mixed with hardener in the ratio of adhesive to hardener of 100:12 by weight as required. Bubbles or voids in the adhesive will alter the accuracy of the test results, either in the shrinkage measurement or the modulus measurement, so the resin and mixture were put into a vacuum chamber before and after mixing. Before pouring the adhesive into the mould, Prekote 700-nc and Gt 85 release agent were sprayed on to the surface. Care was exercised to prevent the entry or entrapment of air when the mixture was poured into the mould and an auxiliary small tube was connected to the tube in tested to help eliminating the bubbles in the ESP110 adhesive. Two temperature ramp rates, 2°C/min. and 4°C/min., were chosen for the two-part and one part adhesives respectively. Temperature was kept constant for 3 hours after temperature had been ramped to the highest cure temperature; the specimen was then allowed to cool down to ambient temperature. The time at which the mixture filled the mould was taken as time zero.

Shrinkage Measurement

Making shrinkage measurements during polymerisation has been an inherently difficult problem since the adhesive changes its state from liquid to solid. It is therefore important to monitor the adhesive temperature and to devise a means of allowing the adhesive to contract and, furthermore, measuring the shrinkage without creating internal cracks and voids. Several different shapes and mould materials were investigated and eliminated(3). A practical measurement mould and test configuration which uses two rubber O-rings which prevent adhesive from leaking during the test, together with the plastic tube offer the additional benefit of easy observation. This apparatus shown in Figure 1, was developed for the purpose of determining the shrinkage during cure at room temperature(4). A constant load was attached to the upper part of top piston so that voids within the adhesive and the meniscus around the top surface of the specimen could be eliminated. Any volumetric changes in the sample, including thermal effects and polymerisation shrinkage were recorded through a linear variable differential transformer (LVDT) by following the change in position of the top piston. Polymerisation shrinkage, as a percentage volume change, was obtained after a single cure heating cycle, and the cycle was then repeated to get the thermal

response for both the sample and on pain(baseline). By a subtracting the baseline from the cure response, the shrinkage as a percentage volume change can be calculated.

One of objectives of this work was to study the effect of temperature on the shrinkage. In a previous paper(4), shrinkage of DER332 + HY951 cured at room temperature was investigated. An alternative cure heating cycle up to 60 °C for DER332 + HY951 was chosen for the purpose of comparison. A thin-walled steel tube, rather than the plastic tube used in previous test was used due to the big deformation of plastic in the elevated temperature test. The magnitude of the load applied to the top piston was decided by the criterion that the force should be just greater than the amount of friction between the piston and the O-ring. The apparatus is shown schematically in Fig 2.

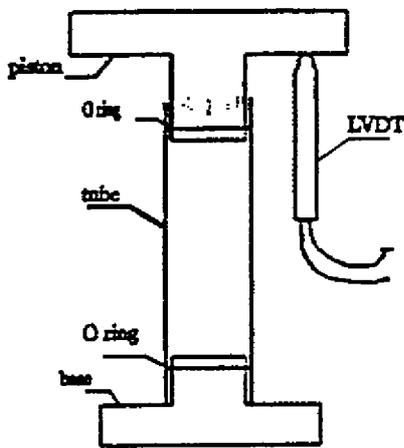


Fig 1. stiff plastic cylindrical tube used for volume change measurement

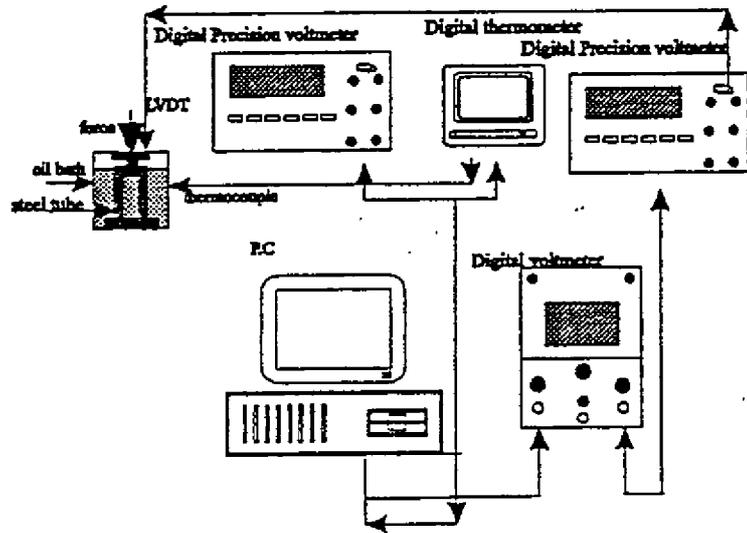


Fig. 2. specimen and instrumentation

Results and Discussion

Effect of temperature on shrinkage

For a specimen 13mm in diameter and 20mm in length, the total shrinkage of the adhesive during cure at 60 ° was measured to be 4.46% by volume over a time period of about 250min.. The effect of temperature on shrinkage was investigated by comparison of the room temperature and elevated temperature cure shrinkage profiles in table 1. Figure 3 is a plot comparing the per cent volume change against time for DER332 + HY951 adhesive cured at elevated temperature and room temperature. The variations of shrinkage with time during cure are shown in Fig 3.

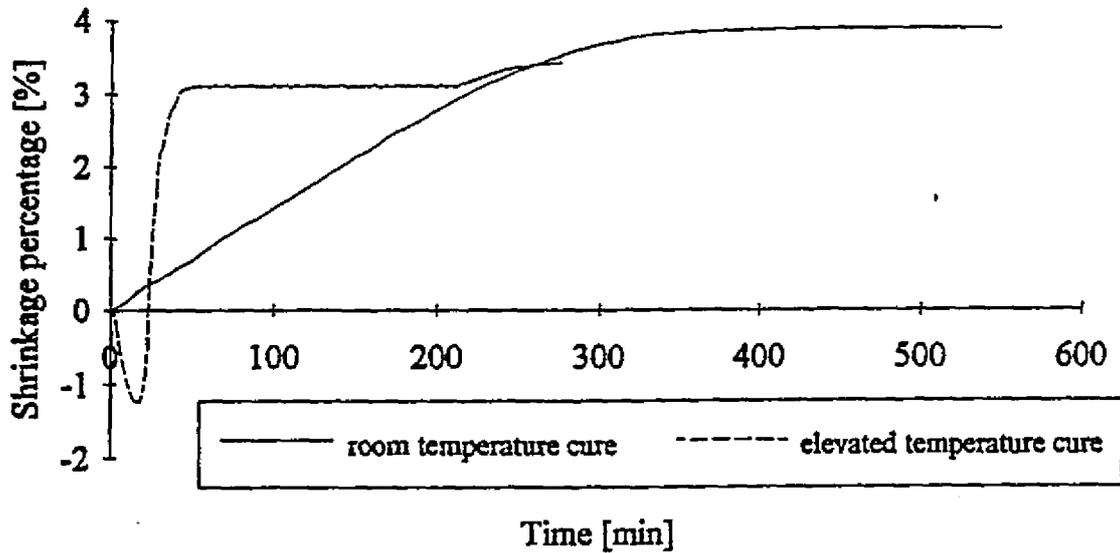


Fig.3. DER332 + HY951 adhesive shrinkage change with time during cure at room temperature and at temperature up to 60 °C

Table I Summary of the adhesives, cure temperatures, and shrinkage in this study

adhesive	Cure temperature	expansion	contraction	shrinkage
DER332+HY951	room temperature	none	3.75%	3.75%
DER332+HY951	60°C	1.16%	3.3%	4.46%
ESP110	135°C	3.51%	1.62%	5.13%

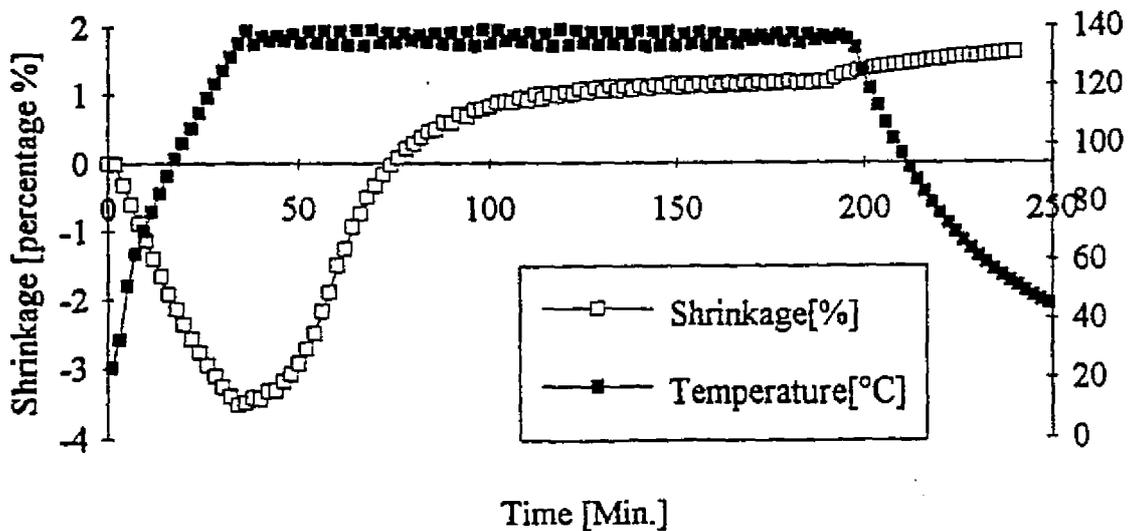


Fig. 4. ESP110 adhesive shrinkage change with time during cure at 130 °C

Comparing the data in Fig.3, it is clear that first, cure shrinkage at 60 °C cure is larger than that when curing at room temperature. Second, as the mixture heats up, the adhesive expands thermally until the reaction begins. Finally, the temperature speeds the reaction rate and thus has a positive effect on the shrinkage. Fig. 4, which shows the shrinkage of the one part epoxy ESP110 during cure also showed the same characteristics.

During the cure process, the adhesive not only changes its state from liquid to solid, but this is also coupled with a strong heat generation due to its exothermic nature of the reaction. We can get the indication of the shrinkage rate, contraction uniformity of adhesive during cure through the variation of temperature of adhesive in tested. One of cure cycles of this adhesive, which is cured at 60° C for 2-3 hour was chosen for this investigation. Two thermocouples were inserted inside the tube which contained the adhesive being tested. The temperature change with time indicated the exothermic effect inside the adhesive is shown in figure 5.

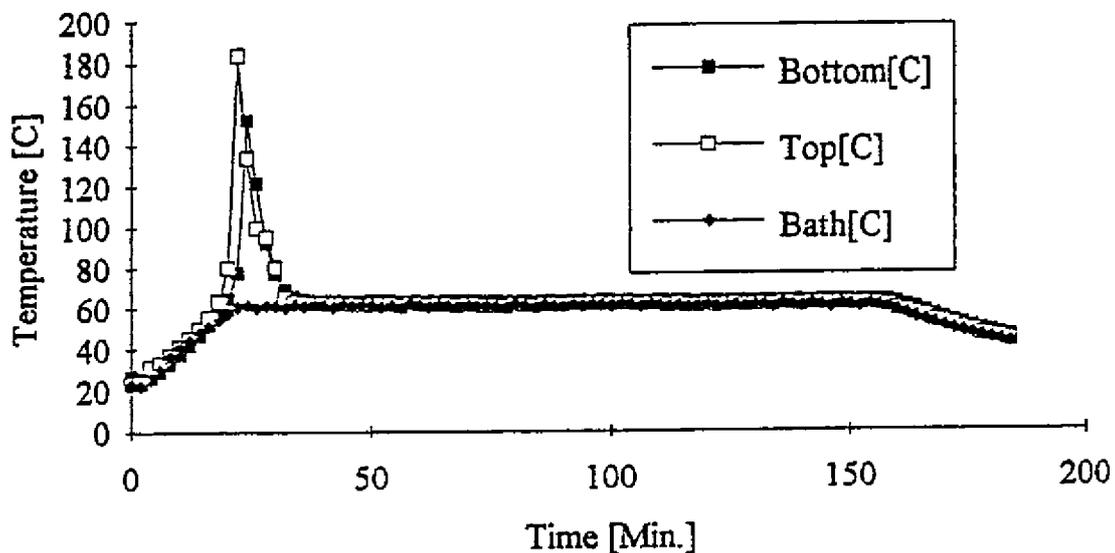


Fig 5. Temperature variation at different positions in the tube with time during cure

Effect of shrinkage on the internal stress

The build-up of a stress state caused by cure over time is controlled by the course of change of volume and stiffness of both adhesive and adherend. Generally speaking, an increment of chemical and thermally induced strain de produced a contribution $d\sigma$ to the stress after completion of the process according to Hooke's law. Thus, in the case of uniaxial stress

$$d\sigma = E de$$

Where E is the elastic modulus at the time of the strain increment. In a previous paper(4), the shrinkage and modulus variation with time during cure at room

temperature were measured for DER332 + HY951 adhesive using a novel vibration method and, the results are shown in Fig. 6.

The internal stress can be calculated by relating the shrinkage and modulus variation with time on the same time scale.

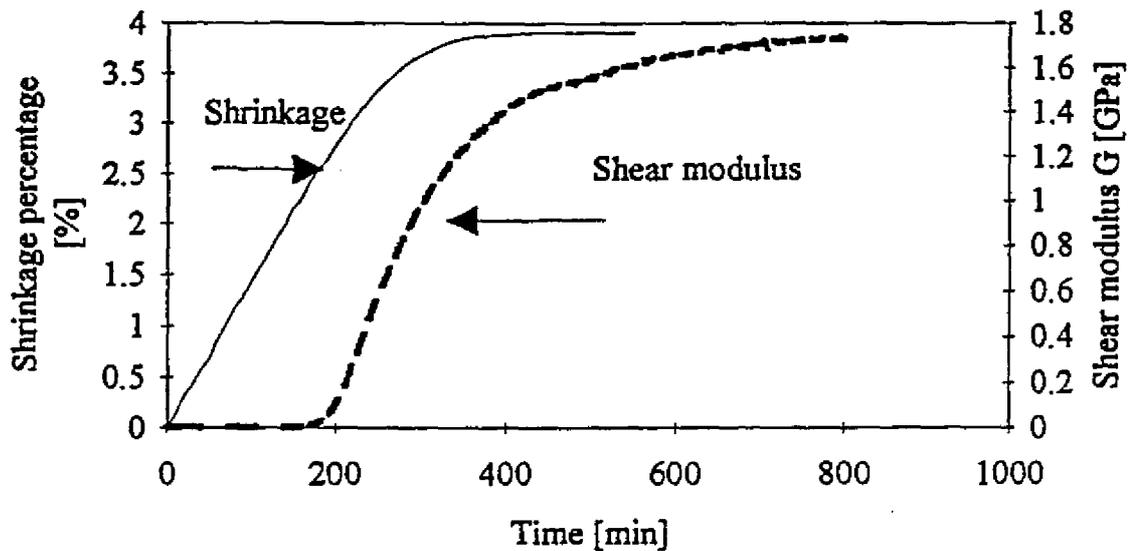


Fig. 6. DER332 + HY951 adhesive shrinkage and shear modulus variation with time during cure at room temperature measured at 600 Hz

Conclusion

The shrinkage changes during the cure process (chemical reaction and cooling) were monitored by a new device. Through the shrinkage and temperature change with time during cure, it is quite clear that shrinkage is non-uniform not only during the cure process, but also within the specimen. Using the shrinkage and modulus variation with time it is possible to predict the contribution from the different parts of the cure process to the overall internal stress build-up.

Reference

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