An aliphatic amine cured rubber modified epoxide adhesive: 1. Preparation and preliminary evaluation using a room temperature cure

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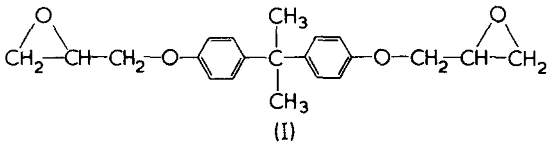
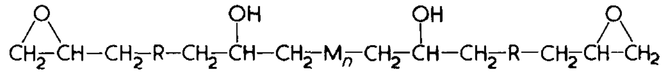
Methods of preparing epoxy resins capable of being cured at room temperature to yield adhesives of high shear and peel strengths are examined. The preferred formulation consists of reacting the diglycidyl ether of bisphenol A with a dicarboxy-terminated butadiene–acrylonitrile (CTBN) rubber (10–15 phr) at 150°C for a minimum period of 2 h. These materials may be cured with diethyleneglycol bis-propylamine at room temperature for 3 days to yield adhesives which have shear and peel strengths of about 32 MN/m^2 and 5 kN/m respectively at 10 phr CTBN and about 26 MN/m^2 and 8 kN/m at 15 phr CTBN.

INTRODUCTION

A method has been previously described whereby epoxides based on the diglycidyl ether of bisphenol A (DGEBA) may be flexibilized by reaction with dienes (M) such as butadiene or isoprene[1]. The process results in a proportion of the DGEBA (structure I) being modified into structure II, where R represents the bisphenol A moiety and *n* averages about six.



(I)



(II)

The reaction product separates into two layers on standing for a few days at room temperature, the top layer being virtually pure modified material II and the bottom layer being principally unmodified DGEBA, (I)[2]. However, the mixture is easily reblended, and when it was tested as an adhesive it was shown to possess up to double the lap shear strength of DGEBA itself[3].

The practical disadvantage of the ready separation of this material was overcome by including acrylonitrile in the reaction mixture and the resulting material, although still two-phase, did not separate over a period of nine months at room temperature[4]. Furthermore, the enhanced adhesive properties were retained and even improved. Thus DGEBA resins are substantially toughened by the chemical incorporation of poly(acrylonitrile–isoprene) components.

The success of this modification procedure led to an investigation of other ways of introducing elastomers into epoxy systems. Carboxy-terminated poly(butadiene–acrylonitrile) CTBN) of about 3000–4000 molecular weight containing 18 or 27% w/w acrylonitrile is commercially readily available, and it seemed attractive to consider methods of making use of this material. The idea of toughening epoxy resins by incorporating CTBN into the matrix is not new – a number of publications and patents have appeared on this subject since 1968, and the field has recently been reviewed[5] – but the relationship between the method of incorporation and the subsequent properties of the cured modified resin has not been satisfactorily reported.

Clearly, the properties of a cured resin system are also largely dependent on the nature of the curing agent. If rigid cured materials possessing strength at high temperatures are required, then curing agents of a stiff, usually highly aromatic character are employed. Conversely, if adhesive systems of high peel strength are sought, then flexible molecules such as terminally functional ethers are likely candidates to effect the cure, as this flexibility is imparted in turn to the crosslinked matrix. Further, when adhesives are required for large-scale application, or for certain specialized operations such as the repair of large components, there is also a need for a reagent capable of curing at room temperature as this obviates the need for equally large ovens. The main class of compounds which exhibits this degree of reactivity toward epoxy groups is that of the primary amines.

The object of the present investigation was to develop a room temperature-curing epoxy adhesive system possessing high peel and shear strength so that, on the basis of the above observations, an oligomeric polyether possessing terminal primary amine groups should be the preferred reagent to act as curing agent for any CTBN modified DGEBA system to be developed. Di-(1-aminopropyl-3-ethoxy)ether (DAPEE) (structure III) is commercially available and has been previously used as a room temperature curing agent.

$$NH_2{-}(CH_2)_3{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}(CH_2)_3{-}NH_2$$

(III)

This compound was therefore exclusively employed as the curing agent for the studies reported in this communication. The process has also been made the subject of a patent application[6].

In this paper, a study of the methods by which CTBN may best be used to modify DGEBA is described, and preliminary shear and peel strength measurements are reported which allowed an evaluation of the effect of the compositional and synthetic changes on the properties of the resulting material. In part II[7], a more rigorous assessment of the properties of the modified epoxy resin which emerged best from this survey is reported.

EXPERIMENTAL

Materials

The materials used in this work were obtained from the following sources and used without further purification: DGEBA epoxide resin (R1877411, B & K Resins), epoxide value 5.2 equiv kg^{-1}; CTBN rubber (Hycar 1300X8, B.F. Goodrich), carboxyl value 0.53 equiv kg^{-1}; 2,4,6-tris(dimethylaminomethyl)phenol (DMP30, K54 catalyst, Anchor Chem Co.); DAPEE (di-(1-aminopropyl-3-ethoxy) ether), (Q19262, B & K Resins). Pure aluminium sheet of 24 swg (0.559 mm) and 12 swg (2.642 mm) to BS 3L61, and aluminium coated aluminium alloy of 16 swg (1.626 mm) to BS 3L73 were supplied by Rapp Metals, and were treated as described below before use as substrates for adhesive joints.

Resin modification procedures

Catalysed precure. The epoxy resin was heated to and held at the required temperature while the CTBN rubber, mixed with catalyst, was brought to the same temperature. The components were then thoroughly blended while the temperature was maintained, and the precure time was measured from the moment of blending. At the end of the required heating cycle the material was poured into a shallow metal tray and cooled rapidly to ambient temperature.

Non-catalysed precure. The epoxy resin and rubber components were mixed thoroughly and heated to the required temperature (150°C). Alternatively, because the rate of increase of temperature was found not to be critical, the components could be prewarmed to facilitate mixing. The mixture was then held at constant temperature for a minimum of 2 h and then allowed to cool. The rate of cooling was likewise not critical.

Curing conditions. The flexibilized epoxide produced by either of the two methods outlined above was blended thoroughly at room temperature with the curing agent (DAPEE). The pot life of a 100 g batch of this mix was typically 20–30 min. The amount of hardener required per 100 g resin was 5.5 x epoxide value of the resin. The curing cycle employed on the adhesive joints before testing was 72 h at room temperature.

Determination of epoxide value (EV)

The method used for determining the *EV* was based on that developed by Jay[8] and by Dijkstra and Dahmen[9]. It is rapid and highly reproducible and is based on the reaction between the epoxide group and a quaternary salt to form the halohydrin ion which is titratable with perchloric acid. The epoxide value is given in equivalents per kilogram.

Physical testing of bonded joints

Maximum bond strengths are obtained on aluminium surfaces by pre-etching with an acid chromate treatment. This method is time-consuming and difficult to reproduce accurately and so, because of the large number of experiments carried out over an extended period, it was decided to use a sand blasting technique instead. Surfaces treated in this way still gave high bond strength joints, and for comparison purposes the reproducibility was excellent.

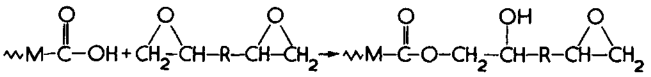
The metal surfaces to be joined were first degreased with chloroform using mechanical scrubbing and then cleaned in a sand blasting machine. The prepared surfaces were finally washed with chloroform and used in the preparation of joints within 1 h. Both the lap shear tests and the 90° peel tests carried out in this work were based on the Ministry of Aviation test specification[10] DTD5577, and were conducted on a Monsanto Type E tensometer. The details of both tests used are recorded in a previous communication[4] and will therefore not be given here. The values of the shear tests quoted are the average obtained with at least five test samples, and those of the 90° peel tests are the average of five minimum recorded peel strengths.

RESULTS AND DISCUSSION

The blending of DGEBA with CTBN results at low rubber concentrations (< 12 phr) in a two-phase system of small rubber particles embedded in an epoxy resin matrix. These phases do not separate out into two layers, and this has been ascribed to the 'solubilizing' effect of the polar nitrile groups in the rubber[4]. At higher concentrations a clear one-phase system is produced.

It is well established that, although some gain in toughness is obtained by blending the rubber component into the epoxy resin, maximum strengths are achieved by chemically linking the elastomer to the resin, so that on curing this component is bound to the epoxy matrix. Preliminary experiments confirmed that only marginal improvement was gained by merely physically mixing DGEBA and non-terminally functional poly(butadiene–acrylonitrile) rubber before cure. For example, unmodified DGEBA gave a 90° peel strength of 0.5 kN/m, which was increased to 1.1 kN/m by incorporating 5, 10 or 15 phr rubber; although this is a doubling of the original strength, the absolute value is still very low and, as will be seen, can be vastly improved by chemical bonding to the matrix.

Methods of reacting CTBN with DGEBA to yield a rubber with epoxide terminal groups were therefore examined[11,12]. This process will be referred to as the precure reaction, and is illustrated in equation (1):



$$\sim\!M{-}\overset{O}{\overset{\|}{C}}{-}OH + \underbrace{CH_2{-}CH}_{O}{-}R{-}\underbrace{CH{-}CH_2}_{O} \rightarrow \sim\!M{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{OH}{\overset{|}{C}H}{-}R{-}\underbrace{CH{-}CH_2}_{O}$$

(1)

This esterification reaction proceeds very slowly even at 120°C, but may be greatly accelerated by the use of certain

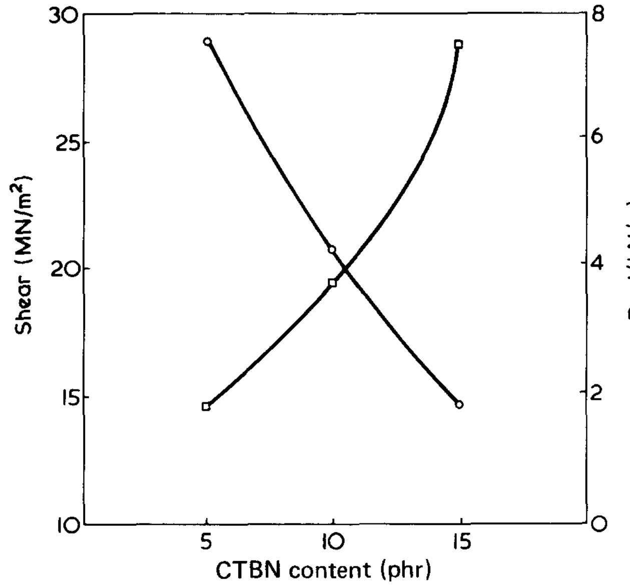


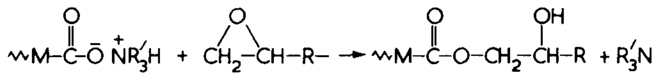
Figure 1 Effect of CTBN on shear (○) and peel (□) strengths of DGEBA after curing; catalysed precure (catalyst content = 1% w/w CTBN)

amine catalysts. Catalysed and non-catalysed systems have therefore been examined in the preparation of the modified epoxy resin, and will be considered separately below.

Catalysed precured systems

The catalysts most commonly used to promote the reaction between a carboxyl and an epoxide end group are tertiary amines, which react via quaternary ammonium salt formation (equations 2 and 3):

$$\sim\!\!\sim M-\overset{O}{\overset{\|}{C}}-OH + R'_3N \longrightarrow \sim\!\!\sim M-\overset{O}{\overset{\|}{C}}-\bar{O}\ \overset{+}{N}R'_3H \qquad (2)$$



$$\sim\!\!\sim M-\overset{O}{\overset{\|}{C}}-\bar{O}\ \overset{+}{N}R'_3H + \overset{O}{CH_2-CH}-R- \longrightarrow \sim\!\!\sim M-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{OH}{\overset{|}{C}H}-R + R'_3N \qquad (3)$$

2,4,6-tris(dimethylaminomethyl)phenol is commonly employed in this role, and only catalytic quantities are required (1–2% w/w of the CTBN rubber content) as larger amounts would result in the direct curing of the epoxy resin. This material was used as catalyst in the present study.

In order to make a preliminary assessment of the effect of rubber concentration on the shear and peel strengths of the cured epoxide, precure conditions of 100°C for 40 min were chosen with a catalyst concentration equivalent to 1% w/w of the rubber. After this treatment the material was cured at room temperature with DAPEE between aluminium strips, as outlined in the Experimental section, and tested. It was found that increasing rubber content gave materials with increasing peel strength, but decreasing shear strength (*Figure 1*). Note that the peel strengths observed are very much greater than those obtained by merely mixing the components. Compositions containing 20 phr and above of rubber became unmanageably thick and, as reasonably high shear and peel strengths were obtained at 5 phr rubber it was decided to concentrate further studies on mixtures of this composition.

At this composition, the catalyst concentration necessary to optimize the shear and peel strengths was then sought. Using the same precure conditions as previously the catalyst concentration was varied up to 10% w/w of the rubber content, and the bond strengths of the subsequent room temperature cured adhesive determined. The results (*Figure 2*) show that optimum values of both shear and peel are obtained at a concentration equivalent to 1.5% of the rubber content.

Finally, having selected the rubber (5 phr) and catalyst (0.075 phr) content of the modified epoxide the effects of temperature and time of precure on the adhesive properties of the material were then examined. Experiments were carried out in the temperature range 80°–100°C with samples being removed at various times. The residual epoxide values were then determined before adhesive strength measurements were carried out on the cured systems. The results of these tests are shown on *Figure 3*.

At all three temperatures, completion of the precure reaction is signalled by a decrease in the rate of loss of epoxide groups at an *EV* of about 4.83. However, the shear and peel strengths are very sensitive to the time of precure. They reach their maxima at times that closely correspond with those for completion of the esterification process, and thereafter deteriorate very rapidly. There is also an indication in the peel strength results that the maximum value increases with the temperature at which the precure reaction takes place.

Possible reasons for these trends will be discussed later. These experiments do show the sensitivity of the mechanical properties of the modified epoxide to the time and temperature of the precure reaction. Thus, although the maximum shear and peel strength values are very good at the highest reaction temperature, these experimental factors make the development of a reproducible synthesis by this method very difficult, particularly if large-scale preparation is contemplated. This is brought out by the differences in absolute values recorded in the first three figures for materials of ostensibly the same composition.

For these practical reasons, further development of the catalysed precured system was not pursued, and attention was turned to a non-catalysed alternative route.

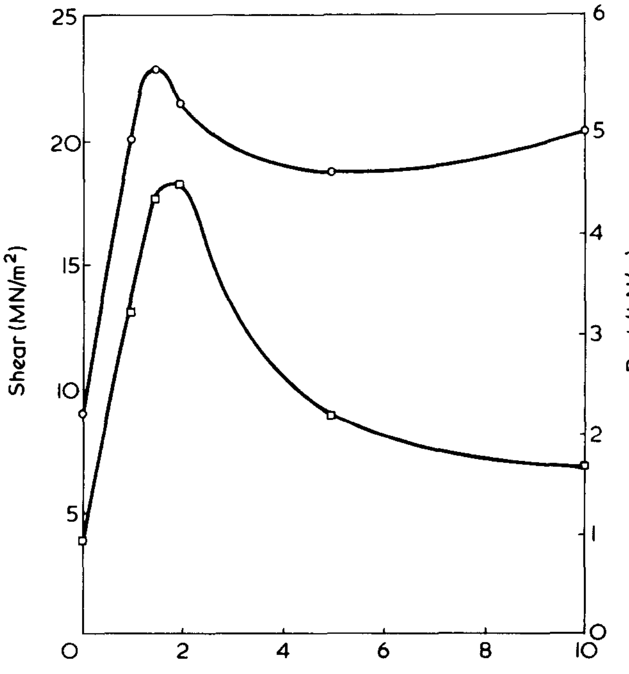


Figure 2 Effect of catalyst content on shear (○) and peel (□) strengths of cured CTBN-modified DGEBA (CTBN content = 5 phr)

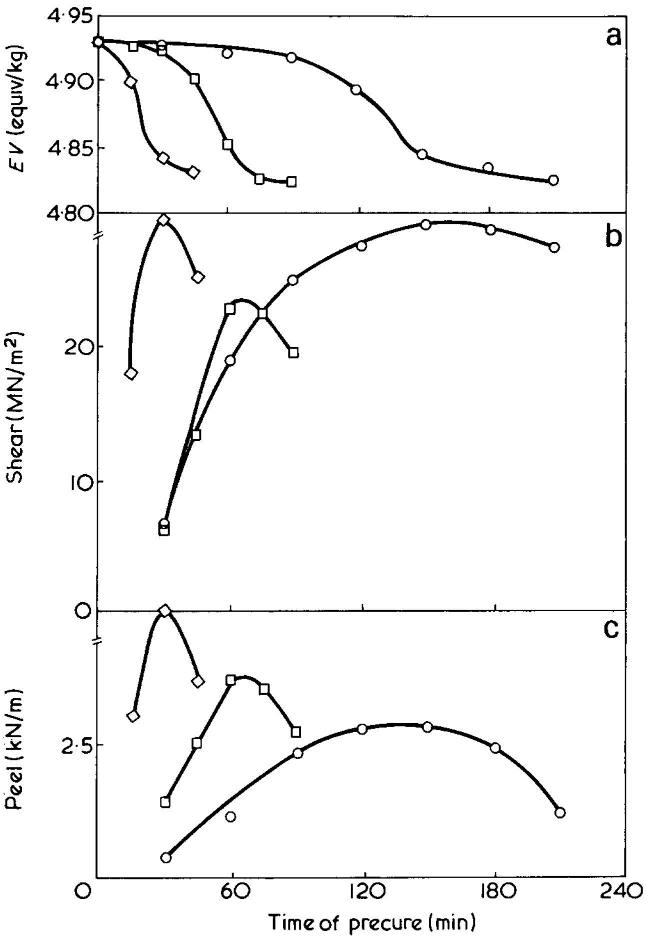


Figure 3 Effect of time of precure at 80°C (○), 90°C (□) and 100°C (◇) on (a) the epoxide value, (b) the shear strength and (c) the peel strength of cured CTBN-modified DGEBA (composition 5 phr CTBN and 0.075 phr catalyst)

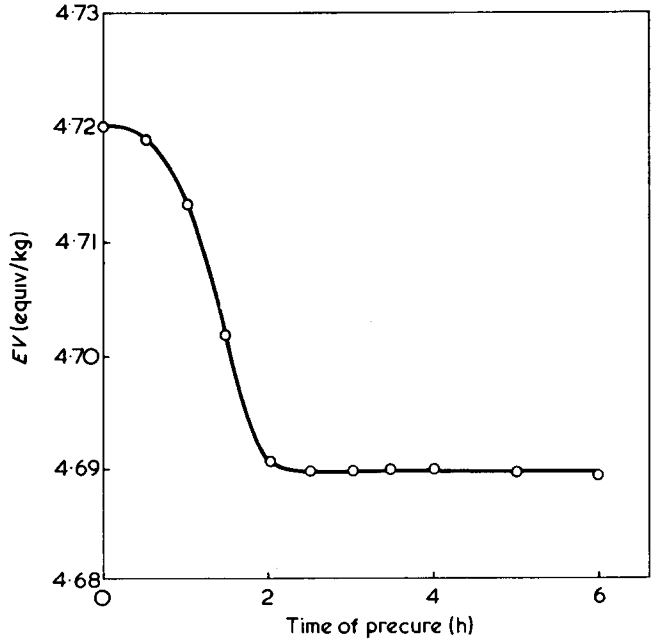


Figure 4 Epoxide value as a function of time in uncatalysed precure of DGEBA and CTBN (10 phr) at 150°C

Non-catalysed precured system

An initial experiment with a mix containing 10 phr CTBN showed that the esterification reaction was very rapid at 175°C, requiring approximately 1 h for the epoxide value to be reduced to a constant value of 4.69. This experiment was then repeated at 150°C, when the time required to reach the same figure was about 2 h (*Figure 4*). These results show that there is no observable fall-off in epoxide value over a 4 h period after attainment of this value, so that the esterification reaction seems to be the only process occurring at these temperatures and in this timescale.

The effect of the time of precure at 150°C on the shear and peel strengths of the subsequently cured materials was then examined, and the trends shown in *Figure 5* for DGEBA modified with 15 phr CTBN are similar to those obtained at other compositions. It is seen that, in contrast to the behaviour of the catalysed precure systems, both strengths rise to plateaux at a time corresponding to the attainment of the minimum epoxide value. The values of the shear and peel strengths on these plateaux are superior to those obtained in the catalysed systems and, like the epoxide value, remain sensibly constant over a further 4 h heating period.

The differences in behaviour between adhesives prepared by the catalytic and non-catalytic routes is probably related to differences in the minimum epoxide values observed in what are otherwise identical materials. This is illustrated by the results listed in *Table 1*. The epoxide value of the starting DGEBA is lowered on addition of CTBN due to a dilution effect (first column), and this is then further reduced by reaction with the terminal carboxyl groups of the rubber. The carboxyl equivalent of the CTBN used is 0.53 mol/kg and the figures given in column 2 are derived on the assumption of one-to-one reaction with epoxide. It is evident that the epoxide values measured for the uncatalysed systems

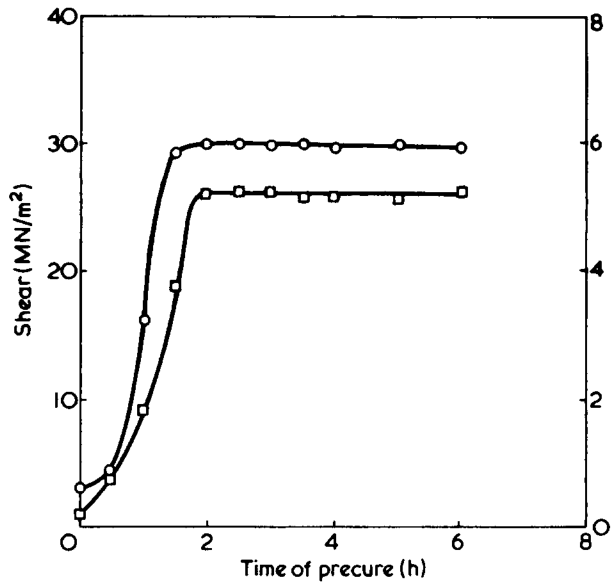


Figure 5 Shear (○) and peel (□) strengths of cured DGEBA modified with CTBN (15 phr) as a function of time of uncatalysed precure at 150°C

Table 1 Comparison of calculated and observed epoxide values of resins modified with CTBN

Composition CTBN (phr)	No reaction *EV* (calc.)	Reaction *EV* (calc.)	Uncatalysed *EV* (obs.)	Catalysed *EV* (obs.)
0.0	5.21	–	–	–
5.0	4.96	4.94	4.93	4.83
7.5	4.84	4.80	4.80	–
10.0	4.73	4.68	4.69	4.52
12.5	4.63	4.57	4.57	–
15.0	4.53	4.46	4.44	–

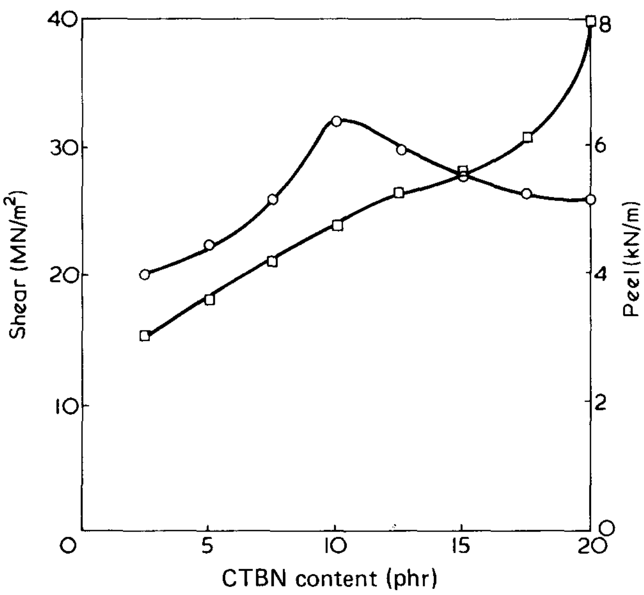


Figure 6 Effect of CTBN content on shear (○) and peel (□) strengths of DGEBA after curing; non-catalysed precure

agree very closely with the calculated figures over a range of rubber concentrations, whereas those obtained from the catalysed systems are significantly lower.

Thus the uncatalysed reaction ceases after esterification of the acid groups, as is reflected in the constancy of the shear and peel properties with extended cure times. The catalysed systems, however, continue to react and the epoxide value falls, presumably by release of the tertiary amine catalyst (equation 3), and this in some way causes the sharp deterioration in the properties of the finally cured product.

The very low shear and peel figures obtained at zero and short precure times (*Figure 4*) deserve comment. This is a consistent feature of a number of experiments carried out with modified DGEBA containing different amounts of CTBN. Significantly higher results at these times are obtained if equivalent amounts of a non-functional poly(butadiene–acrylonitrile) rubber are employed as a diluent for DGEBA, and so the fall is connected with the carboxyl groups of the CTBN. The explanation must therefore be that, as the resin contains residual carboxyl groups until the precure time of 2 h is reached, these can rapidly interact with the primary amine groups of the curing agent which is subsequently added. This reduces the amine content from the optimum number capable of effecting the complete cure of the resin, and so the observed low figures obtained largely reflect the degree of undercure of the adhesive caused by this interaction.

Taking 150°C and a minimum time of 2 h as being suitable conditions of precure to maximize the properties of the resulting systems, a series of resins were prepared with CTBN concentrations up to 20 phr. The shear and peel strengths of these were then determined after a room temperature cure with DAPEE and the results are recorded on *Figure 6.*

Unlike the results given in *Figure 1* for the catalysed system, a maximum value of shear strength of about 32 MN/m^2 is obtained at 10 phr CTBN, at which point the peel strength is about 4.8 kN/m. Thereafter the peel strength may be increased, and it reaches a value of 7.9 kN/m at 20 phr CTBN, but at the expense of the shear strength which is reduced to 25.6 MN/m^2. Clearly adhesives for which high values of both these properties are required should possess CTBN rubber in the range 10–15 phr. These results also underline the superior properties of adhesives prepared in this way rather than by the catalysed route.

It is relevant at this point to comment on some of the morphological aspects of these adhesive systems. With very low CTBN content (< 1 phr) and at high CTBN content (> 15 phr) the material appears as a homogeneous single phase at room temperature. In between these limits the system consists of a mechanically stable dispersion of spherical rubbery particles in the epoxide matrix. However, materials in this range may be homogenized by raising the temperature 10° to 15°C above ambient, and those compositions which are single-phase at room temperature may be converted into dispersions by cooling. Both these processes are reversible. The particle sizes are in the range 3–7 μm and are independent of the nature of the thermal cycles the material has undergone. The same results apply whether the mix has been precured or not.

It is common practice to add fillers to epoxy resins to thicken them and thus improve their handling characteristics and, by suitable choice of filler, mechanical properties such as peel strength can sometimes be significantly enhanced. For these reasons a preliminary study of the effect of adding fibrous asbestos filler to variously prepared modified resins was carried out. The shear and peel strengths at two filler loadings were compared, and the results are listed in *Table 2.*

The addition of asbestos filler seems to have no marked effect on the strength of the cured product, although the handling characteristics of the filled material are improved. The unfilled compositions are quite mobile liquids and the thickening effects of filler result in easier laying up of joints.

The bulk of the experiments described were carried out on small-scale (100 g) batches. For technological significance these systems must be capable of ready scale-up without loss of the properties observed at the laboratory level. Clearly the catalysed systems, which exhibit high sensitivity to time and temperature of precure, were not favoured for this role as difficulties in quickly cooling batches of variable size would be considerable. Instead, the high-temperature non-catalysed system was chosen for the scale-up experiments, and two compositions (10 and 15 phr CTBN) were prepared in batch sizes of 2 kg. Tests carried out on the products showed that the shear and peel results obtained on the laboratory scale were retained in the larger batches.

Table 2 Effect of fibrous asbestos filler on peel and shear strengths of various modified epoxy resins

Composition	Filler added (phr)	Shear strength (MN/m^2)	Peel strength (kN/m)
CTBN 5 phr	0	29.1	5.3
catalysed	5	30.4	5.6
precure	10	30.1	5.4
CTBN 5 phr	0	21.6	3.6
uncatalysed	5	20.9	3.7
precure	10	21.9	3.7
CTBN 10 phr	0	31.7	4.9
uncatalysed	5	32.0	5.0
precure	10	31.1	5.0
CTBN 15 phr	0	27.3	5.6
uncatalysed	5	26.9	5.6
precure	10	26.9	5.7

CONCLUSIONS

(1) Modification of DGEBA commercial epoxy resin by reaction with CTBN yields materials which, with the flexible curing agent DAPEE, result in cold-curing high-shear and high-peel-strength systems.

(2) If the flexibilizing reaction is carried out with 2,4,6-tris(dimethylaminomethyl)phenol as catalyst, an adhesive system containing 5 phr CTBN with shear and peel strengths in the range 30 MN/m^2 and 5 kN/m respectively is produced. The properties are, however, very sensitive to the precure conditions and fall dramatically if the recommended values of time and temperature are not strictly adhered to.

(3) If the flexibilizing reaction is carried out without catalyst at higher temperature (150°C), the precure time is far less critical and heating times considerably in excess of the minimum of 2 h have little effect on the adhesive properties of the product. The CTBN compositions of the resins which give good adhesive properties range from 10 to 15 phr depending on whether the shear or the peel strength is to be optimized. At 10 phr values of about 32 MN/m^2 and 5 kN/m respectively have been achieved, and at 15 phr, values of about 26 MN/m^2 and 8 kN/m.

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