An anionically prepared flexible adhesive:
4. Acrylonitrile modified adhesive

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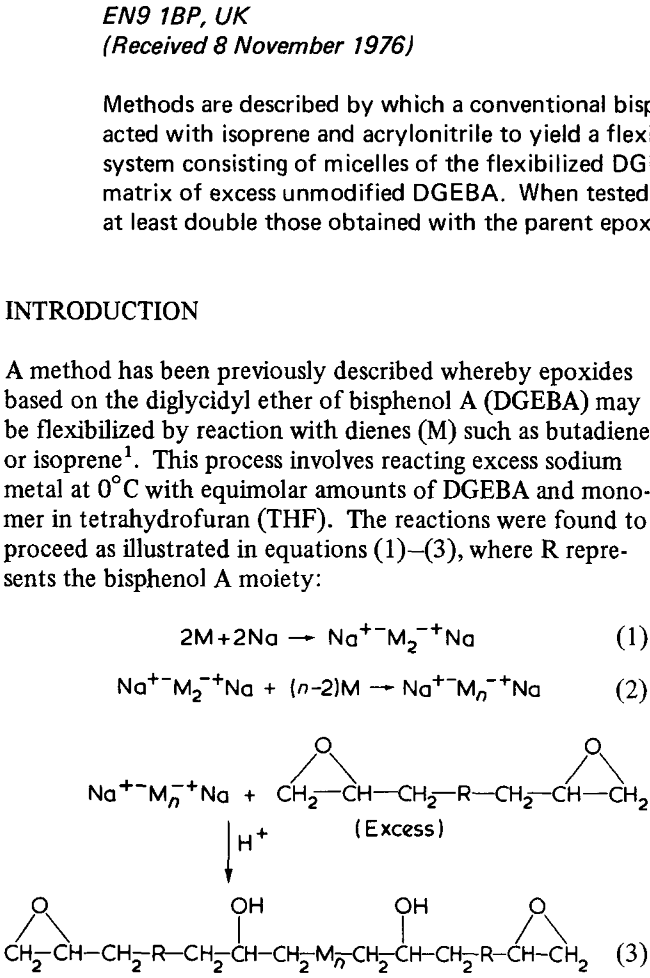
Methods are described by which a conventional bisphenol A based epoxy resin (DGEBA) may be reacted with isoprene and acrylonitrile to yield a flexibilized product. This material is a stable two phase system consisting of micelles of the flexibilized DGEBA of about 10 μm diameter suspended in a matrix of excess unmodified DGEBA. When tested as an adhesive, the product gave lap shear strengths at least double those obtained with the parent epoxy resin.

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]. This process involves reacting excess sodium metal at 0°C with equimolar amounts of DGEBA and monomer in tetrahydrofuran (THF). The reactions were found to proceed as illustrated in equations (1)–(3), where R represents the bisphenol A moiety:

$$2M+2Na \rightarrow Na^{+-}M_2^{-+}Na \qquad (1)$$

$$Na^{+-}M_2^{-+}Na + (n-2)M \rightarrow Na^{+-}M_n^{-+}Na \qquad (2)$$



(3)

(I)

The value of n obtained in species I under these conditions averaged around six for either diene[2]. The isolated material was found, however, to separate into two layers on standing for a few days at room temperature, and ^{1}H n.m.r. analysis showed that the top layer primarily consisted of species I, whilst the bottom layer was principally composed of unreacted DGEBA, although there was some mutual solubility of the components[2]. Nevertheless, when this material was reblended, and subjected to lap joint tests with a variety of curing agents, the lap shear results were significantly superior to those obtained with DGEBA under the same conditions[3]. Maximum synergism occurred at about 20% of the flexibilized component, the proportion produced using equimolar reagents.

Thus the flexibilization of DGEBA results in improved adhesives strengths, although the disadvantage of the incompatibility of the two phases still remains. This requires that careful blending procedures have to be employed to ensure reproducible results and, because the rate of separation is increased as the temperature is raised, problems can arise relating to the inhomogeneity of the product when high temperature curing agents are employed.

It has been recognized that for high strength materials, not only is a degree of elastomer–resin compatability important but so also are the needs of achieving a dispersed phase and maintaining its particle size[4]. Significantly, systems in which DGEBA is blended and prereacted with carboxy-terminated poly(butadiene–acrylonitrile) copolymer (CTBN) show this type of compatibility and a stable dispersed rubber phase is obtained. Again, these materials exhibit properties superior to those of the base resin; a review of such systems has recently been published[4].

Thus it appears that the presence of acrylonitrile units in the rubbery phase increases the compatibility of the two components to the point where phase separation is not observed. If, therefore, the anionic polymerization method outlined above were modified to include acrylonitrile, the product might well retain the improved shear strengths reported previously, whilst maintaining a stable dispersed rubbery phase.

Fetters[5] has divided monomers capable of undergoing anionic polymerization into five categories of increasing susceptibility. The least reactive monomers, which include the dienes, fall into the first category, and these consequently generate the most reactive carbanions. Acrylonitrile falls in the fourth category, and monomers in this classification can be initiated by weak nucleophiles such as alkoxide ions. Anions generated from members of a higher numbered group cannot initiate members of a lower numbered group so that, although polydienyl anions will initiate acrylonitrile, the reverse does not occur.

Acrylonitrile may therefore be introduced into the reaction at one of two points; either in the initial stage, or after the diene–DGEBA reaction is over and the excess metal removed, but before hydrolysis of the product has taken place. In the latter case the acrylonitrile should be polymerized by the alkoxide ions created from the reaction of the polydiene dianions with the DGEBA epoxide groups (equation 3). Thus with this technique acrylonitrile should be incorporated only as oligomeric grafts on the rubber backbone. Introduction of the acrylonitrile as a comonomer with the diene results in a more complicated situation. It may react with any dienyl anions generated, and so become incorporated into the polymer chain as terminal unit(s), or it may compete directly with the diene for reaction sites on the sodium surface, thus producing dianionic acrylonitrile dimers and subsequently oligomers. It may also be polymerized by any alkoxide ions generated by direct reaction of the dienyl anions with epoxide groups. These possibilities are examined in the text in more detail.

This communication describes the preparation of flexibilized epoxide by both these methods, and discusses the morphological properties of the materials obtained. An account is then given of their evaluation as adhesives. The process is the subject of a patent application[6].

EXPERIMENTAL

Materials

15 mm diameter sodium pellets (BDH) were washed with low boiling petroleum ether under a blanket of dry nitrogen, and cut into thin slices.

THF was first dried over molecular sieves and then treated, under dry nitrogen, with a solution of sodium naphthalene in THF until a permanent green colour, characteristic of the complex, remained to indicate a complete drying. The solvent was subsequently distilled under dry nitrogen, stored over fresh sodium wire, and used within two days. The diepoxide was a diglycidyl ether of bisphenol A supplied as either MY750 (Ciba–Geigy) or Epikote 828 (Shell), and used without further purification.

Isoprene was used freshly distilled from powdered calcium hydride.

Acrylonitrile was taken from the middle cut after distillation from calcium hydride.

The two curing agents, triethylenetetramine (TETA) (Ciba HY951) and diethyleneglycol bispropylamine (DGPB) (B & K Resins, Q19262), were used as supplied.

Styrene–acrylonitrile block copolymer (Kostil AF/ATX, Montedison UK Ltd) was used as supplied.

Polyacrylonitrile was prepared in these laboratories using sodium ethoxide as initiator. Its molecular weight was not determined.

CTBN (Hycar, B. F. Goodrich Chemical Co.) contained 18% w/w acrylonitrile.

Infra-red

Infra-red measurements were recorded on a Perkin–Elmer 157G double beam grating i.r. spectrometer. Samples were examined either as THF solutions run against solvent, or as resins pressed between sodium chloride plates.

Synthetic methods

The synthetic methods employed were adaptations of the basic procedure outlined in part 1[1] in which a glass, multinecked 'spiked' and flanged flask of 2 litres capacity was used as the reaction vessel. Typical experiments to prepare 6% w/w acrylonitrile modified epoxide (AN–Is–DGEBA), firstly, by the method in which the acrylonitrile is added after completion of the sodium–isoprene–DGEBA reaction, and secondly by reacting acrylonitrile and isoprene as mixed monomers, will now be described.

The reaction flask was charged with 1 litre of THF containing 280 g (0.8 mol) DGEBA. It was cooled and kept at 0°C whilst purified nitrogen was bubbled through to maintain an inert atmosphere. With constant stirring a two-fold excess, 37 g (1.6 mol), sliced sodium metal were added, followed by 54.4 g (0.8 mol) isoprene. The nitrogen flow was then very much reduced to minimize evaporation. Following a short induction period of about 10 min the metal surface became yellow, thus indicating that the reaction had started. After about 4 h the reaction mixture had become fairly viscous with signs of gel formation, the metal surface had reverted to a dull grey, and the reaction was deemed to be complete. The solution was then siphoned into a 3 litre flask under nitrogen, and the residual gel attached to the sodium metal and the walls of the flask was loosened with about 100 ml fresh THF. This was then also siphoned into the receiver.

A solution of 20.1 g (0.38 mol) acrylonitrile in 200 ml THF was slowly added to the reaction products with constant stirring over a period of 10 min, and the mixture was allowed to react under nitrogen for a further 3 h. During the addition some heat was evolved and the colour of the mixture slowly darkened from a straw colour to one of reddish brown. The work-up procedure was the same as that for the mixed monomer method, and will be described after this alternative method has been detailed.

In this process, 20.1 g (0.38 mol) acrylonitrile were added as comonomer with the isoprene, the quantities of all other ingredients remaining the same as described above. The induction period before the onset of a yellow colouration on the sodium was increased to about 1 h by the presence of acrylonitrile. Once reaction had started the colour of the solution steadily deepened to the reddish-brown observed finally in the other method. The reaction time, as judged by the onset of a dull grey colour to the sodium surface, also increased and averaged about 7 h. Again, the product was a solution containing gel, which was separated from the excess sodium metal by the process described above. It should be recorded that both the induction period and the polymerization time is directly dependent on the acrylonitrile content.

The work-up procedure employed to isolate the product, although the same for both types of materials, is different from that given in part 1 for isoprene modified DGEBA (Is–DGEBA)[1]. It is now recommended that the procedure to be described be applied to that system also, as it has been found to be easier, faster and to give a higher yield of product.

800 ml THF and 1 litre of about 95% saturated brine were added to the separated solution, and the mix was vigorously stirred. A 10% acetic acid solution in brine was then slowly added until external indicator paper showed the pH to be 7. The aqueous solution was allowed to separate, when it was removed leaving the organic phase to be dried with magnesium sulphate. The solution was then filtered, the THF was stripped off using a rotary evaporator, and the final traces of solvent were removed by evaporation under high vacuum.

Analysis

The epoxide content of the product was determined by a titration method developed by Jay[7] and by Dijkstra and Dahmen[8].

The nitrogen content was evaluated by another Department of this Establishment using a Perkin–Elmer 240 Elemental Analyser. The apparatus was calibrated using acetanilide.

Cure conditions

The same cure conditions were employed with both the curing agents used (TETA and DGBP). They were two days at room temperature under compression, followed by a post cure at 80°C for 2 h.

Test methods

Test specimens for lap shear evaluations[9] were prepared from mild steel sheets of 0.064 in. gauge, cut into 4 in. x 1 in. strips. Immediately prior to use they were mechanically scrubbed with chloroform, sand blasted to give an even surface etch, and then washed again with chloroform. The cleanliness of the surface was judged by the absence of streaking in the final wash, and the strips were used within 2 h of the cleaning operation.

The cleaned strips were assembled in pairs and the adhesive, prepared by mixing resin and curing agent, was applied to a length across the end of each specimen sufficient to cover a space at least 0.25 in. longer than the 0.5 in. overlap required. The joints were then assembled, held rigidly under slight pressure, and allowed to cure for the recommended time. Glue line thickness was controlled at 0.1 mm by inserting into the joints two or three very short lengths of wire during the joint assembly.

Testing was carried out using a Monsanto Type E tensometer adjusted to ensure that the breaking load of the specimen fell between 15 and 85% of full scale capacity. The joint was held by a suitable pair of self aligning grips allowing the outer inch of each end to be firmly engaged. Loading was applied at a constant crosshead speed of 5 mm/min, and continued until failure occurred.

The 90° peel test[9] was carried out with two aluminium sheets (BS 3L61) 10 in. x 8 in. of 0.51 mm (24 SWG) and 2.06 mm (12 SWG) thickness respectively. These were surface treated as described above, and then the adhesive mixture applied to each sheet over an area 8 in. x 8 in. leaving an area 8 in. x 2 in. unbonded. The two sheets were then assembled, held rigidly under pressure, and allowed to cure. Glue line thickness was controlled at 0.4 mm with wire and, after curing, five 10 in. x 1 in. strips were cut from the sheet.

Testing was again carried out on the Monsanto Type E tensometer at a peeling rate of 100 mm/min, and a graphic trace of load *versus* peeled distance recorded. The trace for the first 25 mm was ignored and the results recorded as the minimum peel strength obtained from the following 150 mm of the bond line.

RESULTS AND DISCUSSION

Both isoprene and butadiene were originally used to prepare diene modified DGEBA materials[1], and it was found that the degrees of improvement obtained in the adhesive properties of both sets of epoxides were similar. It was therefore decided to concentrate more detailed study on those materials prepared using isoprene, principally because of the greater experimental ease in handling a liquid rather than a gaseous monomer. This philosophy was continued in the present work, so that the results quoted are those obtained from materials flexibilized with isoprene (Is–DGEBA). Furthermore, the relative concentrations of isoprene and DGEBA were held constant at equimolar, the point at which maximum synergism was observed in the Is–DGEBA system, and only the acrylonitrile concentration was changed.

A preliminary survey was first carried out to examine qualitatively the effect of adding acrylonitrile in various polymeric forms to Is–DGEBA on the time required for the rubber and resin phases to separate. Blending was effected by mixing solutions of the two components, and removing the solvents in a rotary evaporator. The samples were then placed in an oven at 50°C to expedite the separation. The results are given in *Table 1*. When acrylonitrile was introduced as the homopolymer or as the component of a block copolymer with styrene, it had very little effect on the separation time whereas, when introduced as CTBN, the separation time significantly increased with acrylonitrile concentration, levelling off at about 5% w/w. Even when DGEBA was added to restore the rubber content to that of the original Is–DGEBA, the separation time was still very substantially greater. These results encouraged the belief that the presence of acrylonitrile in the dispersed rubber phase stabilized that phase, and hence that its incorporation in the anionic polymerization process developed for Is–DGEBA should yield materials similarly stabilized.

Synthetic method and product composition

In initial experiments carried out to prepare acrylonitrile–isoprene modified DGEBA (AN–Is–DGEBA) by both methods, the work up procedure followed was that described in part 1[1]. In all cases, and particularly at high acrylonitrile concentrations, severe emulsion problems were encountered which were only partly and irreproducibly resolved. Consequently, the adhesives isolated from repeat experiments had variable composition and, when tested for lap shear strengths, gave an unacceptably wide spread. The new isolation procedure reported here largely eliminates this problem, and the reproducibility of the product as measured by epoxide value and lap shear strength (*Tables 2* and *3* respectively, 6% acrylonitrile results) is now acceptable. The high recovery of product is an added advantage of this procedure. Products with theoretical acrylonitrile contents up to 10% were handled successfully in this way, although the difficulty in totally preventing emulsification increases with the acrylonitrile content – at the highest values the THF–brine mixtures had to be centrifuged after titration to ensure complete separation. This was unnecessary at the 6% added acrylonitrile level, whether the monomer was added in the initial mix or subsequently and, as will be seen later, this was the composition selected as having the best combination of properties.

The analytically determined acrylonitrile contents of the products were consistently lower than those introduced into the reaction mixture (*Tables 3* and *4*), indicating that incorporation of the monomer was not complete. The analytical values were employed to apply weight corrections to the system, in particular to evaluate EV^0 from EV (see later) but for simplicity the product will be designated in the text by the percentage acrylonitrile introduced into the reaction system.

Table 1 Effect on the time of phase separation of mixing nitrile containing polymers into isoprene modified DGEBA

Acrylonitrile (% w/w)	Source	Separation time at 50°C
0		<15 h
1	CTBN	2 days
2	CTBN	2 weeks
5	CTBN	3 weeks
10	CTBN	3 weeks
6	CTBN	>10 days[a]
5	polyacrylonitrile	<3 days
5	poly(styrene-*b*-acrylonitrile)	<3 days

[a] DGEBA added to maintain percentage rubber phase at 20% v/v

Table 2 Yields, epoxide values and infra-red data of AN–Is–DGEBA materials prepared by the mixed monomer method using the revised work-up procedures

Acrylonitrile (% w/w)					Infra-red relative absorbances	
Introduced	Analysed	Yield (%)	*EV* (equiv./kg)	*EV*^{0} (equiv. kg DGEBA^{-1})	4.45 µm	4.55 µm
DGEBA		–	5.20	5.20	–	–
Is–DGEBA		98	3.62	4.32	–	–
2	1.7	96	3.51	4.25	0.24	0.26
4	3.1	98	3.58	4.39	0.36	0.71
6	4.7	>81	3.64	4.42	0.60	0.85
6	–	97	3.68	4.46	0.50	1.00
6	–	95	3.64	4.42	0.45	0.91
8	5.3	99	3.73	4.66	0.85	1.15
6[a]	4.8	89	3.48	4.34	0.60	0.83

[a] Prepared by post addition method

Table 3 Shear strengths of AN–Is–DGEBA adhesives prepared by the mixed monomer method using the revised work-up procedure and cured with primary amines

Acrylonitrile introduced (% w/w)	Average shear strength (MN/m^2)	
	TETA	DGBP
DGEBA	12.1, 11.8, 12.3	14.7
Is–DGEBA	22.8	22.2
2	27.9	29.5
4	26.0	32.3
6	25.4	32.8
6	25.9	33.0
8	25.9	32.0
6[a]	27.0	28.0

[a] Prepared by post addition method

It was found, as was expected, that the time taken for the product to separate into two layers increased with the acrylonitrile content of the original charge. At 50°C this period ranged from about a week to several months over the range tested, and no evidence of gross phase separation has been found with 6% acrylonitrile after nine months storage at room temperature. Micrographs of this last product (*Figure 1*) show a two phase system containing spherical particles of the modified material with diameter of about 10µm embedded in the DGEBA resin. Thus the requirement of a long shelf life for these modified adhesives may be achieved by incorporating acrylonitrile in the reaction system.

The nature of the induction period in the mixed monomer method was studied by taking samples out of a typical reaction (5% acrylonitrile) with time, and subjecting them after hydrolysis to infra-red analysis. *Figure 2* shows the relative absorbances of peaks at 4.45, 4.50 and 4.55 µm as a function of time. They have been normalized relative to the peak at 4.85 µm due to the DGEBA moiety. The peak at 4.50 µm is characteristic of the acrylonitrile monomer, whilst the other two are products of its polymerization and will be discussed later. It is seen that over the first hour very little acrylonitrile reacts, but that propagation proceeds rapidly thereafter and in the succeeding hour the monomer is essentially consumed. The end of the induction period coincided with the observed change in aspect of the sodium metal from a dull grey to a yellow colour. However, the yellow colouration persisted for some hours after the acrylonitrile had been consumed, showing that isoprene was still present in the reaction mixture. The reaction in fact continued for a further 6 h after the induction period, as evidenced by the deepening of the colour of the solution and the gradual production of gel.

An interesting difference is observed in the epoxide values (*EV*) of materials prepared by the two synthetic methods using the same amounts of starting ingredients (*Table 2*). 6% acrylonitrile material prepared by the post addition method has a significantly lower *EV* than that prepared by the mixed monomer technique. In fact the fall in *EV* in the former material from the value obtained with the Is–DGEBA intermediate can be accounted for by a dilution effect only, so that their epoxide values per kilogramme of DGEBA present (*EV*^{0}) are substantially the same. Thus the propagating acrylonitrile anion does not appear to attack further epoxide groups under the experimental conditions of the preparation. This independence of *EV*^{0} on acrylonitrile content was demonstrated with products possessing a range of compositions prepared by the post addition method (*Table 4*).

In contrast to this behaviour, the *EV*^{0} values of materials derived from the mixed monomer approach increase with

Table 4 Epoxide values of AN–Is–DGEBA materials prepared by the post addition method using Part 1 work-up procedures[1] and their shear strengths when cured with primary amines

Acrylonitrile (% w/w)				Average shear strength (MN/m^2)	
Introduced	Analysed	*EV* (equiv./kg)	*EV*^{0} (equiv. kg DGEBA^{-1})	TETA	DGBP
DGEBA		5.20	5.20	12.3	14.6
Is–DGEBA		3.82	4.55	22.3	28.4
1	0.8	3.78	4.54	24.1	30.1
2	1.0	3.77	4.53	25.3	31.5
4	1.5	3.75	4.52	20.7	32.3
6	2.2	3.75	4.56	21.2	35.0

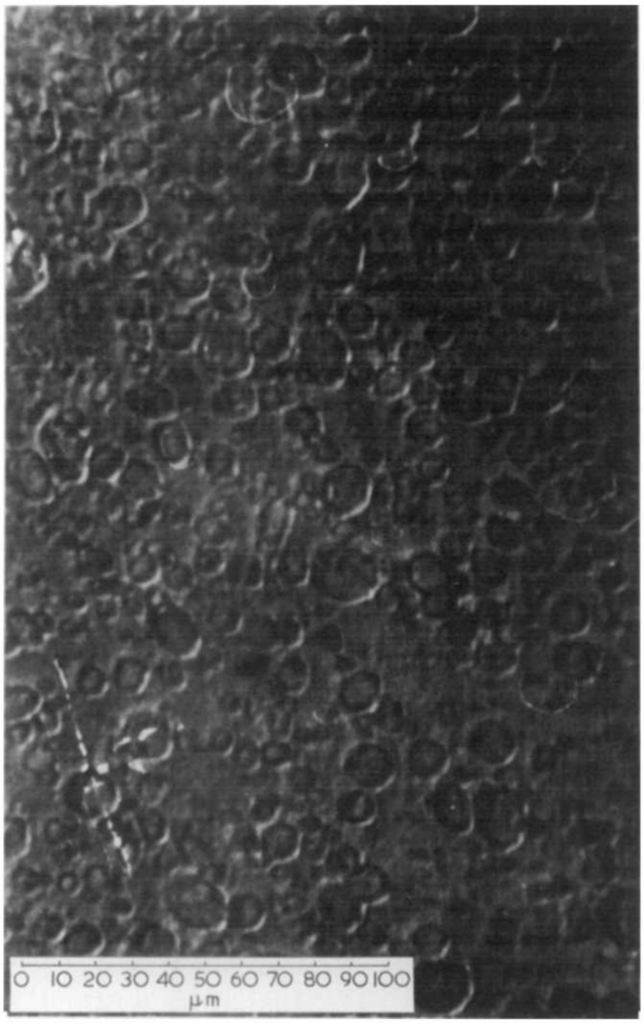
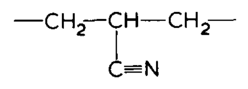


Figure 1 Micrograph of 6% AN–Is–DGEBA uncured material

their acrylonitrile content. This implies that fewer epoxide groups are attacked as the acrylonitrile content increases, although i.r. analysis (*Table 2*) shows that acrylonitrile is incorporated into the product in direct relation to its concentration in the reaction. These two apparently contradictory results have to be reconciled.

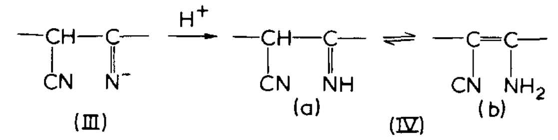
Let us first consider the nature of the absorptions recorded at 4.45 and 4.55 μm. The former has been identified as being due to the pendant nitrile group[10], as in structure II:



$$-CH_2-\underset{C\equiv N}{CH}-CH_2-$$

(II)

and the same authors have shown that the enaminonitrile species (IV) generated by the iminonitrile anion (III) as shown in equation (4) absorbs at 4.55 μm.

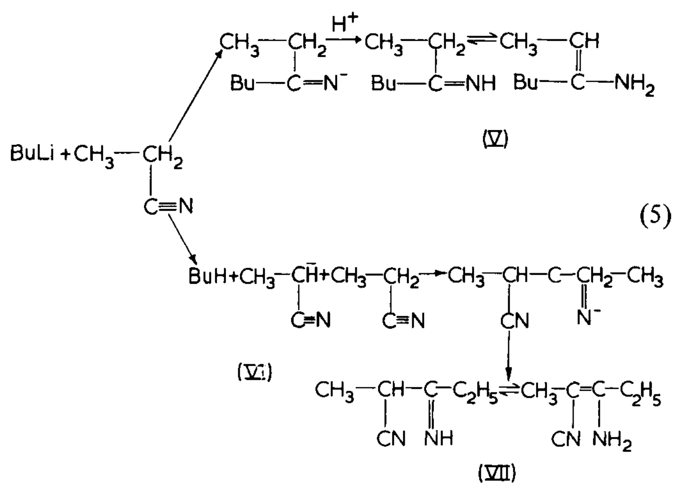


$$\underset{(III)}{-\underset{CN}{CH}-\underset{N^-}{C}-} \xrightarrow{H^+} \underset{(a)}{-\underset{CN}{CH}-\underset{NH}{C}-} \rightleftharpoons \underset{(b)}{-\underset{CN}{C}=\underset{NH_2}{C}-} \quad (4)$$

(IV)

This species is present due to finite probability of attack of the propagating polyacrylonitrile anion across the nitrile group of a preformed chain. The species responsible for the absorption at 4.55 μm is IV(b) since, when acrylonitrile is replaced by methacrylonitrile, this form cannot be generated and no absorption at this frequency occurs.

This species may also be generated by direct attack of a carbanion on a nitrile, as was demonstrated by reacting butyl lithium with propionitrile in THF. Again the hydrolysed product gave a strong absorption at 4.55 μm. The two possible reactions[11] which can occur are shown in equation (5):



The addition reaction yields on hydrolysis an imine (V) which absorbs around the 6.1 μm region[11], but proton abstraction to give the carbanion VI can also occur, and this would

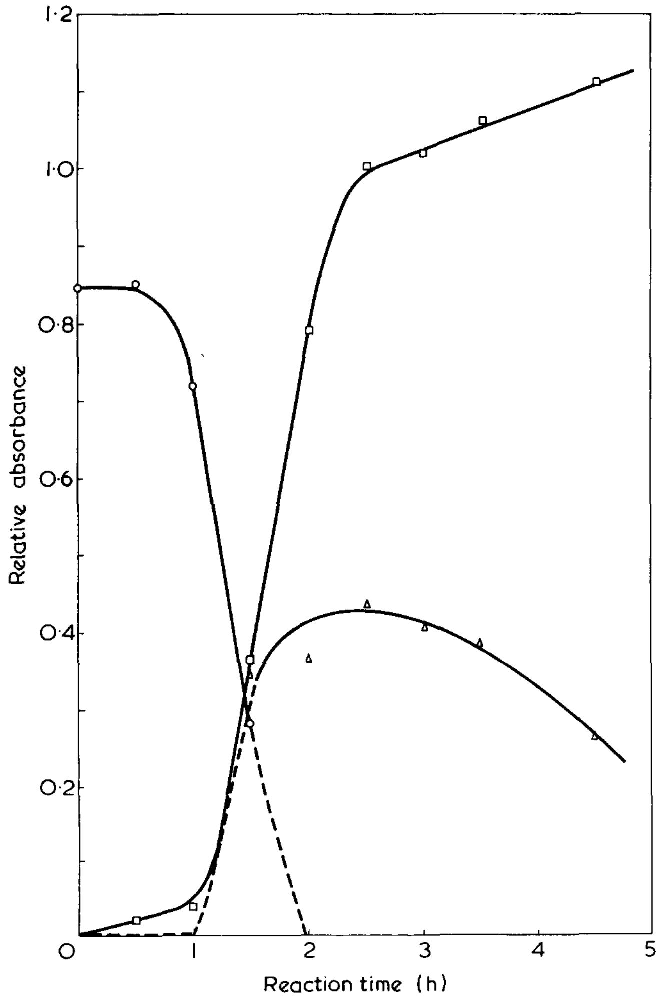


Figure 2 Infra-red measurement of acrylonitrile polymerization with time in a 5% w/w acrylonitrile mixed monomer reaction. ○, 4.50 μm; △, 4.45 μm; □, 4.55 μm

attack a nitrile to give on hydrolysis the enaminonitrile (VII) which does absorb at 4.55 μm.

This reaction scheme is clearly a model for that occurring in the mixed monomer system, and confirms that the absorption observed at 4.55 μm is due to species of type VII. The generation of these species, however, requires that the polyisoprene ends involved are proton terminated, and therefore do not link into the DGEBA structures. Although the extinction coefficient of species VII is unknown, it is likely to be at least as high as that of the isolated nitrile unit, so that the mole fraction of enaminonitrile units formed, and hence polyisoprene ends proton terminated, is probably quite small. Now that the absorbing species have been identified, the trends observed in *Figure 2* may be considered in more detail.

The rapid drop in acrylonitrile concentration observed after the initial induction period, is accompanied by correspondingly rapid increases in absorption due to species II and species IV. After consumption of the acrylonitrile, the peak at 4.55 μm continues to increase slowly whilst that at 4.45 μm falls. This is seen as the formation of species analogous to V and VII due to the action of the isoprenyl anions. Clearly, from the recorded drop in EV^0 of the products, the epoxide groups are also attacked by isoprenyl anions to generate alkoxide ions, and these are active centres for propagating acrylonitrile polymerization during the initial reaction stage. Nevertheless, as the epoxide groups are in direct competition with the nitrile moieties for reaction with these anions, it is to be expected that the fraction destroyed will be inversely related to the nitrile content of the charge, and that is what is recorded in *Table 2.*

Since the product of the post reaction method has EV^0 very close to that of the intermediate Is–DGEBA, alkoxide initiation of acrylonitrile appears to be the exclusive process occurring, so that the absorption at 4.55 μm recorded with this material is due to species of type IV formed exclusively during the polymerization of acrylonitrile. On this basis, it must be regarded as coincidental that the intensities observed with products prepared by both methods are similar. Certainly the structures of the two materials would be, on this analysis, very different. The post reaction product should have a main chain structure identical to that of Is–DGEBA with acrylonitrile units as side chains, whereas that formed by the mixed monomer approach should possess a much more complex structure, with acrylonitrile units linked by isoprenyl oligomers. Despite these differences, however, it will be seen that these two materials possess very similar adhesives properties.

Lastly, comment must be made on the analytical figures obtained for the nitrile content of these isolated products. Although the reproducibility of the results was not very good, the analyses consistently showed that only about 50% of the acrylonitrile introduced into the reaction system reappeared in the product. Experiments of the type illustrated in *Figure 2* indicate that the acrylonitrile is virtually completely polymerized under these conditions, and so the most likely explanation is that homopolyacrylonitrile of low molecular weight is formed in both methods which, being insoluble in the media employed, is adsorbed on to the surfaces of the reaction vessel or appears as a slight scum at the brine–THF interface and is then discarded. Homopolyacrylonitrile may be formed by a chain transfer process in the post addition method, and by this process also in the mixed monomer method together with direct reaction with sodium metal. In the latter method it will remain as the homopolymer only if not attacked and solubilized by isoprenyl anions.

Physical testing

The main purpose in testing the shear and peel strengths of the AN–Is–DGEBA materials was to compare their strengths with those of Is–DGEBA under similar conditions. For this reason, shear strength measurements were carried out with mild steel substrates which had been merely given a sand blast treatment before being made up. This technique does not yield the maximum strengths achievable by more sophisticated, but time-consuming, treatments, but were deemed sufficiently good to yield reliable comparative figures. In all cases to be discussed, the results quoted are the average from five testpieces.

The same surface treatment given to the aluminium strips for the 90° peel test were not so effective, and only qualitative trends could be observed.

Shear strength

Average shear strengths of materials prepared by the mixed monomer method are listed in *Table 3.* Higher shear strengths were obtained with DGBP than with TETA, but with either curing agent the values in the middle acrylonitrile range were appreciably higher than those obtained with Is–DGEBA. Comparison with the strengths given with unmodified DGEBA shows that this modification yields a product with a shear strength about double that of the original epoxide.

The shear strengths of a sample prepared by the post reaction method are also included in the Table, and they have values very close to those obtained with its analogue prepared by the alternative route.

A number of experiments had been previously carried out to prepare materials by the post reaction method, but using the isolation technique given in part 1[1]. As mentioned earlier, the separation was bedevilled with emulsion problems, but these were less acute at lower acrylonitrile concentrations, and some of these were successfully isolated. *Table 4* lists some results obtained from these products. Again the independence of EV^0 on acrylonitrile content is demonstrated, and the shear strengths obtained correspond reasonably well with those given by the mixed monomer products.

It therefore appears that the properties of these modified adhesives depend primarily on their overall chemical composition rather than the method of synthesis.

90° Peel strength

90° peel measurements were also carried out on the same materials as listed in *Tables 3* and *4,* but the results obtained were quite scattered and not consistent enough to be tabulated. Evidently peel strength measurements, which use aluminium rather than mild steel substrates, are very susceptible to surface preparation, and a more sophisticated technique should be adopted to obtain quantitative evaluations. Nevertheless, certain trends were observed which are worth recording: (a) the peel strengths obtained with DGBP were higher than those with TETA; (b) peel strengths were insensitive to acrylonitrile content in the range 0 to 6% w/w, above which fall-off was observed; (c) both types of modified materials had values at least double those obtained with DGEBA; and (d) the maximum peel strength observed with 6% acrylonitrile material was 2.4 kN/m.

CONCLUSIONS

(1) Incorporation of acrylonitrile into isoprene modified DGEBA systems yields two phase materials with greatly enhanced stability.

(2) The time taken for separation into two layers increases with acrylonitrile content; 6% acrylonitrile material had not separated after 9 months storage at room temperature.

(3) The behaviour and adhesive strengths of the modified materials were independent of the method of manufacture, although it was shown that the products from the two processes were structurally probably quite distinct.

(4) 6% w/w acrylonitrile material was chosen as the product which best combined ease of manufacture with long storage life and good shear properties.

(5) This material gave shear strengths up to 33 MN/m^2, significantly higher than Is–DGEBA, and double that of unmodified DGEBA.

(6) 90° peel strengths were widely scattered, but also showed a large increase over those obtained with DGEBA.

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