## Short-Term Aging Effects in a Nitrile-Epoxy Structural Adhesive

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## ABSTRACT

The aging of a carboxylated nitrile rubber-epoxy structural film adhesive at 40°C over a period of 15 d has been examined. Properties of the uncured adhesive, the curing reaction, and properties of the cured adhesive have been studied by a number of instrumental techniques. It was found that significant changes occurred in the solubility, epoxy content, and the molecular weight distribution. The cure reaction was "advanced" but not altered in general form, and the flow during cure was substantially reduced but the mechanical performance of the adhesive was only slightly affected. These results have been interpreted in terms of a carboxyl-epoxy reaction involving the nitrile rubber and epoxy resin.

## INTRODUCTION

Film adhesives now find extensive application in the structural bonding of aircraft. The one-part form, which requires only heat to

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effect its cure, has many advantages in terms of ease of use but the short shelf life, commonly 6 months at -18°C, is a serious disadvantage. Adhesives of this type are proprietary formulations and no information on their composition is supplied by manufacturers. In addition, the acceptance criteria laid down in various specifications are based wholly on mechanical tests with no account being taken of the acceptable levels of variation of the composition. The propensity of manufacturers to modify the composition without notification also causes additional processing problems.

The use of adhesive bonding in critical areas in aircraft, including primary structure, has led to greater interest in studies on chemical-based quality control techniques. The present work is part of a program on aging studies of various classes of film adhesives: the aim of these studies is to elucidate the reactions occurring during storage so as to relate the chemistry of the aging processes in uncured adhesives to the performance of those adhesives when subsequently cured. These considerations are especially important in Australia as all adhesives of this type are imported and must be transported over long distances and stored at subambient temperatures before use.

In the present work the aging of a carboxylated nitrile-rubber modified epoxy film adhesive has been examined at 40°C over a period of 15 d. The manufacturer's recommendation on "useful life" for this adhesive is 15 d at 32°C or 30 d at 4°C; that is, its performance as an adhesive may be impaired after this thermal history. The normal cure cycle is 1 h at 120°C and 0.34 MPa (50 psi).

## EXPERIMENTAL

The adhesive used in these studies was one of the so-called "second generation" nitrile-epoxy adhesives extensively used in aircraft applications. The adhesive, in the form of a film of thickness 0.13 mm, consisted of an organic matrix incorporating a polyester fiber mat support. Each side of the film was protected by a release paper. The overall composition [1] is shown in Table 1.

The adhesive film, with its backing paper undisturbed, was aged in an oven at 40°C. Samples were removed at intervals and, as necessary, stored in sealed plastic bags at -18°C.

Infrared (IR) spectra of soluble fractions of the adhesive, cast as films on KBr plates, were recorded on a Jasco IR-G spectrophotometer. Spectra of the whole adhesive film, for aging and curing studies, were examined by internal reflectance spectroscopy (IRS) using a model TR-25 IRS accessory and a KRS-5 crystal on a Perkin-Elmer 125 spectrophotometer. For studies at elevated temperatures a special IRS holder was made which incorporated wafer heaters on each side, the mass of the holder being adjusted so as to give similar

TABLE 1.  Composition of Nitrile-Epoxy Adhesive

| Component | % by Weight |
|---|---|
| Epoxy resin | 68 |
| Carboxylated nitrile rubber[a] | 15 |
| Dicyandiamide | 4 |
| 3-(p-Chlorophenyl)-1,1-dimethyl urea[b] | 2 |
| Chromium oxide | 0.7 |
| Polyester mat (Dacron) | 10 |

[a]Approximate composition:  butadiene 60%, acrylonitrile 35%, acrylic acid 5%.
[b]Monuron.

temperatures on each side (within 1°C).  Heat up time to 110°C was 6-7 min.

For examination of the cure reactions at 110°C, the absorption bands at 2170 cm$^{-1}$ due to the dicyandiamide curing agent were measured directly.  The absorbance when 110°C was reached was taken as zero % reaction and the constant value at the apparent end of the reaction as 100%.  In the case of measurements of absorbance from the epoxide group near 915 cm$^{-1}$, the results were normalized against the intensity of the band near 825 cm$^{-1}$ (aromatic ring 1,4 substitution).  This procedure highlighted changes in the epoxide content due to aging.

Epoxy equivalent weights were determined by a slightly modified version of the standard nonaqueous titration method [2].

Scanning electron micrographs were obtained using a Cambridge Stereoscan Mk. II instrument.

Gel permeation chromatography studies were conducted on a modified Varian 8500 high pressure instrument incorporating an Altex model 153 UV detector operating at 254 nm and a Waters model R401 refractive index (RI) detector in series.  The $\mu$Styragel columns were of nominal porosities $10^4$, $10^3$, 500, and 100 Å, and the solvent was freshly distilled tetrahydrofuran (THF).

A Du Pont model 900 Thermoanalyzer was used for thermal analysis.  The DSC cell was used for differential thermal analysis (DTA) of samples approximately 3 × 10 mm twice folded and pressed firmly to the base of the aluminum pan by the inverted lid.  The DTA was performed in air, and the area under the DTA curve determined by instrumental integration.  The heat of reaction is expressed in arbitrary units, as the calibration coefficient of the earlier DSC cell is temperature dependent; the values are consistent with those of amine-cured epoxy systems.  The softening point was determined with the

model 941 TMA, at 5°C/min, using the penetration probe loaded with
1 g. For isothermal examination of the cure reaction the tempera-
ture was maintained at 126°C; in the dynamic studies a heating rate
of 10°C/min was used.

To determine the extent of flow during curing, a 50 × 50-mm sample
of adhesive was placed between sheets of Teflon-coated glass cloth
and heated in a platten press for the recommended cure cycle–heated
to 120°C under 0.34 MPa pressure in 45-60 min, then held for 1 h at
120°C at the same pressure. Measurements with a planimeter were
used to calculate the percent increase in area from flow during the
cure cycle.

Single overlap and T-peel joints were made with 2024-T3 alumi-
num which was prepared for bonding by degreasing with 1,1,1-tri-
chloroethane followed by a chromic acid etch. Joints were made in
accordance with specified procedures [3] and the recommended cure
cycle for the adhesive in a heated platten press. The bond strength
was measured on either an Instron model TT-C-L or model 1026
tensile testing machine, depending on the load.

Fracture toughness was assessed by measurements on bonded
tapered double cantilever beams of 7075-T6 aluminum [4]. The sur-
faces were prepared for bonding by the same method as above, the
assemblies cured in an oven at 120°C, and tested on an Instron model
1026 machine.

Dynamic mechanical analysis studies employed a Rheovibron
model DDV-II Dynamic Viscoelastometer operating over the tempera-
ture range -100°C to 150°C. Samples of adhesive were cured between
Teflon-coated cloth using a template of polyester film (Melinex) to
control the thickness, four samples being cured at one time to ensure
equivalent thermal histories.

## RESULTS

The overall composition of the adhesive has been determined and
is given in Table 1. It has been shown [1] that the epoxy resin is
wholly of the diglycidyl ether of bisphenol A (DGEBA) type, that the
nitrile rubber contains some carboxyl groups and has a molecular
weight of approximately 30,000, and that the epoxy and the nitrile
rubber have not been prereacted together. The IR spectrum of the
acetone-soluble fraction of the adhesive (all except the pigment and
support) is shown in Fig. 1.

## Changes in Properties of the Uncured Adhesive

The changes in epoxy content and solubility in acetone and toluene
are shown in Figs. 2 and 3.

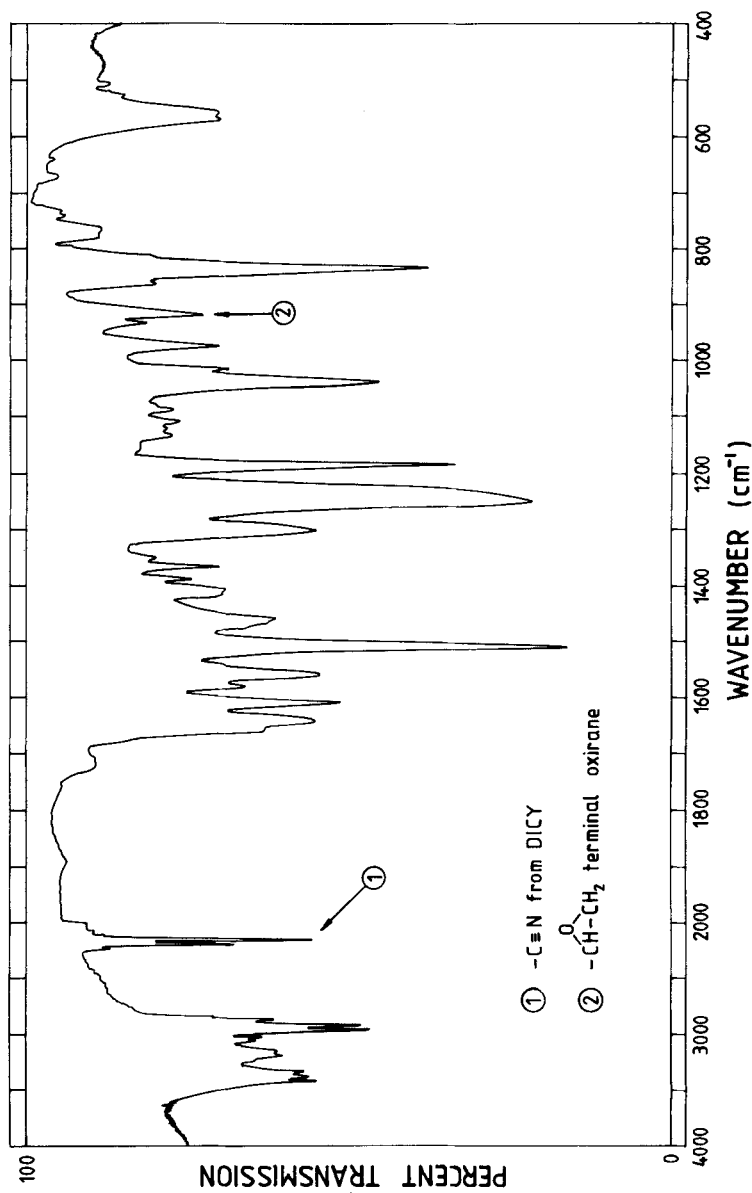Fresh material when dropped into a container of acetone dispersed

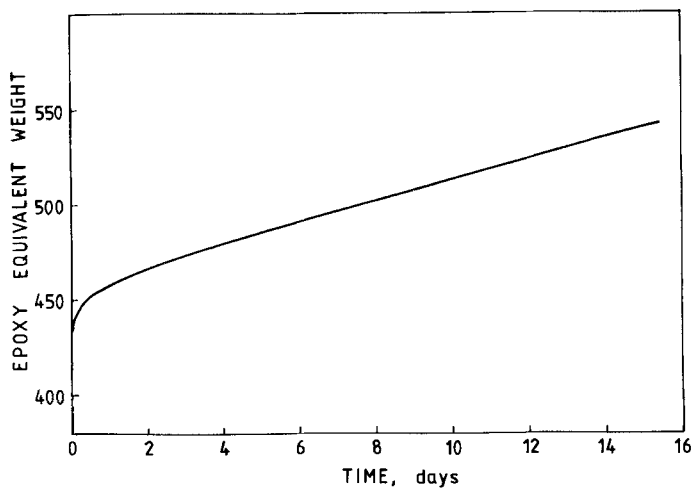FIG. 1. IR spectrum of acetone extract of nitrile-epoxy adhesive.

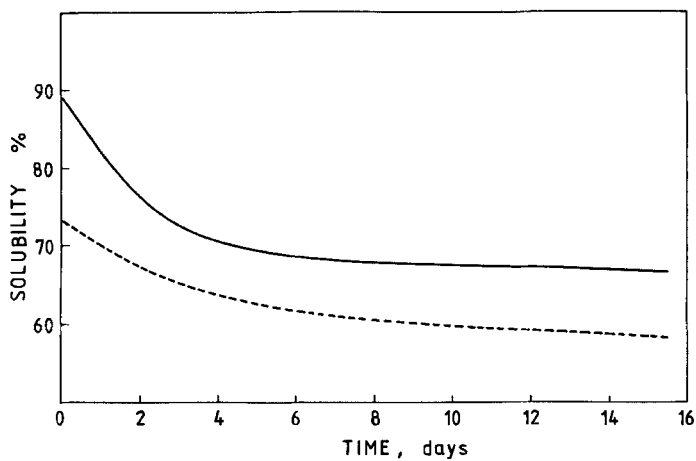FIG. 2.  Change in epoxy equivalent weight with aging time.
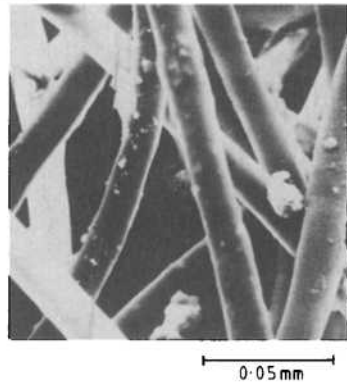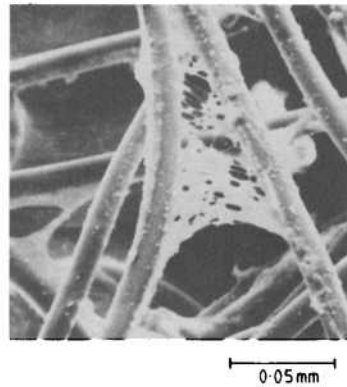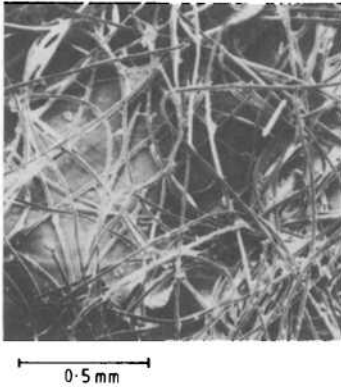


FIG. 3.  Change in solubility with aging time.  (——) Acetone, (- - -) toluene.

## Initial



0·5 mm

0·05 mm

## 0·17 days
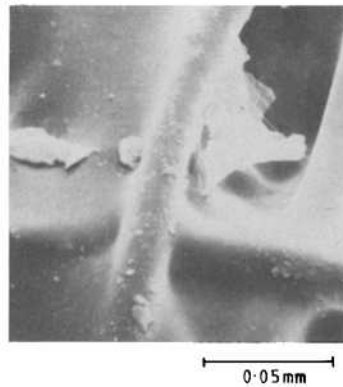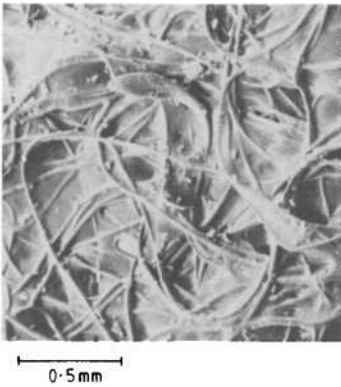


0·5 mm

0·05 mm

## 0·35 days



0·5 mm

0·05 mm

FIG. 4. Scanning electron micrographs of acetone-extracted
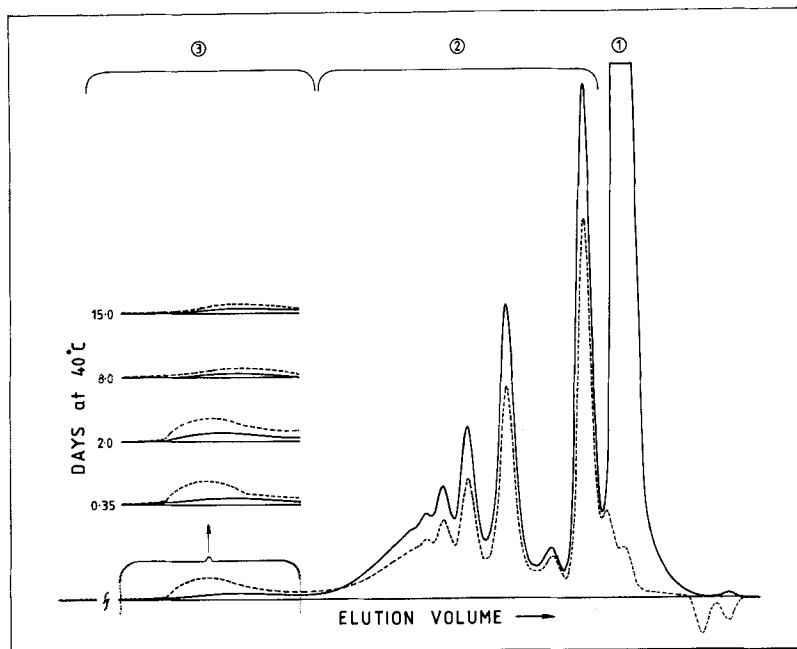Dacron support from fresh and aged adhesive.

FIG. 5. Gel permeation chromatographs of THF-soluble component of adhesive. (—) UV detector, (- - -) RI detector. ① Monuron, ② epoxy oligomers, ③ nitrile rubber.

immediately, leaving the support and a fine green precipitate (chromium oxide). After even a few hours at 40°C (or about a day at RT) this dissolution was perceptibly slower and the support retained a greenish appearance. After 2 d at 40°C, adhesive dropped into acetone appeared to be unaffected; that is, the green mat remained intact and no precipitate was formed, but analysis showed that some 68% of the mass was extracted.

Scanning electron micrographs of the extracted support are shown in Fig. 4. A deposit on the polyester fibers is visible in the aged samples. This deposit, which coats the fibers and forms a rather stringy web between fibers, retains the pigment particles within the mat, thus conferring the green coloration. IR examination of this deposit indicated a combination of rubber and epoxy resin with a substantial ester carbonyl content. The acid carbonyl peak, present in the spectrum of the rubber separately, had disappeared.

Gel permeation chromatograms of the THF-soluble material (all constituents except the pigment and support) are shown in Fig. 5. The nitrile rubber does not absorb at 254 nm but is visible to the RI detector in series. Aged samples increasingly showed high molecular
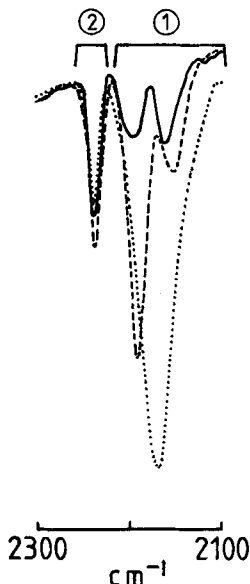
FIG. 6. IR (IRS) spectra of adhesive film. (—) Cold, (- - -) 110°C, (···) after 1 h at 110°C. ① Dicy bands, ② nitrile rubber band.

weight material detectable by UV at an elution volume corresponding to the nitrile rubber position. Further details on peak identification are given elsewhere [1]. From about 2 d aging onward, the amount and the molecular weight of the rubber component diminished; that is, material at the high molecular weight end of the distribution became increasingly insoluble in THF and was filtered out.

Infrared IRS examination of the solid adhesive film showed that significant changes occured on aging in the absorbance of the —CN bands due to the dicyandiamide (dicy) near 2200 cm$^{-1}$. However, independent determination of the overall concentration of dicy showed that no change occurred during aging.

Thermal analysis indicated that the softening temperature of the adhesive was initially about 4°C and increased to about 9°C after 15 d at 40°C.

## Changes in the Curing Reaction

The curing reaction at 110°C was studied by IR spectroscopy on samples previously aged at 40°C. Attention concentrated on the region around 2200 cm$^{-1}$ (the —CN dicy bands) and the epoxy band at 915 cm$^{-1}$. On heating to 110°C, the shape and position of the dicy
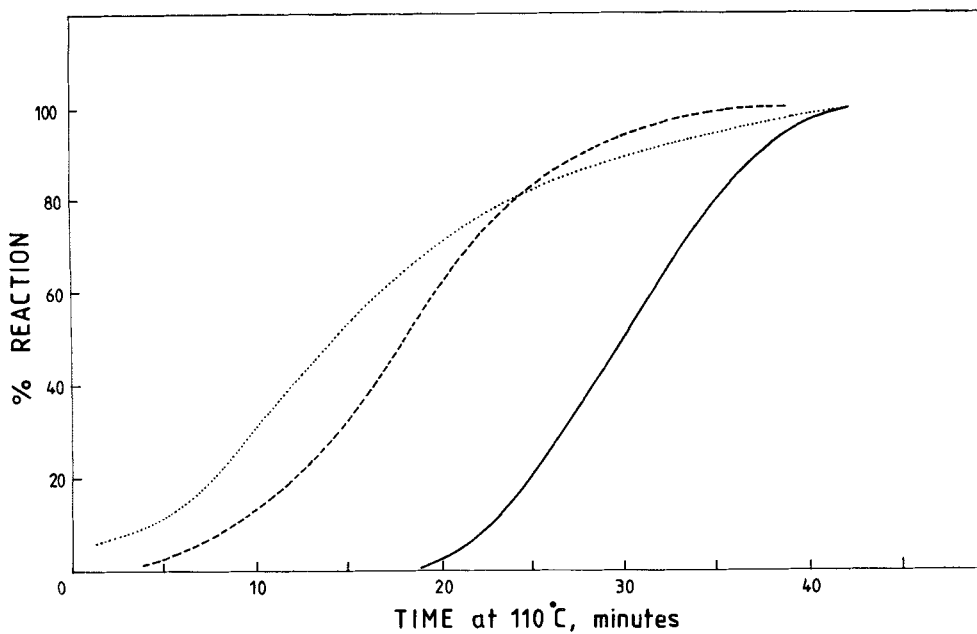
FIG. 7. Effect of aging on band near 2170 cm$^{-1}$. (——) Fresh adhesive, (- - -) after 4 d at 40°C, (···) after 15 d at 40°C.
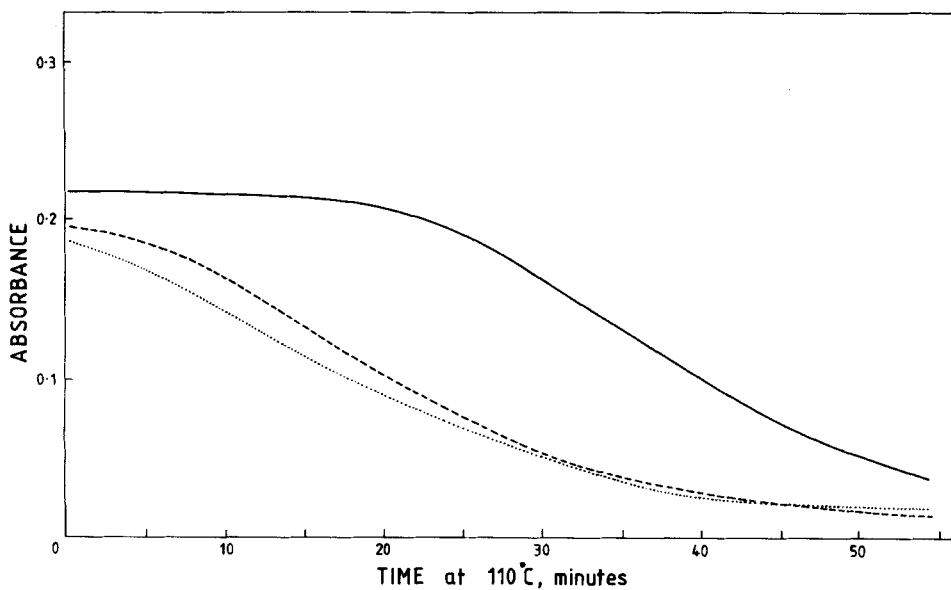


FIG. 8. Effect of aging on epoxy band near 915 cm$^{-1}$. (——) Fresh adhesive, (- - -) after 4 d at 40°C, (···) after 15 d at 40°C.
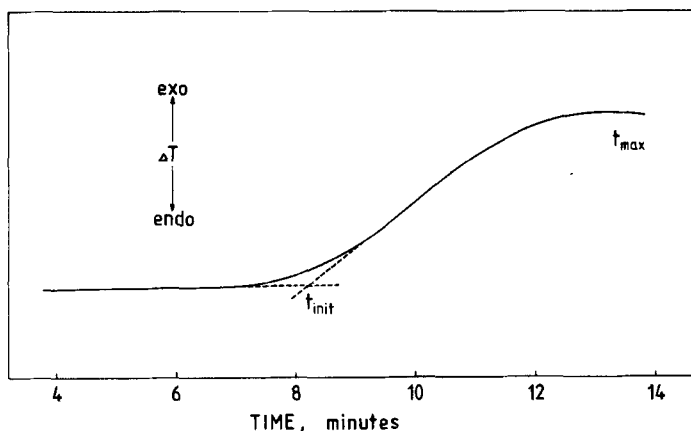
FIG. 9. Isothermal DSC trace.

doublet changed due to dissolution of the dicy in the resin, and a strong band was formed centered at 2188 cm$^{-1}$ (Fig. 6). In the initial stages of cure a new band near 2170 cm$^{-1}$ appeared and that at 2188 cm$^{-1}$ decreased. The epoxide band near 915 cm$^{-1}$ also decreased at this time. The changes in the 2170 and 915 cm$^{-1}$ bands during cure are shown in Figs. 7 and 8. In the latter case, the loss of epoxide during aging is responsible for the diminishing initial values.

The cure reaction was also monitored by thermal analysis on samples aged at ambient temperature. In an isothermal mode at 126°C the overall picture was similar to that shown by IR spectroscopy; that is, an "induction" time followed by an exothermic reaction (Fig. 9). Aging of the samples shortened the "induction" time and the time to maximum rate of reaction (Table 2).

In a dynamic heating mode the temperature of onset of reaction and the peak temperature were both shifted to lower values with increasing age of the sample (Fig. 10). The degree of conversion at the point of acceleration ($T_{init}$) was low, assuming that the heat of reaction is constant. There was relatively little change in the overall heat of reaction and the peak-temperature/heating-rate relationship suggests only slight changes of activation energy of the reaction (Table 2).

The flow during cure was also assessed as a function of the aging time. It was found that the flow was reduced essentially to zero after 2 d at 40°C (Fig. 11).

## Changes in Properties of the Cured Adhesive

The adhesive properties of the aged material were examined by means of bonded aluminum-aluminum joints. The most pertinent

TABLE 2.  Thermal Analysis of Aged Adhesive

| Isothermal Studies (126°C) | | | | | |
|---|---|---|---|---|---|
| Time at room temperature (d) | 0 | 3 | 8 | 14 | 42 |
| $t_{init}$ (mins)[a] | 7.0 | 6.0 | 5.0 | 4.5 | 1.5 |
| $t_{max}$ (mins)[a] | 12.5 | 12.0 | 11.0 | 10.0 | 8.0 |

| Dynamic DTA (10°C/min) | | | | | | |
|---|---|---|---|---|---|---|
| Time at room temperature (d) | 0 | 5 | 7 | 12 | 42 | 130 |
| $T_{init}$ (°C)[b] | 155 | 148 | 142 | | | |
| $T_{max}$ (°C)[b] | 166 | 166 | 164 | 165 | 160 | 158 |
| $\Delta H$ (arbitrary units) | 19 | 18 | 18 | 17 | 16 | 15 |
| Conversion at $T_{init}$ (%) | 2.5 | 0.4 | 0.2 | - | - | - |

[a]See Fig. 10.
[b]See Fig. 11.

features affecting the preparation of the joints were loss of tack, which made initial assembly more difficult, and more significantly, loss of flow.

For single overlap joints, the values of the tensile-shear strength at ambient temperatures (30 MPa) were effectively unchanged for material aged up to 15 d at 40°C. However, the appearance of the broken joints altered, with a significant increase in the proportion of adhesive (interfacial) failure. The coefficient of variation for the six samples measured in each case increased from less than 1% for the initial samples to around 10% for the latter, aged samples.

Peel strength was measured for joints made with fresh adhesive and material aged for 15 d at 40°C. The values (about 135 N/cm) were similar, with again a suggestion of an increased proportion of adhesive failure.

Fracture toughness determinations were made with fresh adhesive and material aged for 15 d. Again the values were effectively unaltered ($35 \times 10^{-2}$ J/m$^2$).

Dynamic mechanical analysis (Rheovibron) on cured samples showed only very minor differences in the modulus and tan δ values between samples aged for 0, 1, 8, and 15 d.
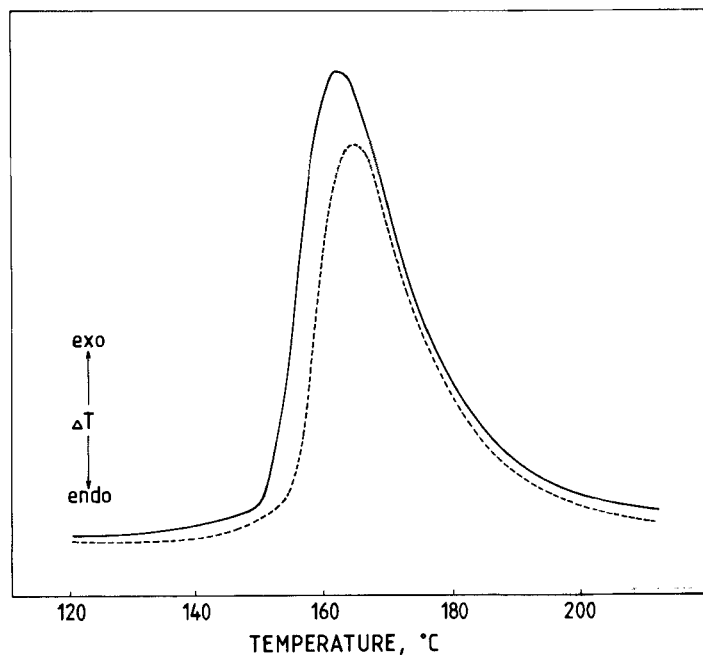
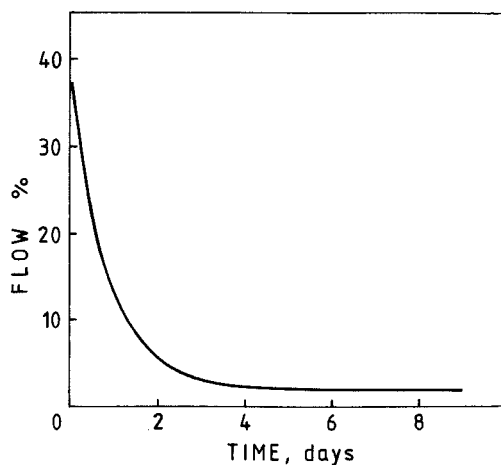FIG. 10.  Dynamic DSC trace. (- - -) Fresh adhesive, (—) after 3 d at ambient temperature.



FIG. 11. Change in % flow with aging time.

## DISCUSSION

The incorporation of nitrile rubber containing some carboxyl groups, usually at terminal positions, into epoxy resins as a means of increasing the fracture toughness has been established for some time [5]. The mechanism by which the toughening occurs is the following: during cure of the epoxy resin the rubber is precipitated as small particles from the initially homogeneous mix and these particles, dispersed in the epoxy matrix, provide the toughening effect. The exact composition of the rubber, especially the acrylonitrile content, affects its compatibility with the epoxy resin and thus the precipitation step [5].

It has been shown that in systems of carboxyl-containing polymers and DGEBA-type epoxies an acid-epoxy reaction occurs preferentially under uncatalyzed or base-catalyzed conditions and, despite a large excess of epoxy resin, dominates other possible epoxide reactions [6, 7]. The curing agent in this system is the dicy-Monuron combination, the mode of action of which is still unclear: however, it is known that dicy is insoluble in epoxy resins below about 80°C. Hence it might be expected that in the present studies at 40°C the formation of epoxy-rubber linkages competes very favorably with the normal epoxide cure reaction.

The change in solubility indicates that an increase in molecular weight occurred on aging and the IR spectra show that the insoluble material was predominantly rubber. From the GPC analysis at the high molecular weight end of the distribution (the nitrile rubber portion), the increase in the UV absorbance over the first 2 d of aging, with no corresponding change in the RI detector response, indicates incorporation of UV-absorbing material into the rubber. After longer aging times the RI response diminished at the high molecular weight end. Material with significantly higher molecular weight and reduced solubility in THF would be filtered out of the system before injection into the instrument. The IR spectrum of the acetone-insoluble material after 2 d aging indicated that effectively all the carboxyl in the rubber was of the ester type rather than the initial acid form.

While these changes in the molecular weight distribution occurred, a small reduction in the overall epoxy content was observed. The drop was initially rapid (about 7% increase in epoxy equivalent weight in the first day) and thereafter slower (less than 2%/d). On the basis of the adhesive formulation containing about 15% nitrile rubber, which itself has an acrylic acid content of about 5%, reaction of all the carboxyl groups with epoxide would account for some 6% of the epoxy content. Thus a network structure was formed over 1-2 d at 40°C which involved virtually all the rubber and perhaps 10% of the epoxy. As the molecular weight of the rubber was initially quite high ($M_n \sim$ 30,000), few cross-links would be necessary to render the rubber portion insoluble. The greatly reduced flow properties of the aged adhesive result from the formation of this network.

Some experiments were conducted on adhesive aged at room temperature where it was found that the solubility and flow changed at about one-sixth the rate at 40°C. However, material stored for more than a year in a freezer at -18°C had apparently not changed. This is doubtless due to the softening point of the uncured adhesive being around 5°C: very limited segmental movement would occur below that temperature.

When the adhesive is heated, the "normal" epoxy curing reaction proceeds. Both IR spectroscopy and thermal analysis indicated that the cure reaction was in its general form unchanged by both aging and the rubber network formation but the "induction time" was shortened.

The precise nature of the CN band at 2170 cm$^{-1}$ in the IR spectrum has not so far been identified but it is associated with the cure reaction in dicy-containing systems. The cure reaction is evidently a series of reactions which are "advanced" to some degree by the aging of the adhesive. The changes in the cure kinetics are not explicable solely on the grounds that the epoxy content was reduced by aging; rather, they suggest that either reactive intermediates normally formed during the initial stages of cure were produced during the aging process or "inhibitors" initially present were consumed during aging. The initial stages of the cure were thus modified when the adhesive was subsequently heated. Although the shape of the dicy doublet near 2200 cm$^{-1}$ altered during aging, the overall dicy content was unchanged. Evidently the cure-related reactions which occur during aging do not directly involve dicy. Further studies of the cure mechanism of dicy-containing systems are in progress to clarify these points.

In spite of various changes in properties of the uncured adhesive and a modification of the cure kinetics, the tensile-shear strength and peel strength at room temperature of aluminum-aluminum joints were effectively unaltered by aging. It would seem that the flow, although slight, was nonetheless sufficient for adequate wetting of the aluminum surfaces. It may be that in systems which rely more heavily on good wetting, such as in bonding honeycomb, the reduction in flow properties would have a more drastic effect. Similarly, the reduction in epoxy content during aging, if it leads to a modification of the cross-link structure, might be expected to affect the high-temperature performance of the adhesive more significantly than at room temperature. Likewise the long-term durability of the bonded joints may be deleteriously affected by the changes accompanying aging. These aspects have not yet been investigated.

It might be thought that the formation of rubber-epoxy linkages during aging would modify the toughness of the cured epoxy matrix. However, this does not appear to be the case. Values of the peel strength and fracture toughness for the adhesive initially and after 15 d at 40°C were essentially the same. In addition, no significant changes were apparent in the Rheovibron curves. The conclusion is that, as indicated above, aging has advanced the initial stages of the cure reaction but not altered its overall course.

## CONCLUSIONS

During storage at 40°C of an uncured, epoxy-based structural film adhesive, modified with carboxylated nitrile rubber, reaction occurs between the epoxide and carboxyl groups which produces an extensive network structure through the film. The presence of this network significantly reduces the flow of the adhesive during cure. However, as only a small proportion of the epoxide content is consumed by the network formation, the general form of the cure reaction is little altered but the "induction" time reduced. Those physical properties of the cured material which are not critically dependent on high flow during cure are little affected by aging over a period of 2 weeks.

## ACKNOWLEDGMENT

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