

Aging and Performance of Structural Film Adhesives.

II. Comparison of Two Nitrile-Epoxy Systems

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Synopsis

The room-temperature aging of two nitrile rubber-epoxy adhesives has been examined. Both are 121°C curing systems, based on DGEBA-type epoxy resins, one of which has been available for about 15 years while the other is a more recent development. It has been found that hydrolysis of the epoxide and polymerization both occur slowly, reducing the epoxide content and solubility. A major reduction in honeycomb peel strength of joints made with aged material was evident in the older system and to a lesser extent in the newer adhesive. This is a result of diminished adhesive flow. Tensile strength was less affected by aging.

INTRODUCTION

Many of the adhesives used for structural applications in aircraft are in the form of one part films of very limited shelf life, even at low temperatures. The increasing use of bonding in critical areas, including primary aircraft structure, has placed additional emphasis on quality control of uncured adhesives, on chemical means of assessing the extent of reaction which has occurred during storage, and the effect of any such reaction on the performance of the cured material. These considerations are of particular concern in Australia, since all adhesives of this type are imported.

In an earlier study on the accelerated aging of a nitrile rubber-modified epoxy adhesive,¹ it was shown that a reaction occurred between the carboxyl groups in the rubber and epoxide groups in the resin. This resulted in the formation of a small amount of a network structure through the adhesive film which significantly modified the flow of the adhesive during cure. In spite of this, values of the tensile-shear and T-peel strength of aluminum-aluminum joints were little affected. However, it was suggested that the strength of joints more critically dependent on flow, such as bonded honeycomb panels, would be more drastically altered. The adhesive in that study was an older type of nitrile-epoxy system which has been used in aerospace applications for at least 15 years. This work has now been extended to the room-temperature aging of this material over longer times, and the results compared with those for a representative of the new-generation, improved nitrile-epoxy systems.

EXPERIMENTAL

The two adhesives used in this work are designated A and B. Both are designed for bonding metal to metal in aerospace applications for service up to

TABLE I
Approximate Overall Composition of Adhesive A

Component	Weight, %
DGEBA epoxy resin ^{a,d}	68
Carboxylated nitrile rubber ^{b,d}	15
Dicyandiamide	4
3-(<i>p</i> -Chlorophenyl)-1,1-dimethylurea ^c	2
Chromium oxide	1
Polyester mat	10

^a Blend of three resins equivalent to Shell's Epon 828 7%, Epon 834 42%, and Epon 1001 18%.

^b Equivalent to Goodrich's Hycar 1072. Approximate composition: butadiene 60%, acrylonitrile 35%, acrylic acid 5%.

^c du Pont's Monuron.

^d The rubber and epoxy resin have not been prereacted.

about 100°C and are based on the diglycidyl ether of bisphenol A type of epoxy resin (DGEBA).

Adhesive A is a nitrile rubber-modified epoxy-based material which has been commercially available for some 15 years. Adhesive B is one of the more recently developed nitrile-epoxy systems. The recommended cure cycle for both is 1 h at 121°C and 0.34 MPa. The composition of these adhesives has previously been studied² and is summarized in Tables I and II.

The shelf life of the two systems is given by the manufacturer of each as six months at -18°C (A) and six months at or below 0°C (B) while the shop life or "out time" is quoted as 10 days at 23°C (A) and 30 days at 23°C (B).

For aging, pieces of adhesive about 30 cm × 30 cm were stored in polyethylene bags at about 23°C and less than 50% RH. Samples were removed at intervals for testing or, if necessary, stored at -18°C until required.

For high-pressure liquid chromatography (HPLC), a modified Varian 8500 instrument was used with an Altex 153 UV detector at 280 nm. The equipment was operated in the reverse-phase, gradient elution mode with a du Pont Zorbax CN column and a combination of tetrahydrofuran (THF) and water as the solvent.

Gel permeation chromatography (GPC) was achieved with the same equip-

TABLE II
Approximate Overall Composition of Adhesive B

Component	Weight, %
DGEBA epoxy resin ^{a,d}	78
Carboxylated nitrile rubber ^{b,d}	13
Carboxy-terminated polybutadiene ^{c,d}	
Adduct of 2,4-tolylene diisocyanate and dimethylamine	5
Blue and yellow dyes	trace
Polyester mat	4

^a Equivalent to Shell's Epon 836.

^b Equivalent to Goodrich's Hycar 1072.

^c Equivalent to Goodrich's Hycar CTB 2000 × 162.

^d The rubber and epoxy resin have been prereacted.

ment with a Waters model R 401 RI detector in series with the UV detector. Five μ Stryragel columns were used (nominal porosities 10^5 , 10^4 , 10^3 , 500, and 100 Å) with THF as the solvent.

Materials associated with selected peaks in the HPLC and GPC traces were collected and identified by infrared analysis using a Perkin-Elmer 580B ratio-recording, double-beam spectrophotometer, interfaced with a model 3500 data handling system. This procedure has previously been described.³

Epoxide content was determined by nonaqueous titration as previously described.³

Flow of the adhesive during cure was assessed by curing a 50-mm-diameter disc of adhesive between release sheets in a heated platen press using the cure cycle recommended for the adhesive. The percent flow was calculated from the mass of material outside the original area.

Single overlap joints were made with 1.6-mm 2024-T3 Alclad aluminum sheet for which the surface preparation was a vapor degrease with 1,1,1-trichloroethane followed by a chromic acid etch. No primer was used. Joints were made in a heated platen press using the cure cycle recommended for the adhesive. Joint geometry and test methods were in accord with standard procedures.⁴ The testing was accomplished with a model TT-C-L Instron tensile testing machine.

Bonded honeycomb panels were made using 9.5-mm cell size aluminum honeycomb 12.5 mm thick with 0.13 mm 2024-T3 face sheets. These panels (75 mm wide) were tested by climbing drum peel.

Dynamic mechanical properties of cured adhesive samples were assessed with a Rheovibron DDV-II-C direct-reading dynamic viscoelastometer. Samples for examination were cured in batches in the press, using a polyester template, to ensure equivalent thermal history. The instrument was operated in the tensile mode at a frequency of 110 Hz and a heating rate of about 2°C/min.

RESULTS AND DISCUSSION

Chemical Studies

The change in epoxide content and in chlorobenzene solubility with time for the two adhesives is shown in Figures 1 and 2, respectively. The rapid initial change in the case of adhesive A has been shown to be due to the interaction of the carboxyl groups in the nitrile rubber with epoxide groups.¹ No such rapid initial change is observed with adhesive B, since the carboxyl and epoxide groups were prereacted as part of the preparation of the adhesive.²

HPLC analyses of the two adhesives were conducted at intervals. Most of the peaks are due to the DGEBA oligomers. For adhesive A, the principal features are the appearance and growth of an additional peak on the more polar side of the epoxy monomer peak and a reduction in the size of the oligomer peaks (Fig. 3). For adhesive B, more complex changes occur since, as well as modifications analogous to those in adhesive A, a number of other additional peaks appear (Fig. 4). The chromatogram for the initial material agrees exactly with that of Epon 836 epoxy resin, with the exception of one additional peak, eluting at about 40% THF, which is due to the curing agent in the adhesive.

Material giving rise to peaks marked B, and A, B, C, and D in Figures 3 and

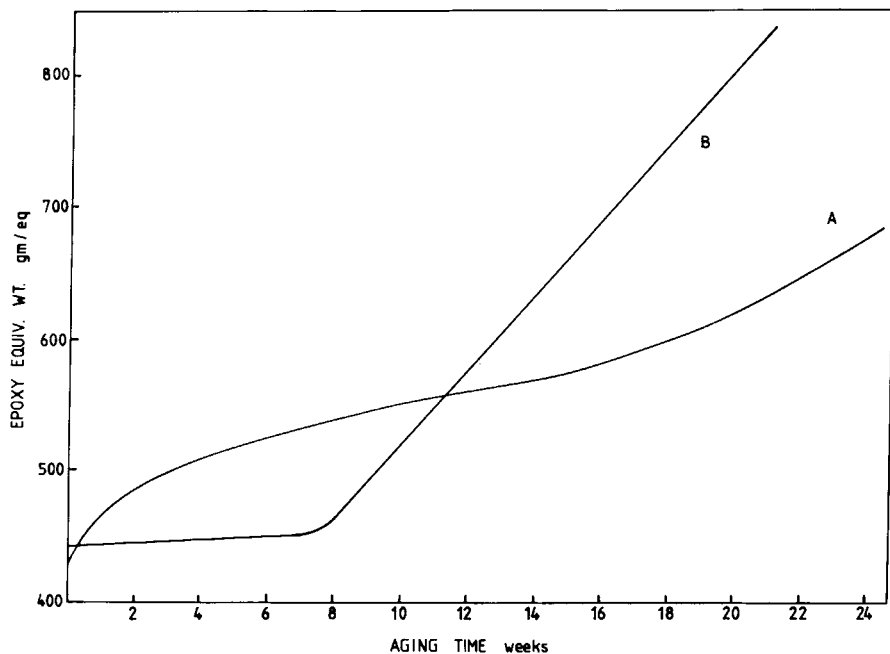


Fig. 1. Change in epoxide content during aging.

4, respectively, was collected and examined by IR spectroscopy (Fig. 5). The material B in each case yielded the same spectrum, consistent with the half-hydrolyzed monomeric epoxy compound. The spectrum of A was consistent with fully hydrolyzed monomer, while those of C and D corresponded to the partly hydrolyzed $n = 1$ and $n = 2$ oligomers, respectively (Fig. 6). The rate of increase of the area of peak B is shown in Figure 7. Initially, both adhesives contain similar amounts of DGEBA monomer (35 to 40% of the total mass).

A recent study on the susceptibility to hydrolysis of a number of epoxy model compounds has indicated that whereas *N*-glycidyl aromatic amines show significant moisture sensitivity, DGEBA-type epoxy compounds do not.⁵ It was shown, for example, that the epoxide content of phenyl glycidyl ether, used as

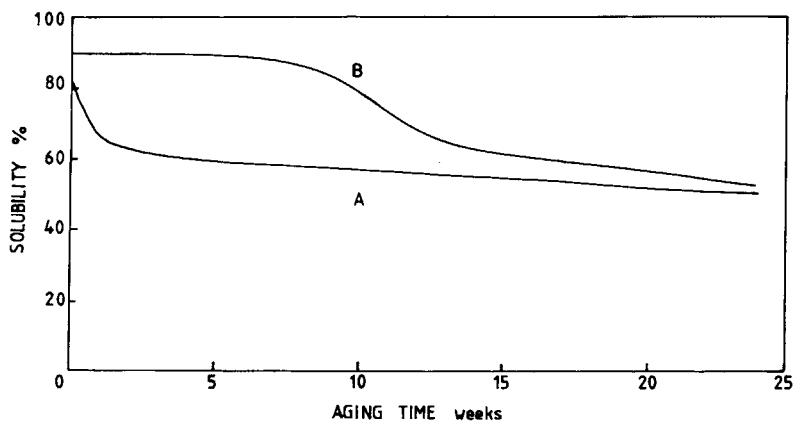


Fig. 2. Change in solubility in chlorobenzene during aging.

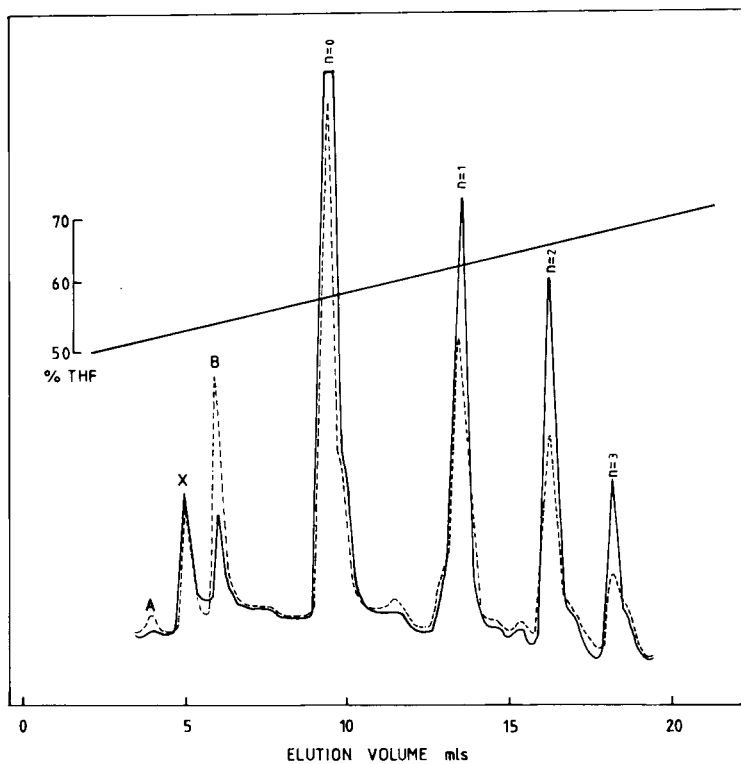


Fig. 3. HPLC analysis of adhesive A: (—) initial material; (---) after 25 weeks of aging. Peaks labeled n are epoxy oligomers; X is Monuron; A and B are hydrolysis products (see text).

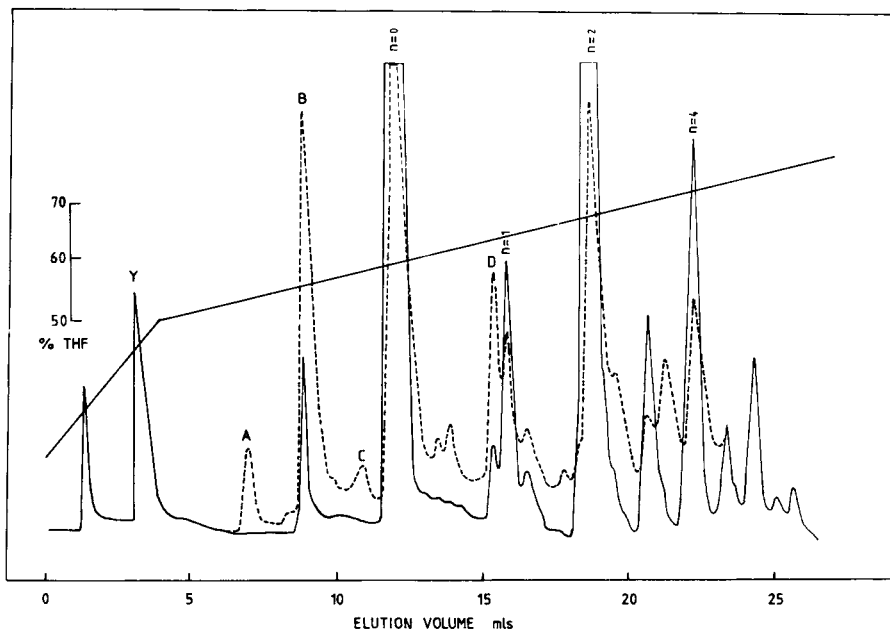


Fig. 4. HPLC analysis of adhesive B: (—) initial material; (---) after 22 weeks of aging. Peaks labeled n are epoxy oligomers; Y is 2,4-tolylene diisocyanate-dimethylamine adduct; A, B, C, and D are hydrolysis products (see text).

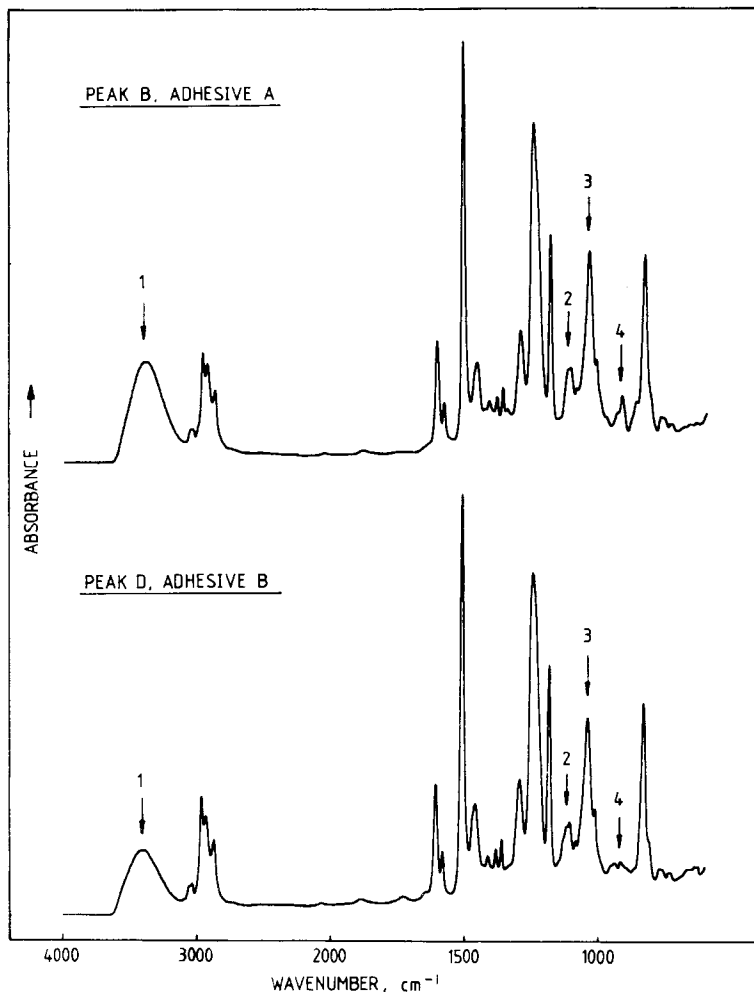


Fig. 5. IR spectra of HPLC fractions. Indicated bands are due to: 1, O—H stretch; 2, C—OH stretch in secondary alcohol; 3, C—OH stretch in primary alcohol + C—O—C stretch in ether; 4, epoxy ring breathing vibration.

a model for DGEBA resins, was unchanged after 130 days at 60°C and 96% RH. This finding is in accord with the well-known stability of DGEBA epoxy compounds. However, a catalytic effect of moisture on the cure of DGEBA epoxy resins has been reported by a number of workers.⁶⁻⁸ Clearly, in the present case of hydrolysis of a DGEBA epoxy compound in formulated adhesives, some other reaction must be operating to produce the observed effects.

A comparison of the composition of adhesives A and B (Tables I and II) shows that the only other components in common are the polyester mat support and the carboxylated nitrile rubber. Mixtures were made of Epikote 828 [made by Shell Chemical (Australia) Pty Ltd]/Hycar 1072 and Epikote 828/polyester mat, each with about 0.5% added water. This resin contained some dihydroxy DGEBA (the half-hydrolyzed $n = 0$) probably arising from the use of partly hydrolyzed epichlorohydrin in its manufacture.^{9,10} The mixtures were kept at

at 60°C. After 45 h, a pattern of HPLC peaks very similar to that developed in adhesive B was obtained, that is, peaks A, B, C, and D were all clearly evident. A mixture of the epoxy and curing agent without added water was unchanged under the same conditions. This topic is being studied further.

The UV detector response was calibrated with pure monomeric DGEBA epoxide (Shell's X22) and also with the half-hydrolyzed compound (peak B), and the extinction coefficients were found to be similar. The extent and rate of the hydrolysis reaction could then be estimated. Initially, in adhesive B the ratio of half-hydrolyzed to monomeric epoxy compound was about 1:12. This was unchanged for about four weeks, after which the amount of the half-hydrolyzed material doubled over the following seven weeks. The presence of the fully hydrolyzed analog (peak A in Fig. 4) was first discernible by HPLC after 11 weeks of aging and reached a proportion of about 1:25 in relation to the initial monomeric epoxy content after 22 weeks. A similar pattern of change occurred with adhesive A but at a slower rate. The initial ratio of half-hydrolyzed compound to parent compound was 1:11, and the amount of the former doubled over about 21 weeks. A trace of the fully hydrolyzed material (peak A, Fig. 3) was discernible in the initial material, and the amount increased somewhat over the 25 weeks of the trial.

In adhesive B, material giving rise to peaks C and D in Figure 4 was collected, and the IR spectra were consistent with those of the half-hydrolyzed $n = 1$ and $n = 2$ compounds. Some at least of the other additional peaks observable in aged adhesive are undoubtedly due to partly and fully hydrolyzed analogs of other oligomers. Slight traces of these higher-molecular-weight compounds were discernible in adhesive A (Fig. 3).

It should of course be noted that these assessments involved only one batch of each adhesive: batch-to-batch variations may be significant. Also, the thermal history of these adhesives prior to receipt in these laboratories is unknown, and this may have exerted a modifying effect. However, both adhesives undergo some hydrolysis; the proportion of the epoxy compounds hydrolyzed under the present aging conditions is fairly small, and adhesive B appears to be more susceptible to hydrolysis than adhesive A.

Considering the reduction in height of the peaks due to the DGEBA oligomers in the two cases, it appears that the rate of change is similar. (Precise calculation is difficult as these peaks are in some instances outside the linear range of detector response.) The rate of change of epoxide content (Fig. 1) follows a different pattern in the two cases. Epoxide loss results from hydrolysis, polymerization (taken to include both chain extension and crosslinking), and, in adhesive A, reaction with carboxyl groups in the rubber. Solubility provides an indication of the extent of polymerization, especially crosslinking. In adhesive A, it was previously estimated¹ that around 6% of the epoxide reacts with carboxyl groups giving rise to the initial changes in epoxide content and solubility. Thereafter, polymerization evidently proceeds slowly, resulting in gradual changes in epoxide content and solubility, with hydrolysis of the resin making a quite minor contribution to epoxide loss. In adhesive B, the sudden change in epoxide content and solubility after 8–10 weeks of aging indicates that polymerization, previously proceeding very slowly if at all, then becomes the dominant reaction, with hydrolysis continuing slowly and involving only a minor proportion of the resin. The reason for the sharp acceleration in rate of polymerization after eight weeks

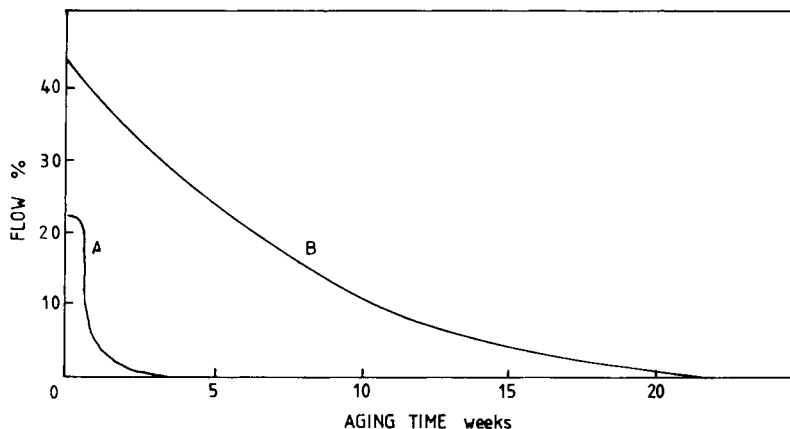


Fig. 8. Change in percent flow on aging.

is unclear at present. Possibilities include the consumption of a stabilizer or the production of some reactive intermediate.

Physical and Mechanical Properties

The change in percent flow for the two systems under the recommended cure conditions is shown in Figure 8. In adhesive A, the flow is reduced to virtually nothing in a short time. This change was observed in the accelerated aging study¹ and was attributed to interaction between the carboxyl groups in the rubber and the epoxy. In adhesive B, the rubber and epoxy are prereacted; as expected, there is a much slower rate of change in its flow properties.

The peel strength of bonded honeycomb panels made with aged adhesive (Fig. 9) changes as a direct consequence of the change in flow properties of the adhesive. The bonding of honeycomb panels relies heavily on good wetting to obtain adequate filleting into the honeycomb cells and thus a strong bond. The small residual peel strength of panels made with adhesive of essentially no flow is a consequence of the honeycomb cutting into the adhesive under the pressure applied during the cure cycle (about 0.28 MPa).

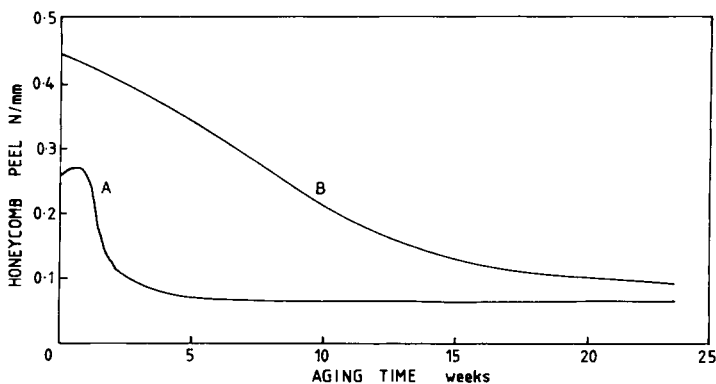


Fig. 9. Change in honeycomb peel strength (climbing drum) on aging.

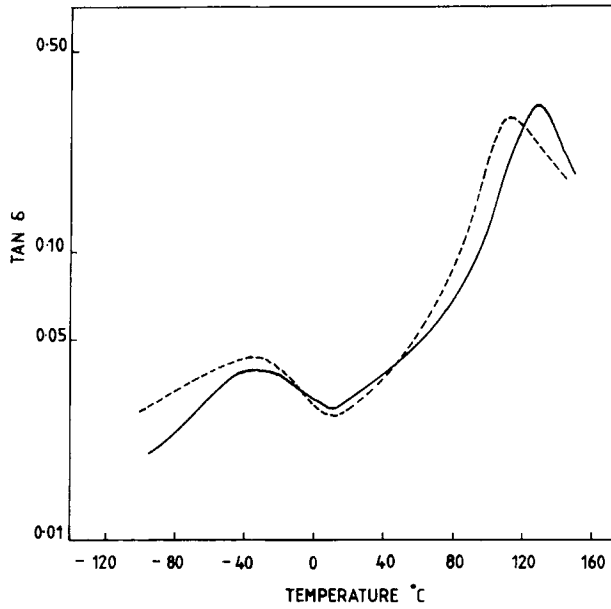


Fig. 10. Dynamic mechanical analysis of adhesive A: (—) initial material; (---) after 22 weeks of aging.

In adhesive B, the flow after four weeks of aging had fallen to about 65% of its initial value. It has been demonstrated that hydrolysis and polymerization had

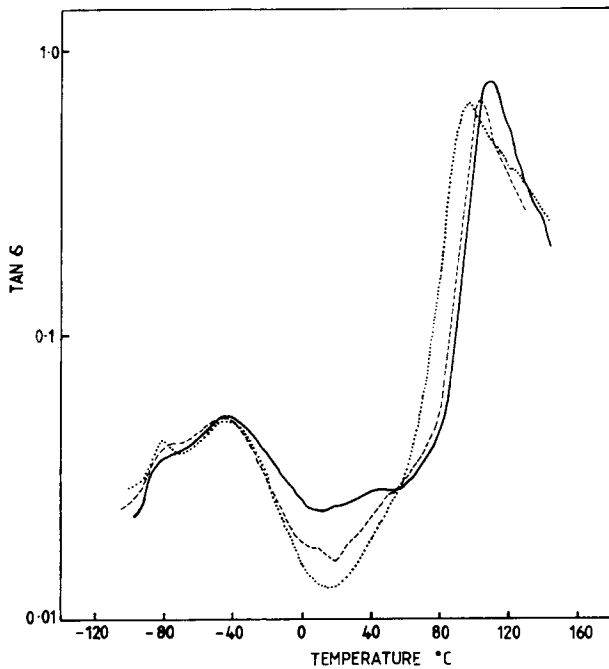


Fig. 11. Dynamic mechanical analysis of adhesive B: (—) initial material; (---) after five weeks; (···) after 22 weeks.

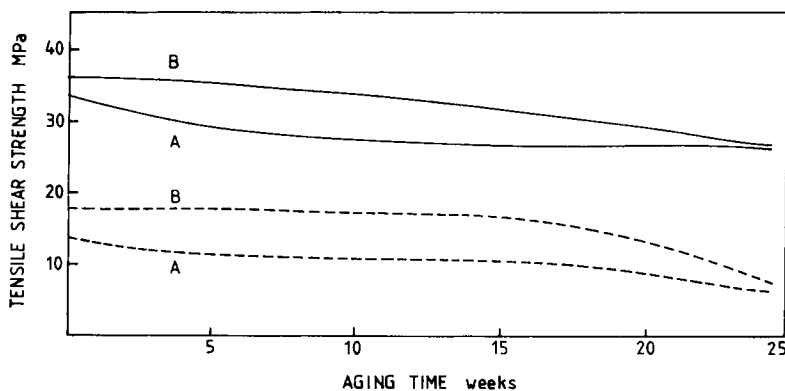


Fig. 12. Tensile shear strength of single overlap joints: (—) tested at ambient temperature; (---) tested at 100°C.

both proceeded to only a very minor extent in that time. The possibility that the carboxylated rubber was not completely prereacted with epoxy during the preparation of the adhesive and that a reaction analogous to that in adhesive A proceeded with the residual carboxyl groups seems unlikely since the solubility of adhesive B was unchanged for the first eight weeks of aging. The sharp change in solubility after 8–10 weeks of aging was not reflected in a rapid change in flow, which had already fallen to about 25% of its initial value by that time. Thus, it would seem the flow properties are strongly influenced in the case of adhesive B by some other factor. In this context, the dynamic mechanical properties of cured, aged samples are interesting (Figs. 10 and 11). For both adhesives, there is a shift in the $\tan \delta$ curve (particularly the α peak) to lower temperatures. For adhesive B, there is also a reduction in the magnitude of the $\tan \delta$ values over the 0–60°C temperature range, even for material aged for only five weeks. This may be related to the flow changes, since most of the adhesive flow occurs in the cure cycle before the adhesive reaches its cure temperature of 120°C.

Tensile-shear strength of lap joints is relatively insensitive to the age of the adhesive (Fig. 12). The applied pressure is evidently sufficient for adequate flow, and thus the bond strength is not greatly affected by aging provided the strength of the adhesive itself is not adversely affected. The loss of epoxide content by hydrolysis can be expected to result in a lower crosslink density when the material is cured and eventually in a reduction in the joint strength at high temperatures, as has been found in other systems.^{3,4} The shift of the maximum of the $\tan \delta$ curves to lower temperatures after 22 weeks of aging (about 16°C down for adhesive A and 13°C for adhesive B) indicates a reduction in the glass transition temperature (T_g). The changes in the tensile-shear strength of lap joints tested at 100°C are ascribable to these effects.

CONCLUSIONS

The rate of change of a number of chemical and physical properties and of adhesive joint performance of two nitrile-epoxy adhesives during room-temperature aging has been examined. Both adhesives are based on DGEBA-type epoxy resins, and it has been shown that under the conditions described in this

work these epoxies are slowly hydrolyzed, although DGEBA resins alone are stable in moist environments. Polymerization also proceeds gradually, leading to a reduced epoxide content and solubility. There is evidence that the more recently developed adhesive system is less stable in these aspects than the older formulation.

Aging is accompanied by a reduction in adhesive flow and in the peel strength of bonded honeycomb panels. This change is especially rapid for the older adhesive system and is a consequence of a reaction between the epoxy and the carboxyl groups in the rubber. The formulation of the newer systems precludes this reaction, but a substantial reduction in peel strength still occurs over a longer time scale. The reason for this is unclear. In terms of the normal use of these two systems, where the total time at ambient temperature might be of the order of several weeks, the newer formulation (B) is clearly substantially more stable.

Hydrolysis of the epoxy resins results in a small fall in the T_g of cured systems and hence in their strength at elevated temperatures.

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