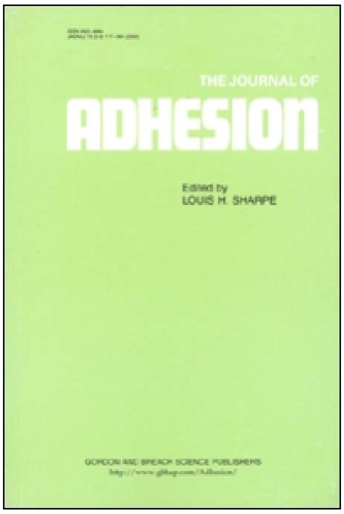

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Characterization of two Nitrile-epoxy Structural Adhesives

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High pressure liquid and gel permeation chromatography, together with infrared studies on particular chromatography fractions, has been used to study two nitrile-epoxy adhesives. One of these materials has been available for some fifteen years while the other is a more modern development. A detailed consideration of the distribution of epoxy oligomers has indicated a change from taffy to fusion process DGEBA resins in recent times. Study of the acrylonitrile content of high molecular weight fractions has shown that whereas the older adhesive only contains a carboxylated nitrile rubber, the newer system also contains some carboxy-terminated polybutadiene.

INTRODUCTION

The increasing use of structural adhesives and of advanced composites in aircraft construction has focussed attention on means of characterizing the organic materials used in these applications. Although most quality assurance specifications for adhesives call only for mechanical tests, such as tensile-shear or peel strength of bonded joints, it has become evident that such tests are insensitive to many variations in chemical composition which could affect performance. The increasing use of these materials in primary aircraft structures has led to increased attempts to devise means of chemically characterizing the proprietary formulations used[1,2]. The aim of these attempts is to be able to define the acceptable limits of batch-to-batch variation and also to assist in assessing the remaining usable life of these materials which frequently have short shelf lives. The latter point is especially significant when the materials must be transported considerable distances at sub-ambient temperatures before use.

The present work describes the characterization of two 120°C curing, nitrile epoxy adhesives extensively used in aircraft applications. One of these has been available for some fifteen years (Adhesive A) while the other is a representative of the newer, improved class of rubber modified epoxy adhesives (Adhesive B). The techniques used for the characterization are mostly various forms of chromatography, the usefulness of which in these applications is increasingly being recognised[3-5]. The aim of this study was to assess the degree to which a formulated film adhesive can be analysed by these techniques as well as to define those features which distinguish the newer nitrile-epoxy adhesives from the older ones.

EXPERIMENTAL

Samples of the adhesives, from a number of different batches, were obtained from Government Aircraft Factory, Melbourne, Victoria, who had imported them from their overseas manufacturer.

Gel permeation chromatography (GPC) was conducted with a modified Varian 8500 high pressure instrument using five μ Styragel columns (nominal porosities 1×10^5, 1×10^4, 1×10^3, 500 and 100Å) and two detectors in series (Waters model R401 differential refractometer and an Altex model 153 UV detector operating at 254 or 280 nm). The equipment was used at room temperature and the solvent was purified tetrahydrofuran (THF) at a flow rate of 1.0 ml/min.

High pressure liquid chromatography (HPLC) was conducted using basically the same equipment in a reverse phase, gradient elution mode, with a 250 mm Du Pont Zorbax CN column, THF and water as the solvent system at a flow rate of 1.0 ml/min and the UV detector.

Infrared 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 films were obtained by internal reflectance spectroscopy (IRS) using a model TR-25 IRS accessory and a KRS-5 crystal on a Perkin Elmer 125 spectrophotometer. IR spectra of fractions separated by GPC were recorded on a Perkin Elmer 580 B spectrophotometer interfaced with a model 3500 data station. NMR spectra were determined on a Varian HA60-1L spectrometer using deuterochloroform or deuteroacetone solutions and tetramethylsilane as the internal lock.

Specimens for mechanical testing were prepared broadly according to specification MMM-A-132[6] and the manufacturer's recommended cure schedule for the adhesive. Type 2024-T3 clad aluminium sheet was obtained from Moorabbin Aircraft Spares Pty Ltd., Melbourne. It was prepared for bonding by vapour degreasing and spraying with 1,1,1-trichloroethane followed by a chronic acid etch. For tensile-shear tests the adherends were 1.6

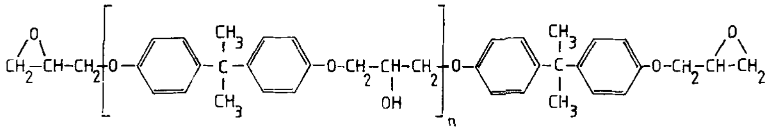
mm thick sheets approximately 203 × 101 mm bonded together with 12.7 mm overlap and cured in a heated platen press. The panels were cut into strips 25.4 mm wide to give six test pieces of 100 × 25.4 mm. The tensile-shear stress was measured on a model TT-C-L Instron tensile testing machine at a cross-head speed of 0.5 mm/min.

Dynamic mechanical properties were assessed by means of a Rheovibron DDV-II-C direct reading dynamic viscoelastometer. Samples for examination were cured in a heated platen press, using a polyester film template, according to the cure cycle recommended by the adhesive manufacturer.

RESULTS AND DISCUSSION

Adhesive A

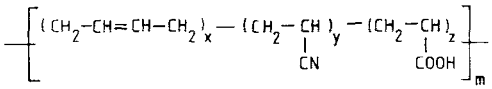
The overall composition of Adhesive A was found to be as shown in Table I. From IR and NMR spectra it was concluded that the epoxy resin is wholly of the diglycidyl ether of bisphenol A (DGEBA) type (I):



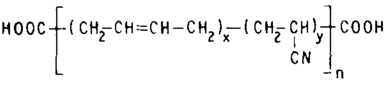
(I)

where $n = 0, 1, 2\ldots$

Nitrile rubbers used to toughen epoxy resins contain some carboxyl groups. From IR evidence and the fact that GPC indicated a relatively high molecular weight for the rubber (>20,000) it was concluded that in the present case a solid, carboxylated nitrile rubber (II) was incorporated in this adhesive rather than one of the carboxy-terminated liquid reactive rubbers (III)[7-9].



$$\left[(CH_2-CH=CH-CH_2)_x-(CH_2-\underset{CN}{\underset{|}{CH}})_y-(CH_2-\underset{COOH}{\underset{|}{CH}})_z\right]_m \qquad \text{(II)}$$



$$HOOC\left[(CH_2-CH=CH-CH_2)_x-(CH_2-\underset{CN}{\underset{|}{CH}})_y\right]_n COOH \qquad \text{(III)}$$

where x, y, z, m and n are integers.

The GPC trace of the THF-soluble material (virtually all except the chromium oxide and polyester mat) is shown in Figure 1 and the identity of compounds responsible for the peaks indicated. The assignment of peaks in GPC and HPLC traces was made on the basis of separate examination of a number of liquid and solid DGEBA epoxy resins and curing system components and by reference to the results of other workers[10,11]. The

TABLE I

Approximate Overall Composition of Adhesive A

Component	% by weight
Epoxy resin	68
Carboxylated nitrile rubber	15
Dicyandiamide	4
3-(4-Chlorophenyl)-1,1-dimethyl urea[a]	2
Chromium oxide	1
Polyester fibre mat	10

[a] Monuron, DuPont

difference between the RI and UV detector curves at the high molecular weight end indicates that the nitrile rubber and epoxy had not been adducted prior to incorporation into the adhesive. (Nitrile rubber does not absorb at 254 nm). The lowest molecular weight material was identified by IR as p-(3-

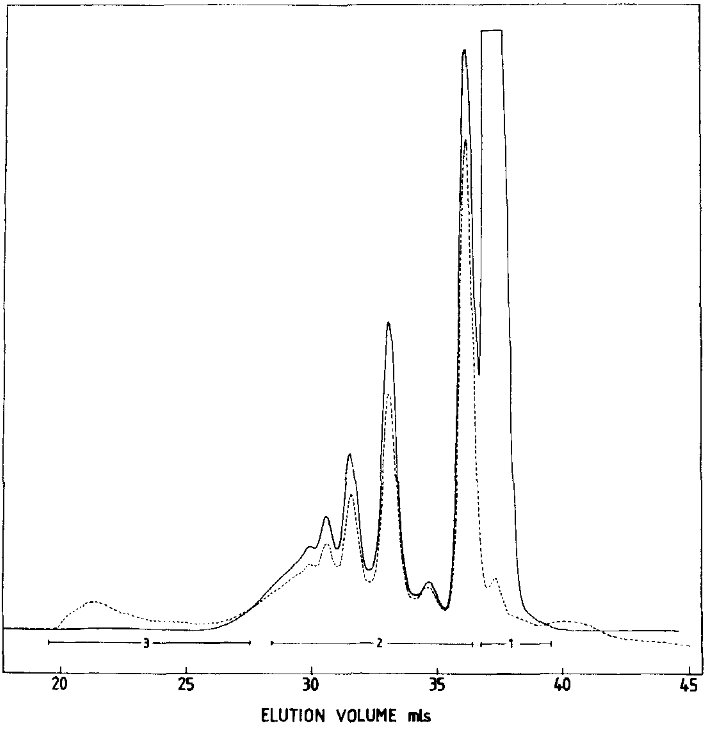


FIGURE 1 GPC analysis of Adhesive A. —— UV Detector; ----- RI detector. 1, Monuron; 2, epoxy oligomers; 3, nitrile rubber.

chlorophenyl)-1,1-dimethyl urea (Monuron). The dicyandiamide content of the adhesive was determined by IR.

As a means of validating the procedures developed for the detailed analysis of structural adhesives an attempt was made to duplicate this adhesive as closely as possible. It was found necessary to blend three DGEBA resins to achieve the desired oligomer distribution. The formulation is given in Table II. IR and NMR spectra of this formulation, designated MRL(F) showed excellent agreement with those of the commercial adhesive. The HPLC trace of the THF soluble portion is shown in Figure 2 together with that of the commercial adhesive. This, and the corresponding GPC analysis, indicates that the overall match is good but the distribution of odd and even numbered oligomers of DGEBA differed in the two cases.

The distribution of oligomers in DGEBA resins depends on whether the "taffy" or "fusion" process is used for their production[10–13]. In the taffy process, bisphenol A is reacted with epichlorohydrin in alkaline conditions: this results in products containing odd and even numbered diepoxide oligomers. The fusion (or advancement) process involves the base-catalysed

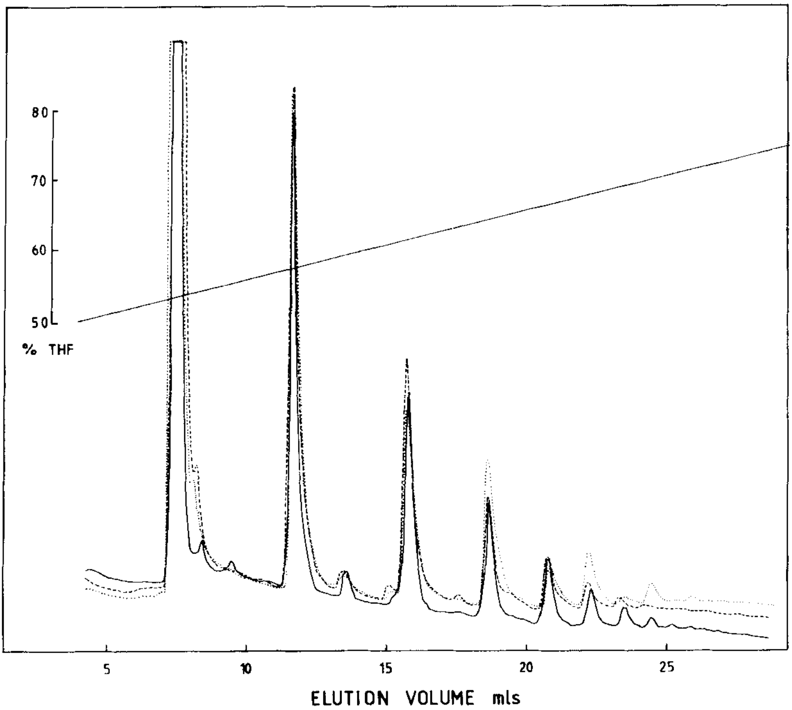


FIGURE 2 HPLC analysis of commercial adhesive (——), MRL(F) (······), MRL(T) (-----). First peak eluted is due to Monuron, subsequent peaks arise from epoxy resin.

TABLE II

Composition of MRL Version of Adhesive A

Component	% by weight
Epikote[a] 834	42
Epikote[a] 1001	18
Epikote[a] 828	7
Hycar[b] 1072	16
Dicyandiamide	4
Monuron	2
Chromium oxide[c]	0.5
Polyester fibre mat	11

[a] Made by Shell Co. of Australia Ltd.
[b] Made by B. F. Goodrich.
[c] Chrome oxide GX from Bayer Australia Ltd.

condensation of bisphenol A with a low molecular weight diglycidyl ether of bisphenol A: this results in substantially the even-number oligomers. The difference in the oligomer distribution in the fusion and taffy process for Epikote 1001 products is illustrated in Figure 3.

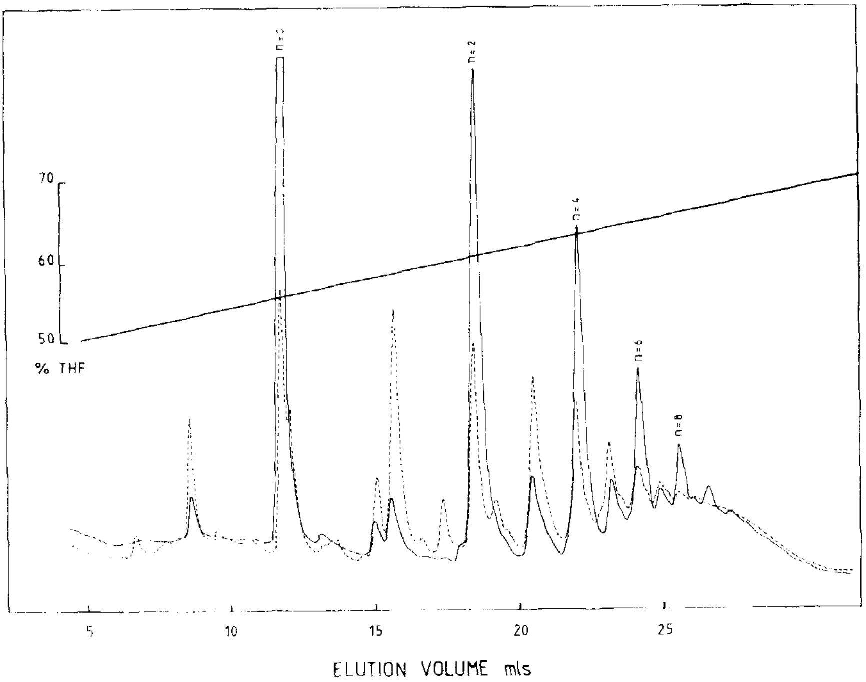


FIGURE 3 HPLC analysis of Epikote 1001 taffy (-----) and Epikote 1001 fusion (——).

The minor peaks and sidebands associated with the DGEBA oligomer peaks in the fusion process resins arise from the presence of monofunctional epoxies in the liquid resin used for reaction with bisphenol A. Hydrolysis of epoxide groups can also occur.[11] In the taffy process incomplete dehydrohalogenation, hydrolysis of epoxide groups and addition of epoxide to secondary hydroxyl groups can all occur giving rise to satellite peaks.[11] In both processes, a further series of compounds arises from the presence of the 3,4′ isomer of isopropylidene diphenol as an impurity in commercial bisphenol A[14]. Overall, the fusion process evidently results in a cleaner product, that is, it contains smaller amounts of side products, and is the preferred process in modern production of DGEBA resins.

A batch of adhesive was made substituting taffy process Epikote 1001 for the fusion process resin in the formulation in Table II. The HPLC trace for this material, designated MRL(T) is also shown in Figure 2. Clearly MRL(T) is a good match to the commercial adhesive.

The performance of the laboratory-made materials as adhesives was compared with that of the commercial material by measurement of the tensile-shear strength of aluminium lap joints. The results were similar for all three (Commercial adhesive 36.1 MPa, MRL(F) 34.2 MPa, MRL(T) 33.6 MPa).

In the course of examining a number of batches of Adhesive A it became evident that the oligomer distribution has been progressively changing with recent batches. The changes in the relative proportions of the first 7 oligomers as determined from HPLC are shown in Table III for 7 batches of the adhesive and the overall effect of this trend is illustrated in Figure 4. These batches were made over a period of 3 years and the progressive changes are evident from Batch 113 onwards. The adhesive manufacturer has indicated no alteration has been made to the formulation. Resin manufacturers do not separately identify fusion and taffy process products and the observed changes in the adhesive probably reflect a change in the process at the resin manufacturer's

TABLE III

Epoxy Oligomer Distribution for Various Batches of Adhesive A

	Relative Proportion of Oligomers						
Batch No.	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
83	51	23	12	6	4	2	2
106	51	26	12	6	3	1	1
113	51	22	15	6	4	2	1
114	53	18	16	5	5	2	1
116	53	19	16	5	4	2	1
124	55	14	19	5	5	1	1
129	60	14	18	3	4	1	0.5

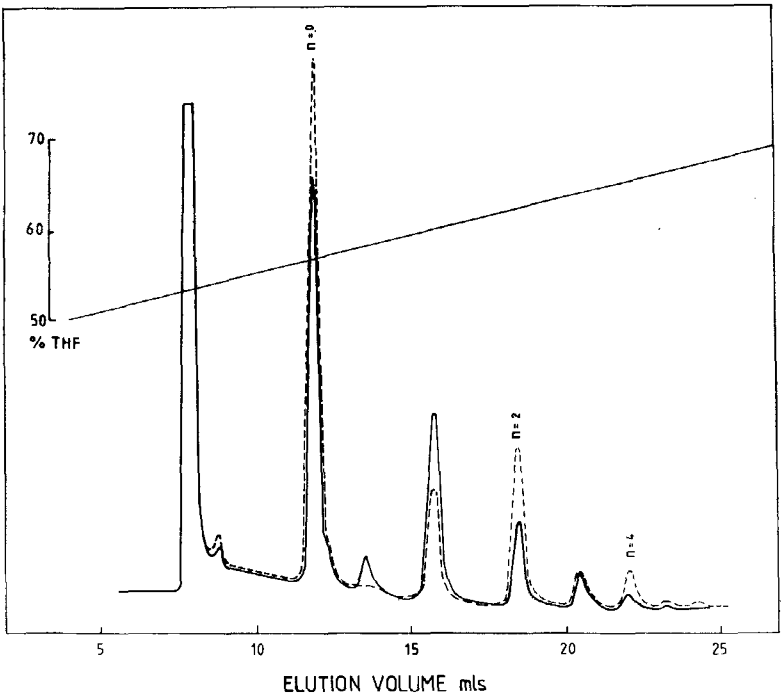


FIGURE 4 HPLC analysis of Adhesive A. Batch 106 (——), Batch 129 (- - - - -). First peak eluted is due to Monuron.

plant or a change in resin supplier. Clearly these batches represent a transition from the use of taffy to fusion process Epikote 1001 or its equivalent.

The effect of the change from taffy to fusion resins on the performance of the adhesive is not known. The long term durability, for example, may be affected by the different impurities, including catalyst residues, incorporated in resins made by different processes. These aspects await further investigation.

Adhesive B

The overall composition of the more recently developed Adhesive B, determined by a combination of chromatography and IR spectroscopy, is given in Table IV. It was again concluded that the epoxy resin is wholly of the DGEBA type. The distribution of epoxy oligomers, as indicated by HPLC, is indistinguishable from that of Shell's Epon 836 (epoxy equivalent weight 290–335)[15].

The GPC analysis of the THF-soluble portion of the adhesive (all except the support) is shown in Figure 5. In this case the curves for the IR and UV

TABLE IV

Approximate Overall Composition of Adhesive B

Component	% by weight
Epoxy resin	78
Carboxy-containing nitrile rubber	13
Adduct of 2,4-tolylene diisocyanate and dimethylamine	5
Soluble dye	>0.1
Polyester fibre mat	4

detectors were very similar at the high molecular weight end of the distribution indicating that the rubber and epoxy had been pre-reacted together. This contrasts with the situation in Adhesive A.

The high molecular weight end of the distribution was collected as two fractions, over the ranges indicated in Figure 5, and the solute examined by IR spectroscopy. The spectrum of each fraction was consistent with a mixture of DGEBA resin and carboxy-nitrile rubber, but the rubber components appeared to differ significantly. A measure of the acrylonitrile content of the rubbers was obtained from the ratio of the nitrile absorption near 2240 cm^{-1} to the *trans* unsaturation absorption near 970 cm^{-1}. From a comparison of nitrile/unsaturation ratios of a series of carboxy-nitrile elastomers of known composition, the acrylonitrile content of the present rubbers was found to be about 35% in fraction 1 and about 6% in fraction 2. A qualitative measure of

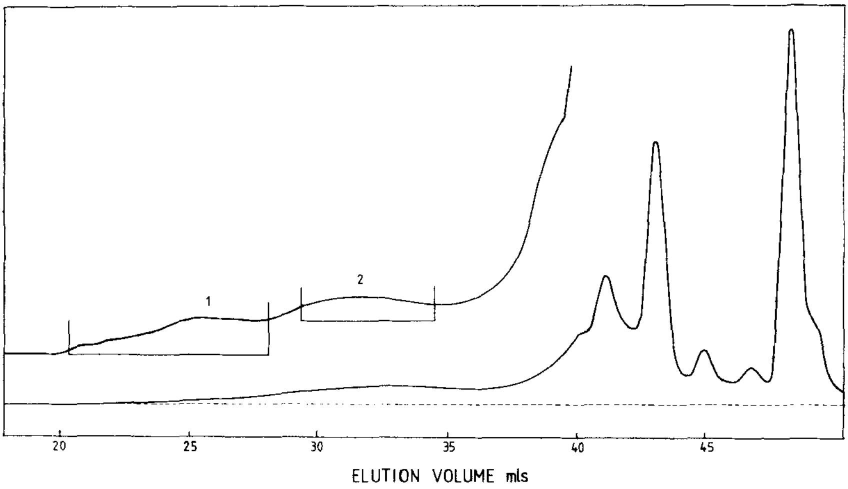


FIGURE 5 GPC analysis of Adhesive B. Upper curve approx. 5 times concentration of lower curve. 1,2 fractions collected (see text).

molecular weight was obtained from the ratio of terminal to *trans* unsaturation, at 910 cm^{-1} and 970 cm^{-1} respectively, using a comparison with elastomers of known composition. This procedure indicated the rubber in fraction 1 was of a high molecular weight while that in fraction 2 was of relatively low molecular weight. Consideration of the carbonyl absorption region suggested a rubber having pendant carboxyl groups, partially adducted, in fraction 1 (complex absorption between 1735 cm^{-1} and 1700 cm^{-1}); the carbonyl absorption in fraction 2 was entirely of the ester type.

Allowing for the fact that the fractions were arbitrary cuts across what are clearly overlapping distributions, the most satisfactory explanation of these results is that the rubber compound in this adhesive is a mixture of a carboxylated nitrile rubber, similar to Hycar 1072 ($M_n \sim 30{,}000$, nitrile content about 35%)[16] and a carboxy-terminated polybutadiene, such as Hycar CTB 2000 × 162 ($M_n \sim 4000$, nitrile content nominally zero but actually about 2% from incorporation of initiator residues)[17,18]. From an estimate of the relative proportions of the two rubbers, an overall nitrile content for the rubber component of the adhesive of about 10% is indicated.

A recent report[19] dealing with the characterization of adhesives included a composition for a material which is probably Adhesive B of this study. It was claimed that the rubber component was consistent with a carboxy-terminated nitrile rubber equivalent to Hycar CTBN 1300 × 8 ($M_n \sim 3500$, nitrile content 17%)[17]. However, the detailed examination of molecular weight distributions reported here indicates that this proposal is incorrect.

Further support for the composition given here is provided by an examination of the dynamic mechanical properties of the cured adhesive as measured by a Rheovibron (Figure 6). The material has a peak in the tan δ curve at −80°C, a broad peak covering the range −60°C to 0°C and the major peak at 110°C. The first two are due to the rubber component and the latter to the epoxy network. The T_g of Hycar CTB 2000 × 162 has been determined by thermal analysis[20] as −80°C and by torsional braid analysis[21] as −74°C. The T_g of the various Hycar CTBN materials are in the range −60°C to −30°C depending on the nitrile content.[18,20,21] Indeed, very few rubbers apart from polybutadiene have a T_g below −75°C[22].

The advantages of using a mixture of a high and low molecular weight rubber in this way are in the production of a bimodal particle size distribution of the separated rubber phase and in giving desirable improvements in performance.[23]

The curing agent in Adhesive B is one of a class of relatively new latent curing agents.[24] Dicyandiamide has been very extensively used in structural adhesives for many years but the need for adhesives of improved shelf life, and especially improved shop life (that is, the usable lifetime at room temperature) has been long recognised. The claimed shop life at 23°C for Adhesive B is 30

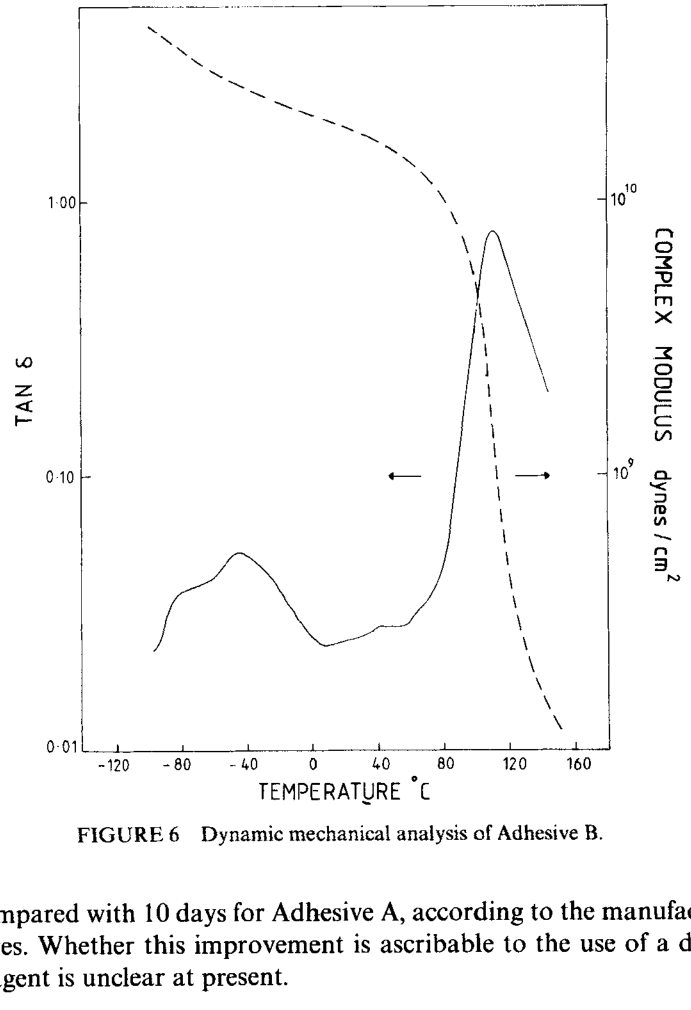


FIGURE 6 Dynamic mechanical analysis of Adhesive B.

days compared with 10 days for Adhesive A, according to the manufacturers' brochures. Whether this improvement is ascribable to the use of a different curing agent is unclear at present.

CONCLUSIONS

Use of high pressure liquid and gel permeation chromatography has permitted detailed studies of the epoxy oligomer distribution and of the extent of adduction of epoxy-rubber blends in two nitrile rubber modified epoxy adhesives. These techniques, together with IR studies on chromotography fractions, has resulted in elucidation of the composition of these two systems.

It has been found that in the older adhesive the epoxy and carboxylated nitrile rubber were not pre-reacted and also that a change from taffy to fusion process DGEBA resins has occurred in recent years. The newer adhesive incorporated a blend of carboxylated nitrile rubber, pre-reacted with epoxy, and a lower molecular weight carboxy-terminated polybutadiene.

Acknowledgements

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