NOTES

Aging of a Two-Part Epoxy Paste Aerospace Adhesive

For minor repairs to bonded aircraft structures it is often more convenient, and adequate, to use a two-part epoxy paste system instead of the film adhesive employed in the original construction. Recently, MRL became interested in the shelf-life (typified by the viscosity) of the resin component of one such system since this appeared, in some instances, to be rather short and to be responsible for a series of bonding failures.

The composition of this adhesive system was determined. The type and extent of the changes that occur under typical storage conditions were examined by monitoring the viscosity of the resin component over 43 days at 25°C and 50% RH, by assessing the amount of the monomeric form of the principal epoxy and of the total epoxide and hydroxyl content before and after aging, and by measuring the tensile shear strengths of adhesively bonded joints using resin both before and after the aging period.

EXPERIMENTAL

This adhesive is qualified to the specification[1] MMM-A-132 Type 1 Class 3. Five examples of the adhesive from three batches were obtained from various sources; duplicates from the one batch thus had different thermal/environmental histories before being received in these laboratories. Further the batches were of different ages since manufacture; namely, samples 1A and 1B were manufactured approximately 9 months before this study commenced, samples 2A and 2B were about 4 months old, and sample 3 about 1.5 months.

For studies on the aging of the resin component, approximately 50 g samples were stored in lightly stoppered glass tubes maintained at 25°C, 50% RH. At intervals, the viscosity of the samples was measured with a Brookfield Model HBTD viscometer using no. 7 spindle at 20 rpm; these measurements were preformed *in situ* by inserting the spindle directly into the storage tubes. Three measurements, each of 60 s, were made on each sample, spaced by 60 s intervals. Values were reproducible to within 3% in most cases, increasing to 5% in a few instances.

Analysis of the resin composition and oligomer distribution was accomplished by chromatography and infrared analysis. Gel permeation chromatography (GPC) employed an Altex Model 110A pump, stabilized tetrahydrofuran as the solvent, a combination of Shodex 801 and 802 columns, and either a Beckman 165 UV detector at 254 nm or a Waters R401 differential refractive index detector. Fractions collected from these studies were analyzed with a Perkin-Elmer 580B dispersive infrared spectrometer equipped with Model 3600 data handling facilities.

Lap shear specimens of standard dimensions[1] were made using 2024-T3 Alclad aluminum for which the surface preparation was vapor degrease in 1,1,1-trichloroethane followed by a FPL chromic acid etch. Parts A and B of the adhesive were conditioned at room temperature, mixed in the recommended ratio (100 : 33), and applied to the prepared aluminum sheets with a spatula. Bond line thickness was controlled by the inclusion of short lengths of 0.1 mm diameter wire. The cure cycle was 1 h at 93°C (200°F) and 0.31 MPa (45 psi), as recommended by the manufacturer. Tensile shear tests were conducted by standard procedures[1] using an Instron Model 1185 tensile testing machine. Values quoted are the average of six replicates.

RESULTS AND DISCUSSION

The composition of the resin component, a gray, thixotropic paste, was found by a combination of GPC and IR analysis to consist principally of triglycidyl *p*-aminophenol and its oligomers, a phenol epoxy novolac, minor amounts of a high molecular weight diglycidyl ether of bisphenol A and of poly(tetramethylene oxide), and (possibly) some other high molecular weight material. In addition, 45% by weight consisted of fillers (a mixture of aluminum filings, aluminum powder, and short glass fibers). Part B, the curing system, comprised triethylene tetramine and a poly-amidoimidazole.
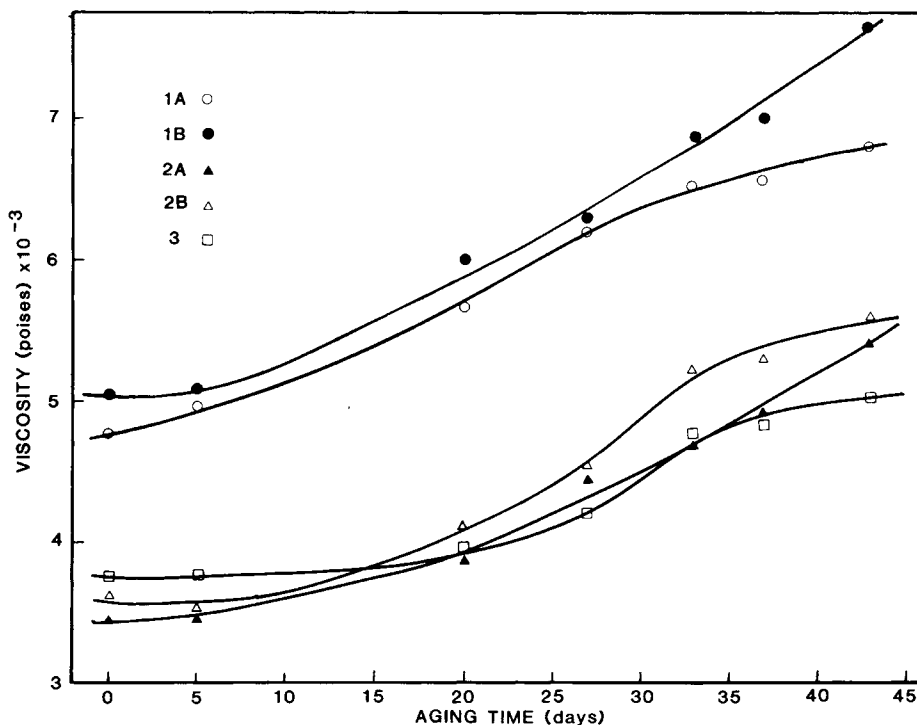
Fig. 1.   Change in viscosity of resin component (part A).

The changes in the viscosity of the resin component (part A) over 43 days at 25°C, 50% RH are shown in Figure 1. All batches increased in viscosity with time; the oldest batch had a significantly higher initial viscosity.

Lap joints were made with the unaged material and after 43 days aging. These joints were tested at room temperature and at 93°C. Results are shown in Figure 2. Overall, the oldest batch, and that with the highest initial viscosity, showed the lowest RT strength, although this value (about 22 MPa) still exceeded the minimum average strength requirement of the relevant aircraft materials specification, 20.7 MPa. However, after aging, during which the viscosity of this batch increased by 40%, tensile shear strength values were somewhat higher (about 24 MPa). Similarly, aged batches 2 and 3, which had about the same viscosity as the unaged batch 1, showed significantly higher joint tensile shear strengths (about 26 MPa). Thus, viscosity per se is clearly not the determining factor for shear strength differences. Similar conclusions can be drawn from the higher test temperature results.

Chemical analysis of the samples relative to each other consisted of assessment of the amount of the monomeric form of the triglycidyl p-aminophenol (by GPC) and of the total epoxide, ether, and hydroxyl content (by IR, using the absorbances near 915, 1110 and 3450 cm^{-1}, respectively). These analyses indicated some minor differences (about 5%, or close to the accuracy of these methods) between the samples at the commencement of this study. IR analysis after aging indicated virtually no change in the total epoxide and ether content while the hydroxyl content in each case, while small, had approximately doubled. An increase in the amount of hydroxyl during aging is not surprising in view of the known susceptibility of triglycidyl p-aminophenol to hydrolysis.[2] Monitoring of the monomeric triglycidyl p-aminophenol by GPC showed only slight differences (a few percent at most) between samples at the beginning and end of this study. Therefore, resin advancement had occurred to only a very minor degree. This conclusion is in accord with the elevated temperature tensile-shear strength of lap joints; earlier studies on the aging of film adhesives has demonstrated that the high temperature performance is the most sensitive to age-related changes in the resin.[3] Thus overall, although the batches displayed significantly different viscosity initially, and the viscosity increased substantially during aging,
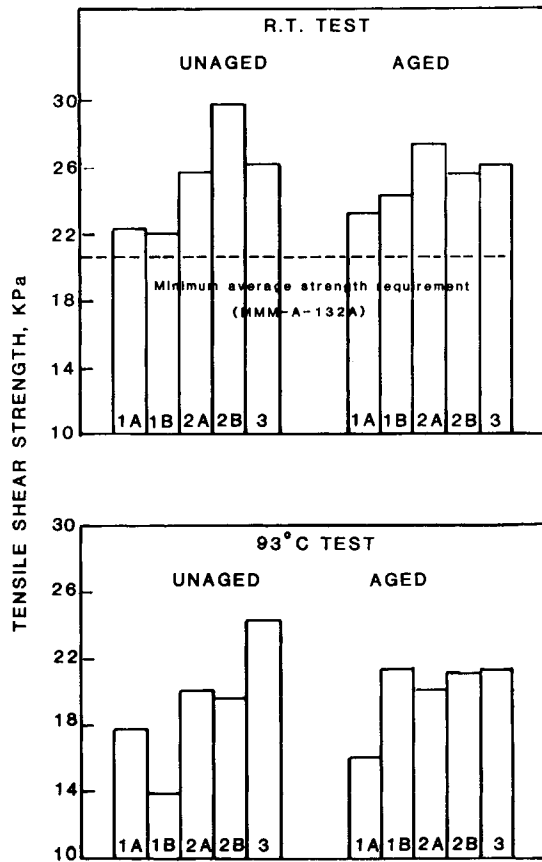
Fig. 2. Tensile shear strength of Al–Al lap joints tested at RT and 93°C.

only very minor differences in composition could be detected between batches and between aged and unaged samples, except for the hydroxyl content, which approximately doubled in each case during aging. These viscosity changes can therefore not be ascribed to resin advancement.

Explanation for the viscosity changes over this age range may thus lie in interaction with the filler. This resin system displays a significant degree of non-Newtonian behavior (thixotropy): For example, for a given temperature and spindle, sample 3 had a viscosity of about 3800 P at 20 rpm, 2700 P at 50 rpm, and 2400 P at 100 rpm. It is therefore suggested that marginal chemical differences result in differences in the extent of interactions with the filler, thereby giving significant changes in viscosity. These interactions, being relatively weak, do not significantly modify the course of the cure reaction or the crosslinked structure produced, and thus the lap shear strength of joints is little affected. The increased viscosity does, however, made handling of the material more difficult and may result in a greater proportion of defects in joints, due, for example, to poor mixing and poor substrate wetting. To this extent the changes in viscosity with aging may result in a greater probability of bonding failures.

In summary, it has been shown that the viscosity of the resin component increases to some extent during aging for 40 days at 25°C and 50% RH but that this increase cannot be accounted for by resin advancement and cannot be correlated with a change in tensile shear strength of lap joints made with aged adhesive. The composition of the adhesive is such that some sensitivity to high humidity would be expected, but only small changes in the hydroxyl content are evident. It is proposed that modification of the degree of interaction with the fillers is the principal reason for the changed viscosity. These changes may have an effect on the performance of the aged adhesive in that handling difficulties are increased and may result in a greater proportion of defective joints.

References

1. U.S. Federal Aircraft Specification MMM-A-132, "Adhesives, Heat Resistant, Airframe Structural, Metal-to-Metal."
2. P. J. Pearce, R. G. Davidson, and C. E. M. Morris, *J. Appl. Polym. Sci.*, **26**, 2363 (1981).
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