The Effect of Freeze–Thaw Cycling on Some Structural Film Adhesives

In the course of a recent study on the room temperature aging of some uncured, epoxy-based, structural film adhesives there were indications of a lower tensile-shear strength for joints made with adhesive which had been repeatedly withdrawn from the storage freezer compared with control joints utilizing adhesive which had not been subjected to extensive temperature cycling.[1] The question of possible deleterious effects of freeze–thaw cycling has important implications in the repair and maintenance of bonded aircraft structures. In that situation, where only small amounts of adhesive are required at the one time, from rolls supplied in lengths of up to 60 yd, the cycle of withdrawing the adhesive from the storage freezer, thawing it out, cutting off a quantity for use, and returning the bulk to the freezer may be repeated many times before the roll is finally used or rejected. Accordingly, the effect of freeze–thaw cycling has been examined for three adhesives, qualified for use in structural aircraft applications, which have previously been the subjects of extensive aging trials.[1,2]

EXPERIMENTAL

The adhesives, one 177°C curing epoxy and two 121°C curing nitrile–epoxy systems, are designated adhesives 1, 2, and 3 for this work. Adhesive 1 is the same as adhesive A in the previously reported aging trial on high temperature curing systems[1] while adhesives 2 and 3 are those designated A and B in the work on nitrile–epoxy systems,[2] except that a thicker version of adhesive 3 was used in the present work (0.21 kg/m^2 compared with 0.15 kg/m^2 in the earlier study). The approximate overall composition of these adhesives is shown in Table I.

Sheets of the adhesives, about 25 × 30 cm, with their backing/release papers intact, were sealed in plastic bags and suspended in a small chest-type freezer. A fan was fitted into a specially constructed lid on the freezer, and the controls of both fan and freezer were connected to a timing device such that the temperature in the chest cycled between about −22°C and ambient (around 18°C) over a 4 h period. The temperature profile, recorded from a thermocouple in a bag adjacent to the adhesive samples, is depicted in Figure 1. As substantial amounts of moisture condensed on the plastic bags during the temperature cycling, some bags contained silica gel in order to assess any effects of possible moisture penetration through the bags.

The studies were run for about 300 cycles. Samples were withdrawn at intervals and tested for solubility in chlorobenzene, epoxide equivalent weight (EEW), and the extent of flow during cure, and subjected to high performance liquid chromatography (HPLC) analysis and determination of the tensile-shear strength of Al–Al lap joints, using methods previously described.[1,2]

RESULTS AND DISCUSSION

Epoxy Adhesive 1

Aging studies showed that solubility of the uncured adhesive is a useful indicator of reaction advancement while changes in EEW provide a direct measure of epoxide consumption. Adhesive solubility and EEW were both unchanged up to 309 cycles (about 64% and 243 g/eq, respectively), including results of samples from silica gel containing bags. Similarly, the extent of flow during cure was in the range 71–74% for nine determinations at different numbers of cycles. No trend in the tensile-shear strength of single lap joints was evident for joints tested both at 20 and 177°C.

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TABLE I
Overall Composition of Adhesives[1,2]

Component	Amount (wt %)
Adhesive 1	
Triglycidyl(4-aminophenol)	33
Cresol novolac epoxy resin	30
Diglycidyl ether of bisphenol A	11
Dicyandiamide	8
Asbestos	8
Woven glass support	10
Adhesive 2	
Diglycidyl ether of bisphenol A	68
Carboxylated nitrile rubber	15
Dicyandiamide	4
3-(*p*-Chlorophenyl)-1,1-dimethyl urea	2
Chromium oxide	1
Polyester mat	10
Adhesive 3	
Diglycidyl ether of bisphenol A	79
Carboxylated nitrile rubber Carboxy-terminated polybutadiene	13
Adduct of 2,4-tolylene diisocyanate and dimethylamine	5
Yellow dye	Trace
Polyester mat	3

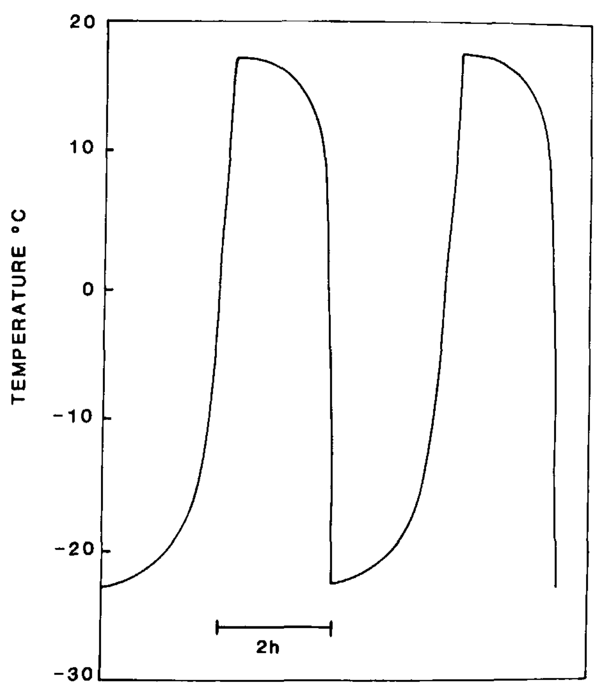

Fig. 1. Typical temperature profiles of the freezing–thawing cycle.

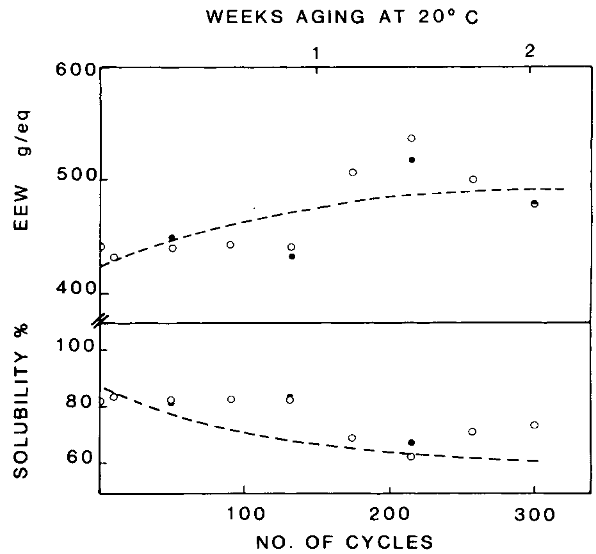

Fig. 2. The effect of freeze–thaw cycling on solubility and EEW for adhesive 2. Open symbols, without silica gel; solid symbols, with silica gel. Broken line illustrates changes during aging at 20°C (from Ref. 2).

The earlier room temperature aging study of this adhesive showed that little change was observable in the solubility, EEW, and flow during cure for about 10–12 weeks. Tensile-shear strength of single lap joints tested at 20°C was essentially unchanged for about 16 weeks while joints tested at 177°C showed decreasing values after about 6 weeks aging.[1] It was also shown that hydrolysis of one of the epoxy resins, detectable by HPLC analysis, was responsible for the majority of the changes in adhesive performance on aging.[1,3] HPLC analysis in the present case has again provided an indication of hydrolysis from the height of the peak due to the monohydroxyl form of triglycidyl(4-aminophenol).[1] After 141 cycles the height of this peak had increased by about a factor of 2.5 while after 298 cycles this peak was about 4.5 times

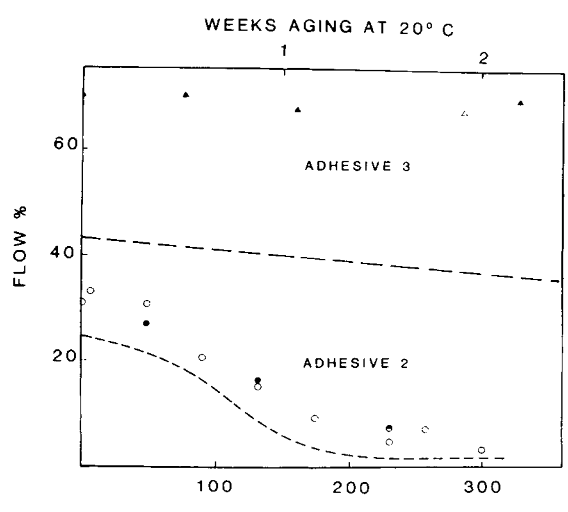

Fig. 3. The effect of freeze–thaw cycling on the extent of flow during cure. (△,○) Without silica gel; (▲,●) with cilica gel; (- - -) changes during aging at 20°C (from Ref. 2).

greater than initially, although the total amount of this compound was still very small. Such an increase corresponds to about 5 weeks room temperature aging of this adhesive.[1]

Nitrile–Epoxy Adhesives 2 and 3

The change in solubility and EEW for adhesive 2 is shown in Figure 2, which also includes an indication of the change in these properties over two weeks at 20°C, as previously reported.[2] These effects are broadly similar to the changes over 300 freezing/thawing cycles. Moisture appears not to be a factor in these changes as the samples stored with and without silica gel were not significantly different.

Adhesive 3 showed a slight drop in solubility and no change in EEW over 329 cycles. The earlier aging studies indicated that adhesive 3 is significantly more stable than adhesive 2, and virtually no change in these parameters was observed up to 8 weeks aging.[2]

As was found in the aging studies, the extent of flow during cure dropped substantially for adhesive 2 and only slightly for adhesive 3 (Fig. 3). The change in this quantity over 2 weeks at 20°C is again indicated. The higher values obtained for adhesive 3 in the present work compared with the earlier studies result from the use of the thicker grade of the adhesive.

Single Al–Al lap joints were tested at 22 and 100°C. Adhesive 2 showed a small drop in the values of those tested at the lower temperature, and essentially no change at 100°C, over 300 cycles. Adhesive 3 showed no change at either temperature over 329 cycles. These results are again consistent with those found over about 2 weeks aging at room temperature.[2]

CONCLUSIONS

The temperature cycling profile shows that for about 1 h of each cycle the temperature was near 18°C. In terms of an "equivalent" time at ambient temperature, 300 cycles would approximate to 13 days. The changes observed to occur during freeze–thaw cycling with the nitrile–epoxy adhesives are thus consistent with those which occurred during an "equivalent" time at about 20°C, that is, no additional changes or greatly increased rate of change arising from the freeze–thaw cycling could be discerned. Similarly, the results for the epoxy adhesive showed no evidence of significant additional deleterious effects of the temperature cycling.

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