Mechanical properties of the glass fibre–polyester interphase

Part II *Effect of water on debonding*

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Experiments are described in which single fibres, embedded in a polyester resin, were immersed in water at various temperatures for various times, and the fibres then pulled out. The effect of the water on the polymer was also investigated. It was found that the fibre–polymer bond strength was reduced almost to zero after 400 h in 75 °C water, but at 60 °C the reduction was only 40%–50%, even after 13 000 h immersion and at 22°C the strength was reduced by 20% after 13 000 h immersion. Bond strength recovered when the samples were dried out at 80° C for 72 h. The polymer was not much affected by the water. Silane coupling agents were found to give considerable protection against water attack, were effective when only present as a very thin chemisorbed layer on the fibres and thin layers gave greater dry bond strengths than thick layers. Excess coupling agent was not only less effective, but also reduced the properties of the polymer, especially with respect to its resistance to water. These results are compatible with well-established concepts, i.e. that water is absorbed preferentially at the fibre surface, and this is inhibited by the silane.

1. Introduction

Glass fibres are usually coated with silanes to enhance adhesion, and convert the glass fibre surface from hydrophilic to hydrophobic. This bestows good water resistance on the fibre composites made with them [1] but does not ensure complete protection. Thus, water permeation still occurs, and increases with increasing stress [2]. It can lead to microcracking of the polymer surface [3], and loss of strength in the composites [4], especially in acid environments [5]. These effects are mainly due to attack on the glass [6].

There is evidence of preferential absorption at the interface or in the interphase [7]. This, together with resin cracking or water segregation into thin sheets, can produce electrically conducting paths in the composite [8]. Fibre "wicking" is not always observed, however [9], and voids appear to provide faster diffusion paths than the interphase [10]. In pure water, osmotic effects are observed; these occur both in the resin, due to leaching of short chain polymers and unreacted monomer, and at the interface due to leaching of ions from the glass [11]. Thus the interphase plays a major role in determining the environmental resistance, or lack thereof, of fibre composites.

This paper is the second in a series of papers which examine the role of water in determining interphase properties. In Part I [12], we examined how the silane coating influenced interphase properties, as measured by direct experiments on the interphase. In Part II, we examine the effect of water immersion on the debonding characteristics of interphases produced by various fibre treatments.

2. Experimental procedure

The materials used, isophthalic polyester resin and E-glass fibres, initially with a polyester-compatible coating on them, and after various surface treatments, were described in Part I [12]. The fibres were used with the coating intact, and also after extraction with tetrahydrofuran (THF), after pyrolysation of the coating, after pyrolysation and then coating with a silane (γ-methacryloxypropyltrimethyl siloxane, MPS) and after coating with the silane and THF extraction of that coating.

The polymer was tested according to ASTM procedures for compression strength, and Izod impact strength, and the fibres were tensile tested. Fibres were embedded in the resin to known depths using the slit rubber stopper method to support the fibre, and then pulled out in an Instron machine. For most experiments the fibre and resin were kept wet during pull out. For this a water bath was used; see Fig. 1. Further details of procedures used may be found in Part I [12].
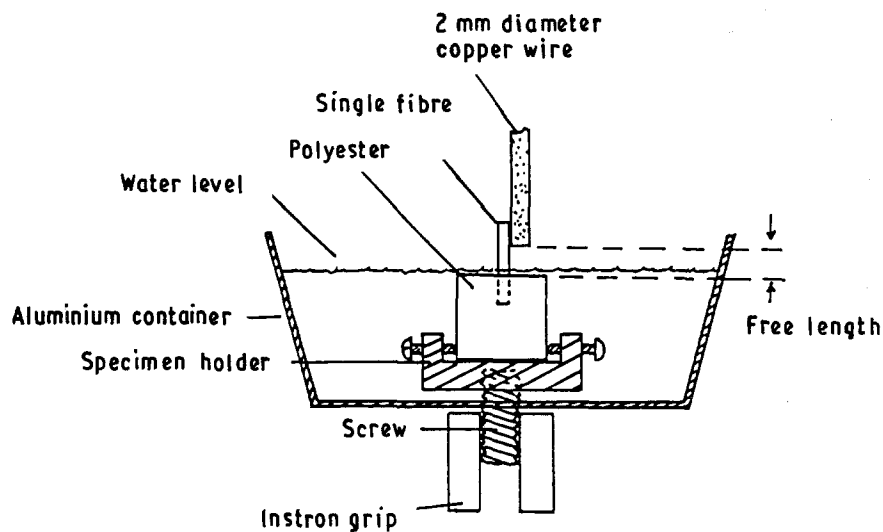
Figure 1 Experimental apparatus for pull-out test.

Fibres, polymer, and fibres embedded in polymer were immersed in water for various periods at 22, 60 and 75 °C prior to testing. The amount of water absorbed by the polymer was measured by comparing the weight after immersion with that of the carefully dried polymer sample prior to the immersion tests. Water diffusion along the interphase was observed using two 2 mm long single fibres, embedded so that they traversed a 2 mm thick polymer film, with tritaited water on the upper side and photographic emulsion underneath. The emulsion (NTB, Kodak Chemicals Inc) was melted at about 40 °C and a layer about 0.2 mm thick was painted on. The time for the appearance of some darkening of the emulsion was noted.

3. Results
3.1. Effect of immersion on the fibres
The strengths of the fibres was reduced by the water immersion at 60°C, Fig. 2. The early loss (100 h) was the greatest, i.e. 12% for the fibres with coating intact, 20% for the pyrolysed fibres, and 10% for the MPS-coated fibres. Thereafter the intact and MPS-coated fibre strengths declined at a rate of about 3% per decade, while the bare fibres suffered a much bigger loss rate after 300 h. Extraction of the initial coating and the MPS coating caused a slight reduction in strength (0.1 GPa) at all stages of the immersion. Immersion at 22 °C had very little effect, while at 75 °C

the losses were slightly greater (by about 0.1 GPa) than at 60 °C.

3.2. Effect of immersion on the polymer
The polymer obeyed Fick's Law, so that the weight gain at time t, M_t, was proportional to $t^{1/2}$ see Fig. 3. M_∞ is the saturation weight gain. When the polymer contained MPS the absorption rate increased, as also shown in Fig. 3. M_∞ values were 1.5% for the polyester, and 1.8% and 2.0% for the polyester containing 30% and 60% MPS, respectively. Similar results were obtained during immersion at 60 °C, but at 75 °C some loss in weight occurred after about 900 h immersion. The diffusion coefficient for the polymer was governed by an activation energy, see Fig. 4, which came to 51 kJ mol^{-1}. When MPS was present in the polymer the activation energy was somewhat higher, as indicated by results at 22 and 60° C, see Fig. 4.

The compression properties of the polymer decreased on immersion at 60 °C, see Figs 5 and 6, and at 75° C these properties decreased more rapidly: 300 h exposure reduced the modulus to 1.9 ± 0.3 GPa and the strength to 60 ± 2 MPa. The impact strength of the polymer was increased about 20% by immersion at 60 °C for 13 kh, while immersion at 22° C had no noticeable effect. Immersion at 75 °C caused a barely significant initial increase (from 2.4 ± 0.4 to 2.6 ± 0.4 kJ m^{-2}) at 70 h followed by a decrease to 1.8 ± 0.3 kJ m^{-2}.
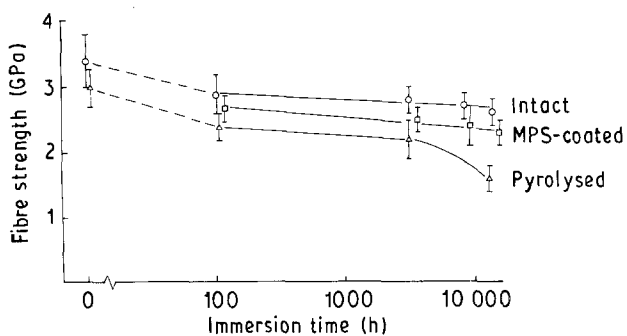

Figure 2 Effect on fibre strength of immersion in water at 60 °C. (The MPS-coated fibres had the same initial strengths as the pyrolysed fibres.)
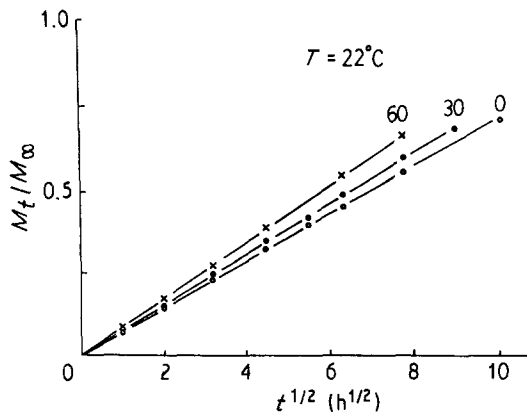
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Figure 3 Water absorption of polyester sheets as a function of immersion time. Polyester contained 0, 30 and 60% MPS.
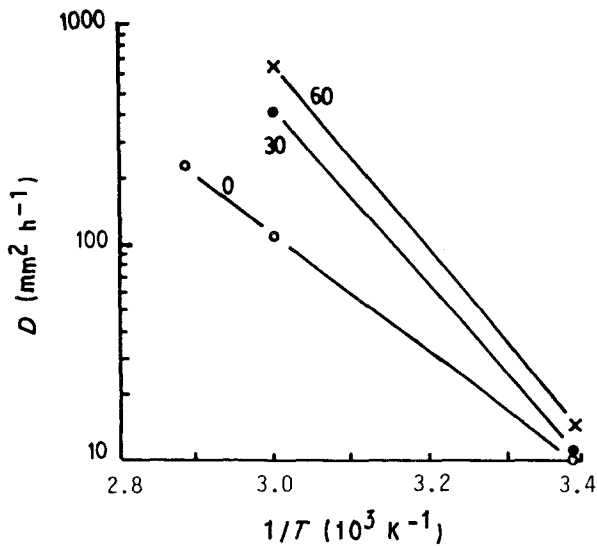

Figure 4 Arrhenius plot for diffusion coefficient for polyester, neat, and with 30% and 60% MPS, as indicated on curves.
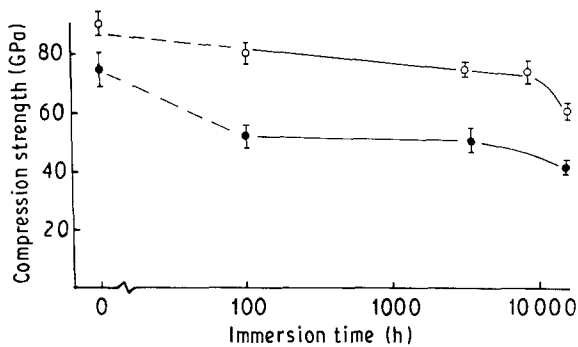

Figure 5 Compression strength of resins versus immersion time in water at 60 °C. (○) Neat polyester, (●) polyester with 60% MPS.

3.3. Effect of water immersion on the interphase

In all the pull-out tests (a total of about 4000 were carried out) the results indicated that the interface did not yield, but rather failed suddenly, giving a debonding force, F_A, versus embedded length, L, plot which was curved, see Fig. 7. Each point plotted is the average of five replicate tests, and subsequent to pull out the fibre was examined in the microscope to verify that the embedded length was indeed the value intended.
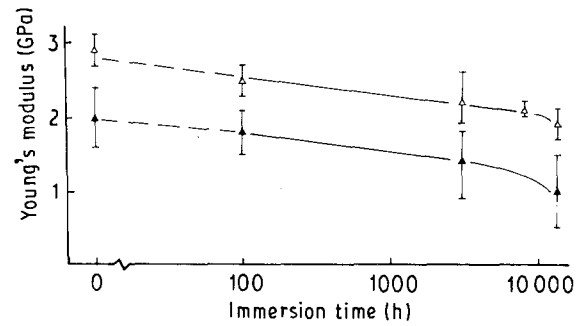

Figure 6 Young's modulus of resins versus immersion time in water at 60 °C. (△) Neat polyester, (▲) polyester with 60% MPS.

The F_A versus L curve may be used to estimate the shear strength of the interface or interphase using the curve fitting technique described by Piggott [13]. Fig. 7 shows results obtained with commercially coated fibres before (upper curve) and after 13 000 h immersion in water at 60° C. The immersion has significantly reduced the debonding force at all embedded lengths.

After immersion in water at 60 °C the interphasial shear strength decreased within 100 h to about 60% of its initial value when the coating was intact. Removal of the coating and its replacement with MPS produced an interphase with almost identical properties, see Fig. 8. Extraction of the interphase material with THF caused a slightly larger proportionate decrease,
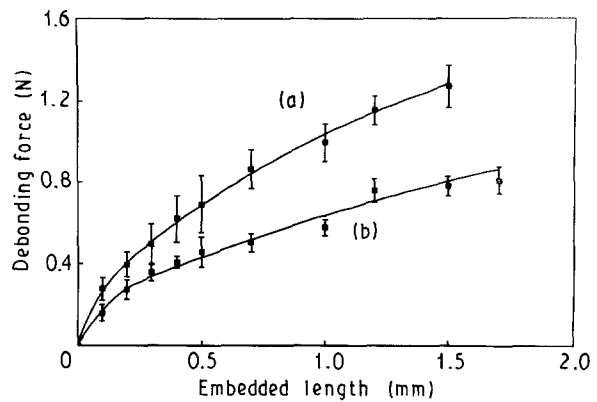

Figure 7 Force versus embedded length for fibre with coating intact (a) before and (b) after 13 000 h immersion in water at 60 °C.
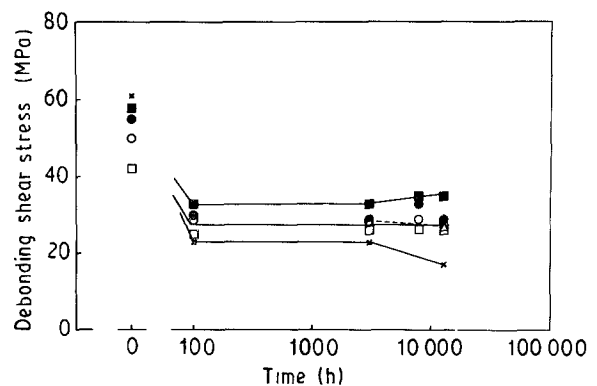

Figure 8 Interphasial work of fracture versus time of immersion in 60 °C water. Upper line, original coating and MPS coating extracted with THF; centre line, coating intact, and pyrolysed then MPS coated; bottom line, pyrolysed fibres.

to 57% of its initial value, and again, extraction of the MPS coating with THF resulted in almost identical behaviour. The bare fibre was much more severely affected, the work of fracture decreasing to only about 38% of its initial value. Further immersion at 60° C had very little effect, except on the bare fibre, where a further decrease to 28% occurred as is also shown in Fig. 8.

Tests at other temperatures (Figs 9 and 10), show that the effect is very much smaller at 22° C, while at 75 °C the interphase is almost completely destroyed after about 300 h immersion. Measuring the debonding force with the specimen still immersed in the water at 60 °C gave about the same result as testing it at room temperature. The fibres used for these tests had been pyrolysed and then coated with MPS (Fig. 9) and had the MPS coating extracted (Fig. 10). The MPS extraction resulted in about the same proportionate loss of interphase properties, i.e. about 20% at 22° C and about 45% at 60 °C in both cases.

The presence of MPS in the polymer hardly affected the result at all, Fig. 11. Relative losses were: for no MPS addition 45%; for 30% addition 48%; and 60% addition 43%. Heating the embedded fibre specimens at 60 °C also had only a small effect, Fig. 12; losses were at most 16% after 13 000 h and were undetectable for the commercially coated fibre. However, heating the embedded fibre specimens at 80° C for 72 h after water immersion restored the interphase, Table I. Full restoration was not always achieved, especially when the immersion loss was very great, i.e. the 75 °C, 300 h immersion specimen.
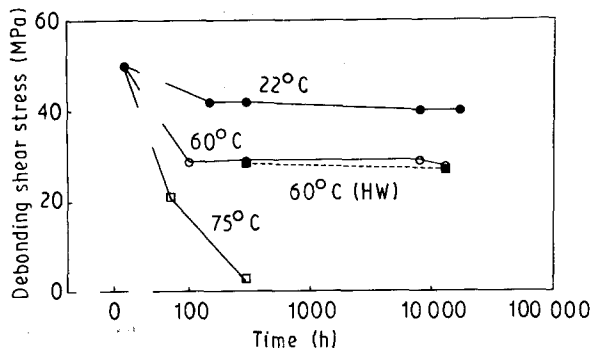

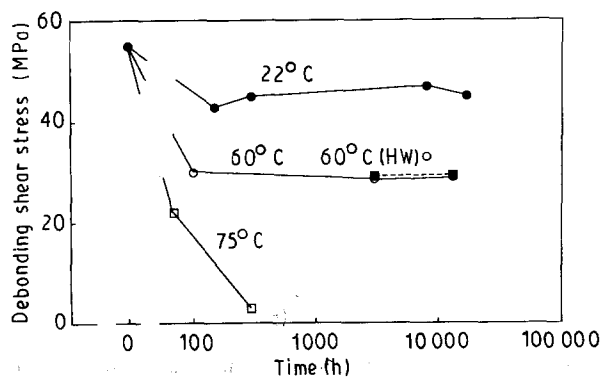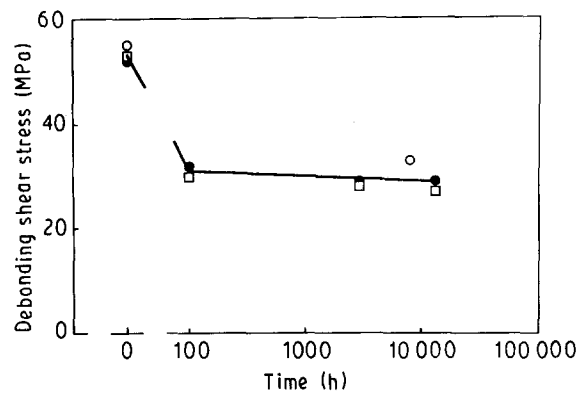*Figure 11* Effect of water treatment on the interphasial work of fracture for MPS-coated fibres in polyester with (□) 60%, (●) 30% and (○) no MPS.
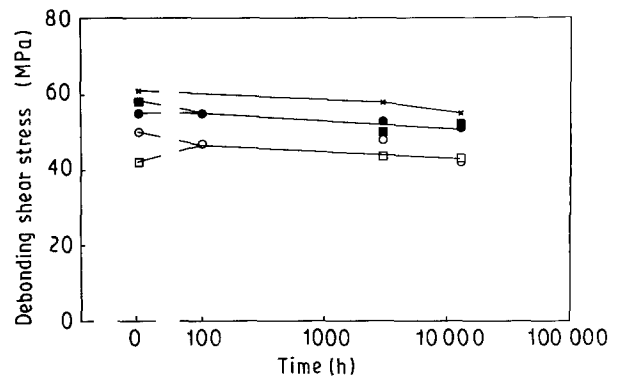

Figure 12 Effect on interphase of heating at 60 °C. (×) Pyrolysed fibres, (■, ●) THF-extracted fibres, (○, □) intact and MPS-coated fibres.

The autoradiographic tests showed that the water diffused preferentially along the interphase, and could be detected within 300 h, see Fig. 13. The actual time depended on the surface treatment, being shortest for the pyrolysed fibre (140 h) and longest for the THF-extracted fibre (310 h) with the intact coating giving a value somewhat closer to the bare fibre (210 h). The MPS coating behaved similarly to the original coating (170 h) and extraction of this with THF also gave similar results (280 h).

4. Discussion

While the water immersion for 100 h did not have a very great effect on the polymer, at least up to 60 °C, where the loss in compression strength was only 12% –13% see Figs 5 and 6, it had a large effect on the interphase, causing a reduction in debonding force of 40% or more, Fig. 8. This loss could have been due to the presence of water in the interphase. The auto-radiographic studies showed that complete penetration along 2 mm of interphase took only 140–310 h at 22° C, it can be expected to be much faster at 60 °C. Also, examination of the specimens in the microscope prior to pull-out testing showed that the water had caused areas of the interface to debond. Such debonding has also been observed in glass fibre-reinforced epoxies, and to a lesser extent in carbon epoxies: the

Figure 9 Effect of water treatment on the interphasial work of fracture for MPS-coated fibres.

Figure 10 Effect of water treatment on the interphasial work of fracture for fibres having MPS coating extracted using THF.

TABLE I   Effect on interphase of immersion and subsequent heating under dry conditions

Fibre surface	Debonding stress, τ_{ed} (MPa)						
	Initial	60°C, 13000h immersion	Restored[a]	75°C, 70h immersion	Restored[a]	75°C, 300h immersion	Restored[a]
Intact	42	26	42				
Extracted[b]	58	35	52				
MPS-coated	50	28	42	21	40	2.3	18
MPS-extracted[b]	55	29	51	22	50	2.4	21

[a] After heating at 80°C for 72 h under dry conditions.
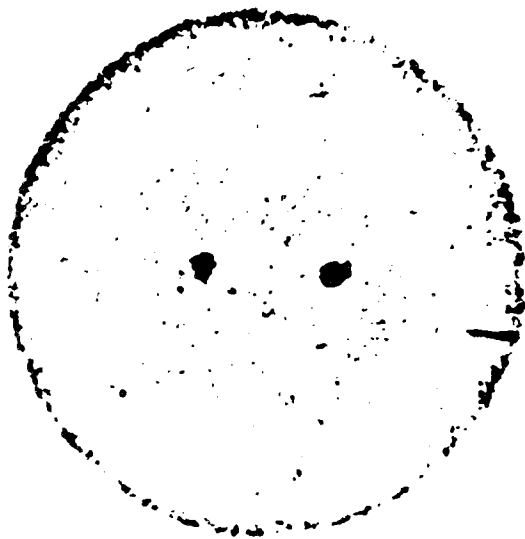[b] Extracted with THF.

Figure 13 Autoradiograph taken after 198 h had elapsed for tritiated water to diffuse through two fibre specimens.

glass fibres were shown to absorb water (in the absence of resin) equivalent to a film 0.02 μm thick at the surface [7]. Complete debonding probably occurs after 300 h at 75° C. The debonding process changed completely: the F_A versus L plots become linear, with slopes corresponding to interfacial shear stresses of less than 3 MPa.

In the case of a specimen immersed at 60 °C the debonded region included about 40% of the surface area of the embedded fibre, suggesting that the loss in bond strength could have been wholly due to this effect. However, debonding does not seem to progress; after more than 100 h there is no evidence of a further decrease in debonding force, except when the immersion temperature was 75 °C. Thus it seems unlikely that debonding can be the only cause of loss of shear strength after immersion. That the effect is due to the water rather than the heat is shown by the relatively small losses observed when the specimens were kept hot but dry, Fig. 12, and by the restoration of properties after heating the immersed specimens (Table I).

The presence of the fibre coating (either commercial or MPS applied in the laboratory) provides some degree of protection against water attack, although it decreased the debonding force prior to immersion,

Fig. 8. This protection was not reduced when the physisorbed layer was removed using THF.

It seems highly probable that the water is preferentially absorbed at the interface, and this weakens the bond, so that the debonding energy is reduced. The presence of a chemisorbed layer of silane reduces the amount of absorption (as indicated by the lower diffusion rate in this case) and so the loss in debonding energy is not so great. When a physisorbed layer is present as well as a chemisorbed layer, more water is absorbed, as indicated by the higher diffusion rate (and the hydrophilic nature of silanes), but still less than in the case of the bare fibre, so that the bond strength is intermediate between the above two cases. Spontaneous debonding probably accounts for some of the loss of apparent bond strength, but appears not to be a progressive process, except for immersion at 75 °C. In this case debonding is complete on a 2 mm length after about 400 h.

The bond appears to be restored by prolonged heating, Table I. This lends support to suggestions that water-induced loss of bonding is a reversible hydrolysis process ([1] p. 105).

Excess sizing has an unfavourable effect on other properties of composites, in addition to lessening the effectiveness of the interphase. Some of it almost certainly dissolves in the polymer, reducing the modulus and compressive strength, and increasing the diffusion and the absorption of water, as indicated by the experiments in which MPS was added directly to the polymer.

5. Conclusion

Water reduces the properties of the polymer, the fibre, and the fibre–polymer interphase. The effect on the interphase is much the greatest and appears to be accompanied by a significant amount of spontaneous debonding. This, however, can be restored, to some degree at least, by high-temperature treatment. Silane coupling agents provide protection against attack by water, and are most effective when present only as a very thin chemisorbed layer. When excessive amounts of silanes are used, the water degradation of the polymer is increased and, in addition, the interphase does not have optimum properties.

Acknowledgements

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