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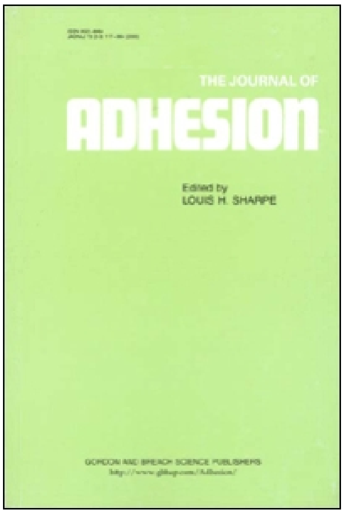

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S. G. Abbott[a]; N. Brumpton[a]
[a] Shoe & Allied Trades Research Association Kettering, Northants, England

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The Effect of Moisture on Polyurethane Adhesives†

S. G. ABBOTT and N. BRUMPTON

Shoe & Allied Trades Research Association, Kettering, Northants NN16 9JH England

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Polyurethane adhesives predominate for bonding shoe soles but the moisture resistance of the adhesive polymer has been questioned. A typical polymer was hydrolytically degraded at 120°C for up to 29 hours and at 20, 30 or 37°C for up to one year and changes in physical and bonding properties monitored. Considerable degradation was necessary before bonding was seriously impaired due to cohesive failure of the adhesive, although heat resistance declined more rapidly. Joints made with undegraded adhesive on exposure to moisture showed rapid loss of strength and cohesive failure at 60 or 70°C, but little loss of strength and failure at or near the interface at 30 or 40°C.

INTRODUCTION

In 1978 U.K. footwear production totalled 157 million pairs,[1] of which 90% depended on adhesive for bonding the sole to the upper. The adhesive has to bond surfaces of widely differing characteristics, e.g., roughed leather, smooth PVC, to produce a flexible, durable joint. Adhesives based on solutions of rubbery polymers in organic solvents have the required versatility. Polyurethane adhesives were introduced in the early 1960's due to their effectiveness in bonding PVC, and now predominate.

Premature hydrolytic breakdown of linear polyester polyurethanes has been a problem in some shoe upper materials, see Hole *et al.*,[2,3] the action of some wearers' perspiration rendering the shoes unserviceable after a few weeks' wear. This caused the moisture resistance of similar adhesive polymers to be questioned. Many upper materials are permeable to moisture from

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perspiration and the wear environment, and allow this to pass to the upper-sole bond line. Hydrolysis of the adhesive could conceivably contribute to bond failure, although obviously deteriorated adhesive had only been noted in a few worn shoes.

A typical polyurethane adhesive polymer was chosen. This was a polyester type, based on adipic acid and butane diol, chain extended with diphenylmethane-4,4′-diisocyanate (MDI); it was fully reacted, with no free isocyanate groups present. The polymer was successively degraded at high and low temperatures to produce a series of polymers; these were used to prepare adhesives and bond test joints.

HIGH TEMPERATURE HYDROLYSIS

Preparation of the polymer series

Chips of the original polymer were hydrolysed in steam at 120°C in a pressure vessel for 1–29 hours. During the process the samples coalesced into slabs, which were allowed to dry under standard conditions (20°C, 65% rh) for two days. Part of each sample was dissolved in butan-2-one (methyl ethyl ketone) to produce the 20% w/w solution typically used as a footwear adhesive.

Characterisation of polymers

The number average molecular weight (M_n) of each polymer was determined by membrane osmometry, using tetrahydrofuran (THF) at 37°C as solvent and cellulose semipermeable membranes. Gel permeation chromatography (GPC) was used to estimate number and weight average (M_w) molecular weight, using 0.1% THF solutions on a polystyrene gel column. Well characterised fractions of the polyurethane were not available and the column was therefore calibrated with polystyrene samples. This may have affected the absolute value of the results. The viscosity of the 20% butan-2-one solutions was measured in a cup and rotating bob instrument over a range of shear rates, and the value at zero shear rate found by extrapolation.

To carry out tensile tests, films of thickness 0.1 mm were cast from the solutions by doctor-blade coating glass plates (treated with trimethylchlorosilane to provide a non-stick surface). The coated plates were allowed to dry at room temperature for two days before removing the film. Ring test-pieces of average diameter 25.4 mm and width 2 mm were cut from the films by press knife and tensile tested at a jaw separation rate of 100 mm/min.

The results of the various determinations are summarised in Table I. Molecular weight decreased steadily with hydrolysis, and viscosity and tensile strength (except for an initial plateau) decreased more rapidly.

TABLE I

Characterisation of polymers after high temperature hydrolysis

Hydrolysis time	M_n by osmometry	M_n by GPC	M_w by GPC	Viscosity at zero shear rate	Tensile strength of film
hours				poise	N/mm^2
0	67 000	55 300	228 000	59	48
1.0		49 100	277 000	39	50
2.0		47 500	265 000	27	51
4.0		44 600	216 000	11.9	51
8.0	48 800	34 800	190 000	4.8	39
15.0		21 100	88 100	1.2	21
18.3	25 300	23 200	86 100		23
21.5		15 900	59 800		13.5
24.5		12 100	38 800		5.9
29.0	12 200	8 840	27 200		0.0

Determination of the activation energy of the hydrolytic degradation

The activation energy for the hydrolysis was estimated from a further series of viscosity measurements on polymer hydrolysed at temperatures between 80 and 120°C. The results for 20% butan-2-one solutions, are shown in Table II. In calculating the activation energy E the hydrolysis was assumed to be a first

TABLE II

Viscosity after hydrolysis at various temperatures

Hydrolysis temperature	Hydrolysis time	Viscosity at zero shear rate
°C	hours	poise
120	1.0	29.0
	2.0	25.0
	4.0	12.0
110	2.0	41.0
	4.0	29.0
	7.75	15.0
100	4.0	28.0
	8.0	18.5
	11.0	11.0
80	16.0	43.0
	32.0	31.0
	64.0	15.5
—	0.0	64.0

order reaction, for which

$$2.303R \log_{10} a_T = -E(1/T_1 - 1/T_2)$$

The scale factor a_T is the relative rate of reaction at temperatures T_1 and T_2 °K.

The times t for viscosity to fall to 10 poise were estimated for each temperature and the time–temperature superposition principle used with a reference temperature of 100°C. An Arrhenius plot of log a_T against $1/T$ was produced from the data in Table III.

The activation energy was calculated from the slope of the Arrhenius plot as 85kJ/mole. The predicted times to reach the same level of degradation at ambient temperatures were estimated by extrapolation. The results indicate that the polymer is moderately stable, although in practice the presence of catalysts is likely to accelerate the hydrolysis.

Adhesive properties of polymers

The bonding properties of the polymer solutions were assessed by standard peel tests using the following SATRA standard substrates (typical good quality shoe materials):

Chrome tanned shoe upper leather — bonding surface buffed on abrasive paper to expose strong fibres

Resin rubber shoe sole material — bonding surface halogenated by dipping in aqueous chlorine (0.1% for one minute, to ensure compatibility with the polyurethane adhesive

PVC coated fabric shoe upper material SD.1
PVC shoe sole material 16/423 — bonding surfaces wiped with butan-2-one to remove plasticiser

TABLE III

Data for activation energy determination

Hydrolysis temperature T	Time t	a_T	$\log_{10} a_T$	T	$1/T$
°C	hours			°K	
120	4.5	3.78	0.577	393	0.00254
110	9.5	1.79	0.253	383	0.00261
100	17.0	1.000	0.000	373	0.00268
80	86	0.198	−0.704	353	0.00283
32	8 500†	0.0020†	−2.70†	305	0.00328
20	33 000†	0.0005†	−3.28†	293	0.00341

† estimated by extrapolation

Adhesive was applied to both surfaces and allowed to dry for one hour; two coats were applied to the leather. The adhesive on the sole material was activated by infra-red heating to 85°C and the adherends assembled and pressed for 15 seconds at 0.55 N/mm^2. After two days conditioning test joints were cut from the assemblies and peeled at a jaw separation rate of 100 mm/min.

Average peel test results are presented graphically in Figure 1. We expect minimum peel strength of 5 N/mm in men's ordinary shoes. Peel strength was maintained at close to the satisfactory value for undegraded polymer with samples hydrolysed for up to about 20 hours, even though by this time molecular weight was around one fifth of the original value. Low bond strengths and cohesive failure of the joint (within the adhesive) were only obtained when a considerable degree of polymer degradation had taken place.

Heat resistance (creep) tests[5] were carried out on PVC upper-rubber test joints. These were preheated for one hour at 50°C, tensioned with fixed weights for 10 minutes and any bond line separation measured, see Table IV.

SATRA guideline figures are maximum separations of 2, 3 and 6 mm with the respective weights. The results show that a serious fall in heat resistance occurs after approximately six hours, i.e. at an earlier stage of hydrolysis than the marked decline in peel strength.

LOW TEMPERATURE HYDROLYSIS

Preparation of the polymer series

Further samples of the adhesive polymer were hydrolysed for up to 52 weeks at 20, 30 or 37°C and over 95% rh. The temperatures are close to those of the wear

TABLE IV

Heat resistance tests after high temperature hydrolysis

	Average length of separation with test weight shown		
Hydrolysis time	0.5 kg	1.0 kg	1.5 kg
hours	mm	mm	mm
0	1	3	2
1.0	1	1	2
2.0	1	2	6
3.0	0	1	5
4.0	1	2	7
6.0	1	19	50+ (in 6 minutes)
8.0	4	31	50+ (in 6 minutes)
15.0	50+ (in 1 minute)	50+ (immediately)	50+ (immediately)
18.3	50+ (immediately)	50+ (immediately)	50+ (immediately)
29.0	— complete failure before adding test weights —		

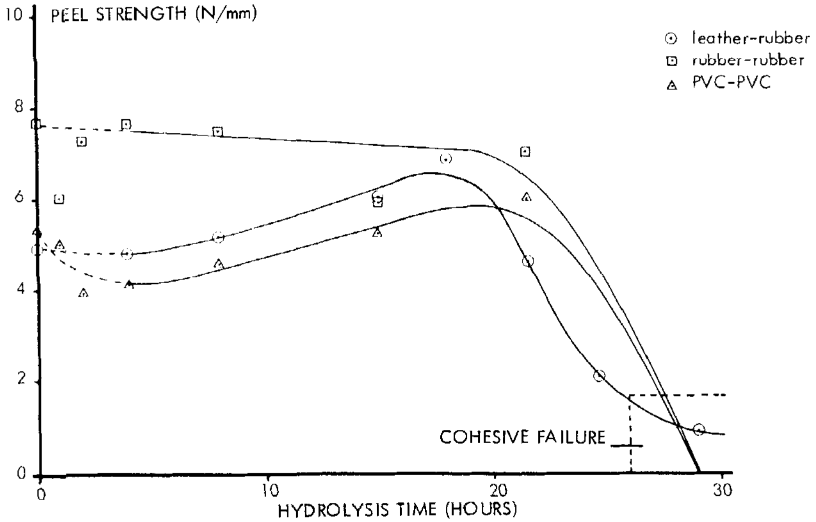

FIGURE 1 Peel strength of joints prepared with adhesive hydrolysed at 120°C.

environment, the aim being to check the validity of the earlier results which could have been influenced by, for example, a different reaction mechanism at high temperatures.

The polymer chips were suspended in small loose weave nylon bags above distilled water in sealed glass jars. The jars were stored at the test temperatures for various periods. The chips were dried at 20°C, 65% rh and 20% butan-2-one solutions prepared.

Characterisation of polymers

The hydrolysed polymers were characterised by tensile tests on films cast from solution. The results are shown in Table V. They show that the polymers degraded relatively slowly, a loss of one third tensile strength being observed after 19 weeks at 37°C, 40 weeks at 30°C and 52 weeks at 20°C.

Adhesive properties of polymers

The solutions were used to bond leather–rubber joints and trends in peel strength are shown in Figure 2. Peel strength showed little decrease, and although the incidence of adhesion failure tended to increase, there was little cohesive failure. Heat resistance was assessed as previously, using PVC upper-rubber joints at 50°C, Table VI.

TABLE V

Tensile strength of polymers after low temperature hydrolysis

Hydrolysis temperature	Hydrolysis time	Tensile strength of film
°C	weeks	N/mm^2
—	—	36
20	10	39
	20	34
	36	37
	52	24
30	6	34
	12	31
	22	33
	40	17
37	5	26
	10	32
	19	23
	26	23

TABLE VI

Heat resistance tests after low temperature hydrolysis

Hydrolysis temperature	Hydrolysis time	Average length of separation with test weight shown		
		0.5 kg	1.0 kg	1.5 kg
°C	weeks	mm	mm	mm
—	—	1	1	1
20	10	1	1	1
	20	1	1	2
	36	1	1	2
	52	1	13	47
30	6	1	2	8
	12	1	1	8
	22	1	10	30
	40	25	50+ (in 7 mins)	50+ (in 3 mins)
37	5	2	22	50+
	10	1	9	39
	19	2	7	25
	26	50+ (in 5 mins)	50+ (in 1 min)	50+ (in ½ min)

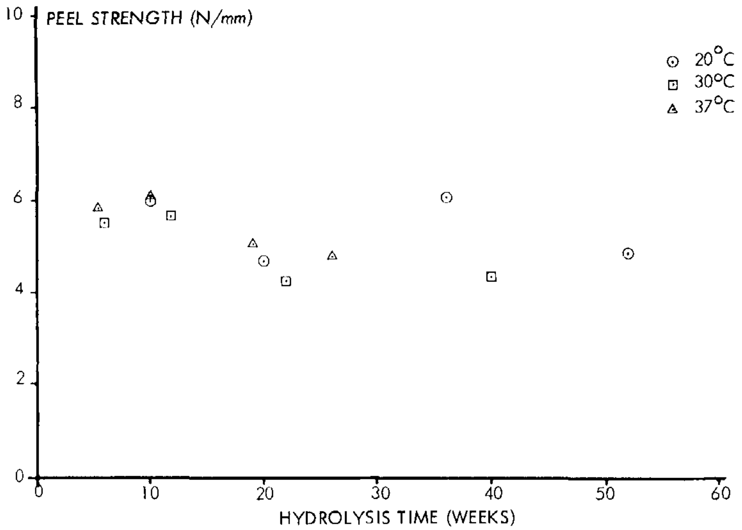

FIGURE 2 Peel strength of leather rubber joints prepared with adhesive hydrolysed at 20°, 30° or 37°C.

As with high temperature hydrolysis, heat resistance declined to an unsatisfactory level more rapidly than peel strength, although at 20°C more than 36 weeks were required.

THE EFFECT OF MOIST ENVIRONMENTS ON BONDED JOINTS

Leather–rubber joints were prepared with a solution of the undegraded polymer and immersed in water for up to 8 weeks at 30, 40, 60 or 70°C. At intervals sets of joints were removed and either conditioned in water at 20°C for two days or allowed to dry for one week at 20°C, 65% rh. Wet and dry joints were then peel tested, see Figures 3 and 4.

At 60 and 70°C a rapid loss of bond strength and onset of cohesive failure occurred, whereas at 30 and 40°C there was little change in bond strength and no cohesive failure. In most cases bond strength was somewhat higher on redrying.

To determine the effect of water on joints which show a consistent mode of failure in peeling, single-sided "half bonds" were prepared. Adhesive (undegraded polymer) was coated onto resin rubber which, to induce adhesion failure, was not surface halogenated but merely freshly abraded. A layer of woven mesh polyester fabric was placed on the wet adhesive layer and a second coat of adhesive applied. The assemblies were left for two days to allow

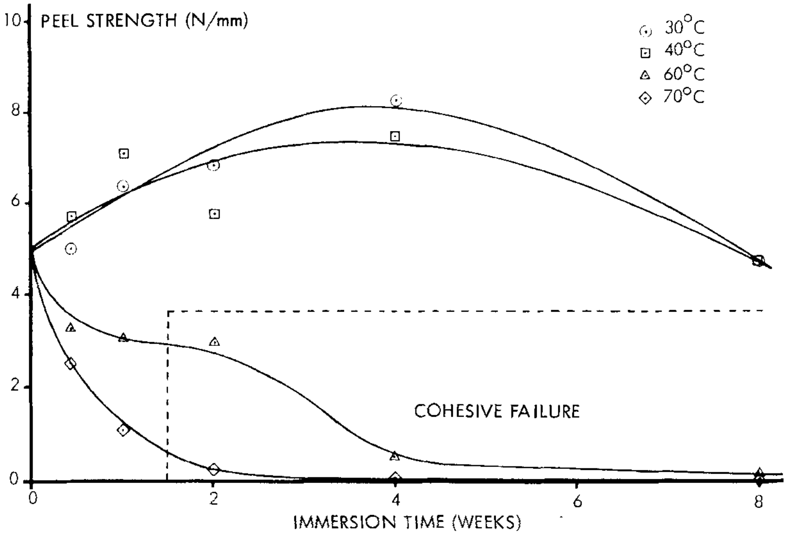

FIGURE 3 Leather–rubber joints immersed in water and peeled wet.

the solvent to evaporate and the polymer to crystallise. The polyester mesh reinforced the adhesive layer so that it could be peeled from the rubber. The "half bonds" were immersed in distilled water at 20, 40 or 60°C for up to 42 days, then reconditioned and peeled, wet or dry, as previously. Results are given in Table VII.

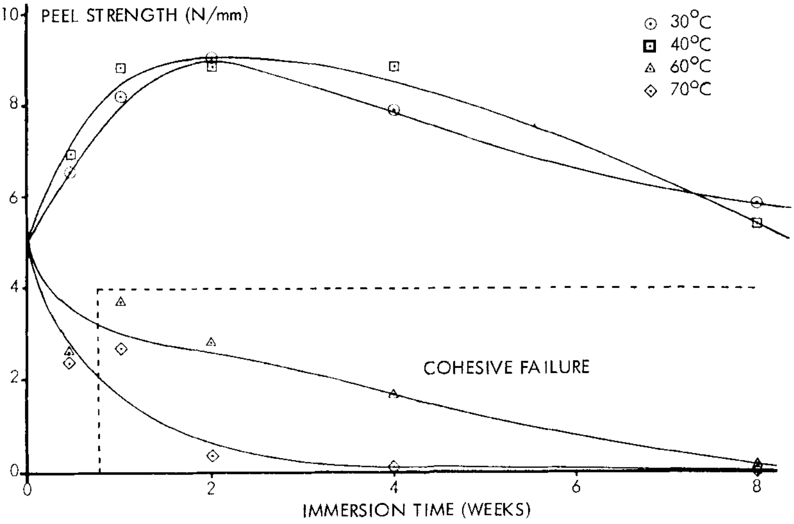

FIGURE 4 Leather–rubber joints immersed in water and peeled dry.

TABLE VII

Peel strength of half bonds after water immersion

Immersion temperature	Test condition	Peel strength (N/mm)				
		Control	3 days	7 days	21 days	42 days
°C						
20	Wet		0.95	0.70	0.80	0.70
	Dry	1.10	1.20	1.00	1.10	0.90
40	Wet		0.70	0.70	0.50	0.50
	Dry	1.10	1.15	1.10	0.65	1.00
60	Wet	—	0.40	0.30	<0.5	<0.1
	Dry	1.10	0.70	0.60	<0.5	<0.1

There was again rapid loss of bond strength at 60°C and relatively slow deterioration at the lower temperatures.

DISCUSSION

The work described confirmed that the physical properties of a polyurethane adhesive polymer are affected by exposure to moist environments. However, a considerable degree of hydrolysis is necessary before the bonding properties of the polymer, when used as a solvent-borne adhesive, are seriously impaired. Bond failure due to breakdown within the adhesive seems unlikely within a normal shoe wear life, although in severe conditions the reduction in heat resistance could be important.

Loss of bond strength of joints soaked in water at 60 or 70°C was more rapid than might be expected from either the polymer hydrolysis experiments or the joints soaked in water at 30 or 40°C. This casts doubt on the usefulness of exposing joints to moisture at temperatures above the decrystallisation temperature (ca. 45°C) of the polymer. Other work as reported by Abbott and Pettit[6] at 40°C or below has confirmed that bond strength eventually declines, but failure is invariably interfacial or within the adherend surfaces. This failure may be accelerated by moisture and warmth but is likely to occur before the adhesive polymer is deteriorated to the level of physical properties at which cohesive failure will occur.

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