

Measurement Note

Characterising the absorbency of porous substrates

Summary

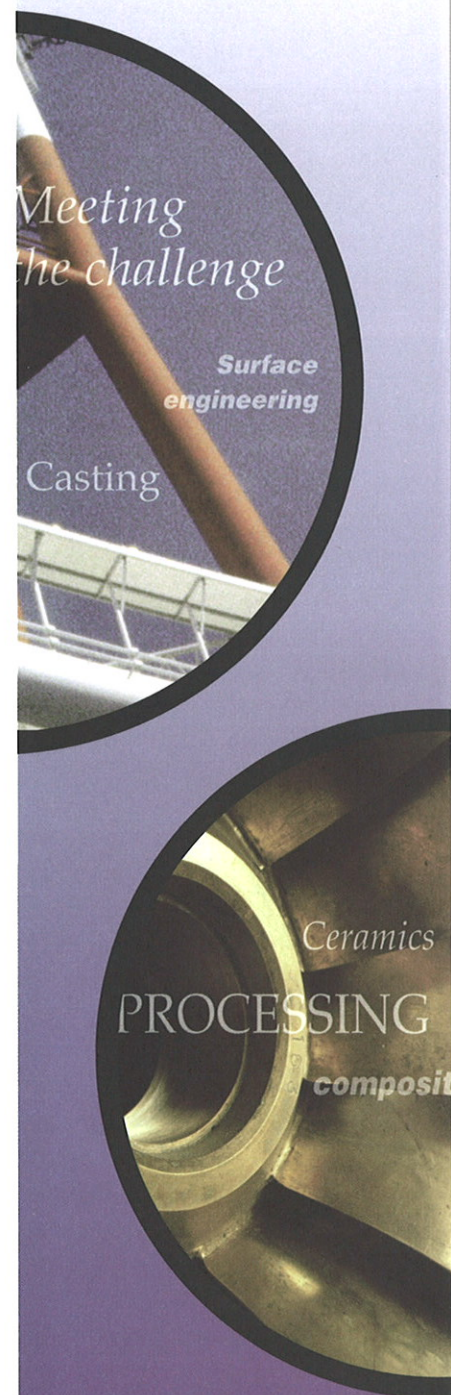
Absorption of adhesive into substrates is of considerable importance in the formation of adhesive bonds. Ingress of the adhesive into pores and rough topography increases the area of intimate contact and can provide mechanical 'keying', which improve the adhesion. However, excess absorption by permeable materials can weaken the subsequent joint. There are no reliable simple techniques to measure absorption of viscous liquid polymers and this Measurement Note describes test methods, using probe liquids such as water, for characterising the absorbency of substrate materials:

- Cobb test is quick to perform and restricts the test to one surface of the substrate, thus simulating adhesive application.
- Edge immersion method allows real-time monitoring of liquid uptake but the main route for ingress is through the 'cut edge'.
- Drying substrates following exposure provides real-time mass loss data but involves both surfaces and the moisture desorption from the sample does not replicate adhesive absorption.
- Vapour exposure measurements, which despite involving both surfaces and absorption from vapour rather than liquid, give approximately the same substrate ranking as the Cobb results.
- Drop volume measurements, using an automated contact angle instrument, show promise but have high relative uncertainties and need to take account of evaporation.

The work was carried out as part of the "Measurements for Materials Systems" (MMS) programme funded by the Department of Trade and Industry.

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March 2005



INTRODUCTION

Industries such as packaging and footwear industries are large users of adhesive bonding technology. However, adhesives and substrate materials tend to receive much less attention than those used in structural engineering applications.

Many of the substrate materials used are rough and/or porous. Ingress of the adhesive into pores and topographic features increases the area of intimate contact and can provide mechanical 'keying', which improve adhesion. However, over absorption into permeable materials can weaken the subsequent joint. Hence, the absorption of adhesive into the substrate material is of considerable importance in the formation of adhesive bonds. This Measurement Note describes some of the methods used to characterise absorption of liquids and the results obtained from the tests.

Absorption of liquids into porous materials can be followed through mass uptake (often known as gravimetric) measurements [1]. Samples can be exposed to the vapour or immersed in the fluid. If the material samples (or components of the material) are soluble in the liquid then mass loss due to leaching of material can also occur and lead to errors in the absorption measurements. Absorption of liquid into a solid material is a diffusion process. Ingress in a porous system will also be driven by capillary forces – interfacial tensions and rheological properties will influence absorption.

METHODS FOR MEASURING ABSORPTION OF MATERIALS

Cobb Test

The Cobb test [2, 3] is used to assess the absorption properties of paper or cardboard. A column of water is placed on

the paper for a set time and the amount of water absorbed is measured. More water resistance will result in a lower Water Cobb result. The test can be run from either the top or reverse side of the sample. Each test evaluates a different property; the coated side test characterises the "openness" of the coating whilst the reverse side test measures the base sheet sizing.

The test is performed by clamping a weighed sample in a Cobb ring with the side to be tested uppermost, as shown in Figure 1. The 100 cm² ring is filled with 100 ml of distilled water. This is left for 45 seconds and then drained. After a further 15 seconds the sample is placed between two sheets of blotting paper and rolled twice with a 10 kg Cobb roller. The sample is immediately weighed to determine the increase in weight due to water uptake. The result, often known as the Cobb₆₀, is expressed in gm⁻².



Figure 1: Cobb test apparatus

Various coated paper and board substrates, conditioned at 23 °C and 50% relative humidity, were evaluated for their ability to absorb moisture by the Cobb method. Both top and reverse surfaces were tested and the results are plotted in Figure 2. There are four materials (nos. 1, 3, 25 and 27) whose reverse (uncoated) surfaces have significantly higher levels of absorbency than the other samples.

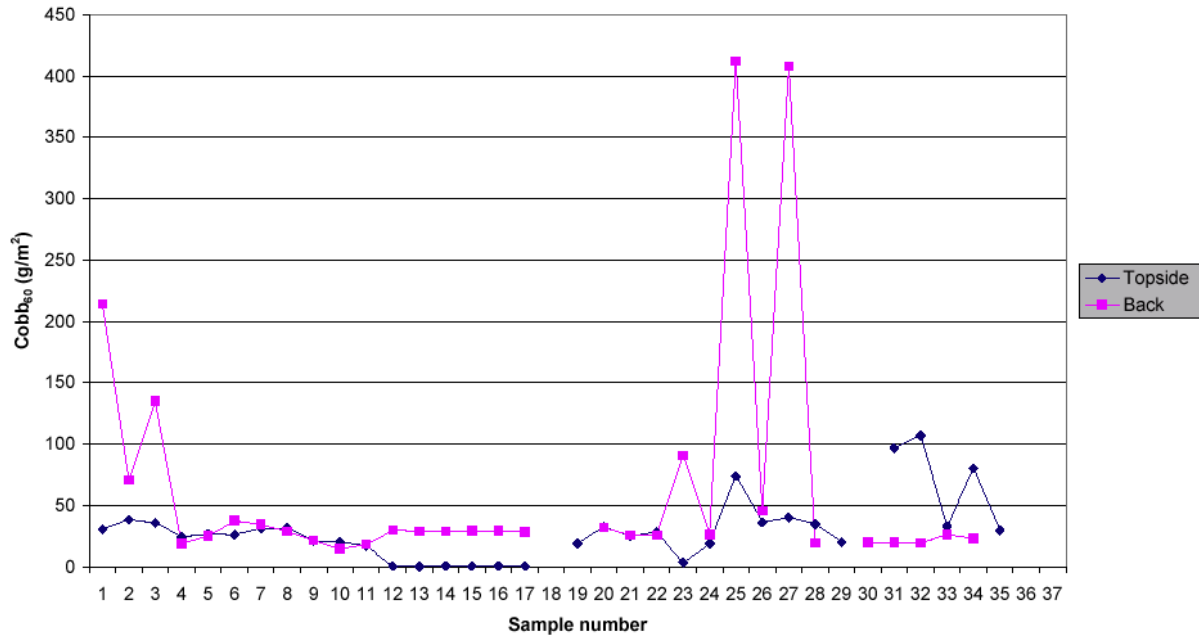


Figure 2: Cobb test results

Table 1: Comparison of Cobb Absorbency and Moisture Uptake

Substrate	Cobb Absorbency (g/m ²)		Edge Immersion (% mass gain)		Vapour Exposure (% mass gain)	
	Top	Reverse	1 hour	24 hours	Peak	Final
Substrate 1	31	214	74 ± 14	105 ± 3	7.2	5.8
Substrate 3	36	135	60 ± 23	100 ± 9	11.1	8.8
Substrate 25	74	413	10 ± 1.5	22.3 ± 1.6	16.2	10.7
Substrate 27	40	408	10.2 ± 0.8	21.2 ± 5.2	14.0	9.9

Edge Absorption Measurements

The four substrates which had high reverse surfaces Cobb absorption levels were investigated using an edge immersion technique. Specimens, cut to 50 by 50 mm square, were suspended from the arm of a calibrated balance with an accuracy of 0.001 grams over a beaker of distilled water, so that one edge of the specimen was just in contact with the water surface. As the moisture absorbs into the specimen, the overall weight therefore increases. This is recorded from the balance's digital

display at periodic intervals. The results are plotted in Figure 3, where they are plotted against the square root of time. The chipboard samples (1 and 3) appear to reach saturation within the duration of the test (48 hours) whilst the boxboard samples (25 and 27) still seem to be absorbing water.

The same substrates were also evaluated for the length of time they took to lose the moisture once it had been absorbed. The specimens were left to absorb water through one edge as before. After various

fixed time periods, the beaker of water was then removed and the specimens left suspended from the balance arm as they dried out. Weights were measured at regular intervals until the specimens had approximately regained the same weight as they had when dry. The results are shown in Figure 4.



Figure 3: Edge absorption tests

The ranking of moisture uptake by edge immersion is the reverse of the Cobb ranking. Table 1 shows that, in the same time, the chipboards absorb over 5 times as much water as the boxboards. It is not unexpected that these results do not correspond with the Cobb results as the main route of moisture ingress in this test is through the cut edge of the card and this may present a very different affinity to moisture than the surface. The method of cutting, the edge used (in materials with a dominant processing or fibre direction) and the depth of immersion will have a considerable influence on the rate of moisture ingress.

The rate at which these substrates lose absorbed moisture was also evaluated. Since the samples are thin, this process should depend mostly on the surface properties. The specimens were allowed to absorb water through one edge as before. After various fixed time periods, the beaker of water was then removed and

the specimens left suspended from the balance arm as they dried out. Weight readings were taken at regular intervals until the specimens had approximately regained the same weight as they had prior to testing. The results are shown in Figure 5. The mass loss appears linear with $\sqrt{t}$ and, unexpectedly, there is no asymptotic approach to zero mass gain, which may suggest that if tests had been continued then net mass loss may have been found. The initial rate of mass loss appears to increase with the moisture level, which is consistent with diffusion processes.

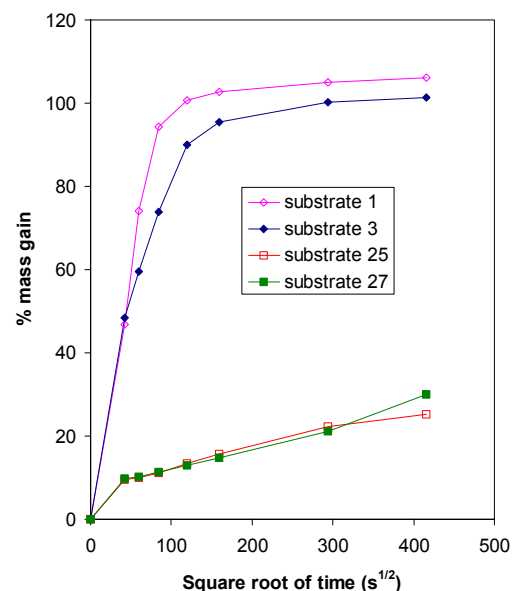


Figure 4: Moisture absorption through specimen edge

Mass Uptake from Vapour Exposure

These substrates were exposed in a Climatic Systems environmental chamber, maintaining 30 °C and 90% relative humidity. Samples were supported vertically in a rack so that the maximum surface area could be exposed to the humid air. Following the procedure of ISO 62 [4], samples were periodically removed from the chamber and weighed. Any condensed moisture on the samples surface was wiped off with an absorbent cloth prior to weighing. The time the sample

was out of the environmental chamber was minimised. The results are shown in Figure 6 and summarised in Table 1.

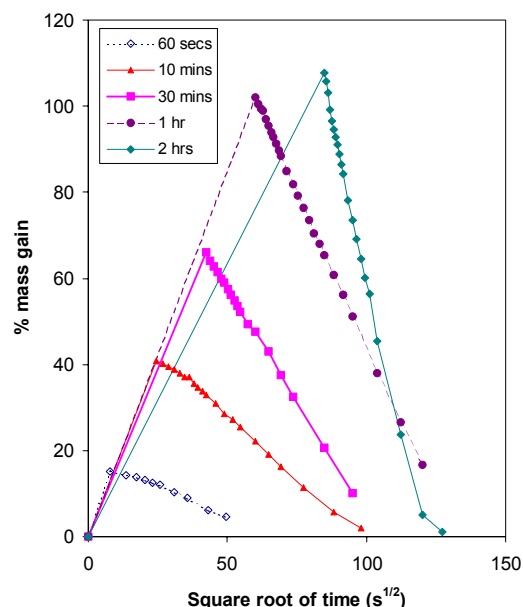


Figure 5: Drying curves for Substrate Sample 1

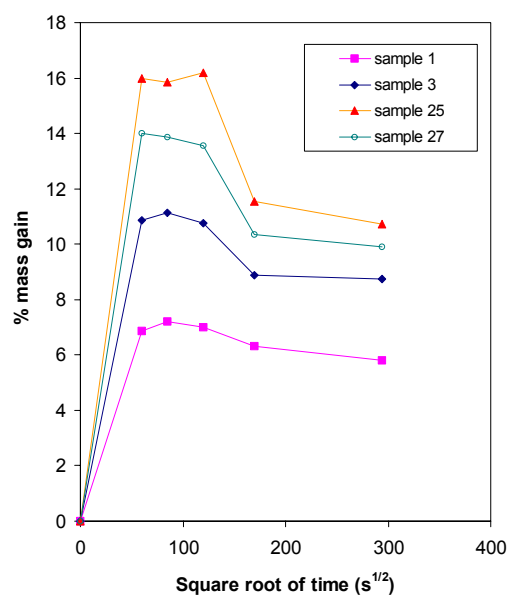


Figure 6: Moisture uptake from a humid environment

There is a rapid increase in mass followed by a peak/plateau and then a decrease in mass to an apparent constant level. The amount of moisture absorbed by the chipboards (1 and 3) is substantially lower than that absorbed in edge immersion experiments. The peak moisture absorption by the boxboards (25 and 27) is

comparable to the edge immersion as similar times. The boxboards absorb more moisture than the chipboards, which is in agreement with the Cobb test results. The decrease in mass observed in all of the tests may result from loss of material from the samples.

Drop Volume Measurement

Liquids that poorly wet surfaces will form as droplets on the surface. The volume of the drop can be determined, assuming the drop is symmetrical, from the shape (width and height) of the silhouette outline of the drop. Automated image analysis routines can be used to continually determine the time evolution of the drop volume. The absorption of liquid drops into a porous substrate was observed and quantified using image analysis routines included in an automated contact angle measurement instrument [5] to calculate drop dimensions. The volume of the liquid on the surface decreases due to both absorption and evaporation. Thus, all measurements need to account for material lost through evaporation. Rates of evaporation can be determined by applying the test liquid to an impermeable surface and following the loss of volume over likely experimental duration. The evaporation correction may large for volatile liquids in low vapour pressure environments the use of liquids with low volatility (e.g. paraffin rather than water) is recommended to reduce corrections.

Figure 7 shows the experimental set-up and the evolution of the shape and volume of a sessile drop on a porous substrate at different times (increasing time from left to right). As time increases the contact angle decreases, the drop height decreases and the drop width increases and then decreases. The drop width and contact angle are influenced by the changing characteristics of the surface due to the presence and adsorption of the liquid, which wets more easily.

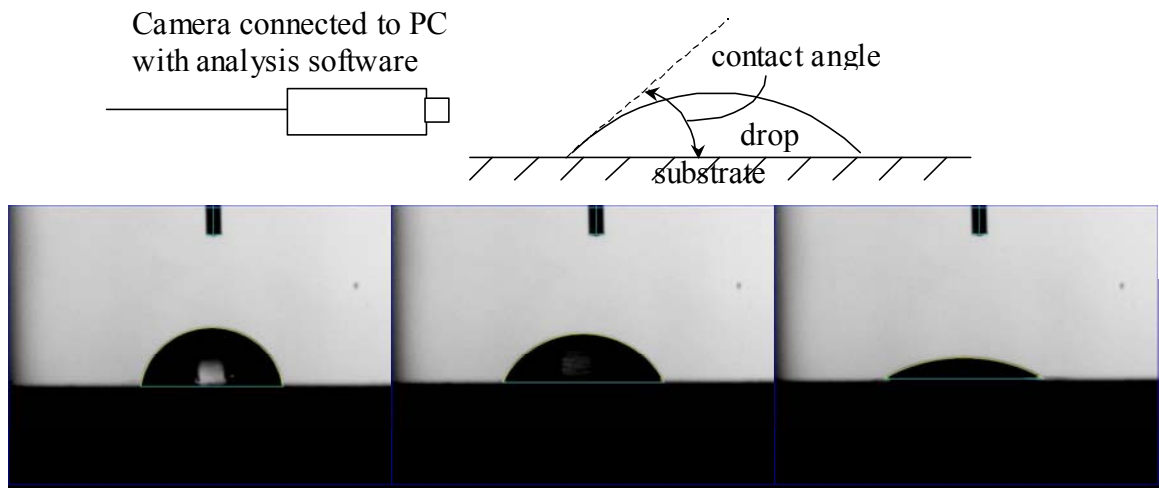


Figure 7: Image analysis of liquid drop absorption

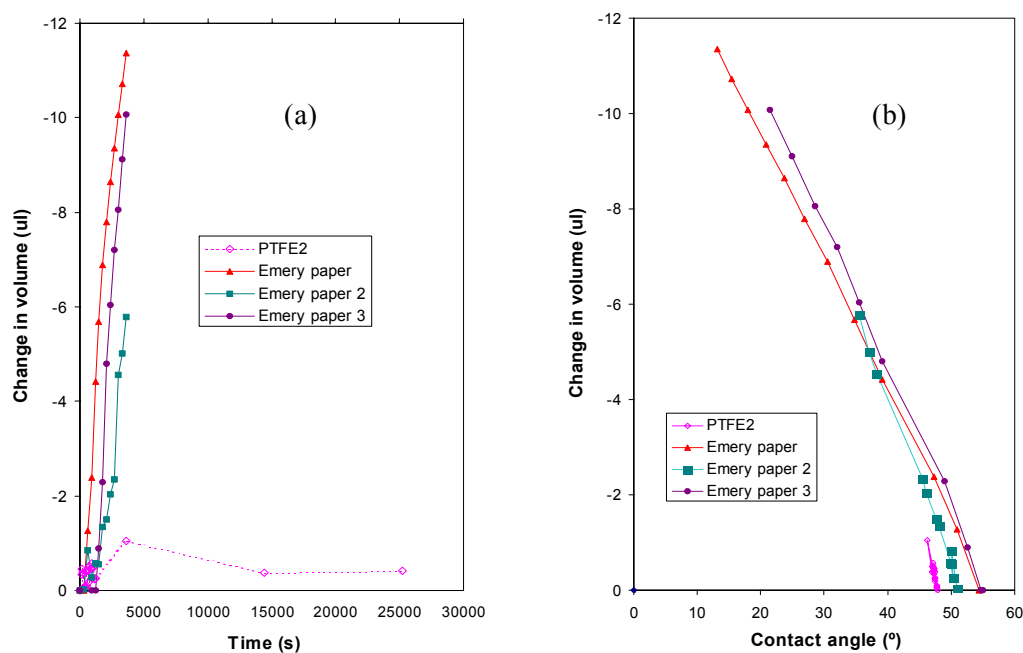


Figure 8: Change in drop volume and contact angle of paraffin

Figure 8 shows drop volume measurements made using paraffin as a probe liquid on an impermeable, low energy surface (PTFE) and a porous surface (the reverse side of emery paper). The initial volumes of the drops applied were between 14 μl and 17 μl .

The measurements of drops on the PTFE surface confirm that paraffin has a very

low rate of evaporation at room temperature. The volume reduction of approximately 1 μl seen in the figure is believed to be an artefact of the measurement method due to uncertainties in drop edge detection and a repeat test indicated a 'gain' in drop volume of approximately 1 μl , which is thought to be a reasonable estimate of uncertainty in the volume measurement.

The three repeat measurements of paraffin drop volume on the emery paper suggest that the rate of absorption into the porous emery paper is relatively constant and could be used as a parameter for characterising the absorbency of substrates. The surface tension of the hydrocarbon paraffin will be similar to those of hot melt adhesives making paraffin a useful analogue for the adhesives.

CONCLUDING REMARKS

Several methods for assessing the absorbency of porous substrates have been discussed. Each has advantages and drawbacks. To be relevant, the duration of the absorbency test should be similar to the time the liquid adhesive is in contact with the substrate before hardening. In a high throughput process this could be as little as a few seconds but in other applications, e.g. with slow curing adhesives, may be several hours.

The Cobb test is quick to perform and restricts the test to one surface of the substrate, thus simulating adhesive application.

The edge immersion method allows real-time monitoring of liquid uptake, which would enable calculation of diffusion constants. However, the main route for ingress is through the 'cut edge', which is not often a critical surface for bonding. The drying method involves both surfaces and the direction of moisture travel out of the sample does not replicate adhesive absorption. Similar criticisms can be levelled at the vapour exposure measurements. Despite the involvement of both surfaces and absorption from vapour rather than liquid, the substrates have approximately the same ranking as the Cobb results. This suggests that the more porous reverse surface dominates the absorption behaviour.

The vapour exposure tests (and consideration of the drying curves) suggest that some of the mass of the substrate may be leached from the samples during mass uptake tests. This may also occur in the Cobb measurements but the standard measurement method is unlikely to reveal this.

Preliminary measurements made using the facility of the automated contact angle instrument to determine drop volumes indicate that absorption can be quantified from the change in volume of the drop. However, uncertainties in the edge detection can produce high relative uncertainties in the volume measurements and the effects of evaporation need to be accounted for when interpreting results.

The methods outlined in the main use water as the probe liquid for absorbency. Water has significantly different surface tension and viscosity to most polymeric adhesives and there is some concern as to how well water will simulate the actual absorption of adhesives. Work on wettabilities suggests that water drop contact angle is not a good predictor of wetting of surfaces by hot melt adhesives [5]. A hydrocarbon-based liquid, such as paraffin, may be a better model for adhesives. Adhesive bond tests or wax pick tests [5] may provide further information on the relationship between water absorbency measurements and adhesive absorption. However, such interpretations would not be straightforward.

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ACKNOWLEDGEMENTS

The research reported in this Measurement Note was carried out as part of project MMS9 of the "Materials for Measurement Systems" (MMS) programme, a programme of underpinning research funded by the United Kingdom Department of Trade and Industry (MMS9/T4/M4).

The authors would like to thank Richard Roberts, Mark Taylor, Russell Musgrove and Doug Leatherdale at Pira for carrying out the Cobb tests and providing samples.

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