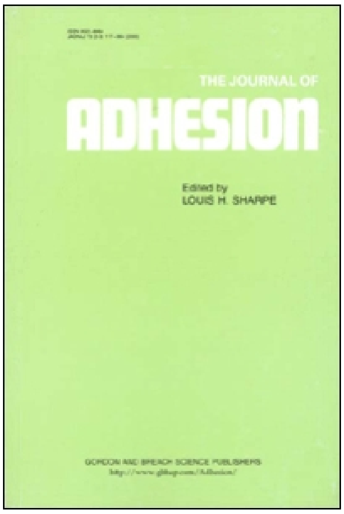

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NOTE

Effect of Relative Humidity on the Wettability of Steel Surfaces

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Metals and metal oxides are usually classed as high-energy solids since in the ultra-clean state they have surface free energies typically greater than 500 mJ/m^2. However, Bernett and Zisman[1] measured the critical surface tension, γ_c, of wetting of various hydrophilic, high-energy, metal oxides and pure metals at two extreme humidities namely 0.6% r.h. and 95% r.h., and found that the surfaces were converted to ones of low γ_c (i.e. about 46 and 38 mJ/m^2 respectively) and, further, the γ_c values were almost independent of the solid surface. They ascribed these observations to the adsorption of water and proposed that the surface free energy of any clean, high-energy surface after exposure to an atmosphere containing water vapour is mainly dependent upon the surface concentration of adsorbed water. Recent studies[2,3] using surface-specific analytical techniques have indicated that the surfaces of high-energy solids are not only covered by adsorbed water but also by other contaminants such as nitrogen and organic adsorbates such as hydrocarbons.

The aim of the present investigation was firstly to extend this earlier work by examining the effect of a range of relative humidities on the wettability of mild-steel surfaces of different rugosities employing Kaelble's analysis[4] where the dispersion, γ_{SV}^D, and polar, γ_{SV}^P, contributions to the solid's surface free energy, γ_{SV}^T, are isolated. Secondly, to consider the implications of such data on the strength of steel-epoxide adhesive joints prepared under different humidities. This letter describes some interesting initial observations.

The mild steel was to specification BS 970, EN 3B and was prepared either (i) by abrasion with various grades of silicon carbide paper followed by polishing on a cloth wheel with 6 μm diamond paste, washing with distilled water, immersion consecutively in liquid- and vapour-degreasing baths of 1,1,1-trichloroethane, or (ii) by degreasing, then grit-blasting with 180–220 mesh alumina, then degreasing again. Advancing contact angles of the various liquids on these surfaces were measured over a range of relative humidities employing an instrument based upon the Fort and Patterson design,[5] in a sealed glove-box (equipped with an electric-fan) in a constant temperature (22° ± 1 °C) room with various humidities maintained by using salt solutions.[6] The steel specimens were equilibrated at the required r.h. for two hours prior to the contact angle determinations.

The measured contact angles are shown in Table I; each result is the mean of ten determinations, the reproducibility was ±2°.

TABLE I

Contact angle results

Liquid	γ^{T}_{LV} (mJ/m)^2	Polished steel surface				Grit-blasted steel surface						
		9%	17%	51%	81%	7%	16%	35%	56%	80%	81%	88%
Water	72.2	63	68	61	72	66	69	76	69	>90	>90	>90
Glycerol	64.0	53	57	62	69	42	48	61	67	83	79	86
Formamide	58.3	43	52	44	55	29	30	42	54	53	56	52
Di-iodomethane	50.8	33	35	39	43	S	S	5	34	33	33	35
1-bromonaphthalene	44.6	S	S	S	27	S	S	S	S	S	S	S
Ethylene glycol	48.3							34		65		54
Polyglycol E-200	43.5							5		36		30
Polyglycol 15-200	36.6							S		S		S

S indicates liquid spread on surface.

These results were used to deduce γ^{D}_{SV} and γ^{P}_{SV} for the polished and grit-blasted steel surfaces at each r.h.[4, 7] and Figure 1 shows γ^{T}_{SV} ($\gamma^{T}_{SV} = \gamma^{D}_{SV}+\gamma^{P}_{VS}$) as a function of r.h. For the polished surface there is a linear correlation and the present results are in good agreement with the previous values for γ_c (1). However, for the rougher, grit-blasted surfaces there is a considerably greater variation in the value of γ^{T}_{SV} with humidity and, as might be expected,[8] the value of γ^{T}_{SV} (rough) is usually greater than γ^{T}_{SV} (polished).

Now, from the values of γ^{D}_{SV} and γ^{P}_{SV}, a wettability envelope may be constructed. For wetting to occur (i.e. the contact angle to be zero) then:

$$\gamma^{T}_{SV} \geqslant \gamma^{T}_{LV}+\gamma^{T}_{LS} \tag{1}$$

where γ^{T}_{LV} and γ^{T}_{LS} are the liquid–vapour and liquid–solid interfacial free energies respectively. But:

$$\gamma^{T}_{LS} = \gamma^{T}_{SV}+\gamma^{T}_{LV}-2(\gamma^{D}_{SV}\cdot\ \gamma^{D}_{LV})^{\frac{1}{2}}-2(\gamma^{P}_{SV}\cdot\gamma^{P}_{LV})^{\frac{1}{2}} \tag{2}$$

Substituting (2) into (1), then for wetting just to occur:

$$\gamma_{LV}^{T} - (\gamma_{SV}^{D} \cdot \gamma_{LV}^{D})^{\frac{1}{2}} - (\gamma_{SV}^{P} \cdot \gamma_{LV}^{P})^{\frac{1}{2}} = 0 \qquad (3)$$

Thus knowing values of γ_{SV}^{D} and γ_{SV}^{P} for a solid surface enables Eq. (3) to be solved to yield values of γ_{LV}^{D} and γ_{LV}^{P} for liquids which would just wet the solid surface and so allows a wettability envelope for the solid to be constructed.

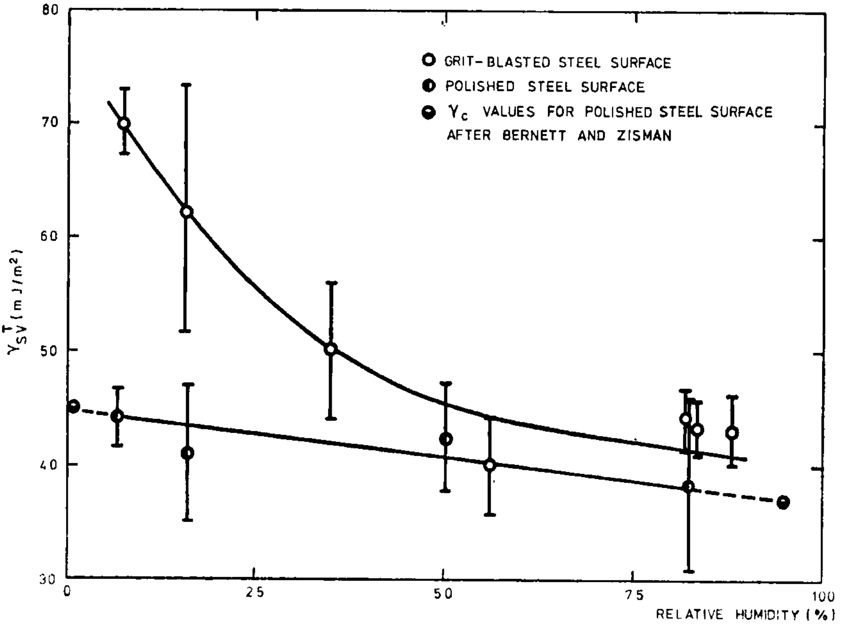

FIGURE 1 Total surface free energy of grit-blasted and polished mild-steel surfaces as a function of relative humidity.

Wettability envelopes for the grit-blasted mild-steel surfaces at different humidities are shown in Figure 2 with the γ_{LV}^{D} and γ_{LV}^{P} values[9] for an epoxide adhesive (a diglycidyl ether of bisphenol A mixed with 9.4 mass per cent of 2,4,6, tris(dimethylaminomethyl)phenol). As may be seen, the γ_{LV}^{D} and γ_{LV}^{P} values for this adhesive lie inside the 7 and 16% r.h. envelopes but outside the 56 and 81% r.h. envelopes, indicating wetting of the steel surface by the epoxide adhesive at the lower humidities but non-wetting at the higher humidities. This was indeed confirmed by contact angle measurements.

To examine the practical implications of these results, coaxial butt joints were prepared consisting of grit-blasted mild-steel cylinders bonded with the epoxide adhesive. The adhesive was applied to the steel surfaces under either a 7 or 56% r.h. and cured for 96 h at 22°C in the relevant r.h. followed

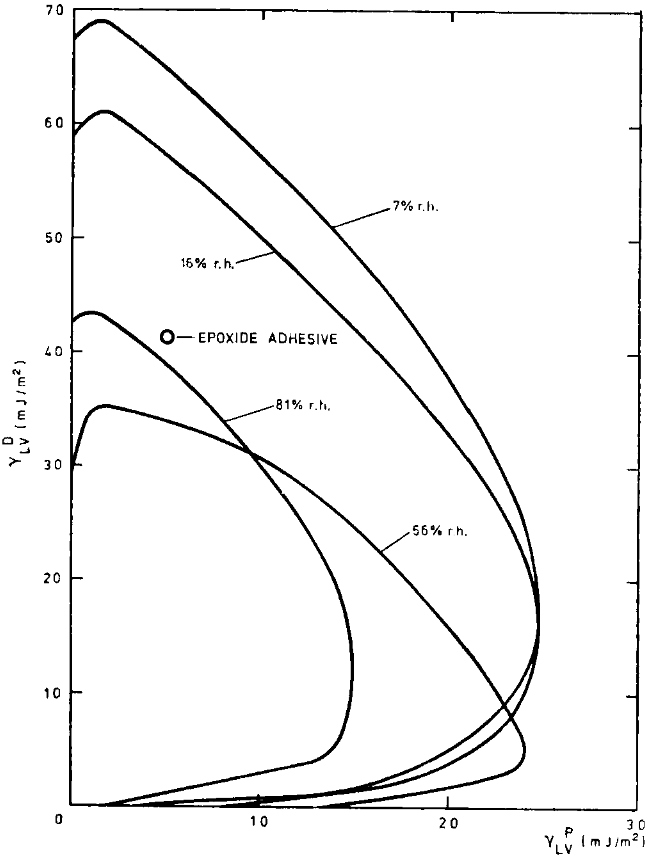

FIGURE 2 Wettability envelopes for grit-blasted mild-steel surfaces at various humidities.

TABLE II
Joint failure studies

r.h. under which adhesive was applied (%)	Butt joint strength[a] (MPa)	Locus of joint failure[b]
7	56.7 (8.5)	44% C and 56% I
56	31.9 (3.8)	19% C and 81% I

[a] Mean of 20 determinations; standard deviations given in brackets.

[b] C: cohesive failure through the adhesive
I: interfacial failure between the adhesive and metal oxide.

by 1¼ h at 100°C and 2½ h at 180°C. The cured joints were kept at 22°C, 55% r.h. for 7 days prior to being fractured in tension under these conditions at a strain-rate of $4.0 \times 10^{-2} s^{-1}$. The results are shown in Table II; the joints prepared under the 7% r.h. are highly significantly stronger (a Student's 't' test gives a 0.1% significance level) and, furthermore, the locus of joint failure occurs more cohesively through the adhesive rather than interfacially. Thus the wetting of the steel surface by the adhesive at the lower humidity, as indicated by the wettability envelopes, is directly reflected in higher joint strengths.

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