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Note

A new calorimetric cell for determining the heat of wetting of substances with a small specific surface

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Replacement of part of a polymer by cheap available fillers necessitates the investigation of surface phenomena at the filler–polymer interface.

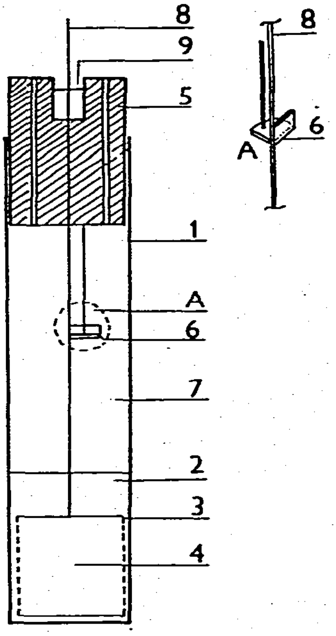
For studying the polymer–filler interaction, we have chosen an immersion calorimetric method which enables the heats of wetting of fillers to be measured and the surface energy of the filler and the energy of adhesion to the filler surface to be evaluated.

The heats of wetting of solid surface are exothermic and usually low. For instance[1], the heat of wetting by water of the high polar energy surface of a water insoluble inorganic salt is 400 mJ m^{-2}, and that of a low energy surface, such as graphite, is 30 mJ m^{-2}. Therefore, a very sensitive apparatus and a specially constructed calorimetric cell with the lowest and well-reproducible blank effect are needed for measurements. Boyd and Harkins[2], Zettlemoyer et al.[3] and Berghausen[4] have described the basic types and construction of calorimeters and the procedures used in the measurement of heats of wetting. In these cases, correction was made for the blank effect caused by breaking the glass ampoule containing the sample, which may assume the values[3-5] of 1.6–2.5 J. It includes the mechanical energy arising from breaking the ampoule, the residual strain in the glass, the $p\Delta V$ work, filling up the residual volume of the ampoule with the wetting liquid and evaporation of the latter into the space formed[4, 5] in the calorimetric cell. The correction for substances, the specific surface of which lies between 3 and 10 m^2 g^{-1}, is often equal to or higher than the thermal effect of wetting.

In this paper, a method is proposed which eliminates these shortcomings.

EXPERIMENTAL

A commercial low-temperature Calvet microcalorimeter[6] (Setaram, Lyon)



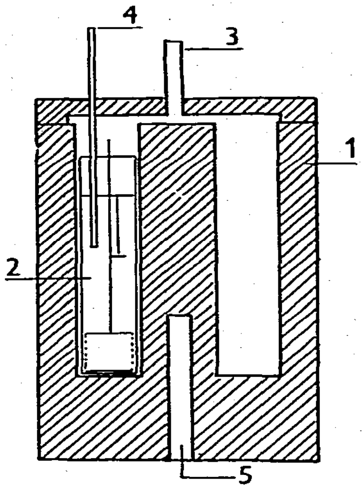


Fig. 1. Calorimetric cell for the measurement of the heat of wetting. 1, Cell; 2, mercury; 3, cage; 4, adsorbent; 5, teflon stopper; 6, safety stop; 7, wetting liquid; 8, pull rod; 9, mercury seal.

Fig. 2. Thermostated aluminium block. 1, Block; 2, cell; 3, vacuum; 4, mercury inlet; 5, thermometer.

operating at temperatures between +200 and −200 °C was used to measure the heat of wetting.

The new calorimetric cell proposed by us is shown in Fig. 1. It consists of a stainless steel cell, 1, 1.7 cm diam. × 8.5 cm long, with a cage, 3, made of stainless steel mesh, containing the adsorbent, 4. The cell is closed by a teflon stopper with a mercury seal, 9, to prevent evaporation of the liquid. Before measurement, adsorbent, 0.5 g, is placed in the cell cage, 3, and freed from the physically bound water by drying at 110 °C in vacuo in a thermostatted aluminium block (Fig. 2). After drying, mercury, 2, is introduced by means of a stainless steel tube, 4 (Fig. 2), under vacuum to fill up the free space of the cage. After releasing the vacuum, the space above the mercury is filled with the wetting liquid, 7. In order to determine the blank effect of the cell, the thermal effect of wetting the empty cage with hexane, a nonpolar substance, and with water, a polar substance, was measured.

For the purpose of illustration, we present the measurement of the heat of wetting of kaolin (Chlumčany, Czechoslovakia) with a specific surface of 8 m^2 g^{-1}, determined by BET with N_2. As wetting liquid, we used twice-distilled water, hexane, undecane, ethanol, hexadecane purified[7] and freed from water vapour by means of a 4 Å molecular sieve.

RESULTS AND DISCUSSION

The construction of the measuring cell led to a considerable decrease in the blank effect. Practically, the correction only involves the heat caused by the transfer of the cage from the mercury to the immersion liquid.

The average of three measurements of the blank effect was 30 ± 3 mJ in hexane and 34 ± 4 mJ in water. In order to verify the reproducibility of the method, ten measurements of the heats of wetting of kaolin with water were performed. The values ($Q_{\mathrm{im}} = 2.222 \pm 0.059$ J g^{-1}) obtained were subjected to the significance test[8]. For determining the interval estimate, the Student *t*-test was used. The 95% confidence interval within which the measured value must lie, was $\langle 2.180; 2.364. \rangle$.

The heats of wetting of kaolin by some liquids are ethanol, $Q_{\mathrm{im}} = 1.775 \pm 0.020$ J g^{-1}; hexane, $Q_{\mathrm{im}} = 0.325 \pm 0.008$ J g^{-1}; undecane, $Q_{\mathrm{im}} = 1.310 \pm 0.006$ J g^{-1}; and hexadecane, $Q_{\mathrm{im}} = 1.340 \pm 0.007$ J g^{-1}.

The proposed calorimetric cell, together with the Calvet microcalorimeter, permit sufficiently precise measurements of the heats of wetting of solids with relatively small specific surface ($\sim$ 10 m^2) to be carried out.

REFERENCES

1 J. J. Chessik and A. C. Zettlemoyer, *Advan. Catal.*, 11 (1959) 263.
2 G. E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, 64 (1942) 1190.
3 A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *J. Phys. Chem.*, 57 (1953) 649.
4 P. E. Berghausen, in A. Clark, J. E. Rutzler and R. L. Savage (Eds.), *Adhesion and Adhesives*, Wiley, New York, 1954, p. 225.
5 G. J. Young and P. P. Barsh, *J. Colloid Sci.*, 15 (1960) 361.
6 E. Calvet and H. Prat, in H. A. Skinner (Ed.), *Recent Progress in Microcalorimetry*, Pergamon Press, Oxford and New York, 1963.
7 J. A. Riddick and W. B. Bunger, *Organic Solvents*, Wiley, New York, 1970.
8 W. C. Hamilton, *Statistics in Physical Science*, The Royal Press Co., New York, 1964.