DISPERSIBILITY OF CARBON BLACK BY POLYVINYL ALCOHOL SOLUTIONS

By G. A. JOHNSON and K. E. LEWIS

The dispersibility of carbon black by eight types of polyvinyl alcohol solution has been studied which differed in their degree of hydrolysis (i.e. amount of free acetate groups) and molecular weight. The degree of hydrolysis varied from 80 to 100% and the molecular weight (viscosity average) from 6000 to 40,000. Adsorption isotherms of the polyvinyl alcohol on to the carbon black and contact angles of water on carbon black on to which polyvinyl alcohol had been previously adsorbed were measured. These results are related to the concentration at which dispersion occurs. It is shown that dispersion occurs when the contact angle falls below 90° but that this does not correspond to monolayer coverage of the polyvinyl alcohol on the carbon black. In fact, dispersion occurs at very low levels of adsorption, suggesting that only a low surface coverage is necessary to produce a hydrophilic surface.

Introduction

Previous work on dispersibility and the formation of dispersions has in many cases not taken into account fully, and in some instances not even reported, the conditions under which dispersions have been made. The process of dispersion of a particulate solid in a liquid may be defined as the complete process of incorporating solid matter into a liquid medium, that is, replacing the solid/solid and solid/air interfaces by solid/liquid interfaces, such that the final state consists of primary particles distributed throughout the liquid medium. Dispersibility is then the ease of forming such a dispersion. The stability of the resulting dispersion may be considered to be a second phenomenon of the system. Often in practice it is difficult to distinguish between the two, although different theoretical factors and parameters are involved. The factors governing dispersibility are discussed below. The production of a stable dispersed system does not necessarily mean good dispersibility and conversely an easily dispersed system, i.e. good dispersibility, does not necessarily imply the formation of a stable dispersion.

It is well known that non-ionogenic polymers are good dispersing agents. Accordingly, the dispersibility of Sterling MT carbon black in polyvinyl alcohol solutions was studied under known controlled dispersion conditions. Sterling MT in water forms a very stable dispersion owing to a large electrostatic repulsion force between primary particles, and hence dispersibility can easily be observed without the complications of producing a flocculating system. To produce such a dispersion in water it is necessary to use ultra-sonic irradiation to break down the aggregates into the primary particles.

Dispersion involves the wetting of aggregates of primary particles which are then broken down either by a mechanical force or spontaneously if the work of wetting provides sufficient energy to overcome adhesional forces. When the surfaces of a solid/solid adhesive system are wetted by water there is a reduction in the adhesive forces operating. Krupp[1] has demonstrated that for an adhesive system where the solid/solid adhesive area is formed before immersion, immersion in water reduces the adhesive force by about one-third of the value in air. This is due to the effect of water between the surfaces on the van der Waals' interaction. Quantitatively this may be accounted for by the change in the dielectric constant of the medium between surfaces, according to the Lifshitz theory of long-range forces of attraction due to electromagnetic fluctuation fields.[2]

It is convenient to divide the wetting process into three parts,[3] adhesion, spreading and immersion. Wetting will be spontaneous when the contact angle θ is less than 90°, whereas for $\theta > 90°$ energy must be supplied to wet the system. However, consideration of the separate stages of wetting shows that energy must be supplied to overcome the work of spreading; at a maximum this would be of the order of γ_{LV} (the surface tension at the liquid/vapour interface) per cm^2. Spontaneous spreading occurs only when $\theta = 0°$.

The addition of a surface-active component causes a reduction in γ_{LV} and if it is adsorbed on the solid surface, as it usually is, it causes a change, most probably a decrease, in γ_{LS} (the surface tension at the solid/liquid interface). Both these effects lead to a reduction in θ and hence to better wetting of the surface.

If the solid is an aggregate of small particles then for complete wetting the liquid must penetrate into the channels or 'pores' of the aggregate. The treatment of wetting as a capillary phenomenon was described by Adamson.[4]

For the purposes of the present investigation the factors which govern the dispersibility of a system can be summarised as: (a) wetting phenomena of the solid surface; (b) the mechanical force, or agitation, supplied to the system to break down the aggregates which has been kept to a minimum by using slow end-over-end rotation of the system; (c) the initial aggregation of the primary particles, which is a function of manufacture and storage. This may be considered to be a second-order effect in relation to (a) for the Sterling MT carbon black.

Experimental

Materials

Carbon black

Sterling MT carbon black (Cabot Carbon Ltd.) was in the form of spherical primary particles with an average particle diameter of 2000–3500 Å. Thus, the surface area is approximately 8 m^2/g and, in the absence of a more reliable value from nitrogen adsorption, this was assumed to be the surface area.

The carbon black was used as received, except in certain experiments for which the surface was pre-treated by cleaning by benzene extraction in a Soxhlet apparatus, further extraction with petroleum ether (b.p. 60–80°) for 3 h and drying in a vacuum oven at 100° overnight.

Sterling S carbon black (Cabot Carbon Ltd.), was similar to the Sterling MT but had an average particle diameter of 500–1000 Å.

Polyvinyl alcohols

The polyvinyl alcohols used are listed in Table I together with their physical properties. The two Alcotex samples were supplied by Revertex Ltd., while all other samples were Gohsenol polyvinyl alcohols from the Nippon Synthetic Chemical Industry Co. Ltd. The % hydrolysis shown indicates residual acetate groups.

The viscosities of the polyvinyl alcohol samples were measured at 25° over a range of concentrations using an Ubbelohde viscometer. For aqueous polyvinyl alcohol solutions:

$$[\eta] = 1\cdot6 \times 10^{-3} P^{0\cdot64} \exp(495/T)$$

where P is the degree of polymerisation of the polymer.[5] The molecular weights obtained are a complex average because of the unknown distribution of the degree of polymerisation for each sample, and hence cannot be considered absolute values.

Analysis of polyvinyl alcohol solutions

Based on the fact that polyvinyl borate solution reacts with iodine to give a blue colour,[6,7] an analytical method for the analysis of polyvinyl alcohol solutions has been developed.

It was found by experiment that the following reagent and method produced reliable results. A solution of potassium iodide (0·025M), boric acid (2·5 g/100 ml) and iodine (25 mg/100 ml), when mixed with an equal volume of a dilute polyvinyl alcohol solution, undergoes a colour change from yellow to green. The intensity of the green colour was shown to be a function of the concentration of the polyvinyl alcohol. The solutions were allowed to stand for 5 min before the optical density was measured. Plots of polyvinyl alcohol concentration vs. optical density at 546, 560 and 600 nm of the polyvinyl borate–iodine solution were straight lines for the concentration range 0–10 mg/100 ml of polyvinyl alcohol. These plots were used to determine the polyvinyl alcohol concentration of the solutions in the adsorption study.

Procedure for determining adsorption isotherms

All experiments were carried out at room temperature (20° ± 2°). Sterling MT (0·1 g) was pre-dispersed in water (25 ml) in a stoppered tube by ultra-sonic irradiation, and polyvinyl alcohol solution (25 ml) of the appropriate concentration was added to give the required final concentration. Effective contact between the solid surface and the solution was obtained by rotating (2 rev/min) the tube end-over-end for a pre-determined time. An aliquot of the liquid was then centrifuged at 55,000 × g for 3 min to remove all suspended carbon black. The clear polyvinyl alcohol solution obtained was removed and analysed according to the above method.

In the rate experiments, all the times quoted are those for end-over-end rotation, actual contact time of Sterling MT with the polyvinyl alcohol solution being some 5 min longer due to the centrifugation.

The results from this method of analysis assume that no polymer is removed by entrapment in the pores of the carbon black or by molecular weight fractionation by the centrifugation process.

Dispersion procedure

Sterling MT carbon black (0·5 g) was put into a stoppered tube which was then filled completely with the appropriate polyvinyl alcohol solution, added so that there were no air bubbles in the tube (about 52 ml). The tubes were rotated end-over-end at 2 rev/min for 1 h and then allowed to stand for a further hour before the degree of dispersion produced was assessed. The slow rotation and absence of air bubbles ensured that the aggregate of carbon black was subjected to very little mechanical agitation.

The degree of dispersion was estimated by measuring the percentage transmission at 490 nm of an aliquot of the suspension taken from the top of the tube.

Rates of dispersion were found by stopping the rotation at pre-determined times and measuring the percentage transmission as above but without allowing the tube to stand for longer than 1 min at any time.

Sterling MT which had been pre-treated was used in some of the rate experiments. The surface of the carbon black was altered by allowing it to pre-adsorb, over 3 h, the appropriate polyvinyl alcohol from a 10^{-2} g/100 ml solution, after which it was washed with water and dried. The state of aggregation was changed by completely dispersing the carbon black in water, using ultra-sonic irradiation, collecting it by centrifugation and then drying it (110°). In one case, polyvinyl alcohol was pre-adsorbed on the re-aggregated material.

Contact angles

A carbon film was formed by coating a glass slide with 'two-sided Sellotape' and dipping the slide into the carbon black powder. Sterling S was used for this because it formed a much more uniformly smooth surface than did the Sterling MT.

The slides were then allowed to stand in contact with the polyvinyl alcohol solution for the required time, rinsed with water and allowed to dry.

The contact angle of a water droplet against the carbon black–polyvinyl alcohol system was measured using a simple projection technique.[8]

Results

The change in dispersibility of Sterling MT in three polyvinyl alcohols, KH 17, GH 20 and NM 14, with change in concentration of these alcohols is shown in Fig. 1; dispersibility is equated to the optical density expressed as percentage transmission at 490 nm of the dispersion. The dispersibilities of Sterling MT in the other five polyvinyl alcohols, GL 03, GL 02, GM 14, Alcotex 88-05 and Alcotex 88-10 are given in Fig. 2. The results of the dispersibility experiments with Sterling S carbon black are given in Fig. 3. The effect of varying the time of end-over-end rotation, from 30 min to 2 h, on the dispersibility of the KH 17 and Alcotex 88-05 systems is shown in Fig. 4.

The rates of dispersion of Sterling MT in solutions of GL 02, GL 03, GM 14, and Alcotex 88-05, each at a concentration of 5 × 10^{-5} g/100 ml, are given in Fig. 5. Figs 6 and 7 show the changes in the rate of dispersion when the

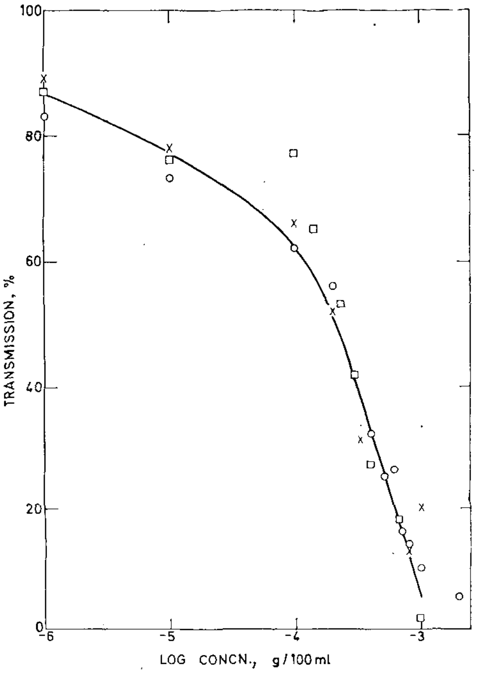

Fig. 1. *Dispersibility of Sterling MT in polyvinyl alcohol solutions*
○ KH 17; × GH 20; □ NM 14

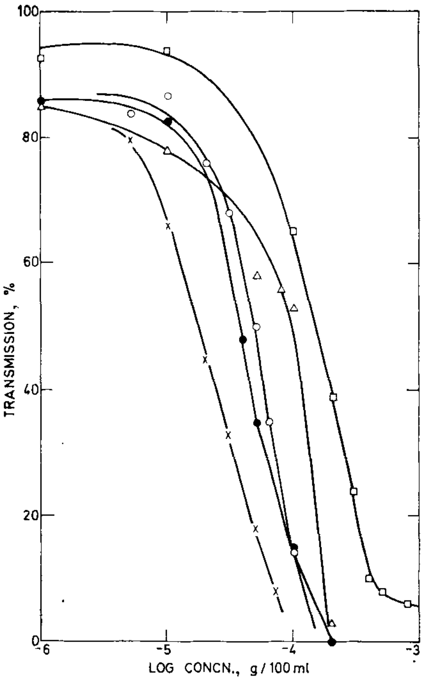

Fig. 2. *Dispersibility of Sterling MT in polyvinyl alcohol solutions*
○ GL 02; × GL 03; □ GM 14; ● Alcotex 88-05; △ Alcotex 88-10

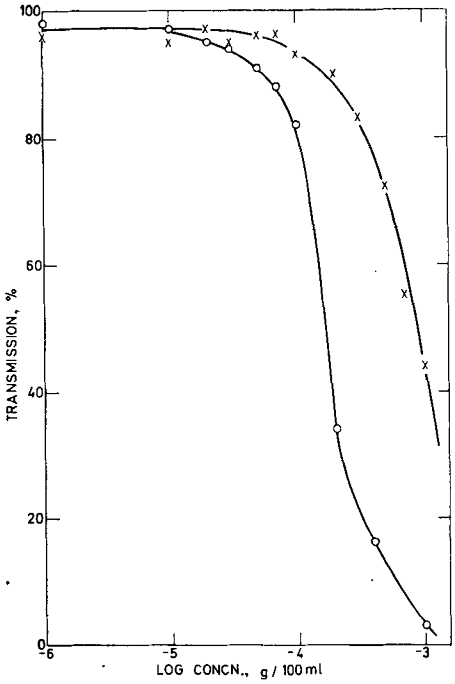

Fig. 3. *Dispersibility of Sterling S in polyvinyl alcohol solutions*
× KH 17; ○ Alcotex 88-05

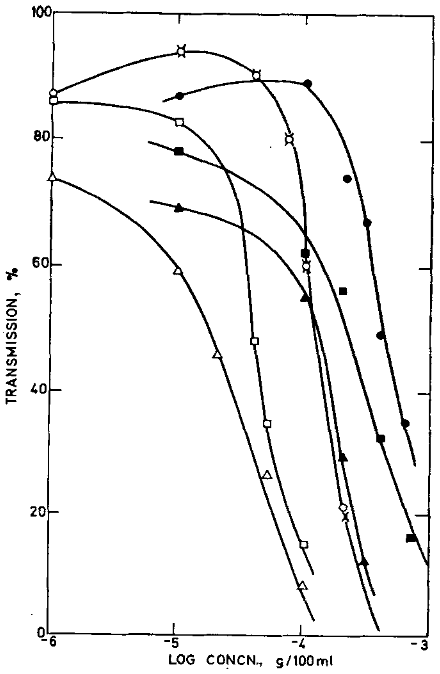

Fig. 4. *Effect of end-over-end rotation time on dispersibility*
Rotation time 120 min: ▲ KH 17; △ Alcotex 88-05
60 min: ■ KH 17; □ Alcotex 88-05
30 min: ● KH 17; ○ Alcotex 88-05
30 min and only 30 min standing: × Alcotex 88-05

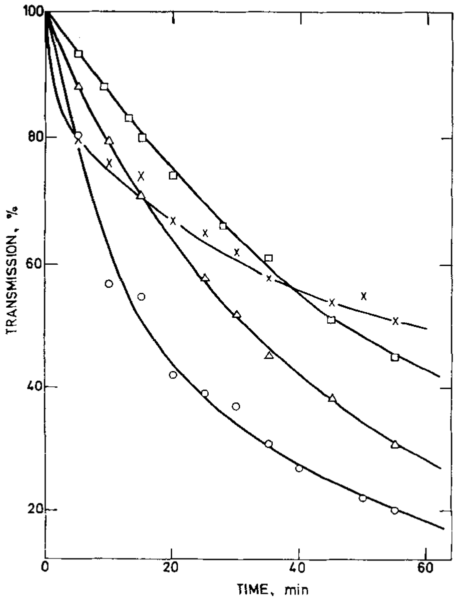

Fig. 5. *Rate of dispersion in solutions of polyvinyl alcohol at a concentration of 5 × 10^{-5} g/100 ml*
□ GL 03; × GM 14; △ Alcotex 88-05; ○ GL 02

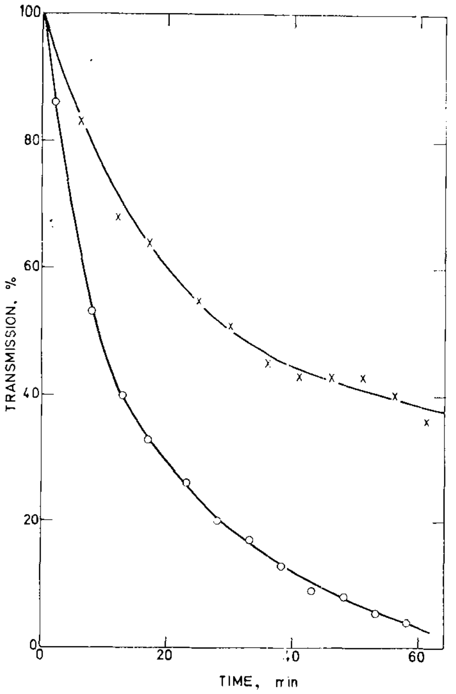

Fig. 6. *Effect of pre-treatment of Sterling MT on the rate of dispersion in solution of polyvinyl alcohol Alcotex 88-10 at a concentration of* 5×10^{-5} *g/100 ml*

× Surface as received; ○ surface with Alcotex 88-10 pre-adsorbed

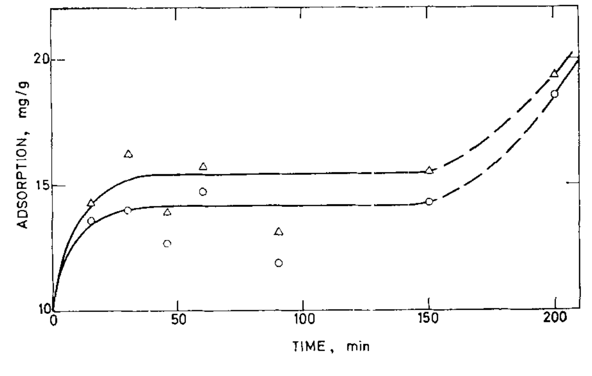

Fig. 8. *Rate of adsorption of polyvinyl alcohol on Sterling MT*
Solution concentration of 5 mg/100 ml, that is, an equilibrium concentration of 1·3 mg/100 ml
○ KH 17; △ Alcotex 88-05

Sterling MT is treated (a) by pre-adsorbing the appropriate polyvinyl alcohol, washing and drying; (b) by completely dispersing in water with ultra-sonic irradiation and then drying; and (c) by a combination of (a) and (b).

The rates of adsorption of two polyvinyl alcohols KH 17 and Alcotex 88-05 on to pre-dispersed Sterling MT are shown in Fig. 8.

The adsorption isotherms for KH 17, Alcotex 88-05 and GH 20 are shown in Fig. 9. In all cases measurements have been made for untreated carbon blacks, and for those extracted with benzene.

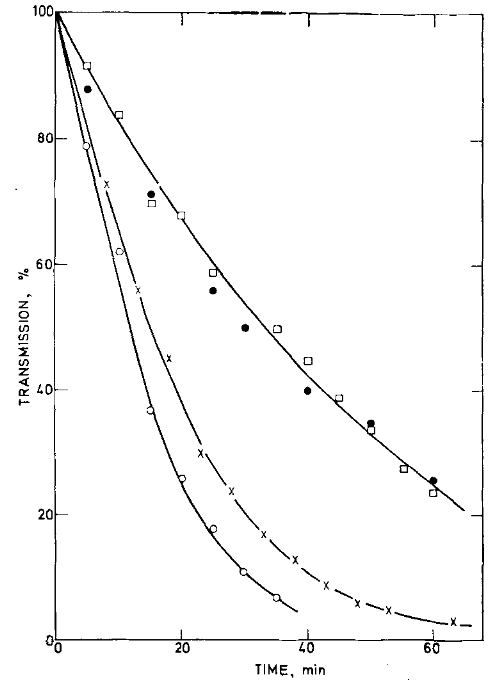

Fig. 7. *Effect of pre-treatment of Sterling MT on the rate of dispersion in solution of polyvinyl alcohol Alcotex 88-05 at a concentration of* 5×10^{-5} *g/100 ml*

● Surface as received; □ pre-ultra-sonified in water; × Alcotex 88-05 pre-adsorbed; ○ as for □ followed by pre-adsorption of Alcotex 88-05

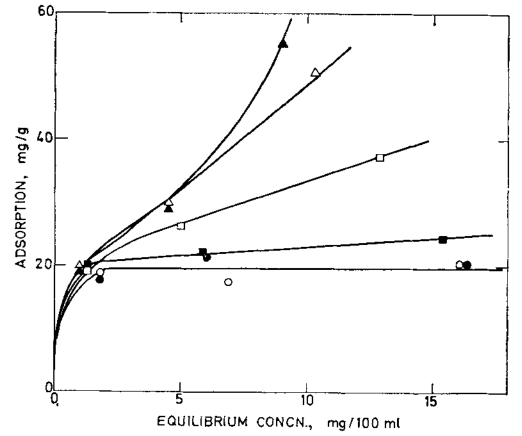

Fig. 9. *Adsorption isotherms for polyvinyl alcohols on Sterling MT*
○ GH 20 (as received), ● (benzene-extracted); △ Alcotex 88-05 (as received), ▲ (benzene-extracted); □ KH 17 (as received), ■ (benzene-extracted)

As the adsorption is rapid, the time effects observed in the dispersibility experiments are not directly related to adsorption but are a function of the dispersion process. They are due to the rate of penetration of polyvinyl alcohol into the 'pores' of the carbon black aggregate. This may be illustrated by examining the rate of uptake of polyvinyl alcohol under the dispersion conditions. Fig. 10 gives the results for GH 20, KH 17 and Alcotex 88-05. The quantities of 1 g of Sterling MT in 50 ml of solutions of concentration 10^{-2} g/100 ml were chosen so that initial aggregation was high (i.e. large number of 'pores') and appreciable dispersion would occur; that is, initially there was a large surface area exposed and subsequent adsorption would have been shown by a very rapid increase in measured uptake.

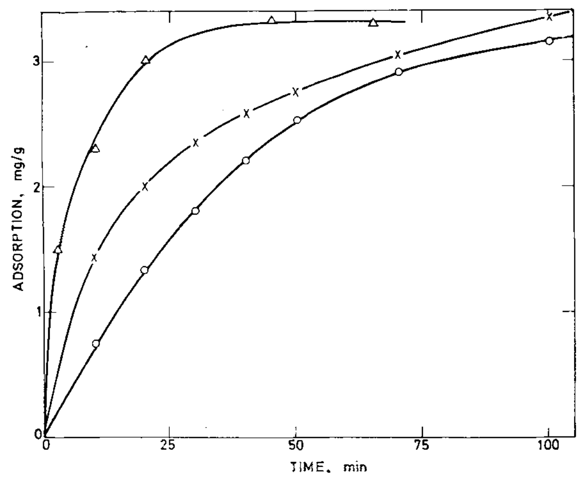

Fig. 10. *Rate of polyvinyl alcohol adsorption on Sterling MT during dispersion*
Solution concentration 10^{-2} g/100 ml
○ KH 17; × GH 20; △ Alcotex 88-05

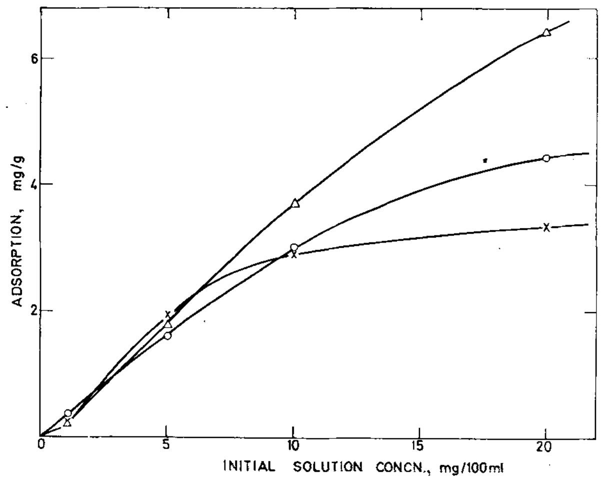

Fig. 11. *Adsorption of polyvinyl alcohol on Sterling MT under conditions of dispersion (3 h)*
○ KH 17; × GH 20; △ Alcotex 88-05

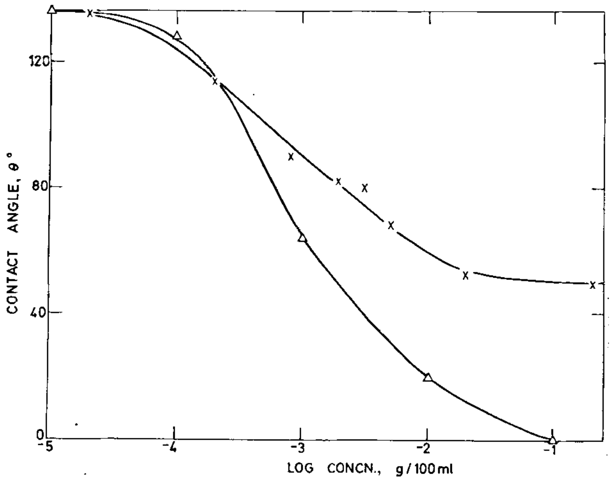

Fig 12. *Contact angle of water on Sterling S after surface exposed to polyvinyl alcohol solution for 1 h*
× KH 17; △ Alcotex 88-05

The adsorption isotherms for the same systems under dispersion conditions are shown in Fig. 11. The results of the contact angle measurements on Sterling S carbon black are shown in Fig. 12.

Discussion

The surface of Sterling MT carbon black is not easily wetted by water and a dispersion in water alone cannot be formed simply by shaking but requires ultra-sonic irradiation. Under the conditions of end-over-end rotation used in these experiments Sterling MT in water remains as a solid aggregate almost indefinitely. The results given in Figs 1–4 show that the dispersibility of Sterling MT in polyvinyl alcohol solutions is directly related to the concentration of the polyvinyl alcohol. Preliminary experiments showed that varying the weight of Sterling MT in the tube (up to 1·0 g) had no effect on the dispersibility results. There is a marked change in the dispersibility at a critical polyvinyl alcohol concentration of between 10^{-5} and 10^{-4} g/100 ml. The spread of results in Fig. 2 is due to the differences in the molecular weights of the polyvinyl alcohol samples.

The greatly increased dispersibility at a critical concentration must be a function of the adsorption of polyvinyl alcohol on the carbon black surface and the associated change this produces, i.e., an increase in the hydrophilic nature of the surface. This should be in accord with the general theory of wetting, that is, a significant change in the term $\gamma_{LV} \cos \theta$ takes place at this concentration. The major change will presumably be in the contact angle, since the critical concentration is so small. This may be demonstrated by the results on Sterling S. Owing to the difference in their particle sizes, the critical concentration of polyvinyl alcohol for dispersions of Sterling S is higher than that for Sterling MT, Fig. 3. The contact angle approaches 90° in the region of the critical concentration (Fig. 12).

Increasing the time of end-over-end rotation (Fig. 4) slightly lowers the critical concentration for dispersion and gives a more diffuse transition. The increase in the dispersibility may be partly explained by the rate of penetration of the polyvinyl alcohol solution into the 'pores' of the aggregate. For long periods of rotation (2 h), penetration will be appreciable at low concentrations and this will cause a measurable change in the percentage transmission.

The increase in mechanical action on the aggregates is insignificant and may be neglected as a contributory factor to increased dispersibility. Also shown in Fig. 4 are the results that were obtained after allowing the dispersion to stand for 30 min (as opposed to 1 h) before measuring the percentage light transmission; it can be seen that the transmission values are unaffected. With a fluctuating dispersion, the percentage transmission would increase with time, and the stability of the system is therefore not interfering with the dispersibility measurements. This is to be expected since Sterling MT has a high negative electrophoretic mobility in water, which produces a large electrostatic repulsion force between particles.

The rates of dispersion of Sterling MT in several polyvinyl alcohols of differing molecular weight, at 5×10^{-5} g/100 ml concentration, are shown in Fig. 5. The results indicate that faster and more efficient dispersion is achieved with the samples of lower molecular weight. This would follow from a consideration of the radii of the 'pores' in the aggregate and the size of the polymer molecules, assuming that they have a random-coil configuration in solution. However, in the initial stages there is no marked dependence on molecular weight, possibly because of large molecular weight distributions in the samples. Low molecular weight polymers, being more rapidly adsorbed from solution,[9] would initially obscure the overall effect of a high molecular weight, as shown by GM 14.

Pre-adsorbing polyvinyl alcohol on to the carbon black surface greatly increases the dispersibility, while, in comparison, changing the state of aggregation does not affect it to any extent (Figs 6 and 7).

The rates of adsorption of the polyvinyl alcohols KH 17 and Alcotex 88-05 on to pre-dispersed Sterling MT are shown in Fig. 8. An apparent equilibrium value is established in less than 20 min, which is rapid for polymer adsorption. There is an indication that a further slow rise in adsorption occurs after 3 h which could be due to re-orientation of the polymer molecules on the carbon black surface. Such behaviour has been reported for the adsorption of polyvinyl acetate from benzene on to chrome plate.[10]

The adsorption isotherms for the three polyvinyl alcohols on to pre-dispersed Sterling MT, after 3 h contact, are given in Fig. 9. The isotherms show a steep increase from the origin in the amount adsorbed, which reaches a plateau value for KH 17 and GH 20. In the case of Alcotex 88-05, no limiting value was found in the concentration range examined, presumably because of the low molecular weight of this polymer. It is usual for the maximum adsorption to increase with increasing molecular weight. The other polyvinyl alcohol samples may be expected to give similar adsorption isotherms. Only GL 02 and GL 03 have molecular weights comparable with that of Alcotex 88-05, and these may therefore give isotherms of the same type. In general, factors which might influence the isotherms have been summarised before.[3,4]

To ensure that extraneous material on the surface of Sterling MT was not influencing the adsorption, the isotherms were repeated on a benzene-extracted sample. For GH 20 and Alcotex 88-05, the isotherms for the extracted and unextracted samples are coincident within experimental error. However, with KH 17, significantly lower adsorption occurs on the benzene-extracted surface than on the normal surface. An explanation for this may be envisaged in terms of the low degree of hydrolysis of KH 17 (80 %) compared with that of the other two polyvinyl alcohols and interaction with the surface tar-like material.

Knowing the degree of polymerisation, it is possible to calculate the average molecular dimensions of an unbranched polymer chain,[11] in particular, the end-to-end distance, h_{av}, and the average radius of gyration, R_G. The polymer chain is assumed to be flexible and in dilute solution it will take up a random-coil configuration. Polyvinyl alcohols formed from the hydrolysis of vinyl acetates have a head-to-tail unbranched chain configuration with as little as 1–2 % of head-to-head sequence.[12] Calculated values of h_{av} and R_G are shown in Table I. Alcotex 88-05 and GL 02 may have molecular weights which are too low for the random-coil configuration to apply reasonably, in which case R_G for these samples is in error.

It is considered[13] that under many conditions polymers adsorb from dilute solutions at the solid/liquid interface in the form of monolayers of molecular coils whose dimensions are proportional to those of the free coil in that particular solution. Hence, assuming that the polyvinyl alcohol molecules are adsorbed in this manner, the maximum adsorption A_∞ in g/g is given by:

$$A_\infty = \frac{SM}{MR_G^2N}$$

where S is the surface area available to the polymer (for Sterling MT this is taken to be 8 m²/g), M is the molecular weight of the polymer and N is Avogadro's number. A comparison of A_∞ values calculated from the above equation and the experimental adsorption plateau values is shown in Table II. It can be seen that this model of the adsorbed layer gives a maximum adsorption which is less than that found experimentally. Therefore, it may be concluded that at high surface coverage the coils are compressed or entangled together, or, alternatively, there may be multi-layer adsorption. In the case of low molecular weight Alcotex 88-05, the adsorption of 50 mg/g is equivalent to a monolayer coverage of 1 molecule per 200 Å², which implies that the polymer molecule is attached at only a few points on the chain. One extreme situation would be single-point attachment, but this probably occurs only with a polyvinyl alcohol which has a much lower molecular weight.

In the dispersion experiments, the critical concentration of 5×10^{-5} g/100 ml for dispersion is not sufficient to give a saturation adsorption for all the surface of the carbon black present. Unfortunately, with the dispersion process it is not possible to know the fraction of the total surface area which is initially exposed or to measure the amount of carbon black which is completely dispersed. Nevertheless, some indication of the degree of polyvinyl alcohol surface coverage that is

TABLE II

Maximum adsorption of polyvinyl alcohol on Sterling MT

Code	A_∞(calc.), mg/g	A_∞(expt.), mg/g
Alcotex 88–05	9·0	> 50
GH 20	9·9	20
KH 17	10·3	24 and > 40 for extracted surface

TABLE I

Physical properties of polyvinyl alcohols

Code	Hydrolysis*, %	Viscosity of 4 % solution,* cP	Intrinsic viscosity [η] ± 0·02	Mol. wt. (viscosity average)	h_{av}, Å	R_g, Å
Alcotex 88-05	88	5	0·22	8500	47	19
Alcotex 88-10	88	10	0·5	30,000	89	36
GL 02	88	2–3	0·18	6000	40	16
GL 03	88	3–4	0·28	11,500	55	23
NM 14	100	21–25	0·49	25,000	84	34
GM 14	88	21–25	0·55	40,000	106	42
KH 17	80	32–38	0·55	35,000	94	38
GH 20	88	40–46	0·72	49,000	113	46

*Manufacturer's data

required to give the Sterling MT an essentially hydrophilic surface may be obtained by measuring the polyvinyl alcohol uptake in a dispersion experiment. Using 1 g of Sterling MT in 50 ml of the appropriate polyvinyl alcohol solution, the adsorption of the polymer was measured after 3 h of end-over-end rotation, that is, under apparent equilibrium adsorption conditions. The results for the three polyvinyl alcohols are given in Fig. 7. In each case, there is an almost linear increase in uptake but not quite all the available polyvinyl alcohol is adsorbed. Assuming that at the high concentration of 2×10^{-2} g/100 ml all the surface area of the carbon black has been exposed to polyvinyl alcohol, which from the appearance of the dispersions produced is reasonable, the amount adsorbed is less than monolayer coverage of coiled polymer chains. Therefore, it would appear that only a low surface coverage of polyvinyl alcohol molecules is necessary to produce a hydrophilic surface. This might be expected if it is considered that the adsorbed polyvinyl alcohol molecule has hydrogen-bonded water molecules associated with its large numbers of hydroxyl groups.

Unilever Research Laboratory,
Port Sunlight,
Wirral,
Cheshire, L62 4XN

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