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International Journal of Pharmaceutics 154 (1997) 9–17

international
journal of
pharmaceutics

Wettability parameters and deformational behaviour of powder–liquid mixes in the funicular agglomeration phase

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Accepted 23 March 1997

Abstract

Wettability of two powdered materials (lactose and sulfadiazine) of similar particle size is quantified as contact angle, spreading coefficients and work of adhesion. On the basis of overwetting tests, performed in a specially-constructed wet-kneading rheometer, the agglomeration phases are distinguished by recording the resistance to mixing as torque exerted on the mixing vessel with increasing quantities of different granulating fluids (water, isopropanol, water/isopropanol mixture and liquid paraffin). Separate powder–liquid mixing experiments are carried out, with selected amounts of liquids, and the tensile strength of the resulting wet masses is measured at different consolidation states together with their resistance to densification. It was found that both the amount of granulating liquid, corresponding to the mean funicular agglomeration state, and the deformational behaviour of wet masses with certain liquid volume fraction, quantified as tensile strength and resistance to densification are related to the work of adhesion but only for liquids of similar viscosity. No correlation was observed between the torque and the work of adhesion or the viscosity of the granulating liquid. © 1997 Elsevier Science B.V.

Keywords: Wettability; Contact angle; Spreading; Adhesion work; Wet granulation; Agglomeration; Tensile strength; Resistance to densification

1. Introduction

In the wet granulation (shear mixing and massing) some physical interactions occur between the binding liquid and the powder substrate, which

affect the rheological behaviour of the wet masses and the quantity of liquid required for optimal granule formation. In practice, the optimal quantity of the granulating liquid to get a given granule size is often fixed empirically but it can also be monitored by recording the resistance to mixing either as torque or as electrical power consumption.

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Table 1

Contact angle of powder substrates with two test liquids and their free surface energy (γ_s)

Powder	Contact angle θ ($^{\circ}$) for:		Surface tension (mN/m)		
	Water	Meth. iodide	γ_s	γ_s^d	γ_s^p
Lactose	30	50	68.9	34.9	34.0
Sulfadiazine	71	54	49.1	33.0	16.1

 γ_s^d is the dispersion component of γ_s . γ_s^p is the polar component of γ_s .

Many investigations have shown that the resistance to mixing profiles are similar when different types of planetary and rapid mixing granulators are used. This similarity has been attributed to the mechanical forces induced by the different types of mixers which have a much smaller influence than the granulating liquid and the powdered material on the resistance to mixing (Hunter and Ganderton, 1973; Bier et al., 1979; Lindberg et al., 1982; Ritala et al., 1988; Wan and Prasad, 1988; Usteri and Leuenberger, 1989; Ritala and Virtanen, 1991). Therefore, the profiles of resistance to mixing allow the comparison of different wet masses irrespective of their processing histories and can be used for quality control, for establishing reproducibility of wet granulation or for developing a formulation (Hancock et al., 1992; Corvari et al., 1992).

The resistance to mixing of wet agglomerates, which describes their deformational behaviour, should be determined from the liquid bridges, the physical, van der Waals', and the mechanical, frictional, interparticle forces. All these are affected from the physical interactions occurring between the binding liquid and the powder substrate (wetting, spreading, adhesion and possibly solvating and swelling of the substrate) and besides the resistance to mixing or torque profiles the deformational behaviour of wet granulations may be represented by the tensile strength and the resistance to densification during their compression.

In the present work, the wettability of two powdered materials (lactose and sulfadiazine) having similar particle size is quantified as contact angle, spreading coefficients and work of adhesion. Then the agglomeration phases are distin-

guished on the basis of overwetting tests performed in a specially-constructed wet-kneading rheometer by measuring the resistance to mixing with increasing quantities of the different granulating fluids (water, isopropanol, water/isopropanol mixture and liquid paraffin). Further separate mixing experiments are carried out, with selected amounts of liquids, and the tensile strength of the resulting wet masses is measured at different consolidation states together with their resistance to densification. The aim of the work is to elucidate the relation between the different wettability parameters, the requirement of liquid and the deformational behaviour of the wet masses in the funicular agglomeration phase corresponding to optimal production of usable granulations.

2. Materials and methods

2.1. Materials

The materials used in this study were: alpha lactose monohydrate (DMV, Veghel, The Netherlands); micro-crystalline sulfadiazine (ACF, Holland); isopropanol (Merck, Darmstadt, Germany); light liquid paraffin (Merck, Darmstadt, Germany) and distilled water. For both lactose and sulfadiazine, the fraction of particles finer than 15 μm was obtained using a zigzag classifier (Multiplex-Alpine, Augsburg, Germany).

2.2. Characterisation of materials

The properties influencing the granulation process were determined, such as: the density (bulk,

Table 2

Surface tension and viscosity of the granulating liquids and contact angle, work of adhesion and spreading coefficients between liquids and powders

Liquid*	Surface tension (mN/m)	Viscosity (cp)	Contact angle with powder substrate θ (°)	Adhesion work (mN/m)	Spreading coefficient (mN/m)	
					λ_{LS}	λ_{SL}
Water _(L)	71.6	1.4	30	133	-9.6	-4.3
Water _(S)	72.2	1.0	71	96	-48.7	-2.5
Water/Iso- propanol _(L)	25.2	3.3	32	88	22.0	-65.5
Water/Iso- propanol _(S)	25.6	3.0	33	67	16.1	-30.9
Isopropanol _(L)	21.8	1.9	35	64	20.7	-73.5
Isopropanol _(S)	21.9	1.9	28	60	16.2	-38.2
Paraffin _(L)	29.6	32.1	39	79	19.4	-59.2
Paraffin _(S)	29.4	29.2	35	72	13.4	-25.9

* Saturated with powder substrate (Lactose_(L) and Sulfadiazine_(S)).

tap and true) of the powders, the wettability or contact angles of powders with the granulating liquids (θ), the surface tension of the liquids (γ_L), the work of adhesion [$W_a = \gamma_L(1 + \cos \theta)$], the spreading coefficients ($\lambda_{LS} = W_a - 2\gamma_L$ and $\lambda_{SL} = W_a - 2\gamma_S$) and the viscosity of the granulating liquids. All the granulating liquids were presaturated with powder material in order to eliminate the solubility effect.

The true density of the powders was measured on an air comparison pycnometer (Beckman, Model 930). The bulk and tap densities were measured in an J. Engelmann volumeter and were found very close for the two powder substrates. The contact angle was determined from the maximum height of a drop on compacts (Kossen and Heertjes, 1965). The surface tension of liquids was measured by using a Du Noüy tensiometer (Krüss 13337, Hamburg, Germany) and the surface free energy of powders, γ_S , was obtained from contact angle measurements with two test liquids, (presaturated water and methylene iodide purchased from Aldrich-Chemie, Germany) and from contact angles of these liquids against sheets of paraffin (Parafilm, American Can Company, Neenach, USA) as described by Malamataris and Pilpel (1982). The viscosity of the granulating liquids was measured

at 25°C with a glass capillary (Ostwald) viscometer. Table 1 gives the contact angle results with the two test liquids and the surface free energy of the two powder substrates employed. Table 2 lists numerical values of surface tension and viscosity of the granulating liquids and of contact angle, work of adhesion and spreading coefficients between liquids and powders.

2.3. Powder–liquid kneading

A specially-constructed wet-kneading rheometer (shear mixing and massing apparatus) was used for measuring both the electric power consumption and the torque exerted on the mixing vessel, which were always proportional. Therefore, only torque will be considered in this investigation.

The wet-kneading rheometer, shown diagrammatically in Fig. 1, was consisted of a three blade impeller placed centrally in a 1-l cylindrical vessel. The impeller was fitted on a stirrer (IKA-RE 162, Staufen, Germany) which was linked to a recorder of the electrical current (ampere) required for maintaining constant the stirring rate. Recording was achieved through a current to voltage transformer and a linear rectification unit.

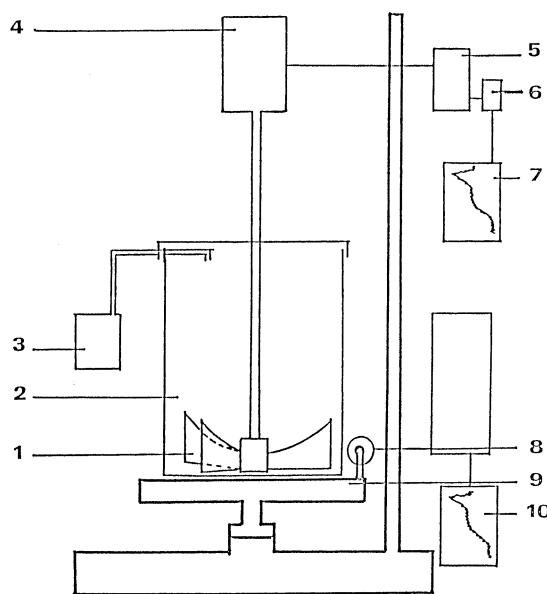


Fig. 1. Diagram of wet kneading rheometer. (1) Three blade impeller, (2) mixing vessel, (3) peristaltic-tube pump, (4) stirrer, (5) stirring speed controller, (6) current to voltage transformer, (7) electric power recorder, (8) load cell and amplifier, (9) rotating platform and (10) torque recorder.

The mixing vessel was mounted on a rotating platform linked tangentially to a dynamometer (100 N load cell with amplifier) connected with a strip chart recorder (Knauer, Berlin, Germany). A peristaltic-tube-pump was employed for the continuous addition of granulating liquid at constant

rate in order to have information about the agglomeration process.

2.3.1. Overwetting tests

Powder–liquid mixing was first performed until overwetting of the powder. Before starting each mixing, a steady baseline of torque value was obtained from the empty mixer over a short period of 30 s. Then a fixed quantity of 150 g powder corresponding to about 500 ml of bulk material was added to the mixing bowl after sieving to destroy the lumps. It was selected as equivalent to 50% of the vessel volume, sufficient to cover the mixing blades at all times.

The powder substrate was dry-mixed in the rheometer for 1–2 min, using speed of 250 rpm, to obtain a stable base line response (D_m , Fig. 2).

Then, the torque recorder was zeroed and the addition of liquid was started. The liquid was added slowly and continuously with the mixer motor running until a rapid reduction of the torque was observed due to overwetting of the powder substrate.

All the overwetting tests were performed in duplicate and from the profiles of torque vs. granulating liquid addition the characteristic agglomeration phases were established and the quantities of granulation liquid corresponding to the boundaries of these phases (S_3 , S_4 and S_5 , Fig. 2) were calculated from the intersection of tangents (Bier et al., 1979).

Table 3
Torque and liquid addition at different agglomeration stages (S_3 , S_4 and S_5)

Powder	Liquid*	Torque (N·m)				Liquid addition (ml)			
		S_3	S_4	S_5	$S_3 + S_4/2$	S_3	S_4	S_5	$S_3 + S_4/2$
Lactose	Water	0.44	0.74	1.52	0.59	5	29	42	17
	Water/Isopropanol	0.32	0.64	1.01	0.48	8	44	57	26
	Isopropanol	0.56	0.79	1.25	0.68	12	60	81	36
	Paraffin	0.47	0.81	1.44	0.64	15	65	83	40
Sulfadiazine	Water	0.57	0.61	1.62	0.59	7	28	41	17
	Water/Isopropanol	0.34	0.54	1.32	0.44	7	34	52	20.5
	Isopropanol	0.51	0.69	1.27	0.60	11	43	62	27
	Paraffin	0.71	1.01	1.86	0.86	19	40	54	29.5

* Saturated with powder substrate.

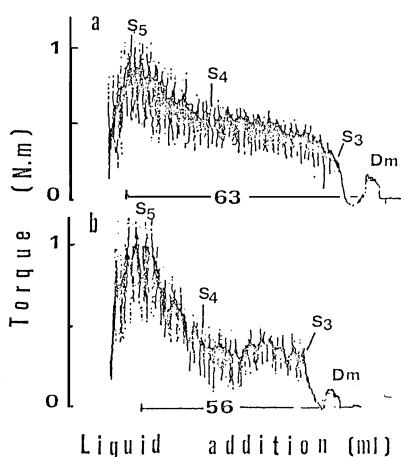


Fig. 2. Torque vs. addition of water/isopropanol mixture in lactose (a) and sulfadiazine (b) powders.

2.3.2. Funicular agglomeration

Further wet-kneading experiments were performed by adding selected amounts of granulating fluids, between the lower and upper boundary of the phase of funicular interparticle bonding, which is necessary for the production of usable granulations. The rate of liquid addition was varied depending on the total amount of liquid added, in order to achieve duration of the granulation between 5 and 10 min. No massing was applied after the end of the liquid addition. The tensile strength at different consolidation state and the resistance to densification of the resulting wet granulations were measured immediately after the wet massing.

2.4. Tensile and densification tests

The tensile strength, T , of wet granulations, corresponding to funicular bonding, was measured at packing fractions, p_f , produced by consolidating them at six stress levels with loads from 10 to 150 N. The apparatus for carrying out the tensile strength measurements was a modified version of the horizontal split cell. It was equipped with a plunger attached to a load platform for

consolidation of the granulations at different interparticulate porosity or packing fraction. Fuller details on the theory and design of the equipment have been published (Ashton et al., 1964; Eaves and Jones, 1972).

Samples were prepared for testing by filling the cell with wet granulations after passing them through a 2.0-mm sieve to avoid lumps. Then the bed of the wet granulations was consolidated by means of the plunger and the tensile strength at the packing fraction achieved was obtained from its weight, the cross-sectional area of the bed and the force required to split it.

The consolidating stress, P , corresponding to a particular packing fraction (p_f) level of 0.5, is defined as resistance to densification. Both T and P , at the fixed p_f were calculated from corresponding logarithmic equations relating them with p_f (Malamataris and Pilpel, 1980): $\log T = A \cdot p_f + B$ and $\log P = A' \cdot p_f + B'$.

3. Results and discussion

Typical profiles of torque exerted on the mixing vessel during the overwetting tests are shown in Fig. 2. These profiles show that, during the initial dry mixing of the substrate powders, the torque responses, D_m , were very similar, probably due to the similar particle properties such as size and density. The five characteristic phases describing the various agglomeration events (Bier et al., 1979) could be distinguished in all the profiles of the overwetting tests and appreciable differences are revealed between the values of both torque and liquid consumption corresponding to the boundaries of the agglomeration phases of the different mixtures. Table 3 gives the liquid addition as well as the torque corresponding to the different boundaries of agglomeration phases (S_3 , S_4 and S_5) and to the mid-stage of the funicular agglomeration ($S_3 + S_4$)/2 for all the mixtures studied.

From the results in Tables 2 and 3 it is seen that the liquid addition, at the mid-stage of funicular agglomeration ($S_3 + S_4$)/2, when the resistance to mixing levels off (Table 3), is inversely

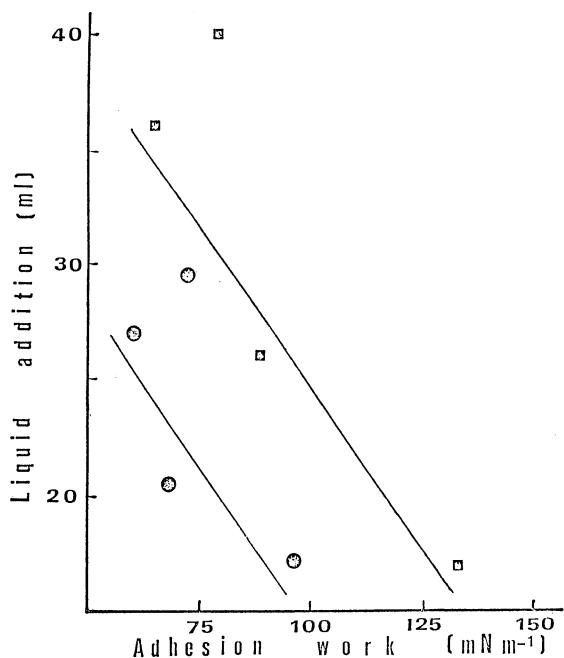


Fig. 3. Liquid addition at the mid-stage of funicular agglomeration $(S_3 + S_4)/2$ vs. adhesion work between liquids and powders: lactose (■) and sulfadiazine (●).

related to the work of adhesion (Fig. 3) with some greater deviation for paraffin which has higher viscosity. The spreading coefficients (Table 3) of granulating liquids on the substrates, λ_{LS} , are negative for water with both the powders used, but those for isopropanol, mixture of water/isopropanol and paraffin are positive, while the coefficients (Table 3) corresponding to spreading of substrate powders on the granulating liquids, λ_{SL} , are all negative showing that this spreading will not be favoured in any of the systems investigated. These data indicate that all the granulating liquids will behave similarly when mixed with the powder substrates and the wet agglomerates are formed in similar way. Also, from the results of Tables 2 and 3, no correlation can be seen between the torque and the work of adhesion or the viscosity of the liquids. The torque expresses the resistance to mixing which is the result of: (i) the development of mobile interparticle (liquid) bridges within agglomerates and (ii) the action of frictional forces between agglomerates. These can be expressed as: (i) tensile strength and (ii) shear strength (i.e. resistance to densification) of the

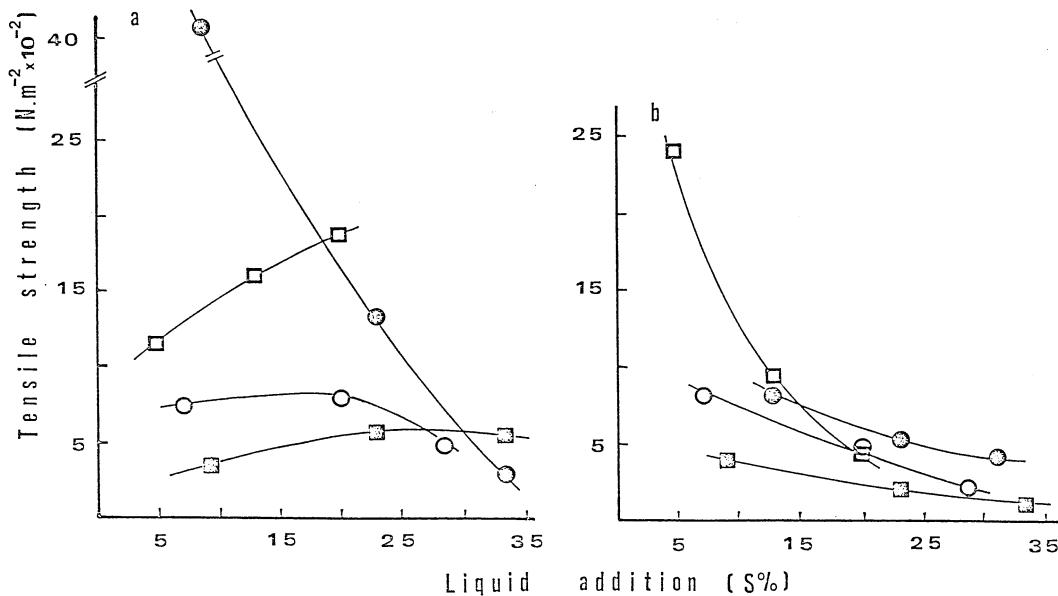


Fig. 4. Tensile strength vs. liquid addition (S%), at p_f 0.5, for wet agglomerates of lactose (a) and sulfadiazine (b) with different liquids: (■) water, (○) water/isopropanol, (□) isopropanol, and (●) paraffin.

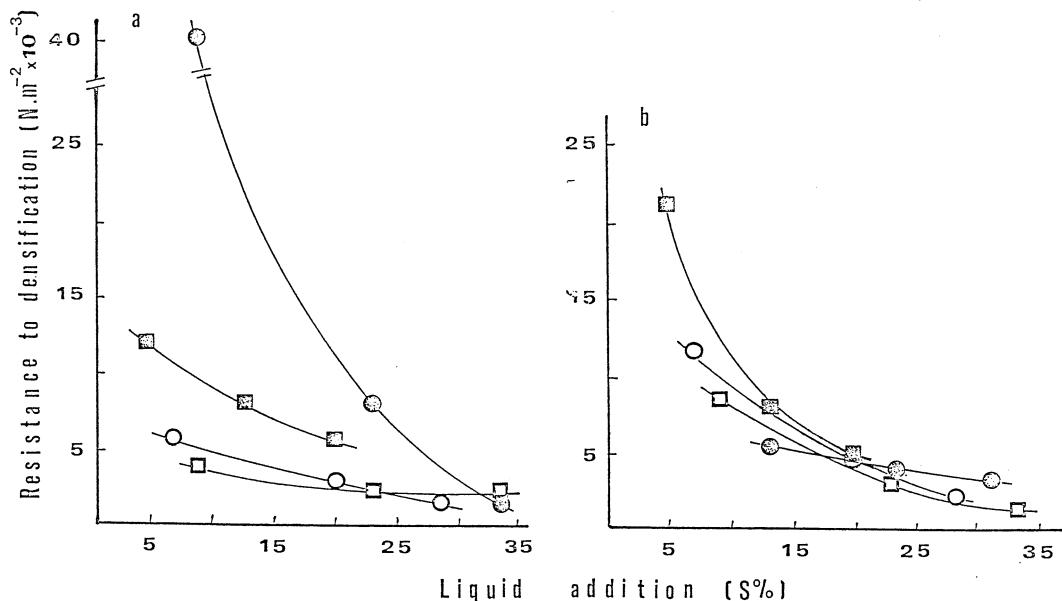


Fig. 5. Applied stress required to achieve p_f 0.5 vs. liquid addition (S%) for wet agglomerates (key as in Fig. 4).

moistened powder bed (Malamataris and Pilpel, 1980).

In Fig. 4 the tensile strength, calculated for a fixed p_f (0.5), is plotted against the quantity of added liquid for different powder–liquid mixes corresponding within the funicular agglomeration phase. The liquid added is expressed in terms of the volume of liquid as a percent of the total volume of true solid plus liquid (S%); this is used because it allows the comparison of powders with different true densities (Hancock et al., 1994).

From the plots in Fig. 4, it is seen that: (a) the tensile strength of lactose increases with the addition of water and isopropanol, (b) with the water/isopropanol mixture, it attains a maximum and then decreases, and (c) in contrast, the tensile strength of lactose decreases with the addition of paraffin.

These tensile strength changes can be attributed to the proportion and strength of lactose–lactose and lactose–liquid bonds developed as well as the strength of liquid interparticle bridges. The initial increase in tensile strength may be the result of liquid bridges acting additionally to the lactose–lactose bonding. The subsequent reduction in ten-

sile strength may be the result of a decrease in the number of lactose–lactose bonds and a predominance of the mobile and weak liquid interparticle bridges. The addition of paraffin to lactose seems to result initially in the development of very strong interparticle liquid bridges due to its high viscosity; such bridges should act in addition to the lactose–lactose bonds. At higher concentration of liquid paraffin the masking of lactose–lactose bonds and predominance of paraffin bridging would result in the continuous tensile strength reduction observed in Fig. 4.

In the case of sulfadiazine, the tensile strength decreases with the addition of all the liquids, as in the case of lactose–paraffin mixtures. The different pattern of tensile strength changes following the addition of liquids to lactose and sulfadiazine can be partially attributed to the higher cohesive-ness of sulfadiazine (The tensile strength at $p_f = 0.5$ for unwetted lactose was 636 and for sulfadiazine 1350 N/m²). On the addition of liquids, the development of weak mobile interparticle bridges, replacing the substrate interparticle attractive forces, should be responsible for the marked reduction in tensile strength.

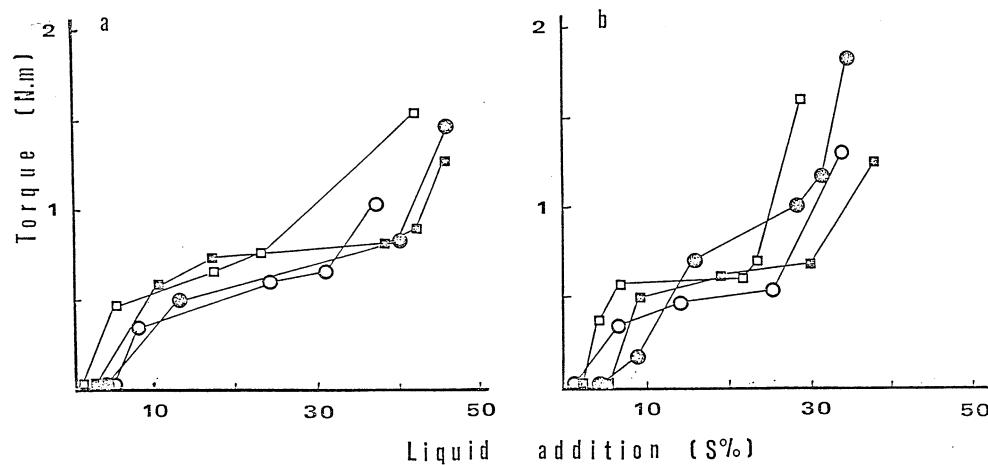


Fig. 6. Torque exerted on the mixing vessel vs liquid addition ($S\%$) during the overwetting tests (key as in Fig. 4).

As far as the resistance to compression is concerned (Fig. 5), there is a decrease for both lactose and sulfadiazine on the addition of all the liquids. Since the resistance to compression depends mainly on the action of frictional, mechanical, interparticle forces, its decrease in Fig. 5 shows that all the liquids are acting as lubricants making easier for the particles to slide past each other during the process of densification due to compression.

In order to compare the tensile strength and resistance to compression results with the wettability parameters, a fixed level of 15% liquid addition ($S\%$) was chosen and their values were

obtained on the basis of their plots vs. $S\%$, shown in Figs. 4 and 5. This level of 15% liquid addition ($S\%$) was selected on the basis of the plots of torque exerted on the mixing vessel during the overwetting tests vs. $S\%$, shown in Fig. 6, because it corresponds to the funicular agglomeration phase for all the systems investigated. Table 4 gives the results of tensile strength and resistance to densification for all the systems together with the work of adhesion. From these results (Table 4), it is seen that both tensile strength and resistance to densification decrease with the work of adhesion except for the case of the more viscous paraffin.

Table 4
Results of work of adhesion, tensile strength (at p_f 0.5) and resistance to densification corresponding to 15% liquid addition

Powder	Liquid*	Adhesion work (mN/m)	Tensile strength (N/m ²)	Resistance to densification (kN/m ²)
Lactose	Water	133	1650	7.2
	Water/Isopropanol	88	810	3.8
	Isopropanol	64	480	3.0
	Paraffin	79	2400	18.2
Sulfadiazine	Water	96	810	7.3
	Water/Isopropanol	67	570	6.4
	Isopropanol	60	390	6.0
	Paraffin	72	770	5.5

* Saturated with powder substrate.

4. Conclusion

In conclusion we can say that both the amount of liquid required for the mean funicular agglomeration state ($(S_3 + S_4)/2$, representing the optimal formation of usable granulations) and the deformational behaviour of wet masses at certain volume fraction of liquid component (quantified on the basis of the tensile strength and resistance to densification) are related to the work of adhesion between the powder substrate and the binding liquid, but only for liquids of similar viscosity.

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