

Adhesion of Pharmaceutical Binding Agents I-Adhesion to polymeric materials

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Abstract :

Adhesion of three commonly used pharmaceutical binding agents, HPMC , PVP and Gelatin to five different polymeric sheet materials was studied. After conditioning, the bond strength of the specimens were measured by shear testing method using a suitably designed apparatus. The results were correlated to the surface energies and the solubility parameters of the adherends. It is concluded that the thermodynamic properties and the solubility parameters are dominant when the mechanisms of adhesion are by adsorption and diffusion respectively.

Key words: Bond strength; surface energy; solubility parameter.

Introduction:

The requirement of an appropriate granule and/or tablet is their withstanding various mechanical stresses during processing and handling. The main factor affecting this property is the bond strength between particles. These bonds are formed from different sources e.g. recrystallisation, binder -substrate adhesion and deformation.

Binder are usually added to improve the strength of most pharmaceutical tableting. Evaluation of binders was investigated by assessing the various properties of granules and tablets (1,2).

The mechanical properties of the binder were related to ultimate bond strength of the

granule and to wetting (3,4). Tensile testing of hydroxypropylmethyl cellulose as a binder to different polymeric sheets was related to the thermodynamic properties of the substrates, spreading coefficients and solubility parameters (5,6,7,8).

The peel strength of the binder was correlated to surface energies of the substrates(9).

Different mechanisms of adhesion (10) that operate simultaneously give wide discrepancies of the results and that are highly depend on the rate of application of testing force (11)

Although selection of binder is mainly based on a particular system of interest as well as the experiences, but was demonstrated (12) by construction adhesive-force curves during different drying stages that are good guiding for selection of binding agents and in the optimization of building up of the granules.

However, bond strength measurements are usually faced with difficulties which are related to the analysis of the stress distribution, particle size, shape, energy contribution etc. On the other hand for sheet materials of well defined shape, there is wide range of test method involved and each of which gives rise to particular set of results that could not be applied in a suitable manner empirically. But in general, bond strength can be related to the ability of the attraction between the two phase irrespective of the nature and method of testing.

In this work, adhesion was carried out experimentally and the results were correlated to the theoretical and literature values.

Materials and Methods:

A. Materials: Three film-forming pharmaceutical binders, Methocel E15 (hydroxypropyl-methyl cellulose), Colorcon, U.K.; Povidon K90 (Polyvinylpyrrolidone, PVP), Fluka, Ag; Switzerland; and Gelation, Byco C, Crodacolloid, Cheshire, England, as aqueous adhesive solution and five polymeric sheets as substrates; Nylon 66, polypropylene (PP) polyethylene (P.E.), Polymethylmethacrylate (PMMA), Plastic former, Denton, Manchester, England, and polytetrafluoroethylene (PTFE), BDH, Poole, England, were chosen.

B. Methods: 1. Specimen preparation; binder solutions were casted between the sheets using micropipette (Lubindustries) then dried at 105°C, conditioned at 11% R.H. and tested.

2. Shear tester apparatus; The apparatus consists of three parts, driving motor supplied with 12 gears, block tester and stainless steel bar supplied with strain gauges. The latter parts were kept in perspex box supplied with low flow of warm air which was adjusted to

25°C by means of thermostat. The breaking loads were recorded using 3 V input and D.C. recorder. The bar was connected to the upper sheet via bended -end steel blade.

3. Surface tension; surface tension of the binder solutions were measured using the Wilhelmyplate method while for other solutions the drop method was carried out.

4. Density; The density of the liquids was determined using densimeter (DMA 60, PAAR) at 20° C.

5. Viscosity; The viscosity of the liquids was determined using U tube Viscometer at 20°C.

6. surface free energy; Surface free energy of the solids were determined using contact angle measurements by means of Σ -H method (14) and introducing into Wu's equation (15).

Results and Discussion:

Table (1) shows details of the properties of liquids used for contact angle measurements while Table (2) shows the experimental and literature values of surface free energy of the substrates and Table (3) indicates surface tension of the 8% W/W binder solutions using Fowkes equation(11).

The ideal bond strength between any two surfaces will be equal to the theoretical work of adhesion (10) only when perfectly rigid and flat surfaces held together and tensile test carried out providing there is no energy expenditure within the adhesive during testing. This ideality is not attainable in practice and so in this study testing conditions have been kept constant. Even with ideal smooth surfaces, the binder films will not necessarily form in an identical manner and so bond strength in this study can only be used for comparative purposes. The results of bond strength are shown in table (4). In order to compare these results with theoretical predictions, the thermodynamic work of adhesion, work of spreading, spreading coefficient and interaction coefficient were calculated for each binder /substrate pairs which are given in table (5). Table (6) shows the interaction coefficient between PVP, HPMC and three substrates based on solubility parameters (δ).

Although work of adhesion differs by a factor of 2-3 for HPMC and PVP, the adhesive bond strength differs from those too weak to handle and measure, less than about 15 Kpa, to 588 Kpa. This emphasizes the importance of smoothness, film formation and surface contamination between binders, that will be affected by film formation, and substrates by surface factors. Despite these restrictions, PVP K90 has the same rank order of bond strength as other thermodynamic parameters for HPMC. The results are similar except for the lower bond strength formed with nylon 66 (Table ,4).

Two models have been proposed (10) based on surface energies by which it is possible to calculate the optimum condition for wetting and hence bond strength.

The first model called interfacial defect, suggests that the spreading coefficient (S) should be maximised.

$$S = 2 \left(\gamma_s \gamma_b \right)^{1/2} - 2 \gamma_b \quad \text{eq (1)}$$

Where ϕ , γ_s and γ_b are interaction coefficient, surface free energy of the substrate and the binder respectively. With the equation, the result depends on the phase to be defined as the adhesive.

The second model, the fracture energy, suggests that the work of adhesion (Wa) should be maximised.

$$W_a = 2\phi \left(\gamma_s \gamma_b \right)^{1/2} \quad \text{eq (2)}$$

Applying the above mentioned equations, the results are maximised when the polarities of the components are exactly matched (10). If it is assumed when a substrate with a surface energy of γ_s and a constant value of ϕ is used, an increase in the binder surface tension will decrease S (eq.1) while increasing W_a (eq.2). Optimum wetting will therefore be obtained when $S=0$ and hence $\gamma_b = \phi^2 \gamma_s$ and $W_a = 2\phi \gamma_s$.

The calculated values for the binders and substrates (Table 5) indicate good agreement between predicted adhesion and bond strength except for Nylon66/HPMC system. Materials with similar value of solubility parameters, which are mutually compatible, were found to give maximum bond strength (17). A plot of bond strength againsts δ of substrate (18) are illustrated in fig(1). It can be seen that there is a good correlation between δ and bond strength. The maximum bond strength is when the δ of the adherends match each other. So the lower result with HPMC/Nylon 66 fits well with the theory of incompatibility. This inturn gives reduction of diffusion and hence bond strength.

Since few values of solubility parameters for rigid materials are found in the literature (1), a rough correlation is drawn here and more values are needed for wide range of materials to show clearly if this correlation would be applied generally.

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Table 1. Some details of the properties of liquids used for contact angle
() measurements.

liquids	$\gamma_{LV}(\text{mJm}^{-1})$	$\gamma_{L}^d(\text{mJm}^{-1})$	$\rho(\text{gmcm}^{-3})$	θ against paraffin at $23\dot{C}\pm 2\dot{C}$
Water	71.8	21.9	0.989	110
Methylene iodide	50.4 [*]	50.4	3.320	0
Liquid paraffine	25.5 ^{**}	25.5	0.866	0

* Ref. (9)

** Ref. (15)

Table 2. Experimental and literature values of surface free energies
and surface tension of materials used.

Polymer	Exp. Water $\gamma_s(\text{mJm}^{-2})$	-Paraffin $\gamma^d(\text{mJm}^{-2})$	Exp. Water $\gamma_s(\text{mJm}^{-2})$	-Me.Iodide $\gamma^d(\text{mJm}^{-2})$	Literature ρ value of γ_s
Nylon 66	50.0	19.6	51.1	22.8	41.3 [*] -44.7 ^{**}
PMMA	43.4	22.7	43.6	25.9	35.4-41.2
P.P.	36.3	21.9	34.7	18.4	30.1 ^{**}
P.E.	27.5	21.3	28.1	22.4	32.4-35.7 ^{**}
PTFE	17.6	15.4	13.7	8.2	15.6 [*] -22.5 ^{**}

* Ref. (16)

** Ref. (17)

Table 3. Surface energy components of the 8% W/W binder solutions.

	$\gamma(\text{mJm}^{-1})$	$\gamma^d(\text{mJm}^{-1})$	$\gamma^P(\text{mJm}^{-1})$
HPMC E15	41.7	24.7	17.0
PVP K90	46.8	15.0	31.0
Gelatine Byco C	32.9	1.1	31.8

Table 4. Comparison of experimental bond strength and calculated work of adhesion for different binders to the polymeric substrates.

	HPMC E15		PVP K90		Gelatine Byco C	
	Cal.(1)	$W_a \text{ exp.}^{(2)}$	Cal.(1)	$W_a \text{ exp.}^{(2)}$	Cal.(1)	$W_a \text{ exp.}^{(2)}$
Nylon 66	87.4	21	96.4	588	70.7	week
PMMA	84.6	75.6	86.9	286	59.5	week
P.P.	77.9	69	76.9	232	49.1	36
P.E.	63.4	45.8	56.4	week	30.4	weak
PTFE	45.4	0	39.1	0	17.9	0

1 : Calculated work of adhesion (mJm^{-2}) given from reference 13.

2 : Bond strength (PKa) obtained after conditioning at 11% R.H. given from reference 13.

Table 5. Bond strengths and the calculated thermodynamic values of interaction between the binder and the substrates in the brackets are the standard deviations.

	HPMC E15					PVP K90					Gelatine Byco C				
	σ (KPa)	W_a	W_s	S	ϕ	σ (KPa)	W_a	W_s	S	ϕ	σ (KPa)	W_a	W_s	S	ϕ
Nylon 66	21(6)	87.4	-161	2.9	0.95	586(160)	96.4	-21.2	2.6	0.66	weak	70.7	-28.1	1.9	0.83
PMMA	75.6(9)	84.7	-18.6	1.2	0.99	286(66)	186.9	-27.1	6.9	0.96	weak	59.5	-31.9	-6.6	0.78
P.P.	69(13)	77.9	-16.1	-6.4	0.99	232(77)	76.6	-24.7	19	0.90	36(17)	50	-47.2	-16.1	0.72
P.E.	45.8(14)	63.4	-22.1	-23.2	0.89	weak	56.4	-36.3	4.2	0.74	weak	30.4	-73.7	-35.2	0.51
PTFE	0	45.4	-34.5	-44.6	0.68	0	39.1	-58.7	60.9	0.57	0	19.9	-85.5	-47.7	0.37

Table 6. Interaction coefficient () of different binders with different substrate based on solubility parameters.

Binders	Substrates		
	PMMA	P.E.	PTFE
HPMC	115.5	52.40	33.83
PVP K90	116.72	62.76	42.41

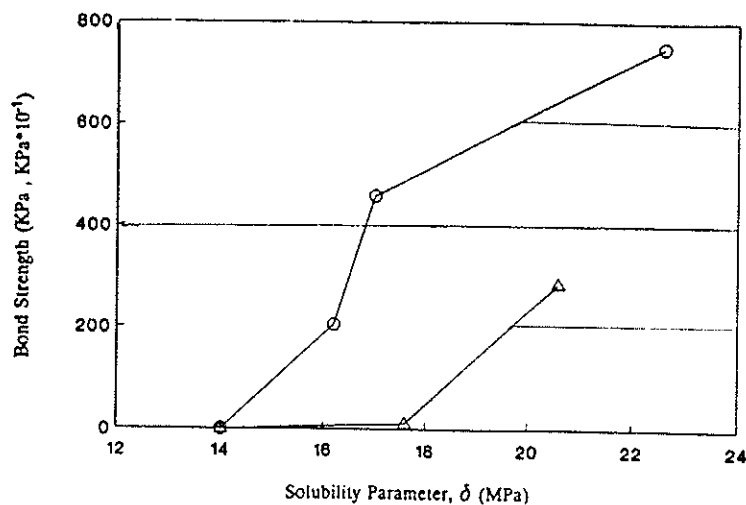


Fig 1. Plot of bond strength against solubility parameter of the substrates.

○ HPMC (KPa * 10^{-1})

△ PVP K90 (KPa)