Measurement of Adhesive Force between Particles of Organic Substances and Polymer Substrates by the Centrifugal Separation Method: Effect of Electrostatic Charge

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Effects of electrostatic force on adhesion between pharmaceutical powder particles (phenacetin and sulfadimethoxine) and various polymer substrates (polyethylene (PE), polyvinylchloride (PVC), Eudragit E100, polyvinylacetal diethylamino acetate (AEA), Eudragit L30D-55) were investigated using the centrifugal separation technique. Two methods were used to attach powder particles to a substrate, the free falling method and the fluidization method. Average adhesive force, f_{50}, and electric potential, V, in the fluidized method were found to be greater than those in the free falling method for all the pharmaceutical powder/polymer substrate systems examined. Average adhesive force, f_{50}, increased with a decrease in surface polarity, P_0, of polymer substrate for each powder.

Key words adhesive force; centrifugal separation method; polymer substrate; electrostatic force; surface electric potential; surface polarity

The adhesive force of powdered materials due to electrostatic charge is known to cause problems in drug manufacturing. Kulvanich and Stewart[1a-c] measured the adhesive property of drug particles on a carrier (glass sphere coated with hydroxypropylmethylcellulose phthalate) by the centrifugal method, as well as by electrostatic charge with an air stream Faraday cage, and discussed the correlation of adhesion and charge. No studies have been reported, however, on direct measurement of the electrical interactive force between a single particle and substrate. In a previous work[2] using pharmaceutical powders, the effect of substrate material on particle adhesion was investigated by the fluidization method, in which particles were fluidized with a jet of air and attached to a substrate in a single layer. Among several substrates, pharmaceutical powder particles attached to polyvinylchloride (PVC) showed extremely large average adhesive force, f_{50}. This is probably due to the electrostatic force produced by the collision and/or friction of the powder to the PVC which has low surface polarity. In the present study, two powders and various polymers having different surface polarities, P_0, were used to measure adhesive force.

Experimental

Materials In Table 1 two sample powders are shown with their physical properties. Average particle diameter (Heywood diameter), d was determind by an image analyzer (Luzex 500, Nireco). Particle density, ρ, was measured using a helium–air pycnometer.

Polymers and Preparation of Polymer Substrate Polyethylene, PE (Sekisui); PVC (HTS625; Takiron); aminoalkyl methacrylate copolymer E, Eudragit E100 (Röhm Pharma); polyvinylacetal diethylamino acetate, AEA (Sankyo); methacrylic acid copolymer LD, Eudragit L30D-55 (Röhm Pharma) were the testing polymers used (Table 2). PE and PVC were supplied as a sheet and plate, respectively. Other polymers were dissolved in the solvents shown in Table 2. A glass plate was dipped in the solution and the solvent was evaporated at room temperature to obtain polymer film.

Determination of Surface Polarity The films and powder compacts compressed by Autograph (Shimadzu) at 118 MN m^{-2} were stored for 24 h in a closed vessel in which air was saturated with the test liquid at 25 °C. A small droplet (25 μl) of water or methylene iodide was placed on the solid surface using a microliter syringe. Contact angle, θ, was determined by photographic recording.

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According to Wu[3] interfacial free energy between a liquid and solid, γ_{SL}, can be estimated by knowing the individual surface free energy (γ_L and γ_S) and nonpolar and polar interaction terms (ϕ^d, ϕ^p)

$$\gamma_{SL}=\gamma_S+\gamma_L-2\phi^d-2\phi^p \quad (1)$$

$$\phi^d=2\gamma_S^d\gamma_L^d/(\gamma_S^d+\gamma_L^d) \quad (2)$$

$$\phi^p=2\gamma_S^p\gamma_L^p/(\gamma_S^p+\gamma_L^p) \quad (3)$$

where γ^d and γ^p are surface free energy of nonpolar and polar components, respectively. The relation of contact angle, θ, γ_S, γ_L and γ_{SL} is expressed by the Young–Dupre equation:

$$\gamma_S=\gamma_L\cos\theta+\gamma_{SL} \quad (4)$$

A combination of Eqs. 1, 2, 3, and 4 yields

$$(b+c+a)\gamma_S^d\gamma_S^p+c(b-c)\gamma_S^d+b(c-a)\gamma_S^p-abc=0 \quad (5)$$

where $a=\gamma_L/4(1+\cos\theta)$, $b=\gamma_L^d$, and $c=\gamma_L^p$.

Surface free energy of the nonpolar and polar components of the two liquids, water and methylene iodide, are known.[3] Thus, if the contact angle of the two testing liquids on a solid is measured, two simultaneous equations can be obtained to solve the two unknowns (γ_S^d and γ_S^p).

The surface free energy of a solid, γ_S, is given as the sum of γ_S^d and γ_S^p and surface polarity index P_0 is determined by the following equation:

$$P_0=\frac{\gamma_S^p}{\gamma_S}\times 100 \quad (6)$$

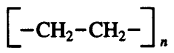
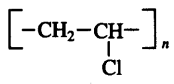
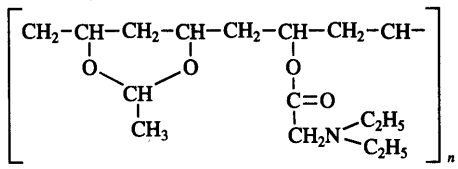
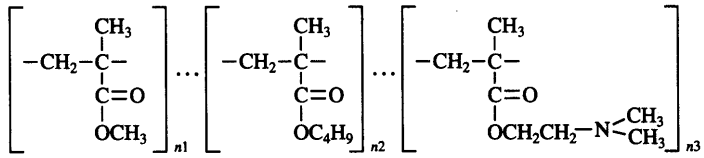
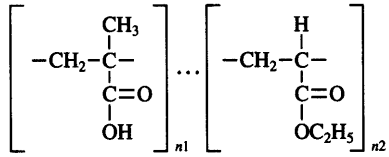
Method of Attaching Particles to Substrate[2] In the free falling method, particles were deposited with very little force by allowing them to freely fall on the substrate.

In the fluidization method, the Air Jet Sieve (200LS, Alpine) was used to attach particles to the substrate. Three hundred mg of sample powder was fed into a container having a capacity of 38.5 cm^3 (70 mm in diameter and 10 mm in depth). A substrate (18 mm in diameter) was stuck on the cover of the sieve with double adhesive tape, and fresh air was blown through the device for 1 min at a flow rate of 3.6 m^3/min. A single layer of particles was obtained on the substrate. This operation was conducted at 25±1 °C and a relative humidity of 40±10%.

Table 1. Physical Properties of Sample Powders Used

Sample	Average particle diameter d (μm)	Particle density ρ (kg/dm^3)
Phenacetin	70.6	1.26
Sulfadimethoxine	79.4	1.48

Table 2. Polymer Substrates Used

Polymer	Structural formula	Type of substrate
PE Sekisui		Sheet
PVC Takiron HTS625		Plate
AEA Sankyo		Film C_2H_5OH (50%)[a] CH_3COCH_3 (50%)
Eudragit E Röhm Pharma E 100		Film C_2H_5OH[a]
Eudragit LD Röhm Pharma L30D-55		Film H_2O[a]

a) Solvent used in preparation of polymer film.

Measurement of Adhesive Force The adhesive force between particles and a polymer substrate was measured by the centrifugal separation method. The cell[4] designed with special attention to air-tightness was fixed in the rotor (RH-150A, Kubota). Some particles were detached from the substrate surface by centrifugal force. Rotation speed (rpm) was measured by a stroboscope, and centrifugation was allowed to continue for 10 min. Centrifugal acceleration, α, was calculated from the angular velocity, ω, and distance between particles and axis of the centrifuge, r. Separation force, f, was obtained from Eq. 7.

$$f=\frac{\pi}{6}\rho d^3 r\omega^2 \tag{7}$$

The percentage of particles adhering to the substrate was determined by counting the number of particles before and after centrifugation using an image analyzer (Luzex 500, Nireco) connected to a microscope. A plot of separation force *vs.* percentage of remaining particles on a logarithmic probability paper yields the average adhesive force, f_{50}, defined as the separation force at which 50% of the particles are detached from the substrate. All measurements were carried out at 25±1 °C.

Measurement of Electric Potential of a Substrate[2] Measurement of the electrostatic properties of the substrates was carried out using a vibrating reed electrometer (Statiron-DZ, Shishido Electrostatic, Ltd.). The surface electric potential of the substrate, V, was indicated directly at the point 22 mm apart from the substrate.

Results and Discussion

(1) Electrostatic Effects on Adhesive Force between Pharmaceutical Powders and Polymer Substrates In Fig. 1 is plotted on log-probability paper the percentage of remaining particles against separation force for the phenacetin/Eudragit E100 system. Average adhesive force, f_{50}, of particles deposited by the fluidization method was greater than that by the free falling method. All adhesion data obtained by the free falling and fluidization methods are shown in Table 3, together with surface electric potential, V. For all pharmaceutical powders and polymer substrate combinations, adhesive force obtained by the fluidization method was several times larger than that by the free falling method. The surface electric potential, V, was also found in all cases to be higher in the fluidization method. It was thus suggested that electrostatic force caused by collision and/or friction of pharmaceutical powder particles to a polymer substrate was probably the most important source of adhesion in the fluidization systems.

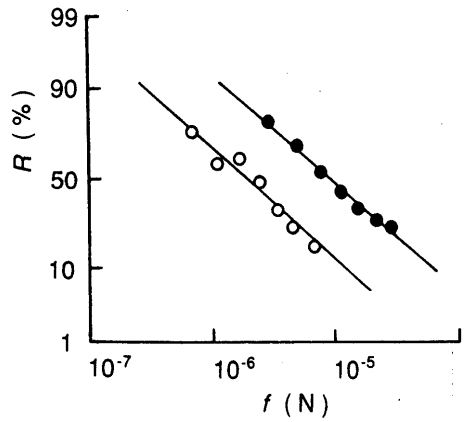


Fig. 1. Plots of Percentage of Remaining Particles, R, against Separation Force, f, on Log-Probability Paper for the Phenacetin/Eudragit E100 System

○, free falling method; ●, fluidization method.

(2) Effects of Surface Polarity on Electrostatic Adhesion between Pharmaceutical Powders and Polymer Substrates The contact angle, θ, surface free energy, γ_S, and surface polarity, P_0, of polymer substrates and pharmaceutical powders are shown in Table 4. Surface polarity, P_0, of the powder compact of phenacetin and sulfadimethoxine was 21% and 28%, respectively, indicating less polarity of phenacetin than that of sulfadimethoxine.

Table 3. Average Adhesive Force and Electric Potential ($n=10$)

Substrate		Phenacetin		Sulfadimethoxine	
		f_{50} (N)	V (kV)	f_{50} (N)	V (kV)
PE	Free falling	1.9×10^{-6}	−0.1	4.2×10^{-7}	0.0
	Fluidization	1.1×10^{-5}	−2.7	8.7×10^{-6}	−2.7
PVC	Free falling	3.2×10^{-6}	−0.2	1.7×10^{-6}	−0.2
	Fluidization	1.2×10^{-5}	−2.6	8.8×10^{-6}	−2.6
Eudragit E 100	Free falling	1.9×10^{-6}	0.0	5.9×10^{-7}	0.0
	Fluidization	9.0×10^{-6}	2.1	1.6×10^{-6}	3.1
AEA	Free falling	1.5×10^{-6}	0.0	2.9×10^{-7}	0.0
	Fluidization	5.7×10^{-6}	2.0	1.5×10^{-6}	2.7
Eudragit L30D-55	Free falling	7.5×10^{-7}	0.0	1.7×10^{-7}	0.0
	Fluidization	3.5×10^{-6}	2.0	1.0×10^{-6}	2.6

Table 4. Contact Angle, Surface Free Energies and Surface Polarity for Various Solids

Solid	Contact angle, θ		γ_s (mN m^{-1})	P_0 (%)
	Water	Methylene iodide		
Phenacetin	68	29	56	21
Sulfadimethoxine	52	16	67	28
PE	90	44	42	9
PVC	75	25	55	16
AEA	59	30	61	27
Eudragit E 100	62	34	58	26
Eudragit L30D-55	53	29	63	30

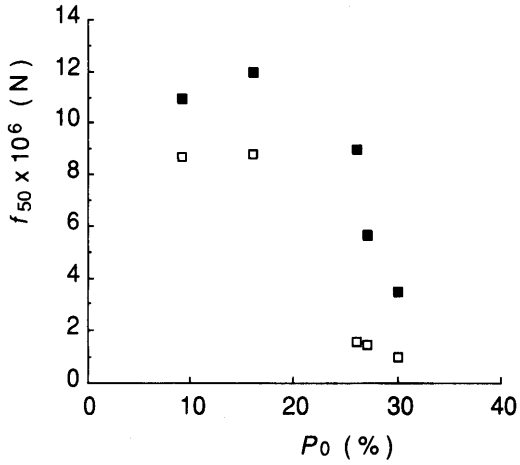


Fig.2. Relationship between f_{50} and P_0
□, sulfadimethoxine; ■, phenacetin.

For the polymer substrate, surface polarity increased in the rank order of PE, PVC, Eudragit E100, AEA and Eudragit L30D-55. Figure 2 shows the relationship between adhesive force, f_{50}, obtained by the fluidization method and surface polarity, P_0, of a polymer substrate. In every polymer substrate, adhesive force, f_{50}, of phenacetin with low surface polarity was higher than that of sulfadimethoxine. Additionally, decreasing surface polarity, P_0, of polymer substrate tends to raise adhesive force, f_{50}, for both powders. These findings imply that the high electrostatic force is produced by use of particles and substrate of low surface polarity in the fluidization method. A few exceptional cases were observed. Despite the considerable difference in surface polarity, P_0, between PE and PVC, adhesive force, f_{50}, of the two powders appeared essentially the same. While there is a possible effect of other surface properties such as surface roughness on adhesion, an obvious reason explaining the results is still unknown.

Conclusions

The adhesive force between two pharmaceutical powders attached to various polymer substrates was determined by the centrifugal method. Electrostatic adhesion force between the powders and a polymer substrate is influenced by surface polarity of the two substances.

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