[Chem. Pharm. Bull. 31(12)4483—4488(1983)]

Measurements of the Adhesive Force between Particles of Powdered Organic Substances and a Glass Substrate by Means of the Impact Separation Method. I.[1] Effect of Temperature

AKINOBU OTSUKA,* KOTARO IIDA, KAZUMI DANJO, and HISAKAZU SUNADA

Faculty of Pharmacy, Meijo University, Yagoto-Urayama, Tempaku-ku, Nagoya 468, Japan

(Received March 15, 1983)

The effect of temperature on the adhesive force between particles of powdered organic substances (butyl *p*-hydroxybenzoate and sulfadimethoxine) and a glass substrate was investigated by means of the impact separation method using a pendulum-type shock testing machine.

At elevated temperatures, a remarkable increase in adhesive force with heating time was observed. The adhesive force at a given heating time increased with rising temperature and a linear relationship existed between the logarithm of adhesive force and the reciprocal of temperature (°K) for each sample. The results were interpreted in terms of the growth of a solid neck between a particle and the substrate.

Keywords——powdered organic substance; butyl *p*-hydroxybenzoate; sulfadimethoxine; adhesive force; centrifugal separation method; impact separation method; pendulum-type shock testing machine; homologous temperature; solid neck formation

It is well known that organic powders are generally difficult to handle in such processes as pulverization, mixing, filling and compression because of their high adhesive and cohesive tendencies. In particular, change in the adhesive force due to the heat generated during the processes sometimes gives rise to unexpected problems, such as sticking in tablet manufacturing and weight variation of tablets or capsules. For these reasons, it is very important to investigate the effect of temperature on the adhesive force of powdered organic substances. There have been two basic approaches for the measurement of adhesive force of powdered materials, one for bulk powders and the other for the individual powder particles. By means of the former, Pilpel and co-workers,[2] and Danjo *et al.*[3] studied the adhesive force of organic powders as a function of temperature. The present work is concerned with the later approach, which is considered to be more fundamental than the former. Among the methods dealing with individual powder particles, the centrifugal separation method has been widely used.[4-6] The principle of this method is to evaluate the average adhesive force of particles statistically by separating them from a substrate by the application of centrifugal force. Recently, Jimbo and co-workers[7] have developed the vibration method and impact method, in which a vibrator and a tapping device are used, respectively. These methods are preferable to the centrifugal method for measurements at higher temperatures. However, neither of these methods can generate enough acceleration to measure adhesive force over a wide range. In order to extend the range of separation force, we attempted to use a shock testing machine (pendulum type), with which high impact acceleration could be obtained.

Experimental

Materials——Powders used are listed in Table I with their physical properties. Particle density was determined

Table I. Physical Properties of Sample Powders Used

Sample	Particle density (g/cm^3)	Particle diameter (μm)	Melting point (°C)
α-Alumina	3.90	62	—
Calcium carbonate	2.61	44	—
Butyl *p*-hydroxybenzoate	1.28	116	68
Sulfadimethoxine	1.42	83	202

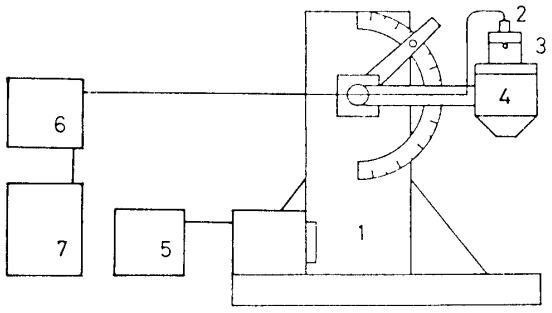

Fig. 1. Schematic Diagram of Apparatus for Pendulum Impact Method

1, impact tester; 2, pick-up for impact acceleration; 3, measuring cell; 4, impact hammer; 5, controller of impact tester; 6, charge amplifier; 7, synchroscope.

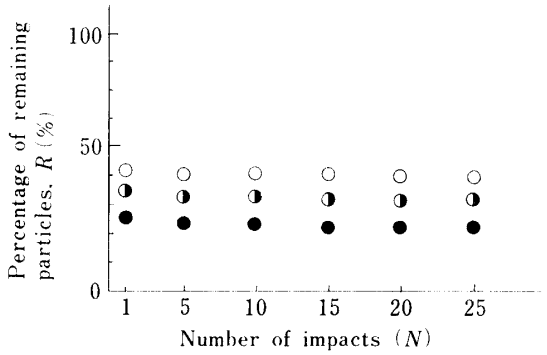

Fig. 2. Percentage of Remaining Particles on a Substrate as a Function of Number of Impacts for α-Alumina

○, 45—55 μm; ◑, 55—65 μm; ●, 65—75 μm.

with a Shimadzu-Micromeritics helium-air type densimeter, particle diameter (Feret diameter) by microscopic measurement, and melting point by DSC (Rigaku Corporation). A microscope slide glass was used as the substrate after being rinsed with methanol and acetone and air-dried.

Equipment and Procedures——(1) Pendulum Impact Method: Figure 1 illustrates the apparatus for the pendulum impact method, in which a shock testing machine (Yoshida Seiki, PST-300) was used. A measuring cell was fixed to an impact hammer which was motor-driven to a desired height and then allowed to fall to impact a shock absorbing mat. Impact acceleration generated was converted to electrical output by a pickup fixed in the measuring cell, amplified by a charge amplifier, projected on a synchroscope as waves, and photographed. The value of impact acceleration was calculated from the height of the first wave. By changing the lift angle of the impact hammer as well as the materials and the thickness of the shock absorbing mat, impact acceleration could be varied up to 5000 g. The impact was repeated 25 times for each test, though almost all the particles to be separated were detached from a substrate by the first impact (Fig. 2).

(2) Tapping Impact Method: A commercially available tapping machine (Seishin Tap Denser, type KYT-1000) fitted with measuring cell and an accelerometer was used.

(3) Centrifugal Method: The measuring cell is rotated around the vertical axis of a motor (Chemy Stirrer B-100, Tokyo Rikakikai) and accelerated to a speed at which the particles on the substrate are detached. The centrifugal acceleration is calculated from the angular velocity and the distance between the particles and the axis of the centrifuge.

Method of Heat Treatment——(1) Procedure I: A dusted substrate was placed in an electric oven. Temperature was measured by the use of a thermocouple which was placed in close contact with the suface of the substrate. The temperature was raised up to a given temperature in about 15 min and maintained at this level (±0.5 °C) for a given time. Then the dusted substrate was cooled for 10 to 15 min in a constant temperature room at 20 °C (±1 °C). The measurements of adhesive force were carried out in this room (Fig. 3a).

(2) Procedure II: As shown in Fig. 4, a measuring cell containing the dusted substrate was completely covered with a mantle heater. The temperature was raised to a given value in about 15 min and maintained at this level (±1 °C) for 30 min. The measurement of adhesive force was performed at this temperature (Fig. 3b).

Determination of Adhesive Force——The particles were subjected to centrifugal force or impact force to separate them from the surface of the substrate. The percentage of particles still remaining on the substrate surface was determined by comparing the photomicrographs before and after the operation, and was plotted on log-probability paper against the corresponding separation force. The average adhesive force f_{50} was defined as the separation force at which 50% of the particles remained on the substrate.

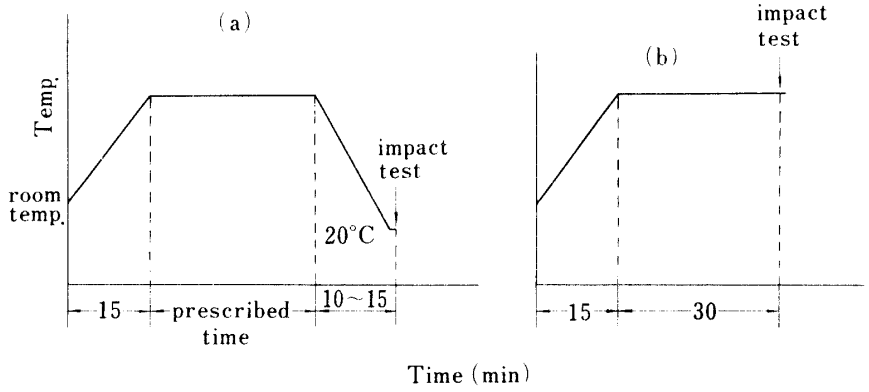

Fig. 3. Schematic Schedules of Heating
(a), Procedure I; (b), Procedure II.

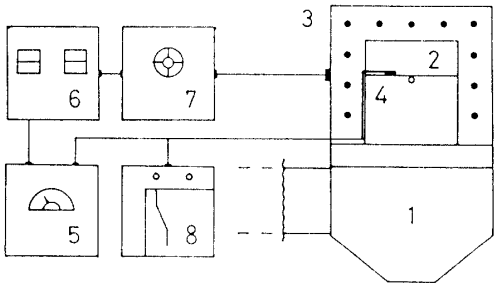

Fig. 4. Schematic Diagram of Heating Apparatus
1, impact hammer; 2, measuring cell; 3, heater; 4, thermocouple; 5, thermoregulator; 6, relay; 7, transformer; 8, recorder.

Results

Comparison of Three Methods

A typical example of measurement by the pendulum impact method is shown in Fig. 5, where the abscissa represents separation force (logarithmic scale) and the vertical axis represents the percentage of remaining particles (probability scale). Table II shows the values for average adhesive force at room temperature for three samples obtained by the three different methods. The values are in good agreement with each other. Nearly the same values were obtained when the measurement was carried out using the sample powders which had been left to stand at room temperature for several hours on the substrate.

Effect of Heat-Treatment Time and Temperature on the Adhesive Force of Powdered Organic Substances

Butyl *p*-hydroxybenzoate (Bu-POB) and sulfadimethoxine (SD) were tested by the pendulum impact method. The samples were heat-treated at a given temperature for a given time, then cooled to 20 °C and subjected to the separation process (Procedure I). Figures 6 and 7 show the effect of heat-treatment time on the adhesive force. At elevated temperatures, a remarkable increase in adhesive force with heating time was observed.

The symbol ⚲ in Fig. 6 represents the value when the particles were allowed to stand at 25 °C with the dusted surface of the substrate downwards. The results showed very little difference from those obtained with the dusted surface upwards. Therefore, under the present conditions, it may not be necessary to take into account the increase in contact area with time possibly caused by the gravitational effect.

The effect of temperature on adhesive force for Bu-POB and SD is shown in Figs. 8 and 9, respectively, where the values for 30 min standing are plotted on the ordinate. The abscissa shows the homologous temperature, which was defined as the ratio of the temperature of measurement, T, to the melting point, T_m, in absolute temperature. The results for the heat

TABLE II. Average Adhesive Forces Obtained by Various Methods

Material		Range of particle diameter (μm)	Relative humidity (%)	Average separation force f_{50} ($N \times 10^7$)		
				Impact method		Centrifugal method
Particle	Substrate			Pendulum	Tapping	
Al_2O_3	Glass	50—70	50—60	9.5	9.8	7.6
$CaCO_3$	Glass	30—70	50—60	1.9	2.7	2.5
$CaCO_3$	Glass	16—24	30—50	—	—	2[a]

a) Value determined by Jimbo *et al.*[5]

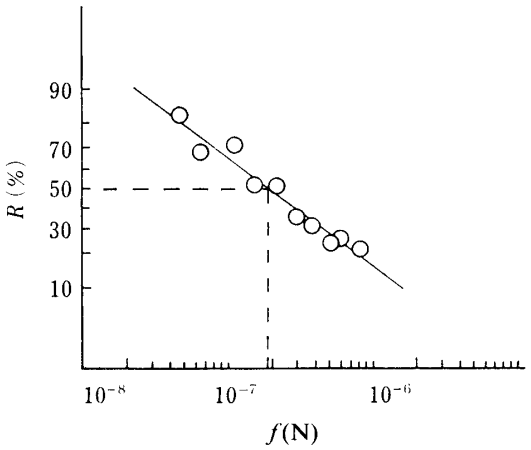

Fig. 5. Plots of Percentage of Remaining Particles against Separation Force on Log-Probability Paper for $CaCO_3$

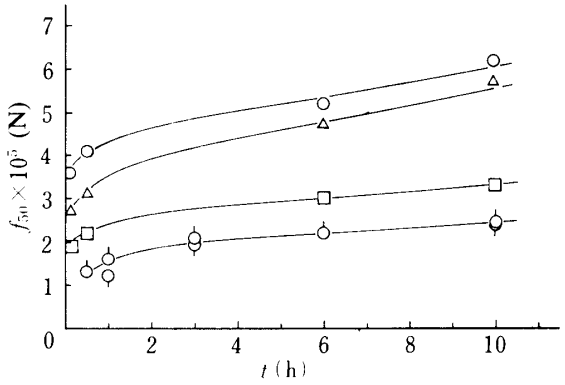

Fig. 6. Adhesive Force as a Function of Heating Time for Bu-POB (Procedure I)

○, 25 °C (with dusted surface upward); ○, 25 °C (with dusted surface downward); □, 34 °C; △, 43 °C; ○, 50 °C.

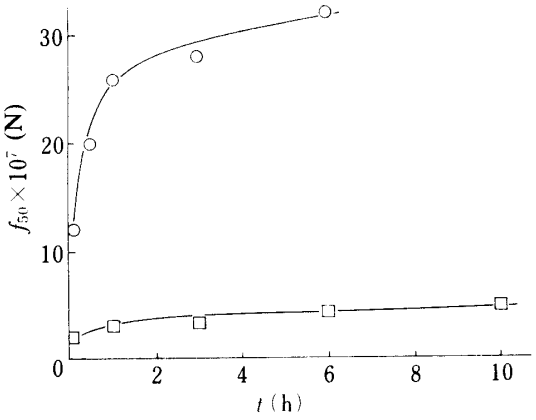

Fig. 7. Adhesive Force as a Function of Heating Time for SD (Procedure I)

□, 25 °C; ○, 155 °C.

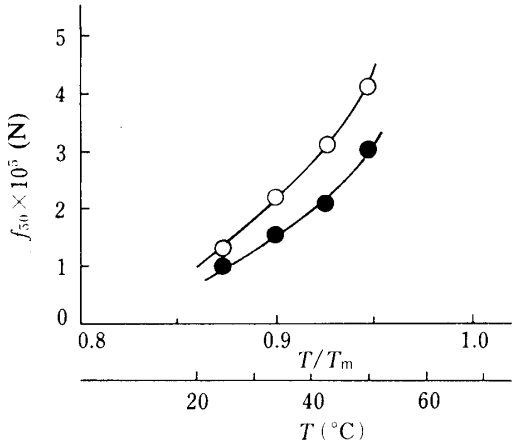

Fig. 8. Adhesive Force as a Function of Homologous Temperature for Bu-POB

○, Procedure I; ●, Procedure II.

treatment by procedure II, where the samples were held at the required temperature for 30 min prior to the determination of adhesive force at that temperature, are shown in Figs. 8 and 9 by black circles.

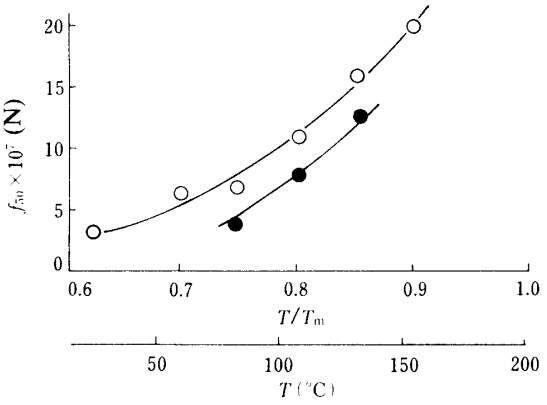

Fig. 9. Adhesive Force as a Function of Homologous Temperature for SD

○, Procedure I; ●, Procedure II.

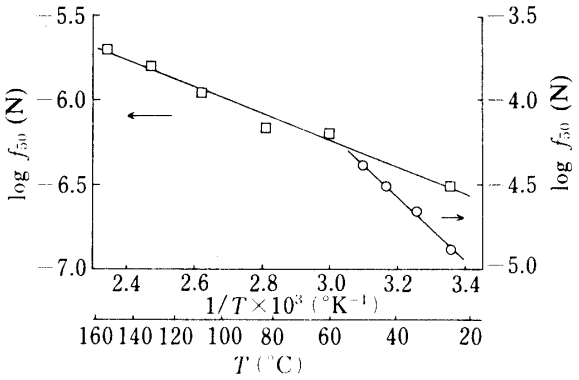

Fig. 10. Arrhenius Plots for the Average Adhesive Force (f_{50})

○, Bu-POB; □, SD.

Discussion

In order to minimize the total surface energy, the movement of surface molecules towards the contact point may occur at temperatures below the melting point of solids and may result in the formation of a neck between particles or between particles and a substrate. Many solid organic substances are at a homologous temperature of over 0.7 even at room temperature because of their relatively low melting points. It is therefore anticipated that an extreme increase in adhesive force accompanied with the growth of a neck will be observed.

Measurements of adhesive force at elevated temperatures have been carried out with gold spheres on gold layers by Polke,[8] who discussed the relationship between adhesive force at a given heating time and temperature. Assuming that the radius of spherical particles (r), heating time (t_a) and temperature (T) are constant, the radius of a neck (a) can be expressed by the following equation:

$$a^n = K_1 e^{-Q/RT} \tag{1}$$

where n is an integer in the Kuczynski equation, K_1 is a constant and Q is the activation energy for the transport mechanism. If the adhesive force (f) can be represented by the product of the adhesive force per unit area (σ) and the contact area between a particle and a substrate (πa^2), Eq. (1) leads to Eq. (2).

$$f = K_2 \sigma e^{-2Q/nRT} = K e^{-A/RT} \tag{2}$$

Figure 10 shows plots of log f_{50} after 30 min standing (procedure I) against the reciprocal of T; a good linear relationship was obtained for each sample. The activation energy for Bu-POB was 36 kJ/mol and that for SD was 15 kJ/mol. Danjo *et al.*[3b] obtained 33 kJ/mol for both methyl and ethyl *p*-hydroxybenzoates as the activation energy by means of tensile strength measurements at various temperatures.

The values for average adhesive force obtained by heat treatment according to procedure II were found to be smaller than those in procedure I. This may be due to the decrease of adhesive force per unit area of contact (σ) with rising temperature.

References and Notes

1) This work was presented at the 101st Annual Meeting of the Pharmaceutical Society of Japan, Kumamoto, April 1981, and The International Symposium on Powder Technology, Kyoto, September 1981.
2) *a*) P. York and N. Pilpel, *Mater. Sci. Eng.*, **9**, 281 (1972); *b*) P. York and N. Pilpel, *Mater. Sci. Eng.*, **12**, 295

(1973); *c*) N. Pilpel and J. R. Britten, *Powder Technol.*, **22**, 33 (1979); *d*) J. R. Britten and N. Pilpel, *J. Pharm. Pharmacol.*, **30**, 673 (1978).
3) *a*) K. Danjo and A. Otsuka, *Yakugaku Zasshi*, **100**, 893 (1980); *b*) K. Danjo, K. Iida, and A. Otsuka, *J. Soc. Powder Technol.* (Japan), **19**, 530 (1982).
4) G. Boehme, H. Krupp, H. Rabenhorst, and G. Sandstede, *Trans. Inst. Chem. Engrs.*, **40**, 252 (1962).
5) S. Asakawa and G. Jimbo, *J. Soc. Material Sci.* (Japan), **16**, 358 (1967).
6) J. Okada, Y. Matsuda, and Y. Fukumori, *Yakugaku Zasshi*, **89**, 1539 (1969).
7) G. Jimbo, R. Yamazaki, and G. Hong, *Rep. Asahi Glass Found. Ind. Technol.*, **38**, 123 (1981).
8) R. Polke, *Bull. Soc. Chim. Fr.*, **1970**, 3241.