Measurement of Adhesive Force between Particles and Polymer Films[1)]

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Adhesion between glass beads and polymer films was investigated using the centrifugal separation method at various relative humidities. The adhesive force depended on the type of polymer, and it was found that there was a close correlation between the adhesive force and the amount of water sorbed by the polymer film. This finding suggests that the polymer surface becomes softened by the sorbed water; consequently, the contact area between a particle and the polymer film increases. The surface treatment of glass beads with trimethylchlorosilane reduced the adhesive property of the particle in every system.

Keywords adhesive force; centrifugal separation method; glass bead; polymer film; surface treatment; moisture sorption

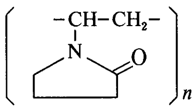
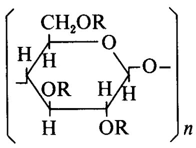
Some polymers are used as materials for various vessels and devices because of their excellent moldability and durability. In pharmaceutical preparations, many types of polymers have been applied, for example, as coating agents and binding agents for tablets and granules. However, adhesion between powdered pharmaceuticals and high polymers seems to be a problem, one which should not be ignored. Kulvanich *et al.*[2)] measured adhesion between glass spheres coated by hydroxypropylmethylcellulose phthalate and powdered pharmaceuticals by the centrifugal separation method using a specially designed cell. They reported that the adhesive force between both particles could be essentially attributed to the Coulombic interaction generated during blending. They also described that the adhesive force decreased during storage, particularly at high relative humidity. In the present study we measured the adhesive force between various polymer films and untreated (hydrophilic) glass beads as well as surface-treated (hydrophobic) beads at the range of relative humidity (R.H.) of 40 to 80%. All the experiments were carefully carried out, avoiding any electrostatic effect.

Experimental

Polymers and Preparation of Polymer Films Polyvinylpyrrolidone, PVP (Kollidon 30; BASF); hydroxypropylcellulose, HPC (EF-P; Shin-Etsu Chemical Co., Ltd.); hydroxypropylmethylcellulose phthalate, HPMCP (HP-55; Shin-Etsu Chemical Co., Ltd.); ethylcellulose, EC (N10G; Shin-Etsu Chemical Co., Ltd.); polymethyl methacrylate, PMMA (Acrylite; Mitsubishi Rayon Co., Ltd.); and polyvinyl chloride, PVC (HTS625; Takiron Co., Ltd.) were used as the testing polymers, and are listed in Table I. Each polymer was dissolved in the solvents shown in Table I, and a glass plate was directly dipped in the solution. The solvent was evaporated at room temperature and a polymer film (5—9 μm) was obtained.[3)]

Glass Beads and Their Surface Treatment Glass beads (Toshiba-Ballotini Co., Ltd.) having a mean particle diameter (Heywood's diameter) of 80 μm were used for the measurement of adhesion to PVC, PMMA, EC and HPMCP film. In case of PVP or HPC film, the adhesive force between particles and film was so great that larger particles

TABLE I. Some Properties of Polymer Used and Solvent for Preparation of Polymer Film

Polymer	Structural formula	Substitutional group[a)]		Mean molecular weight[a)]	Solvent	Symbol
PVP-K30 BASF Kollidon30				4.5×10^4	C_2H_5OH	□
HPC Shin-Etsu EF-P		$-O[-CH_2-CH(CH_3)-O-]_mH$	63.8%	5.6×10^4	C_2H_5OH	◇
HPMCP Shin-Etsu HP-55 200731		$-OCH_3$ $-COC_6H_4COOH$ $-O[-CH_2-CH(CH_3)-O-]_mH$	19.1% 32.5% 5.8%	4.5×10^4	C_2H_5OH CH_2Cl_2	○
EC Shin-Etsu N10G		$-OC_2H_5$	49.2%	7.9×10^4	C_2H_5OH CH_2Cl_2	△
PMMA Mitsubishi Rayon Acrylite	$[-CH_2C(CH_3)(COOCH_3)-]_n$			—	CH_3COCH_3	▽
PVC Takiron HTS625	$[-CH_2-CH(Cl)-]_n$			—	$C_6H_{10}O$	⬡

a) Manufacturer's data.

(diameter = 150 μm) had to be employed. Particle density ρ, measured with a Shimadzu-Micromeritics helium–air pycnometer, was found to be 2.40 g/cm^3. Surface treatment of glass beads was carried out as follows. Glass beads (30 g) were shaken with 80 ml of a 10 v/v% benzene solution of trimethylchlorosilane at 25 °C for 24 h and filtered off. After being washed with benzene and acetone, the trimethylsilylated (TMS) glass beads were dried at 140 °C for 24 h.

Measurement of Adhesive Force The adhesive force between the particles and the various polymer films was measured using the centrifugal separation method.[4-6] The schematic diagram of the apparatus and the cell is shown in Fig. 1. Measuring cells equipped with a rotor (RH-150A, Kubota) were rotated around the vertical axis of a centrifuge (KH-180, Kubota). The cell was designed with special attention to air-tightness. In order to avoid electrification of either the particles or the polymer film, sample particles were gently put on polymer film without friction. The film surface of the cell was then faced downward and kept at a given humidity for 24 h in a desiccator. Saturated solutions of $K_2CO_3 \cdot 2H_2O$, NH_4NO_3 and KCl were used to obtain R.H. of 43, 62, and 84% respectively. Shutting the cock, the cell was fixed in the rotor. Some of the particles were detached from the film surface by centrifugal force. Rotational speed (rpm) was measured by a stroboscope, and further centrifugation was allowed to continue for 10 min. The centrifugal acceleration is calculated from the angular velocity and the distance between particles and the axis of the centrifuge.

The percentage of particles remaining on the film was determined by counting the number of particles before and after centrifugation by means of 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}, which was defined as the separation force at which 50% of the particles remained on the film after separation. The experiments were carried out at 25 ± 1 °C.

Measurement of the Amount of Water Sorbed by Polymer Film The amount of water sorbed by polymer film at 25 °C was measured using gravimetry. Each polymer film was placed in a weighing bottle. After standing under vacuum at 25 °C for 24 h, the weighing bottle was transfered into the box where the R.H. was kept constant. An increase in the weight of polymer film was measured after 24 h.

Measurement of Apparent Plasticity of Polymer Film Untreated glass beads were put on polymer film in the cell and kept at a constant temperature and humidity for 24 h. Then the cell was set in a reverse direction in the rotor and centrifuged, so that pressure was applied to the surface of the polymer film by the glass beads. The resulting dents on the polymer film were observed by means of scanning electron micrograph (SEM). From 13—15 SEM photographs of the dent profile, the mean sectional area, *A*, was calculated. The apparent plasticity of each polymer film, *P*, was given by following equation:

$$P = \frac{A}{F} \qquad (1)$$

where *F* is the compression force.

Results

Effect of Standing Time on the Adhesive Force Change in adhesive force, f_{50}, with standing time at a given humidity was investigated. The results are shown in Fig. 2. The adhesive force, f_{50}, reaches an almost constant level after 24 h.

Effect of Humidity on the Adhesive Force The adhesive force, f_{50}, between the untreated glass beads and polymer film was measured at various R.H.s and the result is shown in Fig. 3. It was found that the higher R.H. gave the larger adhesive force for all the polymers. As to PVP, its f_{50} value abnormally decreased at R.H. 80%, where it was observed that PVP dissolved in the adsorbed water. The f_{50} value decreased in the following rank order of PVP, HPC, HPMCP, EC, PMMA, and PVC.

Amount of Water Sorbed on Polymer Film Figure 4

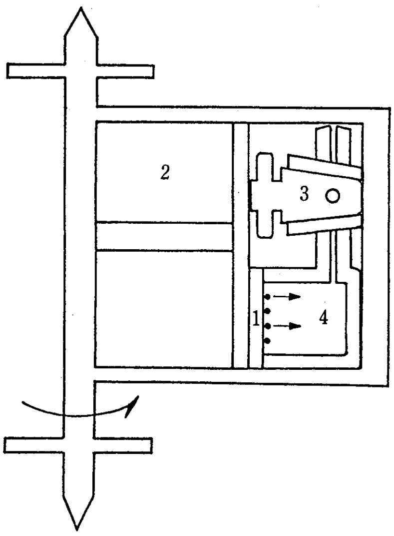


Fig. 1. Schematic Diagram of Apparatus for Centrifugal Separation Method

1, substrate; 2, rotor; 3, cock; 4, glass cell.

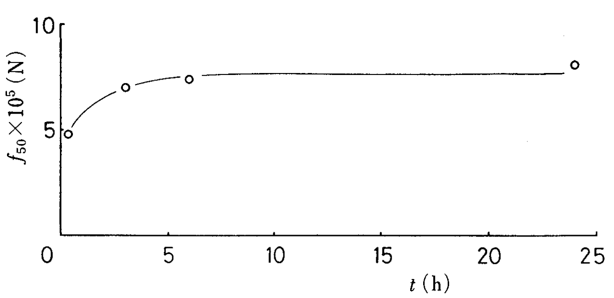


Fig. 2. Variation of Average Adhesive Force f_{50} with Standing Time

Particle, untreated glass; polymer, HPMCP; R.H., 43%.

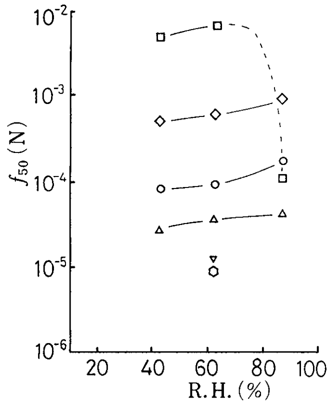


Fig. 3. Relationship between f_{50} and R.H. for Untreated Glass Beads/Polymer Film System

□, PVP; ◇, HPC; ○, HPMCP; △, EC; ▽, PMMA; ○, PVC.

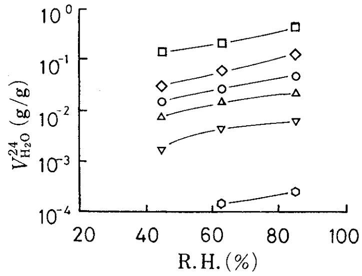
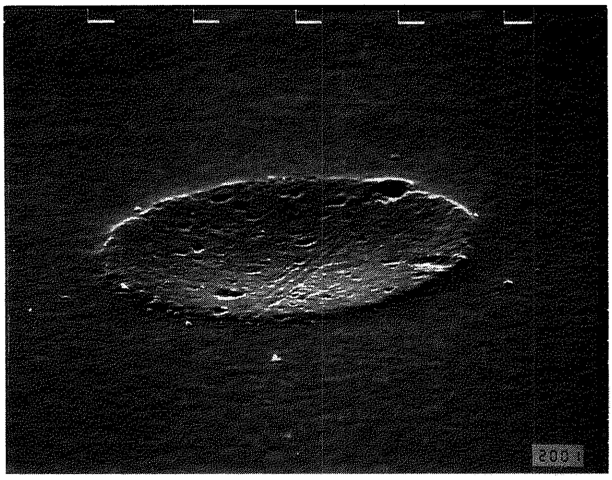


Fig. 4. Relationship between R.H. and Amount of Water Sorbed on Polymer Film

□, PVP; ◇, HPC; ○, HPMCP; △, EC; ▽, PMMA; ○, PVC.



10 μm

Fig. 5. SEM of Dent on Polymer Film

Polymer, HPC; R.H., 62%.

Table II. Apparent Plasticity of Polymer

Polymer	$P \times 10^2$ (cm^2/N)$^{a)}$ ± S.D.
PVP	3.69 ± 0.34
HPC	2.73 ± 0.50
HPMCP	2.49 ± 0.78
EC	1.99 ± 0.82
PMMA	—
PVC	—

a) R.H.: 62%.

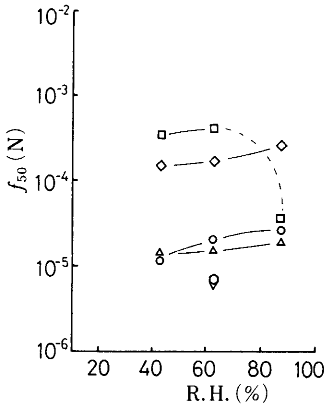


Fig. 6. Relationship between f_{50} and R.H. for Treated Glass Beads/Polymer Film System

□, PVP; ◇, HPC; ○, HPMCP; △, EC; ▽, PMMA; ○, PVC.

shows the amount of water sorbed after 24 h ($V^{24}_{H_2O}$), which increased with increasing R.H. In regard to the type of polymer, the rank order of the amount of sorbed water was found to be the same as the adhesive force.

Apparent Hardness of Polymer Film The SEM photographs of the dents on the polymer film is shown in Fig. 5. The apparent plasticity, P, of each polymer is shown in Table II. The value of P decreased in the rank order of PVP, HPC, HPMCP, and EC, while in PMMA and PVC no dents were observed.

Effect of Surface-Hydrophobicity of Glass Beads The adhesive force, f_{50}, between TMS-treated (hydrophobic) glass beads and polymer film is shown in Fig. 6. Compared with untreated glass beads with a hydrophilic surface (Fig. 3), the f_{50} values were smaller.

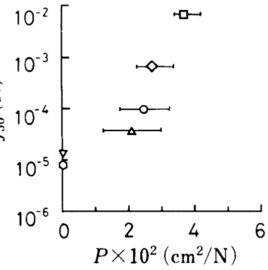


Fig. 7. Relationship between f_{50} and Apparent Plasticity of Polymer Film

□, PVP; ◇, HPC; ○, HPMCP; △, EC; ▽, PMMA; ○, PVC. R.H., 62%.

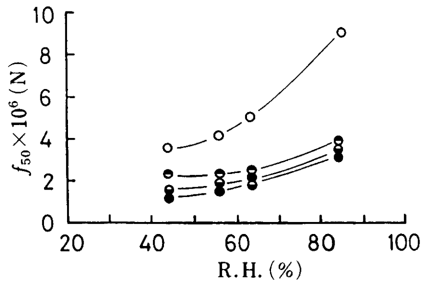


Fig. 8. Relationship between Average Adhesive Force f_{50} and R. H. for Glass Beads/Glass Plate System

○, untreated glass beads/untreated glass plate; ◓, treated glass beads/untreated glass plate; ◒, untreated glass beads/treated glass plate; ●, treated glass beads/treated glass plate.

Discussion

It is considered that the three factors controlling the adhesive force between glass beads and polymer film may be the apparent plasticity of the polymer film as well as the surface properties of the polymer and particles. In Fig. 7, the f_{50} values at R.H. of 62% are plotted against P values. It was found that the f_{50} value increased as the P value increased. This finding suggests that the surface of polymer film becomes soft with sorbed water, and the larger contact area gives a larger adhesive force.

Comparison between Figs. 3 and 6 reveals that the adhesive force is affected by the hydrophilicity of the particles. In order to confirm the influence of the surface property on the adhesive force, measurements of the adhesive force were carried out using untreated and TMS-treated glass beads and glass plates. The results are shown in Fig. 8. Since the glass plate is rigid, plastic deformation at the point of contact with the particles can be neglected; consequently, the values of the adhesive force are very low. However, it was found that the adhesive force between the untreated glass beads and the untreated glass plate was always largest at any R.H., and that the TMS-treatment of either particle or plate reduced the adhesive force. This tendency was more evident at a higher R.H.

It may be concluded that the adhesive force between glass beads and polymer film is influenced by the surface softening of the polymer film due to water sorption. On the other hand, the effect of the surface polarity of glass beads should not be ignored.

References and Notes

1) This work was presented at the 110th Annual Meeting of the Pharmaceutical Society of Japan, Sapporo, August 1990.
2) *a*) P. Kulvanich and P. J. Stewart, *Int. J. Pharmaceut.*, **35**, 111 (1987); *b*) *Idem*, *ibid.*, **39**, 51 (1987); *c*) *Idem*, *J. Pharm. Pharmacol.*, **40**, 453 (1988).
3) It was confirmed that the effect of film thickness could be neglected within the present experimental condition.
4) A. Otsuka, K. Iida, K. Danjo and H. Sunada, *Chem. Pharm. Bull.*, **31**, 4483 (1983).
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