Effect of Surface Treatment of a Polymeric Filler on its Interaction with a Plasticizer

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Synopsis

The interfacial behavior of a filler–plasticizer system was investigated using the pair poly(sodium methacrylate-co-divinylbenzene) beads–diisooctyl phthalate. The effect of various surface treatments of the filler was studied. These consist of a selective extraction of surfactant used in its preparation by emulsion copolymerization and in the adsorption of other types of surfactants. Changes in the compatibility between the two basic components were determined from measurements of the rate of penetration of the plasticizer through the filler bed, from the rheological behavior of concentrated suspensions and from the extractability of the filler from the plasticized PVC matrix.

INTRODUCTION

A characteristic feature of filled polymer systems is their considerable interfacial area, and their behavior is therefore markedly determined by the interaction between components in the interface. It is known that interfacial interactions may be altered by the adsorption of surface-active compounds on the scattered solid component. The role of surface modifiers in models of composite materials was studied in detail by Tolstaya.[1,2] From her studies, exclusively devoted to inorganic fillers, it may be deduced that the distribution of filler particles in the polymeric matrix depends on both opposite parts of the surfactant. The polar group decides about the strength of the filler—surfactant bond (either chemisorption or physical sorption), while the nonpolar group decides about the so-called polymerophility of the surfactant. The chemical similarity between the nonpolar part of surface-active compounds and the polymeric matrix has led to an improvement in the dispersion of fillers. No studies could be traced in the available literature in which the effect of surface modification in the case of polymer filler is examined. Our interest was focussed on a corpuscular polymer filler based on poly(sodium methacrylate-co-divinylbenzene) developed for the hydrophilization of plasticized PVC.[3] Since diisooctyl phthalate is an important component of plasticized PVC as a continuous phase, the filler–plasticizer system was investigated as a simplified model of composite material.

In this model system, interfacial forces are described by the wettability of the solid phase with the liquid phase, i.e., with the plasticizer. The wettability of powderlike materials is investigated most often by direct optical measurement of contact angles on tablets of compressed powder.[4] In our case such a method was not suitable because filler particles are hollow beads of different

wall thickness coated on the surface with emulsifiers used in the preparation of the filler. For this reason, the wettability of the filler was investigated by using the measurement of the rate of penetration of the wetting liquid through a powder bed[4]; the method is based on the assumption that pores in the powder bed can be modelled by a bundle of capillaries.[5] Mathematical treatment of the penetration method is based on the theoretical Washburn equation[6] derived for the rate of penetration of a liquid through a vertical capillary. Assuming small pore radii in the bed and small penetration heights, the rate of penetration of a liquid through the powder bed is described by the equation

$$\frac{dh}{dt} = \frac{k\bar{r}\gamma_L}{4\eta h}\cos\theta t \qquad (1)$$

where h is the penetration height during the time t, $\bar{r}$ is the effective capillary radius, k is a constant expressing the curvature of the capillary in the bed, η is the viscosity of the penetrating liquid, γ_L is the surface tension of the penetrating liquid, and θ is the contact angle.

In addition to changes in the interface, however, modification of the surface of filler particles is also reflected in interactions of the particle–particle type. In wettability measurements by penetration, particles are fixed in the bed and no particle–particle interactions can be observed; they are, however, the decisive factor of the flow behavior of suspensions.[7,8] Due to attractive forces, solid suspension particles form strong three-dimensional thixotropic structures which are destroyed due to shear stress, but are again formed due to London–van der Waals forces, if the suspension is at rest. The degree of destruction of thixotropic structures is proportional to the magnitude of the shear rate.[9,10]

EXPERIMENTAL

Preparation of Surface-Treated Samples. The starting hydrophilic filler (sample HF1) is a product of the emulsion copolymerization of divinylbenzene and sodium methacrylate carried out in water in the presence of two emulsifiers in the mass ratio 1 : 1, viz., Dowfax 2A1 (4'-dodecyldiphenyl ether-2, 4-sodium disulfonate, anion-active surfactant) and Slovafol 909 (25-(p-nonylphenoxy)-3,6,9,12,15,18,21,24-octaoxa-1-hexacosanol, nonionogenic surfactant). The water emulsion thus obtained was dried on a spray drier, where the final product is in the form of hollow beads[3] (cf. Fig. 1). The surface of the starting sample HF1 was further treated by selective extraction with methanol and by adsorption of four surface-active compounds from methanolic solutions (1% by mass). Table I contains a survey of the samples used and of their surface treatments. The latter were carried out as a single operation within 24 h at room temperature, with stirring and in an excess of the medium. In the case of sample HF2, the extract was analyzed by the IR spectrometric method, and it was found that the noninogenic emulsifier is selectively washed out. Of all samples, fractions 32–63 μm stored over P_2O_5 were used in the measurements.
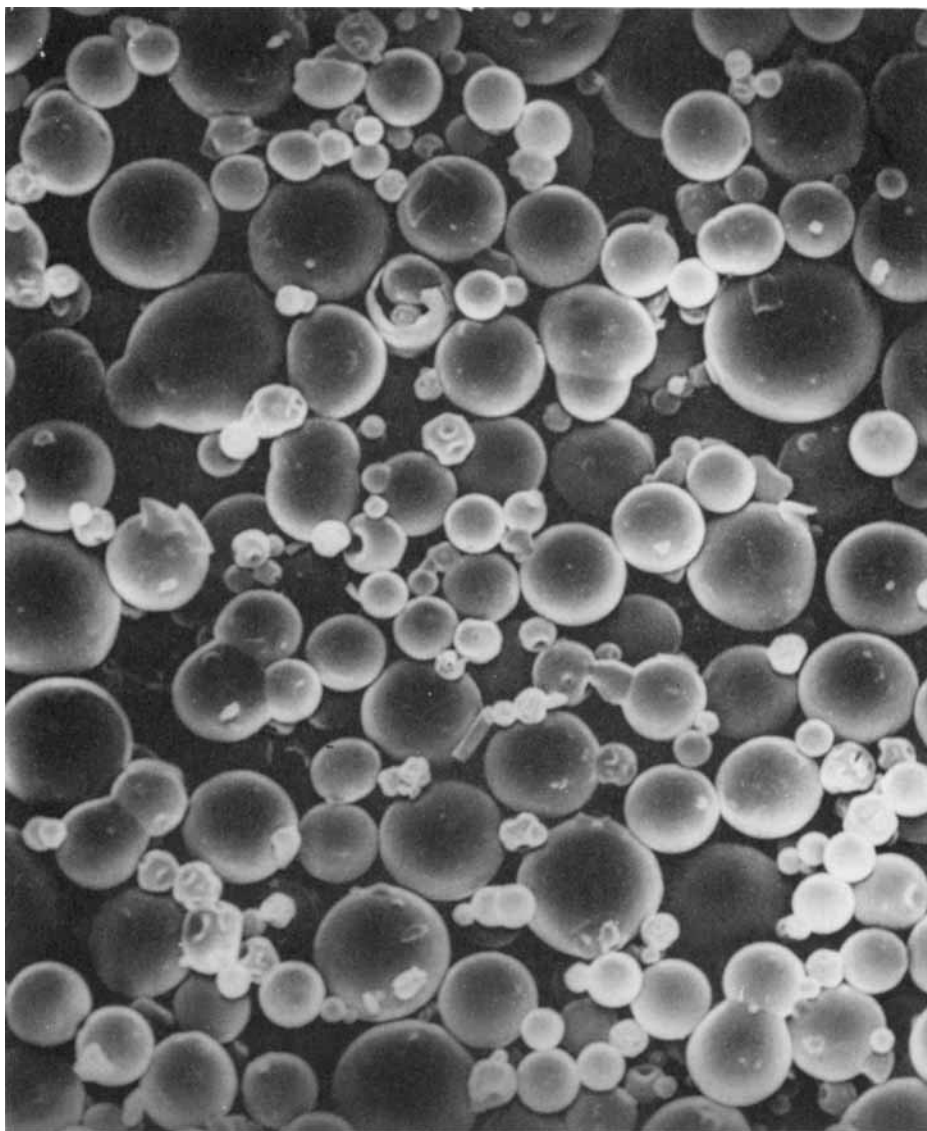
Fig. 1.   Micrograph of polymer filler obtained with a scanning microscope JSM 35 (magnified 750 ×).

Penetration Rate Measurements. The penetration rate of diisooctyl phthalate into the bed of powder filler was investigated in glass tubes, 1 cm in diameter, terminated with a glass filter (pores 15–40 μm). The tubes were filled by hand in very small sample doses, and each dose was pressed by hand with a glass piston. The height of packing was kept constant; the reproducibility of filling was checked by weighing. The lower end of the sample column was adjusted to the diisooctyl phthalate level by means of the mechanical part of a microscope. The height of the liquid in the bed was read off by means of a cathetometer in short times intervals.

TABLE I
Survey of the Samples

Sample	Surface treatment of filler
HF1	Starting sample (anion-active + noninogenic surfactants on the surface)
HF2	With methanol in excess (noninogenic surfactant was extracted)
HF3	1% by mass methanolic solution of anion-active surfactant Kicker–FK 201 [mixture of zinc(II) and cadmium(II) salts of higher aliphatic acids]
HF4	1% by mass of methanolic solution of monocetyl phthalate (weakly anion-active surfactant, chemically similar to plasticizer)
HF5	1% by mass methanolic solution of cation-active surfactant Septones {[1-(ethoxycarbonyl)pentadecyl] trimethylammonium bromide}
HF6	1% by mass methanolic solution of cation-active surfactant Ajatin (dimethylbenzyl–dodecylammonium bromide)

Measurement of Flow Curves. The experiments were carried out with filler suspensions (40% by mass) in diisooctyl phthalate in a rotational viscometer with concentric cylinders Rheotest 2 (VEB Prüfgeräte-Werk Medingen, East Germany), with an attached line recorder (TZ 4221-Laboratory Instruments, Prague). A data record is shown schematically in Figure 2, where part a demonstrates the time régime of action of shear rates on the suspensions and b is a record of the shear stress from the recorder corresponding to the respective shear rates. The steady value of shear stress at a given shear rate for samples of variously surface-treated filler was used as the measure of the magnitude of particle–particle interaction. To guarantee the same hydrody-
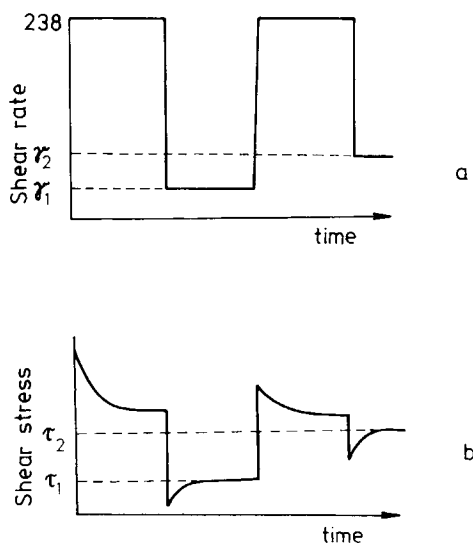

Fig. 2. Schematic view of rheological measurements.

namical history of suspensions before each measurement of the steady shear stress value, the suspension was stirred for 10 min at the shear rate 238 s^{-1}. This value is the highest possible shear rate of the viscometer used at which the most flocculated suspension of sample HF2 could still be measured (discussion in the following chapter). The period of 10 min was sufficiently long for all samples. The suspensions were deaerated before measurement and predried in a desiccator over P_2O_5.

Preparation of Samples of Filled Matrices. Weighed components (45 g PVC–Vestolit 7012 + 53 g diisooctyl phthalate + 15 g filler) were stirred by using a laboratory stirrer and then homogenized on a three-roll friction calender. The paste thus formed was deaerated and gelatinized by means of a special depositing device (Werner-Mathis AG, Zürich). Gelatinization to the first degree proceeded at 115–120°C for 10 min; the final gelatinization took place at 190°C for 2 min. Silicone paper was used as support. The deposit thickness was 2 × 0.25 mm. Along with samples of filled matrices, a control film without filler was prepared by the same procedure from 50 g PVC + 50 g DOP.

Measurement of the Filler Extractability from Matrices. Specimens, 2 × 5 cm^2 in size, were cut out from the films and conditioned 48 h in a desiccator over P_2O_5. After that they were extracted with water in a Soxhlet apparatus for 5 h and dried 72 h over P_2O_5.

RESULTS AND DISCUSSION

One series of experimental penetration data, viz., the penetration height h in a time t, has been plotted in Figure 3 for four samples, HF1, HF2, HF4, and HF5. Results obtained with the sample HF3 has not been plotted for the sake of clarity. The h^2 vs. t plots were linear in all cases, and the data could be treated using the integrated form of eq. (1): $h^2 = A \cos \theta t$, where A = const $= k\bar{r}\gamma_L/2\eta$. The straight lines in the figure are a result of correlation obtained from three independent experiments. The wettability of the samples was not characterized directly by the $\cos \theta$ values, as no liquid could be found suitable for the determination of the numerical value of the constant of the filler bed $k\bar{r}$, the contact angle of which would be close to zero and which at the same time would not affect the particle size by swelling. Therefore, the $A \cos \theta$ values used for the characterization were calculated by the least squares method and are summarized in Table II, together with those of the correlation coefficients of linear regression, r_{xy}. A comparison between the $\cos \theta/\cos \theta_1$ values for the individual samples shows that the wetting of modified samples with diisooctyl phthalate has been impaired with respect to the original sample only in the case of extraction with methanol (HF2). On the contrary, adsorption of all surfactants from the methanolic solution has improved the wettability. The samples can be arranged in the following order according to the improving compatibility between the filler and the plasticizer: HF2 < HF1 < HF3 < HF4 < HF5.

The decreased penetration rate observed with HF2 samples is obviously due to a decrease in the total concentration of surfactants on the particle surface below the effective concentration range after the nonionogenic emulsifier has been extracted with methanol. In samples HF3–HF5 the excess methanolic
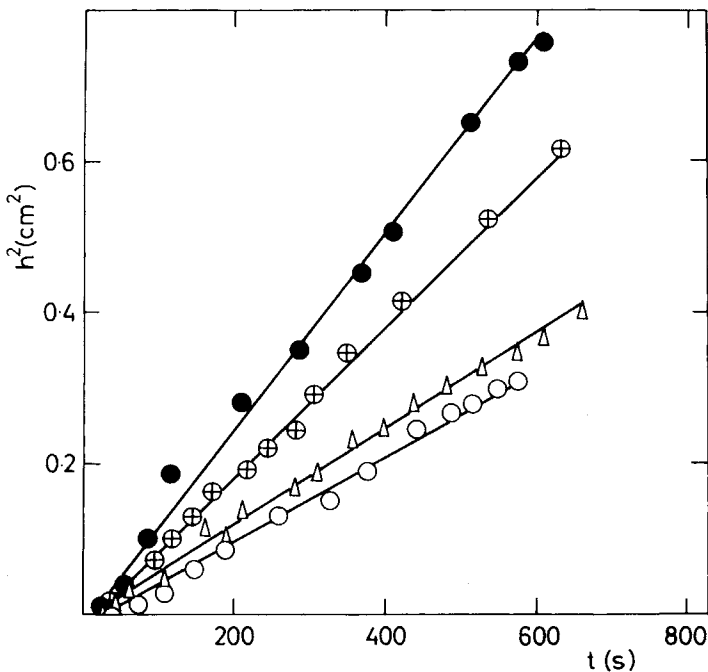
Fig. 3. The effect of modification of the filler surface on the penetration rate of samples: (△) HF1; (○) HF2; (⊕) HF4; (•) HF5.

solution of a further surfactant also causes a simultaneous desorption of the nonionogenic emulsifier, followed by the adsorption of the new surfactant. Assuming approximately the same degree of desorption in all samples, the adsorbed amount of the new surfactant is determined by its structure, because experimental conditions were chosen so as to establish the equilibrium adsorption. Wettability of the filler with the plasticizer became markedly improved after the adsorption of the cation-active surfactant Septonex, probably due to a dipole interaction between its cation-active group and the anion-active group of the emulsifier Dowfax, which remains on the particle surface also after the extraction with methanol. The surface treatment with monocetyl phthalate which is chemically very similar to the plasticizer appeared to be less effective.

We do not report the result of measurement of sample HF6 by the penetration method. Particles of this sample, even if perfectly dry, adhered to

TABLE II
Effect of Modification on Wetting ($A \cos \theta$)

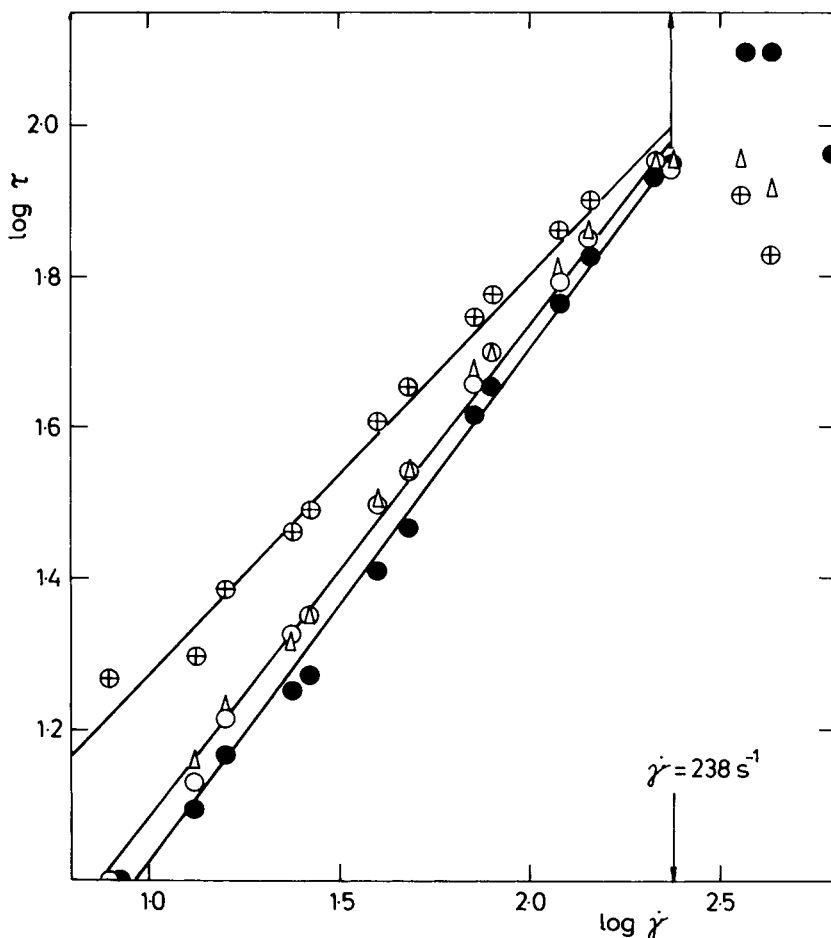| Sample	$10^3 A \cos \theta$	$\cos \theta / \cos \theta_1$	r_{xy}
HF1	0.716	1.000	0.945
HF2	0.650	0.908	0.962
HF3	0.937	1.309	0.995
HF4	1.174	1.640	0.993
HF5	1.304	1.820	0.993

Fig. 4. Changes in the steady values of shear stress τ (Pa) vs. shear rate $\dot{\gamma}$ (s^{-1}) as a consequence of modification of the filler surface for samples: ($\triangle$) HF1; ($\circ$) HF2; ($\oplus$) HF4; ($\bullet$) HF5.

each other, which caused difficulties in filling the columns, and the condition of the method, viz., identical geometry and pore size in the bed, was probably not satisfied.

The results of rheological measurements of filler suspensions in diisooctyl phthalate are given in Figure 4 where the steady values of shear stress τ are plotted on a logarithmic scale against the shear rate $\dot{\gamma}$, for the same four samples, which were used in the penetration measurements. The HF3 sample has been omitted for a better clarity of the figure. The log τ vs. log $\dot{\gamma}$ plots were linear for all samples in the range $\dot{\gamma} < 238$ s^{-1}, which enabled the data to be treated by means of an empirical relation utilized for the flow of non-Newtonian liquids of the so-called power law[11]

$$\tau = B\dot{\gamma}^n \tag{2}$$

where B and n are constants; the constant B has a physical meaning of

TABLE III

Flow Behavior of Suspensions ($\tau = B\dot{\gamma}^n$)

Sample	n	B	r_{xy}	$\dot{\gamma}_{max}$ (s^{-1})
HF1	0.660	2.608	0.997	357
HF2	0.655	2.715	0.998	238
HF3	0.613	3.403	0.991	428
HF4	0.533	5.489	0.994	642
HF5	0.677	2.228	0.996	1312
HF6	0.712	1.909	0.996	> 1312

extrapolated shear stress at a unity shear rate, the constant n expresses a deviation from the Newtonian behavior of the liquid. The values of the constants B and n were calculated by a linear regression of logarithmic data of three independent experiments for the shear rate range $\dot{\gamma} < 238$ s^{-1}. The results of numerical treatment are summarized in Table III (where r_{xy} again represent values of the correlation coefficients) and are represented by straight lines in Figure 4.

Assuming similar τ vs. $\dot{\gamma}$ dependences for all suspensions in the range of very low shear rates, one may regard the extrapolated B value as a measure of the strength of thixotropic structures, and thus also of the magnitude of particle–particle interactions. By arranging the samples according to increasing value of B, we obtain a series of samples with increasing tendency towards the formation of thixotropic structures: HF6, HF5, HF1, HF2, HF3, and HF4. It can be seen that the first places in this series are occupied by samples which have been surface-treated with cation-active surfactants and which, according to the penetration method, possess the best wettability with the plasticizer. The n values show that these samples are also closest to the Newtonian flow. Surprisingly, the measured shear stress values of samples HF4 and HF3, surface-treated with weak anion-active surfactants, are quite high. The strong tendency of these suspensions towards the formation of thixotropic structures which was not expected on the basis of penetration measurements could not be satisfactorily explained.

The effect of cation-active surfactants in the range of shear rates above 238 s^{-1} appeared to be of interest. In these cases at a certain shear rate the measurement of suspensions was accompanied by a steep drop of the shear stress, and its value could not be read off due to great instabilities of the record. A similar behavior of concentrated suspensions has also been observed by other authors[12,13] and has been described as a cohesive fracture of dispersion. Small shearing forces acting on the suspension cause a partial destruction of three-dimensional thixotropic structures to aggregates of particles. An increase in the acting force above a certain value, however, leads not only to the destruction of the thixotropic structures, but also to the decomposition of the aggregates of particles, which is reflected in a sudden drop in the shear stress of the suspension. From the rheological viewpoint it is assumed that this phenomenon takes place after the laminar flow has ceased due to the high shear rates acting upon concentrated suspensions. In Table III we give the maximal shear rate values $\dot{\gamma}_{max}$ for the individual samples of the suspensions at which some partial flow disturbances could indeed be observed; yet the

TABLE IV
Extractability of Filler from PVC Matrix

Sample	Δ%
HF1	75.6
HF2	79.1
HF4	65.6
HF5	39.9

average shear stress value could still be determined. If the measured suspensions are arranged with respect to the increasing $\dot{\gamma}_{max}$ values, the same order of samples is obtained as in the case of penetration experiments, where the samples were arranged with respect to the increasing $A \cos \theta$ values, i.e., according to the improving compatibility between filler and plasticizer. From the agreement between the results, we may deduce that the decisive factor for the fracture of the suspensions is the magnitude of the filler–plasticizer interactions.

The results concerning extractability of the filler from the PVC matrix with hot water are summarized in Table IV, where for matrices filled with the described filler samples we give weight percentages of filler losses from the matrix with respect to the initial weighed amount of the filler (15 g). The matrix filled with HF3 was not prepared. The order of the samples with respect to the decreasing quantity of extracted filler coincides with that with respect to improving compatibility between filler and plasticizer obtained from penetration experiments.

CONCLUSION

Evidence is given of the effect of modification of the surface of a polymer hydrophilic filler of the poly(sodium methacrylate-co-divinylbenzene) type by various ionogenic surfactants, not only on the plasticizer–filler interaction, but to a great extent also on the type of the particle–particle interactions in the suspensions under study. The use of cation-active surfactants appeared very favorable, since it helped to improve greatly the compatibility of the two components of the polymer filler–plasticizer system investigated in this study. An investigation of the plasticizer–filler system as a simplified model of filled plastified PVC has been found to be justified. Also, it has been found that the simple and experimentally not demanding penetration method is a suitable tool for the evaluation of compatibility between filler and plastifier, which plays a decisive role in the extractability of filler from the PVC matrix.

References

1. S. N. Tolstaya, *Faserforsch. Textiltechn.*, **29**, 19 (1978).
2. S. N. Tolstaya, *Problemy Polimernykh Kompozitnykh Materialov*, Izd. Naukova Dumka, Kiev, 1979, p. 3.
3. F. Juračka and S. Hudeček, Czech. Pat. 185 863 (1981).
4. A. W. Neumann and R. J. Good, *Surface and Colloid Science*, Plenum, New York 1979, Vol. 11, Chap. 2.
5. D. D. Ely and D. G. Pepper, *Trans. Faraday Soc.*, **42**, 697 (1946).
6. E. W. Washburn, *Phys. Rev.*, **17**, 374 (1921).

7. W. B. Russel, *J. Rheol.* **24**, 287 (1980).
8. I. Jalchenyak and I. Chtivitsch, *Polymer*, **22**, 847 (1981).
9. Y. Otsubo, M. Horigome, and K. Umeya, *J. Coll. Interface Sci.*, **83**, 241 (1981).
10. T. Shikata and T. Kotaka, *Rep. Prog. Polym. Phys. Jpn.*, **25**, 179 (1982).
11. F. R. Eirich, *Rheology*, Academic, New York, 1960, Vol. 3.
12. T. A. Strivens, *J. Coll. Interface Sci.*, **57**, 476 (1976).
13. J. Ferguson, G. F. Bradley, and J. Beresford, *Rheol. Acta*, **10**, 479 (1971).