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RHEOLOGICAL BEHAVIOUR OF PIGMENT FILLED POLYMER DISPERSIONS: THE INFLUENCE OF ELECTRIC FIELD[1]

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Abstract

Rheological properties of materials are related to their response to applied stress. The field induced chain formation of a large number of organic and inorganic substances such as starch, aluminium oxide, ferric oxide, carbon black, ion-exchange resins, and polymer powders have been studied mainly in insulating oils.

Much less is studied and understood the electrorheological effect of pigments in polymer dispersions. Titanium dioxide is one of the most frequently used surface coatings due to its high-quality and ecologically acceptable properties. In the present paper the authors first review the basic principle of electrorheology, then it is followed by experimental studies on structuring and rheological properties.

Keywords: electrorheology, dielectrophoresis, polymer dispersions, viscosity.

1. Introduction

Electrostatic spray painting is widely used in order to enhance the paint transfer efficiency. It is based on strong Coulombic interactions between paint particles and surface to be coated. An electrostatic field is created and as a result, the paint particles pick up electrons and become ionised. The grounded work piece attracts the negatively charged paint particles and thus the transfer efficiency is increased significantly. Another electrostatic effect is based on the polarisation of dispersed particles in electric field. Small particles in the size range from about one micron up to one millimetre dispersed in non-conducting medium, mainly in organic solvents, can respond to an applied electric field by rapidly changing their apparent viscosity. Such a colloidal solution is called *electrorheological fluid* and the interaction with the field is often designated as *dielectrophoresis*. The dielectrophoresis refers to the

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force exerted on the induced dipole moment of an uncharged particle by nonuniform electric field. The polarised particles interact not only with the imposed field, but also with each other. At close spacing these interaction forces can be quite strong. The particles attract each other when aligned parallel to the applied field, or repel each other when in perpendicular alignment. The attractive forces between particles lead to *chain formation*. The pearl chain structuring makes possible far reaching implication in particulate science. The field induced chain formation of a large number of organic and inorganic substances such as starch, aluminium oxide, ferric oxide, carbon black, ion-exchange resins, and polymer powders have been studied mainly in insulating oils.

Much less is studied and understood the electrorheological effect of pigments in polymer dispersions. Titanium dioxide is one of the most frequently used surface coatings due to its high-quality and ecological acceptable properties. In the present paper the authors first review the basic principle of electrorheology, then it is followed by experimental studies on structuring and rheological properties.

2. Electrorheological Effects

The terms of electrophoresis and dielectrophoresis imply the interplay between electrical phenomena and motion. Dielectrophoresis is the translational motion of neutral particles in nonuniform electric field due to polarisation. Although polarisation effects are often considered to be weak, there are several examples where they are far more effective than Coulomb forces, since polarisation forces can act directly on an uncharged particle. Electrorheology is based on dielectrophoretic effects.

All materials experience forces or torques when subjected to electric field. These interactions are strong in the case of certain solid materials, but rather weak in fluid systems. In order to enhance the influence of the external fields on the fluid-like properties, it is necessary to combine solid like and fluid like behaviours. Since polymer dispersions contain substantial amount of liquid, it is possible to fabricate a field sensitive fluid, called complex fluid. A complex fluid contains dispersed small particles in the size range of nanometers to micrometers [1]. Respondig to an applied field the particles in the fluid couple the viscosity, yield stress and other physical properties to the external. The response time can approach the order of millisecond [2]. If we incorporate polarisable colloidal particles into a polymer solution, due to an imposed electric field, the particles experience a dielectrophoretic force. Since the particles move together with the fluid, all of the forces acting on the particles are transmitted directly to the polymer dispersion resulting in peculiar rheological behaviour.

If an electrorheological fluid is exposed to an external field, two distinct types of interactions can be identified: *field–particle* interaction, as well as *particle–particle* interaction. If the field is nonuniform, then the field–particle interactions are dominant. Particles experience a dielectrophoretic force, f_{DEP}. As a result the particles are attracted to regions of stronger field intensities [3]:

$$f_{\mathrm{DEP}} = 2\pi \varepsilon_1 R^3 K \nabla E^2, \tag{1}$$

where ε_1 denotes the dielectric permittivity of the solvent, R stands for the radius of colloidal particle. The symbol ∇ represents the gradient operator. The quantity K, known as the Clausius–Mossotti function, provides a measure of the strength of the effective polarization of the spherical particle with a dielectric permittivity of ε_2:

$$K(\varepsilon_1, \varepsilon_2) = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}. \tag{2}$$

Eq. (1) reveals the most important feature of electrophoretic effects. It says that the electrophoretic force is proportional to the particle volume of the individual particles dispersed in the liquid. f_{DEP} is also proportional to the dielectric permittivity of the medium in which the colloidal particles are suspended. It is important to mention that the dielectrophoretic force vector is directed along the gradient of the square of electric field intensity, ∇E^2 which is, in general, not parallel to the electric field vector, E. It is also seen that f_{DEP} depends on the sign and magnitude of the Clausius–Mossotti function. In the case of $K > 0$ the colloidal particles are attracted to electric field intensity maxima and repelled from minima. The direction of the field does not play any role.

In uniform fields the situation is completely different. Due to the lack of field gradient, there are no attractive or repulsive field–particle interactions. The particle–particle interaction becomes dominant. The imposed field induces electric dipoles. As a result, mutual particle interactions occur if the particles are so closely spaced that the local field can influence their neighbours. This mutual interaction can be very strong leading to a significant change in the structure of particle ensembles. The particles attract each other when aligned end to end, and repel each other in side by side situation. Due to the attractive forces the pearl chain structure may develop. This field induced chaining has been found to influence the value of viscosity and yield stress. In nonuniform field both phenomena, the dielectrophoretic force as well as the structure formation occur.

3. Experimental Part

The model system of our studies was based upon the dispersion of TiO_2 in silicon oil.

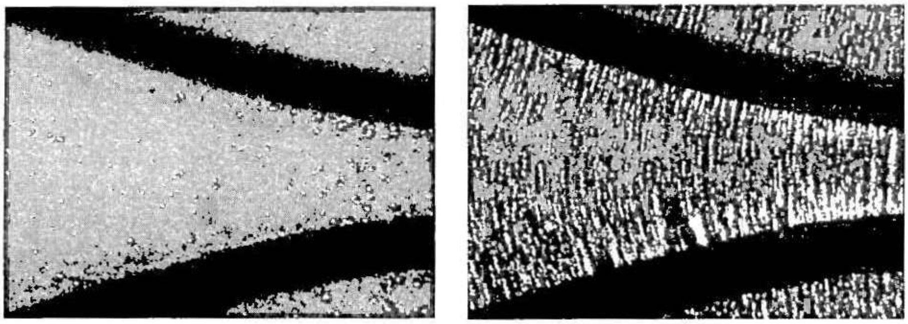
TiO_2 (rutil) TRONOX T R-HP-2 (Kerr-McGEE PIGMENTS GmbH & Co.) was used. The BET surface is 7 m^2/g. The average particle size is 0.4 μm.

The silicon oil (DC200) was obtained from Fluka. The viscosity of the silicon oil is 1 Pas at 25 °C. The suspension was prepared by first adding surfactant TWEEN-65 (Merck) to the pure silicon oil in a concentration of 0.4 m%.

Optical microscopical studies of structure formation due to electrorheological effects were undertaken by Hund Wetzlar H-500 microscopic set connected to a video camera (Sony CCD-IRIS /RGB). The TiO_2 dispersion was placed in a channel formed by fixing two stainless steal wire electrodes on the surface of the microscope slides. The electric field was generated by applying voltage to the wires. Because the high turbidity of the TiO_2 dispersions, optical visualization was only possible for dilute dispersions. The concentration of the dispersion was 15.24 m%.

A viscosimeter with electrically insulated rotational elements was implemented in the determination of the influence of the electric field. The rheological experiments were performed on Rheostress RS 100 dynamic rheometer with parallel plates measuring head which was modified for the application of large electric fields. The electric field was applied by a homemade power supply. Rheological measurements were performed by shearing the suspension at constant shear stress (5 Pa) both in lack of electric field and under the influence of field. Low oscillating load with small amplitude was used in order to study the temporal structural changes due to the imposed DC electric field. The real part of the complex viscosity was recorded in time.

All the measurements including visual observations and viscosity measurements were performed at ambient temperature.

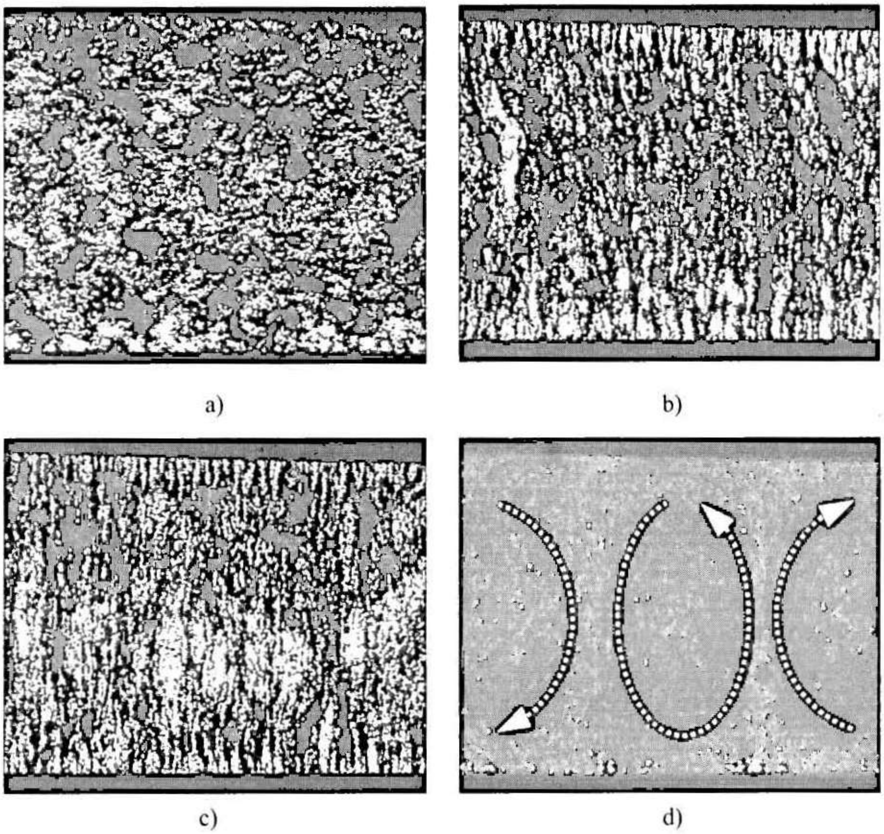


a b

Fig. 1. Development of TiO_2 particle alignment under non-uniform electric field observed microscopically. a) no electric field applied, b) the voltage between the wires is 215 V. The TiO_2 are dispersed in silicon oil. The gap distance varies from left to right from 675 μm to 200 μm

4. Results of Visual Observations

Fig. 1 shows the effect of nonuniform electric field on the TiO_2 suspension. The field intensity increases from left to right in the figure. As a result, a field gradient perpendicular to the direction of the field develops. The field intensity varies from 2 kV/cm to 6.5 kV/cm.


a)

b)

c)

d)

Fig. 2. The effect of the uniform electric field intensity on the structure formation of TiO_2 suspension. a) no external field is applied, b) field intensity: 4 kV/cm, c) field intensity: 12.5 kV/cm, d) field intensity: 50 kV/cm

In nonuniform field at least two phenomena occur. Due to the field gradient the particles are forced to move to the higher field intensities (field–particle interaction). The other effect is the particle–particle interaction, which results in alignment and chaining. On the basis of this figure, it may be concluded that the particle–particle interactions are much stronger than the particle–field interactions. The pearl chain structure is stable under the electric field; the dielectrophoretic force is not enough to destroy the fibrillation. It is important to mention that particle alignment takes only place if the field intensity does not exceed a critical value. At high electric fields electroconvection of the suspension occurs. This is demonstrated in *Fig. 2.*

This figure also shows the pearl chaining under the influence of the electric field. As far as the intensity of the electric field is smaller than 20 kV/cm the particles form chain-like structures. Above this field intensity the order structure is destroyed by the streaming of the suspension. In the figure this convective motion can hardly be seen, therefore we have denoted the motion of the fluid by dotted white curves. The convection occurs at high field intensities, it is very similar to the hydrodynamic pattern formation, called Benard-instability.

5. The Influence of Electric Field on the Rheological Behaviour

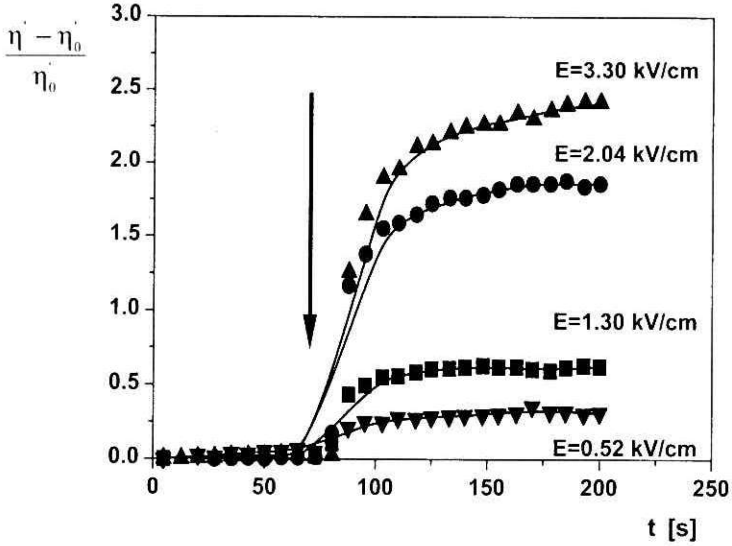


Fig. 3. The influence of electric field on the viscosity of the TiO_2 suspension. The arrow indicates the time when the external field was switched on. The field intensities are shown in the figure.

Structure formation is expected to strongly influence the rheological properties. This is demonstrated in *Fig. 3* where the relative increase of viscosity is plotted against time. A significant increase in the viscosity has been observed. The measure of the viscosity enhancement strongly depends on the applied field. It was found that not only the field intensity, but also the concentration of TiO_2 particles play a decisive role in the viscosity increase. For more concentrated suspensions we have found a ten-fold increase. In our lecture we provide more experimental evidence for the influence of electric field on the rheological behaviour. A theoretical interpretation will also be provided in order to help the application-oriented research. The electric field sensitivity of pigment filled polymer systems may be exploited to develop new type of paints or/and painting methods.

Acknowledgement

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