# THE ELECTRORHEOLOGY OF DISPERSED SYSTEMS

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The rheoelectric and electrorheological effects are considered for dispersed systems.
The effects are due to polarization and interaction of particles of the dispersed phase in
electric fields.

A basic problem in modern rheology is to relate the mechanical properties of a dispersed system
to the structure, and this demands combined use of rheological, optical, electrical, and other methods.

One can obtain valuable information on the nature of such systems, including polymer melts and solu-
tions, by combining steady-state rheological methods (constant shear stress, constant strain rate, etc.)
with dynamic and frequency-varying methods. This enables one to characterize the relaxation spectrum
in relation to deformation, and it has been found [1] that the dynamic elastic moduli and the low-frequency
loss are much reduced on going from a state of rest to one of steady-state flow, which indicates that a
flow increases the importance of rapidly relaxing bonds between structure elements and decreases that of
bonds with long relaxation times.

It is very valuable to combine rheological methods with the use of polarized light. Flow birefringence
and light scattering for polymer solutions indicate the size and shape of the macromolecules [2]. There is
considerable birefringence in some nonaqueous plastic systems of thickened-lubricant type [3]. Frozen
flow patterns are formed when a flow is stopped rapidly, i.e., the particles retain the orientation corre-
sponding to the strain rate. The effect is dependent on the capacity of such a lubricant to restore its struc-
tural framework rapidly and enables one to observe a flow structure at rest. However, polarized light often
cannot be used because these concentrated systems are largely opaque.

Joint use of electrical and rheological effects opens up considerable scope for research; the inter-
action between these reveals many structural features undetectable by either method alone. Also, elec-
trical methods offer much scope for influencing the structure.

Electrorheology involves research on the above relationships and the control of mechanical prop-
erties via electric fields. The following three main trends may be distinguished in electrorheology re-
search.

1. The effects of particle charge on rheological behavior (the electroviscosity effect).

2. The effects of shear, tension, and compression on structure and dielectric properties (the rheo-
electric effect).

3. The effects of electric fields on structure and rheological behavior (the electrorheological effect).

There are the following three reasons for viscosity increase in charged suspensions and polyelec-
trolyte solutions: a) shear in the diffuse part of the electrical double layer (first electroviscous effect); b)
overlap and repulsion of double electrical layers at relatively high concentrations (second electroviscous
effect); c) coiling of molecular chains and increase in clump size in polyelectrolyte solutions by repulsion
between ionic groups (the third electroviscous effect) [4]. A fourth electroviscous effect is expected at
high shear rates and high concentrations on account of deformation of ionic shells in the flow and conse-
quent increased particle interaction.

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The rheoelectric effect gives information on particle shape, orientation, and clumping.

Shear reduces the electrical conductivity because the conducting structural framework is disrupted; the recovery at rest is due to the converse effect [5-7]. However, shear can raise the conductivity in a hydrocarbon dispersed system on account of charge transfer by collision [8] or because the free-charge concentration is increased by stripping of the diffuse part of the double layer [9].

Shear affects the dielectric constant because of orientation of polarizable anisodiametric particles, deformation of soft particles, and structure disruption [11-18]. The orientation effect increases with the dipole moment of the particles; dielectric and other measurements indicate that the particles can have induced and permanent dipole moments [19-21, 24]. The induced part can be due to surface polarization (Maxwell—Wagner polarization [22], polarization of the double electrical layer [23, 25, 26]) or to bulk polarization [27]; it is governed by the dielectric parameters of the medium and the dispersed phase as well as by the state of the phase interface. Hydroxyl groups linked by hydrogen bonds play a large part in particle polarization; protons can migrate along such chains and produce high polarizability [28, 29].

The permanent moment can be discussed via electrooptic effects [19, 20]. A rigid moment is due to spontaneous (unipolar) orientation of dipole molecules at the particle surface.

The shear response of the dielectric constant has been used in research on orientation as it affects the anisotropy in mechanical properties, stress relaxation at stresses less than the shear strength, irreversible structure change at the yield point, and structure recovery [30, 31]. The dielectric and mechanical losses are of great interest in relation to relaxation in polymer systems [32, 33].

The rheoelectric effects include a potential difference between the electrodes of a rotating plastoviscosimeter containing a nonaqueous plastic dispersion [34, 35]. The sign of the difference reverses as the speed increases because of structural change in the system, including features of the boundary layer.

An electrorheological effect can arise from particle displacement and deformation and also by deformation of the structural framework. See [36, 37] on particle orientation and deformation in combined electrical and shear fields. Viscosity equations have been checked on water—oil and oil—oil emulsions. The viscosity change in an electric field is dependent on the electrical, physicochemical, and rheological properties as well as on the characteristics of the fields.

The largest electrorheological effect occurs in a system that acquires a structure in an electric field, in particular hydrocarbon suspensions of silica, metals, oxides, salts, ferrites, polymers, and carbon black, and water—oil emulsions [8, 10, 40-43, 52]. Particularly detailed studies have been made on the effects of electric fields on the viscosity of $SiO_2$ suspensions [41, 42]. The effect increases with the volume percent of the dispersed phase, the field strength, and the temperature but decreases as the shear rate increases. The initial viscosity is recovered after a certain time when the field is removed. The water content influences the effect. The field can raise the viscosity by a factor $10^4$, which opens up practical uses.

This viscosity increase is due to particle interaction via polarization, the field acting on the induced moments. Here the important aspects are the polarization mechanism and the role of surface and bulk effects.

The best particles for producing fibers are [40] solid semiconductors with high dielectric constants. $SiO_2$ particles clump by migration to the regions of highest field strength; they then join end to end into chains. This occurs particularly at the ends of long particles and at defects in spherical particles. Gindin et al. [44, 45] observed a similar mechanism in hydrocarbon suspensions of metals and soaps. The suspended particles move rapidly when a field appears between the electrodes. Strip structures appear at 8 kV /cm, which are attached to one of the electrodes. It has been found [46] that acicular dendrites appear in soap suspensions in response to electric fields.

Klass and Martinek [41] concluded for $SiO_2$ suspensions that the electrorheological effect is due to structures arising from polarization of the double layer and from interaction of induced dipoles; the bulk electrical properties of the dispersed phase were considered to be of secondary importance. The surface mechanism is confirmed by the positive temperature coefficient of the electrorheological effect (due to facilitated polarization of the double layer). No particular migration was observed on microscopic examination. Clumping without visible migration has been observed for other systems, in particular water dispersions of polyvinyl acetate stabilized by polyvinyl alcohol [47].

Efremov and Us'yarov [48, 49] examined the effects of electric fields on particle interaction in colloidal systems. A polymer suspended in an organic liquid produces chains by polarization of the ionic atmosphere; polarization of the material itself had little effect. The external field reduces the energy barrier to particle interaction and so accelerates coagulation. The polarization interaction increases the structure strength and determines the limiting shear stress, and an equation for this [50] is in good agreement with experiment. Reversible and irreversible forms of aggregation are of particular importance, especially as affected by field strength and surface state (charge, solvation, surfactant adsorption).

The framework may be charged in a plastic dispersed system, in which case a field causes compression at one electrode and release of dispersion medium at the other [51]. This is reversible in its initial stages. The higher concentration of the medium at one electrode increases the boundary-layer slip, and this can produce large changes in deformation resistance.

If the potential difference is reversed, the layer with more dispersion medium can shift to various positions, and the deformation accompanying the shift can result in disruption and thixotropic recovery (oscillatory shear stress).

An electric field may raise the deformation resistance by structuring or reduce it on account of electrokinetic effects, the nature of the lubricant and the electrical state of the interface being the decisive factors.

A hydrocarbon dispersion in a strong field shows not only translational motion (electrophoresis etc.) but also rotation and circulation between the electrodes [38, 39], which is due to electrical inhomogeneity of the phase interface on account of inhomogeneity in the dispersed phase and the very low conductivity of the hydrocarbon medium. Oil-soluble surfactants influence the electrical properties of the surface, and charge reversal in some areas causes rotational motion to replace translational. Here there is considerable interest in the effects of electrical inhomogeneity on the electroviscosity and electrorheological effects.

This brief survey shows that major topics in electrorheology are polarization, interaction of polarized particles, and the relation of these to mechanical behavior.

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