Changes of Non-Newtonian Behavior of Carboxylated Acrylate Dispersions During Alkalinization

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Synopsis

Changes of flow curves of the carboxylated acrylate latex dispersions during alkalinization were described in terms of parameters of the Cross theory of aggregation of disperse particles. It was found that the dependence of viscosity on pH has a maximum at pH $\simeq 9.3$ where a yield stress appears.

INTRODUCTION

The shape of the flow curves of concentrated polymer latex dispersions depends on their microstructure and may differ. If disperse particles aggregate,[1] the viscosity at very low velocity gradients is constant and identical with η_0, the viscosity at zero shear rate (first Newtonian region), because it reflects the character of aggregates unperturbed by flow. With increasing shear rate, disaggregation in flow sets in, and becomes stronger with increasing flow rate. The viscosity of nonaggregated disperse particles is lower, and after complete disintegration of the aggregates at high shear rates, it decreases to η_∞, the viscosity in the second Newtonian region.

The flow mechanism of latex dispersion, whose particles carry dissociable groups, may be rather different. Due to charges of ionized groups, the particles may repulse each other so strongly that no aggregation occurs, and a very stable three-dimensional space structure is formed, in which the thermal motion of disperse particles is suppressed. The flow mechanism of such pseudoaggregated network systems differs qualitatively from the former but the shape of the flow curves is similar.[2,3] The viscosity decreases with the velocity gradient owing to the three-dimensional structure being reorganized into a planar one, consisting of disperse particles situated in layers. Due to a certain stability of the structural order, the onset of flow may require application of a yield stress.

In some dispersions the viscosity at high velocity gradients does not reach the constant limiting η_∞ value. It passes through a minimum and then increases with the shear rate, either continuously or with a discontinuous jump. This effect is explained by arguing that the two-dimensional order of disperse particles is not able to adapt itself to the flow rate and is changed into an amorphous structure where the energy dissipation at flow is higher.

In this article we present the results of measurement of rheological behavior of acrylate dispersion—containing a small amount of acrylic acid—during

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alkalinization. When neutralizing the originally acid dispersion of this co-
polymer, we found that in alkaline regions their flow curves changed in an
interesting way: the dependence of η on pH had a maximum. The rise in
viscosity before the maximum was reached and its subsequent drop was larger
at smaller shear rates. At maximum viscosity, the dispersion lost its fluidity
and the space structure appeared. A similar shape with the maximum depen-
dent on pH of the hydrodynamic size of carboxylic acid latex particles was
found by sedimentation and photon correlation spectroscopy.[4]

The aim of our study was to describe this behavior in terms of some
objective parameters of flow curves in order to obtain a better elucidation of
the changes which occur in the microstructure of these systems under the
given conditions.

EXPERIMENTAL

A latex dispersion of the copolymer of butylacrylate and methylmethacry-
late with 2 wt% acrylic acid and a small amount of methacrylamide was
produced under the trade name SOKRAT 6492 (Chemical Works Sokolovo
Czechoslovakia). A series of 12 samples in the pH range 7.58–9.90 was
obtained by alkalinization of the stock dispersion (49.5 wt% of solid) with a
mixture of ammonium hydroxide (26%, reagent grade) and water to various
pH values so that the concentration of disperse particles in all samples was
the same (48.0 wt%).

Viscosity of the dispersions was measured in the range of velocity gradients
1.5–1312 s^{-1} at 25°C, using a rotational viscometer Rheotest 2 (manufactured
by VEB Prüfgeräte-Werk Medingen, Dresden GDR), with coaxial cylinders.
All obtained viscosity–shear rate dependences decreased continuously.

pH values were measured with a digital pH meter 64 (manufactured by
Radiometer Copenhagen) with a combined electrode CK 2321 C.

EVALUATION OF FLOW CURVES

Although many relations have been suggested[5–14] for the description of the
non-Newtonian behavior of polymer latexes, none of them can be recom-
mended unequivocally for our purpose. Some of them are semiempirical and
their parameters have no physical meaning, others are impractical because of
a great number of constants. Our study used the Cross relation[8] based on the
theory of formation of aggregates of disperse particles in the form of randomly
kinked chains and their destruction by flow. In the past it proved to be of
general use for the description of the non-Newtonian viscosity of various
disperse systems. It is represented by a four-parameter equation

$$\eta = \eta_\infty + 1/(A + B\dot{\gamma}^n) \qquad (1)$$

$\dot{\gamma}$ is the velocity gradient, the parameters A and B are defined by $A \propto k_1/k_0$
and $B \propto k_2/k_0$. k_0 and k_1 are, respectively, the rate constants of link
formation and rupture by thermal motion, and k_2 is the rate constant of link

rupture by flow. With $\eta = \eta_0$ at $\dot{\gamma} = 0$, we have $A = 1/(\eta_0 - \eta_\infty)$ and $B = \alpha/(\eta_0 - \eta_\infty)$, where $\alpha = k_2/k_1$.

The advantage of the Cross equation compared with other relations is the small number of parameters and relative simplicity. The parameters are determined from the intercept A and slope B of the linear plot of $(\eta - \eta_\infty)^{-1}$ vs. $\dot{\gamma}^n$.

The physical meaning of the exponent n is not clear. Cross[8] reports that this quantity depends on the polydispersity of the system; the upper limit for a monodisperse system is $n = 1$. For a number of non-Newtonian liquids, $n = 2/3$ appeared to be the universal value.

We suppose that the equation based on the aggregation theory can be used to describe the flow behavior of latex dispersions which have a polyelectrolyte character and where reorganization of the space structure of disperse particles influences the flow. One can imagine that a kinetic equilibrium, dependent on the flow conditions, exists between the three-dimensional and planar structures.

RESULTS

As the exponent $n = 2/3$ was found to be the optimal choice for all of our sample latex dispersions, the parameters η_0, η_∞, and α could be obtained together by optimization, using the least-squares method, to estimate the correlation coefficient ϵ of plotting the straight line through experimental points. The results obtained with the Wang 2100 desk computer are summarized in Table I. High values of the correlation coefficient show that the Cross equation is suitable to fit the flow curves of carboxylated dispersions at various conditions. It can be seen that the alkalinization of the dispersion is accompanied by a steep rise in both η_0 and α to immeasurably high values at pH 9.29 (Figs. 1 and 2) and by a subsequent decrease at higher pH values. Unlike η_0, the change in η_∞ with pH is much less and the dependence has only a slight maximum. The shape of the dependence of α on pH indicates that the non-Newtonian behavior is extremely pronounced at around pH 9.29.

TABLE I
Parameters of Flow Curves of the Dispersions During Alkalinization

pH	η_0 [mPa's]	η_∞ [mPa's]	α [s$^{2/3}$]	ϵ
7.58	149	13.1	0.13	0.9991
8.17	196	15.0	0.17	0.9996
8.46	267	15.2	0.17	0.9997
8.80	925	21.6	0.50	0.9999
9.03	3160	27.9	1.4	0.9999
9.15	4520	28.6	2.0	0.9999
9.22	1.37×10^5	31.2	60.0	0.9998
9.29[a]	∞	32.5	∞	0.9997
9.44	1.85×10^4	30.3	7.7	0.9998
9.50	7580	30.0	3.3	0.9999
9.56	5290	29.4	2.2	0.9999
9.90	4150	27.8	1.8	0.9999

[a] $\tau_0 = 22.2$ mPa.
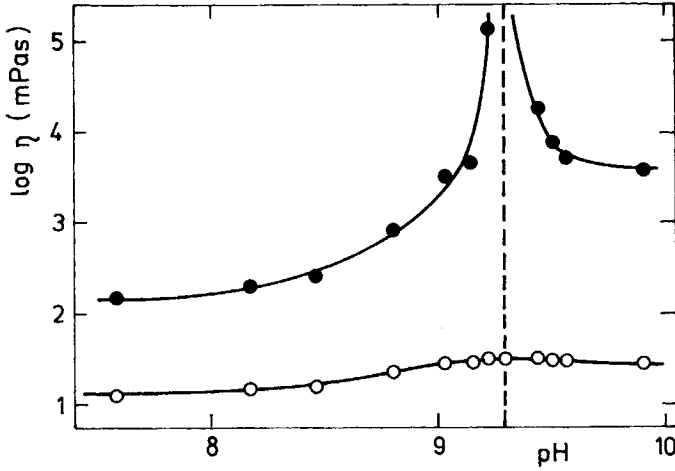
Fig. 1.   Dependence of the η_0 and η_∞ values on pH. Notation of points: (●) η_0; (○) η_∞.
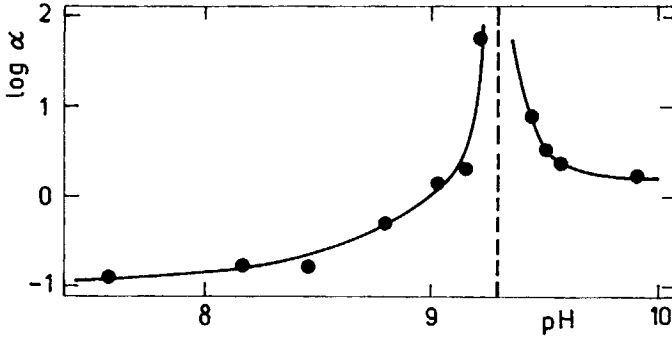

Fig. 2.   Dependence of the parameter α on pH.

If pH reaches the value corresponding to $\eta_0 \to \infty$, parameter A becomes zero and the viscosity is given by

$$\eta = \eta_\infty + 1/B\dot{\gamma}^{2/3} \tag{2}$$

We assume that after reaching this pH value, where a yield stress appears, parameter A remains zero and Eq. (2) may be used also. The total shear stress may be then expressed by the equation

$$\tau = \tau_0 + \left(\eta_\infty + 1/B\dot{\gamma}^{2/3}\right)\dot{\gamma} \tag{3}$$

and the viscosity as the ratio of the total shear stress and the velocity gradient is

$$\eta = \tau/\dot{\gamma} = \tau_0/\dot{\gamma} + \eta_\infty + 1/B\dot{\gamma}^{2/3} \tag{4}$$

By applying this equation to our experimental data at pH 9.29, the yield stress value, $\tau_0 = 22.2$ mPa, was obtained from the intercept of the linear plot $(\eta - \eta_\infty)\dot{\gamma}$ vs. $\dot{\gamma}^{1/3}$.

Our modification of the Cross theory has an advantage in that it can be used to evaluate the non-Newtonian behavior of disperse systems even if a yield stress is not present. This is not the case with other equations, for example, the often used Cason formula[7]

$$\tau^{1/2} = \tau_0^{1/2} + \eta_\infty^{1/2}\dot{\gamma}^{1/2} \tag{5}$$

which for $\tau_0 = 0$ predicts only Newtonian flow.

DISCUSSION AND CONCLUSION

Let us consider the physical meaning of the extension of the Cross theory to systems where $\eta_0 = \infty$. The steepness of the flow curves depends on the value of α, that is the ratio of the rate constants k_2 and k_1. The fact that α tends to infinity (cf. Fig. 2) may be explained by assuming the constant k_1 to tend to zero, which means that the disaggregation by thermal motion of the three-dimensional structure of disperse particles has been suppressed.

To explain the changes which occur in the latex structure with changes in pH, we assume two competing effects: On the one hand, alkalinization brings about dissociation of the carboxylic groups on the particles. Consequently, the ionic atmosphere becomes larger and the hydrodynamic volume of dispersed particles is increased (first electroviscous effect). At the same time, the interaction of particles becomes stronger (second electroviscous effect) and may lead to a three-dimensional pseudoaggregated system at higher concentration.

On the other hand, alkalinization by ammonium hydroxide raises the concentration of NH_4^+ counterions which screen charges on the latex particles and gradually suppress electroviscous behavior of the system.

It seems that all these changes of the dispersion structure may be described very adequately by the parameters of the Cross equation. We admit that objections can be raised against the theoretical competency of this method for latex dispersions with polyelectrolyte character. In an extreme case, the parameters of this equation may be regarded as useful semiempirical constants.

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