The analysis of phenomena and factors having an effect on the sedimentation stability and rheology of water-based dispersions of MMA/BA/MAA copolymer in xylene

Edwin Makarewicz *, Anna Zalewska

*Faculty of Chemical Technology and Engineering, University of Technology and Agriculture,
3 Seminaryjna str., Bydgoszcz, 85-326, Poland*

Abstract

This paper presents essentially the results of sedimentation and rheological studies on aqueous dispersed systems of copolymer methyl methacrylate with butyl acrylate and methacrylic acid (MMA/BA/MAA) in a xylene solution. Non-ionic surfactants such as oxyethylenated unsaturated fatty alcohol, lauryl alcohol and oxyethylenated amines were used as well as the thickening agents: polyvinyl alcohol, sodium salt of carboxymethylcellulose (CMC-Na) and water-soluble polyurethane oligomer. The properties of surfactant water solutions were determined with the use of tensiometric and viscometric methods. The structure of the obtained copolymer was analysed by gel chromatography. The sedimentation experiment was a basic test used to determine the stability of aqueous dispersions of the obtained copolymer in xylene. It consisted in determining types of phases occurring in sedimentation equilibrium. The formation of a foamed copolymer phase was the most interesting phenomenon. A rheological test was carried out by using the so-called stable phase and was aimed to define maximum viscosity, pseudoplasticity and activation energy of a viscous flow. Moreover, the reduced viscosity, a limiting viscosity number and the Huggins constant were also determined. The relationships between these quantities were established indicating the dependences, which were the best interpretation describing interactions between particles in the dispersed system. Basing on rheological and sedimentation tests, the most probable mechanisms of stability in systems of this type were determined. The factors reducing their stability and concerned with flocculation and coalescence of particles have been defined.

1. Introduction

Considering ecological restrictions, the paint and lacquer industry often applies painting materials free from organic solvents. Therefore, water-soluble paints are nowadays recommended for common use. Water used instead of toxic and flammable organic solvents improves the conditions of the paint production and application. Depending on the type of binding material, waterborne paints are based on aqueous polymer dispersions or on water-soluble polymers. Dispersions are two-phase non-equilibrium and irreversible systems, in contrast to soluble one-phase and reversible systems.

Polymer dispersions are much more common than their water solutions, since they contain a higher amount of polymer and their costs of production are lower. The most important features providing a wide range of applications of acrylate polymers are as follows: transparency of coating, full gloss, resistance to UV radiation as well as to weather and chemical conditions, excellent physicochemical properties [1–4]. Aqueous emulsion paints are typical lyophobic, thermodynamically non-equilibrial and unstable systems. The differences between rheological behaviour of the stable and unstable dispersed systems are conditioned by their tendency to form associated emulsion particles. In thinned dispersed systems, this difference is insignificant because association runs slowly and it is completed by a total separation into two phases. In concentrated dispersed systems, the aggregates of

* Corresponding author.
E-mail address: edwin.makarewicz@atr.bydgoszcz.pl (E. Makarewicz).

particles can be so strong that they do not disintegrate completely while flowing. Besides, separation into two phases does not always occur during aggregation. The associated particles can form chains making a network penetrating the whole volume of the system. Thus, most dispersed systems demonstrate a non-Newtonian flow [5–8].

Copolymer particles in dispersed systems are often named globules because of their spherical shape, which results from an action of interfacial tension forces fully sufficient for the system to accept a minimum in Gibbs energy. Copolymer particles are formed as a result of coalescence in the various processes of agglomeration of small particles. The size of the particles and their granulometric distribution belong to the very important properties of dispersed systems. There is a strong relationship between the particle sizes and the viscosity in the dispersed system [9].

The viscosity of dispersed systems depends on the properties of the protective or surface-active layers existing on particle surfaces. Rheological studies permitted defining some parameters describing the structure of a dispersed system. Most dispersed systems are characterised by the features of non-Newtonian flow affected by various factors, such as: dimensions of particles, type and quantity of stabilizers, hydration degree of the particle adsorption layer, charge of particles and interactions between suspended particles, presence of functional groups, pH, temperature, etc. The destruction of internal structures in a definite dispersed system consists in increasing Gibbs energy, and their reconstruction runs spontaneously after removing shear stress. This process rate has an effect on the thixotropy of the system [10,11].

The relationship between the viscosity of the dispersed system and the volume of the dispersed phase does not satisfy the Einstein equation even in the range of Newtonian flow. In case of diluted suspensions of non-interacting spherical particles, the relationship is defined by the equation [12]:

$$\eta = \eta_r(1 + 2, 5C_V), \tag{1}$$

where η is the viscosity of the dispersed system, η_r the viscosity of the dispersing phase, $C_V = (V_C/V_O)$ V_C the volume of the dispersed phase, and V_0 is the total volume of the dispersed system.

The concentrations of dispersed systems are usually much higher than the concentrations where interactions among particles may be neglected and, therefore, additional terms of power series should be introduced into the above equation. The obtained Einstein equation does not take into consideration the Smoluchowski electroviscous effect concerning the influence of the charge of the particles on the viscosity of the tested system.

The addition of a stabilizer usually makes the viscosity of the system increase. While saturating particle surfaces and forming polymeric micelles, significant increase in viscosity of the system caused by the formation of internal structures is observed. The effect is stronger after introducing thickening agents. The structural viscosity is strongly reduced as the temperature rises. Among others, it is due to dehydration of the surface-active films [13,14].

The physical grounds of non-Newtonian flow of liquids – in this case dispersed systems composed of mutually interacting particles – can be brought into the so-called activation or orientation mechanism. According to Frenkel [15] and Eyring [16,17], the activation flow is related to the structure of the fluid and to thermal motion of the particles. Ree and Eyring [18] stated that viscosity can be unequivocally determined on the basis of the shear rate during the stabilized flow.

The characteric of structural viscosity consists in the fact that during flow the super-molecular structure of polymer undergoes reversible destruction which is stronger the higher the shear tension is. Rebinder [19] defined the time of thixotropic recreation of the internal structures after their destruction. The destruction of the structure occurs in such a manner that the formed copolymer segments retain energy allowing their re-transiting to the initial state [20].

The approximate mechanism of structural viscosity refers to systems with particles having an extended form or forming chains. The particles take the unidirectional orientation in a stream of fluid during transition from low to high shear rates. Many researchers tried to describe the structural viscosity of dispersed systems by using the Eyring mechanism, not taking into account the destruction of its internal structure [21]. Ree and Eyring [22] disagree with that point of view considering it unsuitable for the description of the flowed dispersed systems flow. In this case, many factors have an effect on the flow, including, e.g. the size of polymeric particles, the presence of polar substituents in the copolymer chain or the particle surface charge. Thixotroping compounds are, among auxiliary substances, purposefully introduced into dispersed systems. They are aimed to reduce the sedimentation of the dispersed component, providing suitable rheological properties [23].

Rheological tests make it possible to define a size and shape of the dispersed particles, having a decisive effect on the stability of their dispersion. For that purpose, rheological models are used, which enable identification of the dispersed phase by determining constant values describing the phase. The non-Newtonian behaviour of the dispersed systems is particularly observable when a solid shows a tendency to swell, solvate, or when it associates with the liquid phase. Thus, the viscosity of non-Newtonian liquids is not a constant value under specified temperature and pressure conditions but it changes, depending on, e.g. the shear rate. Paints belong to typical plastic materials. At rest, they show a three-dimensional structure characterized by elasticity sufficient to resist every shear stress lower than a flow limit. However, in case the flow limit has been exceeded, the structure is destroyed and a Newtonian liquid is being formed at this moment. The structure becomes reconstructed when shear stress is lower than the flow limit. The flow curve of the pseudo-plastic liquid gets a nonlinear form but it becomes a straight line at high shear rates. It can also be observed that the ratio of shear stress to shear rate decreases as the shear rate increases. This type of flow is described by the Oswald-