Analysis of shear-induced coagulation in an emulsion polymerisation reactor using computational fluid dynamics

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Abstract

Shear-dependent coagulation is a costly problem for the latex manufacturing industry, due to product degradation and reactor downtime. In this study, a method for calculating the shear-dependent coagulation rate in emulsion polymerisation is developed. The method combines simple models for coagulation (only binary collisions being considered) with the effects of rheology on the flow field, using computational fluid dynamics (CFD) to solve the detailed flow field in the reaction vessel. By using the local shear rates (LSR), the method developed provides a more detailed and system-specific assessment compared with using an average shear rate (ASR) for calculating the coagulation rate. The difference in the predictions between the ASR and the proposed LSR method was investigated. It was found that the ASR and LSR methods predict different coagulation rates, especially for more sophisticated coagulation models where the coagulation rate is not linearly dependent on the shear rate. The LSR method was also used to study the effect of the rheology of the latex, of the impeller speed and of the reactor design on the coagulation rate. It was found that the LSR method is useful for providing both visual and numerical means to identify regions with elevated coagulation rates in the modelled reaction vessel. The treatment provides estimates of the amounts of coagulum formed on the vessel walls and on the impeller.
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1. Introduction

Emulsion polymerisation is widely used in industry to produce products ranging from bulk commodities to consumer goods. The process is preferred because the reaction medium (water) facilitates agitation and ease of heat and mass transfer whilst being environmentally-friendly, as well as providing an inherently safe process. However, modelling and simulation of emulsion polymerisation is a challenging task because complex physico-chemical sub-processes exist within the multi-phase process.

Coagulation in the form of small aggregates, filterable solids and macroscopic coagulum on the walls and the impeller is a major cost to the latex manufacturing industry. The phenomenon may have an adverse effect on the product quality and causes large costs for product loss, cleaning and reactor downtime. Even in processes with best-practice levels of coagulum (well below 1%), slow build-up of coagulum on walls, baffles and impellers requires downtime for cleaning during a campaign, because the coagulum diminishes the efficiency of heat exchange. Coagulum formation is one of the major problems when scaling up a reaction from laboratory to industrial size, as the agitation regime in the reactor changes. The key factors that induce the formation of coagulum are fluctuations in ionic strength, temperature, effects at the gas–latex interface (Lowry et al., 1986),

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in situ formulation of polymeric flocculation agents, and shear, acting alone or together. While good mixing of the ingredients is important to ensure reactor homogeneity, it is also the cause of shear-induced coagulation. This poses a significant performance trade-off for the manufacture of latex by emulsion polymerisation. The development of models for this effect would improve the production process and scale-up.

Many attempts have been made to develop mathematical models describing emulsion polymerisation [see Coen et al. (2004) for a partial listing] in order to predict the particle size distribution (PSD). Few of these models include coagulation, as there is no validated kinetic model for predicting shear-induced coagulation in emulsion polymerisation. In the models where coagulation has been included (Araujo et al., 2001; Coen et al., 1998, 2004; Gao and Penlidis, 2002; Immanuel and Doyle, 2003; Richards et al., 1989) only the effect due to Brownian motion (perikinetic coagulation) is incorporated. Other workers (Chern and Kuo, 1996; Lowry et al., 1984, 1986; Mayer et al., 1996) have addressed the issue of shear-induced (orthokinetic) coagulation by its inclusion as a specific compartment in their model. However, the shear-induced coagulation as used in these models makes use of a simplistic method which uses an averaged shear strain rate over the entire reactor as a function of the impeller type and/or the power usage. Although this method may provide an estimate of the effect of shear on the PSD, it does not take into account the fact that the shear-induced coagulation rate will vary spatially in the reactor. Another key element absent from previous shear-induced coagulation models is the change in the dynamic viscosity of the latex during the course of the reaction. The rheology changes throughout the reaction due to particle growth and subsequent evolution of the PSD and the solid content. The latex evolves from a low viscosity Newtonian fluid to a highly viscous non-Newtonian fluid (Bird et al., 1987; Larson, 1999). Additionally, the physical measurement of the local shear rates and viscosities is not practical for large-scale industrial reactors. These points demonstrate the limited suitability of the average shear rate (ASR) method in predicting shear-induced coagulation. As is well known, this limitation can be overcome by the use of computational fluid dynamics (CFD).

In this study, the importance of using the local shear strain rates is shown, by using CFD to evaluate the detailed flow field in the reactor for modelling of shear-induced coagulation and design of emulsion polymerisation reactors. A method combining coagulation theory and the effects of rheology on the flow field using CFD in order to provide an assessment of the coagulation rate and colloidal stability is proposed. Although the method is applied here to a laboratory size reactor, it could easily be applied to an industrial-scale reaction vessel. As an industrial application it could be used to improve reactor design and scale-up for any emulsion polymerisation system with respect to both mixing and reduction of coagulation formation.

2. Fundamentals of coagulation

2.1. Coagulation theory

A number of models describing emulsion polymerisation including coagulation have been developed. The most general approaches are based on the theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) (see, e.g., Russel et al., 1989) which provides a qualitative explanation of the interaction between the attractive van der Waals forces and the electrostatic repulsion between two particles. It is admitted that the quantitative applicability of the particular implementation of DLVO theory used here is questionable (e.g., Kostansek, 1996; Ottewill and Shaw, 1966), but it will certainly be semi-quantitatively adequate; better, but more computationally complex, DLVO treatments are available, (e.g., Behrens et al., 2000; Peula et al., 1997; Scales et al., 1998), which could be implemented if desired.

The present treatment is restricted to binary particle collisions, and it is assumed here that coagulation does not alter the PSD. This omits some clearly important effects, such as that of flocs of coagulated particles catalysing further coagulation, i.e., coagulation is an autocatalytic process (Feeney et al., 1985). This is not as restrictive as it appears, because the primary goal of industry is to minimise coagulation; since coagulation must always start with binary particle coagulation, any indications from the modelling presented here that such coagulation is occurring significantly in a particular region and under particular conditions can be used to reduce this occurrence.

Given the assumption of only binary collisions in a monodispersed latex, the total number concentration of particles, N_c, can be evaluated using

$$\frac{dN_c}{dt} = -2BN_c^2, \tag{1}$$

where B is the coagulation rate coefficient (note that this definition of the loss rate involving identical species takes account of a factor of 2 difference between the US and IUPAC definitions—see, e.g., Russell, 2002).

The *stability ratio W* is commonly used to quantify coagulation rates. This is defined as the ratio of the "slow" coagulation rate (i.e., the actual rate in a particular system) to the "fast" rate (i.e., that in the same system but with the addition of, e.g., large amounts of electrolyte). Theories of coagulation start with diffusion in a potential and/or flow field, described by the appropriate conservation equation (Russel et al., 1989). Assuming that any particle which goes over the repulsive barrier between the particles (through shear and/or Brownian motion) undergoes irreversible coagulation, this may be solved (Blackley, 1997) to yield W for binary collisions:

$$W = 2a \int_{2a}^{\infty} \exp\left(\frac{V(r) - 16Ga^4/r}{kT}\right) \frac{dr}{r^2}, \tag{2}$$