Shear Driven Colloidal Aggregation and Its Application in Nanocomposites

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Shear Driven Colloidal Aggregation and Its Application in Nanocomposites

A thesis submitted to attain the degree of DOCTOR OF SCIENCES of ETH ZURICH

presented by

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Abstract

The intense shear-driven aggregation kinetics, cluster structure evolution and phase transition behaviours have been systematically investigated for single colloidal systems that are well stabilized at rest. The obtained results and the methodologies are then applied to study shear-driven aggregation of binary colloidal systems—a new approach proposed in this thesis to prepare composite materials with homogenous distribution of one colloid in another.

In the first part of the thesis, we investigate the shear-driven aggregation of polystyrene (PS) colloids that are stabilized by both fixed and surfactant charges, using a microchannel (MC) device, at various particle volume fractions. The time evolutions of the primary particles to big clusters and cluster morphology along the shear-driven process are monitored, which are featured by an induction time followed by an explosive increase when the cluster size reaches a certain critical value. These observations confirm the self-acceleration kinetics developed in the literature. The critical size of the clusters that lead to the self-acceleration kinetics has been quantified for the first time, and its scaling with the shear rate follows well the literature prediction. Moreover, along the shear-driven aggregation, we have observed rich phase transition phenomena. Depending on the particle concentration, besides a liquid-like fluid of clusters and a solid-like gel, there is another solid-like state: Wigner glass of clusters.
The Wigner glass occurs in a large range of the particle concentration. A phase diagram is proposed that describes how the three phases evolve at the aggregation steady-state in the colloidal interactions vs particle concentration plane.

In the second part, we have performed intense shear-driven (hetero-) aggregation of binary colloidal dispersions in the MC, a general methodology proposed here for preparing composite materials with the different components homogeneously distributed at nano-scale. To demonstrate its feasibility, we have applied it to stable binary colloidal dispersions that are composed of 43 nm PS particles and 280 nm poly-methyl methacrylate (PMMA) particles. The PS particles are shear-active, i.e., undergoing the shear-driven aggregation, and the PMMA particles are shear-inactive. The result demonstrates that the shear-driven hetero-aggregation of the binary colloidal system does occur, and the formed clusters are composed of both the PS and PMMA particles. The SEM picture shows that the PMMA particles are homogeneously and randomly distributed among the PS particles in the clusters. A capture mechanism is proposed to explain the hetero-aggregation process in the MC, where the extremely high shear drives the particles to aggregate within extremely short time, such that the homogeneously mixed colloids are “frozen” into solid. The obtained nanocomposites can be in the form of either clusters or gels.

In the last part of the thesis, a methodology is proposed to investigate the effect of dispersed nanoparticles (NPs) on bulk polymerization of methyl methacrylate (MMA), based on DSC experiments and modelling of the bulk polymerization kinetics. We have applied it to polymer (PTFE and PS) NPs, which have been surface-modified by cross-linked PMMA (cPMMA). To quantify the net effect of the NPs on the bulk polymerization, we have first quantified the effect of the cPMMA without the NPs, and then subtracted the effect of the cPMMA to get that of the NPs. The presence of
dissolved linear PMMA during the MMA bulk polymerization has also been studied. It was found that the effect of the linear PMMA on the MMA bulk polymerization is as if the system was pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. With respect to the linear PMMA, the cPMMA retards the MMA polymerization kinetics, and such retardation increases as the cross-linker in the cPMMA increases. After subtracting the role played by the cPMMA, we found that the PS NPs behave like (inert) dead volume, changing only the effective concentrations of the components in the system. The CryoSEM imagine of the bulk PMMA indicates that grain-like microstructure is formed in the presence of the NPs.
Zusammenfassung

In dieser Arbeit wurde die Kinetik der scherungsinduzierten Aggregation, die zeitliche Veränderung der Aggregatmorphologie und der Phasenübergang im Fall von stabilen, kolloidalen Dispersionen systematisch untersucht. Die Ergebnisse dieser Untersuchungen und die daraus resultierenden Methoden wurden dann zur Studie von der scherungsinduzierten Aggregation binärer kolloidaler Systeme angewandt, und damit einen neuen Weg zur Synthese von Kompositmaterialien vorgeschlagen, welche eine homogene Verteilung des einen Kolloids in das andere aufweisen.

Im ersten Teil dieser Arbeit wird die scherungsinduzierte Aggregation tensid- oder ladungsstabilisierter kolloidaler Polystyrenpartikeln (PS) mithilfe eines Mikrokanals (MK) bei verschiedenen Partikelkonzentrationen untersucht. Die Entwicklung von Aggregaten aus primären Partikeln sowie die zeitliche Entwicklung der Aggregatmorphologie konnte beobachtet werden. Letztere ist gekennzeichnet durch eine Induktionsphase, und sobald die Aggregatgrösse einen gewissen Schwellenwert erreicht hat, ist sie gefolgt von einer explosionsartigen Wachstumsphase der Aggregate. Diese Beobachtungen stimmen mit der selbstbeschleunigten Kinetik aus der Literatur überein. Der Schwellenwert der Aggregatgrösse konnte hiermit zum ersten Mal quantifiziert werden, und deren Skalierung mit der Scherung stimmt mit der in der

Im zweiten Teil dieser Arbeit wird die intensive scherungsinduzierte Aggregation im MK für binäre kolloidale Systeme bearbeitet. Um deren Funktionsweise aufzuklären wurde die Methode auf eine stabile Dispersion von 43 nm PS Partikeln und 280 nm Polymethylmethacrylat (PMMA) Partikeln angewandt. Die PS Partikeln sind scherungsaktiv, dh. bilden unter intensiver Scherung Aggregate, während die PMMA Partikeln scherungsinaktiv sind. Mit Hilfe der Rasterelektronenmikroskopie (REM) konnte gezeigt werden, dass die so gebildeten Aggregate PS und PMMA Partikeln enthalten und desweiteren eine homogene Verteilung der PS Partikeln innerhalb der PMMA Partikeln vorliegt. Dazu wird ein Einfangmechanismus zur Erklärung dieser scherungsinduzierten Hetero-Aggregation vorgeschlagen, wobei die extrem starke Scherung einen sehr schnellen Aggregationsvorgang verursacht, so dass die homogen dispergierten Partikeln wie „schockgefroren“ in den Aggregaten fixiert werden. Desweiteren konnte gezeigt werden, dass das so gebildete Material sowohl in der Form von Aggregaten als auch in Gelform gebildet werden kann.

Im letzten Teil dieser Arbeit wird eine Methode entwickelt um die Effekte von dispergierten Nanopartikeln auf die Massenpolymerisation
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Chapter 1

Introduction

1.1 Colloids and Colloidal Stabilities

Colloid is defined as a system where small particles are dispersed in a medium purely by the thermal energy (Brownian motion). Thus, such particles are also called thermal particles, which are typically of nano- and submicron sizes. Colloidal systems are very common in our daily life and in various industrial processes related to food, paint, ceramics, paper, polymer, pharmaceutical products, wastewater treatment, etc. Handling and applications of colloidal systems always involve two issues. On the one hand, the colloidal particles have to be well stabilized in the medium to avoid any
possible aggregation among them such as during the production of polymer latexes, biomedicines, paint composites, etc. On the other hand, there are applications where destabilizing the particles is necessary during their applications such as coagulation of polymer latexes to separate the polymer from the medium, fabrication of porous materials and ceramics, and productions of tofu and cheese\textsuperscript{1-3}. A huge number of experimental and theoretical studies have been carried out in more than a century to have accumulated a large amount of information on how to describe the colloidal stability, aggregation kinetics, and the structure of the formed clusters\textsuperscript{1-3}. In addition, colloidal systems have also been considered as excellent model systems that bring the possibility of studying various problems in physics such as phase transitions of the atomic systems, liquid crystals, Brownian motion, multi-body interactions, percolation and gelation phenomena\textsuperscript{4-12}.

In general, NPs in a colloidal system are kinetically stabilized by surface charges, which generate the electrostatic repulsion among the particles. Such a stabilization mechanism can be well described by the classical DLVO (Derjaguin-Landau-Verwey-Overbeek) theory\textsuperscript{1,13}, which accounts for both the van der Waals attraction and the electrostatic repulsion. Applications of the DLVO theory can explain various aggregation phenomena under stagnant conditions related to the role played by electrolytes. Besides the DLVO interactions, there are also various non-DLVO interactions such as short-range hydration, steric and depletion forces\textsuperscript{1}. Recent studies have demonstrated that the non-DLVO interactions generated by the surfactant layer adsorbed on the particle surface can substantially affect the stability of colloidal systems in intense shear flow\textsuperscript{14}. 
1.1.1 Brownian motion-induced colloidal aggregation and gelation

Colloidal aggregation under stagnant conditions has been widely studied in the literature\textsuperscript{15-35}. In the early 1980s, Forrest and Witten\textsuperscript{36, 37} noticed that the clusters generated by aggregations of colloidal particles can be well described by the fractal geometry, which was originally introduced by the French mathematician, Benoit, in 1960s\textsuperscript{1, 38, 39}. For a fractal object, its mass, $i$, with respect to its radius, $R$, follows the scaling, $i \sim R^{d_i}$, where $d_i$ is the fractal dimension, with a value $d_i \in (1,3)$. With respect to non-fractal object (i.e., the case with $d_i = 3$), to construct a fractal object of the same size, due to $d_i < 3$, the required mass is substantially smaller and decreases as $d_i$ decreases. The $d_i$ value of the fractal clusters can be characterized by the static light scattering, specifically from the slope of the power-law regime of the scattering structure factor of the clusters\textsuperscript{32, 40-42}.

It has been well documented that the colloidal aggregation under stagnant conditions can be classified into two classes, characterized with some so-called “universal” features, based on the interaction energy barrier between particles\textsuperscript{43, 44}. In the case of vanishing interaction energy barrier, the colloidal particles are completely destabilized, and the aggregation takes place upon every collision in Brownian motion, i.e., the rate of the aggregation is fully controlled the particle diffusion rate. Thus, the aggregation is referred to as diffusion-limited cluster aggregation (DLCA). In the case of presence of a small interaction energy barrier, only a small fraction of collisions results in successful aggregation, and the aggregation rate is significantly slower with respect to the DLCA process. Thus, it is called reaction-limited cluster aggregation (RLCA). The $d_i$ value of the DLCA clusters is always in the range between 1.75 and 1.85, independent of the materials of the particles and the electrolytes, while that of the
RLCA clusters is in the range between 2.05 and 2.15. Thus, the RLCA clusters are more compact with respect to the DLCA ones.

When the aggregation of colloidal particles is carried out at relatively high particle volume fractions, since the growth of the clusters follows the fractal scaling and the density of the clusters decreases as the size increases, at a certain degree of aggregation the available space would be fully occupied by the clusters. It follows that the clusters would interconnect, leading to a space-filling network—a low density disordered arrested (solid-like) state. Such a process is referred to as colloidal gelation and the formed solid-like state is called a gel. The dynamic arrest, specifically gelation or glass transition in colloidal systems, is a fundamental issue in soft matter physics.

Under equilibrium conditions, the state of a colloidal system could be determined by the inter-particle interaction energy and the particle volume fraction. In one extreme case of such a phase diagram, non-interacting particles or hard spheres at very high volume fractions lead to a glass state, whose solid-like properties originate from the permanent trapping of particles by their nearest neighbours. In another extreme case where strong attraction between particles occurs at low particle volume fractions, the particles interconnect into a space-filling network, whose solid-like properties result from the connectivity of the particles. However, when a long range repulsion is combined with a short range attraction between the colloidal particles, the phase diagram becomes complicated, and an equilibrium cluster phase should be introduced. Different states of a colloidal system could be obtained through the equilibrium route. For example, by gradually removing the dispersion medium from the system, we could observe the phase change from a liquid state to a glass state and finally to a densely packed, crystal state. This phase transition could be also achieved through an extremely fast, non-equilibrium route, by a sudden change in
the properties of the colloidal system. For example, we can decrease the repulsive energy between particles by adding electrolytes. In this way, the colloid would be quenched from a liquid state into a solid-like state due to the fast aggregation, without reaching the equilibrium.

A remarkable case of this non-equilibrium route is through the DLCA process. In this case, a colloidal system would be quenched to a solid-like state at low particle volume fractions due to the attractive force, which is much larger than $k_B T$ where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature, leading to irreversible bonding. If a small energy barrier remains, i.e., in the case of RLCA, since the aggregation rate is slower and the formed clusters are more compact (with a larger $d_*$), the corresponding gelation point would be located at a larger particle volume fraction. Ideally, if one could find a proper method to change the interaction potential gradually, an equilibrium route of phase transition might be reached.

For those colloids where very high interaction energy barriers are present, they are stable under stagnant conditions, but aggregation may take place under flow conditions, driven by shearing forces, such as in a stirred tank, rheometer or microchannel device. The shear-driven aggregation and gelation are the major topics of this thesis, of which systematic studies allow us to apply them to engineer new nanocomposite materials.

### 1.1.2 Shear-driven aggregation and gelation

Colloidal systems under shear demonstrate complex rheological behaviours such as yield stress, shear-thinning, shear thickening, thixotropy or rheopexy\textsuperscript{49, 50}, depending on the nature of their microscopic constituents. In order to understand these non-Newtonian behaviours, we need to get insight into the interactions between the formation and breakage of the micro-scale structures, thus to call for insight into the interplay among the particles under the shear flow.
Since the pioneering work of von Smoluchowski in deriving the equation for the purely shear-driven aggregation of fully destabilized colloidal systems in 1917\textsuperscript{51,52}, an enormous amount of experimental and theoretical studies have been carried out on the aggregation phenomena under shear at low particle volume fractions ( $\phi < 0.01$ ). Various investigations in stirred tanks allow one to substantially understand the aggregation, fragmentation and cluster morphology in flow fields\textsuperscript{53-61}. More recently, theoretical and experimental progresses have been made in the shear-driven aggregation of the colloidal systems that are stable or partially stable, \textit{i.e.}, in the presence of interaction energy barriers between particles\textsuperscript{51,62-65}. Zaccone \textit{et al.}\textsuperscript{66-71}, starting from the two-body Smoluchowski equation for interacting colloidal particles under shear, have derived an approximate theory for the irreversible aggregation kinetics of colloids in linear flows. In particular, let us consider a dispersion of interacting colloidal particles with a certain interaction potential, which are exposed in a linear velocity field. The stationary particle concentration field $c(r)$ is governed by the following two-body Smoluchowski equation with convection\textsuperscript{66,67,69-72}:

\[
\nabla \left\{ \frac{D}{k_B T} [\nabla U(x) + 4\pi \eta a v(x)] - D \nabla \right\} c(x) = 0 \quad (1.1)
\]

Where $D$ is the mutual diffusion coefficient of the particles [ $D = 2D_0 G(x)$ , with $D_0$ the diffusion coefficient of an isolated particle and $G(x)$ the hydrodynamic function for viscous retardation], $U(x)$ is the colloidal interaction energy, $\eta$ is the viscosity of the solvent, $a$ is the particle radius, and $v(x)$ is the flow velocity.

In the frame of the classical DLVO theory, $U(x)$ is the sum of the van der Waals attractive interaction ($U_A$) and the electrostatic repulsive interaction ($U_R$)

\[
U(x) = U_A(x) + U_R(x) \quad (1.2)
\]
According to the Hamaker relationship, the expression for $U_A$ is given by

$$U_A = -\frac{A_H}{6} \left\{ \frac{2}{l^2 - 4} + \frac{2}{l^2} + \ln\left[1 - \frac{4}{l^2}\right] \right\}$$  \hspace{0.5cm} (1.3)

Where $A_H$ is the Hamaker constant, and $l = x / a$. The modified Hogg-Healy-Fuersteneau expression is commonly used to describe the electrostatic repulsion:

$$U_R = \frac{4\pi\varepsilon_c\varepsilon_0 a\psi^2}{l} \ln[1 + \exp(-\kappa a(l - 2))]$$  \hspace{0.5cm} (1.4)

where $\varepsilon_c$ is the permittivity constant of the dispersion medium, $\varepsilon_0$ is the permittivity of vacuum, and $\psi$ is the surface potential. The quantity, $\kappa$, is the reciprocal Debye length, which is defined as:

$$\kappa \equiv \left( N_A e^2 \sum_i C_i z_i^2 / \varepsilon_c \varepsilon_0 k_B T \right)^{1/2}$$  \hspace{0.5cm} (1.5)

Where $N_A$ is the Avogadro constant, $e$ is the electron charge, and $C_i$ and $z_i$ are the bulk concentration and charge valence of the $i$-th ion, respectively.

The boundary conditions for the irreversible aggregation problem are: $c(x) = 0$ at $x=0$ (irreversible stick upon contact) and $c(x) = c_0$ at $x = \delta / a$. The $\delta$ value can be estimated from the boundary layer approximation:

$$\delta / a \sim \sqrt{1/\kappa a / Pe}$$  \hspace{0.5cm} (1.6a)

where $Pe = \frac{3\pi\eta \dot{\gamma} a^3}{k_B T}$ is the Peclet number, with $\dot{\gamma}$ the shear rate. An analytical expression for the rate constant of aggregation between two particles forming a doublet is obtained by solving Eq. (1.1) with the above boundary conditions.
\[ k_{1,1} = \frac{8\pi D_0 a}{\delta i a} \int_0^{\delta i a} dx \frac{dx}{\sqrt{G(x)(x+2)^2}} \exp \left[ \int_{\delta i a}^{\delta i a} \frac{dU(x)}{k_B T} dx + Pe\bar{v}_j dx \right] \]  

(1.6)

where \( \bar{v}_j \) is the effective flow velocity for aggregation. Eq. (1.6) is validated by comparing its predictions with the numerical simulations of the full convective-diffusion equation, Eq. (1.1), and as shown for example in Figure 1.1, the agreement between the two approaches is excellent\(^7\). Since the rate constant of doublet formation under stagnant DLCA conditions is given by

\[ k_{1,1} = 8\pi D_0 a , \]  

(1.7)

a generalized stability ratio, which is valid for arbitrary \( Pe \) numbers and interaction potentials, can be defined from Eq. (1.6):

\[ W_G = \int_0^{\delta i a} dx \frac{dx}{\sqrt{G(x)(x+2)^2}} \exp \left[ \int_{\delta i a}^{\delta i a} \frac{dU(x)}{k_B T} dx + Pe\bar{v}_j dx \right] \]  

(1.8)

In the limit \( Pe \to 0 \), Eq. (1.6) reduces to the well-known Fuchs’ formula for the stability ratio accounting for the particle interactions but in the absence of flow. Therefore, the combined effects of convection and particle interactions can either diminish or augment the aggregation rate, which can be simply expressed as the DLCA rate divided by a factor, \( W_G \):

\[ k_{1,1} = \frac{8\pi D_0 a}{W_G} \]  

(1.9)

By further simplification and approximation in the frame of the DLVO interactions, the following expression in the Arrhenius form for the doublet formation rate constant is obtained:
\[ k_{1,1} \approx 8 \pi D_0 a \sqrt{\frac{P e - \frac{U_m}{k_B T}}{k_B T}} \exp \left( \frac{U_m}{k_B T} + 2\alpha P e \right) \]  

(1.10)

Where \( U_m \) is the particle interaction barrier and \( \alpha \) is a geometrical parameter. The exponent in Eq. (1.10) illustrates the competitive roles played by the colloidal interactions (\( U_m / k_B T \)) and the shearing force (\( P e \)) in the shear-driven aggregation process. At smaller \( P e \) values, or sufficiently high interaction barrier \( U_m \), the exponent is negative and the aggregation rate is rather small. This corresponds to the region close to the left hand side of the vertical line in Figure 1.1. Once \( P e \) increases to a certain critical value (\( P e_c = \frac{U_m}{2\alpha k_B T} \)), further increase in \( P e \) will lead to a sign change of the exponent from negative to positive, and the aggregation rate increases substantially due to the exponential form. When the \( P e \) value becomes sufficiently large, the role of \( U_m \) becomes negligible, and the aggregation rate is controlled purely by shear. This corresponds to the region on the right hand side of the vertical line in Figure 1.1 where the \( k_{1,1} \) values of the three different cases merge to a single curve.

\[ \text{Figure 1.1.} \quad \text{Aggregation rate (} k_{1,1} \text{as a function of Peclet number) calculated based on Eq. (1.4) and compared with numerical simulations of the full convective diffusion equation, Eq. (1.1). (from}^{71} \)
It should be particularly noticed that the Peclet number in Eq. (1.10) is defined by Eq. (1.6a), where the radius of the particles, $a$, has a power of 3, indicating a strong dependence of the aggregation rate on the particle or cluster size. Then, along the shear-driven aggregation, the $Pe$ value of clusters would increase drastically as the sizes of the clusters increase. It follows that even though initially the exponent in Eq. (1.10) is negative, corresponding to low aggregation rate, as the radius of the clusters grows to a certain value, the exponent would become positive, leading to self-acceleration of the aggregation rate. The critical size ($a_{cr}$) after which such self-acceleration kinetics starts can be obtained by setting the exponent in Eq. (1.10) to zero:

$$a_{cr} = \left( \frac{U_m}{6\pi \mu \alpha \gamma} \right)^{1/3} \quad (1.11)$$

The above self-acceleration kinetic theory has been well demonstrated by experiments$^{67}$. Typical examples are shown in Figure 1.2, corresponding to shear-driven aggregation of PS particles in a rheometer. For a given shear rate, the shear viscosity is initially low and slightly increases, and when the shearing time reaches a certain value, the viscosity increases sharply and explosively, corresponding to the transition from slow to fast (accelerated) growth of the clusters, leading finally to space-filling by the clusters, thus explosive increase in the shear viscosity.
Figure 1.2. Suspension shear viscosity as a function of the shearing time under steady shear for charge-stabilized colloids at $\phi = 0.23$. From\textsuperscript{67}

Similar to the gelation process under stagnant conditions, shear-driven gelation can also occur when the aggregation reaches a certain degree such that the generated fractal clusters can fill the entire space\textsuperscript{67,71,73}.

The above theory of the shear-driven self-accelerating aggregation kinetics can be well applied to explain the jamming phenomena of well-stabilized colloidal systems after disturbed by shear in concentrated conditions, which are of practical interest in industrial processes. This theory establishes also the basis for the first part of the research activities presented in this thesis.
1.2 Nanocomposites

Nanoparticles, when properly imbedded into polymer matrices, can improve substantially the thermal, mechanical, electric or optical properties of the matrix polymers. Thus, such polymer matrix nanocomposites have received great attention in the last decades. The concept of polymer-nanocomposites was first introduced in the early 1990s, when imbedding organophilic clay into nylon-6 showed dramatic improvements in mechanical and physical properties of nylon-6. Then, researchers have applied the concept to prepare nanocomposites using a wide variety of polymers including epoxies, unsaturated polyester, poly(caprolactone), poly(ethylene oxide), polystyrene, polyimide, polypropylene, poly(ethyleneterephthalate) and polyurethane. Nowadays, more and more polymer matrix nanocomposites are designed to improve the mechanical, optical, electronic properties of polymers, and the embedded nanoscale fillers are in the form of fibres, whiskers, platelets or particles. The filler materials can be metals, metal oxide, inorganic clays, carbon nanotubes, etc.

Several methods have been developed to prepare the nanocomposites in industry, such as melt mixing, film casting, in situ polymerization, in situ particle generation, etc. Melt mixing or melt compounding is the most popular procedure used in industry, which has been explored for a wide range of materials such as oxides and carbon derivatives (carbon nanotube, graphite and graphene, etc.). However, due to the high viscosity of the polymer melts, breaking aggregates during the melt process is often difficult. Film casting is to disperse hydrophobic NPs in a polymer solution, which could be casted in moulds or coated on the surface. A good solubility of polymer and a good dispersity of the NPs are crucial for the homogeneity of the composite materials. Film casting is also widely used for preparing nanocomposite films.
However, the thickness of the material is limited by the casting and drying process which normally takes days and is followed by hot pressing of the composite in order to completely remove the solvent.

In the case of in-situ polymerization, NPs are pre-dispersed in a monomer of low viscosity to form a stable colloid. The homogeneity of the dispersion can be achieved by modifying the particle surface with some functional groups. The aim of surface modification is either to introduce surface charges or to graft some bulk polymers to generate a steric or lyophilic force. There are three different types of modifications that are introduced in the literature. The simplest method is to attach amphiphilic surfactant molecules such as bulk acid, which can adsorb on the particle surface by ionic attractions. In this case, the surfactant does not participate in the bulk polymerization. The second method is called grafting to process, which is to chemically anchor polymer chains to inorganic particle surface. Among the used polymers, the so-called polymerizable surfactant is the most popular in recent studies. Grafting from techniques is to functionalize the inorganic particle surface with (polymer) initiating groups. In this method, the particles act like initiator for the polymerization. It can be applied for various types of polymerization including anionic, cationic or free radical polymerization.

Since the method based on in-situ polymerization always faces the problem of homogeneously dispersing the surface-modified particles in a monomer, in-situ generation of NPs in the presence of a polymer or monomer has been developed recently. A sol-gel process is applied to generate different inorganic particles. As occurred in the other methods, agglomerates may form, and the control of the preparation conditions limits its application in industry production.
Therefore, properly dispersing the NPs in a polymer matrix during the nanocomposite manufacture is a rather complicated topic, which requires a deep understanding of the stability and aggregation behaviour of NPs in the medium, which is typically either a polymer melt or an organic solvent. In order to get into this problem, the first step is to understand the interaction of the particle surface with the medium. It is known that NPs not only can improve the properties of a polymer but also affect the kinetics during the in situ polymerization process.\textsuperscript{76} However, due to the complexity of the system, engineering nanocomposites is still upon the experimental level without a universal model regarding to the behaviour of polymer nanocomposites and the effect of the NPs.\textsuperscript{84}

### 1.3 Outline of the Present Work

The objective of this thesis is twofold. First, we systematically investigate the shear-driven aggregation process, aiming to get insight into the aggregation mechanism and kinetics, as well as the resulting phase behaviour. Second, we apply our understanding in the shear-driven process, as well as the other colloidal engineering concepts, to develop a new approach, based on shear-driven hetero-aggregation, to engineer nanocomposite materials.

In Chapter 2, we investigate the shear-driven aggregation of PS colloids that are stabilized by both fixed and surfactant charges, using a microchannel device (MC), in various particle volume fractions. The objective is to understand how the primary particles evolve to clusters with shearing time, how the cluster morphology develops along the aggregation with the effect of breakage and restructuring, and whether non-DLVO interactions are present, affecting the kinetics. The time evolution of the primary particle conversion to big clusters is characterized by an induction time
followed by an explosive increase when the cluster size reaches a certain critical value, which confirms the self-acceleration kinetics developed in the literature. The critical clusters have been quantified for the first time, and the scaling of their size with the shear rate follows well the literature prediction. Moreover, analysis of the shear-driven kinetics confirms the presence of substantial non-DLVO interactions in the given system.

In Chapter 3, we study the phase evolution along the shear-driven aggregation again in the microchannel device under intense shear, for the same PS colloids used in Chapter 2, whose high interaction energy barrier ensures the high stability of the particles and clusters before and after shearing. The short residence time of the microchannel allows us to snapshot the phase evolution by repeatedly cycling the colloid in the microchannel. It is found that, depending on the particle concentration, besides a liquid-like fluid of clusters and a solid-like gel, there is another solid-like state between them: Wigner glass of clusters. Their transitions occur in a large range of particle concentration. A phase diagram has been proposed that describes how the transitions of the three phases evolve at the aggregation steady-state in the colloidal interactions vs particle concentration plane.

In Chapter 4, intense shear-driven hetero-aggregation of a stable mixture of two colloidal dispersions was raised, which is proposed in this work as a general methodology for preparing composite materials where the different components are homogeneously and randomly distributed at nano-scale. Its feasibility has been demonstrated using a stable binary colloidal dispersion composed of 43 nm PS particles and 280 nm PMMA particles. The PS particles alone undergo the shear-driven aggregation (shear-active), while the PMMA particles alone do not (shear-inactive). It is found that the shear-driven hetero-aggregation of the binary colloidal system does
occur, and the formed clusters are composed of both the “shear-active” PS and “shear-inactive” PMMA particles. The SEM picture demonstrates that the PMMA particles are homogeneously and randomly distributed among the PS particles in the clusters, confirming the feasibility of the proposed methodology. Mechanism leading to the hetero-aggregation has been proposed based on the experimental observations.

The work in Chapter 5 is motivated by an industrial project where (polymer) NPs-in-PMMA matrix nanocomposites need to be prepared in both lab and industrial scales. The key issue in the applications of the nanocomposites requires that the NPs are homogeneously and randomly distributed in the PMMA matrix, with negligible agglomeration. Although the goal has been successfully reached, due to industrial application proprietary, details about the development cannot be disclosed in this thesis. Thus, only the part of the work that is irrelevant with the industrial application proprietary has been included in this thesis. In particular, we have designed a standard methodology to investigate the role played by NPs during the in-situ bulk polymerization of MMA, which is based on the DSC experiments and the kinetic modelling of the bulk polymerization. Both PTFE and PS NPs have been applied in this work, which, due to their incompatibility with MMA, have been surface-modified by cross-linked PMMA (cPMMA). Then, to quantify the net effect of the NPs on the bulk polymerization, we have first quantified the effect of the cPMMA without the NPs, and then subtracted the effect of the cPMMA to get that of the NPs. Moreover, the presence of dissolved linear PMMA during the MMA bulk polymerization has also been studied and compared with that of the cPMMA. It was found that the effect linear PMMA on the MMA bulk polymerization is as if the system was pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. The cPMMA retards the MMA polymerization kinetics. Such retardation increases as the cross-linker in the cPMMA
increases. After subtracting the role played by the cPMMA, we found that the PTFE NPs behave like (inert) dead volume, changing only the effective concentrations of the components in the system, while, with respect to PTFE NPs, the dispersed PS NPs can promote the MMA bulk polymerization. In addition, the CryoSEM imagines show that the NP dispersion leads to formation of microstructure in the PMMA matrix. Although only model NP systems are used in this work, the developed methodology can be applied to more complicated NP systems, to explore the effect of various different surfaces by quantitative design of the NP surface.
Chapter 2

Kinetics and Cluster Morphology

Evolution of Shear-Driven Aggregation of Well Stabilized Colloids

2.1 Introduction

Shear-driven aggregation of colloidal dispersions has received great attention in recent years, not only because of fundamental interests in soft-matter physics, but also due to its importance in biology\textsuperscript{85, 86}, structured materials\textsuperscript{87} and industrial productions
of polymers and biological drugs. These colloidal particles are often kinetically stabilized by surface charges, and the electrostatic repulsion of the charges together with the van der Waals attraction, i.e., the well-known DLVO interaction, generates an interaction energy barrier, which warrants the particles with no tendency to aggregate at rest. Thus, for the shear-driven aggregation to occur, one has to impose a shear force that can drive the particles to overcome the energy barrier.

As it was demonstrated in the last chapter, the interplay between the shearing force and the interaction energy barrier in destabilizing colloidal dispersions has been well described in the literature. Eq. (1.10) can be rewritten as the following expression for the aggregation rate constant $k_{1,1}$ between two particles or clusters:

$$k_{1,1} \sim \sqrt{(3\pi\alpha\mu\gamma a^3 - U_m^*)/k_B T} e^{-(U_m - 6\pi\alpha\mu\gamma a^3)/k_B T}$$

(2.1)

Within the exponential term, when $U_m \gg 6\pi\alpha\mu\gamma a^3$, the exponent is negative, and the aggregation rate is very small. Thus, to have efficient shear-driven aggregation, one needs to increase the shear rate, $\dot{\gamma}$, so as to have $U_m \ll 6\pi\alpha\mu\gamma a^3$, leading to a positive exponent. This has been well demonstrated by various experiments. On the other hand, even though initially $U_m \gg 6\pi\alpha\mu\gamma a^3$ with very slow aggregation, after a period of (induction) time when the cluster radius reaches a critical value,

$$a_{cr} = (U_m / 6\pi\alpha\mu\gamma)^{1/3}$$

(1.11)

the exponent becomes positive, and the aggregation would accelerate dramatically. Under such situations, since a large number of big clusters are formed in short time, which are fractal objects, their packing fraction would increase substantially, leading to an explosive increase in the shear viscosity.

Although the induction time and the evolution of the shear viscosity along the
shear-driven aggregation have been well described by the above self-accelerating theory, no detailed investigations have been reported in the literature on the shear-driven aggregation kinetics and the cluster structure evolution, where, apart from the aggregation, cluster breakage and restructuring should also play an important role. For example, when the shear-driven aggregation was conducted in a MC where the shear rate is extremely high \( \dot{\gamma} \sim 10^6 \text{ s}^{-1} \) but the residence time of the clusters in the MC is extremely short (\( \sim \) few tens of \( \mu \text{s} \)), the fractal dimension of the formed clusters was \( d_f = 2.40 \pm 0.04 \); instead, when it was done in a rheometer where the shear rate is in the order of \( 10^3 \text{ s}^{-1} \) but the residence time of the clusters in the rheometer is substantially long, the \( d_f \) value was \( 2.7 \pm 0.1 \). This difference clearly implies the effect of shearing history on the cluster structure. Further, the above self-accelerating theory predicts the presence of a critical cluster radius, \( a_c \), given by Eq. (1.11), and only when \( a > a_c \) the self-acceleration in the shear-driven aggregation occurs. However, such a critical cluster radius has never been identified experimentally.

In this chapter, we systematically investigate the time evolutions of the cluster size and morphology along the intense shear-driven aggregation process in the MC device. To realize these, we have to thank the MC device for its very short residence time such that by repeatedly cycling back the colloidal system from the outlet of the MC to the inlet, we can not only reach the desired residence time but also characterize the state of the colloidal system after each cycle (conversion of primary particles to big clusters, average cluster size, cluster fractal dimension, the critical cluster radius, \( a_c \), etc.). Moreover, since the shear rate generated by the MC is extremely large, if there is only the DLVO interactions, we often found that \( U_m \ll 6\pi\alpha\mu\dot{\gamma}a^3 \), and it follows that we cannot have the critical cluster radius \( a_c \) significantly greater than that of the primary
particles. Thus, in this work, we not only use a very small radius of the primary particles, but also add certain amount of ionic surfactant to the particle surface, which generates some non-DLVO interactions (e.g., repulsive short-range hydration force), such that we have initially $U_m \gg 6\pi \mu \gamma a^3$.

2.2 Experimental Methods

2.2.1 The colloidal system.

The PS dispersion was synthesized in our lab by conventional emulsion polymerization using 5% weight fraction of DVB as cross linker, with KPS (potassium persulfate) as initiator and SDS (sodium dodecyl sulfate) as surfactant. The mean radius of the primary particles was $a_p = 21.5$ nm and the polydispersity was around 0.05, determined by dynamic light scattering (DLS). The particles were stabilized by both fixed surface charges from polymer chain end (sulfate) groups and the surfactant (25% coverage regarding to the saturated adsorption of SDS on PS surface). The pH values of the latexes are measured by the SevenEasy pH meter (Mettler Toledo). The $\zeta$-potential of the colloidal system is measured by Zetasizer Nano (Malvern, UK) instrument at $\phi = 1.0 \times 10^{-4}$, was $-40$ mV. The CCC (critical coagulant concentration) value for complete destabilization of the colloid was measured, equal to 0.2 M NaCl.

2.2.2 Shear-driven aggregation/gelation in the MC.

The shear-driven aggregation of the above synthesized colloid was carried out using a commercially available device, Homogenizer HC-5000 (Microfluidics), equipped with a z-shape MC of a rectangular cross section of $5.26 \times 10^{-8}$ m$^2$ with a length of $5.8 \times 10^{-3}$ m$^3$. The intensive shear in the MC was generated by forcing the colloidal system to pass through the MC under high pressure. A pressure gauge was
settled before the inlet of the MC to measure the instantaneous pressure drop ($\Delta P$) through the MC. The relation between the shear rate in the MC and $\Delta P$ is $\dot{\gamma} \in [2 \times 10^5, 1.5 \times 10^6] \text{s}^{-1}$ corresponding to the pressure drop $\Delta P \in [20, 150] \text{ bar}$, reported by the device supplier using water as the test media. The residence time of the fluid in the MC is in the range of 121-38 $\mu$s corresponding to the range of $\Delta P$. All the aggregation experiments were performed without adding any electrolytes, in the range of the particle volume fraction, $\phi \in [0.02, 0.12]$. The shear-driven aggregation kinetics was obtained by passing the dispersion through the MC many times. In a typical experiment a fixed amount (300 mL) of the dispersion was poured into the sample container and pumped completely through the MC. The effluent from the outlet of the MC was collected in a bottle, and when completed pour it again into the sample container for the next pass. After each pass, 5 mL of the sample was taken for characterization of the aggregation extent and cluster morphology. All the particles and clusters practically experience the same residence time in the MC. Thus, the shearing time is defined as the total residence time, calculated as $t = N_p \times \tau_p$, where $\tau_p$ is the residence time of a single pass in the MC and $N_p$ is the number of passes.

2.2.3 Conversion of primary particles to big clusters.

It has been well documented\textsuperscript{14, 92, 93} that a colloidal system, after passing through the z-MC, is composed of two distinct classes of clusters: Class 1, constituted mainly of primary particles and some very small clusters, and Class 2, constituted of big clusters with an average size at least two orders of magnitude larger than that of Class 1. To determine the conversion of the primary particles to big clusters, we diluted each sample (5 mL) into 10 mL and centrifuged at 4500 rpm for 15 min to separate the big clusters. The liquid part was disposed and the solid part was washed with 10 mL of
water and centrifuged again. The sample was weighted after drying in the oven at 60 °C for 8 hours, which defines the value of the conversion, \( x \).

### 2.2.4 Characterization of cluster size and fractal dimension.

The radius of gyration \( R_g \) and fractal dimension \( d_f \) of the big clusters after the MC were determined by small-angle light scattering (SALS) instrument, Mastersizer 2000 (Malvern, U. K.). The sample was diluted with deionized water without filtration. The details of the measurements and characteristics of the SALS instrument could be found elsewhere\(^{14} \). It should be pointed out that since the interactions among the primary particles are repulsive, the clusters formed under the intense shear are also repulsive. Thus, the stability of the clusters during the sample preparation and characterization is guaranteed.

### 2.3 Results and Discussion

#### 2.3.1 SDS-Induced Non-DLVO interactions

Although the DLVO interactions generated by the adsorbed SDS can be well quantified using the generalized stability model\(^{95} \), as shown in the Appendix I, it is difficult to quantify the additional non-DLVO interactions. To evidence the SDS-induced non-DLVO interactions, we took part of the latex and cleaned up all the surfactant (as well as all the ions) in the system by mixing it with a mixture of cationic and anionic exchange resins (Dowex MR-3, Sigma-Aldrich), according to a procedure described elsewhere\(^{93} \). We prepared two colloidal systems: one with the latex before cleaning and another with the latex after cleaning, both at \( \phi = 2.0\% \), and let them pass through the MC one time at \( \dot{\gamma} = 1.5 \times 10^6 \) s\(^{-1} \), and then measured the conversion \( x \) of the primary particles to the big clusters. The obtained \( x \) value is extremely small.
(approaching zero) for the one before cleaning, while the \( x \) value reaches 78\% for the one after cleaning. This result indicates that the adsorbed SDS improves the shear stability of the particles. However, for the given shear rate, we have computed the value of the term, \( 6\pi\alpha\mu\gamma a^3 \) in Eq. (1.11), which is \( 1.56 \times 10^3 k_B T \), while the \( U_m \) value, as shown in the SI, is \( 42.2 k_B T \) and \( 348 k_B T \), respectively, for the cleaned and non-cleaned latexes, i.e., in both cases, we have \( U_m \ll 6\pi\alpha\mu\gamma a^3 \). Based on the principle of the shear-driven aggregation, this means that the aggregation process is controlled purely by the shearing force, independent of the height of the (DLVO) interaction energy barrier. This is obviously contradictory with the experimental result, thus demonstrating the presence of the non-DLVO interaction, particularly the hydration interaction generated by the adsorbed SDS layer\(^{96}\). Further discussion and quantification of the non-DLVO interactions will be given in Section 2.3.4.

2.3.2 Shear-driven aggregation kinetics and cluster morphology.

The shear-driven aggregation kinetics at \( \dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1} \) and three particle volume fractions (\( \phi = 3.0\%, 4.0\% \) and \( 5.0\% \)) are given in Figure 2.1 in the form of the time evolution of the primary particle conversion to big clusters, \( x \). In all the cases, there is clearly an induction period where the conversion remains practically zero, and then the conversion turns up rapidly. This is very similar to the time evolution of the shear viscosity observed during the shear-driven aggregation in a rheometer\(^{71, 73, 94}\), though the shear viscosity is only a lumped macro-quantity and the \( x \) values represent the detailed kinetics. We also investigated the aggregation kinetics at even larger \( \phi \) values (data not shown), and it was found that for \( \phi > 6\% \), no induction time is observed, and the big clusters are formed and the conversion enters into the fast increasing regime immediately after one pass. The system becomes more and more viscous with the
shearing time and eventually become a solid-like gel. When the viscosity reaches a
certain level, the poor flow ability of the dispersion cannot allow us to pour it back to
the inlet of the MC for further shearing. This is the reason why the plateau was not
reached in the cases of higher particle volume fractions. For $\phi > 15\%$, a solid-like gel is
obtained just after passing through the MC one time.

![Figure 2.1](image)

**Figure 2.1.** Time evolution of the conversion of primary particles to big clusters ($x$)

Figure 2.2 shows the inverse of $\phi$ as a function of the induction time $t_i$, which well
exhibits a linear relationship. Considering that the aggregation process follows a
second-order kinetics and in the early stage of doublet formation, we have that
$\frac{d\phi}{dt} \propto \phi^2$, and it follows that $t_i \propto 1/\phi$. It should be noted that, rigorously, the
induction time is not for doublet formation, instead, for the formation of the critical
radius of the small clusters, $a_{cr}$, which leads to self-acceleration kinetics. However,
once the doublets are formed, they grow further and very quickly to larger clusters, due
to the strong dependence of the rate constant on the cluster radius, $a$ in Eq. (2.1). It follows that the induction time is practically controlled by the doublet formation.

\[ \text{Figure 2.2} \] The experimentally measured linear correlation between the induction time ($t_i$) and the inverse of the initial primary particle volume fraction ($1/\phi$), at $\dot{\gamma} = 1.5 \times 10^6$ s$^{-1}$.

The time evolutions of the average radius of gyration of the big clusters, $R_g$, of the three systems are reported in Figure 2.3. It is seen that in each case the $R_g$ value jumps sharply to a local maximum within a very short time and then decreases progressively with time to a plateau value (~10 µm). Such an overshooting in the cluster size was reported in the literature for the aggregation in a stirred tank in the presence of salts.\textsuperscript{66,97} Selomulya et al.\textsuperscript{97} proposed that the overshooting phenomenon is due to restructuring of the clusters when they grow big enough to feel the flow. In our recent work\textsuperscript{98}, we explained the overshooting behavior occurred in a stirred tank for the aggregation of PS particles at pH < 7 by considering irreversible increase in the particle surface roughness (resulting from inter-particle/cluster collisions) with time. Since the adhesive energy between particles reduces as the surface roughness increases, the breakage rate of the
clusters would increase, leading to decrease in the average cluster size. Since we also use PS particles and the pH value of the three systems in Figure 2.1 is 2 to 3, we have to verify if our overshooting is related to the surface roughness variations. Considering that it is difficult to measure the surface roughness of so small particles, we have tuned the pH = 8, where no overshooting was observed previously, and repeated the same experiments in Figure 2.1. We found again the overshooting phenomenon (data not shown), and it follows that our overshooting is independent of pH. It should be noted that the polystyrene particles used in the previous work were charged with carboxylic groups, while the present particles were charged with sulfate groups. In addition, the present particle surface was covered by the adsorbed SDS, while the previous latexes were surfactant free. Further difference is that the previous particles were fully destabilized by adding salts, while in the present systems no salts were added. The operation time was in minutes or hours, while in this work it is in microseconds. All these differences make us difficult to compare overshooting phenomena in this work with those in the previous work. Thus, we cannot conclude that the present overshooting is related to the variations in the surface roughness.
To better understand the oversooting behavior of our systems, first we note that the fractal dimension of the clusters increases with the shearing time. Figure 2.4 compares two scattering structure factors, $S(q)$, at $t = 350 \mu s$ and $810 \mu s$, in the case of $\phi = 4.0\%$, where the slope of the power-law region is obviously larger (thus a larger $d_f$ value) at $t = 810 \mu s$. In all our cases, typically, the $d_f$ value after the first pass is equal to $2.40 \pm 0.05$, as observed previously\(^9^3\), and then increases progressively as the pass number (shearing time) increases until reaching a value of $2.80 \pm 0.05$. This is in good agreement with the experimental and numerical findings in the literature for fully destabilized systems\(^9^8\), where the $d_f$ value also increases with the shearing time in the range of $2.4 \leq d_f \leq 2.8$, resulting from breakage and restructuring induced by intense flow. Second, we calculated the average mass (number of primary particles) in one big cluster based on the fractal scaling, $i = k \cdot (R_g / a_p)^{d_f}$, where $k = 4.46 \times d_f^{-2.08}$\(^9^3\), using
the experimentally measured $d_f$ values. Figure 2.5 shows the time evolutions of $i$ for the three systems. It is evident that the overshooting also occurs in $i$, indicating that after reaching the local maximum, the average mass of the clusters indeed decreases as the conversion (or time) increases. Therefore, based on the above discussion and experimental evidences, we may describe the overshooting phenomenon of our systems as follows. Initially, since the concentration of the small clusters (including primary particles) is very high, the generation rate of the big clusters is very large but the resulting concentration of the big clusters is still low, thus low breakage rate as well. This leads to sharp increase in the size of the big clusters. Then, as the concentration of the big clusters increases and that of the small clusters decreases with time, the breakage and restructuring events become dominant, and consequently both the average size and mass of the big clusters decrease.

**Figure 2.4.** The scattering structure factors, $S(q)$, of the clusters at two shearing times, as a function of the normalized wavevector, $q \times R_g$, in the case of $\phi = 4.0\%$ and $\dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1}$. 
Figure 2.5. Time evolution of the conversion of the average mass of a big cluster (i)

As mentioned above, the shear-driven aggregation leads to a bimodal cluster distribution, and the Class-1 (small) clusters are dominated by primary particles, due to the strong dependence of the kinetics on the cluster size in Eq. (2.1). Thus, the generation rate of the big clusters depends practically on the volume fraction of the remaining primary particles, \( \phi_{\text{rem}} \). In principle, the \( \phi_{\text{rem}} \) value can be simply estimated from \( x \), based on \( \phi_{\text{rem}} = \phi \cdot (1 - x) \). However, since the big clusters are rather compact, their occupied volume is poorly accessible to primary particles. It follows that the accessible free volume decreases as \( x \) increases. Thus, to better understand the kinetics of the primary particle conversion to the big clusters, we should consider the effective volume fraction of the remaining primary particles, \( \phi_{\text{rem,e}} \), which can be expressed as

\[
\phi_{\text{rem,e}} = \phi \times (1 - x) / (1 - \phi_e)
\]

where \( \phi_e \) is the volume occupied by the big clusters. The time evolutions of \( 1/\phi_{\text{rem,e}} \)
computed from Eq. (2.2) are shown in Figure 2.6. It is found that the time evolutions of the $1/\phi_{\text{rem,e}}$ curves of the three systems at $\phi = 3.0\%$, $4.0\%$ and $5.0\%$ have basically collapsed to a single curve, except for the few points within the induction time. This is not surprising when one recalls that the induction time for the formation rate of the critical clusters is controlled by the doublet formation rate. The formation rate of the big clusters should be controlled by the doublet formation rate as well, again due to the strong dependence of the rate constant on the cluster radius, $a$ in Eq. (2.1). This means that the entire shear-driven aggregation process is controlled by the doublet formation rate, thus controlled by the primary particle concentration, i.e., at the same primary particle concentration, the shear-driven aggregation kinetics is the same, independent of the presence of big clusters.

**Figure 2.6.** Time evolution of the conversion of the inverse of the remaining effective volume fraction of primary particles ($1/\phi_{\text{rem,e}}$).
It should be noted that if we calculate the $\phi_{\text{rem}}$ value, based on $\phi_{\text{rem}} = \phi \cdot (1 - x)$, the collapse of the $1/\phi_{\text{rem}}$ values of the three systems is not as good as that of the $1/\phi_{\text{rem,e}}$ values in Figure 2.6. This further confirms that the conversion of the primary particles to the big clusters is determined by the effective volume fraction of the primary particles and the big clusters behave as if inert objects, occupying only effectively the available space.

2.3.3 The critical radius of the small clusters ($a_{\text{cr}}$) for the self-acceleration kinetics.

The critical radius of the small clusters ($a_{\text{cr}}$) after which the shear-driven aggregation accelerates is theoretically given by Eq.(1.11), derived from Eq. (2.1), but its experimental identification has never been reported in the literature. In Figure 2.4, the bending of the $S(q)$ curve at $t = 350 \mu s$ in the range of $q < 1 \times 10^{-3} \text{ nm}^{-1}$ clearly indicates the existence of small clusters ($< 1 \mu m$). In order to identify the critical clusters, we have taken samples near the induction time and determined their composition based on the SALS measurements. Since the difference in size between Class-1 and Class-2 clusters is orders of magnitude, it is possible to separate them by careful centrifugation.

Figure 2.7 compares the $S(q)$ curves before and after centrifugation in the case of $\phi = 3.0\%$, $\dot{\gamma} = 1.12 \times 10^6 \text{ s}^{-1}$. From the $S(q)$ curve before centrifugation, we can well determine the $R_g$ value of the big clusters from the Guinier regime in the range of $q < 10^{-4} \text{ nm}^{-1}$, and the obtained value is $R_g = 30.9 \mu m$. The bending in the range of $q > 1 \times 10^{-3} \text{ nm}^{-1}$, though clearly indicating the presence of small clusters, cannot be used to correctly estimate their size because of the contamination from $S(q)$ of the big clusters. Instead, the $S(q)$ curve after centrifugation in Figure 2.7 perfectly overlaps with that
before centrifugation in the large $q$ range, while it is flat in the region of $q < 1.0 \times 10^{-3}$ nm$^{-1}$, indicating that the big clusters are completely eliminated and the small clusters remain. The radius of gyration of the small clusters obtained from the Guinier plot of the $S(q)$ curve after centrifugation is $a_\text{cr} = 435$ nm, and these clusters are considered as the critical clusters.

**Figure 2.7** A typical scattering structure factor, $S(q)$, before and after centrifugation, for the sample taken near the induction time in the case of $\phi = 3.0\%$ and $\dot{\gamma} = 1.12 \times 10^6$ s$^{-1}$. The inset shows how the $S(q)$ curve after centrifugation evolves with the shear rate.

It was found that at a fixed shear rate, $\dot{\gamma}$, the evaluated $a_\text{cr}$ value of the critical clusters is practically independent of the $\phi$ value. Then, we have varied the $\dot{\gamma}$ value in order to determine the relation between $a_\text{cr}$ and $\dot{\gamma}$. The $S(q)$ curves for the samples prepared at four different $\dot{\gamma}$ values after centrifugation are shown in the insert of Figure 2.8, and as can be seen, the Guinier region moves towards a smaller $q$ value (i.e., a
larger $a_c$ value) as $\dot{\gamma}$ decreases. In Figure 2.8 the obtained $a_c$ values are plotted as a function of $1/\dot{\gamma}^{1/3}$, and as expected from Eq. (1.11), they well exhibits a linear relationship. This result not only confirms the scaling of $a_c$ with $\dot{\gamma}$ given by Eq. (1.11), but also supports that the small clusters identified after centrifugation are indeed the critical clusters for starting the self-acceleration aggregation kinetics.

![Graph](image)

**Figure 2.8.** The critical radius of the small clusters that leads to the self-acceleration kinetics, determined from the approach in Figure 2.4, as a function of $1/\dot{\gamma}^{1/3}$, in the case of $\phi = 3.0\%$.

### 2.3.4 Evaluation of the colloidal interaction energy barrier.

The slope of the plot in Figure 2.8 is equal to $1.22 \times 10^{-4}$, which based on Eq. (1.11) corresponds to

$$(U_m/(6\pi\alpha\mu))^{1/3} = 1.22 \times 10^{-4} \quad (2.3)$$

Then, if we know the flow parameter, $\alpha$, we can estimate the value of the
interaction energy barrier, $U_m$. To estimate the $\alpha$ value, let us consider the scaling of
the induction time in shear-driven aggregation:\textsuperscript{67}

$$t_1 \sim \frac{1}{k_{1,1}} \sim \frac{1}{\sqrt{(3\alpha mU' - U_m)/k_BT}} e^{(U_m - 6\pi a \dot{\gamma}^2)/k_BT} \quad (2.4)$$

For a given system, $U_m$ and its second derivative, $U''_m$, are constant. In addition,
as shown in the Appendix II, typically $-U''_m \gg 3\alpha \mu \dot{\gamma}^3$, and we have

$$t_1 \sim \frac{1}{k_{1,1}} \sim \frac{e^{U_m/k_BT}}{\sqrt{(-U_m)/k_BT}} e^{-6\pi a \dot{\gamma}^2/k_BT} e^{-e^{-6\pi a \dot{\gamma}^2/k_BT}} = e^{-\alpha(2Pe)} \quad (2.5)$$

where $Pe \equiv 3\pi \mu \dot{\gamma}^3 / k_BT$ is the Peclet number. Thus, the slope of the $-\ln(t_1)$ vs
$2Pe$ plot leads to the estimate for $\alpha$. Figure 2.9 shows such plots for our system at three
NaCl concentrations, where the values used for the known parameters are $\mu = 0.001$
Pa-s, $a = 22.1\times10^{-9}$ m. Note that here the variations in $Pe$ are only due to the shear rate,
$\dot{\gamma}$. It is seen that the three lines are practically parallel, with the slope equal to $\alpha = 0.092$
$\pm 0.0024$. Such a result also confirms the validity of the scaling, Eq. (2.5), and the
obtained $\alpha$ value represents indeed the flow property of the MC system. It should be
mentioned that although the flow in the MC is turbulent\textsuperscript{67}, the obtained $\alpha$ value is
surprisingly close to the value of $\alpha = 1/(3\pi)$ for simple shear flow\textsuperscript{67}.
Figure 2.9. Induction time of the shear-driven aggregation, $t_i$, obtained at various NaCl concentrations, as a function of the Peclet number. $\phi = 3.0\%$.

Using the obtained $\alpha$ value, from Eq. (2.4) we obtain the value for the energy barrier of our colloidal system, $U_m = 7.64 \times 10^5 k_B T$. This $U_m$ value is three orders of magnitude larger than that estimated from the DLVO interaction ($325 k_B T$) and is too large to be realistic for a DLVO system. It is thus confirming that our PS particles are stabilized not only by the DLVO but also non-DLVO interactions (e.g., the short-range repulsive hydration force generated by the adsorbed surfactant). This result indicates that through quantification of the critical radius of the small clusters ($a_{cr}$) for the self-acceleration kinetics, one may understand if non-DLVO interactions play a significant role in stabilizing a colloidal system.
2.4 Conclusions

For a PS colloid that is stable at rest, its intense shear-driven aggregation kinetics has been studied through a microchannel device in the range of the particle volume fraction, $\phi \in [0.02, 0.12]$. We have monitored the time evolution of the conversion of the primary particles to big clusters, and average radius of gyration and fractal dimension of the big clusters.

The time evolution of $x$ is typically composed of three stages: induction, sharp increase and slow increase stages. In the induction stage, $x$ is practically zero; in the sharp increase stage, the average size of the big clusters increases also sharply, leading to an overshooting; in the last stage, both the average size and mass of the big clusters decrease to reach a plateau. The fractal dimension of the big clusters increases with the shearing time from the initial value of $2.40 \pm 0.05$ to reach $2.80 \pm 0.05$. Thus, along the shear-driven aggregation, both breakage and restructuring play an important role.

The presence of the induction stage followed by a sharp increase in the conversion confirms the theory of shear-activated aggregation with the activation energy, $E_a = U_m - 6\pi\alpha\mu\gamma a^3$. The induction time implies an initial $E_a > 0$, and the aggregation rate is very small; as the radius of the clusters, $a$, increases progressively to reach a critical value, $a_c$, $E_a \leq 0$, and the aggregation accelerates. The size of the critical clusters for the self-acceleration kinetics has been quantified for the first time, and the scaling of the obtained $a_c$ value with the shear rate follows well Eq. (1.11).

Moreover, after quantifying the flow parameter, $\alpha$ from the induction time scaling, Eq. (2.6), we are able to estimate the interaction energy barrier, $U_m$, from Eq. (1.11) The
obtained $U_m$ value is three orders of magnitude larger than that calculated from the measured $\zeta$-potential, confirming the presence of substantial non-DLVO interactions in the given system.
Chapter 3

Snapshotted Glass and Gel Transitions of Stable Colloidal Dispersions after Shear-Driven Aggregation

3.1 Introduction

Colloidal dispersions with different inter-particle interactions show a variety of phase behaviour. Spherical particles with a steep repulsive potential exhibit a progressive phase transition from a fluid to a jamming state and then to a fully
crystallized state as the particle volume fraction, $\phi$, increases. The jamming state is a glassy state, referred to as repulsive glass or Wigner glass, which may occur in a large range of $\phi$, depending on the range of the repulsion and temperature$^{11}$. For strongly attractive colloids, the system arrests at relatively low particle densities ($\phi < 0.2$), resulting from irreversible inter-particle bonding of fractal scaling, and the arrested state is often referred to as a gel$^{10}$. For the colloidal systems whose interaction potential is attractive at a short distance and repulsive at a long separation, such competing interactions may lead to rich hierarchical self-organization behaviour such as finite sizes of clusters$^{10, 72, 99-102}$, dynamical arrest to form a Wigner glass of clusters$^{99, 102, 103}$, or percolation of clusters to form a gel$^{104, 105}$.

On the other hand, even for colloids with a steep repulsive potential such that they are extremely stable at rest, proper shear forces can drive them to aggregate, leading to phase transition, if the primary (minimum) well of the interactions is deep enough$^{69}$. Such shear-driven transition from liquid-like colloids to solid-like gels has been shown experimentally for various systems with strong DLVO type interactions. The mechanism for the transition was proposed to be similar to that under stagnant conditions, resulting from percolation of fractal clusters at high packing fractions$^{69, 106}$. However, a clear picture how different phases evolve and transfer along the shear-driven aggregation has not been given in the literature. Therefore, this work is dedicated to detailed investigations of the shear-driven phase evolution for a colloidal system that is strongly stabilized by surface charges and surfactants. It will be seen that along the shear-driven aggregation process, we are able to observe progressively three phases: fluid of clusters, Wigner glass of clusters and gel. The presence of the Wigner glass of clusters evidences strong repulsion among the clusters, originating from the strong repulsion of the primary particles.
3.2 Experimental Methods

3.2.1 The colloidal system

We use aqueous dispersions of polystyrene particles as model colloidal systems, which were synthesized in our lab by conventional emulsion polymerization with KPS (potassium per-sulphate) as initiator and SDS (sodium dodecyl sulphate) as surfactant. The mean radius of the particles was $a = 21.5$ nm, determined by dynamic light scattering. The particles were stabilized by both fixed surface charges from polymer chain end (sulphate) groups and the surfactant (25% coverage regarding to the saturated adsorption of SDS on polystyrene surface). The $\xi$-potential of the primary particles after removing the surfactant, measured by Zetasizer Nano (Malvern, UK) instrument at $\phi=1.0\times10^{-4}$, is $-45$ mV. Thus, the primary particles are well stabilized with no tendency of aggregation at rest.
Sketch 3.1. The microchannel system for the shear-driven aggregation experiments, based on the commercial device, Homogenizer HC-5000 (Microfluidics, USA), equipped with a z-shape microchannel (MC) of a rectangular cross section.

3.2.2 The shearing device and procedure

The shear-driven aggregation of the above colloid was carried out using a commercially available device, Homogenizer HC-5000 (Microfluidics), equipped with a z-shape microchannel (MC) with a rectangular cross section of ~0.05 mm$^2$ and length of 5.8 mm, about which details can be found elsewhere$^{14}$. A schematic illustration of the device is given in Sketch 1. The intense shear in the MC is generated by forcing the colloid to pass through the MC under high pressure. A pressure gauge is settled in the front of the MC inlet to measure the instantaneous pressure drop ($\Delta P$) through the MC. The relation between the shear rate $\dot{\gamma}$ in the MC and the pressure drop $\Delta P$, reported by the device supplier, is $\dot{\gamma} [1/s] = 1.02 \times 10^4 \Delta P [\text{bar}]$, where $\Delta P \in [20,150]$ bar. It is worth noting that the residence time of the particles or clusters in the MC is extremely short (e.g., ~27 µs at $\Delta P = 150$ bar, i.e., at $\dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1}$). This means that we are
able to snapshot the aggregation status of a colloidal system in very short time intervals.

Moreover, when one notices that the cross section of the MC is only ~0.05 mm$^2$, while the cross section at its outlet is ~20 mm$^2$ (400 times), we can consider that the shear is immediately removed outside the MC and all the shear-driven events (aggregation, breakage and restructuring) take place only within the MC. Then, due to the strong repulsion, the Brownian motion-driven aggregation and breakage are negligible, and the formed clusters are practically “frozen” outside the MC. Therefore, with the above features, after a dispersion passes through the MC, we can offline characterize it and then send it back to the inlet for further shearing. When we repeat such experiments for many cycles, we are able to monitor the shear-driven phase evolution.

For a typical shearing experiment, the tube connected to the MC outlet introduces the sheared dispersion directly to the chamber at the inlet such that the shearing process is continuous, as indicated in Sketch 3.1. The shearing time is computed by $t = 0.8 \times N_c$, where $N_c$ is the number of pulses and 0.8 is the pumping time of each pulse in second. The shear rate is fixed at $\dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1}$ in this study. We explored the phase transition behavior of the shear-driven aggregation process in the range of the particle volume fraction, $\phi \in [0.02, 0.15]$.

3.3 Results and Discussion

3.3.1 Time evolution of the shear-driven process

It has been well documented$^{14, 93}$ that the shear-driven aggregation leads to clusters of bimodal distributions: the average size of the first class is not far from the primary particles, while that of the second class is orders of magnitude larger than that of the
first. Thus, by centrifugation we can easily isolate the big clusters and quantify the conversion of the primary particles to the big clusters, $x$, which is defined as the total mass of the big clusters divided by the total mass of the initial primary particles. Then, the radius of gyration ($R_g$) and fractal dimension ($d_f$) of the big clusters can be determined by small-angle light scattering measurements$^{42}$. Fig. 3.1 shows the time evolution of $x$, $R_g$ and $d_f$ in the case of $\phi = 3.0\%$. The conversion shows a sharp upturn after an induction time, which is related to the activation energy barrier, $U_{act} = U_m - 6\pi \alpha \mu \dot{\gamma} R_g^3$, of the shear-driven aggregation kinetics, $k_{1,1} \sim \sqrt{(3\pi \alpha \mu \dot{\gamma} R_g^3 - U_m')/k_BT} \times e^{-U_{act}/k_BT}$ ($\alpha$ is a coefficient related to the type of flow, e.g., $\alpha = 1/3\pi$ for simple shear flow$^{67}$, $\mu$ is the viscosity of the system, $U_m$ is the colloidal interaction barrier, and $U_m'' < 0$ is the second derivative of $U_m$)$^{67}$. Since $U_{act}$ is positive, initially, the aggregation is very slow; when a certain cluster size, $R_g = (U_m'/6\pi \alpha \mu \dot{\gamma})^{1/3}$, is reached, $U_{act}$ vanishes and then even becomes negative, and the aggregation becomes much faster and goes with the cube of $R_g$ in the exponent. The $R_g$ evolution exhibits an overshoot; the maximum $R_g$ appears just after the upturning point of $x$, indicating that once the critical cluster size is reached, the extremely fast aggregation rate leads to the clusters growing larger and larger in an extremely short time$^{67}$. The fractal dimension of the clusters increases with time from $d_f = 2.4 \pm 0.05$ to $2.8 \pm 0.05$, suggesting occurrence of the shear-driven restructuring$^{69,107,108}$.

It is evident that the size and fractal dimension of the clusters result from dynamic equilibrium among the shear-driven aggregation, breakage and restructuring$^{109}$. Initially, aggregation is dominant, and big clusters are formed in an extremely short
time associated with the vanishing of the activation energy barrier. Then, as the conversion and number of clusters increase, breakage and restructuring start to play an important role. In fact, from computations of the average cluster mass ($i$) based on the fractal scaling, $i = k(R_g / a)^d$ with $k = 4.46 \times d_f^{-2.08}$, using the measured $R_g$ and $d_f$, we found that, after the $R_g$ maximum, the region where $R_g$ decreases with the shearing time in Figure 3.1 is indeed related to not only compacting (restructuring) but also breakage of the big clusters (i.e., $i$ decreases with time)$^{108}$. Figure 3.2 shows the typical shape and morphology of the big clusters in the later stage. It is seen that the shape of the big clusters is rather irregular, and the scanning electron microscope confirms that the big clusters are very compact. After $x > 0.6$ in Figure 3.1, since the primary particle concentration reduces to $\sim 1/3$ of the initial concentration, the rate of the aggregation, as a second-order process, would reduce one order of magnitude, and it follows that the increase in $x$ with time becomes much slower. Thus, it is difficult to reach 100% conversion at low particle concentrations. This is the reason why we decided to carry out our experiments in the range of $\phi \in [0.02, 0.15]$. Note that also due to the concentration effect, the induction time decreases as $\phi$ increases, and it approaches zero when $\phi > 5.0\%$. Moreover, when $\phi > 15\%$, the system gels directly after passing through the MC just one time.
**Figure 3.1.** Time evolution of the conversion ($x$) of the primary particles to big clusters and the average radius of gyration ($R_g$) of the big clusters, after shearing at $\dot{\gamma} = 1.5 \times 10^6$ s$^{-1}$, in the case of $\phi = 0.03$. Inset: the corresponding time evolution of the fractal dimension ($d_f$) of the big clusters.
Figure 3.2. Typical shape (a) and detailed structure (b) of the big clusters generated by the MC, characterized by an optical microscope and a scanning electron microscope, respectively.

3.3.2 Time evolution of the phases and phase transition

As the packing fraction of the clusters increases with the conversion, at a certain point, the liquid-like state eventually transfers to a solid-like state. To have a glance of the state transition, we show in the insert of Figure 3.3 some pictures taken at different shearing times in the case of $\phi = 5.0\%$. It is evident that the samples in the first three pictures at $t = 0$ s, 20 s and 50 s are liquid-like, while the last two at $t = 80$ s and 180 s are solid-like. However, for the two solid-like samples when we performed dilution experiments with water\textsuperscript{111}, the sample at $t = 80$ s can be completely dispersed after gentle shaking, while the one at $t = 180$ s cannot, keeping its shape for days. This
clearly indicates that in the former the clusters are not interconnected and repel each other, while in the latter they are interconnected. Thus, the former is a Wigner glass of clusters, and the latter is a gel. Further evidence is that the scattering structure factor of the former is typical of fractal clusters, as it is shown in Figure 3.4a, flat in the small $q$ range and has only one bending (Guinier) regime. For the latter, we have to use a glass bar to mash the gel flocks and then further disperse them by mechanical agitation. Obviously, in this way, the gel and cluster structure can be significantly altered, thus not reported here. However, we found that at $t = 150$ s, the gel can still be dispersed in water by substantial stirring (without using a glass bar to mash). This indicates that at $t = 150$ s the percolation has started towards the gel but not yet completed. The obtained scattering structure factor is shown in Figure 3.4b, and it has two bending regimes, characteristic of a gel, one related to the clusters and another to the secondary structure made of cluster interconnection. It is therefore concluded that along the shear-driven aggregation, three states can exist: fluid of clusters, Wigner glass of clusters and gel.
Figure 3.3. Time evolution of the packing fraction of total big clusters ($\phi_c$), after shearing at $\dot{\gamma} = 1.5 \times 10^6$ s$^{-1}$, at various values of the initial particle volume fractions ($\phi$). Insets: pictures of the colloidal system after shearing for different times in the case of $\phi = 0.05$. 


Figure 3.4. Structure factor of the clusters, $S(q)$, (a) after dilution from a glass state at shearing time of 80 s and (b) after dilution from a gel state at shearing time of 150 s. $\dot{\gamma} = 1.5 \times 10^6$ s$^{-1}$; $\phi = 0.05$.

The presence of the Wigner glass state is obviously related to the repulsive nature
of the system, which remains even after forming clusters. The occurrence of the gel state after the glass state is different from the phase transition of repulsive spherical particles, where the glass state is followed by a fully crystallized state. This arises because of two factors: 1) for our system a strong attraction exists at the extremely short screening length, which can be reached under the intense shear, and 2) the clusters are of irregular shape and surface. Thus, once the clusters are connected at the attraction well, it is difficult for them to relax to a crystal state.

With the visual observation and dilution experiment mentioned above, as well as light scattering characterizations, we are able to define the transitions of different phases. Note that the glass transition is typically defined in the literature as the point where the viscosity becomes larger than $10^{13}$ poise, or when the non-ergodic behaviour (by light scattering) persists for an observation timescale longer than $10^2$ s. The former is somewhat empirical, and the latter cannot be realized for our system, because at the given $\phi$ range, the dispersions are too turbid to perform such light scattering experiments. The obtained phase evolution diagram is shown in Figure 3.3, in the form of the packing fraction of the total clusters, $c_\phi$, as a function of the shearing time. The $c_\phi$ values are computed by $c_\phi = x\phi k^{-1} (R_g / a)^{3-d_f}$, and the $x$, $R_g$ and $d_f$ values are determined experimentally. The two broken lines are found experimentally, which divide the plane from small to large $c_\phi$ values into three phases: fluid of clusters, Wigner glass of clusters and gel.

In the case of the initial particle volume fraction, $\phi \leq 3\%$, the system is always liquid-like in the entire shearing time. The $c_\phi$ value exhibits a local maximum and then decreases with the shearing time, because the generation rate of new clusters slows down with time and $d_f$ increases, i.e., the clusters become more and more compact. In
the range of $3\% < \phi < 5\%$, the system evolves with the shearing time from the fluid of clusters to the Wigner glass of clusters in the end. In this $\phi$ range, the final conversion can reach $x = 80\%$ but further increase needs extremely long time. For $\phi > 5\%$, the system covers all the three phases and ends with a gel. As indicated by the two broken lines in Figure 3.3, the glass state occurs in a large range of the cluster packing fraction, $0.48 < \phi_c < 0.72$. This is related to the irregular shape and polydispersity of the clusters. A polydisperse system would lead to a wider range of glass transition compared with a monodisperse system$^9$.

Figure 3.5 shows the effective volume fraction of the primary particles forming the clusters, $\phi_e (= x\phi)$, as a function of $\phi$ along the phase evolution. The two broken lines represent the two transitions between Fluid and Glass and between Glass and Gel, respectively. It should be emphasised that since we are discussing the phase evolution along the shear-driven aggregation, Figure 3.5 should not be considered as a phase diagram at the steady state of the shear-driven process, and each point in the diagram is associated with a set of values for $\phi$, $\dot{\gamma}$, $x$, $R_g$, and $d_f$ at a specific time. It is seen from Figure 3.5 that the $\phi_e$ range for the glass phase increases as $\phi$ increases. This is mainly due to the position of the Glass-Gel transition line, which increases with $\phi$ substantially. This is related to the average size of the clusters at the transition, which was found experimentally decreasing with $\phi$, while the fractal dimension was practically identical ($d_f = 2.65 \pm 0.04$). It is known that if the fractal dimension is the same, the smaller is the cluster size, the higher the particle density within the cluster$^{41}$, and it follows that the $\phi_e$ value at the transition increases as $\phi$ increases. To explain why the cluster size at the Glass-Gel transition decreases with $\phi$, we recall that the percolation to gelation occurs only after the MC, and within the MC, the system has to
be a fluid due to the extremely high shear. Then, as $\phi$ increases, in order for the system to be a fluid, the cluster size within the MC has to decrease. In Figure 3.5, no phase transition data are reported for $\phi > 12\%$, because in this range the shear-driven gelation occurs after the system passes through the MC just one time. Thus, all the phase transitions occur within the residence time of the MC.

![Phase evolution diagram along the conversion of the primary particles to big clusters at different initial particle volume fraction, displayed in the plane of the effective particle volume fraction to the big clusters ($\phi_e = x\phi$) vs the initial particle volume fraction ($\phi$).](image)

**Figure 3.5.** Phase evolution diagram along the conversion of the primary particles to big clusters at different initial particle volume fraction, displayed in the plane of the effective particle volume fraction to the big clusters ($\phi_e = x\phi$) vs the initial particle volume fraction ($\phi$).

3.3.3 **Construction of a steady-state phase diagram for the shear-driven process**

The phase diagram in Figure 3.5 is related to the dynamic evolution of the shear-driven process, out of the aggregation steady state. In fact, the conversion values are all far from $x = 1$. However, there is one point, P, which is the intersection of the glass and gel transition lines, and, not coincidently, P is located on the $x = 1$ line. This
means that the system corresponding to Point P is at the steady state. However, P is
difficult to reach experimentally because of the finite shearing time. On the other hand,
it is true from the experimental data in Figure 3.5 that all the systems with the \( \phi \) values
smaller than that at P, \( \phi_p \), would never reach the Wigner glass or gel phase, while those
with \( \phi > \phi_p \) would sooner or later become a Wigner glass and then a gel phase. Thus,
the existence of Point P is confirmed. Of course, Point P varies with systems and shear
forces, \( i.e. \), with colloidal interactions and Peclet number ( \( Pe = 3 \pi \mu \gamma a^3 / k_B T \)).
However, for a given \( Pe \), a steady-state phase transition diagram may be drawn based
on Point P.

To construct such a phase diagram, we note that \( Pe \) affects both the aggregation
and breakage, resulting in the steady-state cluster size and structure. Thus, the crucial
quantity that governs the steady-state cluster morphology is the difference between the
energy barriers for aggregation (\( U_a \)) and breakage (\( U_b \)), \( \Delta U = U_a - U_b \), as illustrated in
the insert of Figure 3.6. It follows that the phase diagram can be defined in the
\( \Delta U / k_B T \) vs \( \phi \) plane, as shown in Figure 3.6. The Wigner glass line is basically the
trajectory of Point P discussed above, which divides the plane into fluids of clusters and
solid-like gels. Increasing \( \Delta U \) means increasing the aggregation barrier or decreasing
the breakage barrier, thus favouring the breakage, and the steady-state cluster size
decreases. Since at a fixed \( d_c \), the smaller is the cluster, the higher the particle density
within the cluster\(^{41} \), more primary particles are required to reach the Wigner glass state;
it follows that the Wigner glass line moves upward to a larger \( \phi \) value. When \( \Delta U \)
increases to reach a certain critical value, the cluster size reduces to the minimum, \( i.e. \),
the size of a primary particle; this means that within the MC, the breakage event is so
strong that the effective aggregation does not occur. An obvious case that corresponds
to such a situation is when $U_b = 0$ ($\Delta U = U_a$), as indicated in Figure 3.6. Therefore, at the critical point, the line of the Wigner glass of clusters will coincides with the repulsive glass of particles under stagnant conditions at $\phi \approx 0.58$. This applies also to even larger $\Delta U$ values; thus, the line of the repulsive glass of particles in this region is vertical. It should be pointed out that in the region of high $\phi$ values, i.e., on the right hand side of the vertical broken line in Figure 3.6, since the particles are already crowded, the interparticle distance may become smaller than the position of the interaction energy maximum, i.e., the particles become attractive. Thus, in this region, different arrested dynamics may occur without shearing, such as attractive glass, dense packing, crystal, etc.

Of course, changing $Pe$ will change the glass transition line in Figure 3.6. However, since $Pe$ affects the aggregation and breakage in rather different kinetics, it is difficult to rationalize how the position and shape of the glass transition line vary with $Pe$. On the other hand, no matter how the systems are different and the $Pe$ value varies, the principle of the phase diagram presented in Figure 3.6 has its general validity.
**Figure 3.6.** Phase diagram at the steady state of the shear-driven aggregation process, presented in the plane of the difference between the aggregation and breakage energy barriers vs. the initial particle volume fraction (i.e., $\Delta U/k_BT$ vs $\phi$, where $\Delta U = U_a - U_b$), at a fixed $Pe$. Inset: illustration of the definition for the aggregation and breakage energy barriers related to colloidal interactions.

### 3.4 Conclusions

We have investigated in this work the phase evolution along the shear-driven aggregation process of a polystyrene colloid in the range of the particle volume fraction, $\phi \in [0.02, 0.15]$, through a microchannel (MC). Since the MC is very short (5.8 mm), the short residence time allows us to snapshot the phase evolution by repeatedly cycling the aggregating system in the MC many times. An important feature of the system is that due to the strong repulsion between the particles generated by charges from the surface fixed charge groups and the adsorbed surfactants, the formed clusters are strongly repulsive as well, thus stable after shearing.

It is found that as the aggregation extent (thus, the cluster packing fraction)
increases with the shearing time, depending on the initial particle volume fraction, we have progressively observed three phases: fluid of clusters, Wigner glass of clusters and gel. The presence of the Wigner glass state is obviously related to the repulsive nature of the system, which remains even after forming clusters. Along the shear-driven aggregation, the Wigner glass of clusters can occur in a large range of the packing fraction of total clusters (0.48<φ<0.72), mostly due to the irregular shape of the clusters.

We have proposed a phase diagram that describes how the transitions of the three phases evolve at the aggregation steady-state in the colloidal interactions vs particle concentration plane. It tells that, as the difference between the aggregation and breakage energy barriers increases, the particle concentration for the occurrence of the Wigner glass of clusters increases. Therefore, the energy barriers for the aggregation and breakage, together with the particle concentration and the shear rate, determine the final clustered state. This scenario brings a clear understanding of the complicated shear-driven aggregation and solidification process and it is of great importance in applications.
Chapter 4

Nanocomposite Materials Prepared by Shear-Driven Hetero-Aggregation of Stable Colloidal Dispersions of Different Miscible Colloids

4.1 Introduction

Nano-hybrid and nanocomposite materials are widely used in practice due to their enhanced optical, electrical, thermal, magnetic and mechanical properties with respect
to those made of individual components\textsuperscript{76, 83}. The most challenging issue in preparing those materials is how to reach distribution homogeneity of all components at the nano-scale\textsuperscript{112}. To this aim, various strategies have been developed such as melt compounding, in-situ generation of one component within another, and drying-aggregation of multi-component colloidal dispersions\textsuperscript{76, 82, 113}. Moreover, composite micro-size clusters formed by nanoparticle assembly have been emphasized recently for medical diagnostics\textsuperscript{114}, drug delivery\textsuperscript{114, 115}, sensors\textsuperscript{116} and electronic devices\textsuperscript{117}, where the self-assembly of nanoparticles was typically realized by hetero-aggregation of particles with opposite charges or binding molecules.

The so-called hetero-aggregation is an aggregation process among colloidal particles with different chemical composition, particle sizes, charges or surface properties. The hetero-aggregation of oppositely charged colloidal particles has been well documented in the literature\textsuperscript{118-120}. When oppositely charged particles are similar in size, the aggregation undergoes in a rapid, random manner due to the attractive electrostatic interactions, and the formed clusters are typically of irregular shape and low fractal dimension. It is evident that in this way the distribution homogeneity of the two components within the clusters cannot be warranted when the particle concentrations are relatively high due to the extremely fast aggregation rate. When the sizes of the two types of particles are substantially different, the smaller particles are likely to adsorb onto the surface of the larger particles to generate stable “core-shell” hetero-clusters. For two types of particles with charges of the same sign, if their separate dispersions are stable, their mixture is typically stable as well. The conventional ways to realize the hetero-aggregation of such systems include adding electrolytes to screen the electrical double layer, introducing bonding molecules or high
molecular weight polymers for depletion aggregation, and changing pH to neutralize pH-sensitive charges\(^{87, 113, 118, 121}\).

Alternatively, without adding any kind of destabilizer, intensive shear can also provide particles, which are well stable at rest, enough kinetic energy to realize aggregation, about which numerous theoretical and experimental studies can be found in the case of homo-aggregation (\textit{i.e.}, single component aggregation)\(^{14, 67, 70, 71, 92-94, 122}\). In the case of purely shear-driven hetero-aggregation, however, no any study can be found in the open literature. There are only a few theoretical investigations for partially or fully destabilized hetero-aggregation systems, focusing on understanding how the shear force affects the doublet formation rate between two particles of unequal sizes or of different materials\(^{123, 124}\). It was found that more stable particles would enhance the tendency towards homo-aggregation of less stable particles, and the aggregation selectivity is determined mainly by the difference in their homo-aggregation rates\(^{123}\). Thus, applications of such hetero-aggregation under shear would lead to full or partial phase separation, instead of homogeneous composite materials. There are also a few experimental studies on hetero-aggregation in the presence of both electrostatic attraction and shear\(^{119, 125}\), where fractal clusters are generated. It was shown that the fractal dimension of such hetero-clusters is strongly affected by the shearing force. However, details of the cluster morphology were not investigated, and it is unclear how the two types of particles of different origins are distributed within the clusters.

In this chapter, we developed a methodology to perform hetero-aggregation purely based on intense shear-driven aggregation without adding any destabilizer (electrolyte, pH, bonding molecules, or depletion polymer). The key feature of this method is that different components with charges of the same sign are first mixed to form a homogeneous stable dispersion, and then the extremely fast aggregation driven by an
intense shear freezes the homogeneity of the mixed colloids. To demonstrate the feasibility of the proposed methodology, we investigate a model binary system that is composed of a shear-active and a shear-inactive colloid. The shear-active colloid can undergo the shear-driven homo-aggregation, while the shear-inactive one at the same shear cannot. Then, after their mixing to form a stable homogeneous dispersion, the shear-driven hetero-aggregation is carried out through a microchannel device. The formed composite clusters are carefully characterized, and the mechanism of the hetero-aggregation is proposed based on the observed phenomena.

4.2 Experimental Methods

4.2.1 The colloidal systems

The polystyrene (PS) and poly-methyl methacrylate (PMMA) dispersions were synthesized in our lab by conventional emulsion polymerization with KPS (potassium persulfate) as initiator and SDS (sodium dodecyl sulfate) as surfactant. The PS particles contain 5% DVB (divinylbenzene) as cross linker. For synthesis of the PMMA particles, we added 1% RhB (rhodamine-B) into the MMA monomer. Thus, the formed PMMA latex has a pink color. RhB was used as the fluorescent label for PMMA particles with excitation and emission wavelength of 540 nm and 595 nm, respectively. The mean diameter is 43 nm for the PS particles and 280 nm for the PMMA particles, determined by dynamic light scattering. The zeta potential measured by Zetasizer Nano (Malvern, UK) instrument at the particle volume fraction, \( \phi = 1.0 \times 10^{-4} \), was \(-40 \) mV for the PS particles and \(-65 \) mV for the PMMA particles. The original latexes were diluted to the desired particle volume fraction and composition using deionized water for the shear-driven hetero-aggregation, without other treatment.
4.2.2 The microchannel device for the hetero-aggregation

Commercially available device, Homogenizer HC-5000 (Microfluidics), with a z-shape microchannel was applied in this work. The intense shear was generated by forcing the colloidal system to pass through the MC under high pressure. In this work, we fixed the pressure at the MC inlet, $P = 150$ bar, which corresponds to the shear rate, $\dot{\gamma} = 1.5 \times 10^6$ s$^{-1}$. In a typical experiment, a stable binary (PS/PMMA) latex passes through the MC one time, and then we characterize the morphology and composition of the formed big clusters, as well as the conversion of the primary particles to the big clusters.

4.2.3 Determining the conversion and the cluster composition

As it was discussed previously, a colloidal system, after shear-driven aggregation through the MC, is composed of two distinct classes of clusters: Class 1, constituted mainly of primary particles and some very small clusters, and Class 2, constituted of big clusters with an average size at least two orders of magnitude larger than that of Class 1. We found that the same behavior occurred also in this shear-driven hetero-aggregation process. To characterize the dispersion after passing through the MC, we diluted a specific amount of the dispersion in a given amount of deionized water and then filtered it by a 5 µm opening filter. The solid part was weighted after drying in an oven at 60 °C for 8 hours. To quantify the ratio of PMMA in the formed PS/PMMA hetero-clusters, we dissolved 1.0 g of the dried sample in 5 mL dioxane and measured the RhB concentration, which is bonded to the PMMA chains, by UV-visible spectrophotometer (300 Scan CARY). Before the measurement, the solution was centrifuged to eliminate the cross-linked PS. The absorption at 595 nm was used to quantify the RhB. The baseline of the absorption curve was corrected by Rayleigh
scattering simulation to eliminate the effect of the dissolved PMMA of high molecular weights. The calibration curve was determined using the powder of pure PMMA-RhB particles. The conversion of the PS primary particles to the big clusters was calculated from the total weight of the clusters and the ratio of the PMMA in the clusters.

### 4.2.4 Characterization of the size and morphology of the big clusters

The radius of gyration ($R_g$) and fractal dimension ($d_f$) of the big clusters were determined by a small-angle light scattering (SALS) instrument, Mastersizer 2000 (Malvern, U.K.). In this case, the sample was diluted with deionized water without filtration. The details of the measurements and characteristics of the SALS instrument could be found elsewhere. In addition, to observe how the two components are distributed in the big clusters, SEM pictures were taken after drying one drop of the diluted dispersion ($\phi \sim 10^{-5}$) on a silicon chip by the microscope, Gemini 1530 (Zeiss, FEG SEM), where the two types of particles can be well identified due to the distinct difference in their sizes.

### 4.3 Results and Discussion

It is well known that PMMA particles in water are more hydrophilic than PS particles, because the surface ester groups from the MMA monomers may lead to a favored tendency of forming ordered water layers, which are the main source of the short-range, repulsive hydration forces\textsuperscript{128}. Such hydration forces, in combination with the DLVO interactions, can provide a high energy barrier for the particles against the shear-driven aggregation\textsuperscript{14}. In fact, for the synthesized PMMA latex after passing through the MC at the given shear rate, $\dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1}$, no any aggregation took place.
at any particle volume fractions (including that of the original latex, $\phi_{\text{PMMA}} = 0.238$), even passing through the MC many times (more than 20 passes tested). Thus, the PMMA particles are referred to as “shear-inactive” particles. Instead, for the synthesized PS latex at the same shear rate, the shear-driven aggregation did occur, i.e., the PS particles are “shear-active”. In particular, for the experiments with the PS particle volume fraction, $0.06 < \phi_{\text{PS}} < 0.15$, big clusters are formed just after passing through the MC one time and the amount of the clusters increases as $\phi_{\text{PS}}$ increases. For $\phi_{\text{PS}} \geq 0.15$, a solid-like gel is formed at the outlet of the MC after one pass due to percolation of the big clusters when their packing fraction reaches a critical value. Now, let us mix the shear-active (PS) and shear-inactive (PMMA) particles to form a stable binary colloidal dispersion to see how the presence of the PMMA particles affects the shear-driven aggregation of the PS particles and the fate of the PMMA particles themselves.

4.3.1 Effect of PMMA particles on the conversion of PS particles to big clusters

Figure 4.1a shows the conversion of the PS particles ($x_{\text{PS}}$) to big clusters as a function of the PMMA particle volume fraction, $\phi_{\text{PMMA}}$ present in the dispersion, when the PS particle volume fraction, $\phi_{\text{PS}}$, is fixed at 0.08, 0.10 and 0.12, respectively. The results demonstrate that $x_{\text{PS}}$ increases as $\phi_{\text{PMMA}}$ increases in all the cases. However, the role of the PMMA particles in increasing $x_{\text{PS}}$ is less significant than that of the PS particles. For example, at $\phi_{\text{PS}} = 0.08$, by adding $\phi_{\text{PMMA}} = 0.02$, the $x_{\text{PS}}$ value increases only from 0.10 to 0.15, while changing the $\phi_{\text{PS}}$ value also by 0.02 from $\phi_{\text{PS}} = 0.08$ to 0.10 in Figure 1a leads to an increase in $x_{\text{PS}}$ from 0.10 to 0.30. The substantial increase
in $x_{ps}$ with $\phi_{ps}$ is obviously due to the second-order kinetics, which is very sensitive to the variations in the PS particle concentration. Then, the less significant role played by the PMMA particles on the PS particle conversion certainly indicates that their presence in the clusters is not due to the second-order kinetics. This means that the PMMA particles do not participate in the shear-driven aggregation process.

**Figure 4.1.** The conversion of (a) the PS particles and (b) the PMMA particles to big clusters,
$x_\text{PS}$ and $x_\text{PMMA}$, as a function of the volume fraction of the PMMA particles in the PS/PMMA binary dispersion, $\phi_\text{PMMA}$, after passing through the MC one time, at various initial PS particle volume fractions, $\phi_\text{PS}$. $\dot{\gamma} = 1.5 \times 10^6 \text{ s}^{-1}$.

On the other hand, the presence of the PMMA particles in the PS particle dispersion can reduce the free volume, leading to increase in the effective volume fraction of the PS particles, which can be expressed as $\phi_{\text{PS},e} = \phi_\text{PS} / (1 - \phi_\text{PMMA})$. Let us now re-plot the $x_\text{PS}$ values in Figure 4.1a as a function of $\phi_{\text{PS},e}$, as given in Figure 4.2. It is seen that all the $x_\text{PS}$ values collapse to a single curve, independent of $\phi_\text{PMMA}$, and they also collapse with the $x_\text{PS}$ values coming from the shear-driven aggregation of pure PS particles. It is therefore concluded that the increase in the PS particle conversion by the presence of the PMMA particles is only a volume effect, i.e., the PMMA particles behave as inert fillers that increase the effective volume fraction of the PS particles during the shear-driven aggregation.

![Graph showing the relationship between $x_\text{PS}$ and $\phi_{\text{PS},e}$](image)

Figure 4.2. The $x_\text{PS}$ values in Figure 4.1a re-plotted here as a function of the effective PS
particles volume fraction ($\phi_{PS,e}$), which is estimated by excluding the space occupied by the PMMA particles.

4.3.2 The fate of the PMMA particles

Although the PMMA particles behave as inert fillers and do not participate in the shear-activated aggregation process, we have indeed detected their presence inside the big clusters. Figure 4.1b shows the conversion of the PMMA particles to the big clusters (i.e., within the big clusters of the PS particles), $x_{PMMA}$, as a function of $\phi_{PMMA}$ in the dispersion. In contrast to $x_{PS}$, $x_{PMMA}$ does not increase with $\phi_{PMMA}$, again confirming that their presence inside the big clusters does not result from the second-order aggregation kinetics. At $\phi_{PS} = 0.08$, $x_{PMMA}$ is basically independent of $\phi_{PMMA}$, with a constant value around 0.03. At $\phi_{PS} = 0.10$ and 0.12, $x_{PMMA}$ even decreases as $\phi_{PMMA}$ increases. To explain why the PMMA particles are present inside the big clusters, we note that at the given shear rate the residence time of the particles within the MC is only about 27 $\mu$s. Then, when the shear-driven aggregation of the PS particles takes place within such a short time interval, since the PMMA particles, though shear-inactive, are distributed among the PS particles, they have no time to escape from the PS aggregation process and are captured during the formation of the big clusters.

In order to get more insight into the proposed capture mechanism, we have calculated the (mass) fraction of the PMMA particles in the cluster phase, $f_{PMMA,c}$, which is defined as the mass of the captured PMMA particles divided by the total mass of the PS and PMMA particles in the cluster phase. Figure 4.3 shows the $f_{PMMA,c}$ values
as a function of the corresponding mass fraction of the PMMA particles with respect to the total mass of the PS and PMMA particles in the initial dispersion, \( f_{\text{PMMA}_i} \). The solid line represents \( f_{\text{PMMA}_c} = f_{\text{PMMA}_i} \), i.e., the fraction of the PMMA particles in the cluster phase is equal to that in the initial dispersion. In this circumstance, the PMMA particles, which are present in the area where a big cluster is formed, are captured 100% by the cluster. In reality, most of the experimental data are located below the \( f_{\text{PMMA}_c} = f_{\text{PMMA}_i} \) line. This indicates that during the shear-driven formation of the big clusters, part of the PMMA particles are able to escape from the aggregation region, avoiding 100% capturing. When the initial mass fraction of the PMMA particles is extremely small (\( f_{\text{PMMA}_i} < 0.05 \) in Figure 4.3), we do have the experimental data located on the \( f_{\text{PMMA}_c} = f_{\text{PMMA}_i} \) line, i.e., the PMMA particles located in the aggregation region are basically captured 100%. Then, the experimental data depart more and more from the \( f_{\text{PMMA}_c} = f_{\text{PMMA}_i} \) line as \( f_{\text{PMMA}_i} \) increases, indicating that the amount of the PMMA particles escaped from the aggregation increases as \( f_{\text{PMMA}_i} \) increases. On the other hand, it is evident that the amount of the PMMA particles captured by the clusters also increases with \( f_{\text{PMMA}_i} \), as clearly demonstrated by the pictures in the insert of Figure 4.3, where the pink color of the cluster phase increases with \( f_{\text{PMMA}_i} \).
Figure 4.3. The mass fraction of the PMMA particles (with respect to the total mass of the PS and PMMA particles) in the cluster phase ($f_{PMMA,c}$), obtained after the shear-driven hetero-aggregation of the PS/PMMA binary dispersion, as a function of the mass fraction of the PMMA particles (with respect to the total mass of the PS and PMMA particles) in the initial dispersion ($f_{PMMA,i}$). Inset: Pictures of the dried cluster phase obtained at $\phi_{PS} = 0.08$, (a) $f_{PMMA,i} = 0.059$, (b) $f_{PMMA,i} = 0.20$, (c) $f_{PMMA,i} = 0.38$, (d) $f_{PMMA,i} = 0.50$, and (e) $f_{PMMA,i} = 0.58$.

Similar to the other colloidal systems, our PS system also shows a shear-driven transition from a liquid-like cluster dispersion to a solid-like gel after passing through the MC one time when the PS particle volume fraction reaches a critical value, $\phi_{PS,cr}$. This critical value in our case of pure PS particles is $\phi_{PS,cr} = 0.15$. For the binary system, we did not find significant influence of the presence of the PMMA particles on the $\phi_{PS,cr}$ value, at least in the tested range of $\phi_{PMMA} < 0.05$. Most importantly, as one expected, for the binary system, once a solid-like gel is formed after passing through the MC one time, all the PMMA particles are entrapped inside the gel, leading to 100% capture efficiency.
In Figure 4.4 are compared the SEM pictures of the clusters formed by pure PS particle dispersion and by the PS and PMMA binary dispersion. In the latter case, it is seen that the (larger) PMMA particles can indeed be found inside the PS clusters, which are homogeneously and randomly distributed among the PS particles. This confirms the validity of the proposed methodology for preparing composite materials with distribution homogeneity of the components at the nano-scale.

Figure 4.4. The SEM pictures of the big clusters formed after the shear-driven aggregation of (a) the pure PS dispersion at $\phi_{PS} = 0.08$ and of (b) the PS/PMMA binary dispersion at $\phi_{PS} = 0.08$
and $\phi_{\text{PMMA}} = 0.08$.

### 4.3.3 Morphology of the hetero-clusters

Since the size and material of the PS and PMMA particles are different, we have explored if the entrapped PMMA particles inside the PS clusters would affect the morphology of the clusters. To this aim, we have characterized, using the SALS instrument, the big clusters formed from the binary colloidal system after passing through the MC one time, at a fixed value of $\phi_{\text{PS}} = 0.08$ but varying the $\phi_{\text{PMMA}}$ value. Figure 4.5 shows the average radius of gyration, $R_g$, as a function of $\phi_{\text{PMMA}}$. It is seen that the $R_g$ value does not change significantly with the presence of the PMMA particles. This arises mostly because the diameter of the PMMA particles (280 nm) is much larger than that of the PS particles (43 nm). In this case, at the same particle volume fraction, the number concentration of the PS particles is about 300 times larger than that of the PMMA particles. Thus, the interconnection among the PS particles is dominant within the cluster, controlling the mechanical strength of the formed cluster against breakage in the MC.
Figure 4.5. The radius of gyration ($R_g$) of the big clusters obtained after the shear-driven hetero-aggregation of the PS/PMMA binary dispersion, as a function of the PMMA particle volume fraction in the initial dispersion, $\phi_{\text{PMMA}}$, at a fixed PS particle volume fraction, $\phi_{\text{PS}} = 0.08$.

Figure 4.6 shows the scattering structure factor, $S(q)$, of the hetero-clusters that contain different amounts of the PMMA particles formed in the MC, as a function of the normalized wavevector, $q \times R_g$, with $q$ the wavevector ($=4\pi n_0 \sin(\theta/2)/\lambda_0$), where $n_0$ is the refractive index of the medium, $\theta$ the detector angle, and $\lambda_0$ the laser wavelength). We reported in our previous study that the $d_f$ value of the clusters formed by pure PS particles after passing through the MC one time is $2.40 \pm 0.04$, independent of the primary particle size and concentration\textsuperscript{93}. The same $d_f$ value has been obtained also in this work in the case of pure PS particles, as shown in Figure 4.6. In the cases of the PS/PMMA hetero-clusters, however, the slope of the power law regime of the $S(q)$ curve in Figure 4.6 is significantly more steep, equal to $-2.60 \pm 0.05$, \textsuperscript{93}.
independent of the amount of the PMMA particles present inside the clusters. If this slope could represent the fractal dimension of the hetero-clusters, the hetero-clusters might be more compact than the homo-clusters. Unfortunately, a proper scattering theory that can describe the structure factor of such hetero-clusters cannot be found in the literature, we are unable to conclude the fractal characteristics of the hetero-clusters from the light scattering results.

Figure 4.6. The scattering structure factors, $S(q)$, of the big clusters formed after the shear-driven aggregation of the pure PS dispersion at $\phi_{PS} = 0.08$ and of the PS/PMMA binary dispersions at $\phi_{PS} = 0.08$ and various $\phi_{PMMA}$ values, as a function of the normalized wavevector, $q \times R_g$. 
4.4 Conclusions

We have proposed a methodology for preparing composite materials with distribution homogeneity of different components at nano-scale. It is based on intense shear-driven hetero-aggregation of a stable mixture of different colloidal dispersions, without using any additives. To demonstrate the feasibility of the proposed methodology, we have prepared a stable binary colloidal dispersion, which is composed of 43 nm PS particles and 280 nm PMMA particles. Both types of the particles are stable at rest, but the PS particles alone undergo the shear-driven aggregation (shear-active) in a microchannel (MC) in a time interval of ~27 μs at a shear rate of $1.5 \times 10^6$ s$^{-1}$, while the PMMA particles at the same shear rate do not (shear-inactive). Since both PS and PMMA particles are negatively charged, the mixture of their dispersions is stable as well. Then, the shear-driven aggregation of the binary colloidal dispersion at different PS/PMMA compositions has been carried out in the same MC at the same shear rate.

It is found that the shear-driven aggregation of the binary colloidal system does occur, and the formed clusters are composed of not only the “shear-active” PS particles but also the “shear-inactive” PMMA particles. The SEM picture demonstrates that the PMMA particles are homogeneously and randomly distributed among the PS particles in the clusters, confirming the feasibility of the proposed methodology.

On the other hand, the experimental results have proven that the presence of the PMMA particles does not change significantly the aggregation kinetics of the PS particles or the average size of the clusters, and they behave as inert fillers. These results allow us to propose the following mechanism for the inclusion of the PMMA particles in the clusters: When the shear-driven aggregation of the “shear-active” PS
particles takes place within such a short time (~27 μs) interval, since the PMMA particles, though “shear-inactive,” are distributed among the PS particles, they have no time to escape from the PS aggregation process and are captured during the formation of the clusters. At low PMMA volume fractions, the capture efficiency can reach 100%, and it is significantly lower at high PMMA volume fractions. However, when the shear-driven aggregation of the binary colloidal system leads to a solid-like gel, the capture efficiency of the PMMA particles reach naturally 100%.
Chapter 5

An Experimental and Modelling Study on the Effect of Dispersed Polymeric Nanoparticles on the Bulk Polymerization of MMA

5.1 Introduction

It is well known that imbedding nanoparticles into polymer matrices to form polymer matrix nanocomposites (PMNCs) can improve thermal, mechanical, electric or optical properties of the polymers\(^{14}\). Due to the large specific surface area of NPs, the
interactions between polymer chains and solid surfaces in the PMNCs may amplify many molecular processes, resulting in “non-classical” responses to thermal, mechanical, electric or optical excitations\textsuperscript{76, 83}. Various methods have been developed for preparing the PMNCs, such as melt compounding, film casting, in-situ polymerization, and so forth\textsuperscript{76, 83}. The procedure of in-situ polymerization involves dispersing the NPs directly in the monomer or monomer solution and subsequent polymerization of the monomer dispersion with standard polymerization techniques. In this case, the surface of the NPs is usually modified to achieve good dispersity of the NPs in monomers, as well as along the polymerization process\textsuperscript{76}.

Recently, many efforts have been made to investigate the role played by NPs during the preparation of the PMNCs through in-situ polymerization\textsuperscript{76}. It has been proven that inorganic particles can interfere the free radical polymerization process, leading to changes in molecular weight, molecular weight distribution and glass transition temperature of the polymer matrices. The presence of nanofillers can either accelerate or retard the free radical polymerization kinetics\textsuperscript{76, 129, 130}. For example, during the bulk polymerization of methyl methacrylate (MMA) in the presence of ZnO NPs, the hydroxyl groups on the ZnO surface may induce a degenerative transfer suppressing the gel effect\textsuperscript{129}. Dimitris et al. investigated the effect of organo-modified montmorillonite NPs on the kinetics of free radical in-situ bulk polymerization of MMA\textsuperscript{78}, and found that the NPs strongly affect the diffusion-controlled processes during the polymerization. Such effect was attributed to the bulk ammonium salt, which was used as the organic modifier. In the work of Siddiqui et al\textsuperscript{79}, it was observed that the existence of rigid phenyl rings in the organo-modifier may result in a hindered monomer movement, especially at high conversions. Thus, most of the results indicate that the role played by the NPs in affecting the in-situ polymerization is related to the
functional groups on the NP surface, due to the high specific surface area of the NPs. However, in all the above studies, due to the difficulties in quantifying the properties of the NPs (shape, size distribution, agglomeration, etc.), the roles played by the NPs themselves and the surface functional groups are difficult to separate.

We believe that to properly understand the role played by the NPs during the preparation of the PMNCs through in-situ polymerization, we should separate the surface effect due to the functional groups from the volume effect of the NPs, as well as additional factors such as existence of small amount of water and/or oxygen in the solution, long chain polymers used as stabilizer, etc. Meanwhile, it is evident that the NPs should be well dispersed, avoiding their agglomeration along the entire in-situ polymerization process. It is very challenging to achieve all these requirements for inorganic NPs/monomer systems due to the complexity of the inorganic NP surface, morphology and agglomeration. On the contrary, the size and functional groups of polymeric NPs can be easily controlled and quantified during their formation through emulsion polymerization. Therefore, polymeric NPs/monomer systems are ideal (model) systems for detailed investigation of the role played by the NPs in in-situ bulk polymerization.

In this chapter, we set up a standard methodology, based on DSC experiments and modelling of bulk polymerization kinetics, to study the role played by polymeric NPs during the MMA bulk polymerization. Two types of polymeric NPs, PS and PTFE, are used in this work, which represent the nanoscale dispersed phase first in MMA and then in PMMA after polymerization. Since both the NPs are not well compatible with MMA, their surface has been modified by cross-linked PMMA. To quantify the net effect of the NPs on the bulk polymerization, we first quantify the effect of the cross-linked PMMA without the NPs, and then subtract the effect of the cross-linked PMMA to get
that of the NPs.

## 5.2 Experimental Methods

### 5.2.1 Materials

MMA monomer with 100 ppm inhibitor, hydroquinone, was washed with a 5% NaOH solution 3 times, followed by deionized water washing two times, dried over sodium sulphate anhydrous and stored at 5 °C before use. Di(trimethylolpropane)tetraacrylate (DTTA), Azobisisobutyronitrile (AIBN), divinylbenzene (DVB) and styrene were purchased from Aldrich and used without removing inhibitors. Potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were purchased from Fluka. Deionized water was used in all processes.

### 5.2.2 Preparation of the NPs

Four types of NPs have been used in this work, which are DVB cross-linked PS, PTFE, DTTA cross-linked poly-methylmethacrylate (cPMMA) and non-cross-linked PMMA. Except for PTFE, which was provided by industry partner, all the others were synthesized in our lab by conventional emulsion polymerization using KPS as initiator and SDS as surfactant. In the cases of PS and PTFE, the surface of the NPs was modified by grafting cPMMA in order to improve their dispersity in the MMA monomer. Details of all the NPs used in this work and their surface modification are summarized in Table 5.1
Table 5.1 Properties of the NPs used in the MMA bulk polymerization.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>NP type</th>
<th>Radius (nm)</th>
<th>Surface Modification</th>
<th>$\varphi_{\text{NP}} / \varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS</td>
<td>31.5</td>
<td>cPMMA, $\varphi_{\text{DTTA}}=2.5%$</td>
<td>34.5%</td>
</tr>
<tr>
<td>2</td>
<td>PTFE</td>
<td>40.0</td>
<td>cPMMA, $\varphi_{\text{DTTA}}=2.5%$</td>
<td>56.2%</td>
</tr>
<tr>
<td>3</td>
<td>cPMMA, $\varphi_{\text{DTTA}}=2.5%$</td>
<td>25.0</td>
<td>_</td>
<td>0.0%</td>
</tr>
<tr>
<td>4</td>
<td>cPMMA, $\varphi_{\text{DTTA}}=7.5%$</td>
<td>25.0</td>
<td>_</td>
<td>0.0%</td>
</tr>
<tr>
<td>5</td>
<td>Linear PMMA</td>
<td>15.0</td>
<td>_</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

For these NPs to be used in the bulk polymerization of MMA, we have to separate them from the disperse medium. We first cleaned up the surfactant and any other electrolytes by mixing the latex with a mixture of cationic and anionic ion-exchange resins (Dowex MR-3, Sigma-Aldrich), based on a procedure described elsewhere. Then, the latex was frozen at $-18$ °C for 24 hours to freeze-coagulate the NPs, and unfrozen afterwards at room temperature to form the clusters of the NPs. The solid part was obtained by filtration and dried under vacuum, and finally we obtained the dried NPs in the form of white powder.

5.2.3 Characterization methods

The NP sizes were characterized by both the static and dynamic light scattering (DLS and SLS) techniques using a BI-200SM Goniometer System (Brookhaven,
U.S.A.), equipped with a solid-state laser, Ventus LP532 (Laser Quantum, U.K.) of wavelength = 532 nm. The solid content of the latex was measured by thermogravimetry using HG53 Halogen Moisture Analyzer (Mettler Toledo, Switzerland).

To take CryoSEM images, we freeze the sample in liquid nitrogen vacuum at −140 °C, followed by 5 min freeze drying at −100 °C. Then, the sample was cracked and the cracked surface was coated with 3 nm Tungsten at varying angles between 45° and 90° at −120 °C. Samples were transferred under vacuum and the coated part was imaged with InLens detector at 2 kV and −120 °C. Samples for TEM images were prepared by dropping dilute latex on a Formvar/carbon-coated copper grid and dried for 12 hours. The images were taken using FEI Morgagni 268 transmission electron microscope.

The residual MMA monomer content in the polymer after bulk polymerization was determined by gas chromatography (GC). The polymer sample from the DSC crucible was dissolved completely in 0.5 mL dichloromethane. Then, 10 mL methanol was added, and the mixture was kept for 10 hours before filtered with a paper filter to eliminate the polymer. The liquid was injected into the GC to quantify the monomer residue.

5.2.4 DSC measurements

MMA bulk polymerization in the presence of different NPs was investigated using Polymer DSC (Mettler Toledo)\textsuperscript{131}. All the samples were prepared in a glove box with nitrogen atmosphere. The mass of the sample was varied in the range of 4 to 80 mg, and the weight fraction of the NPs was in the range of 0 to 15%. The samples were sealed in a 40 µL or 160 µL aluminium crucible. The crucible was placed into the appropriate
position of the instrument, and an identical empty crucible was placed as heat reference. The temperature was maintained constant at 70 ± 0.05 °C during the bulk polymerization. The reaction exothermal was recorded as a function of time in the unit, mW. The effective conversion-time (x-t) curve was calculated from the integrated area at time \( t \) divided by the total integration area according to Eq. (5.1)

\[
x(t) = \frac{\int_{t_0}^{t} HF(t)dt}{\int_{t_0}^{t \text{end}} HF(t)dt} \times x_{\text{end}}
\]  

(5.1)

where \( x(t) \) and \( HF(t) \) are the conversion and the heat flow at time \( t \), respectively; \( t_0 \) is the starting time; \( t_{\text{end}} \) is the end time of the polymerization; \( x_{\text{end}} \) is the monomer conversion at the end of the polymerization, which is calculated from the final monomer residue.

For all our DSC experiments, 4 to 6 parallel measurements were conducted for each polymerization conditions, in order to avoid small differences in sample preparation. Figure 5.1 shows typical experimental \( HF-t \) curves from four measurements of the same sample (MMA with 5% cPMMANPs) at different masses of the polymerization system. It is seen that the position of the gel effect peak for the four experiments is practically identical, confirming the reliability of our DSC experiments.
The isothermal polymerization is confirmed by the negligible temperature shift in the DSC crucible (70 ± 0.05 °C) during the entire course of polymerization. Further confirmation of the isothermal condition arises from Figure 5.1, where, though different MMA loadings were used, which signify different heat transfer distances, the identical gel effect peak position indicates that heat transfer resistance in the small crucible is negligible.

5.3 Modelling of MMA Bulk Polymerization

The kinetic model for the MMA bulk polymerization has been well studied in the literature, and can be generally described as:
Initiation:

\[ I \xrightarrow{k_I} 2R \cdot \]
\[ R \cdot + M \xrightarrow{k_2} R_1 \cdot \]

Propagation:

\[ R_n \cdot + M \xrightarrow{k_p} R_{n+1} \cdot \]

Termination:

\[ R_n \cdot + R_m \xrightarrow{k_{tc}} P_{n+m} \]
\[ R_n \cdot + R_m \xrightarrow{k_{td}} P_n + P_m \]

where \( I \) is the concentration of initiator; \( R_n \cdot \) is the concentration of a free radical containing \( n \) monomer repeat units; \( P_n \) is the dead polymer chain containing \( n \) monomer repeat units; \( k_d, k_p, k_{tc} \) and \( k_{td} \) denote the respective rate constants of the initiator decomposition, propagation, termination by combination and termination by disproportionation.

Long chain hypothesis is typically assumed in deriving the differential equations of the system, and quasi-steady-state assumption is applied for the free radical of primary initiator. Detailed derivation of the differential equations can be found in the literature\(^{131-133}\), and we use the following equations to compute the \( x-t \) evolution.

\[
\frac{dl}{dt} = -k_d I - \frac{\varepsilon I}{1 + \varepsilon x} \lambda_0 (1-x) k_p \quad (5.2)
\]

\[
\frac{dl}{dt} = -k_d I - \frac{\varepsilon I}{1 + \varepsilon x} \lambda_0 (1-x) k_p \quad (5.3)
\]

\[
\frac{dx}{dt} = k_p \lambda_0 (1-x) \quad (5.4)
\]
\[
\frac{d\lambda_0}{dt} = -\frac{\varepsilon \lambda_0^2}{1 + \varepsilon x} (1 - x)k_p + 2f k_d I - k_t \lambda_0^2 \tag{5.5}
\]

where \( x \) is the fractional monomer conversion, defined as \( x = \frac{M_0 V_0 - MV}{M_0 V_0} \), where \( M \) and \( V \) are the monomer concentration (mol L\(^{-1}\)), and the sample volume (L), respectively, and \( M_0 \) and \( V_0 \) are their initial values; \( \lambda_0 \) is the zero moment of the growing radicals; \( \varepsilon \) is the volume expansion factor determined by

\[
\varepsilon = \frac{d_{\text{MMA}} - d_{\text{PMMA}}}{d_{\text{PMMA}}} \]

where \( d_{\text{MMA}} \) and \( d_{\text{PMMA}} \) are densities of the monomer and polymer, and \( f \) is the efficiency factor for primary initiator radical (\( R \cdot \)) consumption.

The gel effect and glass effect, which affect \( k_p \) and \( k_t \), are incorporated into the mathematical description. The constitutive equations used in this model are:

\[
\frac{1}{k_p} = \frac{1}{k_p^0} + \Theta_p \exp(\lambda_0 - \frac{2.3 \Phi_m}{A + 0.03 \Phi_m}) \]
\[
\frac{1}{k_t} = \frac{1}{k_t^0} + \Theta_t \exp(\lambda_0 - \frac{2.3 \Phi_m}{A + 0.03 \Phi_m}) \tag{5.6}
\]

where \( \Theta_p \), with unit of time, can be viewed as a characteristic migration time of the growing radicals; \( \Theta_t \) is the characteristic time of the monomer diffusion; \( \Phi_m \) is related to the monomer conversion by

\[
\Phi_m = \frac{1 - x}{1 + \varepsilon x} \tag{5.7}
\]

The values of the parameters used in this work are taken from the literature\textsuperscript{131,134,135}, as shown below:
$f = 0.58; \quad A = 0.152$

$k_d = 6.32 \times 10^6 \exp(-1.54 \times 10^4 / T) \quad \text{(min}^{-1})$

$k_p^0 = 2.95 \times 10^7 \exp(-2.19 \times 10^3 / T) \quad \text{(L mol}^{-1} \text{ min}^{-1})$

$k_p^1 = 5.88 \times 10^9 \exp(-3.53 \times 10^2 / T) \quad \text{(L mol}^{-1} \text{ min}^{-1})$

$\Theta_p = 5.48 \times 10^{-16} \exp(-1.40 \times 10^4 / T)$

$\Theta_i = 1.135 \times 10^{-22} \exp(-1.74 \times 10^4 / T) / I_0$

The $x$-$t$ and $HF$-$t$ plots are the two main outputs from the model simulation. The $HF$-$t$ plot is calculated from $x$ using Eq. (5.9):

$$HF = \Delta H_p r_p V \times \frac{1000}{60} \quad \text{(mW)} \quad (5.9)$$

where $r_p = dM / dt \quad \text{mol L}^{-1} \text{min}^{-1}$, $M = (1-x)M_o / (1+\varepsilon x) \quad \text{mol L}^{-1}$ and $\Delta H_p$ is the standard heat of polymerization of methacrylate double bounds ($\Delta H_p = -54900 \ J \text{mol}^{-1}$)\textsuperscript{136}.

The initial total volume for determining the concentrations of initiator, polymer and NPs was calculated as follows, accounting for differences in density and mass fraction of the species:

$$V_i = \frac{m\varphi_{NP}}{d_{NP}} + \frac{m(\varphi - \varphi_{NP})}{d_{PMMA}} + \frac{m(1-\varphi)}{d_{MMA}} \quad (L) \quad (5.10)$$

where $m$ is the mass of the solution sealed in the crucible, $\varphi_{NP}$ is the mass fraction of the NPs, and $\varphi$ is the mass fraction of the NPs plus the PMMA mass for the surface modification. It should be noted that since the NPs are in solid state, inaccessible for the monomers and initiator, to correctly calculate the concentration of each component in the system, we need to exclude the volume occupied by the solid NPs and to use the following effective volume as the initial volume:
\[ V_0 = \frac{m(\varphi - \varphi_{NP})}{d_{\text{PMMA}}} + \frac{m(1-\varphi)}{d_{\text{MMA}}} \text{ (L)} \quad (5.11) \]

Thus, the correct initial concentrations for the initiator and monomer are given by

\[ I_0 = \frac{m\varphi_{\text{AIBN}}}{M_{\text{W,AIBN}}} V_0 \times f_e \text{ (mol L}^{-1}) \quad (5.12) \]

\[ M_0 = \frac{m(1-\varphi)}{M_{\text{W,MMA}}} V_0 \text{ (mol L}^{-1}) \quad (5.13) \]

with \( M_{\text{W,AIBN}} \) and \( M_{\text{W,MMA}} \) being the molecular weight of the initiator and monomer, respectively. Table 5.2 lists the values of the parameters used in the model simulations.

**Table 5.2** Values of parameters used in the model simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{\text{PMMA}} )</td>
<td>1.2 g/L</td>
</tr>
<tr>
<td>( d_{\text{MMA}} )</td>
<td>0.94 g/L</td>
</tr>
<tr>
<td>( d_{\text{Polystyrene}} )</td>
<td>1.05 g/L</td>
</tr>
<tr>
<td>( d_{\text{PTFE}} )</td>
<td>2.1 g/mL</td>
</tr>
<tr>
<td>( x_{\text{AIBN}} )</td>
<td>1.66 %</td>
</tr>
<tr>
<td>( M_{\text{W,MMA}} )</td>
<td>100 g/mol</td>
</tr>
<tr>
<td>( M_{\text{W,AIBN}} )</td>
<td>164 g/mol</td>
</tr>
</tbody>
</table>

In order to check the model prediction, we have performed the bulk polymerization of MMA, in the absence of the NPs, with AIBN as initiator (0.094 mol L\(^{-1}\)), using the DSC instrument under isothermal conditions (70 °C). Then, the model was used to fit the DSC results. Two parameters have been tuned in order to best fit the experimental data. First, we have noticed that the efficiency of our initiator, AIBN, is only 80\% of that reported in the literature. It follows that we have multiplied an efficiency parameter,
\( f_e = 0.8 \) in Eq. (5.12), for the used initiator. Second, the value for the prefactor of \( \Theta_p \) in Eq. (5.8) has been changed from \( 5.48 \times 10^{-16} \) to \( 4.81 \times 10^{-17} \) in order to correctly simulate the intensity of the gel effect. After the tuning, the model with the new set of the parameters establishes a basis for exploring the effect of the NPs on the bulk polymerization of MMA.

### 5.4 Results and Discussion

#### 5.4.1 Dispersity of the surface-modified NPs in MMA

Accurate quantification of the NP surface effect requires that the NPs are mono-dispersed in the monomer, avoiding significant NP aggregation. In the cases of PTFE and PS NPs without surface modification, it was found that due to their poor compatibility with MMA, their dried powders were very difficult to re-disperse (forming big agglomerates) in MMA. Thus, their surface is modified by a layer of cross-linked PMMA (cPMMA), which is highly compatible with MMA, such that, instead of the PTFE or PS NPs, the cPMMA layer contacts directly with MMA. To verify the dispersity of the surface-modified NPs in MMA, we have added the dried surface-modified PS NP powder into MMA and monitored, using SLS, the average radius of gyration \( (R_g) \) of the PS NP agglomerates as a function of the sonication time.

As shown in Figure 5.2, the \( R_g \) value decreases as the sonication time increases, and after sonication for 40 min, the \( R_g \) value reaches a plateau of 25.1 nm, which does not change even after 3 hours sonication. This plateau \( R_g \) value, based on \( R_g = (3/5)^{0.5} R_p \), corresponds to a radius of a sphere, \( R_p = 32.4 \) nm. This is very close to the radius of the PS NPs in the latex before surface modification, 31.5 nm, determined by DLS, confirming that the surface-modified PS NPs in the powder have been well dispersed in
MMA with negligible agglomerates.

![Figure 5.2](image)

**Figure 5.2.** The average radius of gyration, $R_g$, of the agglomerates of the surface-modified PS NPs dispersed in MMA as a function of sonication time.

To further confirm the good dispersity of the surface-modified NPs in MMA, we have taken TEM pictures of the surface-modified PTFE NPs in MMA after dispersing the NP powder for 40 min. As can be seen in Figure 5.3a, indeed, the NPs are well separated, with negligible aggregation. Such good dispersity maintains even after bulk polymerization to form a PMNC. Figure 5.3b shows a CryoSEM picture of the fractured PMNC, demonstrating a homogeneous dispersion of the spherical NPs over the fractured surface.

In Table 5.1, apart from the surface-modified PTFE and PS NPs, Samples 3 and 4 are pure PMMA NPs with different amounts of the cross-linker, DTTA, leading to different levels of swelling in MMA, while Sample 5 is pure PMMA NPs without using any cross-linker, thus dissolvable in MMA. These PMMA NPs are also used in the
DSC experiments in order to identify the differences in the MMA bulk polymerization compared to the presence of the surface-modified PTFE and PS NPs.

Figure 5.3. (a) TEM picture of a NPs/MMA dispersion after sonication for 40 minutes, and (b) CryoSEM picture of the fracture surface of a bulk PMMA with dispersed PTFE NPs. The measured diameter of the PTFE NPs is 79.4 nm.

5.4.2 Role of presence of linear PMMA in MMA bulk polymerization

Let us first consider the simplest case: we explore if the presence of linear PMMA in MMA affects the bulk polymerization process or not. This can be done by using Sample 5 in Table 5.1, the PMMA NPs produced without using a cross-linker, thus composed of linear polymers. When the powder of these PMMA NPs was added into
MMA, the NPs disappeared and all the linear polymer chains were dissolved in the monomer. The DSC experiments of the bulk polymerization were carried out at a fixed initiator mass fraction, $\varphi_{AIBN} = 1.66\%$, and temperature, $T=70\, ^\circ\text{C}$, but at five different mass fractions of the PMMA NPs, $\varphi = 0.0\%$, 2.0\%, 5.0\%, 7.5\% and 10.0\%, respectively. The measured $HF\text{-}t$ and $x\text{-}t$ curves (symbols) are shown in Figure 5.4. It is seen that the gel effect peak moves progressively towards a shorter time as the mass fraction of the dissolved linear PMMA increases. Note that the differences in the peak height are due to the differences in the mass of the system. The results in Figure 5.4 indicate that the presence of the linear PMMA enhances the MMA polymerization kinetics.

When the five sets of the experimental data are simulated by the model described in Section 5.3, it is found that, considering only the volume effect of the dissolved linear PMMA, we are unable to simulate the DSC data in Figure 5.4. Then, we considered the dissolved linear PMMA as pre-polymers, i.e., assuming that the system is pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. In this way, we have replaced the conversion, $x$ with $x_0+x$, in all the model equations, where $x_0 = \varphi$. The continuous curves in Figure 5.4 correspond to the model simulation; the agreement with the DSC data is excellent. This result signifies that the effect of the presence of the dissolved linear PMMA on the MMA bulk polymerization is as if the system was pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. In this sense, the dissolved linear PMMA does affect the MMA polymerization kinetics.
Figure 5.4. The $HF-t$ and $x-t$ curves of the MMA bulk polymerization in the presence of different mass fractions of the linear PMMA NPs (Sample 5), $\varphi$. The bulk polymerization conditions: $\varphi_{\text{AIBN}} = 1.66\%$; $T = 70 \,^\circ\text{C}$. The continuous curves are model simulations by assuming $x_0 = \varphi$.

5.4.3 Role of presence of cPMMA NPs in MMA bulk polymerization

When cross-linked PMMA (cPMMA) NPs are added into MMA, though they can be swollen by MMA to a certain extent, depending on the amount of the cross-linker
(DTTA) used during their preparation, they cannot be dissolved in MMA. Let us now compare the effect of the cPMMA with linear PMMA on the MMA bulk polymerization. In particular, we consider Sample 3 (cPMMA with $\varphi_{\text{DTTA}} = 2.5\%$) and Sample 5 (linear PMMA). Figure 5.5 shows the experimental $HF\cdot t$ data in the presence of different amounts of the cPMMA NPs, $\varphi = 0.0\%, 5.0\%$ and $10.0\%$, respectively. In the same figure we also show the $HF\cdot t$ curve in the presence of $10.0\%$ linear PMMA NPs. It is evident that, both at $\varphi = 10.0\%$, the gel effect peak in the case of cPMMA occurs later than that in the case of linear PMMA. Recall the role of the dissolved linear PMMA discussed above, which is as if the system is pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. Now, it is obvious that the role played by the cPMMA is not the same as that by the linear PMMA. In the other words, with respect to the linear PMMA, the presence of the cPMMA seems affecting the MMA polymerization kinetics—retarding the gel effect.
Figure 5.5 The $HF$-$t$ curve of the MMA bulk polymerization in the presence of different mass fractions of the cPMMA NPs (Sample 3 in Table 5.1). $\varphi$. As a comparison, the same curves in the presence of the linear PMMA NPs at $\varphi = 10.0\%$ are also shown. The bulk polymerization conditions: $\varphi_{AIBN} = 1.66\%; T = 70\, ^{\circ}\mathrm{C}$. The continuous curves are model simulations.

Since the only difference between Samples 3 and 5 in Table 5.1 is the presence of 2.5\% cross-linker in the former, the observed kinetic retarding effect in Figure 5.5 must be related to the cross-linking in the cPMMA NPs. To confirm this point, we have prepared the cPMMA NPs with even higher cross-linker (7.5\%), i.e., Sample 4 in Table 5.1. Figure 5.6 compares the $HF$-$t$ curve among the three cases: in the presence of the linear PMMA (Sample 5), cPMMA with $\varphi_{\text{DTTA}} = 2.5\%$ (Sample 3) and cPMMA with $\varphi_{\text{DTTA}} = 7.5\%$ (Sample 4), all at $\varphi = 10.0\%$. As can be observed, the gel effect peak moves progressively towards a longer polymerization time as the amount of the cross-linker used in the cPMMA NPs increases, thus confirming that the kinetic retarding strongly links to the cross-linking in the cPMMA NPs.
It is difficult to explain why the cross-linking in the cPMMA NPs can retard the MMA bulk polymerization kinetics. The first thought we have is that since increasing the cross-linking decreases the possibility for the NPs to swell. Then, in the MMA bulk polymerization system there are two distinct regions: the pure MMA region and the region occupied by the swollen NPs. One can expect that the polymerization kinetics should be different in the two regions, but still we cannot connect such difference to the overall retarded polymerization kinetics. Our second thought is that the swelling inside the cPMMA NPs by MMA is inhomogeneous. Specifically, there might exist small domains inside each NP, which are unable to swell at all. These non-swollen domains are basically inert for the MMA bulk polymerization, and behave as a dead volume. To demonstrate the possibility of the second thought, we have performed the model simulations as follows. We consider that for the added amount of the cPMMA NPs, $\varphi$, only its certain fraction behaves as the linear PMMA, i.e., as pre-polymers affecting the MMA bulk polymerization kinetics discussed in the previous section, while the remaining fraction, $\Delta$, is inert, like a dead volume. Thus, during the model fitting, the dead volume should be subtracted from the total volume, and the initial concentrations of all the components in the system should be re-calculated accordingly. The amount of the dead volume is estimated by fitting the HF-t curve, so as to reach $x_0 = \varphi - \Delta$. Let us first use this approach to simulate the data in the case of cPMMA with $\varphi_{DTA} = 2.5\%$ in Figure 5.5. It is found that, with respect to $\varphi = 0.0\%, 5.0\%$ and $10.0\%$, we have obtained $x_0 = 0.0\%, 4.0\%$ and $8.0\%$, respectively, and the corresponding $\Delta$ values are $0.0\%, 1.0\%$ and $2.0\%$. This result indicates that when the cPMMA NPs prepared with 2.5% cross-linkers are added in MMA, there are 20% of cPMMA that are unable to swell, behaving like dead volumes. Let us now perform the same simulation for the
DSC data in Figure 5.6, in the case of cPMMA with $\phi_{\text{DTTA}} = 7.5\%$, at $\phi = 10.0\%$. The obtained results are $x_0 = 7.0\%$ and $\Delta = 3.0\%$. Thus, the non-swollen domains have increased to 30% for the cPMMA NPs with $\phi_{\text{DTTA}} = 7.5\%$. From the above simulations, the presence of non-swollen domains inside the cPMMA NPs when they are dispersed in MMA can be considered as a proper explanation for the observed kinetic effect.

**Figure 5.6.** The $HF\cdot t$ curve of the MMA bulk polymerization in the presence of the cPMMA NPs with $\phi_{\text{DTTA}} = 7.5\%$ (Sample 4 in Table 5.1) at $\phi = 10.0\%$, compared with those in the presence of the linear PMMA NPs (Sample 5 in Table 5.1) and the cPMMA NPs with $\phi_{\text{DTTA}} = 2.5\%$ (Sample 3 in Table 5.1) also at $\phi = 10.0\%$. The bulk polymerization conditions: $\phi_{\text{ABN}} = 1.66\%$; $T = 70$ °C. The continuous curves are model simulations.

### 5.4.4 Role of presence of PTFE and PS NPs in MMA bulk polymerization

The results and discussion presented in the above two sections have established a good basis for us to investigate the role played by the real NPs, PTFE and PS, during the MMA bulk polymerization. Recall that both the PTFE and PS NPs are
surface-modified by the cPMMA with $\varphi_{DTTA} = 2.5\%$. Since the cPMMA on the surface can be swollen by MMA and its effect on the MMA bulk polymerization has been investigated in Section 5.4.3, we can consider separately the role played by the cPMMA on the surface and the PTFE (or PS) NPs. In particular, for a given total mass fraction of the PTFE (or PS) NPs, $\varphi$, we divide it into two parts: the net mass fraction of the PTFE (or PS) NPs, $\varphi_{NP}$, and the mass fraction of the cPMMA, $\varphi - \varphi_{NP}$. The results obtained in the previous sections about the role played by the cPMMA are applied directly for the cPMMA part. After subtracting the role played by the cPMMA part, we can understand the role played by the PTFE (or PS) NPs.

Let us first consider the surface modified PTFE NPs, i.e., Sample 2 in Table 5.1. We have performed two sets of the DSC experiments at $\varphi = 8.9\%$ and 13.4%, respectively, and the experimental data are shown in Figure 5.7. It is seen that the gel effect peak moves towards a shorter polymerization time as $\varphi$ increases, thus indicating the presence of the effect of the surface modified PTFE NPs on the polymerization kinetics. For a given $\varphi$ value, we can compute from the specifics in Table 5.1 the mass fraction of the cPMMA, $\varphi - \varphi_{NP}$, and the net mass fraction of the PTFE (or PS) NPs, $\varphi_{NP}$, which are 3.9% and 5.0% in the case of $\varphi = 8.9\%$, and 5.9% and 7.5% in the case of $\varphi = 13.4\%$. As mentioned above, for the cPMMA part, we apply directly the results obtained in the previous sections in the case of the cPMMA NPs with $\varphi_{DTTA} = 2.5\%$. That is, within $\varphi - \varphi_{NP}$, there are 80% behaving as the linear PMMA and 20% as inert, dead volume. For the net mass fraction of the PTFE NPs, $\varphi_{NP}$, let us first assume that they behave as inert, dead volume. Then, plus the dead volume from the cPMMA part, the total dead volume is $\Delta = \varphi_{NP} + 0.2(\varphi - \varphi_{NP}) = 5.78\%$ and
8.68%, respectively, for $\phi = 8.9\%$ and 13.4%. The remaining, $0.8(\phi - \phi_{NP})$, as the linear PMMA, is set to the amount of pre-polymers, $x_0 = 3.12\%$ and 4.72%, respectively, for $\phi = 8.9\%$ and 13.4%. With such estimated values for $x_0$ and $\Delta$, we have performed the model simulations, and the results are shown in Figure 5.7 (continuous curves). It is seen that the agreement between the experimental data and the model simulations is excellent, thus supporting our above hypothesis. It is therefore concluded that the PTFE NPs dispersed in MMA do not interfere specifically the MMA bulk polymerization process.

![Diagram](image)

**Figure 5.7** The $HF\cdot t$ curve of the MMA bulk polymerization in the presence of surface modified PTFE NPs (Sample 2 in Table 5.1), at $\phi = 8.9\%$ and 13.4%. The continuous curves are model predictions, as described in the text. The bulk polymerization conditions: $\phi_{ABN} = 1.66\%; \ T = 70 \ ^\circ C$.

Now, we apply the same approach to explore the role played by the surface-modified PS NPs, *i.e.*, Sample 1 in Table 5.1, in the MMA bulk polymerization.
We have prepared two sets of the DSC experiments at $\varphi = 7.25\%$ and $14.5\%$, respectively, and the DSC data are shown in Figure 5.8. As a general observation, the trend in Figure 5.8 is very similar to that in Figure 5.7 in the case of the surface-modified PTFE NPs. With the $\varphi$ values, based on the specifics of the PS NPs in Table 5.1 and the parameter estimation methodology used above, we have obtained the values for $x_0$ ($\Delta$) to be 3.8% (3.45%) and 7.6% (6.9%) for $\varphi = 7.25\%$ and $14.5\%$, respectively. The model simulations with the estimated $x_0$ and $\Delta$ values are shown in Figure 5.8. It is interesting to have found that the model simulations significantly deviate from the experimental data. Particularly, the predicted gel effect peak is located at a longer polymerization time, with respect to the experimental one, in both cases. Such deviation is obviously caused by the PS NPs, which behave not only as inert, dead volume, but also as promoter for the MMA polymerization.

**Figure 5.8** The $HF$-$t$ curve of the MMA bulk polymerization in the presence of surface modified PS NPs (Sample 1 in Table 5.1), at $\varphi = 7.25\%$ and $14.5\%$. The continuous curves are model predictions, as described in the text. The bulk polymerization conditions: $\varphi_{\text{AIBN}} = 1.66\%$;
It is difficult to explain why the dispersed PS NPs can promote the MMA bulk polymerization. However, we have noticed that, when we disperse the powder of the surface-modified PS NPs into MMA, the plateau $R_g$ value after a long sonication time was 25.1 nm, as shown in Figure 5.2. This corresponds to a radius of a sphere, $R_p = 32.4$ nm. Since the TEM picture confirms that the PS NPs are very mono-disperse in MMA, and the surface cPMMA is invisible due to the refractive index matching, the obtained $R_p (=32.4$ nm) value must be the radius of the PS NPs in MMA. This value is slightly larger than the radius of the PS NPs (31.5 nm) in water before surface modification. This may indicate that the PS NPs in MMA were slightly swollen by MMA. Similar to the swollen PMMA, the swollen PS might also promote the MMA bulk polymerization.

5.4.5 NP-related microstructure in bulk PMMA

Apart from the linear PMMA, for both the cPMMA NPs and the surface-modified PTFE (or PS) NPs, after dispersed in MMA, their identity does exist. Then, a question arises whether the presence of these NPs would lead to changes in the microstructure of the bulk PMMA. As fracture surfaces often provide information about microstructure, to explore our NP effect on the microstructure, we have selected three bulk PMMA samples: PMMA from pure MMA, PMMA with dispersed cPMMA NPs, and PMMA with dispersed PTFE NPs. Then, we have fractured them under cryogenic conditions and taken the CryoSEM images of their cracking surface, which are shown in Figure 5.9. In the case of the PMMA produced from pure MMA in Figure 5.9a, the microstructure of the fracture surface is random and homogeneous. However, when the cPMMA NPs (Figure 5.9b) or PTFE NPs (Figure 5.9c) are introduced in the
bulk PMMA, we have observed grain structures. It is worth noting Figure 5.9d, where each PTFE NP is located in the centre of a grain and the boundary is pulled out during the sample fracturing. This has strongly evidenced that the formation of the microstructure is related to the dispersed PTFE NPs. In Figure 5.9b, we cannot see any NPs in the centre of the grains, because the cPMMA NPs are swollen by the MMA. This typical grain structures were also observed when nano-fillers as a second phase were included in nanocomposites\textsuperscript{139}, or can be formed during the crack propagation when there are impurities in the polymer\textsuperscript{137, 138, 140, 141}. However, since the cPMMA NPs are swollen by MMA before bulk polymerization, they do not form a second phase. We believe that the microstructure in our cases might be related to NP-induced property distribution inside the polymer, such as molecular weight, different branching or different monomer conversion. As a reasonable assumption, the grain structure is probably related to NP-induced changes in the local kinetics of the diffusion limited polymerization. Even though the detailed observation of the molecular weight distribution along the fracture surface needs extremely high resolution microscope, the above results clearly indicate the role played by the NPs in varying the microstructure of a bulk PMMA.
**Figure 5.9.** CryoSEM pictures of the fracture surface of the bulk PMMA samples prepared from (a) pure MMA, (b) MMA with 2.5% cPMMA NPs, and (c) MMA with 1% surface modified PTFE NPs.

### 5.5 Conclusions

We have designed a standard methodology to investigate the role played by NPs during the in-situ bulk polymerization of MMA, which is based on the DSC experiments and the kinetic modelling of the bulk polymerization. Both PTFE and PS
NPs have been applied in this work, which, due to their low compatibility with MMA, have been surface-modified by cross-linked PMMA (cPMMA). Then, to quantify the net effect of the NPs on the bulk polymerization, we have first quantified the effect of the cPMMA without the NPs, and then subtracted the effect of the cPMMA to get that of the NPs. Moreover, the presence of dissolved linear PMMA during the MMA bulk polymerization has also been studied and compared with that of the cPMMA.

In the case of dissolved linear PMMA chains in MMA, it is found that their effect on the MMA bulk polymerization is as if the system was pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. Thus, the dissolved PMMA chains do affect the MMA bulk polymerization kinetics. The role played by the dispersed cPMMA is different from that by the linear PMMA. We observed that with the same dispersed mass, the gel effect peak appears later for the cPMMA than for the linear PMMA. Thus, the cPMMA retards the MMA polymerization kinetics, with respect to the linear PMMA. Such retardation increases as the cross-linker in the cPMMA increases.

For the dispersed PTFE NPs in MMA, which are surface-modified by the cPMMA, after subtracting the role played by the cPMMA, we found that the PTFE NPs behave like (inert) dead volume, changing only the effective concentrations of the components in the system. For the dispersed PS NPs, instead, we have indeed observed their role in promoting the MMA bulk polymerization, with respect to the PTFE NPs. This may be related to possible swelling of the PS NPs in MMA.

Moreover, we have examined the microstructure of the final PMNCs in the presence of different NPs through cryogenic cracking and CryoSEM imaging. When the cPMMA NPs or PTFE NPs are introduced during the MMA bulk polymerization, we have observed grain structures in PMMA. In particular, each PTFE NP is located in
the centre of a grain and the boundary is pulled out during the sample fracturing, indicating that the formation of the microstructure is related to the dispersed PTFE NPs.
Chapter 6

Conclusions

In this thesis, the kinetics of the shear-driven aggregation of a well stabilized colloidal system and the phase behaviour have been investigated from experimental and theoretical perspectives. A PS colloid which was stable at rest was used to perform the aggregation studies through a microchannel device which can generate high shear rates (up to $1.5 \times 10^6 \text{ s}^{-1}$), with a short residence time (short to 27 $\mu$s). The obtained results strongly support the self-accelerating kinetics in the shear-driven aggregation where high energy barrier exists. The observed phase evolution brings the systematic understanding of the shear driven gelation phenomena in the MC, based on which we developed a new approach to prepare composite materials with homogenous distribution of one colloid in another.

Besides the main stream of shear driven aggregation system, we have also prepared another type of polymer-based nanocomposites by free radical bulk polymerization of MMA. In particular, we have designed a standard methodology
to investigate the role played by NPs during the in-situ bulk polymerization of MMA, which is based on the DSC experiments and the kinetic modelling of the bulk polymerization.

**Aggregation kinetics under the intensive shear**

We have monitored the time evolution of the conversion ($x$) of the primary particles to big clusters, and average radius of gyration and fractal dimension of the big clusters. The time evolution of $x$ is typically composed of three stages: induction, sharp increase and slow increase stages. In the induction stage, $x$ is practically zero; in the $x$ sharp increase stage, the average size of the big clusters increases also sharply, leading to an overshooting; in the last stage, both the average size and mass of the big clusters decrease to reach a plateau. The fractal dimension of the big clusters increases with the shearing time from the initial value of $2.40 \pm 0.05$ to reach $2.80 \pm 0.05$. Thus, along the shear-driven aggregation, both breakage and restructuring play an important role.

The presence of the induction stage followed by a sharp increase in the conversion confirms the theory of shear-activated aggregation with the activation energy, $E_a = U_m - 6\pi\alpha\mu \dot{\gamma} a^3$. The induction time implies an initial $E_a > 0$, and the aggregation rate is very small; as the radius of the clusters, $a$, increases progressively to reach a critical value, $a_c$, $E_a \leq 0$, and the aggregation accelerates. The size of the critical clusters for the self-acceleration kinetics has been quantified for the first time, and the scaling of the obtained $a_c$ value with the shear rate follows well the theoretical prediction.

The interaction energy barrier ($U_m$) was estimated to be four orders of magnitude larger than that calculated from the measured $\zeta$-potential, confirming the presence of
substantial non-DLVO interactions in the given system.

**Phase evolution and the steady state-phase diagram**

The short residence time allows us to snapshot the phase evolutions of the PS colloidal system by repeatedly cycling the aggregating system in the MC many times. An important feature of the system is that due to strong repulsion between the particles generated by charges from the surface fixed charge groups and the adsorbed surfactants, the formed clusters are strongly repulsive as well, thus stable after shearing.

It is found that as the aggregation extent (thus, the cluster packing fraction) increases with the shearing time, depending on the initial particle volume fraction, we have progressively observed three phases: fluid of clusters, Wigner glass of clusters and gel. The presence of the Wigner glass state is obviously related to the repulsive nature of the system, which remains even after forming clusters. Along the shear-driven aggregation, the Wigner glass of clusters can occur in a large range of the packing fraction of total clusters ($0.48 < \phi_c < 0.72$), mostly due to irregular shape of the clusters.

We have proposed a phase diagram that describes how the transitions of the three phases evolve at the aggregation steady-state in the colloidal interactions vs particle concentration plane. It tells that, as the difference between the aggregation and breakage energy barriers increases, the particle concentration for the occurrence of the Wigner glass state increases. Therefore, the energy barriers for the aggregation and breakage, together with the particle concentration and the shear rate, determine the final clustered state. This scenario brings a clear understanding to the complicated shear-driven aggregation and solidification process and it is of great importance in applications.
Application of the shear-driven aggregation to prepare nanocomposites

Based on the above understanding, we propose a methodology for preparing composite materials with distribution homogeneity of different components at nano-scale. To demonstrate the feasibility of the proposed methodology, we have prepared a stable binary colloidal dispersion, which is composed of 43 nm PS particles and 280 nm PMMA particles. Both types of the particles are stable at rest, but the PS particles alone undergo the shear-driven aggregation (shear-active), while the PMMA particles at the same shear rate do not (shear-inactive). Since both PS and PMMA particles are negatively changed, the mixture of their dispersions is stable as well. Then, the shear-driven aggregation of the binary colloidal dispersion at different PS/PMMA compositions has been carried out in the same MC at the same shear rate.

It is found that the shear-driven aggregation of the binary colloidal system does occur, and the formed clusters are composed of not only the “shear-active” PS particles but also the “shear-inactive” PMMA particles. The SEM picture demonstrates that the PMMA particles are homogeneously and randomly distributed among the PS particles in the clusters, confirming the feasibility of the proposed methodology.

On the other hand, the experimental results have proven that the presence of the PMMA particle does not change significantly the aggregation kinetics of the PS particles or the average size of the clusters, and they behave as inert fillers. These results allow us to propose the following mechanism for the inclusion of the PMMA particles in the clusters: When the shear-driven aggregation of the “shear-active” PS particles takes place within such a short time (~27 μs) interval, since the PMMA particles, though “shear-inactive,” are distributed among the PS particles, they have no time to escape from the PS aggregation process and are captured during the formation
of the clusters. At low PMMA volume fractions, the capture efficiency can reach 100%, and it is significantly lower at high PMMA volume fractions. However, when the shear-driven aggregation of the binary colloidal system leads to a solid-like gel, the capture efficiency of the PMMA particles reach naturally 100%.

**The effect of dispersed polymeric NPs on the bulk polymerization of MMA**

We have designed a standard methodology to investigate the role played by NPs during the in-situ bulk polymerization of MMA, which is based on the DSC experiments and the kinetic modelling of the bulk polymerization. Both PTFE and PS NPs have been applied in this work, which, due to their incompatibility with MMA, have been surface-modified by cross-linked PMMA (cPMMA). Then, to quantify the net effect of the NPs on the bulk polymerization, we have first quantified the effect of the cPMMA without the NPs, and then subtracted the effect of the cPMMA to get that of the NPs. Moreover, the presence of dissolved linear PMMA during the MMA bulk polymerization has also been studied and compared with that of the cPMMA.

In the case of dissolved linear PMMA chains in MMA, it is found that their effect on the MMA bulk polymerization is as if the system was pre-polymerized at a conversion equal to the dissolved amount of the linear PMMA. Thus, the dissolved PMMA chains do not interfere specifically the MMA bulk polymerization. The role played by the dispersed cPMMA is different from that by the linear PMMA. We observed that with the same dispersed mass, the gel effect peak appears later for the cPMMA than for the linear PMMA. Thus, the cPMMA retards the MMA polymerization kinetics. Such retardation increases as the cross-linker in the cPMMA increases.

For the dispersed PTFE NPs in MMA, which are surface-modified by the cPMMA,
after subtracting the role played by the cPMMA, we found that the PTFE NPs behave like (inert) dead volume, changing only the effective concentrations of the components in the system. For the dispersed PS NPs, instead, we have indeed observed their role in promoting the MMA bulk polymerization, with respect to PTFE NPs. This may be related to possible swelling of the PS NPs in MMA.

Moreover, we have examined the microstructure of the final PMNCs in the presence of different NPs through cryogenic cracking and CryoSEM imaging. When the cPMMA NPs or PTFE NPs are introduced during the MMA bulk polymerization, we have observed grain structures in PMMA. In particular, each PTFE NP is located in the centre of a grain and the boundary is pulled out during the sample fracturing, indicating that the formation of the microstructure is related to the dispersed PTFE NPs.

**Outlook of this thesis**

As shown in Chapter 4, shear-driven aggregation of the binary colloidal systems leads to the micro-scale clusters of composites, due to the “shear-active” PS particles that capture the “shear-inactive” PMMA particles during their aggregation. Theoretically, based on the inter-particle interaction energy between the two types of particles, various possible mechanisms will occur during the hetero-aggregation. Different combinations of binary colloidal systems are shown in Table 6.1. The PS/PMMA system which was discussed in this thesis corresponds to Case 1, where A and B represent the “shear-active” PS and the “shear-inactive” PMMA particles, respectively. It has to be noted that “active” and “inactive” are terms describing the relative shear behaviours of the two distinct colloids. The inter-particle interaction curve of B-B sketched in Table 6.1 (1) is an extreme case, indicating that in the absence of the primary minimum, B will never aggregate under shear. In the reality, B is unnecessarily strictly “shear-inactive”. As long as the difference in the aggregation
rates between the “shear-active” A-A and the “shear-inactive” B-B is significant and there is no A-B aggregation, the hetero-aggregation can be achieved by the “capture” mechanism described in Chapter 4. Moreover, the difference in the aggregation kinetics between the two types of particles is not only in the properties of the materials, but also determined by the surface, such as surface charge, surfactant, etc. For Case 2 in Table 6.1, A-A and B-B have similar interaction curves, representing that both shear-driven A-A and B-B aggregation can take place, while A-B cannot. As a reasonable assumption, during the induction time, A and B will form small homo-clusters until their sizes reach $a_i$, and then the self-acceleration of A-A or B-B shows up. Due to the very fast reaction, co-aggregation occurs to form micro-clusters. In this case, since the non-self-accelerated particles are already in the form of small homo-clusters, they are captured inside the composite in the form of small homo-clusters, instead of primary particles. For Case 3 in Table 6.1, shear-driven A-A, B-B and A-B aggregations are all possible. This leads to a competition between A and B during the process, and the results, similar to copolymerization, could be determined by the activity ratio, $r_{A,B}/r_{A,A}$. For the last case, Case 4 in Table 6.1, neither A nor B could form homo-aggregates, but introducing the second type of particles leads to the aggregation of the entire system. The scenario is similar to the binary colloids composed of particles with opposite charges under the stagnant condition where one particle will be bonded with the other particles of different materials. It should be pointed out that the above discussion is based on a rational “imagination” based on the colloidal interactions. A large amount of work needs to be carried out in order to understand the reality of these processes and corresponding kinetics.
Table 6.1. Different combination of the binary colloids in the study hetero-aggregation

<table>
<thead>
<tr>
<th>Case No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>B-B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>A-B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
</tbody>
</table>

Besides the effect of the colloidal interactions between the two types of particles, there are other factors which affect the composition and morphology of the composites such as the size ratio between the two types of particles, shape of the particles, shear rate, etc. Further experiments have to be done in order to clarify those effects.

Moreover, it is worth mentioning that the shear-driven aggregation in preparing homogeneous nanocomposites can be well applied to industry production due to ease of operation, high speed and relatively low cost. For example, in the case of our lab-scale MC system at $\Delta P = 150$ bar, the flow rate can already reach about 300 ml/min, indicating a production facility of 5.4 kg of composite material per hour, if we use a latex with $\phi = 0.3$. Furthermore, a large variety of composite materials can be prepared using this method, including polymer composites and polymer/inorganic composites.
Notation

\( a \)  
Radius of colloidal particles or clusters, m

\( a_{cr} \)  
Critical activated size of particles or clusters, m

\( A_m \)  
Hamaker constant in Eq. (1.3), J

\( C_0 \)  
Concentration of particles in the bulk in Eq. (1.6), mol/L

\( C_i \)  
Bulk concentration of electrolyte in Eq. (1.5), mol/L

\( D \)  
Mutual diffusion coefficient of the particles in Eq. (1.1), m\(^2\)/s

\( D_0 \)  
Diffusion coefficient of an isolated particle in Eq. (1.1), m\(^2\)/s

\( d \)  
Density, kg/m\(^3\)

\( d_f \)  
Fractal dimension

\( e \)  
Electron charge in Eq. (1.5), C

\( E_a \)  
Activation energy, J

\( f \)  
Efficiency factor for the primary initiator radical consumption

\( f_{PMMA,c} \)  
Fraction of PMMA in the cluster phase

\( f_{PMMA,i} \)  
Fraction of PMMA initially

\( G(\tau) \)  
Hydrodynamic function for viscous retardation (1.1)

\( HF \)  
Heat flow, mW

\( \Delta H_p \)  
Standard heat of MMA polymerization, J/mol

\( i \)  
Average cluster mass

\( I \)  
Initiator concentration

\( k \)  
Pre-factor in computation of the average cluster mass based on the fractal scaling

\( k_{1,1} \)  
Rate of doublet formation

\( k_B \)  
Bolzmann’s constant

\( k_d \)  
Rate constant of the initiator decomposition, min\(^{-1}\)

\( k_p \)  
Rate constant of the propagation, L/(mol·min)

\( k_p^0 \)  
Rate constant of the propagation at zero conversion, L/(mol·min)

\( k_{tc} \)  
Rate constant of the termination by combination, L/(mol·min)

\( k_{td} \)  
Rate constant of the termination by disproportionation, L/(mol·min)

\( k_t^0 \)  
Rate constant of the termination at zero conversion, L/(mol·min)

\( m \)  
Mass of the sample, g

\( M \)  
Monomer concentration, mol/L

\( M_0 \)  
Initial monomer concentration, mol/L

\( M_{w,ABN} \)  
Molecular weight of the initiator, g/mol

\( M_{w,MMA} \)  
Molecular weight of the monomer, g/mol

\( N_A \)  
Avogadro constant

\( N_0 \)  
Refractive index of the dispersion medium
$N_p$ Number of passes in the shearing experiments
$\Delta P$ Pressure drop through the microchannel, bar
$Pe$ Peclet number defined in Eq. (1.6a)
$q$ Scattering wave vector modulus, nm
$r_p$ Rate of polymerization
$R_g$ Radius of gyration of a cluster or particle
$R_p$ Hydrodynamic radius of the particle
$S(q)$ Scattering structure factor
$T$ Absolute temperature, K
$t$ Ending time of the polymerization
$t_i$ Induction time in shear driven aggregation
$U$ Colloidal interaction energy in Eq. (1.2), J
$U_A$ Van Der Waals interaction in Eq. (1.3), J
$U_m$ Particle interaction energy barrier in Eq. (1.10), J
$U_R$ Electrostatic interaction in Eq. (1.4), J
$U_a$ Energy barrier for aggregation, J
$U_b$ Energy barrier for breakage, J
$\Delta U$ Difference between the $U_a$ and $U_b$, J
$v$ Flow velocity in Eq. (1.1), m/s
$V$ Volume of the sample, L
$v_e$ Effective flow velocity for aggregation (1.6), m/s
$W_G$ Coefficient in describing the rate of shear-driven aggregation in Eq. (1.9)
$x$ Conversion
$x_0$ Initial polymer conversion used in model simulation
$x_i$ Initial fraction of the linear polymer
Greek Symbols

\( \alpha \) Geometrical parameter of the shear flow

\( \dot{\gamma} \) Shear rate, \( \text{s}^{-1} \)

\( \varepsilon \) Volume expansion factor in MMA bulk polymerization

\( \varepsilon_0 \) Permittivity of vacuum in Eq. (1.4), F/m

\( \varepsilon_r \) Permittivity of the dispersion medium in Eq. (1.4), F/m

\( \phi \) Volume fraction of colloidal particles in the dispersion

\( \phi_c \) Volume occupied by the big clusters

\( \phi_{\text{rem}} \) Remaining volume fraction of primary particles

\( \phi_{\text{rem,c}} \) Remaining effective volume fraction of primary particles

\( \phi_{\text{PS,e}} \) Effective volume fraction of the PS particles

\( \varphi_{\text{NP}} \) Mass fraction of the NPs

\( \varphi_{\text{NP,\text{+}}} \) Mass fraction of the NPs plus the PMMA mass for the surface modification

\( \varphi_s \) Mass fraction of the PMMA mass for the surface modification

\( \varphi_{\text{DTTA}} \) Mass fraction of the cross linker (DTTA) in the cross linked PMMA

\( \Theta_p \) Pre-factor, characteristic time of the free radical diffusion

\( \Theta_t \) Pre-factor, characteristic time of the monomer diffusion

\( \Phi_{\text{in}} \) Factor determined in Eq. (5.6)

\( \psi \) Particle surface potential (1.4)

\( \delta \) Thickness of the boundary layer, m

\( \Delta \) Deviation of the simulated initial conversion from the experimental polymer volume fraction, \( \Delta = \varphi_{\text{NP}} - x_0 \)

\( \kappa \) Reciprocal Debye length (1.5), \( \text{m}^{-1} \)

\( \mu \) Viscosity of the dispersion medium, Pa·s
Appendix I

The colloidal systems used for this study were aqueous dispersions of polystyrene particles produced by emulsion polymerization with SDS (sodium dodecyl sulfate) as surfactant and KPS (potassium persulfate) as initiator. The radius of the particles is 21.5 nm by DLS measurements. The particle volume fraction ($\phi$) of the original latex is 0.15. The aggregation systems with different $\phi$ were prepared by direct dilution of the original latex with deionized water. This leads to changes in the SDS adsorption isotherm and the ionic strength at different $\phi$ values and consequently to the changes in the interaction energy barrier ($U_m$), which should be estimated. To this aim, the generalized stability model developed previously has been applied\textsuperscript{95}, which accounts simultaneously for the interactions among three important physicochemical processes: adsorption equilibrium of surfactants, association equilibria of the ionic surfactants with counter ions, and colloidal interactions. The following describes briefly the quantities that we considered in the generalized stability model:

1. The DLVO interactions.

According to the DLVO theory, the interaction energy between two colloidal particles, $U$, is the sum of the van der Waals attractive interaction ($U_A$) and the electrostatic repulsive interaction ($U_R$)

$$U = U_A + U_R$$

(1.2)

According to the Hamaker relationship, the expression for $U_A$ is given by

$$U_A = -\frac{A_H}{6} \left[ \frac{2}{l^2} + \frac{2}{l^2} + \ln \left( 1 - \frac{4}{l^2} \right) \right]$$

(1.3)
where $A_H$ is the Hamaker constant, and $l = x / a$. The modified Hogg-Healy-Fuersteneau expression is commonly used to describe the electrostatic repulsion\textsuperscript{95}:

$$U_R = \frac{4\pi \varepsilon_r \varepsilon_0 \psi^2}{l} \ln\left\{1 + \exp[-\kappa a(l - 2)]\right\} \quad (1.4)$$

where $\varepsilon_r$ is the permittivity constant of the dispersion medium, $\varepsilon_0$ is the permittivity of vacuum, $\psi$ is the surface potential which is obtained from $\zeta$-potential measurement\textsuperscript{142} and $\kappa$ is the reciprocal Debye length, which is defined as:

$$\kappa \equiv \left( N_A e^2 \sum_i c_i^{b_i} z_i^2 / \varepsilon_r \varepsilon_0 k_B T \right)^{1/2} \quad (1.5)$$

where $N_A$ is the Avogadro constant, $e$ is the electron charge, and $c_i^{b_i}$ and $z_i$ are the bulk concentration and charge valency of the $i^{th}$ ion, respectively. The constants used in calculating $U$ is listed below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_H$</td>
<td>J</td>
<td>$1.37 \times 10^{-20}$\textsuperscript{143}</td>
</tr>
<tr>
<td>$N_A$</td>
<td>1/mol</td>
<td>$6.022 \times 10^{23}$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>J/K</td>
<td>$1.381 \times 10^{23}$</td>
</tr>
<tr>
<td>$F$</td>
<td>C/mol</td>
<td>$9.65 \times 10^{4}$</td>
</tr>
<tr>
<td>$e$</td>
<td>C</td>
<td>$1.602 \times 10^{19}$</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>298</td>
</tr>
<tr>
<td>$\varepsilon_r \varepsilon_0$</td>
<td>C/V/m</td>
<td>$6.950 \times 10^{10}$</td>
</tr>
</tbody>
</table>

In order to estimate the DLVO interaction of the colloidal systems, several parameters has to be described:

2. Charges on the particle surface

The colloidal systems of this work contain the SDS surfactant, which adsorbs on the particle surfaces based on the adsorption isotherm and their dissociation leads to the formation of negative charges on the surface. Since the adsorption is reversible, the charges deriving from the surfactant molecules are referred to as mobile charges ($\text{E}^{-}$).
Besides, the polymer end group which comes from the initiator KPS contribute to the fixed charge (L⁻) on the particle surface.

3. Ionic strength

Since the colloidal systems which are used in the experiment are directly diluted from the original latex, the change of ionic species in the bulk liquid phase causes the redistribution of the ionic species, which in turn changes the association equilibria between the ionic surfactant adsorbed on the particle surface and the counter-ions in the bulk phase. Specifically, two sets of ionic specious SDS and KPS are considered in this calculation. The dissolved SDS in the bulk can be calculated according to the Langmuir-type adsorption isotherm of SDS on polystyrene nanoparticles:

\[
V_{c_{\text{SDS}}} + \frac{K_{c_{\text{SDS}}}}{1 + K_{c_{\text{SDS}}}} \Gamma_{\infty} S = V c_0
\]  

(AI-1)

where \( K = 1.208 \times 10^5 \text{ cm}^3/\text{mol} \); \( \Gamma_{\infty} = 7.257 \times 10^{-10} \text{ mol/cm}^2 \); \( c \) is the SDS concentration in the bulk and \( c_0 \) is the total SDS concentration and \( S \) is the total surface area of the polystyrene particles in the latex and \( V \) is the total volume.

During the emulsion polymerization, besides the part which initiates the free radical polymerization, KPS will also be hydrolysed according to the following reaction:

\[
\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{SO}_4^{2-}
\]  

(AI-2)

Consequently, \( \text{H}^+ \) and \( \text{SO}_4^{2-} \) will be generated and contribute to the ionic strength.

Since the \( \text{H}^+ \) concentration is significant in our system (pH= 2-3), in order to simplify the calculation, we only consider the association of \( \text{H}^+ \) with \( \text{SO}_4^{2-} \) in the bulk.
and the $-\text{SO}_4^-$ groups (L$^-$ for fixed charge) on the polystyrene particle surface. The association of ions such as Na$^+$ and K$^+$ with anions is neglected.

$$
\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^- \quad K_{\text{HSO}_4^+} = \frac{c_{\text{HSO}_4^-}}{c_{\text{H}^+}c_{\text{SO}_4^{2-}}} \quad (\text{AI-3})
$$

$$
\text{H}^+ + \text{L}^- \rightleftharpoons \text{LH} \quad K_{\text{LH}} = \frac{c_{\text{LH}}}{c_{\text{H}^+}c_{\text{L}^-}} \quad (\text{AI-4})
$$

### 4. Surface charge density and surface potential

As discussed above, two species contribute to the surface charge: the mobile charge from adsorbed surfactant ($E^-$) and the fixed charge from polymer end group (L$^-$.). The total surface charge density:

$$
\sigma_0 = \sigma_{0,E} + \sigma_{0,L}
$$

Where $\sigma_{0,E} = Fc_E^S$ and $\sigma_{0,L} = Fc_L^S$. $c_E^S$ and $c_L^S$ are the concentration of surfactant and the fixed end group on the particle surface (mol/m$^2$), respectively. The surface potential of the particle is related to the surface charge by Eq. (AI-5)$^{144}$

$$
\sigma_0 = -\sum_j c_j^b \left[ \exp\left( \frac{Z_j e \psi_0}{k_B T} \right) - 1 \right] \quad (\text{AI-5})
$$

where $R_0 = 2F e \varepsilon N A k_B T / e$, $\psi_0$ is the surface potential and $c_j^b$ is the concentration of the $j^{th}$ ion in the bulk.

In order to estimate the fixed charge density, we have mixed part of the original latex with a mixture of cationic and anionic exchange resins (Dowex MR-3, Sigma-Aldrich), according to a procedure described elsewhere$^{145}$. This procedure can clean up all the SDS (adsorbed and dissolved), as well as all the other possible ions, leaving only the counterions (H$^+$) of the surface fixed charges. Then, we dilute this cleaning latex to $\phi = 1.0 \times 10^{-4}$ with water in the presence of small amount of NaCl,
$c_{\text{NaCl}} = 0.01 \text{ mol/L}$, which is considered as the model system. The $\zeta$-potential of the model system was measured using Zetasizer Nano instrument (Malvern, UK), equal to -45 mV, which is computed from the measured mobility using Smoluchowski approximation. Then, from the generalized stability model, we estimated the fixed charge of the polystyrene particles, whose value is 0.012 C/m$^2$. Sample No. 1 in Table AI corresponds to the model system.

With this model system together with the above descriptions of all the quantities, we are able to describe well the colloidal interactions of all the systems used for the shear-driven aggregation, which are listed in Table AI.

Table AI  Properties and colloidal interaction quantities of all the dispersions used in this work

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\phi$</th>
<th>$a$</th>
<th>$\psi_0$</th>
<th>$s$</th>
<th>Total $I$</th>
<th>$I/k$</th>
<th>$U_m$</th>
<th>$a_{cr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>mV</td>
<td>C/m$^2$</td>
<td>mol/m$^3$</td>
<td>nm</td>
<td>$k_B T$</td>
<td>nm</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$10^{-4}$</td>
<td>21.5</td>
<td>-45.0</td>
<td>0.012</td>
<td>20.0</td>
<td>3.04</td>
<td>21</td>
<td>31.2</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>21.5</td>
<td>-158.8</td>
<td>0.083</td>
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<td>79.7</td>
</tr>
<tr>
<td>3</td>
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<td>-152.2</td>
<td>0.091</td>
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<td>325</td>
<td>77.9</td>
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<td>4</td>
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<td>0.098</td>
<td>21.5</td>
<td>2.93</td>
<td>280</td>
<td>74.2</td>
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<td>5</td>
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<td>-120.7</td>
<td>0.107</td>
<td>57.2</td>
<td>1.78</td>
<td>218</td>
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<tr>
<td>6*</td>
<td>0.02</td>
<td>21.5</td>
<td>-54.0</td>
<td>0.012</td>
<td>1.3x10$^{-4}$</td>
<td>1202</td>
<td>42.2</td>
<td>39.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\phi$</th>
<th>$c_{\text{SDS}}$</th>
<th>$c_{\text{H}^+}$</th>
<th>$c_{\text{Na}^+}$</th>
<th>$c_{\text{Cl}^-}$</th>
<th>$c_{\text{SO}_4^{2-}}$</th>
<th>$c_{\text{SO}_3^{2-}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>mol/m$^3$</td>
<td>mol/m$^3$</td>
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*: is corresponding to the latex after cleaning.
Appendix II

In shear-driven aggregation, the rate constant of the doublet formation is given by Eq. (2.1)\textsuperscript{92}.

Consider the case of the DLVO interactions. The total interaction energy is a sum of van der Waals attractive energy and the electrostatic repulsive energy Eq. (1.3) and Eq. (1.4).

The first derivative of $U$ reads:

$$U' = -\frac{A_{m}}{6} \left[ -\frac{4a^{2}r}{(r^{2} - 4a^{2})^{2}} - \frac{4a^{2}}{r^{3}} + \frac{8a^{2}}{r^{3} - 4a^{2}r} \right] \frac{4\pi \varepsilon \varepsilon_{0} a^{2} \psi^{2}}{r^{2}} \ln[1 + \exp[-\kappa(r - 2a)]]$$

$$+ \frac{4\pi \varepsilon \varepsilon_{0} a^{2} \psi^{2} \kappa}{r^{2}} \frac{1}{1 + \exp[\kappa(r - 2a)]]}$$

At $r = r_{m}$, $U' = 0$ and $U = U_{m}$. The second derivative reads:

$$U'' = -\frac{A_{m}}{6} \left[ - \frac{4a^{2}}{(r^{3} - 8a^{2}r + 16a^{3} / r)^{2}} (3r^{2} - 8a^{2} - 16a^{3} / r^{3}) \right]$$

$$\quad + \frac{12a^{2}}{r^{4}} - \frac{8a^{2}}{(r^{3} - 4a^{2}r)^{2}} (3r^{2} - 4a^{2}) + \frac{8\pi \varepsilon \varepsilon_{0} a^{2} \psi^{2}}{r^{3}} \ln[1 + \exp[-\kappa(r - 2a)]]$$

$$\quad + \frac{8\pi \varepsilon \varepsilon_{0} a^{2} \psi^{2} \kappa}{r^{2}} \frac{1}{1 + \exp[\kappa(r - 2a)]} + \frac{4\pi \varepsilon \varepsilon_{0} a^{2} \psi^{2} \kappa^{2}}{r} \frac{\exp[\kappa(r - 2a)]}{[1 + \exp[\kappa(r - 2a)]]^{2}}$$

For the colloidal system used in this work, we have $a = 23$ nm, $\varepsilon, \varepsilon_{0} = 6.950 \times 10^{-10}$ C/V/m, $1 / \kappa = 9.62 \times 10^{-9}$ m, and $A_{m} = 1.30 \times 10^{-20}$ J. With these values, considering the surface potential in the range of $\psi \in [0.005, 0.1]$ V, we obtain that at $r = r_{m}$, $U''_{m} \in [-2.07 \times 10^{-4}, -1.79]$. Instead, for the term, $3\pi \alpha \mu \dot{\gamma} a^{3}$, with the values, $\alpha = 1 / (3\pi), \mu = 0.001$ Pa·s and $\dot{\gamma} = 10^{6}$ s$^{-1}$, we have $3\pi \alpha \mu \dot{\gamma} a^{3} = 1.22 \times 10^{-20}$. Therefore, it can be concluded that in general, we have $3\pi \alpha \mu \dot{\gamma} a^{3} \ll -U''_{m}$, and for given colloidal interactions, the rate constant, Eq.(2.1), can be simplified as follows:
\[
\frac{1}{k_{1,1}} \sim \frac{e^{U_m / k_BT}}{\sqrt{\frac{U_m}{k_BT}}} e^{-6\pi eT^2 / k_BT} \sim e^{-6\pi eT^2 / k_BT} = e^{-\alpha(2Pe)}
\]
Bibliography


