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Invited review

Gelation of polymeric nanoparticles

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ABSTRACT

We review how, starting from polymeric nanoparticles, to generate clusters of fractal morphology and to expand the entire space and interconnect to form gels, through either Brownian motion or intense shear-induced aggregation. In the case of Brownian motion-induced gelation, specific techniques developed to obtain uniform structure of gels under both reaction-limited and diffusion-limited cluster aggregation conditions have been described. In the case of intense shear-induced gelation as a newly developed technique, our focus is on its principle, theoretical development and advantages with respect to Brownian motion-induced gelation in practical applications. We consider gelation of both rigid and soft particles. As a physical process, the bonding between the particles within gels is owed to van der Waals attractions, thus being easily broken. However, in the case of soft particles that can coalesce upon contact, the coalescence can allow the particles to stick together forming permanent gels. In this case, the gel structure can be controlled by controlling the degree of coalescence. Techniques used to control the degree of coalescence have also been described.

Contents

1. Introduction

In most cases, polymers can be produced through emulsion polymerization, and are in the form of nano- or colloidal particles dispersed in water, which is referred to as latex. One of the most attractive features of latexes is that when they are properly destabilized the nanoparticles can aggregate to form clusters that are typically mass fractal objects (Lin et al., 1989; Lin, Lindsay, Weitz, Ball, et al., 1990; Lin, Lindsay, Weitz, Klein, et al., 1990; Majolino, Mallamace, Migliardo, Micali, & Vasi, 1989). Thus, their structure can be defined by the following fractal scaling (Kerker, 1969):

$$i = k_f \left(\frac{R_g}{a}\right)^{D_f}, \quad (1)$$

where i and R_g are the mass (i.e., number of particles) and gyration radius of the cluster, respectively, a is the nanoparticle radius, D_f (<3) is the mass fractal dimension, and k_f is the scaling prefactor.

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Extensive numerical simulations (Ehrl, Soos, & Lattuada, 2009) have shown that k_f is well correlated with D_f:

$$k_f = 4.46 D_f^{-2.08}. \quad (2)$$

Therefore, the structure of fractal clusters with a given mass i is characterized by the unique parameter D_f. Since the D_f values are often significantly smaller than 3, from Eq. (1) only a very small amount of mass i is required to form a cluster with a radius R_g.

More importantly, when the aggregation of the nanoparticles is carried out at high particle volume fractions, since the growth of the clusters follows the fractal scaling, the available space would be occupied by all the clusters at a certain degree of aggregation. The clusters would then interconnect, leading to a liquid-like to solid-like transition (Carpineti & Giglio, 1992, 1993; Krall & Weitz, 1998; Kroy, Cates, & Poon, 2004; Lattuada, Wu, & Morbidelli, 2004; Mellema, Heesakkers, van Opheusden, & van Vliet, 2000; Sciortino & Tartaglia, 1995; Wu & Morbidelli, 2001; Wu, Xie, Lattuada, & Morbidelli, 2005). The solid-like matter that is formed is called a gel, and the process is generally referred to as gelation. It is evident that, due to the fractal nature of the clusters, the formed gels are of open structures. Furthermore, it has been observed that during aggregation, depending on the nature (rigid or soft) of the polymeric nanoparticles and their surface properties, upon contact the particles can either retain their original identity within the clusters or partially or fully coalesce (Arosio, Xie, Wu, Braun, & Morbidelli, 2010; Chevalier et al., 1992; Gauer, Wu, & Morbidelli, 2009a, 2010; Jia, Wu, & Morbidelli, 2007; Roldán-Vargas et al., 2008; Roldán-Vargas, Barnadas-Rodríguez, Quesada-Pérez, Estelrich, & Callejas-Fernández, 2009; Urbina-Villalba, 2009; Xie, Arosio, Wu, & Morbidelli, 2011). Since different degrees of coalescence lead to different compactness of the clusters forming the gels, starting from polymeric nanoparticles gels of different structures can be obtained by controlling the degree of coalescence.

In this article, we first review the most common techniques used to generate physical gels from polymeric nanoparticles and discuss their advantages and limitations in practical applications. Then, we describe how to make permanent gels from the physical gels in the case of soft particles through controlled inter-particle coalescence.

2. Gelation of rigid nanoparticles

2.1. Fractal gels from Brownian motion-induced gelation

Due to thermal energy, the polymeric nanoparticles in a latex follow Brownian motion, and collisions between the particles frequently occur. For a stable latex, because charges are typically present on the particle surface, the electrostatic repulsion together with the van der Waals attraction constitutes the so-called DLVO (Derjaguin–Landau–Verwey–Overbeek) interaction, which generates an interaction barrier between the particles (Berg, 2010; Evans & Wennerström, 1999). Thus, the particles repel each other when they collide. If additional electrolytes (salts) are introduced into the latex, screening and counter-ion association effects reduce the interaction barrier (Ehrl, Jia, et al., 2009; Jia et al., 2006). When the barrier is reduced to a certain level, Brownian motion allows the particles to overcome the barrier, leading to effective aggregation between two particles during collision and the formation of a doublet. The bonding between the particles in these cases is typically located in the deep well of the interaction potential, and thus in most cases is irreversible. Of course, the aggregation continues from the doublets to form fractal clusters.

2.1.1. RLCA gels

Depending on whether a small interaction barrier is present, there are two aggregation regimes (Lin et al., 1989):

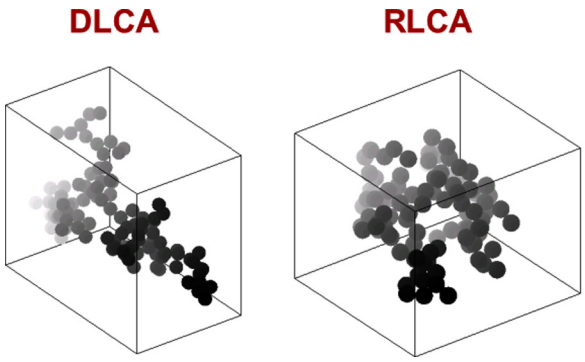

Fig. 1. Typical structures of clusters formed under DLCA and RLCA conditions generated through Monte Carlo simulations.

reaction-limited cluster aggregation (RLCA) in the presence of a small interaction barrier and diffusion-limited cluster aggregation (DLCA) in the absence of any interaction barrier. Moreover, the aggregation kinetics and cluster structure follow certain so-called universal behaviors (Lin et al., 1989; Lin, Lindsay, Weitz, Ball et al., 1990; Lin, Lindsay, Weitz, Klein et al., 1990; Sandkühler, Lattuada, Wu, Sefcik, & Morbidelli, 2005). In the RLCA regime, the average cluster size exponentially increases with time, and the fractal dimension D_f is in the range 2.05–2.15. In the DLCA regime, the aggregation kinetics follows a power-law and the D_f value is in the range 1.75–1.85, that is, more open structures are obtained with the DLCA regime than with the RLCA regime. It should be noted that in both regimes the D_f values are considerably less than 3, leading to very open structures of the clusters, as represented by the clusters generated through Monte Carlo simulations in Fig. 1. With such open structures, the growing clusters can easily fill the entire space, and interconnection among the clusters occurs, leading to the transition from the initial liquid-like latex to a solid-like state, that is, the gel mentioned above. The most attractive feature of Brownian motion-induced gelation is that a solid-like gel can be easily formed with a particle volume fraction $\phi > 2\%$ (Lattuada et al., 2004). This indicates that with ideal Brownian motion-induced gelation, materials can be generated with void greater than 90%.

Brownian motion-induced gelation is commonly carried out under RLCA conditions (Gisler, Ball, & Weitz, 1999; Krall & Weitz, 1998; Poon & Haw, 1997; Sandkühler, Sefcik, & Morbidelli, 2004a, 2005; Sonntag & Russel, 1987; Wu, Xie, Lattuada, Kohlbrecher, & Morbidelli, 2011; Wu et al., 2005; Wu, Xie, & Morbidelli, 2013), because in RLCA the aggregation rate can be easily controlled by tuning the height of the interaction barrier, thus ensuring homogeneity of the gel morphology. Although a gel is solid-like, it shrinks if it is dried due to the nature of the physical bonding. Thus, the structure characterized by normal scanning electron microscopy (SEM) or transmission electron microscopy (TEM) does not represent the true structure of a gel before drying. Using a cryo-SEM or TEM technique through gel vitrification, one may obtain true images of gels. Wyss, Hütter, Müller, Meier, and Gauckler (2002) performed cryo-SEM in the case of gelation of silica particles (Fig. 2(a)). However, due to the very high volume fraction of silica particles ($\phi = 40\%$) and the projection effect of all the particles, pores cannot be clearly seen inside the gel. Instead, the image obtained from the Brownian dynamic simulations under the same conditions, but with fewer particles, clearly shows the presence of pores (Fig. 2(b)). Light scattering techniques are commonly used to characterize structures of fractal clusters, but gels formed from most polymeric nanoparticles at high particle volume fractions are too turbid to be characterized by light scattering techniques.

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