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Short communication

Trace the polymerization induced by gamma-ray irradiated silica particles

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HIGHLIGHTS

- Pre-irradiation of γ-ray enables an effective synthesis of polymer/inorganic nanocomposites toward pre-selected properties.
- Solution dynamics and electron microscopic studies reveal the formation mechanism of the nanocomposites.
- Reaction time is a critical parameter to achieve desirable organic/inorganic nanocomposite structure in a given system.

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ABSTRACT

A γ-ray irradiation to inorganic particles is a promising technique for preparation of organic/inorganic composites as it offers a number of advantages such as an additive-free polymerizations conducted under mild conditions, avoiding undesired damage to organic components in the composites. Herein, we demonstrated a step-wise formation mechanism of organic/inorganic nanocomposite hydrogel in detail. The γ-ray irradiation to silica particles dispersed in water generates peroxide groups on their surface, enabling surface-initiated polymerization of acrylic acid from the inorganic material. As a result, poly (acrylic acid) (PAA) covers the silica particles in the form of a core-shell at the initial stage. Then, PAA-coated silica particles associate with each other by combination of radicals at the end of chains on different particles, leading to micro-gel domains. Finally, the micro-gels are further associated with each other to form a 3D network structure. We investigated this mechanism using dynamic light scattering (DLS) and transmission electron microscopy (TEM). Our result strongly suggests that controlling reaction time is critical to achieve specific and desirable organic/inorganic nanocomposite structure among core-shell particles, micro-gels and 3D network bulk hydrogel.

1. Introduction

Nanocomposites have attracted tremendous scientific and technical interests due to their exceptional mechanical, (Afroze et al., 2016; Lee et al., 2013; Ye et al., 2007) electrical, (Chapman and Mulvaney, 2001; Ye et al., 2007) optical, (Chapman and Mulvaney, 2001; Wang et al., 2015; Wilson et al., 2002) and thermal properties (Balayeva and Mamiyev, 2016; Ye et al., 2007; Yoon et al., 2002). In particular, organic/inorganic nanocomposites have been extensively explored as the platform allows modifying a variety of properties by realizing their potential from bulk to molecular level (Burnside and Giannelis, 1995). A γ-ray irradiation method has been considered as one of promising techniques for an effective synthesis of organic/inorganic nanocomposites, as the process is easily controlled and the system is simultaneously sterilized effectively. Furthermore, since γ-ray initiates polymerization or induces crosslinking in the nanocomposites, the resulting composites do not include any additives such as initiators and crosslinkers or by-products which possibly degrade desired properties in the composites (Chapiro, 1964; Huang et al., 2007).

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Therefore, γ-ray irradiation has been utilized to tailor the properties of materials to make them more versatile for further applications such as semiconductors, (Xie et al., 1999) membranes, (Kim et al., 2016) food packaging, (Madera-Santana et al., 2016) smart adhesive plasters (Yoshii et al., 1995) and hydrogels (Carenza, 1992).

However, direct high-energy γ-ray irradiation to organic materials such as monomers or polymers can induce undesirable chemical reactions such as decomposition or unintended cross-linking in resulting composites. Thus, the resulting chemical/physical structure and properties are not rationally predicted. To address this challenge, a pre-irradiation method has been proposed and explored where the inorganic materials such as silica fillers directly are treated with γ-ray irradiation which produces peroxide groups on their surfaces (Griscom et al., 1994; Lee et al., 2013). The peroxide groups undergoes homolytic cleavage to result in silyloxy radicals on particle surfaces which allows surface-initiated polymerization (SIP) at mildly heated environment, *e.g.* 40 °C. Therefore, the pre-irradiation method enables avoiding any damages to organic components in nanocomposites during γ-ray irradiation process.

Using this method, we previously reported an additive-free preparation of polymer/inorganic particle nanocomposite hydrogel which exhibited high mechanical strength (Koo et al., 2012; Lee et al., 2013). The results strongly suggested that pre-irradiation method provided an efficient route to tailor physical properties in soft materials, however, details in the mechanism to form the final structure has not been investigated yet. Herein, we systematically studied how the system evolves from γ-ray treated silica nanoparticles, silica/PAA core/shell nanoparticles to microgels by combining solution dynamics and microscopic studies using dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques. Careful examination of the process as a function of reaction time allows us to gain deep understanding in the formation of 3D network gel structure. Furthermore, current studies highlight the potential of γ-ray to synthesize various types of organic/inorganic nanocomposites from suitable monomer and inorganic particles to achieve desirable properties for target applications.

2. Experimental details

2.1. Materials

Tetraethyl orthosilicate (TEOS), ethanol, aqueous ammonia solution (NH_4OH) and acrylic acid (AA) were purchased from Sigma Aldrich and were used without further purification. Deionized water (DI water, resistivity of > 18.2 MΩ cm) was obtained using Milli-Q system.

2.2. Silica particle synthesis

Silica particles were synthesized using Stöber method (Stöber et al., 1968). A solution of ethanol (150 mL), TEOS (9 mL) and NH_4OH (3 mL) in a 250 mL volumetric flask was stirred for 24 h, resulting in spherical silica particles with a radius of 63 nm. The solution was washed thrice with ethanol and subsequently with DI water twice.

2.3. Surface modification of silica particles by γ-ray irradiation

An aqueous solution of silica particle (2 wt%) in a narrow-necked ampoule (2 cm in diameter and 5 cm in length) was subjected to ^{60}Co γ-rays at a dose of 10 kGy h^{-1} (at KAERI, Jeongeup, Korea) at ambient conditions for 2 h to create peroxide groups on the surfaces of silica particles. The resulting samples were stored at 0 °C before the polymerization process.

Following previous studies on peroxide formation on the silica surface, (Griscom, 1985; Imai and Hirashima, 1994; Kokatnur and Jelling, 1941) the formation of peroxide groups on the silica particle was confirmed using iodometry which is a common method to verify peroxide groups in various systems (Kim et al., 2009). Potassium iodide and isopropyl alcohol were added to the irradiated silica particle solution. After a reflux for 30 min, the solution gradually turned to yellow color which indicates the formation of I_2, confirming the presence of peroxides on the silica particle. Generated peroxide group by γ-ray irradiation is used as an initiator for surface-initiated polymerization.

2.4. Synthesis of PAA/silica nanocomposite

1 mL of Acrylic acid was added to 2 mL of γ-ray irradiated 2 wt% silica particle solution, then dissolved gas was removed by freeze-pump-thaw process for three times. Then, the solution was heated up to 40 °C to initiate the polymerization. The polymerization times was controlled for 30 min, 2 h, 6 h and 12 h, to trace surface-initiated polymerization process.

2.5. Characterizations

DLS experiments were performed with a UNIPHASE He-Ne laser operating at 632.8 nm. The detector equipment employed optical fibers coupled to an ALV/SO-SIPD/DUAL detection unit with an EMI PM-28B power supply and ALV/PM-PD pre-amplifier discriminator. An ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels was used to produce correlation functions. The laser beam passed through a cylinder scattering cell which was located in a bath of decaline as a refractive index matching solvent, then passing through a 400 nm pinhole before reaching the detector.

The decay rate (Γ) was calculated from the Eq. (1) with correlation functions obtained at nine scattering angles in 30–150°,

$$\Gamma = 1/\tau \tag{1}$$

where τ is an average decay time. The diffusion coefficient (D_t) was calculated using Eq. (2) and Eq. (3).

$$\Gamma = D_t q^2 \tag{2}$$

$$q = (4\pi n/\lambda)\cdot sin(\theta/2) \tag{3}$$

where n is a refractive index of a solvent, q is a scattering vector, λ is the wavelength of incident light and θ is a scattering angle. The hydrodynamic radius (R_h) is obtained from D_t using Stokes-Einstein equation (Eq. (4)),

$$R_h = k_b T/6\pi\eta D_t \tag{4}$$

where k_b is Boltzmann constant, T is temperature and η is solvent viscosity.

TEM and STEM images were obtained with JEOL JEM-2100F with operation voltage of 200 kV. Aliquots were taken after desired reaction time, followed by exposing to air with cooling down for quenching. Then a drop of sample was placed on 200 mesh copper Formvar carbon coated TEM grid.

3. Results and discussion

The gel formation process can be explained with four stages: (1) initiation on silica nanoparticle surface, (2) propagation of AA