

Interpenetration of polymer chains on particle surfaces in latex films determined by small-angle X-ray scattering

Polymeric latex films play important roles in industrial coatings, paintings, and adhesives. Water-borne latex films are particularly interesting in this context, as they are obtained by evaporating water from aqueous dispersions of polymeric latex particles, and thus reduce/circumvent the use of volatile organic compounds (VOCs) during film formation. To prepare water-borne latex films, the glass-transition temperature T_g of the particles should ideally be lower than the drying temperature, i.e., the hydrophobic particles should be allowed to interpenetrate each other after the evaporation of water (Fig. 1(a)). However, water-borne latex films usually show poor mechanical strength as is usually the case with latex polymers with a low T_g [1,2]. Thus, tremendous efforts have been devoted to the structural analysis and the understanding of the toughness of latex films. Nevertheless, a method for the quantitative analysis of the interpenetration between polymer chains on particles remains elusive. In this study, small-angle X-ray scattering (SAXS) was applied to characterize latex films.

Here, the latex films were prepared with three types of particle synthesized by mini-emulsion polymerization under the same conditions. The tested particles are rotaxane crosslinked (RC), chemically crosslinked (CC), and non-crosslinked (NC) particles, respectively (Fig. 1(b)). The rotaxane crosslinking points affect the flexibility of the polymers in the particles (the so-called ‘stress relaxation’). In addition, annealing increased the fracture energy of the latex films used in this study and was more effective for latex films composed of RC particles than for those composed of NC and CC

particles [1,2]. Accordingly, chemically ‘clean’ latex-film systems were suited as models for the evaluation of the interpenetration of polymer chains.

The latex films were examined at 25°C under vacuum by SAXS using synchrotron X-rays sourced at SPing-8 BL03XU. The SAXS profiles of dry RC, CC, and NC films are displayed in Fig. 2(a). For all films, peaks were observed in the range of the measured scattering vector (q). These peaks seem to reflect the ordered structure of the particles in the films and are the Bragg peaks derived from face-centered cubic colloidal crystals. However, detailed information on the interpenetration of near-surface polymer chains on these microspheres remains unclear.

To quantitatively analyze the interpenetration degree of polymer chains on the particles in these latex films, we used SAXS analyses to determine the thickness of the domain boundaries in the block copolymers [3]. For those cases, a model for the trapezoidal electron-density variation for the domain structure was developed, where the block copolymer forms the domain structure (the so-called ‘pseudo-two-phase system’). In brief, this method examines the SAXS intensity in the high- q region. According to Ruland’s theory for two-phase materials with diffuse boundaries, the domain boundary thickness can be determined using Porod’s law by analyzing the deviation of the scattering curves in the high- q region, where the intensity is expressed by $I(q) = Cq^{-4} \exp(-\sigma^2 q^2)$, with C being a constant and σ the diffuseness of the boundary. Consequently, a plot of $\ln[q^4 I(q)]$ as a function of q^2 affords a straight line, wherein the slope affords the parameter σ .

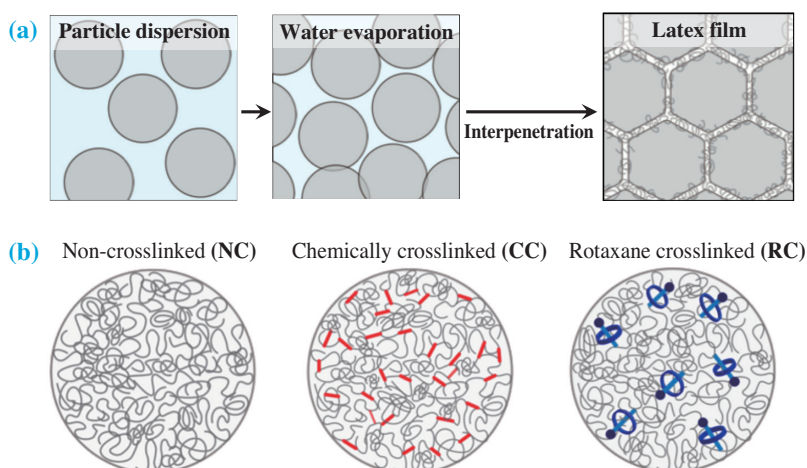


Fig. 1. (a) Scheme of latex film formation and (b) illustrations of the tested non-crosslinked (NC), chemically crosslinked (CC), and rotaxane-crosslinked (RC) particles. [4]

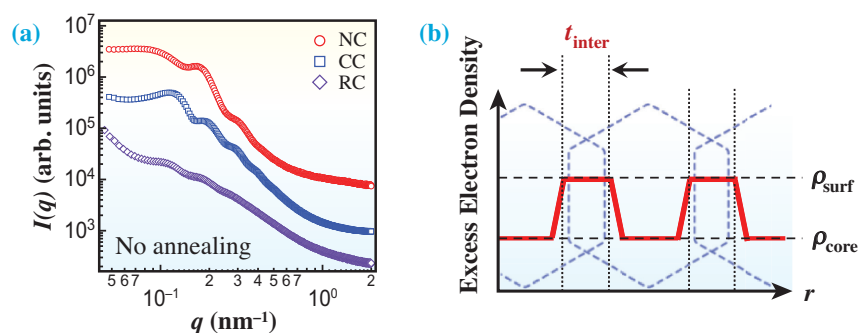


Fig. 2. (a) SAXS intensities of NC, CC, and RC latex films obtained at SPring-8 BL03XU. The data are reprinted from Ref. 4. (b) Model of trapezoidal electron-density variation (red line) for the packed structure of the particles (blue dashed line).

Here, the domain boundary thickness (t_{inter}) is given by $t_{\text{inter}} = (2\pi)^{1/2}\sigma$. In the latex films, we assumed the pseudo-two-phase system that consists of a low-density particle core (ρ_{core}) and a high-density interphase between the particle surfaces (ρ_{surf}) (Fig. 2(b)). Thus, t_{inter} can be regarded as the characteristic interfacial thickness and/or the degree of interpenetration of the polymer chain on the particles.

The obtained t_{inter} exhibited the annealing time dependence (Fig. 3(a)). Without annealing (0 h), t_{inter} decreases in the order of NC (3.3 nm) > RC (3.1 nm) > CC (2.5 nm), which indicates that NC particles exhibit high deformability and flexibility due to the lack of crosslinking. Moreover, the difference between RC and CC particles may be due to the fact that the rotaxane crosslinking points endow the polymer chains in the individual particles with mobility during the formation

of the films. On the other hand, the interpenetration of polymer chains on CC microspheres may be suppressed owing to the increased rigidity of the individual particles.

Furthermore, t_{inter} of latex films strongly affects their toughness, i.e., fracture energy (Fig. 3(b)). In particular, the increments of both t_{inter} and the fracture energy of the RC latex film are higher than those of the NC films, resulting in a relatively steep slope. The rotaxane crosslinker thus enhances the interpenetration with and without annealing. Therefore, the rotaxane crosslinker provides synergetic effects in the film in terms of both polymer interpenetration on the particle surface and stress relaxation [4]. We are convinced that the proposed method represents a universally applicable strategy to quantitatively analyze microscopic interdiffusion in latex films and, potentially, in other colloidal crystals [5].

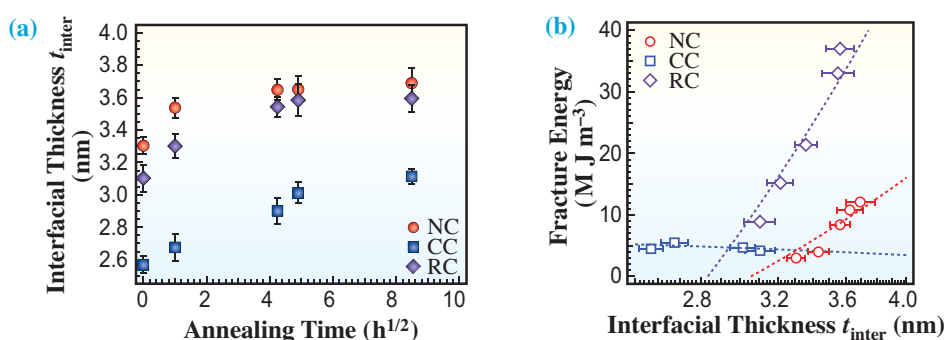


Fig. 3. (a) Interfacial thickness (t_{inter}) of the tested latex films. (b) Relationship between t_{inter} and the fracture energy of NC, CC, and RC latex films. [4]

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