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Fabrication and evaluation of one-component core/shell structured latex adhesives containing poly(styrene) cores and poly(acrylate) shells

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ABSTRACT

A one-component, non-crosslinked, and ambient temperature-cured core/shell (CS) structured waterborne poly(styrene-acrylate) (PStA) latex adhesive was prepared by two-stage seeded emulsion polymerization. The first-stage polymers were non-polar styrene-based copolymers with T_gs ranging from 86 °C to 41 °C and the second-stage polymer was polar acrylate-based copolymer having a T_g of 8 °C. The effect of latex particle morphology and film microstructure on the CS structured PStA latex adhesive was examined by evaluating film thermal properties and mechanical performance. The results have shown that incorporation of soft shell polymers into hard core polymers can improve adhesive properties without compromising film-forming ability. Wood adhesive performances of latex adhesive were measured by shear strength and boiling water resistance of glued wood blocks. The utilization performances of the one-component CS structured PStA latex adhesive were found to largely depend on CS morphological character and the interfacial compatibility between various polymeric constituents, demonstrating that fabrication of CS latex particles provides a promising approach to realize high-performance latex adhesives.

1. Introduction

The outstanding properties of polymer colloids make them promising candidates as waterborne products for various industrial applications [1,2], especially in the field of adhesives [3]. Moreover, there is also a scientific need for sufficient understanding to permit the development of high-performance latex adhesives that are environmentally friendly. In recent decades, poly(styrene-acrylate)-based (PStA) wood adhesives have attracted great interest due to their low cost, good adhesion performance, non-pollution, and excellent cold water-resistance. However, a major issue which is associated with PStA latex adhesives arises from the competition between latex film formation and mechanical properties of the resultant film. Latex film, mainly regarded as glueline, is one of the most decisive control factors during the conventional gluing process. It has been demonstrated that PStA emulsions composed of low glass transition temperature (T_g) polymers, although exhibiting good film-forming abilities, often result in poor mechanical properties upon adhesion to a substrate [4]. On the contrary, high-T_g polymer-based PStA emulsions exhibit difficulty forming a continuous glueline on a substrate at ambient temperature, or the resultant film formed is so brittle that it cannot form a strong bonded joint. In order to simultaneously improve the film-forming ability and mechanical properties of a PStA latex adhesive, a film-forming aid is commonly added to the formulation prior to the film forming process. However, film-forming aids usually contain volatile organic compounds (VOC), which can lead to environmental pollution and a health hazard [5]. Therefore, another significant driving force for the development of high-performance waterborne PStA latex adhesives is the demand to decrease the VOC emissions from film coalescing agents used during the bonding process.

Numerous studies have reported on possible approaches to overcome the lack of film-forming ability and/or mechanical strength to improve the performance of PStA latex adhesives [6–8]. Those that have been more successful have tended either to incorporate copolymers, or to introduce crosslinking within the PStA polymer network. In fact, no simple one-component PStA formulation is commercially available that can offer the potential to overcome all of the shortcomings of PStA latex adhesives. Among the various methods considered, fabricating core/shell (CS) structured composite latex particles is an alternative strategy to resolve this dilemma [9,10]. CS emulsions comprise composite particles which are composed of a polymer core engulfed in a polymer shell. CS composite particles that consist of two or more different homopolymers or copolymers with distinguishing thermodynamic properties can be produced in a two-stage emulsion polymerization process, especially in semi-continuous starved

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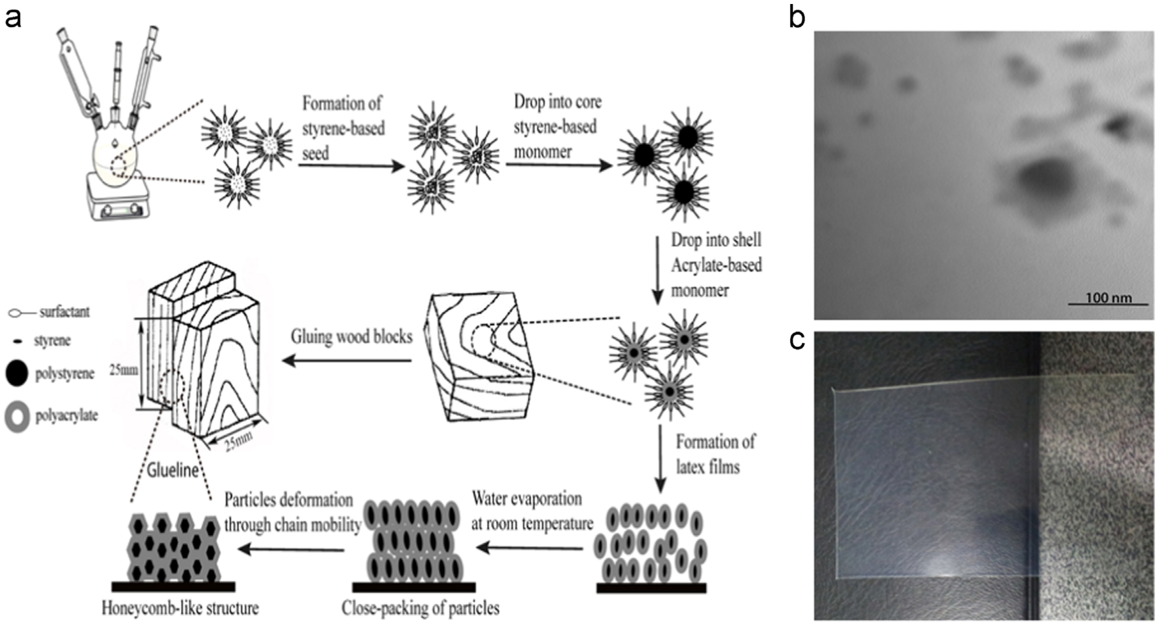

Fig. 1. (a) Schematic diagram showing the fabrication process of CS latex particle and its film. (b) TEM image of produced CS latex particle (CBA2). (c) Photograph of obtained transparent film (CBA6).

mode. CS latex polymers can display a wide range of tailored physical or chemical properties because of their various phase morphological features and compositions. It has been well accepted that the ultimate morphology of a CS latex particle is controlled by a combination of thermodynamic and kinetic factors [11,12]. However, this is an oversimplified description and the full analysis to this complicated subject is much more diversified [13,14]. Nevertheless, in past decades, numerous investigations have emerged to reveal the phase structure of CS latex particles [15–18], facilitating the development of high-performance composite emulsions with tailored properties.

The attractive aspect of CS morphology in a PStA latex adhesive is that it provides a way to control latex film structure and morphology at the nanoscale. The film-forming process from the CS structured latex is illustrated in Fig. 1(a). Upon drying, close-packed latex particles could deform into a honeycomb-like structure, however, retaining the special architectural characteristics of CS morphology [1,19]. Thus the properties of the resultant CS latex film can be largely dependent on the morphological features of the original composite latex particles [20]. It is anticipated that in a CS structured PStA latex adhesive, the combination of the hard non-film-forming poly(styrene)-based core together with a soft poly (acrylate)-based shell that forms a film at ambient temperature, could result in an adhesive that results in a hard glueline formed at low temperature without releasing VOCs from film-forming aids. The corresponding dry films can be described as equivalent to continuous honeycomb-like morphological matrices containing discrete rigid inclusions. Cavaille et al. [21,22] reported the improved mechanical performances of latex films obtained from CS structured poly(styrene)/poly(butyl acrylate-methacrylic acid) emulsion polymers than those of either random copolymerization or blending of the same compositions. However, the structure-property relationship of the latex particle morphologies and the structured PStA latex adhesive has not been fully investigated. Therefore, it is considered that there are both scientific and application reasons for designing and manufacturing CS structured PStA latex adhesives.

In this study, one-component, non-crosslinked, and ambient temperature-cured CS structured poly(styrene-acrylate)-based latex adhesive has been synthesized by a two-stage seeded emulsion polymerization process. The first-stage poly(styrene-co-butyl acrylate) core, was prepared with varying amounts of butyl acrylate, and the identical second-stage monomers were introduced into the core particles by a semi-continuous starved addition mode, producing a poly(butyl acrylate-co-methyl methacrylate-co-acrylic acid) shell. Thermal and mechanical properties of CS structured PStA latex adhesive were characterized by differential scanning calorimeter (DSC), dynamic mechanical analyzer (DMA), and universal testing machine. Wood adhesive performances of PStA latex adhesive were measured through shear strength and boiling water resistance. Evaluations of adhesive films and glue bonds of CS structured PStA latex adhesives were undertaken in order to investigate the relationships between latex particles morphology and adhesive performance.

2. Experimental

2.1. Materials

Styrene (St) was purchased in reagent pure grade (99.8%) from Tianjing Fuchen Chemical Reagents Factory. The other monomers, including butyl acrylate (BA, $\geq$99%, Tianjing Fuchen), methyl methacrylate (MMA, 99%, Tianjing Guangfu), and acrylic acid (AA, 99%, Tianjing Kermel) were purchased in reagent pure grade and used without further purification. Initiator ammonium persulfate (APS, $\geq$98%, Tianjing Kermel), buffering agent sodium bicarbonate ($NaHCO_3$, $\geq$99.5%, Tianjing Kermel), anionic emulsifier sodium dodecyl sulfate (SDS, $\geq$99%, Guangdong Xilong), and nonionic emulsifier octylphenol polyoxyethylene ether (OP-10, Tianjing Kermel) were purchased in reagent pure grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Latex preparation

All the synthesis were performed in a 500 mL four-necked flask with a reflux condenser, a thermometer, a mechanical stirrer and a feeding tube for monomer mixtures and initiator solutions. The reactor was immersed in a thermostatic water-bath for controlling