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## The effect of core–shell particle morphology on adhesive properties of poly(styrene-co-butyl acrylate)

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## ABSTRACT

The objective of this work was to develop poly(styrene-co-butyl acrylate) emulsion based adhesives that simultaneously exhibit high cohesive and adhesive strength via structured core–shell particle design. The structure–property relationship was examined and optimized through changing the core–shell ratio, crosslinking of the core by using ethylene glycol dimethacrylate (EGDMA) crosslinker and modification of the soft shell by varying the concentration of a thiol based chain transfer agent (CTA). The prepared polymers were characterized by size-exclusion chromatography (SEC), cryogenic transmission electron microscopy (cryoTEM), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Crosslinking of the core part enables high cohesive strength of the adhesive, whilst the relatively soft shell facilitates adhesion by enabling the proper wetting of the substrate. The optimal adhesive performance in terms of tack, peel strength and shear strength was achieved when the latex particles had a crosslinked core, a shell prepared without CTA and a core–shell ratio of 1:1.5. Thus, we achieved the goal of combining sufficient energy storage and energy dissipation properties in one particle through structured particle design.

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## 1. Introduction

Replacement of solvent-based adhesives by environmentally sound waterborne products that practically emit insignificant amounts of volatile organic compounds (VOCs) and that also otherwise meet the performance requirements of adhesives has been a topic of intensive research during the past decades. Nowadays aqueous polymer emulsions have found wide use as binders, adhesives, paints and inks, etc. [1–7]. However, in recent years the adhesive industry has faced yet another challenge related to the elimination of so-called secondary emissions from construction adhesives. One recent representative example of such a secondary pollutant compound is 2-ethyl-1-hexanol, which may

*Abbreviations:* VOCs, volatile organic compounds; MFT, minimum film formation temperature;  $T_g$ , glass transition temperature; CTA, chain transfer agent; DSC, differential scanning calorimetry; SEC, size exclusion chromatography; CryoTEM, cryogenic transmission electron microscopy; DMA, dynamic mechanical analysis; BuA, butyl acrylate; St, styrene; AA, acrylic acid; EGDMA, ethylene glycol dimethacrylate; Dm, 1-dodecanethiol; KPS, potassium persulfate; TBHP, tert-butyl hydroperoxide; NaOH, sodium hydroxide solution; THF, tetrahydrofuran; Mn, number average molecular weight; Mw, average molecular weight; PDI, polydispersity index; LT-ELSD, low temperature evaporative light scattering detector; PSA, pressure sensitive adhesive; Mc, molecular weight between crosslinks

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be hazardous or pose a risk to human health and/or environment [8]. This indoor air polluting component is mainly generated from the decomposition of poly(2-ethyl hexyl acrylate) or its copolymers via hydrolysis under strongly alkaline conditions (pH 13). Still today, 2-ethyl hexyl acrylate (EHA) is a commonly used monomer in commercial waterborne adhesive emulsions [9–11]. As a consequence, the objective of this work was to develop an EHA-free waterborne adhesive emulsion without sacrificing the crucial adhesion properties.

Besides today's ecological necessities there are several other basic requirements that need to be fulfilled. The adhesive must have proper rheology to ensure surface wetting and adhesion, but also good cohesion to deliver mechanical strength. From a practical point of view, these are expressed as a proper combination of tack, peel and shear strength [12]. In addition, the minimum film formation temperature (MFFT) is required to be low to attain film formation at ambient application temperatures. The fulfillment of these prerequisites is closely related to the structural features of latex such as particle size, particle morphology, crosslink density, gel content, molecular weight and its distribution as well as the glass transition temperature ( $T_g$ ) [13,14]. These characteristics in turn mainly depend on the polymer's chemical composition and process conditions. The nature of emulsion polymers is referred to as “products by process” which implies that the main properties of latex are determined during the polymerization process itself [1].

Consequently, the choice of latex components, polymerization parameters and the design of latex particles are critical for optimizing adhesive properties and the adhesive's performance in the intended end-use applications. Among various emulsion based adhesives, poly(styrene-co-acrylate) latexes are well-known for their versatility as adhesives and coatings [6]. Latexes with different combinations of soft and hard segments provide diversity in performance, as the soft polyacrylate promotes tack and the hard polystyrene enhances mechanical strength. In addition to the main monomers, a small quantity of an acid-functional monomer (no more than 1.5% of dry polymer), such as acrylic acid (AA), is required in the latex formulation. The repulsive negative charges on the latex particle surfaces enhance the colloidal stability and also improve peel and shear strength by enabling ionic bonding [6,15]. Additional components such as emulsifiers, initiators, redox agents and pH adjusters are also of great importance for achieving optimal properties of the final latex. Special attention has been paid on the emulsifier systems, and endocrine disruptive compounds such as alkylphenol ethoxylates (APEO) are increasingly replaced by alternative nonionic emulsifiers that comply with the concept of sustainability [16,17].

Today, poly(styrene-co-acrylate) based emulsions with a uniform particle morphology are most commonly applied as pressure sensitive adhesives (PSAs) and because of their relatively low mechanical strength they are not ideal as load bearing adhesives per se. On the other hand, high strength poly(styrene-co-acrylate) latexes intended for construction adhesives can be achieved via proper design of particle morphology. Core-shell emulsions are commonly used representatives of heterogeneous structures used to design emulsion polymers with versatile properties [4,14,18]. The difference in the microstructure of the core and the shell enables the combination of sufficient energy storage and dissipation properties in the same particle [19,20]. In addition to different ratios of soft and hard monomers in the core and the shell, crosslinkers and chain transfer agents (CTAs) can be used to further create distinctive properties in the named layers. Crosslinkers improve cohesive strength by creating a rigid polymer network structure, whereas the use of CTA enhances polymer chain flexibility and mobility, which in turn enables enhanced adhesion by allowing the polymer chains to interpenetrate into the voids of the substrate. Generally, the core-shell particles can be built up of a rigid core and a soft shell or vice versa. In the case of an emulsion based adhesive, the rigid core-soft shell type is preferable, as the crosslinked core offers sufficient cohesive strength, and the flexible shell consisting of a low molecular weight polymer simultaneously provides enhanced wetting and adhesion to a substrate [6].

In this work, a series of waterborne poly(styrene-co-butyl acrylate) latexes with a rigid core and a soft shell structure have been synthesized via semi-batch emulsion polymerization, and the chosen chemical and particle design parameters have been correlated to the adhesion performance. Thus, the overall objective has been to design latexes with low VOCs, that are free of endocrine disrupting substances and that exhibit an enhanced adhesion performance in terms of a balanced combination of tack, peel strength and shear strength compared to conventional latex particles with a uniform composition.

Samples have been characterized by differential scanning calorimetry (DSC), size-exclusion chromatography (SEC), cryogenic transmission electron microscopy (cryoTEM) and laser diffraction techniques. In addition, dynamic mechanical analysis (DMA), tensile and shear tests have been utilized for determining mechanical properties of the adhesive films.

## 2. Experimental procedures

### 2.1. Materials

The following chemicals were used: Disponil FES 32 (BASF, 31%), Disponil NG 3070 (BASF, 70%), butyl acrylate (BuA) (Dow, 99.5%), styrene (St) (Sigma Aldrich, 99%), acrylic acid (AA) (Ecem, 99.5%), ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, 98%), 1-dodecanethiol (Dm) (Sigma Aldrich, 98%), potassium persulfate (KPS) (BASF, 99%), tert-butyl hydroperoxide (TBHP) (AkzoNobel, 70% in H<sub>2</sub>O), the reduction agent Bryggolit C (Bruggemann Chemical, 40%), the preservative Proxel (Arch, 9.25%), sodium hydroxide solution (NaOH, 13.5%) (J.T. Baker, 99.7%), tetrahydrofuran (THF) (Sigma Aldrich, 99%) and methanol (Sigma Aldrich, 99%). Distilled water was used in all polymerizations. All chemicals were of commercial grade and were used as received.

### 2.2. Polymer latex preparation

The poly(styrene-co-butyl acrylate) latexes were synthesized via semi-batch emulsion polymerization, which were carried out in a 1 L five-neck glass mantled reactor equipped with a thermostated water bath, a mechanical agitator with a perforated steel paddle, a reflux condenser as well as two feeding inlets for pre-emulsion and initiator solutions, respectively. Peristaltic pumps were used to ensure an even feeding of the solutions.

Both core and shell pre-emulsions were prepared by mixing emulsifiers and monomers (i.e. BuA, St and AA) for 15 min at room temperature. Distilled water, Disponil FES 32, Disponil NG 3070 and KPS solution were charged into the reactor, while pre-heating to 80 °C under agitation (200 rpm). Core pre-emulsion and the corresponding KPS solution were simultaneously fed into the reactor over 1 h and subsequently post-polymerized for 30 min. Then shell pre-emulsion and the corresponding KPS solution were simultaneously fed into the reactor for 1 h 40 min. After finalizing the feed, the temperature was set to 65 °C and the agitation speed was adjusted to 300 rpm. The system underwent post-polymerization for 2 h before the redox agents (TBHP and Bryggolit C) were successively dropped into the reactor within 20 min in order to ensure the consumption of monomer residues. The system was left to react for an additional 30 min at 65 °C before being cooled down to 20 °C and then being charged with the preservative. To enhance the colloidal stability, 1 wt% of Disponil NG 3070 was post added. Then the pH was adjusted by 13.5% NaOH solution to 6. The obtained milky latex was weighed and vacuum filtered through a pre-weighed 125 µm filter screen in order to measure the amount of coagulum in the latex.

The basic formulation of the sample 0 is shown in Table 1. Based on the basic formulation (Table 1), other samples were synthesized by changing the following variables: the incorporation of the crosslinker EGDMA in the core, different concentration of CTA in the shell and varying the ratio of core to shell (1:1.5 and 1:1). The samples were labeled, for example, sample 0-O-0-1:1.5 (sample code-O (without crosslinker)/X (0.45% crosslinker EGDMA)-CTA amount-ratio of core to shell). The general information on different samples and their particle sizes are shown in Table 2.

### 2.3. Characterization

#### 2.3.1. Characterization of the polymer emulsion and films

The coagulum amount and solid content were determined gravimetrically. The coagulum amounts of all samples were determined to be less than 0.1%. The solid contents of all samples were 49.4% (± 0.4%). Latex particle sizes were measured using a laser diffraction instrument (LS 13 320 Particle Size Analyzer,

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