



# Modification of latex microstructure and adhesive performance using d-Limonene as a chain transfer agent



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## ABSTRACT

Core-shell latex-based pressure-sensitive adhesives comprising n-butyl acrylate, styrene and acrylic acid were prepared via two-stage seeded semi-batch emulsion polymerization. d-Limonene (Lim) was used as a renewable chain transfer agent. Adhesive performance was modified by manipulating the microstructure of both the latex particle cores and shells. In the first stage of the polymerization, the concentrations of Lim and divinylbenzene (DVB) crosslinker were varied to alter the core microstructure and thus, the cohesive strength of the adhesive films. The particle shell microstructure was modified in the second stage of the polymerization by varying only the amount of Lim. As a result, a variety of particle microstructures and morphologies were generated. Tack and peel strength decreased with increasing Lim concentration while shear strength showed a maximum at a moderate core Lim concentration of 2 phm. Empirical models were developed using stepwise regression to correlate tack, peel strength and shear strength to Lim concentration in the core/shell and DVB concentration in the core.

## 1. Introduction

Water-based pressure sensitive adhesives (PSAs) are in high demand for packaging applications because they have a high solids content and are devoid of hazardous solvents. Latex-based adhesives have found wide application as labels, food-contact packaging, medical tapes and many others. Acrylic adhesives demonstrate the advantage of colorlessness, excellent cohesive strength and necessary tack and peel strength, as well as good resistance to heat and aging [1,2].

In a typical latex-based acrylic adhesive formulation, one finds a combination of “soft” monomers, “hard” monomers and some functional monomers [3]. Soft monomers, whose polymer have a low glass transition temperature ( $T_g$ ), such as n-butyl acrylate (BA,  $T_g = -54\text{ }^\circ\text{C}$ ) and 2-ethylhexyl acrylate ( $T_g = -50\text{ }^\circ\text{C}$ ), provide viscosity, flow and wetting abilities, which ultimately impart properties such as tack and peel strength to the PSA film. Hard monomers, whose polymer have a high  $T_g$ , such as styrene (Sty,  $T_g = 100\text{ }^\circ\text{C}$ ) and methyl methacrylate ( $T_g = 105\text{ }^\circ\text{C}$ ), offer hardness and internal strength to the PSA. The addition of small amounts of functional monomers such as acrylic acid (AA) can impart polarity and balance the viscous-elastic properties, adhesion and internal strength of the PSA film [4–6]. In recent years, latexes with a core-shell particle morphology have enabled outstanding control over the adhesive properties by combining polymers with

different microstructures in the same particle [7–11].

Crosslinker and chain transfer agent (CTA) are two common modifiers used to tailor polymer microstructure and properties. In general, the addition of a CTA would increase the flexibility and mobility of adhesive polymers by reducing the molecular weight and the gel content level [12]. An increase in crosslinker concentration would result in an increase in gel content, which improves the rigidity and the internal strength of the PSA [13,14]. Manipulating both CTA and crosslinker concentrations simultaneously allows for a broad range of polymer microstructure and adhesive performance [15–18]. Thiol compounds such as tert-butanethiol and n-dodecanethiol, are the most commonly used CTAs in emulsion polymerization due to their water solubility and high efficiency [19–21]. However, thiols exhibit an unpleasant odor and are considered as a VOC which is counter to sustainable practice.

Terpene is one of the largest naturally occurring chemical feedstocks, and is a constituent of essential oils found in many conifer and citrus plants. d-Limonene (Lim) is a cyclic monoterpene with two unconjugated double bonds in its backbone (see Fig. 1). Previous studies have reported that the allylic hydrogen is very active and leads to a degradative chain transfer during polymerization with acrylic monomers [22–24]. Lim has been used as a CTA and solvent in ring-opening polymerizations and metallocene polymerizations of olefins [25,26].

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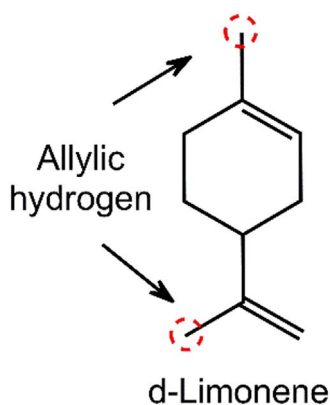


Fig. 1. d-Limonene and allylic hydrogen.

In this work, a core-shell latex-based PSA was prepared using Lim as a renewable CTA. The shell polymer was designed to achieve a lower  $T_g$  and viscosity than the core polymer, in order to offer better flow ability, substrate wettability and thus, better adhesion, and increase energy dissipation during the debonding process. To balance the viscoelasticity behaviour of the PSA, the core was designed with higher  $T_g$  and higher crosslinking density to ensure adequate cohesive strength of the PSA film. By simultaneously manipulating the crosslinker and Lim concentrations, the gel content and molecular weight were modified, and their influence on the adhesive performance (i.e., tack, peel strength and shear strength) was investigated. To our knowledge, this is the first reported use of a renewable CTA used for the modification of PSA performance properties.

## 2. Experimental

### 2.1. Materials

The monomers styrene (Sty, Sigma-Aldrich, 99%), n-butyl acrylate (BA, Sigma-Aldrich, 99%), and acrylic acid (AA, Acros, 99.5%), and the solvent, tetrahydrofuran (THF, Fisher, 99.9%) were used as received without further purification. d-Limonene (Lim, Fisher, 96%) was distilled under vacuum at 65–70 °C before use to remove tocopherol inhibitor. A biodegradable anionic surfactant, EF-800 (49–51 wt% aqueous solution), was donated by Cytec (USA) and used as received. Potassium persulfate (KPS, Sigma-Aldrich, 99%) initiator, sodium bicarbonate buffer, and divinylbenzene (DVB, Sigma Aldrich, 80%) crosslinker, were all used as received. Distilled deionized (DDI) water was used throughout the experiment. Poly(vinylidene fluoride) (PVDF) porous membranes (47 mm diameter, 5  $\mu$ m pore size, Cole-Parmer) were used in gel content measurements.

### 2.2. Latex preparation

Polymerizations were carried out at 80 °C in a 1 L Mettler-Toledo LabMax® jacketed glass reactor equipped with an anchor stirring blade, reflux condenser, and inlets for nitrogen, monomer, and initiator semi-batch feeds. The latexes were prepared using a two-stage seeded semi-batch polymerization process (Table 1).

#### 2.2.1. Core-stage

A mixture of surfactant, buffer, and DDI water was initially charged into the reactor. Nitrogen purging was started and the temperature of the reaction was gradually increased to 80 °C within 30 min, while stirring (220 rpm). To start the polymerization, 42 g of monomer mixture and the 15.4 g KPS aqueous solution were charged into the reactor as single shots. After a 30 min seed production stage, a sample was taken to measure latex particle size and monomer conversion. The

Table 1  
Latex formulation by seeded semi-batch emulsion polymerization at 80 °C.

Latexes	Stages	Component	Amount (g)
Core-stage polymerization	Initial charge	Water	313
		EF-800 <sup>a</sup>	24
		Sodium bicarbonate	0.4
		BA	33
		Sty	9
	Semi-batch feeding	2.5 wt% KPS solution	15.4
		BA	197.8
		Sty	40.2
		AA	9.5
		Lim	4.8
Shell-stage polymerization	Initial charge	DVB	0.48
		2.5 wt% KPS solution	82.1
		core latex	287
		Water	56.6
		Sodium bicarbonate	0.16
	Semi-batch feeding	2.2 wt% KPS solution	15.4
		BA	189.7
		Sty	17.1
		AA	8.3
		Lim	6.2
		2.2 wt.% KPS solution	86.9

core monomer mixture and the remaining initiator solution were then fed to the reactor over 3 and 3.5 h, respectively. After completing the feed, the system was then allowed to react for an additional 40 min to increase the conversion. The latex was then cooled to 30 °C.

#### 2.2.2. Shell-stage

Buffer, DDI water and core latex were weighed and charged into the 1 L reactor. The reactor temperature was increased to 80 °C within 30 min under nitrogen atmosphere. The stirring speed was maintained at 280 rpm throughout the polymerization. A 15 g KPS solution was then charged into the reactor. After 5 min, a mixture of monomers and Lim, and the remaining initiator solution were fed into the reactor over 3.5 and 4 h, respectively. At completion of the feed procedure, reaction was continued for 40 min and then cooled to 30 °C. Samples were taken to monitor particle growth and monomer conversion. The final latex was stored at room temperature for further characterization.

A series of core-shell latexes were prepared by varying the concentration of Lim (0/2/5 phm, parts per hundred parts monomer) and crosslinker divinylbenzene (0.2/0.3 phm) in the core, and the concentration of Lim (0/3 phm) in the shell-stage polymerization. For all cases, BA and Sty were used as monomers with a BA/Sty composition of 80/20 mol/mol (core) and 90/10 (shell). To maintain consistency in core properties, each batch of core latex was split and used separately with a different shell formulation. The experimental design and latex properties for 6 core latexes and 11 core-shell latexes are given in Table 2. All latexes were colloidally stable for over one year and no coagulum was observed during polymerization. A final conversion beyond 96 wt% was achieved for all runs. The solids contents for the core and final latexes were  $42.5 \pm 0.5\%$  and  $51.0 \pm 1\%$ , respectively. The average particle diameters were between 71 and 73 nm for the core latex, and between 107 and 115 nm for the final latexes. The core-shell mass ratio was designed to be 1:1.75. This ratio would ensure complete coverage of all core particles.

### 2.3. Characterization

Solids content was measured gravimetrically. Latex particle size and polydispersity index (PDI) were measured using a Malvern NanoS Zetasizer Dynamic Light Scattering (DLS) instrument at room tempera-

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