



Emulsion-based pressure sensitive adhesives from conjugated linoleic acid/styrene/butyl acrylate terpolymers



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ABSTRACT

Free radical emulsion terpolymerizations of conjugated linoleic acid (CLA), styrene (Sty), and butyl acrylate (BA) were performed at 80 °C. Terpolymers were characterized for composition, conversion, molecular weight and glass transition temperature, latexes were characterized for viscosity and particle size while adhesives were characterized for tack, peel strength, shear strength, storage modulus, loss modulus and tan delta. One impurity commonly found in CLA, oleic acid, was shown to influence the reaction kinetics significantly. Adhesive performance was tuned using divinylbenzene (DVB) crosslinker to keep the terpolymer molecular weight in a desired range. By using a constrained mixture design, the influence of terpolymer composition, chain transfer agent (CTA) concentration, DVB concentration, molecular weights, viscosity and particle size on tack, peel strength and shear strength was investigated. The final forms of the resulting empirical models allowed the creation of 3D response surfaces for pressure sensitive adhesive (PSA) performance optimization.

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1. Introduction

Polymer production using renewable sources such as plant oils can address several green chemistry principles [1,2]. Plant oils, or triglycerides, are made of three fatty acid chains bonded to a glycerol backbone (see Fig. 1.a). The polymerization of plant oils is made difficult due to steric hindrance which can be overcome by the use of its component fatty acid chains such as linoleic acid (see Fig. 1.b) [3,4]. Because of the ability of conjugated oils to copolymerize [5], conjugated linoleic acid (CLA) was chosen for free radical polymerization (see Fig. 1.c). With the prohibitive cost of high purity CLA [6,7], an affordable CLA containing impurities such as oleic acid (see Fig. 1.d) and saturated fatty acids (see Fig. 1.e) presents an interesting option for polymerization. Oleic acid has been used as a surfactant replacement in the emulsion homopolymerization of styrene without any signs of copolymerization [8]. Oleic acid is also known for its electron trapping ability [9] where the oleic acid radicals are resonance stabilized [10]. Oleic acid also was shown to influence the reaction kinetics significantly for bulk copolymerizations and terpolymerizations involving CLA, Styrene (Sty) and n-butyl acrylate (BA) [6,7]. In this study, low-cost CLA containing oleic acid and saturated fatty acids was used to produce terpolymers with Sty and BA with the goal of producing

pressure-sensitive adhesives (PSA) with a significant concentration of a renewable component.

PSA's are characterized by instantaneous adhesion upon application of light pressure [11]. They are soft and tacky with a low glass transition temperature within the –60 to 20 °C range. While an acrylic polymer such as poly(BA) can be soft and tacky, thus providing good tack and peel strength, it often lacks in shear strength. The addition of a “hard” monomer such as Sty is useful to regulate tack, peel strength and shear strength [12,13]. Monomers with functional groups such as acrylic acid (AA) can be added to improve peel strength, shear strength and film formation, but at the expense of reducing tack [14]. In this study, the effect of terpolymer composition, chain transfer agent (CTA) concentration, divinylbenzene (DVB) concentration, molecular weight, viscosity and particle size on tack, peel strength, and shear strength were evaluated for CLA/Sty/BA systems prepared by emulsion terpolymerization.

2. Experimental

2.1. Materials

An affordable conjugated linoleic acid (CLA, Penta, 74% CLA, 13% oleic acid and 13% saturated fatty acid) was chosen for practical reasons and used without further purification. Sty (Sigma-Aldrich, 99%), BA (Sigma-Aldrich, 99%) and all solvents (e.g., acetone

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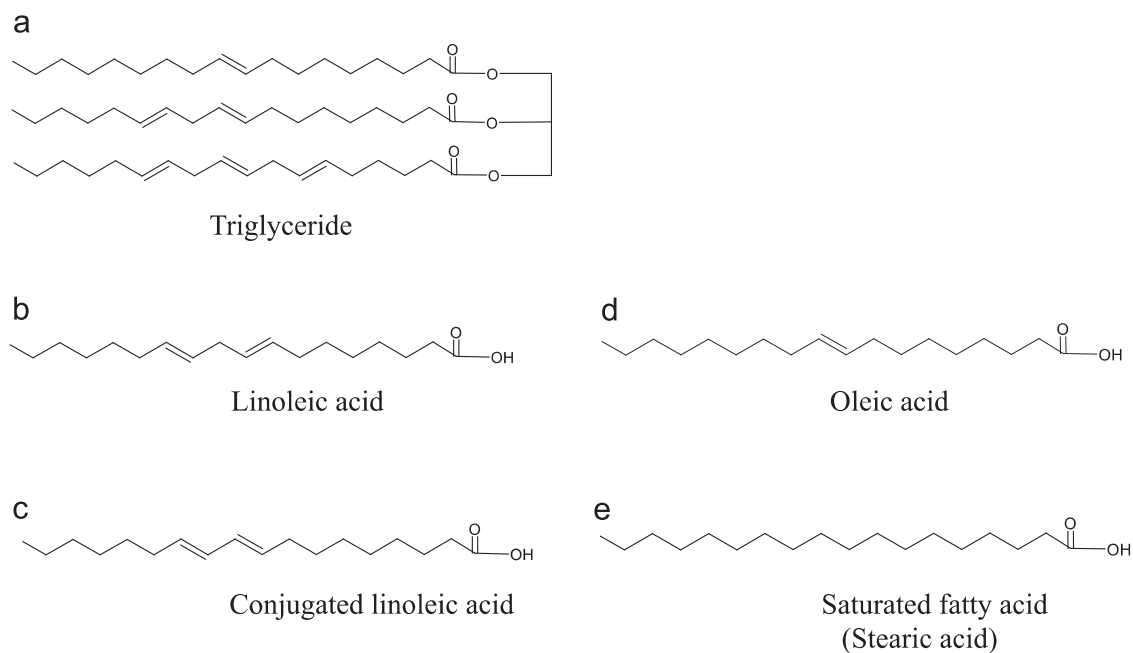


Fig. 1. Molecule of a) triglyceride, b) linoleic acid, c) conjugated linoleic acid, d) oleic acid, and e) saturated fatty acid.

(Fisher, 99%), tetrahydrofuran (THF, Fisher, 99.9%) and chloroform-d (Cambridge Isotope Laboratories, 99.8%) were used as received. The water soluble initiator, potassium persulfate (KPS, Fisher, 100%), and the emulsifier, sodium dodecyl sulfate (SDS, EM Science, 100%) also were used as received while the solvent phase was distilled deionized (DDI) water. In some instances, sodium bicarbonate (NaHCO_3 , Fisher, 100%), n-dodecyl mercaptan (CTA, Sigma-Aldrich, 98+%), acrylic acid (AA, Acros, 99.5%) and divinylbenzene (DVB, Sigma Aldrich, 80%) were added to modify the latex properties.

2.2. Polymerizations

Batch emulsion polymerizations were performed at 80 °C in a 1.2 L, jacketed glass reactor (LabMax, Mettler-Toledo) and stirred at 200 rpm. The reactor was equipped with a nitrogen pressurizing line, a sampling line, a vent with reflux condenser, and a port for an IR probe. CLA, Sty, BA, CTA, AA, DVB were mixed for 15 min, while DDI water, SDS, and NaHCO_3 were also mixed for 15 min in separate beakers. The two solutions were then combined and mixed for 45 min before being poured into the reactor. Oxygen was purged from the reaction mixture with nitrogen for 45 min while the reaction temperature was raised. After the reaction mixture reached 80 °C, a deoxygenated initiator solution was pumped into the reactor and this marked the beginning of the polymerization. Samples were taken regularly through the sampling line for offline analyses by gravimetry and $^1\text{H-NMR}$ spectroscopy. As shown in Table 1, three different feed compositions were used repeatedly in this study (f_i is mole fraction of monomer i in the feed). Based on previous knowledge [13], polymer compositions were selected to produce PSAs with acceptable adhesive performance. The Sty feed composition was set to 10 mol% while the CLA in the feed was added at the expense of the BA fraction normally used [6,7]. It should be noted that due to its high molar mass, the mass fractions of CLA were quite elevated despite the relatively low mol fraction (see Table 1). All additional ingredient concentrations are listed in Table 2.

Table 1

Monomer feed composition for emulsion terpolymerization.

Feed formulation	f_{CLA} (wt. frac.)	f_{CLA} (mol frac.)	f_{Sty} (mol frac.)	f_{BA} (mol frac.)
A	0.16	0.08	0.10	0.82
B	0.23	0.12	0.10	0.78
C	0.30	0.16	0.10	0.74

Table 2

Emulsion formulations (phm=parts per hundred parts monomer on a weight basis).

Emulsion formulation	AA (phm)	KPS (phm)	SDS (phm)	CTA (phm)	DVB (phm)	Feed formulation (from Table 1)
1	0.0	0.5	0.5	0.0	0.0	A
2	0.0	0.2	1.0	0.0	0.0	A
3	0.0	1.0	1.0	0.0	0.0	A
4	0.0	0.5	1.0	0.0	0.0	A
5	4.0	0.5	1.0	1.0	0.0	A
6	4.0	0.5	1.0	1.0	0.1	A, B, C
7	4.0	0.5	1.0	1.0	0.2	A, B, C
8	4.0	0.5	1.0	1.0	0.3	A, B, C
9	4.0	0.5	1.0	0.5	0.2	A
10	4.0	0.5	1.0	0.3	0.2	C
11	4.0	0.5	1.0	0.0	0.2	C
12	4.0	0.5	1.0	0.0	0.4	C
13	4.0	0.5	1.0	0.0	0.6	A, B, C
14	4.0	0.5	1.0	0.0	0.8	A, B, C
15	4.0	0.5	1.0	0.0	1.0	A, B, C

2.3. Experimental design

A series of experiments (see Table 2) was designed to further our understanding of the CLA/Sty/BA emulsion terpolymerization kinetics while evaluating PSA performance. Some formulations were replicated more than once and all reactions were run at 80 °C and 50 wt.% solids content. The concentrations of water and NaHCO_3 were kept constant at 90 and 0.15 phm, respectively, where phm represents parts per hundred parts monomer on a

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