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Plant oil-derived copolymers with remarkable post-polymerization induced mechanical enhancement for high performance coating applications

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HIGHLIGHTS

- High oleic soybean oil (HOSO) derived copolymers were prepared using a semi-batch emulsion polymerization method.
- Successful polymerization of soybean monomer with various co-monomers resulted in latexes with tailorable properties.
- A simple auto-oxidative crosslinking of latex films provided excellent mechanical enhancements.

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ABSTRACT

Polymer coatings have been heavily utilized in many industrial and civil applications where a protective thermoset material with enhanced properties such as chemical and physical resistance, thermal stability, and tailorable mechanical properties is desired. Plant oils are a class of promising biomass toward sustainable polymers, but have yet to be fully harnessed in tailorable thermoset coatings due to the challenging functionalization and extensive crosslinking processes required to achieve desirable thermomechanical properties. In this work, we demonstrated that soybean methacrylate (SBMA) from high oleic soybean oil (HOSO) can be utilized to produce bio-based acrylic thermoset copolymers through an industrially viable semi-batch emulsion polymerization process with various commonly used co-monomers such as methyl methacrylate, styrene, and butyl acrylate. A wide range of monomer feed ratios with SBMA from 0 to 50 wt% was easily achieved with minimal modifications allowing for good tunability of thermal and mechanical properties in the prepared latexes. More importantly, a simple and effective auto-oxidative crosslinking of the latex films provided extreme mechanical enhancements making these thermosets good candidates in ultra-strong, ultra-tough, and high T_g coating applications.

1. Introduction

Thermoset polymers have been widely used as high performance coatings in many industrial applications due to their thermal stability, chemical and mechanical resistance, facile processing, and tailorable mechanical properties. Chemically and mechanically resistant thermoset polymers are frequently used as specialized coatings on substrates for heavy duty work such as laboratory benches, automotive parts, and construction materials. Resins, including epoxy and phenol, are widely used as durable coating materials due to their low cost and facile crosslinking chemistry [1,2]. Unfortunately, the curing agents, solvents, and additives in thermoset resin materials often pose health hazards, such as known carcinogenic formaldehyde or suspected endocrine disruptor bisphenol A [3]. Extensive efforts have been focused on replacing these hazardous components with benign bio-derived alternatives [4–10]. On the other hand, acrylate-based thermoset systems present an alternative with better tailorable properties, owing to their greater structural diversity and safer options for post-polymerization functionalization [11]. Acrylate monomers of various structures and chemical compositions can be copolymerized with a variety of co-monomers including styrenes, vinyl ethers, and other (meth)acrylates [12]. Higher molecular weight and better chemical composition control can be achieved in comparison to the epoxy and phenolic resin-based systems as the initial polymerization and subsequent crosslinking occur in two separate steps. Furthermore, crosslinking in these systems can be conveniently achieved by utilizing light and/or heat without the need to use toxic catalysts or other additives [13–15]. However, these acrylate-based materials have relied primarily on petrochemicals raising

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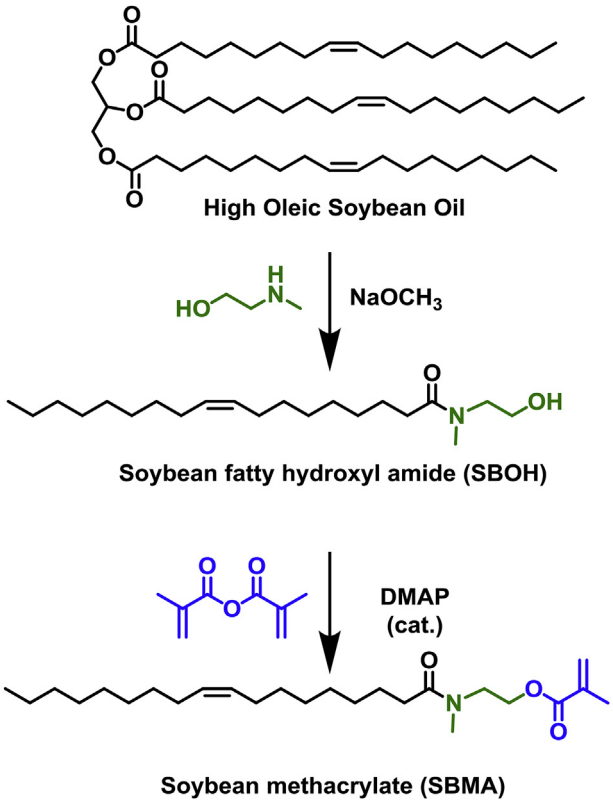
large environmental and sustainability concerns.

In searching for new approaches to preparing more robust and environmentally benign, high performance coatings from plant oils, we realized that utilizing free radical emulsion polymerization to obtain higher molecular weight acrylate polymers with preserved functional groups for facile post-polymerization modification could provide convenient access to desirable mechanical properties. Biomass encompasses a variety of structures that have shown promise in a range of polymer applications, including coatings for biomaterials and adhesives [16–23]. Plant oils have shown great potential as biomass resources to replace petrochemicals in polymer materials [24–28]. Owing to their versatility in structures, various functionalization can be easily carried out to produce a range of materials from thermoplastics to thermosets [17,29–34]. Fatty acid-derived acrylate polymers have also shown facile crosslinking via UV exposure or simple auto-oxidation, resulting in high performance coatings useful in pressure sensitive adhesives [35–37]. To our knowledge, no prior reported work has focused on utilizing plant oil acrylates to obtain stiff, tough, high T_g performance coatings competitive with current epoxy and phenolic resins. The robust free radical emulsion polymerization process allows for easy preparation of higher molecular weight polymers and thus better mechanic properties, and hence has been heavily utilized in industry to produce acrylic coatings with optimal properties [38–40]. In addition, various types of co-monomers can be easily incorporated to prepare copolymers in the emulsion polymerization process offering a convenient tuning of the physical and mechanical properties. More importantly, the resulting waterborne polymers can be used directly without the need for removing harmful organic solvents, making them the most sought-after high volume materials in applications pursuing high environmental and health standards. Therefore, increasing amount of attention has centered on the more efficient and effective incorporation of sustainable and bio-based materials in high volume polymers to reduce the carbon footprint [41–44].

Unfortunately, due to their strong hydrophobicity and unique inherent reactivity, bio-based acrylic monomers from plant oils, and other hydrophobic biomass sources, have been largely ignored in emulsion-based free radical polymerization until recently [44–52]. Voronov and co-workers recently highlighted the potential of plant oil-based monomers to produce latex polymers with high bio-based content (up to ~ 60 wt%) via a more feasible batch process indicating the practicality of utilizing plant oils to produce waterborne latex polymers [53]. Recent success in adapting hydrophobic acrylate monomers (such as methacrylated methyl oleate) in conventional batch emulsion polymerization process has aspired us to examine the possibility and potential of high oleic soybean (HOSO)-based monomers in a more industrially relevant semi-batch emulsion polymerization process [22,54,55]. It is worthwhile to note that *ab initio* emulsion polymerization has achieved great success on the incorporation of hydrophobic monomers including plant oil-derived monomers, though the process is less appealing in scaling [56–59].

Herein we report a study on the semi-batch emulsion copolymerization of a soybean methacrylate monomer (SBMA) with various co-monomers to prepare waterborne latex polymers with tunable compositions and thermomechanical properties. The bio-based acrylic monomer, SBMA, can be readily prepared in a highly efficient and scalable two-step process from HOSO (Scheme 1) [32,33,60]. The homopolymer of SBMA (PSBMA) has a unique soft and tacky nature and can serve as a renewable replacement for other low T_g acrylic polymers such as butyl acrylate polymers in current acrylic coatings. The pendant unsaturated fatty side chain in SBMA can be used for post-polymerization oxidative crosslinking to further improve the properties and performance of bio-based latex polymers, without the need for further functionalization [61,62]. In this work, we also demonstrate that simple oxidative curing of the prepared bio-based latex films can lead to remarkable enhancement in mechanical properties, resulting in ultra-strong, ultra-tough thermoset materials competitive with high performance coatings.



Scheme 1. Synthesis of soybean methacrylate (SBMA) starting with high oleic soybean oil via a fatty amide alcohol intermediate.

2. Materials

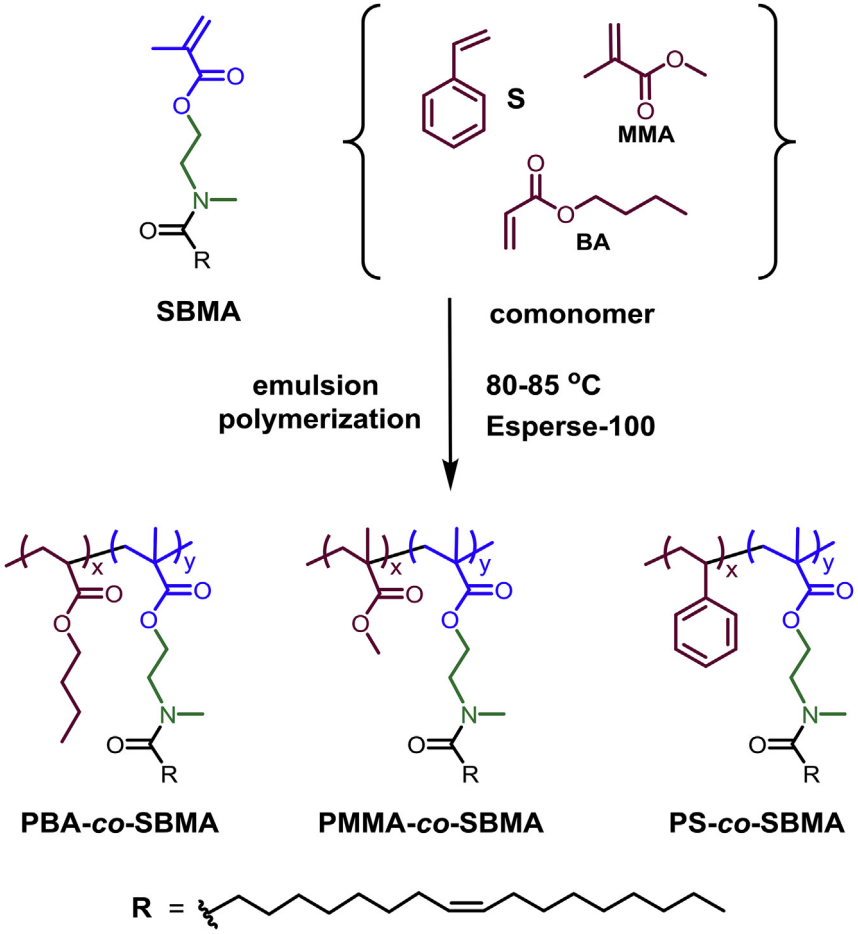
Plenish™ high oleic soybean oil (HOSO) was provided by DuPont Pioneer. E-Sperse® 100 was provided by Ethox Chemicals. Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized twice from methanol. Monomers were passed through basic alumina to remove inhibitors in reactivity studies and were used as received in emulsion polymerization studies. All other reagents were purchased from commercial resources and used as received unless otherwise mentioned. SBMA was prepared in a 3 kg batch according to our previously reported procedures (Scheme 1 and Fig. S1) [32,33]. Solution polymers used for reactivity ratio determination were synthesized using free radical polymerization in a previously reported procedure [32,33,63].

2.1. Characterization

^{1}H NMR spectra were recorded on a Bruker Avance III HD 300 spectrometer using $CDCl_3$ as solvent with tetramethylsilane (TMS) as reference. Zetasizer nano instrument, equipped with an 830 nm wavelength laser, was used to determine the particle size for all emulsion polymers. Solid content was determined by drying ~1 g of latex on an aluminum pan at 55 °C overnight, using the equation (1) below. W_i is the initial mass of latex used and W_f is the final mass of dried latex.

$$\textit{solid content} = \frac{W_f}{W_i} \times 100 \quad (1)$$

The glass transition temperature (T_g) of polymers was tested through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 °C to 200 °C at a rate of 10 °C/min. After cooling down to −70 °C



Scheme 2. Synthesis of copolymers by free-radical emulsion polymerization using soybean methacrylate (SBMA) and a variety of co-monomers including methyl methacrylate (MMA), styrene (S), and butyl acrylate (BA). Copolymers contain between 10 and 50 wt% SBMA.

at the same rate, the data was collected from the second heating scan. About 8 mg of each sample was used for the DSC test, under nitrogen gas at a flow rate of 50 mL/min. Tensile stress-strain testing was carried out on an Instron 5543 A testing instrument. Dog-bone shaped specimens were cut from the cast film with a length of 20 mm and width of 5.0 mm. The thickness was measured prior to each measurement. Testing was done at room temperature with a crosshead speed of 20 mm/min. Five replicate samples were used to obtain an average value for each.

3. Methods

3.1. Synthesis of emulsion copolymers

A pre-emulsion was prepared by mixing 40 mL of DI water, 60 g (in total) of monomers (methyl methacrylate (MMA), styrene (S), or butyl acrylate (BA)), and 4.8 g of E-Sperse® 100 (8 wt% of total monomer feed), and homogenized. The reactor charge was prepared by mixing ~10% v/v of the above pre-emulsion and 50 mL of DI water, and placed in a cylinder reactor vessel (with overhead mechanical stirring). The reactor charge was heated until the internal temperature of the reactor charge reached 80 °C. The initial catalyst solution, 0.1 g of ammonium persulfate (APS) in 1 mL of DI water, was injected. The reaction was kept at 80–85 °C for 20 min to allow particle formation. The remaining pre-emulsion was slowly pumped in over 3 h *concurrently* with the delay catalyst solution, 0.18 g of APS (0.3 wt% of total monomer feed) in 30 mL of DI water. After pumping finished, the emulsion was stirred for 30 min. Finishing catalyst, ammonium persulfate (0.1 g in 1 mL DI water) was added and stirred for 15 min. The mixture was then cooled to 65 °C. Once cooled, redox catalysts were added in the following order; iron (II) sulfate (0.1 g in 1 mL DI water), ammonium persulfate (0.1 g in 1 mL DI water), and sodium bisulfite (0.1 g in 1 mL DI water). After stirring for 30 min, the emulsion was cooled to room temperature and filtered through fine mesh to remove any particulates.

3.2. Preparation of copolymer films

Emulsion copolymer latexes (6 mL each respectively, MMA20–50, S20-50, and BA20-50) were poured into Teflon molds. The latex films were obtained by drying at 55 °C over 48 h and then at 75 °C for 24 h under vacuum. Samples were cut for tensile testing.

3.3. Preparation of crosslinked films

The crosslinked latex films were obtained by placing the above films in the oven under air at 125 °C for 16 h. After cooling to room temperature, the crosslinked films were cut for tensile testing and Soxhlet extraction.

3.4. Model study of auto-oxidative curing

High oleic soybean oil and oleic acid (2 mL of each) were placed in two different aluminum pans. Pans were placed in an oven at 125 °C for 16 h.

3.5. Soxhlet extraction

Solvent extraction of latex and crosslinked films were carried out by Soxhlet extraction using tetrahydrofuran (THF) as the solvent for 36 h. A 500 mL round bottom flask filled with 300 mL THF was connected to a Soxhlet extractor. All samples were vacuum dried, weighed, packed in filter papers, and inserted into the extractor. The extracted samples were dried at 40 °C under vacuum for 36 h and weighed. The procedure was repeated twice to obtain an average. The sol contents of all films were calculated according to the following previously reported equation (2),

$$\textit{Crosslinked content}\ (\%) = 100 - \left(\frac{W_i - W_f}{W_i}\, x\ 100\right) \quad (2)$$

where W_i is the sample weight before extraction and W_f is the sample weight after extraction and vacuum dry [64].

4. Results and discussion

4.1. Synthesis of latex polymers

Latex copolymers of varying wt. % of soybean monomer (SBMA) with three common co-monomers (MMA, S and BA) were prepared via emulsion polymerization (Scheme 2). A semi-batch process that starves the reaction of both monomer and initiator was chosen, allowing for more manageable exotherms and better control of the polymerization [65]. E-Sperse® 100 was selected over the common sodium lauryl sulfate (SLS) as the surfactant to prepare a stable pre-emulsion of SBMA with other monomers. E-Sperse® 100 was found to have overall better performance in the surfactant screening test showing little to no emulsion breakdown in 72 h. The pre-emulsion mixture was also homogenized to further ensure its good stability during the delayed pumping stage.

To start each polymerization, a small fraction of pre-emulsion was diluted with additional water, homogenized, and heated to 80 °C before the initial catalyst (ammonium persulfate, AP) was added. This initialization step was easily identified by the onset of a blueish color in the solution due to the micellar formation. Next, the reaction propagation was maintained at 80–85 °C and starved by the slow addition of remaining pre-emulsion mixture and delay catalyst (AP) solution. In the finishing step, a chase catalyst (AP) was added at the reaction temperature before the reaction mixture was cooled down to 65 °C. Afterwards, a redox finishing catalyst (AP, iron (II) sulfate, and sodium bisulfite) was added to push the complete consumption of residual monomers and achieve a high conversion [66]. Each type of catalysts serves a unique role in our polymerization. The delay catalyst is added into the starved reaction to initiate any monomers in situ and propagate the reaction. The chase catalyst serves to initiate any residual monomers and allows for movement into the larger growing polymer particles. The finishing catalyst works uniquely at a lower temperature to ensure all monomers in the liquid phase and can be brought into particles and incorporated into the final polymers in order to achieve high conversion. Detailed procedure is provided in the Methods section in the SI.

The prepared latexes were characterized using a variety of methods, and results were provided in Table 1. All polymers are named using their co-monomers followed by the weight percentage of SBMA. For example, **MMA10** is referred to as the copolymer of poly(methyl methacrylate-*co*-soybean methacrylate) (PMMA-*co*-SBMA) with 10 wt% SBMA. Auto-oxidative crosslinked samples are denoted with a "**C**" in the end. For example, **S40C** is referred to the crosslinked copolymer of poly(styrene-*co*-SBMA) (PS-*co*-SBMA) with 40 wt% SBMA.

To our satisfaction, SBMA showed good overall incorporation with a variety of co-monomers. Little to no coagulation was observed with these polymerizations, likely due to the robust semi-batch process (good heat dissipation and smooth reaction rate) together with the excellent cross-reactivity between SBMA with co-monomers (Fig. S2 and Table S1). As a result, molar ratios in monomer feed and in the final polymers were in good consistency (Figs. S3–S5). High conversions (> 95%) for both SBMA and co-monomers were confirmed using ^{1}H NMR. Slight decrease in co-monomer conversion (styrene, methyl methacrylate, and butyl acrylate) was observed with higher SBMA content in all copolymerizations. All latexes have a relatively small particle size (below 100 nm), likely due to the relatively high surfactant content (3 wt% overall) in the current recipes. Particle size was also found to decrease with increasing SBMA content regardless of comonomer composition, which was speculated to result from the structural similarity of SBMA monomer to the surfactant (Fig. S6). Solid contents of all latexes was consistent and in line with the expected ~30%, reaffirming the high level of conversion achieved in our emulsion polymerizations.

Glass transition temperatures (T_g) of the latex copolymers were found to follow a predicted trend consistent with those calculated from the Fox equation. Unfortunately, the observed T_g has a very broad (Fig. S7). Styrene and methyl methacrylate copolymer latexes showed decreases in T_g with increasing SMBA content. This is well expected considering the T_g of homopolymer PSBMA is around −6 °C. Increasing SBMA fraction would result in a drastic decrease in T_g of the copolymers with MMA or S (Note that the homopolymers of PMMA and PS have their T_g's of 105–120 °C and 100 °C, respectively). Alternatively, an increase of SBMA content in the butyl acrylate copolymers should cause an increase in T_g (Note that the homopolymer PBA has a T_g of −54 °C).

Molecular weight data is not readily available for these copolymers due to solubility issues. All copolymers are only fully soluble in dichloromethane and chloroform. However, they are sparingly soluble in the operable solvents (tetrahydrofuran and dimethylformamide) with our GPC systems. Despite repeated attempts, the copolymer samples could not be fully dissolved leaving significant an amount of residue when passing through 0.2 μm filter. Therefore, data was not collected considering the partially soluble samples may likely interfere with GPC measurements and produce inaccurate molecular weight information.

4.2. Mechanical properties of latex copolymers

Latex copolymers of soybean methacrylate with styrene and methyl methacrylate, respectively, were capable of forming free-standing films when the SBMA content was 20–50 wt% but became too brittle as the SBMA content dropped to 10 wt%. All latex copolymers of SBMA and butyl acrylate were too soft to form free-standing films. The tensile curves are shown in Fig. 1. Complete mechanical data is summarized in Table 2.

Elasticity of the copolymer film was found to increase with the increasing soy monomer content in the latex copolymers. The elasticity enhancement was dramatic on latex films made with styrene copolymers (**S20–S50**). For example, the tensile strain increased from 36.5% for **S40**, to 359% for **S50** when SBMA content increased from 40 to 50 wt%. Generally, styrene copolymer films were tougher than methyl methacrylate copolymer films of a similar level of SBMA content. For example, the toughness of copolymer latex films nearly doubled from **MMA40** to **MMA50** but quadrupled from **S40** to **S50**. Higher soy content, in general, resulted in longer elongation and decreased stress at break. It is most notable that increasing SBMA content caused decreases in stiffness but sizable increases in toughness. This trend was observed in both copolymers of styrene and methyl methacrylate respectively. For instance, **MMA20** showed toughness of only 0.55 MJ/m^3 and Young's modulus of 928.4 MPa. In comparison, **MMA50** demonstrated a toughness of 5.98 MJ/m^3, a nearly ten-fold increase, and Young's modulus of 240.0 MPa, about three-quarters loss. Similarly, **S50** showed toughness of 12.8 MJ/m^3, a nearly ten times increase compared with **S20** (0.38 MJ/m^3), and Young's modulus of 5.4 MPa, a decimating loss in comparison to **S20** (1300.7 MPa). This observed trend is likely due to the long fatty chain of soybean monomer acting as a plasticizer in the copolymers prepared with stiffer co-monomers such as styrene

Table 1
Characterization of latex copolymers containing soybean methacrylate (SBMA).

Copolymer	Molar Ratio in Feed (X/SBMA)[a]	Molar Ratio in Polymer (X/SBMA)[b]	Conv. (%) (X/SBMA)	Particle size (nm)[c]	Solid content (%)	T_g (°C)[d]
MMA10	1.0/0.028	1.0/0.025	99/99	97.0 (± 21)	33	87
MMA20	1.0/0.055	1.0/0.05	98/99	66.1 (± 17)	35	79
MMA30	1.0/0.11	1.0/0.13	98/99	52.8 (± 15)	33	74
MMA40	1.0/0.2	1.0/0.18	97/99	49.3 (± 13)	29	54
MMA50	1.0/0.26	1.0/0.23	96/98	45.8 (± 14)	30	42
S10	1.0/0.029	1.0/0.035	99/99	102.8 (± 24)	29	75
S20	1.0/0.064	1.0/0.07	97/99	77.0 (± 19)	34	72
S30	1.0/0.11	1.0/0.11	96/99	68.4 (± 18)	31	61
S40	1.0/0.26	1.0/0.3	95/99	66.2 (± 16)	27	50
S50	1.0/0.32	1.0/0.37	95/98	62.8 (± 15)	29	40
BA10	1.0/0.036	1.0/0.045	99/99	78.8 (± 16)	28	−47
BA20	1.0/0.081	1.0/0.12	99/99	77.5 (± 17)	30	−40
BA30	1.0/0.14	1.0/0.19	99/99	67.6 (± 18)	28	−32
BA40	1.0/0.32	1.0/0.38	97/99	64.2 (± 17)	25	−29
BA50	1.0/0.46	1.0/0.52	97/98	50.5 (± 15)	31	−20

[a] X = comonomer.
[b] Molar ratio in polymer was determined using ^{1}H NMR (for details, see Figs. S3–S5 in the SI).
[c] The number-average particle size determined using DLS.
[d] T_g of dried latex determined using DSC (2nd heating cycle).

and methyl methacrylate. Similar toughness enhancement has been observed in earlier works of incorporating plant oil-based monomers into polymer systems and has been considered a promising attribute in coating applications [67,68].

4.3. Auto-oxidative crosslinking

Plant oils possess crosslinkable alkene functional groups on their fatty chains. Our HOSO-derived SBMA has one alkene group per fatty chain on average, composed of a variety of saturated, mono-unsaturated, and polyunsaturated fatty acids. These alkene groups, when exposed to atmospheric oxygen at elevated temperatures, can undergo auto-oxidation and form crosslinked structures in polymers [69,70]. This oxidative crosslinking process can be accelerated by the addition of metal salts, or enzymes [71,72]. High crosslinking is important in thermosets for high performance coating applications as they dictate many of the necessary thermomechanical and chemical resistance properties [1]. Most likely the presence of a low fraction of linoleic acid would trigger the auto-oxidation, which could further propagate the crosslinking reaction involving the majority of oleic groups. A model auto-oxidative study using our soybean oil and oleic acid (typically contaminated with 5–10% linoleic acid and linolenic acid) confirmed the occurrence of crosslinking in both cases (available in SI).

Our bio-based latex copolymers contained 10–50 wt% SBMA and were able to achieve high levels of crosslinking without the need for catalysts. Dried latex films were placed in an open oven at 125 °C and allowed to crosslink over 16 h. Soxhlet extraction was carried out to help examine the level of crosslinking present in the films. The crosslinked content can be estimated by the weight percentage of the non-soluble content of the films after exhaustive extraction. Details of the extraction procedure are provided in the SI. Both non-crosslinked copolymers samples (**MMA10–50** and **S10–50**) and crosslinked samples (**MMA10C–50C** and **S10C–50C**) were examined for comparison purposes (Fig. 2). Butyl acrylate copolymers were not examined with Soxhlet extraction. The low T_g of these samples made it too difficult to extract and accurately weigh both initial residual samples without sample loss due to their tacky nature. All non-crosslinked samples (**MMA10–50** and **S10–50**) were found to fully dissolve upon exhaustive

Table 2
Tensile properties of latex copolymers containing soybean methacrylate.

Copolymer	Stress at break (MPa)	Strain at break (%)	Toughness (MJ/m^3)	Young's Modulus (MPa)
MMA20	28.6 (± 0.4)	4.1 (± 0.2)	0.55 (± 0.02)	928.4 (± 10.2)
MMA30	9.7 (± 0.3)	19.8 (± 0.4)	1.91 (± 0.2)	379.5 (± 6.6)
MMA40	9.9 (± 0.4)	29.6 (± 0.4)	2.75 (± 0.3)	355.3 (± 5.6)
MMA50	11.0 (± 0.2)	56.4 (± 2.1)	5.98 (± 0.6)	240.0 (± 3.2)
S20	29.1 (± 0.3)	3.8 (± 0.3)	0.38 (± 0.01)	1300.7 (± 12.1)
S30	38.8 (± 0.5)	5.7 (± 0.8)	0.99 (± 0.03)	532.1 (± 7.8)
S40	9.7 (± 0.4)	36.5 (± 0.8)	3.63 (± 0.3)	361.2 (± 4.4)
S50	9.7 (± 0.6)	359.0 (± 7.2)	12.8 (± 0.9)	5.4 (± 0.5)

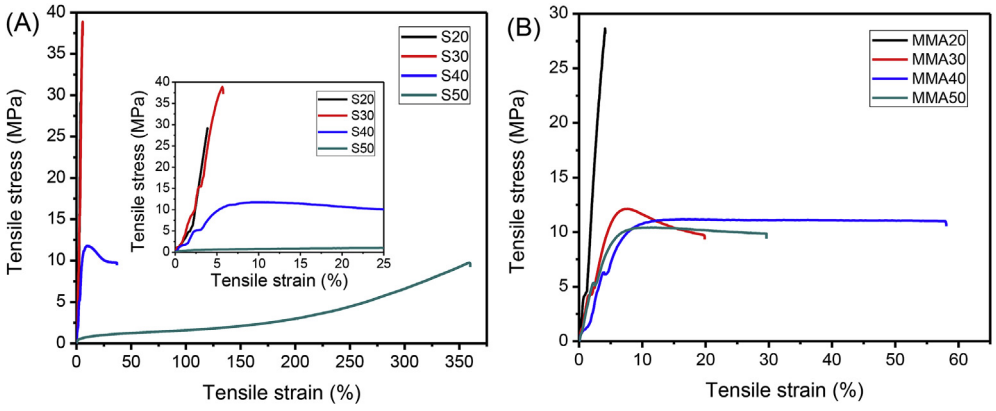


Fig. 1. Tensile curves of (A) PS-*co*-SBMA, inset magnifies graph to show tensile strain between 0 and 25%, and (B) PMMA-*co*-SBMA copolymers.

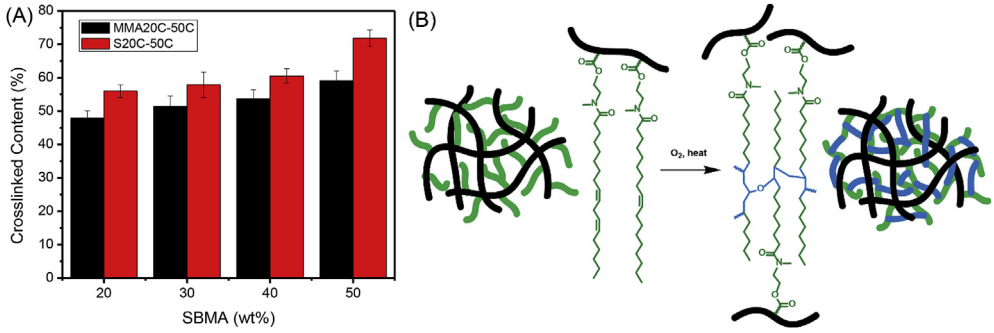


Fig. 2. (A) Crosslinked content of copolymers as determined by Soxhlet extraction of crosslinked films (**MMA20C–50C** and **S20C–50C**). (B) A schematic presentation of the auto-oxidative crosslinking process involving the oleic amide chains.

extraction. In contrast, all crosslinked films were found to have a significant amount of non-soluble content upon exhaustive extraction (Fig. 2). All thermally processed latex films had a high level of crosslinking at > 50%. Furthermore, crosslinked latex films showed a qualitative correlation between SBMA content and crosslinked content, where higher SBMA content resulted in higher crosslinked content. Interestingly, all styrene copolymers were found to achieve higher levels of crosslinking than methyl methacrylate films. For example, the styrene copolymer with 50 wt% of SBMA was found to reach a crosslinked content around 73% (**S50C**) whereas the counterpart methyl methacrylate copolymer was found to have a crosslinked content of around 60% (**MMA50C**).

4.4. Mechanical properties of crosslinked latexes

All crosslinked latex films were found to have dramatically enhanced mechanical properties (Fig. 3). The most remarkable increase in properties was seen in the crosslinked methyl methacrylate copolymer **MMA20C** and styrene copolymer **S20C**, which were found to reach a tensile strength of 122.5 and 131.3 MPa respectively. This corresponds to a four-folded enhancement than non-crosslinked samples. In general, copolymer films with higher soy content were found to increase in elasticity but decrease in strength upon crosslinking. Both crosslinked copolymer films made with methyl methacrylate (**MMA10–40C**) and styrene (**S10–40C**), respectively, showed an overall increase in strength, toughness, and stiffness, but marked decrease in elasticity (Table 3). All crosslinked butyl acrylate copolymer films, despite being quite soft, were able to form free-standing films, showing a marked improvement over their viscoelastic non-crosslinked counterparts (Fig. S9). All butyl acrylate copolymers showed increasing stress at break with increasing soy content (Table 3). For example, crosslinked butyl acrylate copolymer with 50 wt% of SBMA (**BA50C**) showed almost doubled stress at break (0.81 MPa) in comparison to the crosslinked counterpart (0.31 MPa) with 10 wt% of SBMA (**BA10C**). A similar trend was observed with toughness, which increased from 0.08 MJ/m^3 for **BA10C** to 0.45 MJ/m^3 for **BA50C**, a significant increase.

Impressive increases in the Young's modulus of the latex films were also observed upon crosslinking. For example, crosslinked methyl methacrylate copolymer **MMA20C** were found to have a drastically higher Young's modulus (5.04 GPa) in comparison with uncrosslinked counterpart (928.4 MPa). Similar enhancements were also readily observable with crosslinked films of **MMA30C**, **S20C**, and **S30C** all showing a much higher modulus of ~3 GPa than their non-crosslinked counterparts (less than 1 GPa). Furthermore, crosslinked copolymer films often showed improved toughness than non-crosslinked counterparts. For example, styrene copolymer with 40 wt% of SBMA was found to have an over 10-fold increase in toughness upon crosslinking (31.08 MJ/m^3 for **S40C** *versus* 3.63 MJ/m^3 for **S40**). However, the crosslinking-induced toughness enhancement appeared to be highly influenced by the copolymer compositions and fluctuate from case to case. For example, crosslinked copolymer **MMA40C** was found to have very marginal improvement in toughness than its non-crosslinked counterparts. Further studies are currently carried out in our laboratory to examine the relationship between the toughness and copolymer composition and structure. Nevertheless, the ultra-high strength, impressive stiffness, and toughness achieved by simple crosslinking of these films indicates potential as acrylic thermoset replacement for current high performance, high T_g coating materials like epoxy and phenolic resins.

5. Conclusions

Soybean methacrylate was copolymerized with a variety of comonomers including styrene, methyl methacrylate, and butyl acrylate

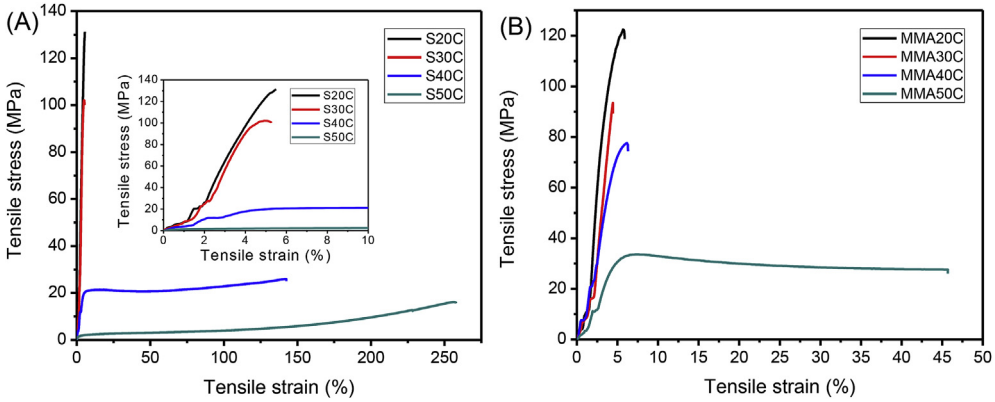


Fig. 3. Tensile curves of (A) PS-*co*-SBMA (**S20C–S50C**), inset magnifies graph showing tensile strain between 0 and 10%, and (B) PMMA-*co*-SBMA (**MMA20C-MMA50C**) crosslinked copolymers.

Table 3
Tensile properties of crosslinked latex copolymers containing soybean methacrylate (SBMA).

Copolymer	Stress at break (MPa)	Strain at break (%)	Toughness (MJ/m^3)	Young's Modulus (MPa)
MMA20C	122.5 (± 0.4)	5.7 (± 0.2)	3.87 (± 0.03)	5041.3 (± 7.2)
MMA30C	93.5 (± 0.3)	4.4 (± 0.4)	1.52 (± 0.01)	3553.9 (± 4.1)
MMA40C	77.6 (± 0.4)	6.2 (± 0.4)	2.69 (± 0.03)	2103.3 (± 2.3)
MMA50C	27.7 (± 0.2)	45.5 (± 2.1)	12.79 (± 0.4)	1065.6 (± 3.1)
S20C	131.3 (± 0.3)	5.5 (± 0.3)	3.23 (± 0.01)	3240.9 (± 9.1)
S30C	102.1 (± 0.5)	4.9 (± 0.8)	2.56 (± 0.02)	3370.4 (± 5.4)
S40C	25.9 (± 0.4)	141.9 (± 0.8)	31.08 (± 0.9)	468.0 (± 2.1)
S50C	16.1 (± 0.6)	256.6 (± 7.2)	25.64 (± 0.2)	10.1 (± 0.3)
BA10C	0.31 (± 0.05)	51.8 (± 1.1)	0.08 (± 0.02)	0.73 (± 0.1)
BA20C	0.32 (± 0.03)	150.6 (± 2.3)	0.30 (± 0.09)	0.60 (± 0.1)
BA30C	0.55 (± 0.1)	51.7 (± 0.5)	0.17 (± 0.03)	1.15 (± 0.05)
BA40C	0.64 (± 0.04)	89.7 (± 0.6)	0.36 (± 0.06)	1.40 (± 0.2)
BA50C	0.81(± 0.06)	98.1 (± 0.9)	0.45 (± 0.06)	1.08 (± 0.1)

using an industrially relevant, safer semi-batch emulsion polymerization method. All polymerizations showed good control with nearly complete incorporation of monomers and predictable properties. Tensile tests on the corresponding polymer films revealed that high soy content improved elasticity and toughness, while low soy content boosted stiffness and strength. Such tunable thermomechanical properties present a useful attribute towards a range of high performance coating applications. Crosslinking of copolymer latex films via facile auto-oxidation provided thermomechanically enhanced materials. Incorporation of plant oil derived methacrylate monomers into polymer latexes has demonstrated good potentials as a cheaper, simpler, and effective strategy to prepare durable, high T_g acrylic coatings with tunable thermomechanical properties. The remarkable enhancement in thermomechanical property also points to great promise for plant oil-based methacrylates in developing further high performing sustainable materials in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.04.072.

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