Emulsion Copolymerization of Vegetable Oil Macromonomers Possessing both Acrylic and Allylic Functionalities

Ethem Kaya, Sharathkumar K. Mendon, David Delatte, James W. Rawlins, Shelby F. Thames*

Summary: A soybean oil-based vegetable oil macromonomer (VOMM) was incorporated as a comonomer into an all-acrylic copolymer via semi-continuous emulsion polymerization. Structurally, VOMMs are comprised of long hydrocarbon fatty acid moieties with allylic double bonds which enable auto-oxidative crosslinking at ambient temperature. VOMMs facilitate low temperature film formation and the fatty acid chains tethered to the polymer backbone auto-oxidize upon film formation to yield crosslinked films. Latexes with varying VOMM levels were synthesized to elucidate the effect of VOMMs on the pre-cure and post-cure glass transition temperature (T_g) and minimum film formation temperature (MFT). Thermoplastic control latexes (without VOMM) were also synthesized via copolymerization of butyl acrylate and methyl methacrylate. This paper details the characterization performed to validate and quantify the VOMM allylic unsaturation retention before, during, and after polymerization, and to quantify and confirm the increase in T_g resulting from auto-oxidative crosslinking via solid state ^{13}C nuclear magnetic resonance spectroscopy and differential scanning calorimetry.

Keywords: auto-oxidation; biopolymers; crosslinking; emulsion polymerization; renewable monomers

Introduction

Traditionally, coatings contain significant amounts of solvents that evaporate into the atmosphere after application and are classified as volatile organic compounds (VOCs). VOCs are an environmental concern because they react with atmospheric nitrogen oxides to form ozone. Environmental Protection Agency (EPA) findings have linked ground level ozone to increased asthmatic and respiratory conditions in humans.[1] Even short-term exposure to ozone can cause chest pain, coughing, nausea, throat irritation, congestion, and reduced lung capacity. In addition, ozone can exacerbate cardiac and lung conditions such as bronchitis, asthma, pneumonia, emphysema, and heart disease. In view of the detrimental effect of ozone, the EPA imposes restrictions on the maximum VOC content permissible in coatings. Although waterborne coatings are regarded as the closest and environmentally favored alternative to solvent-based coatings, they are often formulated with significant amounts of solvents to facilitate good film formation of high glass transition temperature (T_g) polymers.

In recent years, advances in designing environmentally friendly and sophisticated polymer latex systems have facilitated exciting developments in the field of coatings. The utilization of renewable resources to synthesize viable alternatives to petroleum-derived raw materials is steadily increasing in popularity for environmental and ecological reasons.

School of Polymers and High Performance Materials, 118 College Drive #5217, The University of Southern Mississippi, Hattiesburg, MS 39406, USA
E-mail: james.rawlins@usm.edu

A number of authors have described the synthesis and utilization of soybean oil derivatives in polymers and coatings.[2–5] Larock *et al.* synthesized a series of methoxylated soybean oil polyols with different hydroxyl functionalities and incorporated them into vegetable-oil-based waterborne polyurethane dispersions.[6] Cadiz *et al.* reviewed developments in biobased polyols and their utilizations in polyurethanes.[7] Soybean oil phosphate ester polyols have been evaluated in low-VOC corrosion resistant coatings.[8] U.S. Pat. No. 7,691,914 to Abraham *et al.* describes soybean oil-based polyols for use in the manufacturing of polyurethane foams.[9] U.S. Pat. No. 7,799,895 to Ddamulire *et al.* describes low-VOC bio-based adhesive compositions utilizing drying oils.[10]

Vegetable oil macromonomers (VOMMs) have been investigated as comonomers for use in emulsion copolymerization of conventional monomers.[11–13] VOMMs, as described below are designed to have three distinct characteristics that are advantageous in the synthesis of environmentally-responsible emulsions: (1) by virtue of its molecular length and large monomer size, the VOMMs are excellent plasticizing monomers that provide a means of coalescence without the necessity for solvent-based coalescing solvents/agents, (2) they readily copolymerize with vinyl monomers through the acrylate functionality and reduce MFT during film formation, and (3) the allylic functionalities within the monomer tail react auto-oxidatively after application at ambient temperature, creating films with crosslinked networks that improve mechanical strength through network connectivity and entangled polymer chains. The synergistic combination of allylic vegetable oil fatty acids and an acrylic backbone provides mechanically stable, self-crosslinking emulsions for utilization in coatings with reduced or zero VOC emissions that result in an unique fundamental structure properties dissimilar to conventional monomers in polymers produced from simple emulsion polymerization and resulting in practical latexes in a ready-to-use form.

The VOMM described in this paper, i.e., soybean oil amide acrylate (SoyAA-1), is a glyceryl ester-free derivative that has been optimized for parameters that influence VOMM incorporation in emulsions, i.e., surfactant choice and quantity, emulsion processing parameters, initiator proportion, comonomer selection, and the structure-property relationship for final emulsion polymer and coating materials. This study focuses on the elucidation of the structure-property relationships of VOMMs in all-acrylic copolymers.

Experimental Part

Materials

Soybean oil was purchased from Alnor Oil Company Inc., Valley Stream, NY. Sodium bicarbonate, ammonium persulfate (APS), methyl methacrylate (MMA), *n*-butyl acrylate (BA), and methacrylic acid (MA) were purchased from Sigma-Aldrich, St. Louis, MO. 2-Amino-2-methyl-1-propanol was purchased from Acros. Surfactants Abex® 2005, Abex 2545, and Abex 2515 were obtained from Rhodia, Cranbury, NJ. Cobalt Hydro-Cure II® was provided by OMG Borchers GmbH, Langenfeld, Germany.

Characterization

Solid-state NMR spectroscopy was performed on a Varian Unity Inova 400 NMR spectrometer using a standard Chemagnetics 7.5 mm CP/MAS probe. The sample was loaded into a zirconia PENCIL™-style rotor sleeve, sealed with Kel-F™ caps, and spun at rates of 3.5 and 4.0 kHz. Spectra were obtained via direct polarization (DP) using the DEPTH sequence[14] to remove or reduce probe background signals. High-power proton decoupling was implemented during data acquisition to remove C–H dipolar coupling. The acquisition parameters for the DP/MAS spectrum were a recycle delay of 55–70 seconds and a ^{13}C 90° pulse width of 5.5 μsec. The common number of scans accumulated for the samples reported herein was 2048, and the acquisition time was 45 msec. Exponential line broadening of 10 Hz and zero-filling of 128 k was applied to the data prior to Fourier transformation. Additional spectra were acquired using the TOSS technique[15] to detect spinning side bands. The baseline was corrected using the Whittaker algorithm[16] as implemented in the MestReNova™ software package.

Latex particle sizes were determined via the Microtrac® UPA 250 Particle Size Analyzer having a sample range capability of 0.003 to 6.54 μm (standard deviation ± 10 nm) after diluting the latexes with 200 times their volume of deionized (DI) water to a concentration of 2.25×10^{-3} g/mL.

Latex MFT was determined visually as the temperature corresponding to the point at which the latex dried to a clear film on the MFFT-BAR instrument (Rhopoint, Inc., temperature range −5–90 °C).

Latex T_g was determined via differential scanning calorimetry (DSC) conducted on the DSC Q1000 (TA Instruments) over the temperature range of −90 °C to 150 °C at a heating rate of 5 °C/min and cooling rate of 10 °C/min for two cycles. Latex films utilized in these studies were coalesced separately under air (with 0.1 wt% cobalt metal on latex solids) and nitrogen (no catalyst).

Dynamic mechanical analysis (DMA) studies on latex films (~ 0.5 mm thick, ~ 5 mm wide) were conducted on a DMA Q800 from TA Instruments under tensile mode at a frequency of 1 Hz, heating rate of 2 °C/min over a range of -50 to 150 °C under strain mode, and gap distance of 5–7 mm.

Latex Synthesis

Seed particles were synthesized utilizing a batch emulsion polymerization process. The seed latex was formulated to a copolymer composition of BA/MMA at 45/55 (by weight) with 0.25 wt% MA. The monomer mixture, DI water, and 4 wt% Abex 2005 surfactant were emulsified by mechanical stirring (1,800 rpm) for 30 min in the reaction kettle. The reaction vessel was then placed in a water bath at 70 °C and purged with nitrogen for 30 min. The reaction was initiated by injecting a solution of 0.67 wt% APS in 10 mL DI water into the reaction vessel. The reaction was continued for eight hours, cooled to ambient, and filtered. The final seed latex was characterized by a solid content of 36% (by weight), unimodal particle size distribution, and mean particle size of 49 nm.

VOMM latexes were synthesized utilizing a starve-fed, semi-continuous polymerization process. The latexes were formulated to a copolymer composition of SoyAA-1/MMA at 10/90, 20/80, and 60/40 (all ratios by weight) with 0.3 wt% MA. Pre-emulsions were prepared by mechanically stirring at 1,800 rpm a blend of the monomers with DI water, 1.6 wt% Abex 2005, 0.5 wt % Abex 2545, 0.5 wt % Abex 2515, 0.67 wt% APS, and 5 wt % seed particles for 30 min. The pre-emulsion pH was adjusted to 7 with 2-amino-2-methyl-1-propanol. The reaction vessel was then placed in a water bath at 80 °C and purged with nitrogen for 30 min before being charged with a solution of DI water, 0.5 wt% seed particles, and 0.4 wt% sodium bicarbonate, while the contents were stirred continuously at 250 rpm. The reaction was initiated by injecting 0.2 wt% APS in 10 mL DI water into the reaction kettle. The reaction was continued under starve-fed conditions at a pre-emulsion feed rate of 0.033 g/sec over 3.5 hours under continuous stirring and a nitrogen blanket. The reaction pH was maintained around 7 by injecting 7 mL of a solution of 2-amino-2-methyl-1-propanol in DI water (30% by weight) with a syringe pump at a feed rate of 0.031 mL/sec. Once the pre-emulsion feed was exhausted, the reaction kettle was maintained in the water bath at 80 °C for another 4.5 hours (total reaction time was 8 hours). The reaction kettle was then cooled to ambient, and the latex was filtered and adjusted to a pH value of 9.0 with 2-amino-2-methyl-1-propanol. The same reaction procedure was used for the control latexes except that SoyAA-1 was replaced quantitatively by BA. All the syntheses were performed in a 500 mL lab scale reaction kettle. Subsequently, S-5 (SoyAA-1/MMA (46/54 w/w)) was synthesized in a 5 gal reactor to confirm the scale-up viability of the synthesis procedure.

Results and Discussion

SoyAA-1 synthesis (Figure 1) has been described elsewhere.[17–18]

SoyAA-1 is characterized by high vegetable oil content (66% by weight), favorable hydrophobic-hydrophilic balance for facile emulsion synthesis under standard conditions, optimal water solubility, retention of allylic unsaturation through the polymerization process, and minimal coagulum during emulsion processing. With a theoretical homopolymer T_g of - 67.5 °C, SoyAA-1 is an excellent flexibilizing comonomer, and has been successfully copolymerized with common monomers such as butyl acrylate and methyl methacrylate in emulsions.

VOMM Copolymer Characterization

Latexes with varying levels of SoyAA-1 and MMA were synthesized to elucidate the effect of VOMMs on the latex T_g and MFT. Control latexes (w/o VOMM) were also synthesized via copolymerization of BA and MMA at varying weight ratios. Table 1 shows the latex compositions and physical properties of the VOMM and control latexes in addition to scale-up latex (S-5). All latexes were over 50% in solid content except SoyAA-1/MMA (60/40 w/w) (S-4). Both VOMM and control latexes exhibited unimodal particle size distribution with typical well-defined

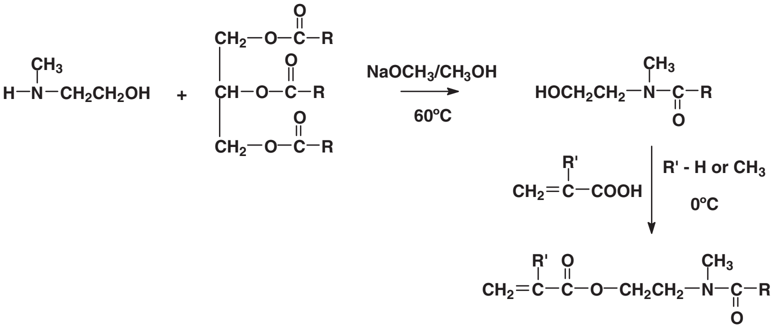


Figure 1.
SoyAA-1 synthesis.

Table 1.
Latex Composition.

Run #	SoyAA-1/MMA	Solids (%)	Particle Size (nm)	T_g (°C)	MFT (°C)
S-1	10/90	52.0	175	101	> 90
S-2	20/80	52.6	142	70	76.4
S-3	40/60	51.6	128	18	22
S-4	60/40	46.0	272	−8	−2.4
S-5	46/54	52.6	141	9	9
	BA/MMA	Solids (%)	Particle Size (nm)	T_g (°C)	MFT (°C)
C-1	10/90	53.9	200	101	>90
C-2	20/80	52.6	291	71	75
C-3	40/60	52.6	277	30	26.3
C-4	60/40	52.4	262	−2.5	−1.8

particle size distribution except for latex S-4 which showed a broad particle size distribution and higher viscosity. With increasing VOMM concentration, the particle size of the polymer dispersion decreased except for latex S-4. On the other hand, the control latexes did not exhibit a particular trend with respect to particle size. As expected, increasing VOMM concentration resulted in decreasing T_g. Although, the T_g values are similar for both VOMM and control latexes up to 20%, the T_g decrease was more pronounced at higher VOMM concentrations.

Ionic surfactants impart colloidal stability to latex particles via electrostatic repulsion. If the surface charge density falls below a critical value, the latex particles coagulate and eventually lead to phase separation of the latex.[19] Figure 2 shows the particle size distribution of SoyAA-1/MMA (46/54 w/w) latex at room temperature and 50 °C. At room temperature, the SoyAA-1/MMA latexes are exceptionally stable and did not exhibit any phase separation or change in particle size distribution even after 10 months at ambient temperature. After a week at 50 °C, the mean particle size of the latex increased to 140.9 nm and increased slightly without phase separation by the end of four weeks.

The MFT measures the temperature at which film formation occurs and corresponds with the temperature at which driving forces for latex particle deformation exceed the forces that resist deformation.[20] For each latex, MFT depends on a number of factors including T_g, plasticization by water and cosolvents, and particle size. Sperry and co-workers suggested two important stages in the process of latex film formation: evaporation of the aqueous solvent and deformation/compaction of particles leading to void closure, and postulated that either of these steps could be rate-limiting, depending on the process temperature.[21] Near its T_g, the rate-limiting step in film formation is particle deformation. At temperature more than 20 K above its T_g, evaporation is the dominant rate-limiting process in film formation.[22] The MFT values of latexes synthesized via copolymerization of SoyAA-1 and MMA are given in Table 1. Unfortunately, these results are hindered by the capabilities of the MFT instrument which is limited to a lower temperature of −5 °C (thus freezing the water and filming capabilities of all samples) and upper temperature limit of 90 °C.

Latexes synthesized using vegetable oil acrylates synergistically combine the advantages of alkyds and emulsions. VOMMs are

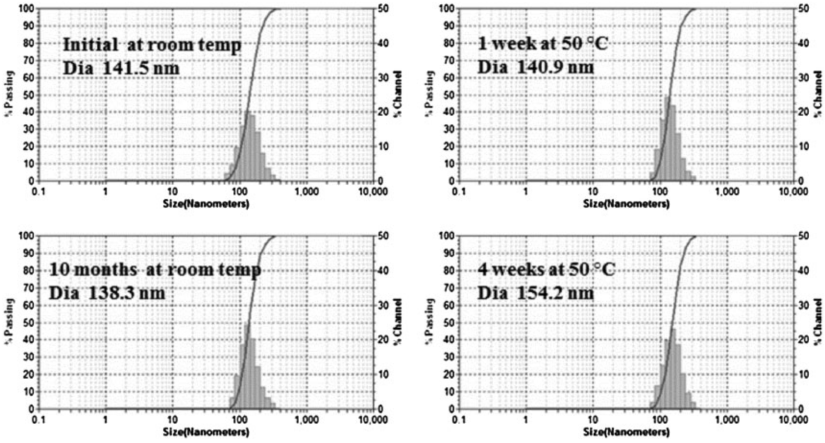
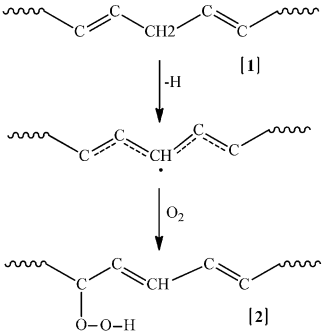


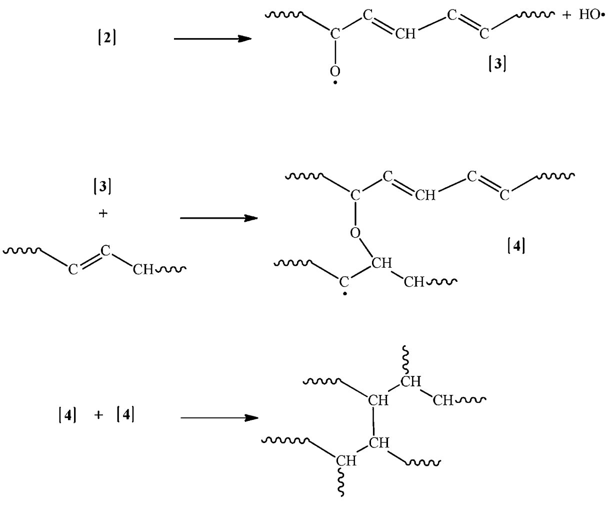
Figure 2.
Stability of SoyAA-1/MMA (46/54 w/w) latex at ambient temperature and 50 °C.



Scheme 1.
Hydroperoxide formation.

comprised of long hydrocarbon fatty acid moieties with allylic double bonds which enable auto-oxidative crosslinking at ambient temperature. Auto-oxidation of fatty acid proceeds through two stages that are promoted by the reactive hydrogen atom on the allylic position of the molecules.[23–26] As the water evaporates after film application, the amount of oxygen dissolved in the polymer matrix increases. The oxygen abstracts an allylic hydrogen from the long hydrocarbon fatty acid moieties to form a fatty alkyl radical which reacts with oxygen to form a hydroperoxide and conjugated double bonds (Scheme 1). Decomposition of these hydroperoxides into alkoxy and peroxy radicals are aided by a transition metal catalyst such as cobalt. Crosslinking comprises the recombination of these radicals to form ether, peroxy, and carbon-carbon (Scheme 2) links which eventually increase the T_g and film durability.

Figure 3 illustrates the T_g changes in SoyAA-1 latexes containing 10, 20, 40, and 60 wt% SoyAA-1 between zero cure (films dried in nitrogen) and films cured in air with 0.1 wt% cobalt metal on latex solids for four weeks. With increasing VOMM concentration, the overall T_g decreased in both cure states. The zero cure data represents a coalescence state where the unsaturated groups of SoyAA-1 have not been exposed to oxygen, thus inhibiting the formation of internal crosslinks. The higher T_g values observed upon ambient cure validate that the fatty acid chains crosslinked auto-oxidatively and catalyzed by cobalt. The difference between zero and final cure T_g, i.e., ΔT_g, is a measure of the auto-oxidation that has occurred in the latex films and corresponds linearly with SoyAA-1 composition (Figure 3). As expected, the ΔT_g increase was more profound for latexes containing 40 and 60% VOMM than latexes containing lesser amounts of VOMMs. The zero and final cure data for



Scheme 2.
Possible crosslinking mechanisms of SoyAA-1.

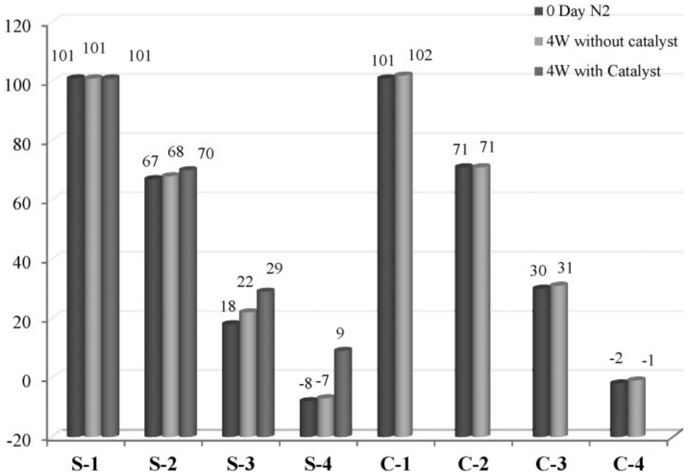


Figure 3.
ΔT_g values as a function of SoyAA-1 and BA content.

control samples (w/o VOMM) are also provided in Figure 3. The lack of autooxidation resulted in no differences being observed in the T_g values over four weeks in the control latexes. It is noteworthy that unlike control copolymers which showed sharp and distinct transitions, the T_g values of VOMM copolymers were very broad and we attributed the breadth to the VOMM's ability to plasticize the polymer matrix.

T_g values as a function of time for SoyAA-1/MMA (46/54 w/w) latex in air with and without 0.1 wt% cobalt metal on latex solids and nitrogen are shown in Figure 4. A slight decrease in the initial T_g was noted upon addition of the cobalt drier and is attributed to the plasticization of the polymer matrix by the solvent content of the commercial catalyst. The latex film with cobalt drier displayed steadily increasing T_g

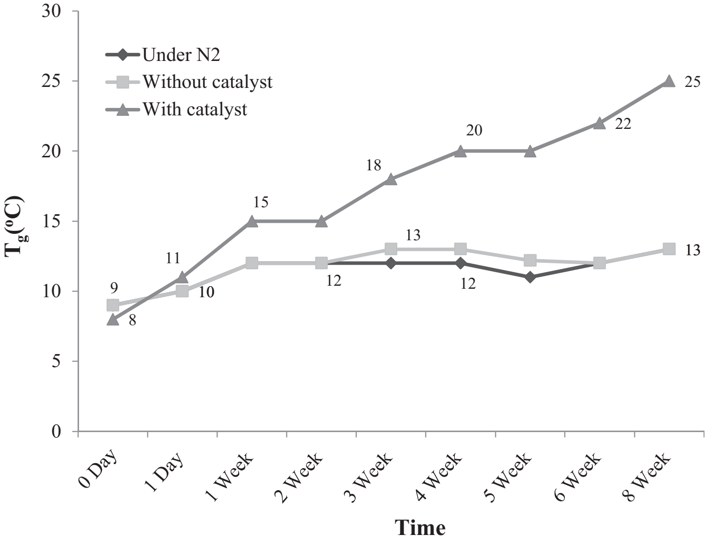


Figure 4.
T_g values as a function of time for SoyAA-1/MMA (46/54 w/w) in air with and without 0.1 wt% cobalt drier and nitrogen.

with auto-oxidative cure at ambient temperature. Continued monitoring validated that within the limits of experimental error, cure was complete at 8 weeks of ambient drying. Latexes cured in air without cobalt drier and under nitrogen showed an initial slight increase of T_g values in the first week of drying, however subsequent T_g values were almost constant.

Solid state ^{13}C NMR spectroscopy is a simple but powerful technique for analyzing a crosslinked system to determine structural changes of the polymer matrix and study cure kinetics. Solid state ^{13}C NMR spectra of SoyAA-1/MMA (46/54 w/w) latex films with 0.1 wt% cobalt metal on latex solids cured at ambient temperature are shown in Figure 5. The peaks appearing between 40–55 ppm are attributed to MMA, while the peaks between 125–135 ppm are associated with allylic double bonds of SoyAA-1. The ratio of allylic double bonds of SoyAA-1 over MMA was quantified via peak integration to determine the percent unsaturation after polymerization and during auto-oxidative curing. Figure 6 summarizes the solid state ^{13}C NMR spectra of the SoyAA-1/MMA copolymer without cobalt catalyst during auto-oxidative crosslinking in air over a drying time of initial, one week, and six weeks. Without the cobalt drier, the peak area of allylic double bonds is almost unchanged, while the same peak decreased noticeably versus time in VOMM films due to auto-oxidative crosslinking catalyzed by cobalt drier (Figure 5).

The cure kinetics of SoyAA-1/MMA (46/54 w/w) latex films were studied over a six week period and the percent unsaturation was determined by solid state ^{13}C NMR spectroscopy (Figure 7). Latex films utilized in this study were coalesced separately to evaluate auto-oxidation of the VOMM under nitrogen, and under air (with and without cobalt drier). The initial value

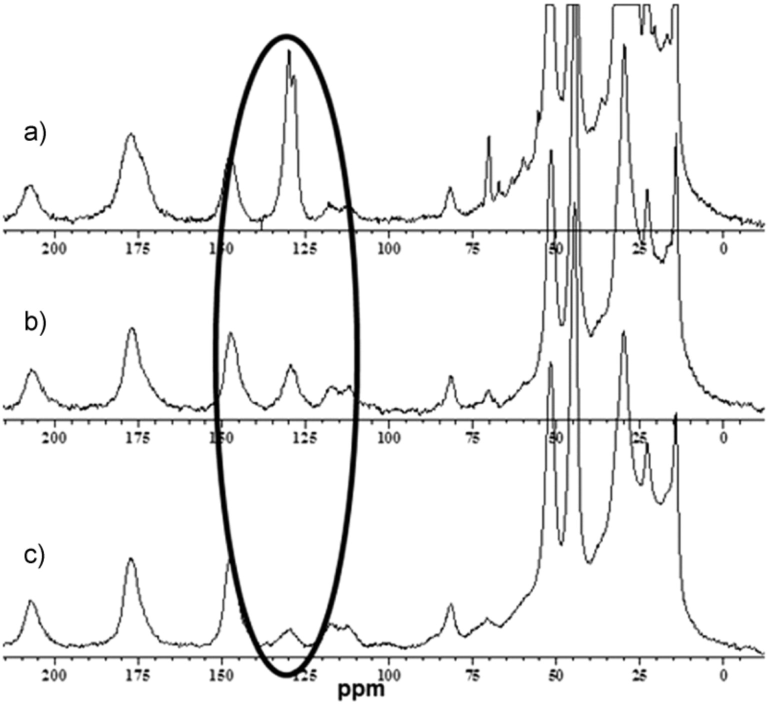


Figure 5.
Solid state ^{13}C NMR spectra of SoyAA-1/MMA (46/54 w/w) latex films with 0.1 wt% cobalt metal on latex solids cured over a) initial, b) 1 week, and c) 6 weeks.

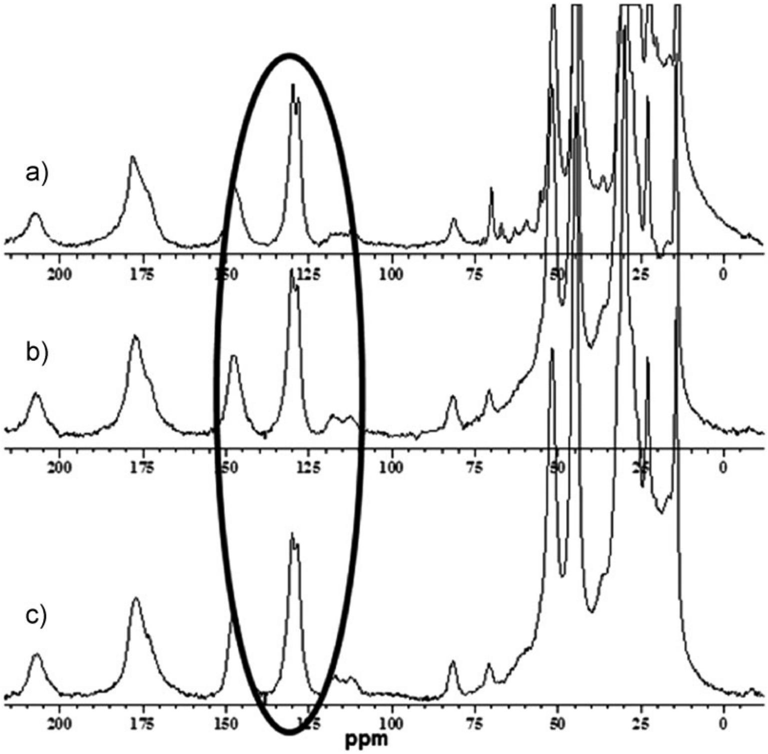


Figure 6.
Solid state ^{13}C NMR spectra of SoyAA-1/MMA (46/54 w/w) latex films without cobalt drier cured over a) initial, b) 1 week, and c) 6 weeks.

of the percent unsaturation of the film cured under nitrogen for four hours was reported as 100% and the preserved unsaturation was calculated based on this value. The amount of double bonds preserved was almost constant in latex films that dried for one day in nitrogen and air, and decreased slightly over six weeks of drying. By this time, the samples cured in nitrogen and air retained 92% of their allylic double bonds within the limits of experimental error. Latex samples containing 0.1 wt% cobalt metal on latex solids lost about 5% of its allylic double bonds within four hours of application. Unlike the films without cobalt catalyst, the latex films with cobalt catalyst retained only 15% of their original double bonds by the end of six weeks, i.e., 85% of the double bonds were consumed via auto-oxidation. The residual unsaturation is probably due to the high degree of crosslinking that limits oxygen diffusion to the deeper layers of the latex film.[27–28] This result is consistent with the T_g change for SoyAA-1 latexes.

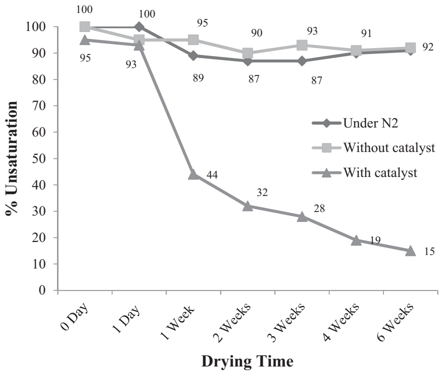


Figure 7.
Percent double bonds preserved during cure for SoyAA-1/MMA (40/60 w/w) latex films in air with and without 1 wt% cobalt drier and nitrogen as determined via solid state ^{13}C NMR.

The similar trends in both the percent unsaturation and T_g change of the film samples cured under air and nitrogen validate the role of cobalt catalysis in auto-oxidative crosslinking. A number of research articles have discussed the effect of cobalt drier on auto-oxidative curing of pure drying oils[29–30] and alkyd coatings.[31,32] Oyman *et al.* [33] studied model compounds including methyl oleate (MO), ethyl linoleate (EL), and methyl linolenate (MLn) emulsified in water to mimic waterborne alkyd paints. After water evaporation, auto-oxidation was monitored via Raman spectroscopy, ATR-FTIR, and ^{1}H NMR. Almost no change was observed for MO and EL without cobalt drier over 130 hours, but all the esters showed significant changes in the presence of cobalt drier within three hours.

Measured variation in dynamic storage modulus as a function of temperature for SoyAA-1/MMA (46:54 w/w) latex film cured in air with and without 0.1 wt% cobalt metal on latex solids is summarized in Figure 8. The films without cobalt lacked the mechanical integrity at higher temperatures to allow above DMA characterization, while all the films cured with cobalt were able to be analyzed over the full temperature range. Dynamic mechanical properties of polymer systems depend on the crosslinking density and storage modulus above T_g increase for higher crosslink systems.[34] In general, storage modulus values of samples with and without cobalt followed similar transition

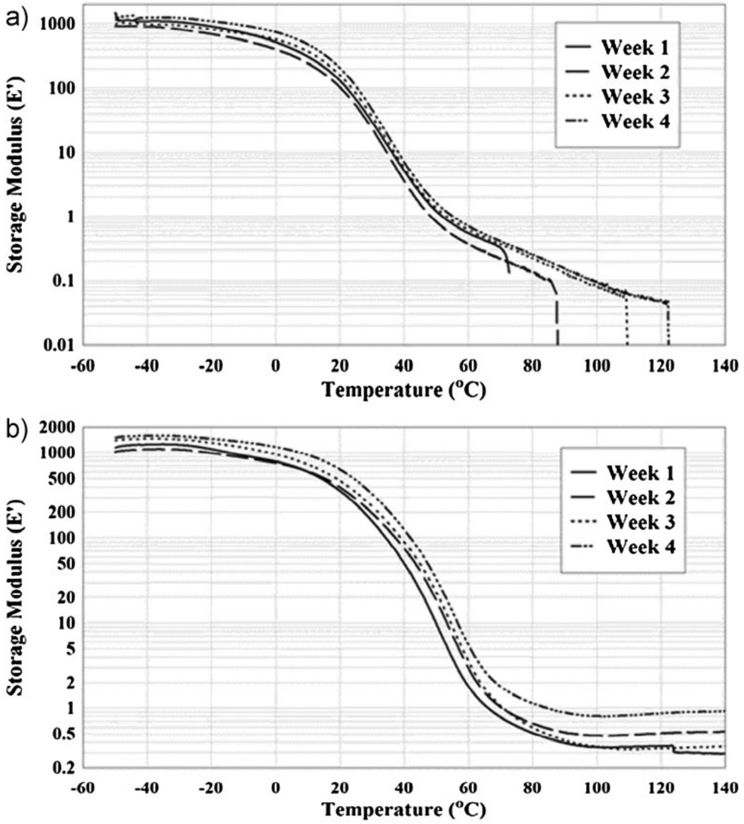


Figure 8.
Storage modulus vs. temperature curves for SoyAA-1/MMA (46:54 w/w) latex films cured in air a) without cobalt metal and b) with 0.1 wt% cobalt metal on latex solids.

trends. As drying/crosslinking progressed, both samples exhibited an increase in storage modulus values in the rubbery plateau.

Tan δ values as a function of temperature for SoyAA-1/MMA (46:54 w/w) latex films dried in air with and without 0.1 wt% cobalt metal on latex solids are shown in Figure 9. Generally, an increase in T_g was noted as the samples were tested over the course of four weeks accompanied by a slight decrease in area under the signal peak due to auto-oxidative crosslinking catalyzed by cobalt. As is generally observed, T_g determined via DMA was higher than that obtained via DSC. The T_g of the latex film with cobalt (determined from the tan δ peak) was 57 °C after one week, and increased with cure time yielding values of 60.1, 60.8, and 62.0 °C for 2, 3, and 4 weeks, respectively. Tan δ peaks of the film samples without cobalt were broader and no significant changes were noted in its form over the duration of drying. T_g values for the air-dried samples were around 44–45 °C but there was no obvious trend of T_g change over the duration of four weeks. The widths of tan δ curves are a further indication of the sample non-homogeneity.[35] Tan δ curves of films with cobalt became narrower with time due to higher degrees of auto-oxidative crosslinking catalyzed by cobalt drier.

Conclusion

A soybean oil macromonomer, SoyAA-1, containing both acrylate and allylic functionalities, was successfully copolymerized with MMA at varying weight ratios. Solid state ^{13}C NMR spectroscopy confirmed the

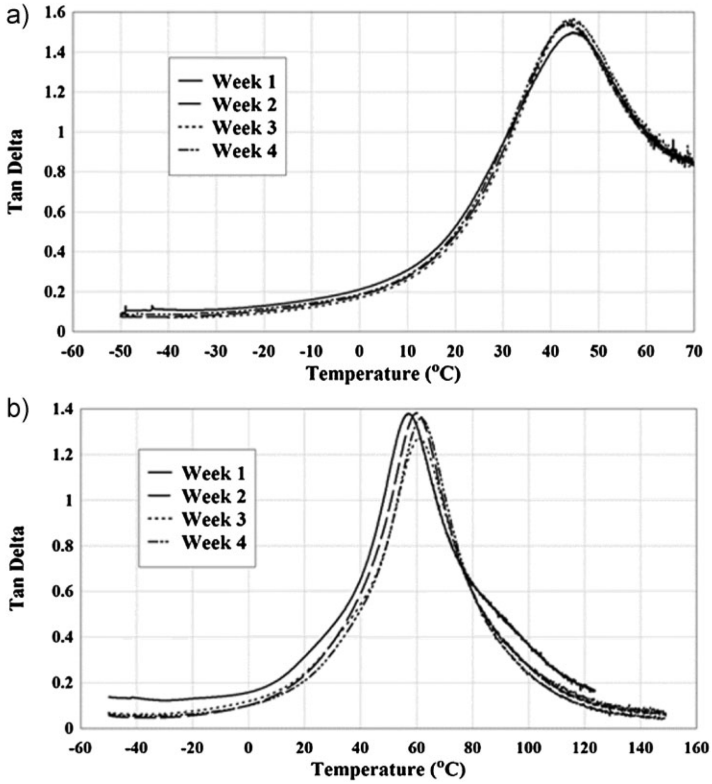


Figure 9.

Tan δ as a function of temperature for SoyAA-1/MMA (46:54 w/w) latex cured in air a) without cobalt metal and b) with 0.1 wt% cobalt metal on latex solids.

preservation of allylic functionalities during emulsion polymerization and was used to investigate the cure kinetics of drying process. The similar trends in both the percent unsaturation and T_g change of the film samples cured under air and nitrogen attest to the role of cobalt catalysis in auto-oxidative crosslinking.

[1] www.airnow.gov, accessed 17 June **2012**.

[2] R. Larock, Y. Lu, *Biomacromolecules* **2007**, *8*, 3108.

[3] V. M. Mannari, J. L. Massingill, *JCT Research* **2006**, *3*, 151.

[4] D. A. Boyles, M. S. D. Al-Omar, US patent application 2009/0275715.

[5] J. M. Behr, US patent application 2008/0250976.

[6] R. Larock, Y. Lu, *Biomacromolecules* **2008**, *9*, 3332.

[7] G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, *Biomacromolecules* **2010**, *10*, 2825.

[8] Y. Guo, V. M. Mannari, P. Patel, J. L. Massingill, *JCT Research* **2006**, *3*, 327.

[9] T. W. Abraham, J. A. Carter, D. Dounis, J. Malsam, US 7,691,914.

[10] R. K. Ddamulari, J. E. Raidy, B. K. Wright, US 7,799,895.

[11] G. Hao, S. K. Mendon, D. E. Delatte, J. W. Rawlins, S. F. Thames, *Proceedings of the 35th International Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, **2008**, 57.

[12] S. F. Thames, *Proceedings of the 25th International Waterborne, High-Solids, and Powder Coatings Symposium*, New Orleans, LA, **1998**, 305.

[13] S. F. Thames, K. G. Panjnani, O. S. Fruchey, US 6,174,948.

[14] D. G. Cory, W. M. Ritchey, *J. Magn. Reson.* **1988**, *80*, 128.

[15] W. T. Dixon, *J. Chem. Phys.* **1982**, *77*, 1800.

[16] P. Eilers, *Anal. Chem.*, **2003**, *75*, 3631.

[17] S. F. Thames, J. W. Rawlins, Proceedings of the Thirty-Sixth Annual International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, **2009**, 5.

[18] S. F. Thames, J. W. Rawlins, S. K. Mendon, D. Delatte, US patent application 2009/0143527.

[19] M. F. Kemmere, J. Meuldijk, A. A. H. Drinkenburg, A. L. German, *Journal of Applied Polymer Science*, **1999**, *74*, 1780.

[20] P. A. Lovell, M. S. El-Aasser, *Emulsion Polymerization and Emulsion Polymers*; John Wiley & Sons, New York **1997**, p. 489.

[21] P. R. Sperry, B. S. Snyder, M. L. O'Dowd, P. M. Lesko, *Langmuir* **1994**, *10*, 2619.

[22] R. A. Pethrick, L. A. Cannon, *Macromolecules* **1999**, *32*, 7617–29.

[23] D. Deffar, M. D. Soucek, *J. Coat. Technol.* **2001**, *73*, 95.

[24] F. Chen, B. G. Bufkin, *J. Appl. Poly. Sci.* **1985**, *30*, 4551.

[25] J. Samuelsson, M. Johansson, *J. Am. Oil Chem. Soc.* **2003**, *80*, 491.

[26] A. Kockritz, A. Martin, *Eur. J. Lipid Sci. Technol. Res.* **2001**, *8*, 719.

[27] C. Stenberg, M. Svensson, M. Johansson, *Ind Crops and Prod* **2005**, *110*, 812.

[28] J. Gardette, J. Lemaire, J. Mallegol, *Prog. Org. Coat.* **2000**, *39*, 107.

[29] S. M. P. Meneghetti, R. F. Souza, A. L. Monteiro, M. O. Souza, *Prog. Org. Coat.* **1998**, *33*, 219.

[30] M. Lazzari, O. Chiantore, *Polym. Degrad. Stab.* **1999**, *65*, 303.

[31] K. H. Zabel, R. P. Klaasen, M. W. F. Nielen, J. O. Hubert, W. J. Muizebelt, *Prog. Org. Coat.* **2000**, *40*, 121.

[32] E. Bouwman, R. Gorkum, *Coordin. Chem. Rev.* **2005**, *249*, 1709.

[33] Z. O. Oyman, W. Ming, R. Linde, *Prog. Org. Coat.* **2003**, *48*, 80.

[34] S. N. Gan, R. Yahya, S. Ataei, *J. Coat. Technol. Res.* **2011**, *8*, 719.

[35] M. Narkis, A. Siegmann, *J. Appl. Poly. Sci.* **2007**, *105*, 885.