

Synthesis and characterization of new vinyl acetate grafting onto epoxidized linseed oil in aqueous media

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ABSTRACT: Modified poly (vinyl acetate) copolymers with epoxidized linseed oil (ELO) as co-monomer have been prepared. The polymerization was performed in aqueous medium without any additional protective colloid in the presence of sodium persulfate as catalyst. The effect of vinyl acetate (VAc)/ELO feed ratio, reaction temperature, reaction time, and catalyst amount has been studied. FTIR spectroscopy showed that the reaction between ELO and VAc resulted in slight decrease and shift in ELO characteristic bands of oxirane groups; and new bands were detected in the copolymer spectra attributed to PVAc and ELO functional groups. Moreover, new signals attributable to the copolymer were observed in the ¹H NMR spectra (δ 4.07 and 1.62 ppm) and in the ¹³C NMR spectra (δ 15.29 and 31.0 ppm). Analysis by differential scanning calorimetry (DSC) showed a single T_g for the copolymerization product of VAc and ELO and two T_g for the PVAc/ELO blend, indicating the chemical reaction between VAc and ELO. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42089.

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INTRODUCTION

Polyvinyl acetate (PVAc) homopolymer is among the main products of the adhesive industry. They are mainly used in wood processing, civil engineering, paper processing, packaging and binding industry adhesives and coatings, construction and many other applications.^{1,2} Their copolymerization with other monomers has found increasing use in more advanced adhesives, exterior and interior paints, carpet backing, and adhesives for clay coatings on paper.¹ These emulsions offer the advantage of high solids content with fluidity since the viscosity of the emulsion is independent of the molecular weight of the resin. However, the adhesives formulated with PVAc-based polymer dispersions have some drawbacks. Because of high polyvinyl acetate thermoplasticity the adhesive joints obtained with PVAc-based formulations are sensitive to moisture and high temperature and have a poor resistance to creep under static load.³ In general, the emulsions utilize poly (vinyl alcohol) (PVOH) protective colloid to form small particles.^{1,4} Nevertheless, the addition of PVOH reduces adhesive water resistance because of the introduction of hydrophilic hydroxyl groups into the system. Moreover, VAc is a polar and very reactive monomer and requires further treatment to copolymerize with less polar and

reactive monomers.^{1,5,6} In addition, the high solubility of VAc monomer in water leads to difficulties during copolymerization with more hydrophobic monomers since the relative concentrations of the copolymerizing monomers in the polymer and water phases are significantly different. As alternative, various monomer feed methods are employed to force random copolymerization with less reactive monomers. In line with this, a large number of patents and other literatures reported methods on how to improve the performances of PVAc adhesives. Among these methods, the utilization of specific functional comonomers in the emulsion polymerization phase, by including polyvalent metals salts in the adhesive formulation or by post-addition thermosetting resins such as urea-formaldehyde (UF), melamine formaldehyde (MF) or polyisocyanates for two components systems.^{7–11} However, the demand for substitution of toxic chemicals and development of environmental-friendly products is constantly increased during recent years. In this context, efforts have been focused on the use of vegetable oils as alternatives to fossil-based chemicals for polymer synthesis, and there is a broad palette of chemical pathways for the preparation of thermosets and thermoplastic polymers based on plant oils.^{12,13} Due to their ready availability, inherent

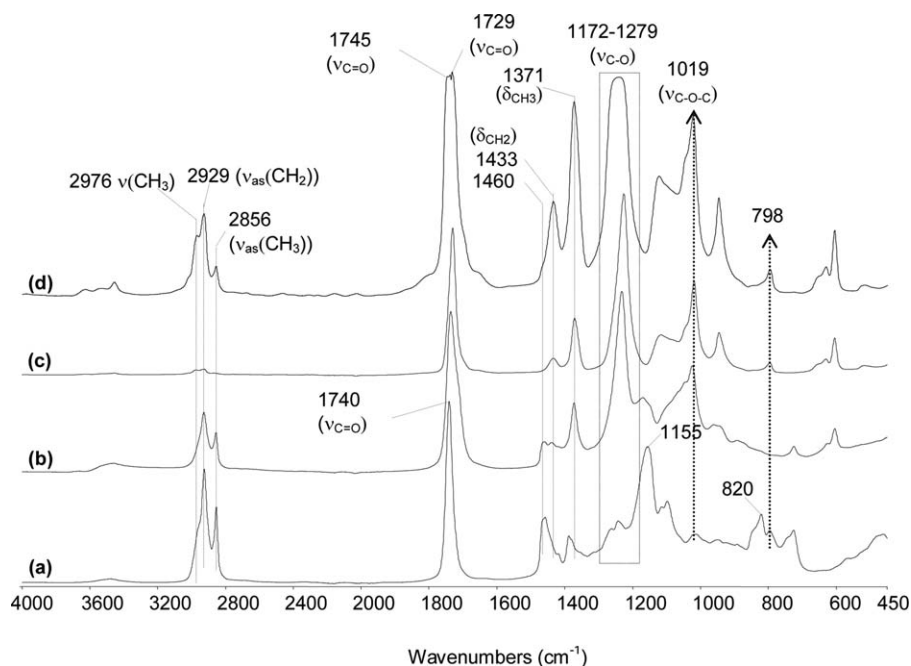


Figure 1. FTIR spectrum of ELO (a), Poly(ELO) (b), PVAc (c), and VAc/ELO (3/1) copolymer (d).

biodegradability and low toxicity, vegetable oils have been largely employed for many years as paints binders or as components in alkyd resins and many other applications. In particular, the use of plant oils, especially drying oils, as co-monomers with VAc have been reported in the literature.^{14,15} However, these studies reported either the resulting products as blends¹⁴ or the synthesis was carried out in organic medium or in water but in the presence of PVOH as protective colloid;¹⁵ in both case a waterproof effect resulted from using plant oil was reported.

In this study, a synthesis of copolymer PVAc-grafted epoxidized linseed oil (ELO) by emulsion polymerization in various compositions without any protective additives was investigated. The resulting copolymers which can produce additional waterproof effect were characterized by FTIR and NMR spectroscopy and thermal analyses.

EXPERIMENTAL

Materials

Epoxidized linseed oil was supplied by Traditem GmbH. Vinyl acetate ($\geq 99\%$, 3–20 ppm hydroquinone) was purchased from Sigma Aldrich. Sodium persulfate was obtained from Merck. All other chemicals were reagent grade and used as received.

Instrumentation

FTIR spectra were obtained using a Perkin-Elmer FTIR Spectrum-two spectrometer on ATR mode (resolution 4 cm^{-1} , 16 scans). Polymers spectra were recorded on films obtained from solutions after solvent evaporation in the range of wavenumbers from 4000 to 450 cm^{-1} . The FTIR spectra were normalized and major vibration bands were associated with functional groups. The spectra of ELO and polymerized ELO were measured by placing directly a film of oily sample on the

surface of ATR diamond and spectra obtained baseline-corrected and normalized using the peak at 1460 cm^{-1} (i.e., CH_2 scissors deformation vibration).

One dimensional ^1H and ^{13}C NMR spectra were recorded in CDCl_3 with a tetramethylsilane internal standard using a Bruker DRX-400 spectrometer. Chemical shifts (δ) are reported in (ppm). Thermogravimetric analysis (TGA) of the obtained polymers was performed using a Mettler-Toledo TGA/SDTA 851e, to determine thermal degradation. Differential scanning calorimetry (DSC) thermograms were recorded on a DSC Mettler-Toledo DSC 820 system under a nitrogen atmosphere. 2–5 mg of the sample was heated in an aluminum crucible. The samples were first heated from 30 to 100°C at $10^\circ\text{C}/\text{min}$ (first scan) to remove thermal history, and then cooled to -50°C . The second heating scans were run from -50 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$. Glass transition temperatures (T_g) were defined as the midpoint temperature of the heat capacity transition in the second heating scan.

Synthesis of Polymers

Synthesis of Poly (vinyl acetate) (PVAc). Totally, 20 g of vinyl acetate was added to a solution of 10 mL of water containing $\text{Na}_2\text{S}_2\text{O}_8$, in a 250-mL three-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser, under nitrogen atmosphere. The temperature was maintained by placing the reaction flask in a controlled-temperature oil bath. Stirring rate was kept constant throughout the reaction. The solution was stirred and heated at 80°C for 2 h. After reaction a white solid polymer was obtained. The solid product was washed several times with diethyl ether and purified by dissolving in acetone and precipitating by adding diethyl ether. The transparent product was then dried in the oven at 50°C under vacuum and 18.7 g of the polymer were obtained (93.7% yield).

Table I. Synthesis of VAc/ELO Copolymers in Varied Conditions: Impact of the VAc/ELO Ratio, Reaction Time, Reaction Temperature, and Catalyst Amount

VAc/ELO (%) ^a	1/0	3/1	1/1	1/3	0/1
Yield (%)	93.7	91.3	54.3	24.4	0
Reaction time (min) ^b	30	60	120	240	360
Yield (%)	4.2	74.2	91.3	89.2	94.6
Reaction temperature (°C) ^c	60	70	80	90	100
Yield (%)	0.6	85.2	91.3	91.2	93.3
Catalyst amount (%) ^d	0.05	0.1	0.25	0.5	1
Yield (%)	13.0	80.7	91.3	90.4	91.0

^aReaction time was 2 h, temperature was 80°C and catalyst amount was 0.25%.

^bVAc/ELO ratio was 3/1, reaction temperature was 80°C and catalyst amount was 0.25%.

^cVAc/ELO ratio was 3/1, reaction time was 2 h and catalyst amount was 0.25%.

^dVAc/ELO ratio was 3/1, reaction time was 2 h and reaction temperature was 80°C.

Synthesis of Poly (epoxidized linseed oil) (PELO). The polymerization of epoxidized linseed oil (ELO) requires acid catalysts for ring opening of the oxirane group. A typical procedure for the ring-opening polymerization of ELO is as follows: 7 g ELO and 3 g acetic acid were added to 250-mL three-necked round bottom flask equipped with magnetic stirrer, condenser and thermometer. The mixture was stirred and heated at 140°C for 4 h and a viscous product was obtained. The obtained product was then washed several times with water to remove and deactivate the catalyst and the remaining residue was dried under vacuum at 80°C to a constant weight to give a 98% yield of reddish polymer. FTIR confirmed the ring opening polymerization of the ELO oxirane groups (Figure 1).

Synthesis of Vinyl Acetate (VAc)/ELO Copolymers in Aqueous Media

The reagent amounts, the reaction conditions and the yields for each copolymer synthesis were reported in Table I. Typically, into a three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser, various VAc/ELO ratios were added to a water solution of Na₂S₂O₈. The solution was stirred at 60, 70, 80, 90, and 100°C for 30 min, 1, 2, 4, and 6 h. The solid product obtained after each preparation was washed several times with diethyl ether to remove unreacted ELO, and dried in the oven at 50°C to a constant weight and the yield was calculated. These products were analyzed by ¹H and ¹³C NMR and FTIR and compared with those obtained from a formulation containing PVAc homopolymer and initial ELO. Thermal properties, water and solvent solubility of the polymers were evaluated as well.

Solubility Test

The solubility of the PVAc, PELO, and PVAc/ELO copolymers was examined with the following method. A 100 mg of copolymer sheets was introduced in test tube and 10 mL of solvent was added. Then the tubes were shaken in the horizontal direction continuously for 36 h at room temperature. The solubility

was assessed in water, and in some organic solvents such as DMF, methanol, toluene, THF, chloroform, acetone, acetonitrile, ethylene glycol, xylene, butanol, diethyl ether. The solubility of the polymers was evaluated visually and results were classified into three categories: soluble (++) , partially soluble (+) and nonsoluble (-). If the result lies between two categories, a combination of two signs separated by slash (/) was used.

RESULTS AND DISCUSSION

Characterization of VAc/ELO Copolymer: Effect of Reaction Conditions

The yields of resulted products of mixing VAc and ELO at various feed ratios and reaction time, reaction temperature and catalyst amount were listed in Table I. The conversion of the monomers to copolymer is greatly influenced by the relative feed composition of the monomers (VAc/ELO). The rate of copolymerization increases significantly as the VAc increases or ELO concentration decreases in the feed. Similar trends were reported in the literature when linseed oil was copolymerized with VAc in organic solvent.¹⁵ The possible reason for this marked influence of ELO concentration on the copolymerization yield could be the high steric effect of the ELO, availability of residual double bonds in ELO and chain transfer which limits the chain growth. The yield of the reaction between VAc and ELO was also found to increase with increasing temperature, reaction time and catalyst amount. However, a significant yield (91.3%) was obtained after 2 h reaction at 80°C with 0.25% catalyst. Accordingly, these relatively mild conditions appear to be adequate for obtaining copolymer with relatively high yield. Almost no reaction was noted at room temperature, and no reaction occurred without catalyst or water. This is a proof of mixture stability at room temperature and the importance of catalyst and water in the reaction. The relatively small yield obtained after 30 min at 80°C (4.2% yield) indicates that the reaction is rather slow.

The ¹H NMR analysis (spectra not shown) of the product obtained at the end of the polymerization test with persulfate, water, and ELO without vinyl acetate showed that neither epoxy groups nor residual double bonds were affected by persulfate radicals. Indeed, the ¹H NMR and FTIR spectra of the obtained product were identical to those of raw ELO. Although this shows that ELO's double bonds and oxirane groups remain unreacted under studied reaction conditions, the presence of polyvinyl acetate radical chains resulted in significant decrease of double bonds and slight decrease of oxirane groups in the products of copolymerization of vinyl acetate and ELO as proved by FTIR and NMR spectra (Figures 1–3).

Spectroscopic Characterization of the Copolymer

In order to characterize the product of the copolymerization, the ELO raw material and the PVAc homopolymer were characterized using FTIR, and ¹H and ¹³C NMR spectroscopy, and the data obtained were reported in Table II, Figures 1 and 4, respectively. These data were in agreement with the literatures.^{3,16–26} The epoxy group number of ELO per molecule, determined by ¹H NMR spectroscopy, was 5.9. The ¹H and ¹³C NMR analyses of the ELO showed also the presence of residual double bonds. Integration of the area under double bonds peak in ¹H NMR

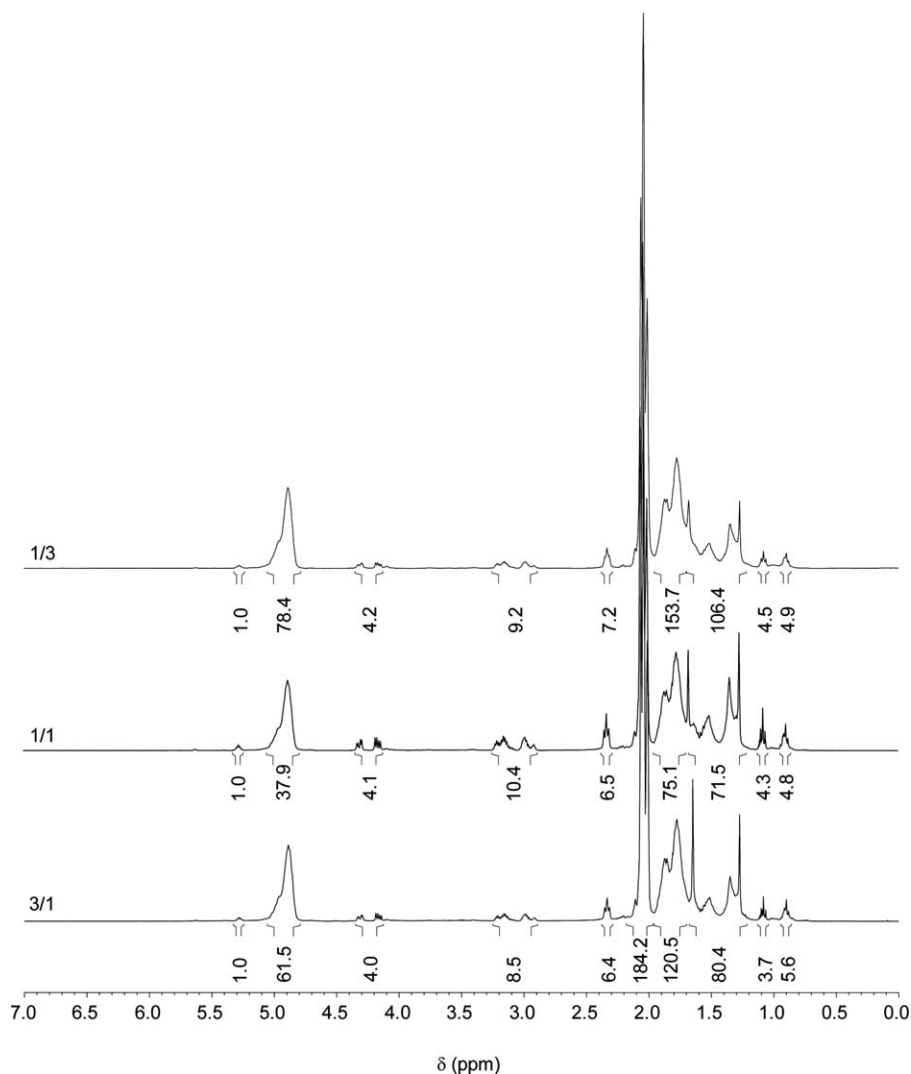
Table II. FTIR Spectral Data (cm^{-1}) for ELO and PVAc Homopolymer

	Epoxy ring (stretching)	CH (stretching)	C=O (stretching)	CH (bending)	C—O (stretching), C—C (stretching)
ELO	820 (w)	2856 (s) 2929 (s)	1740 (vs)	1457 (m) 1371 (s)	1155 (s) 1242 (w)
PVAc		2973 (w) 2926 (w)	1729 (vs)	1433 (w)	1018 (m) 1225 (vs) 1370 (s) 1115 (w)

spectra showed that ELO has (0.1) residual double bonds per ELO molecule.

The chemical changes due to the copolymerization of VAc and ELO were determined by spectroscopy FTIR, ^1H and ^{13}C NMR, and the obtained results were compared with those of PVAc homopolymer obtained under same conditions and with raw ELO. While, the physical changes, were evaluated by analyzing the thermal behavior of the copolymer, and the obtained data

were compared with those of the PVAc homopolymer and PELO. The FTIR was used to prove the reaction between VAc and ELO by qualitative identification of the main characteristic bands from ELO and PVAc. ELO is characterized by the stretching vibration of the epoxide moieties (C—O—C) at 820 cm^{-1} , and the copolymerization reaction between ELO and VAc resulted in decrease and shift of this band to lower wavenumbers (Figure 1). New bands were also observed in the copolymer

**Figure 2.** ^1H NMR spectra of VAc/ELO copolymers at different feed ratios.

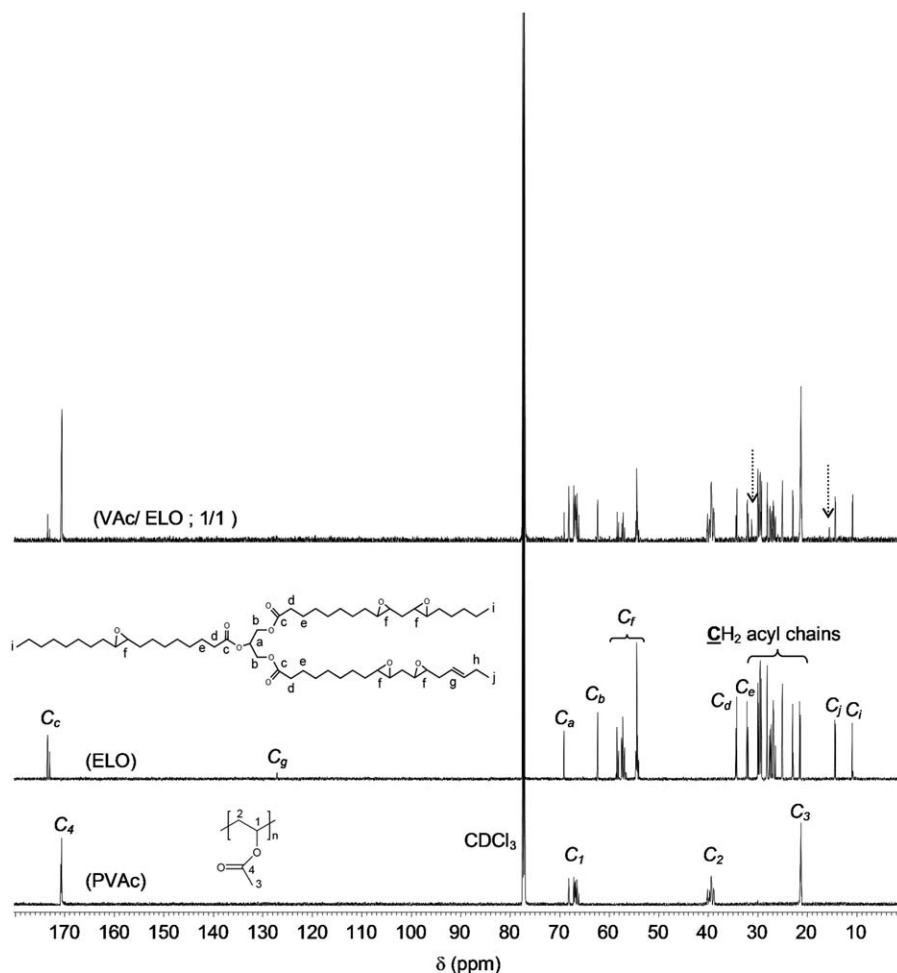


Figure 3. ^{13}C NMR spectra of PVAc homopolymer, ELO, and VAc/ELO (1/1) copolymer.

spectra in the range $2950\text{--}3000\text{ cm}^{-1}$, which were assigned to the new alkyl groups generated from the reaction of ELO and PVAc. The broad absorptions at $1729\text{--}1745\text{ cm}^{-1}$ region, and at $1172\text{--}1279\text{ cm}^{-1}$ region assigned to carbonyl group and C—O respectively, indicates the coexistence of C(=O)—O—C of PVAc and triglyceride moieties.

FTIR spectra of polymerized ELO (PELO) using acetic acid as catalyst was analyzed and compared with those of ELO, PVAc, and VAc/ELO copolymers. ELO spectra is characterized by the characteristic oxirane absorption at 820 cm^{-1} (Figure 1), which was completely disappeared in PELO spectra, while in the copolymer spectra, it was slightly decreased and shifted to low wavenumbers with respect to its location in the ELO spectrum. This is most likely because of the grafting of PVAc onto ELO. Copolymers were also analyzed by $400\text{ MHz } ^1\text{H}$ and ^{13}C NMR to confirm the incorporation of ELO into PVAc (Figures 2 and 3). Figure 2 shows the ^1H NMR spectra of VAc/ELO copolymers at different feed ratios. The signals at $\delta 1.75$, 2.02 , and 4.86 ppm in the ^1H NMR spectrum are attributable to the PVAc backbone, in agreement with the homopolymer data (Figure 4). The signal at $\delta 5.24$ ppm corresponds to the hydrogen of the methine proton $-\text{CH}_2-\text{CH}-\text{CH}_2-$ of the glycerol backbone. The methylene protons $-\text{CH}_2-\text{CH}-\text{CH}_2-$ of the glycerol

backbone were also observed at $\delta 4.1\text{--}4.32$ ppm. By using the signal at $\delta 5.24$ ppm (methine proton) as internal standard, the integral (I) of the peaks at $\delta 4.1\text{--}4.32$ ppm was between 4.0 and 4.2. Peaks at $\delta 3.22\text{--}2.86$ ppm (integral values ranged from 8.5 to 10.4) correspond to epoxy groups. Peak at $\delta 2.31$ ppm ($I = 6.4 - 7.2$) corresponds to the methylene hydrogens alpha to carbonyl groups ($-\text{CH}_2-\text{C}(\text{O})-\text{O}-$). The hydrogens of the triglyceride ending methyl groups ($\text{CH}_3-(\text{CH}_2)_n-$) appear at $\delta 1.06$ ppm and 0.87 ppm. These analyses showed that some signals attributable to ELO fragments appeared modified in their intensity with respect to those of unreacted oil. In particular, the intensity of the signals at $\delta 3.22 - 2.86$ ppm region (oxirane groups) decreased slightly with respect to the unreacted ELO. Two new signals, which correspond neither to the PVAc homopolymer nor to ELO, were appeared at $\delta 4.07$ and 1.62 ppm, which are attributed respectively to proton resonance signal of the PVAc—CH—ELO and ELO—CH—PVAc linkage. Similar results were reported by Salvini *et al.*¹⁵ when they modified PVAc with linseed oil (LO) in the presence of cobalt acetate as catalyst in organic solvent and Poly (vinyl alcohol) as protective colloid. For the studied ELO/VAc feed ratios (3/1, 1/1, and 1/3), ELO inclusion was found to be respectively 1.63, 2.64, and 1.27 mol % by taking the ratio of the signals at 5.24 ppm (methine triglyceride) and at 4.86 ppm (PVAc methine).

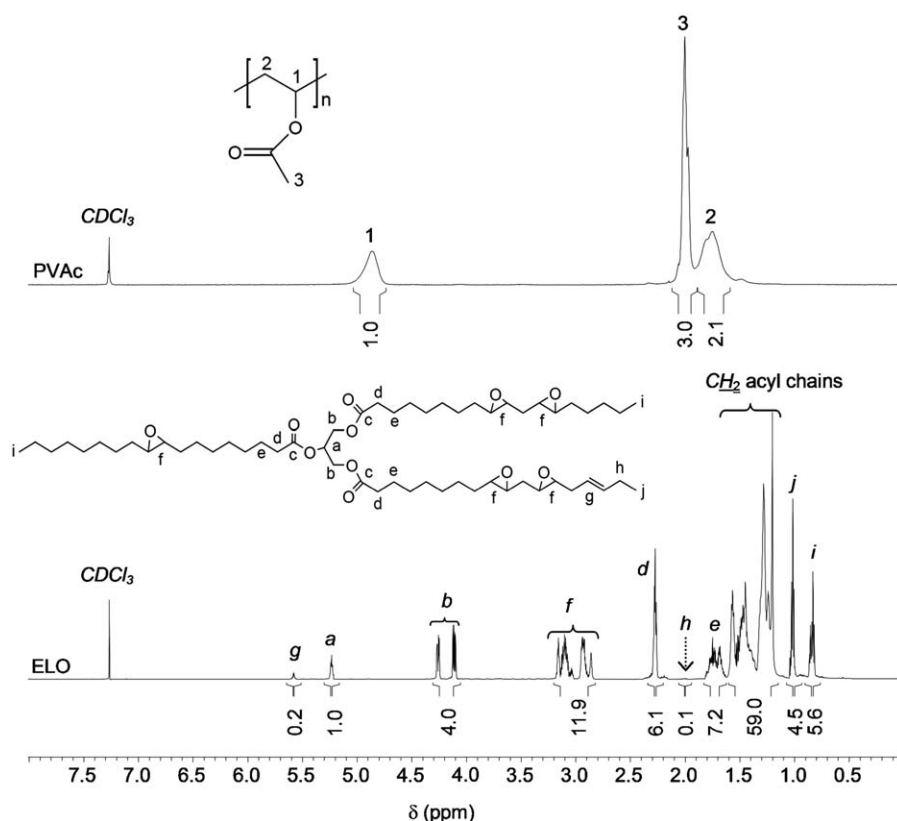


Figure 4. ^1H NMR spectral data (δ , ppm, CDCl_3 as solvent).

Figure 3 shows the ^{13}C NMR spectrum of the PVAc homopolymer, ELO and ELO/VAc (1/1) copolymer. The spectrum of VAc/ELO copolymer clearly shows the presence of ester carbonyls (δ 173.2–173.3 ppm) from oil triglyceride structure and ester carbonyl from PVAc at δ 170.4 ppm. This spectrum shows also clearly the complete disappearance of the peak at δ 126.8 ppm which correspond to carbons of double bond ($\text{CH}=\text{CH}$), and the appearance of two new peaks at δ 31.0 ppm and δ 15.29 ppm, which corresponds respectively to the carbons of $\text{ELO}-\text{CH}-\text{CH}-\text{PVAc}$ linkage and the carbon of the end methyl group of the acyl chain which reacted with PVAc (Figure 5). Control experiment using linseed oil (LO), which has more double bonds than ELO, has been performed under same conditions as VAc/ELO showed no reaction between LO and VAc. This result shows that the epoxidation of some double bonds in plant oils makes the residual double bonds much more reactive than those naturally present in the plant oils. This could be explained by the inductive effect changes resulting from the epoxidation of some double bonds.

Thermal Characterization

The glass transition temperature (T_g) is one of the principal polymer characteristic related to polymer properties and processing. For most of thermoplastic, mixing of two incompatible polymers (Polymer blends) shows in general two distinct T_g , while, a random copolymer obtained from reaction of two monomers shows in general a single T_g situated between the two T_g of the corresponding homopolymers. ELO and PVAc are not compatible, thus the formation of VAc/ELO copolymer was

also confirmed by differential scanning calorimetry (DSC) analysis by analyzing PVAc homopolymer, PELO, VAc/ELO copolymer, and PVAc/ELO blends (Figure 6). These analyses shows a T_g value of 38°C for PVAc homopolymer which is in accordance with the literatures,^{1,15} while the T_g of PELO was found to be around -20°C . Whatever the mixture ratio of PVAc and ELO in the blends, the analyses showed two distinct T_g , indicating the incompatibility of these two polymers. However, the VAc/ELO copolymer showed a single T_g (26°C) which is lower than that of PVAc homopolymer due to the ELO incorporation and its plasticizing effect resulted from its flexibility and relatively short chains in the copolymers.

The thermal degradation of PVAc homopolymer, ELO and VAc/ELO copolymers were shown in the Figure 7. In general, the thermal degradation of PVAc starts at $150-220^\circ\text{C}$.^{1,27} The polymer can be heated at 125°C for hours without changing, but at 150°C it gradually darkens, and at over 225°C it liberates acetic acid, forming a brown, insoluble resin. The volatilization occurs very rapidly at 300°C .^{1,28} It was found that the thermal degradation rate was independent of the molecular weight of PVAc.²⁹ The decomposition occurs in two stages; in the first stage only acetic acid is lost followed by the main loss of weight above 300°C due to the polyester chain scission.³⁰ ELO shows better thermal stability and the degradation start above 300°C , and only one stage was observed. TGA of copolymers shows similar behavior as PVAc homopolymer in the first degradation stage, and slight differences in behavior above 350°C were observed, most likely because of the incorporation of the ELO units in the

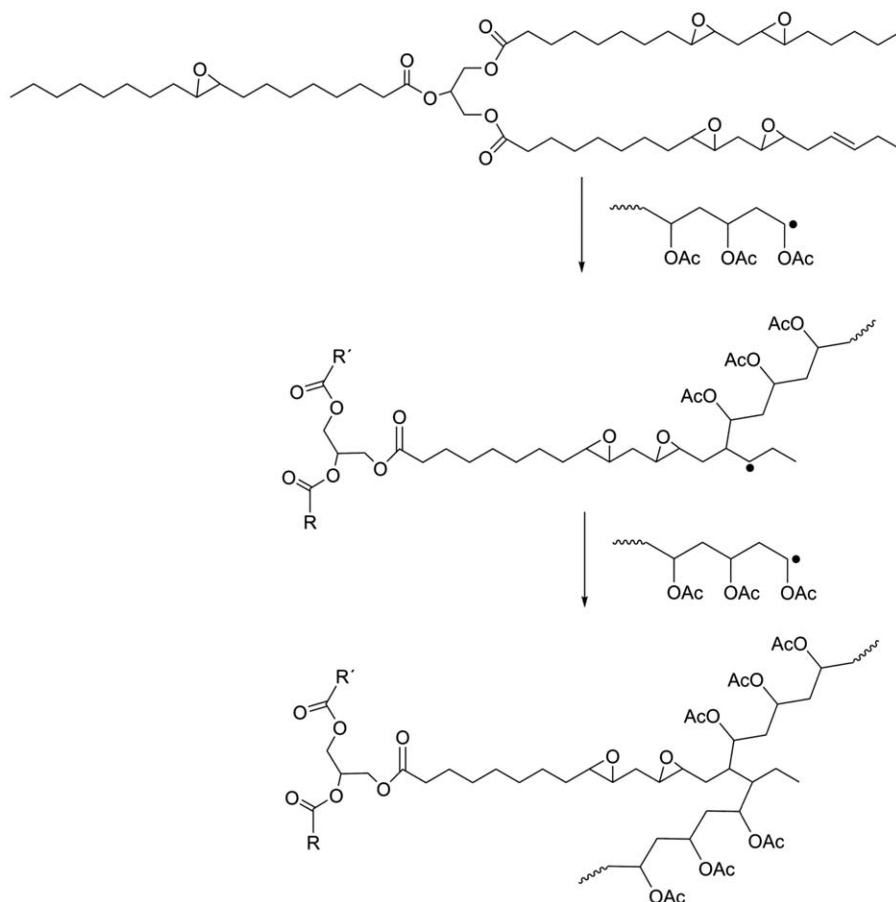


Figure 5. Polymerization reaction mechanism and VAc/ELO copolymer structure.

PVAc. The first step is degradation of the PVAc backbone to give acetic acid and other chemicals followed by the degradation of the incorporated ELO units (above 350°C). The differences observed in the copolymers thermal behavior above 300°C could be explained by the amount of ELO incorporated in the PVAc. Indeed, the estimation of the ELO/VAc ratio in the final

product showed that some copolymers contain different amount of ELO depending on the initial feed ratio.

The incorporation of ELO group into PVAc provides slight effect on the degradation rate at higher temperatures. The degradation pattern of the copolymers seemed to be similar to

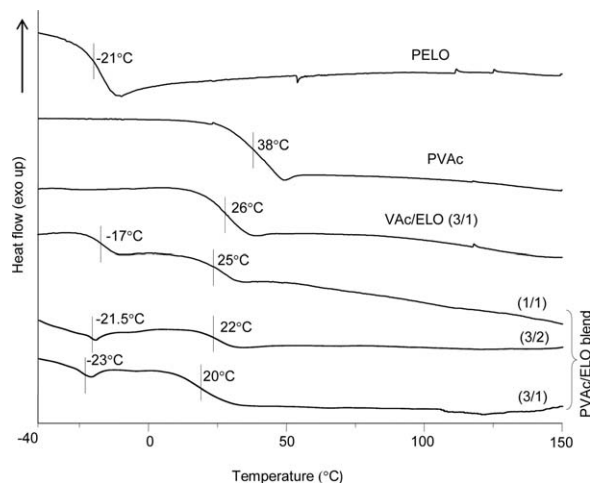


Figure 6. DSC thermograms of PVAc homopolymer, ELO, VAc/ELO (3/1) copolymer, and PVAc/ELO blend.

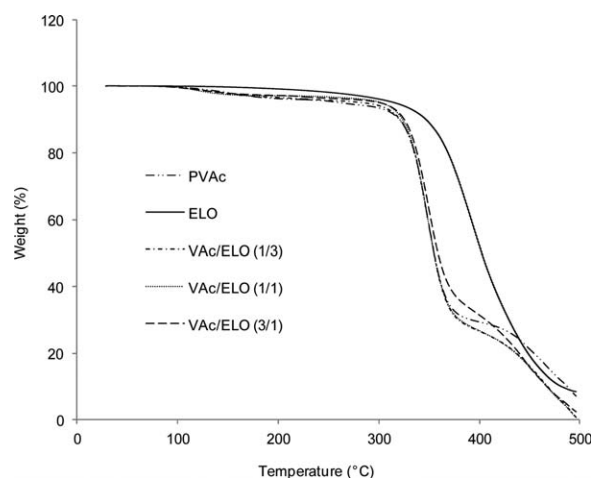


Figure 7. TGA thermograms of PVAc homopolymer, PELO, and PVAc/ELO copolymers.

Table III. Solubility Test Results of PVAc Homopolymer, Poly (ELO), and VAc/ELO Copolymer

Solvent	Material		
	PELO	Copolymer VA/ELO = 3/1	PVAc
DMF	++	+	+
Methanol	++	++/+	+
Toluene	++	+	+
THF	++	++/+	+
Chloroform	++	+	+/-
Acetone	++	++/+	+
Acetonitrile	++	++/+	++/+
Water	-	-	-
Ethylene glycol	-	-	-
Xylene	++	+/(swollen)	+/(swollen)
Butanol	++	-	-
Diethyl ether	++	-	-

PVAc homopolymer behavior, and this could be explained by the fact that a few ELO units were incorporated into PVAc.

Solubility Tests

It was clear that the Poly (ELO) was soluble in solvents such as DMF, methanol, toluene, THF, chloroform, whereas PVAc was slightly soluble in signified solvents as shown in the Table III. Because of the presence of drying oil in the PVAc chains, it was showed good hydrophobicity and significant improvement in the water resistance. Slight increasing in the copolymers solubility was obtained because of the incorporation of oil moieties. The application of PVAc-based polymer dispersion in adhesives formulations implies using poly (vinyl alcohol) as protective colloid which result in products with high moisture and water sensitivity. Incorporation of ELO which is hydrophobic into PVAc polymer chains will result in products with waterproofing properties. Also the residual oxirane groups in the copolymer product can play a role of internal hardener and discard using external hinders. The environmental concerns and the cost of the systems currently available in the adhesives market and the growing interest in using renewable materials such as plant oils, have also emphasized the incorporation of renewable and waterproofing agent to the PVAc backbone to enhance adhesives performances.

CONCLUSIONS

In conclusion, we have shown that it is possible to incorporate the renewable ELO into polyvinyl acetate in aqueous media. The reaction yield can be controlled by varying the concentration, reaction time, temperature, and amounts of catalyst. The copolymer formation was confirmed on the basis of the spectroscopic characteristics. The copolymerization reaction between ELO and VAc resulted in slight decrease and shift in the characteristic groups of oxirane groups; and new bands were detected in the copolymer FTIR spectra attributed to PVAc and ELO functional groups. Moreover, new signals attributable to the copolymer were observed in the ^1H NMR spectra (δ 4.07 and 1.62 ppm) and in

the ^{13}C NMR spectra (δ 15.29 and 31.0 ppm). The results obtained were in agreement with the thermal analyses, which shows a single T_g (26°C) for the VAc/ELO copolymers, which is lower than T_g of PVAc homopolymer and higher than that of PELO. ^1H NMR spectra shows also the presence of unreacted oxirane groups in the copolymer product which is potentially interesting for subsequent hardening. An improvement of the water resistance has been observed due to the presence of ELO.

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