

New Polymers from Epoxidized Soybean Oil with Pyridine Derivatives

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Received 9 July 2010; accepted 7 December 2010

DOI 10.1002/app.33917

Published online 30 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study 4-methylpyridine (4MP), 4-vinylpyridine (4VP) and poly(4-vinylpyridine) (P4VP) were separately reacted with epoxidized soybean oil triglycerides (ESO) to give plant oil based thermoset polymers. The addition reaction of pyridine with epoxide followed by a rearrangement results in formation of pyridone units and these were polymerized via a Diels–Alder reaction. DMA, DSC, TGA and IR spectroscopy were used for the characterization of the products. 4MP-ESO, P4VP-ESO and P4VP-ESO-*in situ* polymers were cross-

linked yielding rigid infusible polymers. Glass transition temperatures (T_g) of 4MP-ESO and P4VP-ESO-*in situ* were found as -10.5 and 70.5 (32.3 as shoulder) °C respectively, by DMA analysis. Storage moduli of 4MP-ESO and P4VP-ESO-*in situ* at 25°C were 13.7 and 187.2 MPa, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2976–2984, 2011

Key words: renewable resources; thermal properties; crosslinking; mechanical properties; biodegradable

INTRODUCTION

The increasing price and the dwindling reserves of petroleum dictate the use of nonpetroleum raw materials for polymer synthesis. The use of plant oil triglycerides as renewable raw materials in polymer production has many advantages; namely, biodegradability, renewability of raw materials, CO₂ emission reduction,¹ energy savings, ease of production,² low price³ and the availability of a variety of chemical transformations on the triglycerides.^{4–6}

In the past we and others have synthesized oil based polymers by placing a polymerizable functional group on the triglyceride and using it to obtain a polymer. Such large monomers usually polymerized in low conversions and gave low molecular weight polymers with low mechanical properties.^{4–9} The strategy used in this work is different. First, a high molecular weight polymer which has suitable functional groups was chosen and the triglyceride derivative was grafted onto this polymer using these functional groups. This ensures that the product has a high molecular weight. The two strategies are shown in Figure 1. In fact we have used this strategy successfully by reacting ESO with styrene-maleic anhydride copolymers¹⁰ and with maleic

anhydride grafted polypropylene.¹¹ In each case the presence of the high molecular weight backbone increases the mechanical properties of the final crosslinked polymers.

When a pyridine derivative is used with an epoxy group, it is natural to expect that pyridine would initiate the homopolymerization of epoxy groups.¹² However, Xue et al. showed that the reaction between pyridine and epoxide groups resulted not only in the homopolymerization of epoxy groups but also in the formation of pyridone structures (Fig. 2).¹³ The addition reaction of pyridine to the epoxide followed by a ring formation and a rearrangement results in formation of pyridone. The *N*-substituted pyridone can no longer aromatize and behaves as a 1,3 diene and/or a dienophile in Diels–Alder reaction.

We note that epoxy-pyridine reactions produce new carbonyl groups belonging to pyridone rings whose IR signals can be used to monitor the extent of the reaction. We also note that due to the competition of epoxy homopolymerization the exact stoichiometry between the pyridine and epoxy groups could not be predicted.

The reaction of pyridines with epoxy group is well documented. In the literature, styrene oxide was reacted with 4-ethylpyridine, pyridine, and 2-methylpyridine. The reactivity was found as 4-ethylpyridine > pyridine >> 2-methylpyridine. Final products gave Diels–Alder type polymerization.¹³ In another example, poly(4-vinylpyridine) and poly(2-vinylpyridine) were reacted with 1,4 butanediol diglycidyl ether to give ladder type

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Contract grant sponsor: Boğaziçi University Research Fund; contract grant number: 02S101.

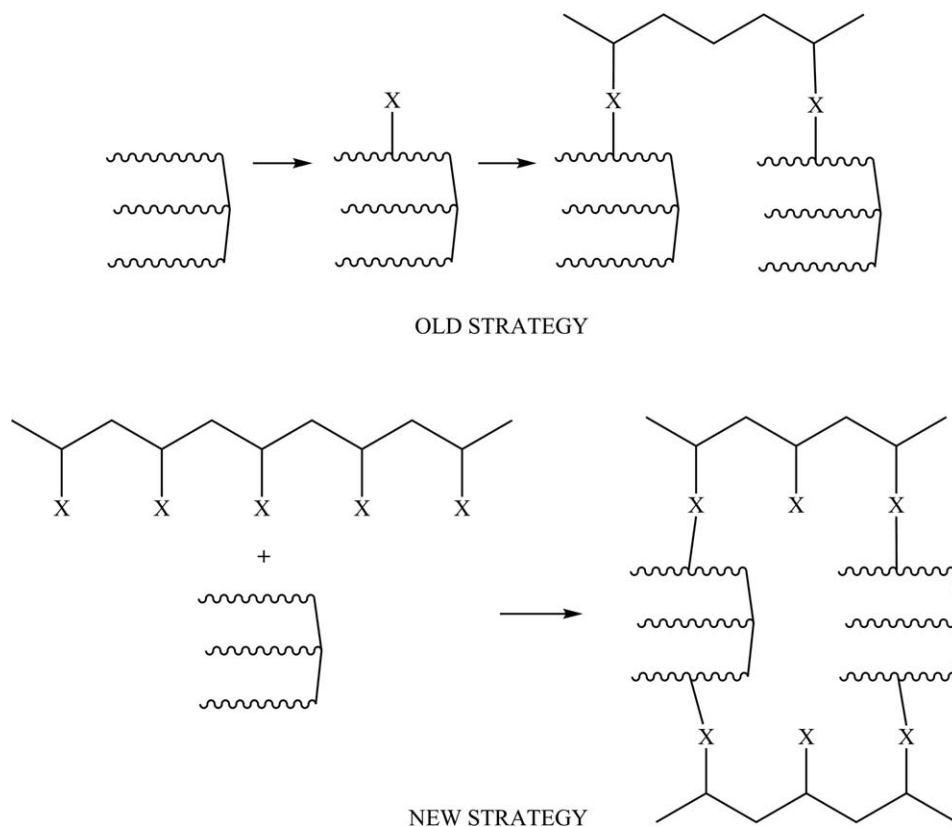


Figure 1 Schematic representation of the old and new strategies.

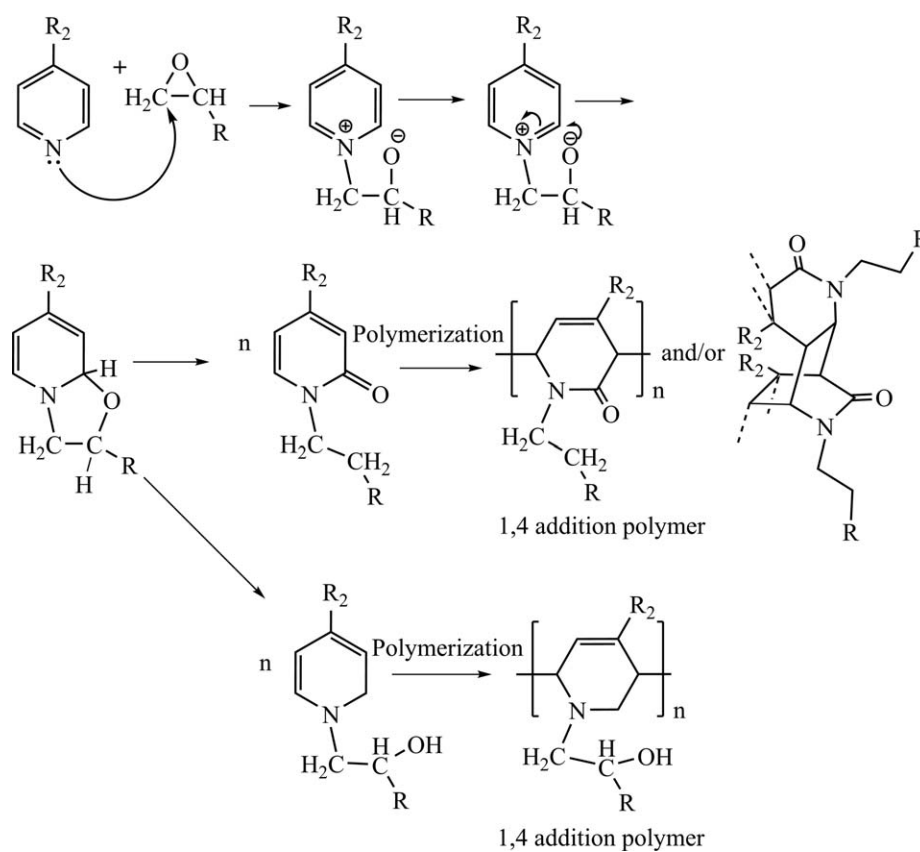


Figure 2 Proposed mechanism of pyridine-epoxy polymerization reaction.⁹

polymerization via Diels–Alder reaction of the pyridones produced. The reactivity of 1,4 butanediol diglycidyl ether with pyridine derivatives was found as poly(4-vinylpyridine) > poly(2-vinylpyridine) > 4-ethylpyridine > pyridine > 2-ethylpyridine.¹⁴ In recent literature, P4VP was polymerized with diglycidyl ether of bisphenol A and oligomeric octahydrosilsesquioxane.^{15,16}

Epoxidized soybean oil (ESO) has frequently been used as the triglyceride component to synthesize crosslinked polymers. Polymerization and crosslinking of ESO with diamines is known.^{17,18}

On the basis of these literature examples, the aim of the present work is to polymerize 4-methylpyridine (4MP), 4-vinylpyridine (4VP) and poly(4-vinylpyridine) P4VP with ESO as shown in Figure 3. 4MP is expected to polymerize only by the 1-4 addition and Diels–Alder routes of the pyridone formed, while 4VP will also undergo double bond addition polymerization in presence of a radical initiator. This allows both the addition polymerization of the functional monomer 4VP, and grafting of the triglyceride to P4VP formed to take place concurrently. Reaction of ESO with P4VP and with 4VP with concurrent addition polymerization of 4VP should essentially yield the same polymer with different amounts of connectivity. This work aims (i) to carry out the synthesis of pyridine-epoxy copolymers of a renewable triglyceride based epoxy, ESO, (ii) to characterize the chemical structures of the new polymers obtained, (iii) to briefly examine the mechanical and thermal properties of the product polymers.

EXPERIMENTAL

Materials and methods

Epoxidized soybean oil (Paraplex G-62) with a molecular weight of *ca.* 1000 g/mol and an oxygen content of 6.8% (4.2 epoxy groups per triglyceride molecule) was provided courtesy of C.P. HALL COMPANY (Chicago, USA), diethyl ether, DMF, 4-methyl pyridine, 4-vinyl pyridine and benzoyl peroxide were purchased from Merck (Darmstadt, Germany).

The IR analysis was performed on a Nicolet 380 FT-IR with Smart Diamond ATR. DSC characterization was performed by “Thermal Analyses” Q 200 instrument with a 10°C/min heating rate. DSC samples were prepared by weighing 7–10 mg of polymer samples in aluminum DSC pans. Temperature scans were run for polymers from –45 to 140°C. TGA characterization was performed by “Thermal Analyses” Q 50 instrument with a 10°C/min heating rate. Balance purge flow is N₂ 40.0 mL/min and sample purge flow is N₂ 60.0 mL/min. TGA samples were prepared by weighing 9–10 mg of polymer samples in platinum sample pan. Temperature scans were run from 25 to 600°C. The dynamic mechanical thermal analysis of the polymer samples were performed by using TA Instrument Q800 Dynamic Mechanical Analyzer (DMA) in single cantilever mode. The average dimensions (*t* × *w* × *l*) of the samples were 0.2 ± 0.2 × 12 ± 0.2 × 35 ± 0.2 mm. Temperature scans were run from –50 to 50°C (4MP-ESO) and –30 to 180°C (P4VP-ESO) at a heating rate of

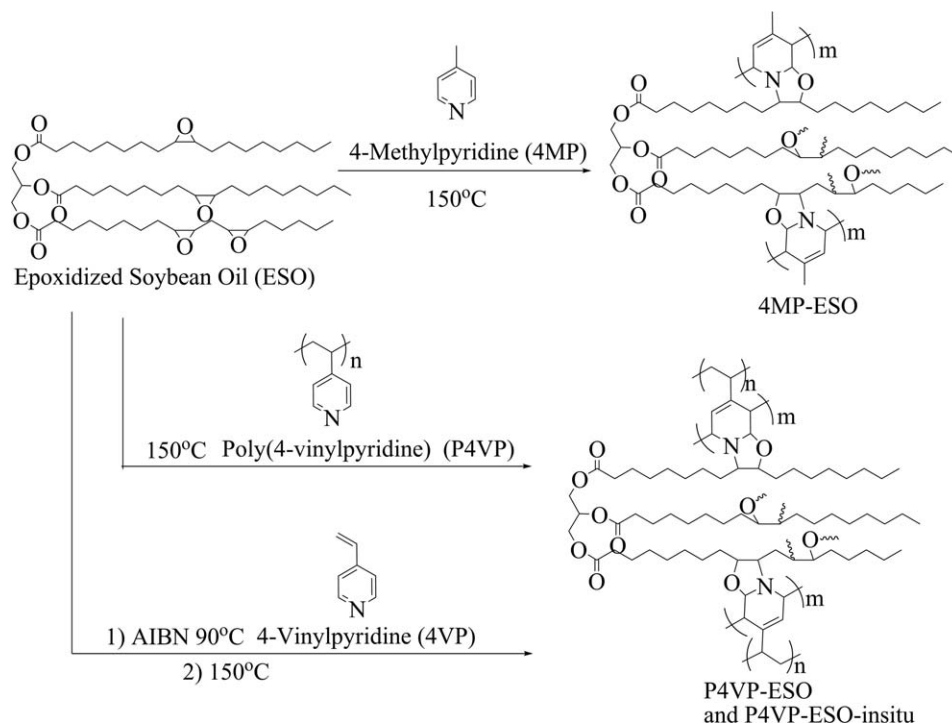


Figure 3 Schematic representation of the new polymers synthesized.

3°C/min with a vibration frequency of 1 Hz. The Zwick/Roell Durometer (Ulm, Germany) with Shore A was used to determine the surface hardness of polymer samples, the test was performed according to ASTM D 2240 standard test. The average dimensions ($t \times w \times l$) of the samples were $.7 \pm 0.2 \times 12 \pm 0.2 \times 12 \pm 0.2$ mm³ and analyses have been done at room temperature (25°C). Hardness values range from 0—for full penetration—to 100—for no penetration. To obtain a reliable analysis data, the samples were tested at least at 10 different points on the same surface.

Polymer synthesis

4MP-ESO

In a typical experiment, 0.4 g 4MP (0.0042 mol) and 1.0 g ESO (0.0042 mol epoxy) were stirred at room temperature for an hour in a mini round bottom flask with a magnetic stirrer. The mixture was transferred to a Teflon® mold and heated for three 4h periods at 120°, 150°, and 190°C under nitrogen. The samples were removed from the mold and extracted with diethylether in a soxhlet apparatus for 6 h to remove unreacted materials and dried in a vacuum oven at 80°C for 4 h. A brown, flexible, soft, thermoset product was obtained in 78% yield after extraction. Conversions could not be improved by prolonged heating, probably due to the solid product obtained which prohibits diffusion of reactive groups. The extract was shown to contain both 4MP and ESO. Proportionately larger samples were used to obtain mechanical test samples.

4MP-ESO

IR (Film) (cm⁻¹): 3000-3600 (br., OH), 2926 (s, CH), 2867 (s, CH), 2854 (s, CH₂, Sym. Stretch) 1734 (s, C=O), 1637 (m, C=C, pyridone), 1598 (m, C-C, Ar.), 1565 (w, C-O, Stretch), 1517 (m, Ar, pyridine), 1460 (m, CH₂, Def.), 1419 (m, C-C, Ar.), 1375 (m, CH₂O, Def.), 1245 (m, C-O-C, Def.), 1176 (s, CO, Def.; C-O-C, Def.), 1102 (m, C-O-C, Def.), 1058 (w, C=O, Str. Vib.), 817 (m, C(-O-)-C(-O)-, Ring Vib.), 814(w, H-Ar), 724 (w, C-C, Skel.Vib.)

P4VP-ESO

In a typical experiment, 0.5 g P4VP (containing 0.0048 mol pyridine units, $M_n = 6000$) and 1.14 g ESO (containing 0.0048 mol epoxy) were dissolved in 10 mL DMF and the mixture was refluxed at 152°C for 8 h. DMF was removed from the solution in rotatory evaporator under vacuum at 100°C. A brown viscous liquid was obtained. It was then transferred into a Teflon® mold and heated at 160°C for 4 h and postcured at 190°C for 4 h under nitro-

gen atmosphere. The polymer samples were extracted with diethyl ether in a soxhlet apparatus for 6 h to remove unreacted materials and dried in a vacuum oven at 80°C for 4 h. A brown, flexible, thermoset product was obtained in 97.1% yield. Proportionately larger samples were used to obtain mechanical test samples.

P4VP-ESO

IR (Film) (cm⁻¹): 3000-3600 (br., OH), 2923 (s, CH), 2857 (s, CH), 2741 (w, pyridine), 1732 (s, C=O), 1639 (m, C=C, pyridone), 1599 (m, C-C, Ar.), 1558 (w, C-O, Stretch), 1461 (m, CH₂, Def.), 1415 (m, C-C, Ar.), 1360 (m, CH₂O, Def.), 1342 (s, pyridone), 1279 (m, CH/CCN bend.), 1241 (m, C-O-C, Def.), 1150 (s, CO, Def.; C-O-C, Def.), 1103 (m, C-O-C, Def.), 1060 (w, C=O, Str. Vib.), 959 (m, C-N, Stretch.), 840 (m, C(-O-)-C(-O)-, Ring Vib.), 817 (m, C(-O-)-C(-O)-, Ring Vib., pyridine out of plane), 814(w, H-Ar), 755 (w, C-H, pyridine), 732 (w, C-C, Skel.-Vib.), 573 (w, Ar., Pyridine).

P4VP-ESO-*in situ* method

In a typical experiment, 0.44 g 4VP (0.0042 mol) and 1.0 g ESO (containing 0.0042 mol epoxy) were stirred at room temperature for an hour. 1% benzoyl peroxide (based on 4VP) was added and the mixture was transferred into a Teflon® mold. The mixture was heated in an oven at 90°C for 4 h under nitrogen atmosphere. The brown gel obtained was cured for another 4 h at 150°C and post cured at 190°C for 4 h under nitrogen atmosphere. Test samples were extracted with diethylether in a soxhlet apparatus for 6 h to remove unreacted materials and dried in a vacuum oven at 80°C for 4 h. A brown, flexible, thermoset product was obtained in 90.1% yield. Proportionately larger samples were used to obtain mechanical test samples.

P4VP-ESO-*in situ*

IR (Film) (cm⁻¹): 3000-3600 (br., OH), 3071 (C-H, m, Stretch., pyridine), 2926 (s, CH), 2854 (s, CH), 1733 (s, C=O), 1637 (m, C-C, pyridone), 1599 (s, C-C, Ar.), 1557 (w, C-O, Stretch), 1487 (w, Ar, Stretch.), 1459 (m, CH₂, Def.), 1416 (m, C-C, Ar.), 1375 (m, CH₂O, Def.), 1244 (m, CH/CCN bend.), 1219 (m, C-O-C, Def.), 1106(s, CO, Def.; C-O-C, Def.), 1071 (w, C=O, Str. Vib.), 1047 (m, C-N, Stretch.), 840 (w, C(-O-)-C(-O)-, Ring Vib.), 823 (m, C(-O-)-C(-O)-, Ring Vib., pyridine out of plane), 749 (w, C-H, pyridine), 7222 (w, C-C, Skel.Vib.), 570 (w, Ar., Pyridine).

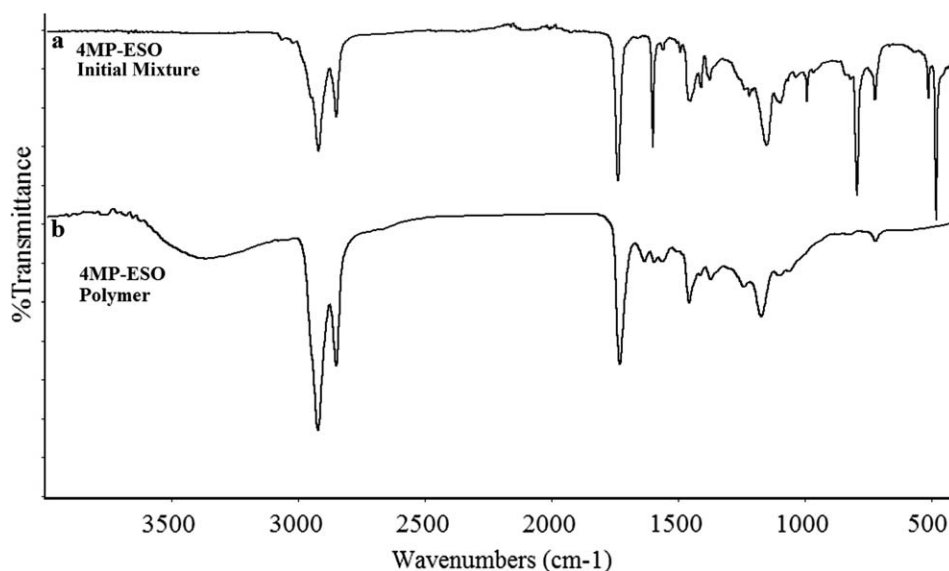


Figure 4 IR spectrum of 4MP-ESO initial mixture (a) and after polymerization (b).

RESULTS AND DISCUSSION

Polymer synthesis and spectral identification

As the polymers synthesized in this work are all insoluble thermosets, IR is the only chemical analysis tool available.⁹ At a first glance the only possible reaction between 4MP and ESO seems to be pyridine initiated ring opening polymerization of ESO. The evidence for this reaction would be increase in intensity of the C–O–C stretching absorption at 1110 cm^{-1} . Surprisingly no such increase was observed.

The IR spectrum of 4MP-ESO initial mixture is shown in Figure 4(a). The C–C stretching of the aromatic pyridine ring shows a strong absorption band at 1604, 1413 cm^{-1} and 840, 821 cm^{-1} absorptions belonging to epoxide rings of ESO. Figure 4(b)

depicts the IR spectrum of 4MP-ESO Polymer after curing and soxhlet extraction process. A new band which belongs to newly formed unsaturated C=C double bonds of Diels–Alder product appears at 1637 cm^{-1} . A sharp decrease in the peak intensities at 1604, 1413, 840, and 817 cm^{-1} indicate that aromatic rings of 4MP and epoxy groups of ESO were nearly depleted. In addition, a hydroxyl band appears at 3335 cm^{-1} due to the ring opening of the epoxide.

Figure 5 shows the IR spectra of ESO, P4VP, and P4VP-ESO polymers, respectively. The C–C stretchings of the aromatic pyridine ring of P4VP show strong absorption bands at 1599 and 1415 cm^{-1} [Fig. 5(b)] 840 and 821 cm^{-1} absorption bands belong to epoxide rings of ESO [Fig. 5(a)]. In Figure 5(c) a new

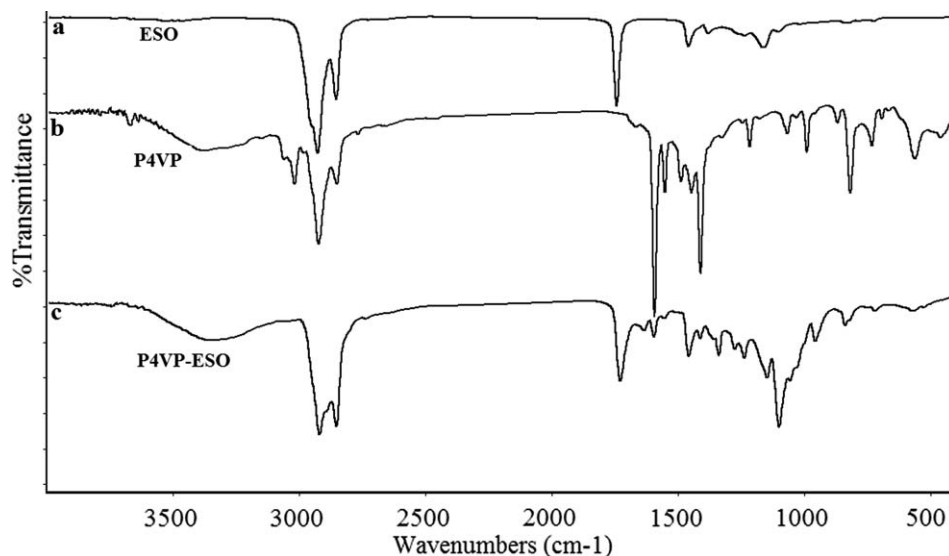


Figure 5 IR spectrum of ESO (a), P4VP (b) and P4VP-ESO, (c) polymer.

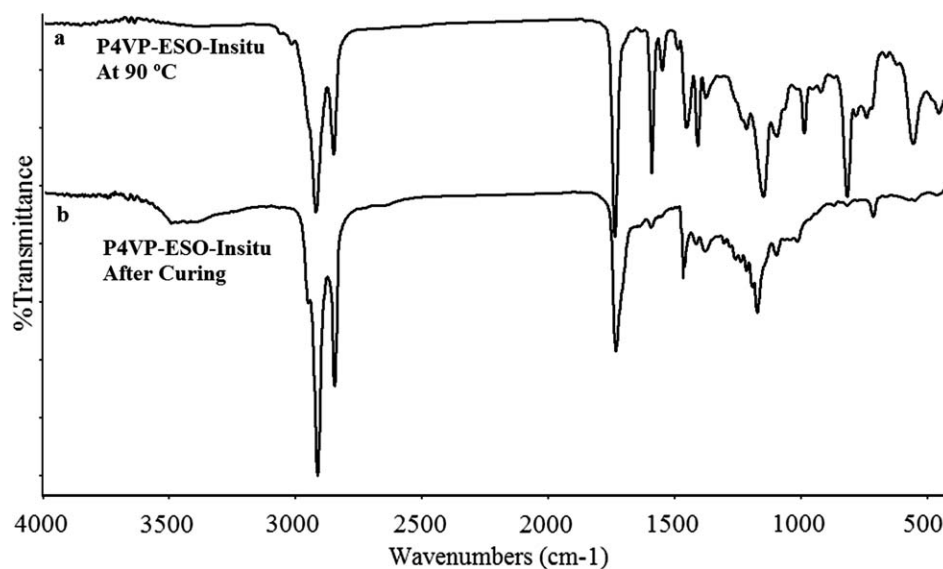


Figure 6 IR spectrum of P4VP-ESO mixture after 4VP converted to P4VP (a) and after epoxy-pyridine reaction is completed (b).

band at 1639 cm^{-1} appears which belong to newly formed unsaturated C-C double bonds of Diels-Alder product. A sharp decrease in the intensities of aromatic pyridine ring of P4VP at 1599 and 1415 cm^{-1} , and epoxide ring of ESO at 840 and 817 cm^{-1} was observed. The band at 1150 cm^{-1} which belong to the ether (C—O—C) did not increase in intensity proving that pyridine initiated homopolymerization of epoxy groups did not take place to a large extent.

Because of the lower electron density on the nitrogen of pyridine and 4VP, both of these compounds did not react with sterically hindered internal epoxy groups of ESO. 4MP and P4VP with electron donating alkyl groups at the 4 position have higher electron density on the nitrogen so that these compounds react with the epoxy groups easily. Figure 6(a) shows IR spectrum of the benzoyl peroxide initiated radical polymerization of 4VP to P4VP in ESO at 90°C . There is no evidence of C—C double bonds of Diels-Alder product absorption band at 1637 cm^{-1} and sharp aromatic pyridine ring absorption bands at 1604 and 1413 cm^{-1} and 840 and 821 cm^{-1} peaks that belong to epoxide rings of ESO remain intact suggesting that 90°C is not enough to start pyridine-epoxy reaction. On the other hand, after curing at 150°C and postcuring at 190°C , IR spectrum [Fig. 6(b)] shows the formation of C—C double bonds of Diels-Alder product absorption peak at 1637 cm^{-1} and a sharp decrease in epoxy peaks at 840 and 821 cm^{-1} proving the completion of pyridine-epoxy reaction. In addition, it is noted that a hydroxyl band appears at 3335 cm^{-1} due to the ring opening of the epoxide. In 4VP-ESO reaction there was no increase in the ether peak (C—O—C) at 1106

cm^{-1}), indicating that pyridine initiated homopolymerization of the epoxy groups is insignificant.

Thermal properties

TGA trace and the temperature at maximum weight loss rate of the polymers synthesized are shown in Figure 7 and Table I. Temperature where 5% weight loss is also given Table I. The TGA trace shows that ESO has the highest and P4VP has the lowest thermal stability. ESO shows a maximum rate of weight loss at 385°C and the ESO containing polymers synthesized also show similar peaks at 383 , 378 , and 377°C . The pyridine containing backbone of the polymers synthesized appears to be more thermally stable, as both the 4MP and 4VP backbones had a second maximum rate of weight loss temperature around 440°C .

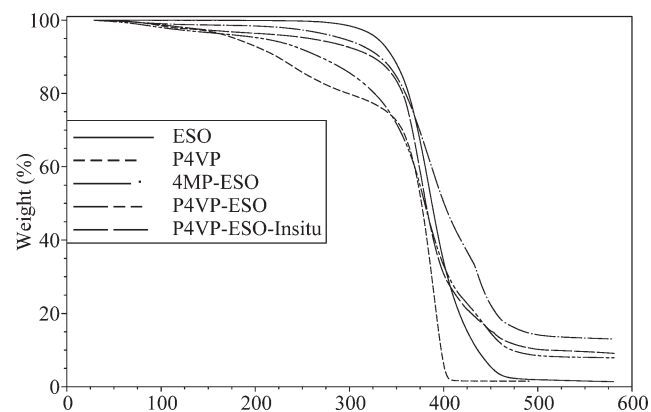


Figure 7 TGA analysis of ESO, P4VP, 4MP-ESO, P4VP-ESO and P4VP-ESO-*in situ* polymers.

TABLE I
TGA Analysis Results of ESO, P4VP, 4MP-ESO,
P4VP-ESO, and P4VP-ESO-*In situ*

Compound	Temperature where maximum rate of weight loss occurs (°C)	5% weight loss temperatures (°C)	% char yields
ESO	385	329	1.4
P4VP	241, 389	178	1.5
4MP-ESO	383, 436	292	13.0
P4VP-ESO	378, 441	207	7.9
P4VP-ESO- <i>in situ</i>	377, 444	257	9.2

DSC analysis shown in Figure 8 does not show a T_g for the synthesized polymers within the temperature range of -45 to 140°C .

Mechanical properties

The storage moduli and DMA obtained T_g 's of the polymers synthesized are expected to increase with the introduction of polymeric pyridine derivatives. Only 4MP-ESO and P4VP-ESO-*in situ* samples could be produced fault free in sizes suitable for DMA.

4MP-ESO product gave a storage modulus of 13.7 MPa at room temperature. The mechanical properties of the P4VP-ESO-*in situ* polymer improve dramatically upon thermal postcuring and the storage modulus of P4VP-ESO-*in situ* polymer is 187.2 MPa at room temperature.

This significant increase is probably due to double bond addition polymerization in the *in situ* method (Table II). In, stress-strain analyses, 4MP-ESO showed a stress at break at 0.25 MPa with 150% elongation and P4VP-ESO-*in situ* showed a stress at break at 1.88 MPa with 78% elongation. This is due to the availability of the P4VP backbone with its

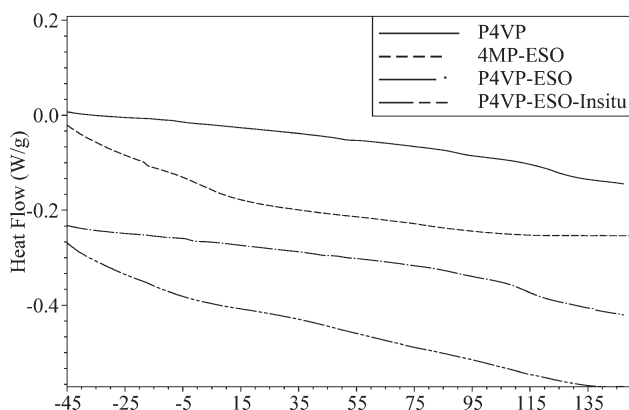


Figure 8 DSC analysis graphs of 4MP-ESO, P4VP, P4VP-ESO and P4VP-ESO-*in situ* polymers.

high molecular weight. DMA is known to be a more sensitive method for determining T_g than DSC. $\tan \delta$ derived T_g 's are 32.3 and 70.5°C for P4VP-ESO-*in situ* and -10.5°C for 4MP-ESO. Two T_g 's observed for P4VP-ESO-*in situ* are probably due to diels alder type ladder polymerized backbone and P4VP backbone segments. The use of polymeric pyridine units not only introduced a new T_g at 70.5°C but also increased the T_g of Diels-Alder polymers from -10.5 to 32.3°C . This clearly shows that T_g increases with increasing use of polymeric pyridine derivatives (Figs. 9 and 10). These improvements in T_g and storage modulus are in perfect agreement with our original postulate.

Results of the surface hardness test are presented in the Table II. Surface hardness of P4VP-ESO polymer is 15 units higher than 4MP-ESO polymer. Also surface hardness of P4VP-ESO-*in situ* is 19 units higher than P4VP-ESO suggests that homogeneity introduced by *in situ* synthesis of P4VP gives superior mechanical properties. Surface hardness results are in good agreement with DMA analysis results.

CONCLUSION

Poly(4-vinylpyridine) was used as the backbone of the polymers synthesized by either using poly(4-vinylpyridine) itself or by polymerizing 4-vinylpyridine *in situ*. The second method gave polymers with better thermal and mechanical properties due to improved homogeneity obtained by the *in situ* synthesis.

Pyridine-epoxy reaction between epoxidized soybean oil triglycerides and 4-methylpyridine and poly(4-vinylpyridine) gave interesting results. The expected pyridine initiated homopolymerization of the epoxy groups did not take place. Instead pyridine addition followed by rearrangement to a pyridone derivative was observed. Diels-Alder and/or addition polymerization of the pyridone gave novel polymers. In the case of poly(4-vinylpyridine), the high molecular weight introduced by the use of a

TABLE II
DMA Obtained T_g 's and 25°C Storage Moduli of
4MP-ESO and P4VP-ESO-*In Situ* Polymers and Surface
Hardness of 4MP-ESO, P4VP-ESO, and
P4VP-ESO-*In Situ* Polymers

Polymer	T_g 's (°C)	Storage modulus at 25°C (MPa)	Surface hardness (shore A)
4MP-ESO	-10.5	13.7	40
P4VP-ESO	—	—	55
P4VP-ESO- <i>in situ</i>	32.3 and 70.5	187.2	74

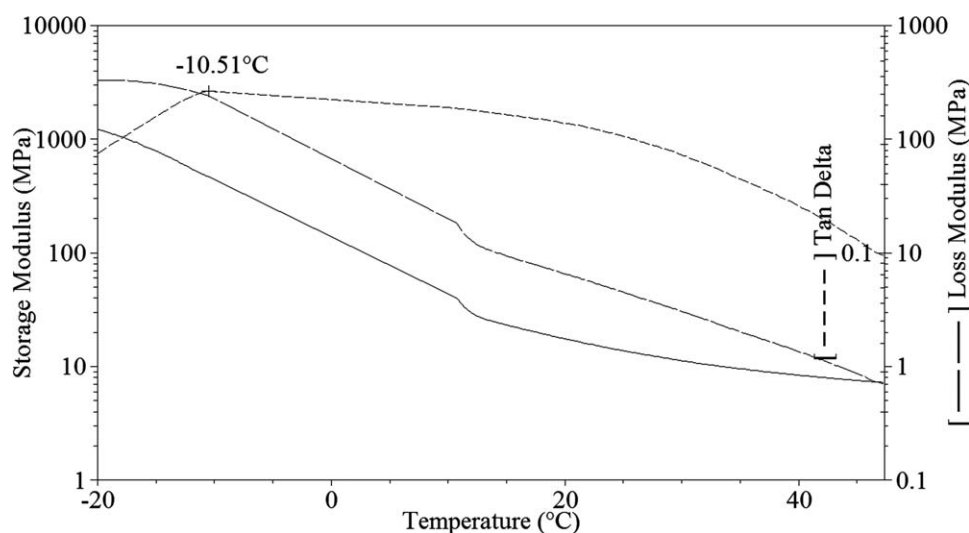


Figure 9 DMA graph of thermoset 4MP-ESO polymer.

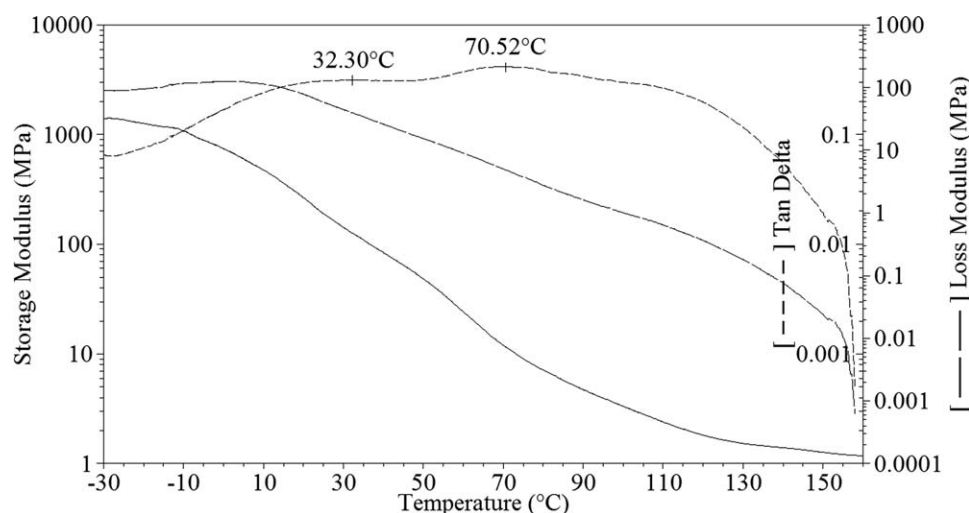


Figure 10 DMA graph of thermoset P4VP-ESO-*in situ* polymer.

polymeric backbone gave superior mechanical properties.

A possible application for the new crosslinked material is its use as a gel molding resin. When 4VP is free radically polymerized using ESO as solvent, P4VP swells in ESO and a viscous, thixotropic, and reactive gel is obtained. This gel is ready to be crosslinked by the reactions described in this article merely upon heating. The gel has no volatile components, takes excellent mold detail, the cure stoichiometry can be optimized by the manufacturer and there are no by products during cure. As such the proposed gel molding compound contains approximately 70% renewable, plant oil based raw material and has a respectable set of mechanical and thermal properties when cured.

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