

Some Epoxidized Polyurethane and Polyester Resins Based on Linseed Oil

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SYNOPSIS

Linseed oil was epoxidized *in situ* with perbenzoic or peracetic acid to produce epoxidized linseed oil (I). Effect of type and concentration of the peracid and the reaction time on the characteristics of the produced epoxidized oil were studied. Various epoxidized polyurethanes (II) with different NCO/OH ratios as well as epoxidized polyesters (III) were prepared from (I). The results obtained for the evaluation of resins (II) and (III) show promising applicability as petroleum pipeline coatings. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Linseed oil is the most widely used drying oil in coatings and varnishes.¹ The three nonconjugated acids, oleic, linoleic, and linolenic, present in the linseed oil, possess one, two, and three double bonds, respectively. Linseed oil can be epoxidized with hydrogen peroxide and acetic acid in the presence of an ion exchange resin as catalyst.² Interpenetrating polymer networks composed of polyurethanes (PUs) and epoxies were prepared by the simultaneous technique.³ PU resins possess good properties as coatings⁴⁻⁸ (chemicals and water resistance). Coated films have excellent adhesion characteristics as well as thermal stability and heat resistance. Also, polyester⁹⁻¹² and epoxide resins¹³⁻¹⁸ are widely used as coatings and adhesives with excellent properties.

In the present work, molecules containing a combination of epoxy, urethane, and ester groups were prepared to be used as petroleum pipeline coatings.

EXPERIMENTAL

Materials

1. Linseed oil: Egyptian alkali refined linseed oil, product of Cairo for Oil Co., having an

average molecular weight of 876; density at 23°C of 0.9271 g/cm³; viscosity at 25°C of 27.4 cS; iodine value of 178; and acid value of 0.75 mg KOH/g oil.

2. Perbenzoic acid: pure grade, 63%.
3. Peracetic acid: pure grade, 60%.
4. Toluene diisocyanate (TDI): mixture of 80% 2,4- and 20% 2,6-toluene diisocyanate.

All other chemicals were pure grade.

Methods

Preparation of Epoxidized Linseed Oil (EL)

Linseed oil (1 mol) was heated under reflux with perbenzoic or peracetic acid at 30°C.¹⁹ At the end of each experiment, the mixture was diluted with benzene (2 L). The benzene solution was desiccated over anhydrous sodium sulfate (40 g). The effects of type, concentration, and reaction time of peracids on the characteristics of produced epoxidized oil were studied (see Tables I, II). The infrared (IR) spectra obtained for the produced EL resin show epoxy absorption bands at 916, 1250, and 2980 cm⁻¹ and hydroxyl absorption bands at 3560 cm⁻¹ indicating that this sample EL was significantly epoxidized.^{20,21}

Preparation of Epoxidized PU (EPU) Resins

Different types of EPUs (EPU₁-EPU₁₀) containing different NCO/OH ratios were prepared by reacting

Table I Characteristics of Different Types of EL

Used Peracids		Produced EL			
Type	Molar Ratio of Acid/Oil	Viscosity at 25°C (cS)	Epoxy Group Content (%)	Hydroxy Value (mg KOH/g Oil)	Acid Value (mg KOH/g Oil)
Perbenzoic acid, 63%	0.7	27.8	2.5	4	3
	1	28.3	3.5	7	5
	1.3	29.4	5.9	9	6
	2	30.7	6.9	11	9
Peracetic acid, 60%	0.7	27.7	2	5	2
	1	28.2	3.5	9	5
	1.3	29.2	4.8	13	7
	2	31.0	5.4	19	11

Reaction time was 20 h at 30°C.

EL with TDI (10 g) (see Table III) using triethanolamine (1% by weight of the reactance materials) as catalyst and a reaction time of 30 min at $60 \pm 5^\circ\text{C}$.²²

Preparation of Epoxidized Polyester (EPE) Resins

Three types of EPE were prepared by reacting EL with phthalic anhydride (PA) in different molar ratios (see Table IV) applying the fusion method.²³

Preparation of Coated Films

Glass or iron plates (2.5×7.5 cm) free from surface imperfections were cleaned using different solvents. The resin was then poured on one edge of the plate that was left in vertical position (to spread the resin uniformly) at average temperature of 30°C for 7 days. The film thickness was measured according to the BS 3900 (part E2).

Evaluation of Coated Films

The drying properties were studied according to ASTM D 1647-59. The chemicals resistance was carried out for 6 months at 30°C according to ASTM D 543-78 and ASTM G 20-72 using coated glass panels. The physical tests were carried out on coated specimens of petroleum pipeline, steel grade API-5L, according to API-PR 5L2 (March 1981).

RESULTS AND DISCUSSION

Epoxidation of Linseed Oil

The epoxidation process of linseed oil without catalysis is governed by many factors, such as the type and concentration of peracid, reaction time, and temperature of reaction. The effect of type and concentration of peracids on the characteristics of the obtained epoxidized oils has been studied and the specification of these products are given in Table I.

Table II Effect of Reaction Time on Characteristics of EL (in Presence of Peracetic Acid, 1.3 mol) at 30°C

Reaction Time (h)	Viscosity at 25°C (cS)	Epoxy Group Content (%)	Hydroxy Value (mg KOH/g Oil)	Acid Value (mg KOH/g Oil)
0	27.4	0.0	0.0	0.75
10	28.0	2.1	5.15	2.1
20	29.46	4.8	13	7.0
30	31.12	4.0	17.6	11.0
40	35.75	3.6	2.9	180
50	52.30	2.7	44	22.0

Table III Air Drying Properties of EPU Resins with Different NCO/OH Ratios

Prepared EPU		Reactance Weights (g)		Air Drying Time of EPU at 30°C (h)		
Type	NCO/OH	TDI	EL	Tacky	Slightly Tacky	Hardening
EPU ₁	1	10	146.6		Not dry	
EPU ₂	2	10	73.3	24	48	120
EPU ₃	3	10	48.8	14	30	48
EPU ₄	4	10	36.6	12	24	40
EPU ₅	5	10	29.3	5	12	30
EPU ₆	6	10	24.4	1	4	17
EPU ₇	7	10	20.9	0.5	1	7
EPU ₈	8	10	18.3	0.5	1	4
EPU ₉	9	10	16.3	0.25	0.5	2
EPU ₁₀	10	10	14.7		Dry immediately	

The data in Table I shows that with increasing the molar ratio of peracid to the oil, the viscosity, epoxy group content, hydroxy value, and acid value of EL increased. Also perbenzoic acid is more effective than peracetic acid at all molar ratios. This could be due to the withdrawing effect of the phenyl group in perbenzoic acid that facilitates the formation of the hydroxonium ion (OH)⁺, resulting from the heterolytic decomposition of the perbenzoic acid, and the (OH)⁺ attacks the carbon-carbon double bond.²⁴ In case of peracetic acid the —CH₃ group, which is an electron repelling group, could make the formation of (OH)⁺ difficult as in case of perbenzoic acid.

The effect of reaction time on the characteristics of the prepared EL with peracetic acid has been studied and the results are given in Table II.

According to the results given in Table II, the epoxy group content increases up to 4.8% through increasing reaction time to 20 h, beyond which it decreases to 2.7% after 50 h. However, viscosity, hydroxy, and acid value are found to increase progres-

sively as a function of reaction time. The decrease of epoxy group content with reaction time is most probably due to a reaction between a portion of the epoxy groups with the water liberated during the reaction to produce glycol.¹⁹ Nevertheless, the resulting increase in viscosity with the reaction time could be due to the increase of crosslinking that leads to the formation of ether linkages. The increase of acid value with time of reaction could result through the formation of free acid under the conditions used where oxidation of the oil (triglyceride) is a favorable reaction.

The experiment was carried out to study the effect of reaction temperature on the properties of EL. When the reaction was conducted at 120°C for 1 h in the presence of peracetic acid 1.3 mol/mol oil, the product was darker in color and had high viscosity (62 cS at 23°C). This indicates an increase in molecular weight of EL. The acid value also increased greatly (25 mg KOH/g oil); this indicates the possible formation of free acids as a result of thermal decomposition of the oil and due to oxidative de-

Table IV Physical Tests for EPU Samples

EPU Type	Film Thickness (μm)	Adhesion Test	Stripping Test	Bending Test	Water Res. Test
EPU ₅	130	Good adhesion	No stripping	No cracking	No change
EPU ₆	140	Good adhesion	No stripping	Cracking	No change
EPU ₇	130	Good adhesion	No stripping	Cracking	No change
EPU ₈	140	Good adhesion	No stripping	Cracking	No change

Table V Characteristics of EL Blend

Average molecular weight	980
Density at 23°C	0.9471 g/cm ³
Viscosity at 23°C	52.4 cS
Epoxy group content	5.1%
Hydroxy value	44 mg KOH/g oil
Acid value	18.3 mg KOH/g oil

composition.²⁵ The hydroxyl value of obtained EL is 49 mg KOH/g oil, epoxy content is 2.5%, and its density at 23°C is 0.9485 g/cm³.

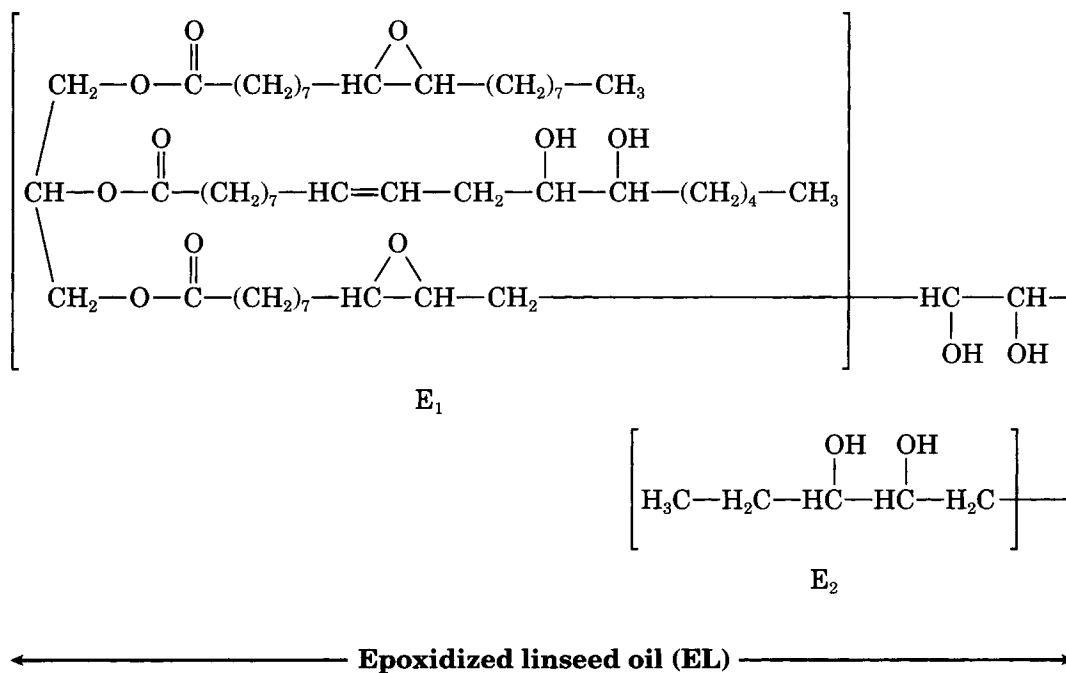
In order to obtain the benefits of the advantages obtained in each product, the EL, prepared in the presence of perbenzoic acid with a ratio of 1.3 mol/mol oil (having relatively higher epoxy group content

of 5.9%), was mixed with the EL prepared in the presence of peracetic acid in a ratio of 1.3 mol/mol oil at 120°C (having higher hydroxyl value of 49 mg KOH/g oil) to obtain a blend of EL. Its characteristics are given in Table V.

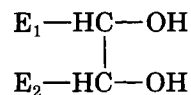
The data given in Table V indicates that the EL blend is more suitable for manufacture of PU and PE. The reaction that proceeds during their preparation necessitates the presence of the hydroxyl group found in the EL.

EPU Coatings

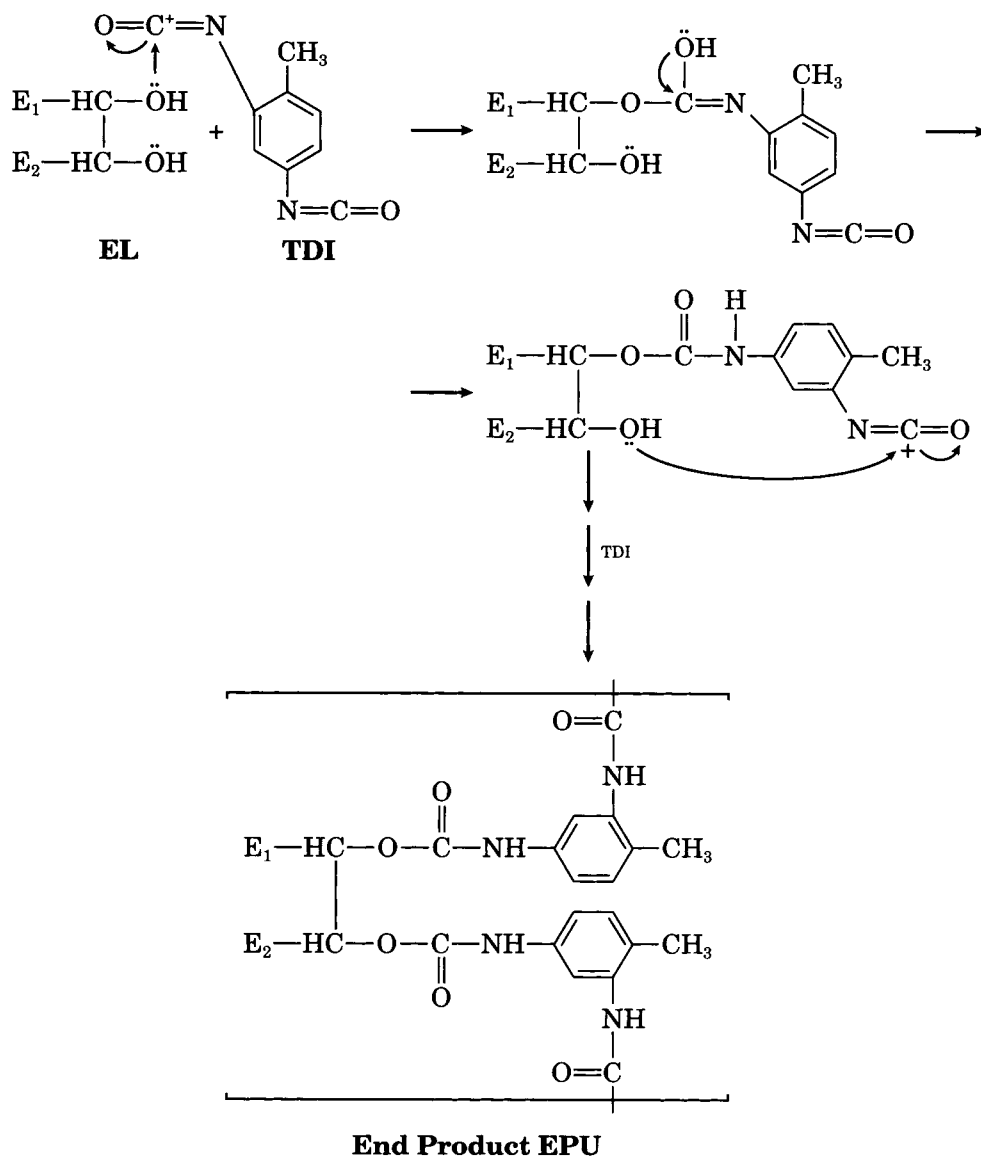
The EPU resins have been prepared via reacting the TDI with EL as polyol and it is rich in OH groups. The suggested mechanism for this reaction may be given as follows:



To simplify this formula for EL, it can be represented by:



So its reaction with TDI to form EPU proceeds as:



It has to be pointed out that the two terminals E_1 and E_2 contain OH groups that are also capable of cross-linking; these hydroxyls react with TDI in the same manner as in the above-mentioned mechanism.

Various types of EPU resins with different NCO/OH ratios have been prepared using NCO/OH ratios of EPU²² ranging between 1 and 10 relative to 10 g of TDI. Its air drying properties at an average temperature of 30°C were studied (see Table III).

According to the results given in Table III, the drying times for the produced samples are found to decrease as the NCO/OH ratio decreases. EPU₁, EPU₉, and EPU₁₀ samples are found to be unsuitable

for using as coating materials because EPU₁ dries very slowly or practically does not dry, whereas EPU₉ and EPU₁₀ dry immediately after preparation.

The prepared coated films EPU were tested for chemicals and petroleum products resistance at an average temperature of 30°C for 6 months. The results obtained are given in Table VI.

The data in Table VI shows that the resistance of EPU toward chemical solutions increases as the NCO/OH ratio increases, which is attributed to the increase of cross linkage in the produced resin. The most resistant samples for chemicals and petroleum products are between EPU₅ and EPU₈.

Table IV gives the data obtained for physical testing of EPU₅, EPU₆, EPU₇, and EPU₈ samples.

From the results given in Table IV, EPU₅ sample has successfully passed all the required physical tests, whereas the remaining samples have been cracked during the tests.

So, EPU₅ sample (NCO/OH ratio = 5) can be considered as the most promising to be used as a successful petroleum pipeline coating material.

This may be attributed to the formation of a complete cross-linked network structure²⁶ of EPU with suitable amounts of EL and TDI.

EPE Coatings

EPE resins were prepared via reacting EL with PA. The reaction taking place is presumed to follow the equations:

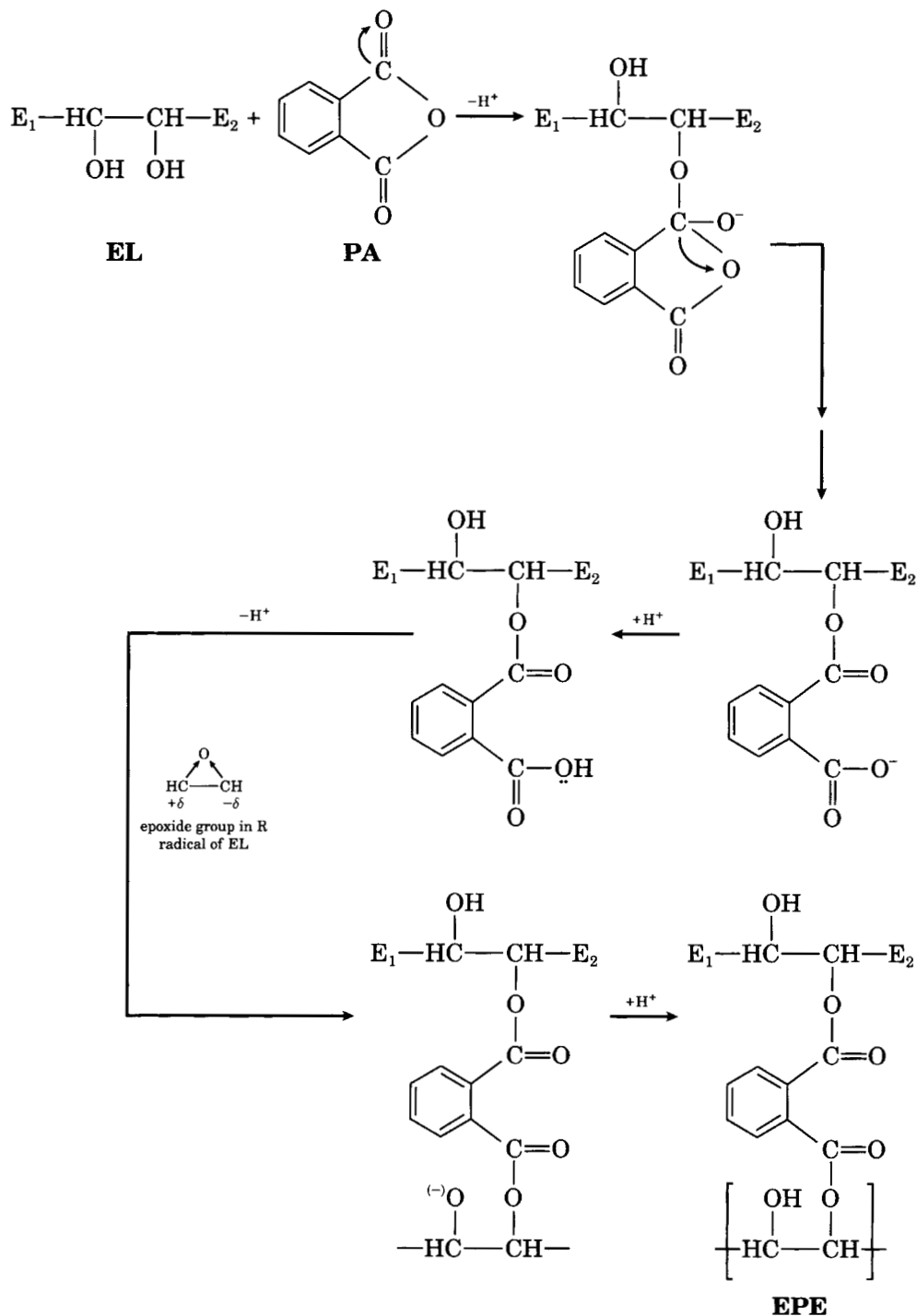


Table VI Chemicals and Petroleum Products' Resistance for EPU Films

EPU Type	Film Thickness (μm)	NaOH, 1%	HCl, 10%	H ₂ SO ₄ , 3%	HNO ₃ , 10%	Acetic			Crude Oil	Gasoline	Kerosine	Gas Oil	Fuel Oil	
						Acid, 5%	NaCl, 10%	Na ₂ CO ₃ , 20%						
EPU ₂	130	P	G	G	G	G	G	G	P	P	P	P	F	F
EPU ₃	140	F	E	G	G	G	G	G	P	F	F	F	G	G
EPU ₄	140	G	E	E	E	E	E	E	P	G	G	G	G	G
EPU ₅	130	E	E	E	E	E	E	E	P	E	E	E	E	E
EPU ₆	150	E	E	E	E	E	E	E	F	E	E	E	E	E
EPU ₇	140	E	E	E	E	E	E	E	F	E	E	E	E	E
EPU ₈	140	E	E	E	E	E	E	E	F	E	E	E	E	E

P = poor, F = fair, G = good, E = excellent.

Table VII Characteristics of Prepared EPE Resins

EPE Type	Reactance Mater. (Mol)		Air Drying Time at 30°C (h)	Hydroxyl Value (mg KOH/g Oil)	Acid Value (mg KOH/g Oil)
	EL	PA			
EPE ₁	1	1	7	30	5
EPE ₂	1	2	5	10	13.2
EPE ₃	1	4	3.5	4	20.7

Table VIII Chemicals' and Petroleum Products' Resistance for EPE Films

EPE Type	Film Thickness (μm)	NaOH, 1%	HCl, 10%	H ₂ SO ₄ , 3%	HNO ₃ , 10%	Acetic			Crude Oil	Gasoline	Kerosine	Gas Oil	Fuel Oil	
						Acid, 5%	NaCl, 10%	Na ₂ CO ₃ , 20%						
EPE ₁	130	P	F	F	F	F	P	P	P	G	G	G	E	E
EPE ₂	120	P	G	G	G	G	G	G	F	G	G	G	E	E
EPE ₃	140	E	E	E	E	E	E	E	G	E	E	E	E	E

P = poor, F = fair, G = good, E = excellent.

Table IX Physical Tests for EPE Films

EPE Type	Film Thickness (μm)	Adhesion Test	Stripping Test	Bending Test	Water Res. Test
EPE ₂	130	Good adhesion	No stripping	No cracking	Swelling
EPE ₃	140	Good adhesion	No stripping	No cracking	No change

Three EPE resins were prepared using different molar ratios (Table VII). The examination data obtained for these resins indicates that the drying time increases in the order: $EPE_3 > EPE_2 > EPE_1$, which is attributed to increasing the hydroxyl value.

Table VIII shows the chemicals' and petroleum products' resistance behavior of the dried EPE resin films. This resistance is found to be in the order: $EPE_3 > EPE_2 > EPE_1$, which is attributed to increasing the crosslinking.

Physical testing of EPE films (Table IX) shows that the EPE_3 sample only appears satisfactory for use as a coating material.

From the experimental data, it can be concluded that the EPU resin (NCO/OH ratio = 5) as well as EPE resin (molar ratio of EL : PA = 1 : 4) can be used as successful petroleum pipeline coating materials.

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