

# Polyurethane Dispersions Based on Interesterification Product of Fish and Linseed Oil

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**Abstract** Alkyd and styrenated alkyd resins based on fish oil and their interesterifications with linseed oil were synthesized. The various properties of fish oil, such as its iodine value, acid value, saponification value and moisture content were determined. The interesterification product of fish oil and linseed oil can be used to partially replace the commercially available linseed oil alkyd resin. Alkyd resin and styrenated alkyd resin were modified with 2,2 dimethylolpropionic acid to introduce acid functionality and then sequentially reacted with isophorone diisocyanate, neutralized with amine, chain extended with ethylenediamine and dispersed in water to form a polyurethane dispersion. The newly synthesized resins and polyurethane dispersions were studied for coating properties such as scratch hardness, adhesion, flexibility, impact, solvent and chemical resistance. The polyurethane dispersions exhibited superior coating properties to those of their respective alkyds and styrenated alkyds.

**Keywords** Fish oil alkyd · Interesterification · Oil modified polyurethane dispersion · Waterborne coating

## Abbreviations

- F Alkyd resin
- S Polyurethane dispersion of styrenated alkyd
- P Polyurethane dispersion of alkyd resin
- A Linseed oil:Fish oil 100:0
- B Linseed oil:Fish oil 75:25
- C Linseed oil:Fish oil 50:50

- D Linseed oil:Fish oil 25:75
- E Linseed oil:Fish oil 0:100
- F<sup>A</sup> Alkyd resin based on linseed oil 100%
- F<sup>B</sup> Alkyd resin based on linseed oil:fish oil 75:25
- F<sup>C</sup> Alkyd resin based on linseed oil:fish oil 50:50
- F<sup>D</sup> Alkyd resin based on linseed oil:fish oil 25:75
- F<sup>E</sup> Alkyd resin based on fish oil 100%
- S<sup>A</sup> Polyurethane dispersion of styrenated alkyd based on linseed oil 100%
- S<sup>C</sup> Polyurethane dispersion of styrenated alkyd based on linseed oil:fish oil 50:50
- S<sup>E</sup> Polyurethane dispersion of styrenated alkyd based on fish oil 100%
- P<sup>A</sup> Polyurethane dispersion of alkyd resin based on linseed oil 100%
- P<sup>C</sup> Polyurethane dispersion of alkyd resin based on linseed oil:fish oil 50:50
- P<sup>E</sup> Polyurethane dispersion of alkyd resin based on fish oil 100%

## Introduction

The surface coating industry has been dominated by alkyd resins for the last few decades due to their excellent gloss, chemical resistance and fast drying. One of their major drawbacks is the emission of high volatile organic components (VOC) that pollute the ecological system, and hence there is an increasing need to formulate coatings that have zero VOC or to substitute solvents with water. Researchers are engaged in using polymer chemistry to design a water dispersible coating [1–3]. Recently, water dispersible polyurethanes have been rapidly gaining importance, mainly due to their easy processing as well as excellent

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chemical and physical properties, which can be tailored to suit a very wide range of applications. Polyurethane dispersions (PUD) made from renewable resources have gained considerable attention these days [4–6]. Renewable resources are used for the production of surface coatings, as petroleum products are costly and are likely to get exhausted. Traditional seeds like linseed, soybean, coconut and castor oils have been commercially used for synthesis. Earlier work on the synthesis of alkyd resin and their coating properties has been reported by Athawale et al. [7]. Marine products are also a renewable resource. Different types of fish are available in the seas and oceans. Fish oil is a by-product of the fisheries; it is more plentiful and cheaper than soybean and linseed oils. Fish oil is derived from the tissues of oily fish. The only drawback of fish oil is its fishy odor. Sardines are abundantly available in the Karnataka region of India; hence, there are many fisheries in this region. Fish oil is recommended for a healthy diet because it contains fatty acids, omega-3 i.e. 5,8,11,14,17-eicosapentaenoic acid (EPA, C20:5) and omega-6 4,7,10,13,16,19-docosahexaenoic acid (DHA, C22:6) [7–11], and their absence in a normal diet may cause various diseases, such as coronary heart diseases, hypertension, cardiac arrhythmias, diabetes, inadequate development of the nervous system, and several inflammatory disorders [12, 13]. EPA and DHA found in marine fish originate from the phytoplankton and seaweed that are the part of their food chain. Variations in their fatty acid composition occur due to fluctuations in the quality and amount of food available, species, size, place, water temperature, feeding and seasons. Little is known about the chemical composition of marine fish oil at present. There may be about 25 individual fatty acids [12, 13] present in fish oil, consisting of saturated and unsaturated fatty acids. The physico-chemical properties and fatty acid composition of fish and linseed oils are given in Tables 1 and 2, respectively. In the present study, long oil alkyd resins (oil length of 65%) based on fish oil and its interesterification products with linseed oil in different ratios were synthesized, and their coating properties were characterized. Fish oil contains highly unsaturated acids, so a careful choice of ingredients is essential to formulate alkyd resin, as otherwise gelation may occur. Fish oil [14] can be used to replace linseed oil, either completely or partially, as it is cheaper than linseed oil.

## Experimental

### Materials

Refined fish oil (FO) was procured from Jantha fishmeals, Mangalore (India). Linseed oil (LO) was supplied by Godrej industries, Mumbai. All the chemicals used in the

**Table 1** The physicochemical properties of fish oil and linseed oil

	Refined sardine fish oil	Linseed oil
Odor	Fishy	Nil
Color	Pale yellow	Pale yellow
Iodine value	180.2	180
% Free acid	3.0	0.5
Saponification no.	190.0	175.0
% Unsaponified matter	0.9	0.8
Specific gravity	0.99	0.99
% Moisture content	0.02	0.01

**Table 2** Fatty acid compositions of sardine fish and linseed oil

	Refined sardine fish oil <sup>a</sup>	Linseed oil <sup>b</sup>
Saturated		
C14 Myristic acid	17.00	–
C16 Palmitic acid	26.20	4.80
C18 Stearic acid	3.00	4.70
Total	46.20	9.50
Unsaturated		
C16:1 Palmitoleic acid	18.20	–
C16:3 Hexadecatrienoic acid	2.56	–
C18:1 oleic acid	5.00	19.9
C18:2 Linoleic acid	5.20	15.9
C18:3 Linolenic acid	1.00	52.70
C20:3 Eicosatrienoic acid	2.00	–
C20:5 Eicosapentaenoic acid-EPA	10.20	–
C22:6 Docosahexaenoic acid- DHA	4.20	–
Others	5.70	2.0
Total unsaturated	53.80	90.00
Total	100.0	100.0

<sup>a</sup> GC analysis of sardine fish oil

<sup>b</sup> Hui YH (1995) Baileys industrial oil and fat product [26]

present work were of AR grade. Glycerol, phthalic anhydride, maleic anhydride, triethylamine, ethylene diamine (EDA), *N*-methylpyrrolidone, di-*tert*-butyl peroxide (DTBP), dibutyltin dilaurate (DBTL), were procured from SD fine chemicals, Mumbai. Styrene (ST), 2,2 dimethylolpropionic acid (DMPA), isophorone diisocyanate (IPDI) were supplied by Fluka. Driers, such as lead octoate, magnesium octoate, and cobalt octoate, were obtained from Alpha Chemie in Mumbai, India.

### Analysis of FO and LO

The physicochemical properties of FO and LO, such as their color, specific gravity, % free acid, saponification

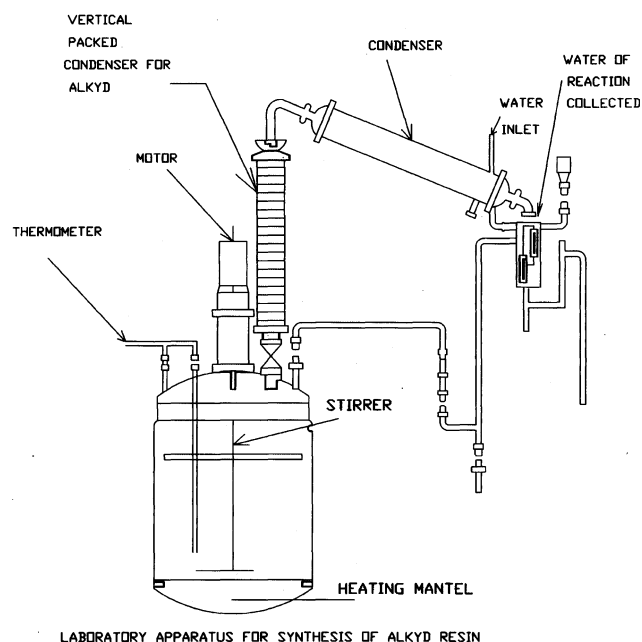
value, moisture content and iodine values, were determined according to standard methods [15] and presented in Table 1.

### Fatty Acid Compositions of Refined Sardine Fish Oil

Fatty acid methyl esters were prepared by a standard method [15] and analyzed by gas chromatography using Agilent-Technologies RT-2650 capillary column (30 m × 0.25 mm, film thickness 0.20 μm). A sample of 1 μL was injected into the capillary column. Nitrogen at a flow rate 1.0 mL/min was used as the carrier gas. The oven and detector temperatures were set at 230 and 250 °C, respectively.

### Synthesis of Alkyd Resins

Several alkyd resins were synthesized with oil lengths of 65% using different ratios of fish oil, linseed oil, glycerol, and phthalic anhydride, according to the formulations given in Table 3. All the alkyd samples were formulated close to alkyd constant 1.00. A resin reactor equipped with a thermometer, mechanical stirrer, Dean-Stark apparatus (Fig. 1) [16] and nitrogen inlet was charged with oil and glycerol in the mole ratio 1:3, and calcium octoate was used as a catalyst (0.01% w/w based on oil). The temperature was slowly raised to 240 °C and maintained until the monoglycerides were formed. The formation of monoglycerides were checked by testing the solubility in methanol. A clear and homogeneous solution was obtained when the reaction mixture and pure methanol were taken in a 1:3 ratio, indicating the formation of monoglycerides. After the formation of monoglycerides was confirmed, the temperature was brought down to 120 °C, and the required amounts of phthalic anhydride, maleic anhydride and



**Fig. 1** Schematic of a laboratory reactor for alkyd synthesis

glycerol were added. The batch was further processed [16, 17] at 220 °C for 8–10 h; water was condensed and collected in a Dean-Stark apparatus. The reaction continued until the acid value decreased below 10 mg KOH g<sup>-1</sup>. The reaction scheme is shown in Fig. 2.

### Grafting of Alkyd Resin

A three-necked round-bottom flask equipped with a thermometer, condenser, and mechanical stirrer was used to carry out the reaction. Alkyd resin was placed in the reactor, and styrene [17, 18] was added drop-wise from a dropping funnel over a period of 2.5 h at 130–135 °C. DTBP was used as the catalyst (0.1% of the weight of styrene) and heating was further continued for 0.5 h to ensure the complete reaction of the styrene.

### Synthesis of Polyurethane Dispersions (PUDs)

Alkyd resin and grafted resin were separately reacted with a known quantity of DMPA to achieve acid functionality. The reaction was carried out at 70 °C for 1 h using DBTL as a catalyst, and *N*-methylpyrrolidone was used as the solvent. The resin mixtures were cooled to 40 °C, and the required quantity of IPDI [18, 19] was added drop-wise from a dropping funnel over a period of 2 h. The temperature was then raised to 60 °C, and each resin mixture was neutralized with triethylamine and maintained at this temperature for an additional 1 h. The product mixtures were transferred into stainless steel

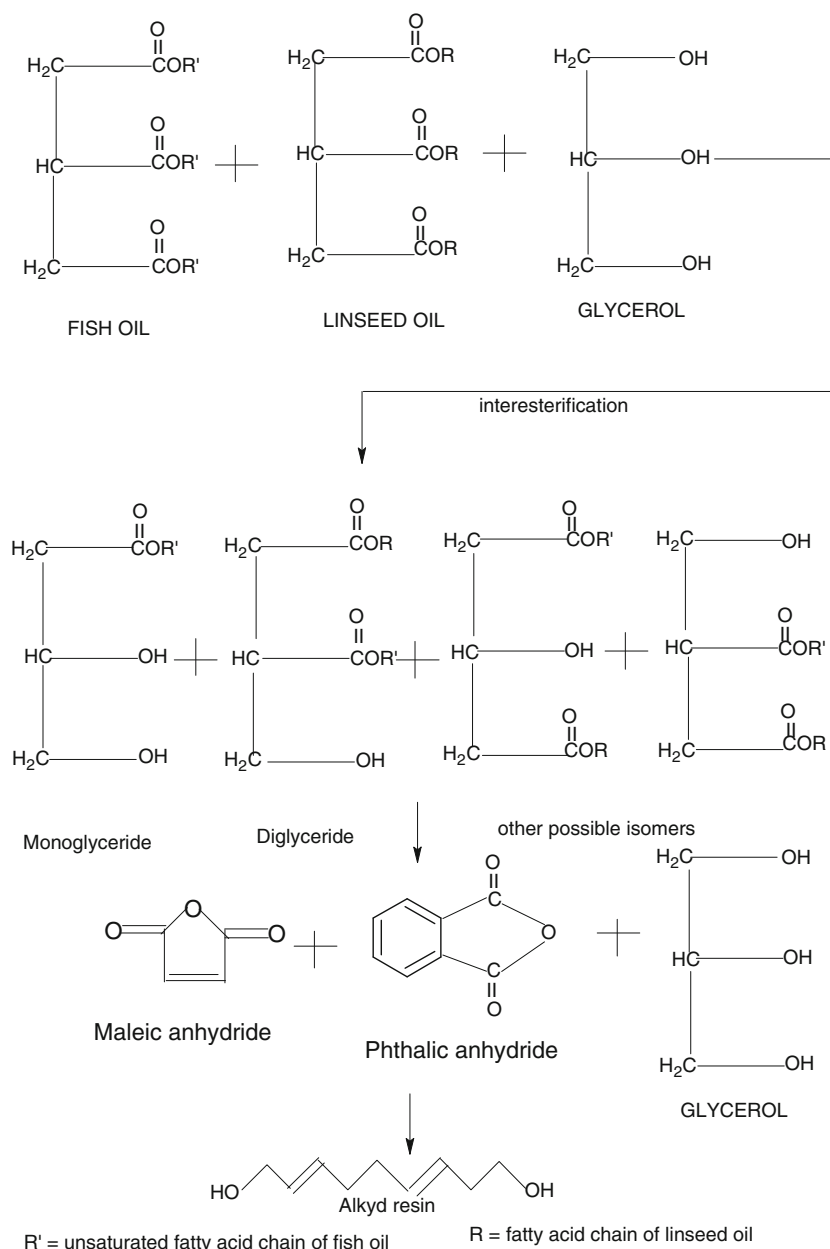
**Table 3** Composition of long oil alkyd resins

Ingredients	Weight (g)				
	F <sup>Aa</sup>	F <sup>B</sup>	F <sup>C</sup>	F <sup>D</sup>	F <sup>E</sup>
Linseed oil	110	82.5	55	27.5	–
Fish oil	–	27.5	55	82.5	110
Glycerol	28.2	28.2	28.2	28.2	28.2
Phthalic anhydride	59	59	59	59	59
Maleic anhydride	1.23	1.23	1.23	1.23	1.23
Xylene	80	80	80	80	80
Solid content %	69.2	69.3	68.9	69.9	69.9
Acid value mg KOH/g	8.34	9.4	8.0	9.68	7.79
Hydroxyl value <sup>b</sup>	36.02	34.9	35.9	34.3	36.8

<sup>a</sup> LO alkyd using commercial sample formulation

<sup>b</sup> Hydroxyl value determine as per reference [13]

**Fig. 2** Reaction scheme of alkyd resin



beakers equipped with high-speed stirrers. The chain extender ethylenediamine and deionized water (about 70% of solid content) were added over 0.5 h under high speed stirring. Each mixture turned into a highly viscous, white opaque liquid at first; however, on further addition of water, the viscosity of the mixture decreased, and thus two polyurethane dispersions (Table 4) of ~30% solids were separately obtained. The reaction scheme is shown in Fig. 3.

## Characterization

### FTIR

IR spectra of fish oil alkyd resin and polyurethane dispersion were recorded using a Perkin Elmer instrument (spectrum one) in the range of 600–4,000  $\text{cm}^{-1}$ . Resin and PUD were dissolved in carbon tetrachloride and placed on KBr pellets to record their IR spectra.

## <sup>1</sup>H NMR

<sup>1</sup>H-NMR spectra of refined fish oil, its alkyd resin and LO:FO (50:50) were recorded using a Bruker 300 MHz NMR spectrophotometer at ambient temperature. Deuterated carbon tetrachloride was used as the solvent.

## Acid Values and Viscosities of Alkyd Resins

Acid values of the alkyd resins and their viscosities were determined by ASTM Method D 465 and ASTM Method D 1200 using a B4 Ford cup, respectively.

## Film Preparation

Mild steel panels (24 gauge, 6 × 4 inch) were coated after being thoroughly cleared of scales by rubbing with emery paper followed by cleaning with acetone as per ASTM D 609-00.

The newly synthesized resin samples were mixed with a combination of different driers (containing cobalt octoate 0.05%, lead octoate 0.2% and magnesium octoate 0.05% w/w of the resin) and coated onto the mild steel panels, using a bar coater (“sheen” make) of 50 microns. The coated samples were studied at 29 °C in 60% humidity for surface and hard drying times as per ASTM D 1640-03. The alkyd resins were allowed to dry at room temperature for a week, and the PUDs were dried at 100 °C for 24 h, to ensure the complete maturation of films before testing.

## Pencil Hardness

A relative measurement of hardness was achieved by rating the hardness of lead pencils as per ASTM D3363-92a.

## Scratch Hardness

The scratch hardness was measured using a scratch hardness tester with a hemispherical hardened steel needle point of 1-mm diameter, according to ASTM D 5178.

**Table 4** Composition of styrenated alkyds and polyurethane dispersions

Ingredients	Weight (g)	
	P <sup>A</sup> /P <sup>C</sup> /P <sup>E</sup>	S <sup>A</sup> /S <sup>C</sup> /S <sup>E</sup>
Alkyd resin (70%)	36	36
Styrene	00	10
DMPA	3.6	3.6
IPDI	5.2	5.2
TEA	0.9	0.9
Water (added under high speed dispersion)	75	75

## Adhesion

A cross-cut adhesion test was performed as per ASTM D-3359-2002. The samples were coated onto mild steel panels and cut into squares of 1 × 1 mm using a crosshatch tester (“sheen make”). Adhesive tape was applied on the cross-cut section, firmly rubbed with a fingertip and removed after 1 min. The number of squares left intact gives a measure of the adhesion of the sample.

### Adhesion (%)

$$= \frac{\text{Number of squares intact in the tape applied area}}{\text{Total Number of squares in the tape applied area}} \times 100$$

## Flexibility

This property is related to the elongation and can be measured by the conical mandrel (1/4”), as per ASTM D 522-939. To check flexibility, samples coated onto tin plates were tested using a conical mandrel and examined visually for cracks in the film.

## Impact Resistance

The impact resistance was measured using a falling weight type impact tester (Komal Scientific, Mumbai, India), as per ASTM D2794.

## Water Resistance

Glass panels coated with the samples were allowed to completely dry and cure at 100 °C for 24 h. Wax was applied to the edges of the glass panels to restrain the migration of water under the film from the open ends. The panels after being dipped in water were examined for changes in appearance after 24 h.

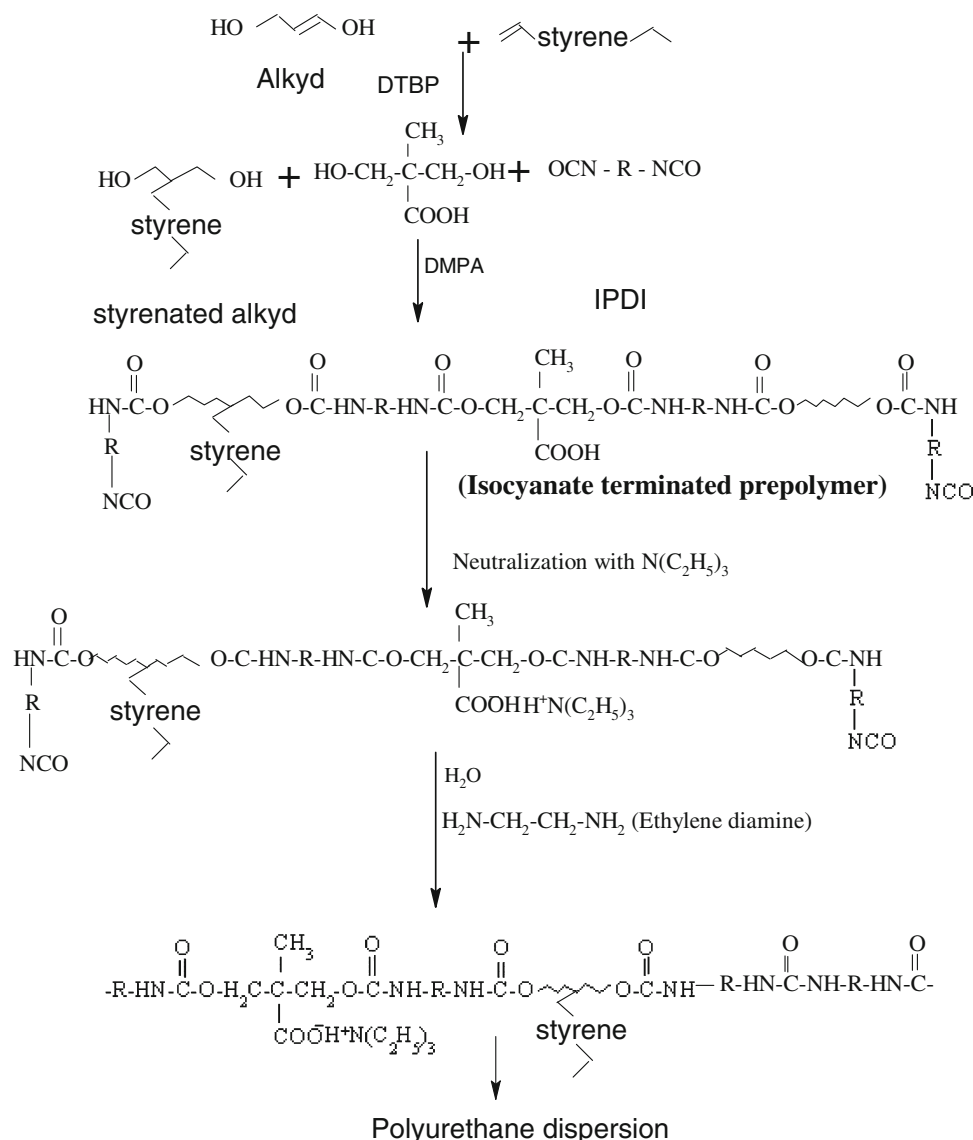
## Acid/Alkali Resistance

Glass panels coated with the samples were dipped in 2% w/w sulfuric acid solution and 2% w/w sodium hydroxide, respectively, and the changes in the appearance of the films were noted after 24 h.

## Salt Water Resistance

Coated mild steel panels were dipped in 5% w/w sodium chloride solution, and the changes in the appearance of the films were noted after 24 h.

**Fig. 3** Reaction scheme of styrenated polyurethane dispersion



### Solvent Resistance

The solvent resistance was carried out as per the “Double Rubs” method (ASTM D 1308) by soaking the cotton in a solvent and rubbing it back and forth on a coated film until the film was detached from the surface. The solvents used were acetone and methyl ethyl ketone (MEK). The number of rubs that the coated film withstood was noted as the solvent resistance.

### Results and Discussion

Fish oil contains a high percentage of unsaturated and saturated fatty acid. Its iodine value is almost equal to that of linseed oil, and it can therefore be used in the synthesis of long oil alkyd coatings, provided its

obnoxious fish odor can be eliminated. A series of long oil alkyd resins were prepared using refined sardine fish oil, linseed oil and different ratios of refined fish oil (FO) and its interesterification with linseed oil (LO). Surprisingly, the fishy odor was significantly diminished at a LO:FO ratio (50:50) in the synthesis of alkyd resin. The processing parameters, such as acid values and viscosities, were determined for all alkyd resins, but only the representative samples of linseed oil and linseed oil: fish oil (50:50) alkyd resins are presented in Table 5. No significant change was observed in the acid values or viscosities between these two resins. It can be observed that the acid value decreases as the reaction proceeds over a period of time. The reaction was stopped when the acid value dropped below 10. The viscosity of each of the resins increased exponentially with the progress of the reaction.

**Table 5** Processing parameters, acid values and viscosities of resins

Time (h)	Acid value mg KOH/g	Viscosity (s)
Linseed long oil alkyd resin		
4	38.2	16
5	28.2	32
6	22.2	44
7	19.2	56
8	14.2	70
9	11.2	99
10	8.34	140
Interesterification of fish and linseed (50:50) long oil alkyd		
4	33.7	17
5	29.9	27
6	22.6	35
7	18.6	49
8	13.5	68
9	10.2	98
10	8.0	125

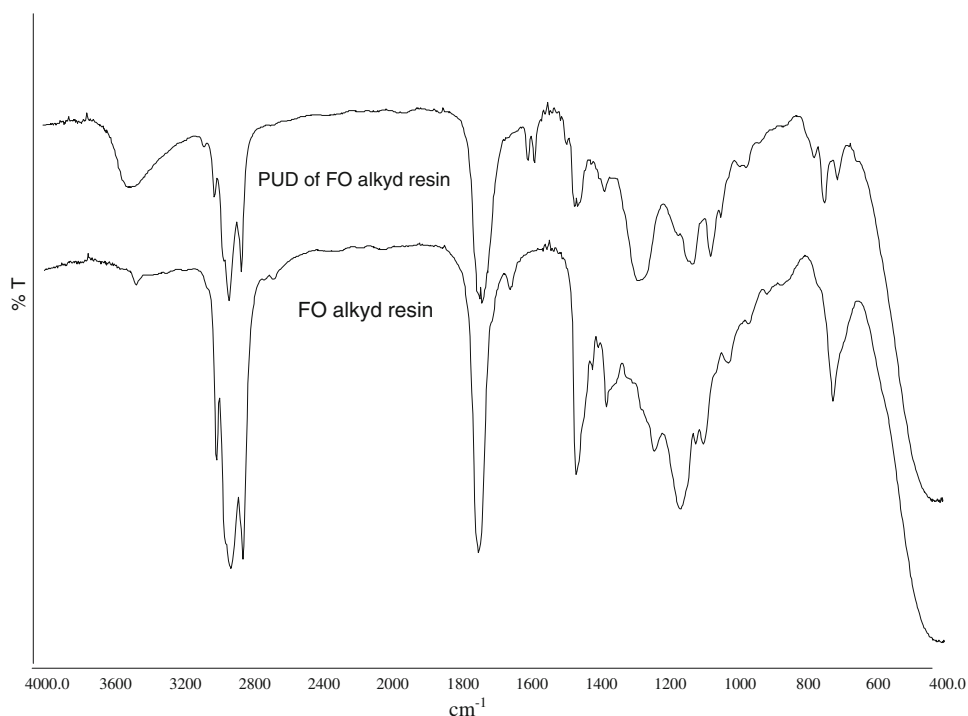
### FTIR

The IR spectra of FO alkyd and PUD of FO alkyd are shown in Fig. 4. The bands at 2,925 and 2,854  $\text{cm}^{-1}$  actually correspond to asymmetric and symmetric stretching of C–H, respectively, both from  $\text{CH}_2$  and  $\text{CH}_3$ . The C–H stretching of  $>\text{CH}$  is clearly seen at about 3,000  $\text{cm}^{-1}$ , which is a clear indication of unsaturation. The formation of urethane was

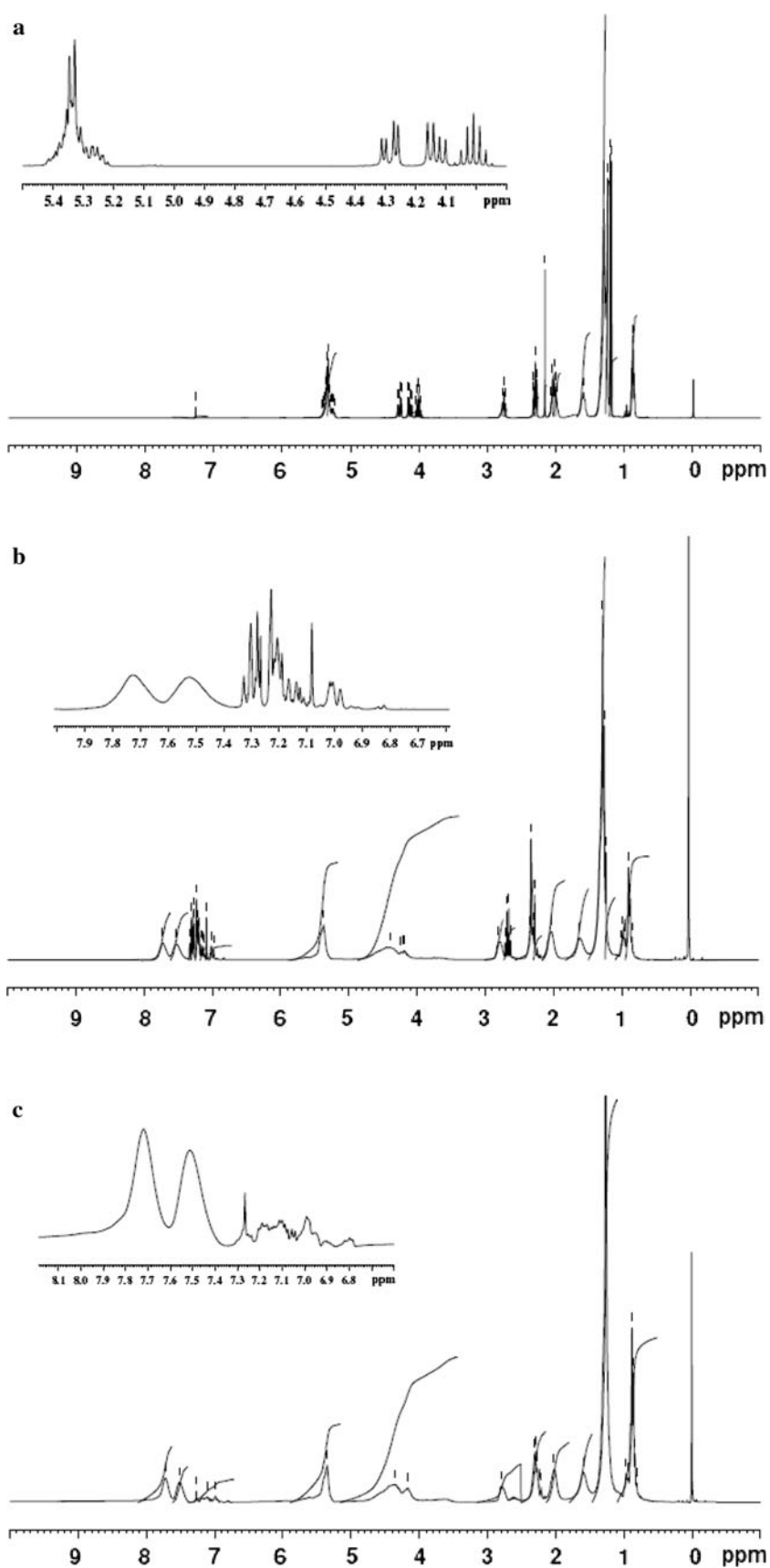
confirmed by the presence of a band at 3,408  $\text{cm}^{-1}$  due to the NH group [4, 11]. The band at 1,730  $\text{cm}^{-1}$  corresponds to C = O stretching from the ester and carboxylic acid groups of the FO alkyd and its PUD. The absence of bands in the range of 2,000–2,300  $\text{cm}^{-1}$  shows that all the diisocyanate groups have reacted completely during polymerization to form urethane linkages and amide groups.

### $^1\text{H-NMR}$ spectroscopy

Figure 5a, b, c show the  $^1\text{H-NMR}$  spectra of refined sardine fish oil, its alkyd resin and its LO:FO (50:50) interesterification product. The signal assignments are listed in Table 6. The peak at  $\delta$  0.84–0.91 ppm corresponds to all fatty acids (FA) except  $\omega$ -3 FA. The huge peak at  $\delta$  1.20–1.35 ppm originates from the fatty acids (FA) except EPA and DHA. The peaks in the range of  $\delta$  2.73–2.77 ppm correspond to polyunsaturated fatty acids [20–23]. The acylglycerol with one proton appear to overlap with the olefinic signal at about  $\delta$  5.25 ppm; on the other hand, the signals of the four protons for the two acylglycerol- $\text{CH}_2\text{OCOR}$  units appear at  $\delta$  4.1 and 4.3 ppm, respectively. The middle range of the proton spectra ( $\delta$  3.3–6.6 ppm) contains the peaks due to vinyl proton of fatty acids (FA) incorporated in the alkyd resins ( $\delta$  5.3), and the protons neighboring the hydroxyl or ester groups. The peaks in the range of  $\delta$  7.2–7.7 ppm correspond to aromatic protons originating from phthalic and maleic ester fragments of the alkyd resin [24, 25].

**Fig. 4** IR spectra of **a** fish oil alkyd, **b** fish oil PUD

**Fig. 5** **a** NMR spectrum of sardine fish oil **b** NMR spectrum of sardine fish oil alkyd resin **c** NMR spectrum of LO:FO alkyd resin 50:50





**Table 6** Signals present in <sup>1</sup>H-NMR spectra of fish oil and alkyd resins and their assignment

Chemical (ppm)	Assignment	Compound
0.84–0.91	–CH <sub>3</sub>	All fatty acids (FA) except ω-3 FA
0.95–1.0	–CH <sub>2</sub>	ω-3 FA
1.20–1.35	–(CH <sub>2</sub> ) <sub>n</sub>	All fatty acids (FA) except EPA and DHA
1.59	–(CH <sub>2</sub> ) <sub>n</sub> –CH <sub>2</sub> –COOH	All fatty acids (FA) except DHA
1.98–2.15	(CH <sub>2</sub> ) <sub>n</sub> –CH = CH	Unsaturated FA
2.27–2.32	–CH <sub>2</sub> –COOH	All fatty acids (FA) except DHA
2.73–2.77	=CH–CH <sub>2</sub> –CH=	Polyunsaturated FA
4.00–4.17	–CH <sub>2</sub> –O–CO–	α position in glycerol
4.27–4.32	–CH = CH–	Olefinic (FA chain)
5.26–5.37	–CH–O–CO–	β position in glycerol
7.2–7.7		Aromatic protons of phthalic and maleic ester

**Table 7** Characteristics of alkyds and polyurethane dispersions

Alkyd/PUD	F <sup>A</sup>	F <sup>B</sup>	F <sup>C</sup>	F <sup>D</sup>	F <sup>E</sup>	P <sup>A</sup>	S <sup>A</sup>	P <sup>E</sup>	S <sup>E</sup>	P <sup>C</sup>	S <sup>C</sup>
Coating characteristics											
Drying time (h)											
Tack free	5	5	5	18	48	–	–	–	–	–	–
Hard dry	18	18	18	48	64	–	–	–	–	–	–
Pencil hardness	4H	4H	3H	3H	2H	5H	6H	5H	6H	5H	6H
Scratch hardness (g)	1500	1400	1200	1000	900	1850	2000+	1900	2000+	1900	2000+
Adhesion	100%	100%	100%	80%	80%	100%	100%	100%	100%	100%	100%
Flexibility	Passes	Passes	Passes	Passes	Passes	Passes	Passes	Passes	Passes	Passes	Passes
Impact resistance <sup>a</sup>											
Direct	50	50	50	37.5	37.5	75	75	75	75	75	75
Reverse	50	50	50	37.5	37.5	75	75	75	75	75	75
Chemical resistance											
Water	NE	NE	NE	SB	SB	NE	NE	NE	NE	NE	NE
Alkali	FR	FR	FR	FR	FR	VSB	VSB	VSB	VSB	VSB	VSB
Acid	NE	NE	NE	SB	SB	NE	NE	NE	NE	NE	NE
Salt	HSB	HSB	NE	SB	SB	SB	SB	SB	SB	SB	SB
Solvent resistance											
Acetone Rub	100	100	100	100	100	50	50	50	50	50	50
MEK Rub	75	50	75	75	50	90	50	80	60	78	50

NE no effect, VSB very slightly blushed, SB slightly blushed, HSB highly blushed, FR film removed

<sup>a</sup> The values are arrived at by multiplying weight of indenter in lbs (6.25 lbs) with the maximum height in inches from where indenter falls without any visible damage of film

### Drying Properties of Alkyds

Drying properties, such as surface and hard dry times, of different interesterification products (IP) of FO: LO alkyd resins are presented in Table 7. It has been observed that the drying time of the FO alkyd alone is very long when compared to its IP with LO. The drying time is reduced with the increase in LO content in the IP ratio. The drying of an alkyd resin depends on the amount of linolenic and linoleic acid present in the oil [10, 13]. Fish oil contains only linoleic acid, which is a semi-drying acid, so it dries

very slowly. The increase in LO contents in IP increases the linolenic acid component, which facilitates fast drying and hence reduces the drying time. At an optimum ratio of LO:FO (50:50), the drying time was almost equal to that of the linseed oil alkyd alone.

### Pencil Hardness

The pencil hardness increased with increasing LO content in the LO:FO alkyd ratio, (Table 7). Among all the resins, the 100% FO alkyd showed the least pencil hardness. This

may be due to the low percentage of linoleic acid present in fish oil. Linseed oil contains higher percentages of both linoleic and linolenic acid [11] which contributes to crosslinking and drying, hence, increased LO content increases the hardness. However, the pencil hardness for 50:50 and 25:75 composition of LO: FO was constant. The maximum pencil hardness was observed at 75:25 LO:FO and 100% LO alkyd. All the styrenated PUDs showed excellent hardness compared to PUDs based on alkyds and their interesterification products.

#### Scratch Hardness

Table 7 lists the scratch hardness comparison data of the tested alkyd resins and PUDs. The FO alkyd alone shows the least scratch hardness. Hardness increased with increasing LO content in the FO:LO alkyd resin. The minimal hardness of the FO alkyd alone may be because of the highly unsaturated fatty acids present in fish oil, which favor short crosslinks. There are two different crosslinkings [11, 13] that influence hardness, (1) due to the double bonds within unsaturated fatty acids in fish oil, which lead to short crosslinks; (2) due to the double bonds of the unsaturated fatty acids of fish oil on interaction with linseed oil, which decrease the short crosslinks. However, the primary reason for the better drying and hardness of IP could be the higher amounts of linoleic and linolenic acids present in LO [13]. The scratch hardness was found to decrease in the order of styrenated PUD of LO > PUD of LO > LO alkyd. A similar trend was observed for FO and LO:FO (50:50) alkyds when converted to their PUDs and styrenated PUDs, respectively. This indicates that styrenation improves the hardness of resins.

#### Flexibility/Adhesion Test

All the samples of alkyds and PUDs passed the flexibility test and showed no cracks in the bent films. This is mainly due to the good flexibility of the films, which is the characteristic feature of both PUDs and alkyds. It can be seen from Table 7 that the fish oil alkyd (100%) and LO:FO (25:75) were inferior in adhesion, while all the other interesterification products of LO: FO, LO alkyd and PUDs displayed 100% adhesion.

#### Impact Resistance

The impact resistance of alkyd resins increased with the increase in LO content (Table 7). The composition of the 100% FO and LO:FO (25:75) alkyds showed the lowest impact resistance. The highest impact resistance was shown by the LO:FO (50:50) alkyd. There was no increase

in impact resistance with LO content in the LO:FO alkyd above 50%. All the styrenated and interesterification products of PUDs showed the highest impact resistance.

#### Chemical Resistance

All alkyd resins exhibited excellent resistance to acid, salt, and water; however, all films were completely removed when immersed in an alkali solution (Table 7). However, PUDs based on alkyd and styrenated alkyd showed fairly good resistance to acid, alkali and salt.

#### Solvent Resistance

The acetone resistances of all PUDs samples were slightly inferior to their respective alkyd resins. This may be due to the presence of acid functionality in the polymer network which makes the PUDs hydrophilic in nature (Table 7). All PUDs were slightly better in MEK resistance; however, in the case of styrenated PUDs, except styrenated fish oil (100%) PUD, the other compositions were inferior to their respective alkyd resins.

#### Conclusions

It can be concluded from the present study that the costlier linseed oil used for making long oil alkyds may be partially replaced by fish oil, a cheap marine resource. Except for pencil and scratch hardness, all the other coating performance properties of the interesterification product of fish oil and linseed oil (50:50) alkyd were similar to those of a standard linseed oil alkyd resin. Polyurethane dispersion of FO alkyd resins exhibited excellent adhesion, impact, flexibility, and chemical resistance, despite the fact that the coating properties of the FO alkyd by itself are not very good. Hence, fish oil may be used to formulate a VOC compliant coating. Polyurethane dispersions of FO:LO (50:50), as well as of styrenated fish oil, exhibited superior coating properties to those of their alkyd resins, respectively.

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