Novel Polyesteramide Resin from Rubber Seed Oil for Surface Coating Application

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Abstract

This paper reports the synthesis of rubber seed oil-based polyesteramide via maleinised rubber seed oil intermediate. Rubber seed oil was modified by treatment with maleic anhydride and subsequently reacted with diethanolamine. The synthesized intermediate and the resin were characterized by measurement of physico-chemical properties (acid value, iodine value, and saponification value), resistance to chemicals (water, dilute alkali, dilute acid, and brine) and drying time in comparison with medium oil-modified alkyd resin. The values of the measurement parameter suggest a potential for the application of polyesteramide resin in surface coating applications.

Keywords: Rubber seed oil, maleinization, polyesteramide resin, low V.O.C., surface coating

1. Introduction

The surface coating industry world over remains strong, with a market value estimated in the tune of billions of dollars (Bourguignon, 1997). A reminisce into its origin dates back into the prehistoric times. Progress in the field is not unconnected to experiences generated over the years by coating chemists and technologist, in the quest to improve or, synthesize superior coating systems, according to the need of the time.

The use of natural raw material like oils and fats (e.g., Linseed oil) as binder has long been reported (Oil and Colour chemist's Association of Australia, 1983). The foremost 100% solid finishes, especially in such applications as wood, steel primers, etc, were oil based coatings. Poor performance properties in its gloss, films, and water resistance, coupled with the more competitive film former, such as, water based latex emulsion, led to decline in their usage (Bentley et al, 1998). The advent of technology-driven natural and synthetic materials, which are economically viable, and offers more efficient polymeric binder systems, such as, polyesters, acrylics, nitrocellulose lacquer, polyurethanes, epoxy resin, etc. (Encyclopedia of Polymer Science Technology, 1964), Payne, (1997), has further displaced these 100% solid oil-based coating.

However, present trends in the coating industries has embraced environmental restrictions and government legislations (Wick et al, 1999), (Anon, U.S. EPA), which has put limit on the volatile organic compound (VOC) content of coatings, especially as it has been found to be the second largest source of VOCs pollutant

responsible for excess ozone depletion in the atmosphere (Bourguignon, 1997). Such VOC emissions in the atmosphere poses serious health hazard, both to material, plants and animals. All these coupled with the high cost of petroleum products has redirected attention on agricultural raw materials which has the advantage of being renewable, biodegradable, and relatively inexpensive (Wick et al, 1999), (Radojevic, 1999), (Azim et al, 2001).

Nonetheless, the shortcomings of natural oils and fats are capable of being obviated by modification via chemical means in order to maximize its performance properties to meet with target end utilizations; this is in spite of their continued use in oleo resinous paints and varnishes, and in inks (Hofer, 1996). Such modification processes include synthetic conjugation of naturally non-conjugated unsaturated oils (e.g., dehydrated castor oil and lesqurella oils), dimerization, copolymerization with polymeric monomers (Shelby et al, 1999), (Anthawale et al, 2000), etc. Also, chemical modification of oils can be effected by treating with maleic anhydride. In the high temperature reaction suited for unconjugated polyunsaturated fatty acid (PUFA), there is formation of succinic anhydride adduct at the double bond carbon of the fatty acid followed by rearrangement (hydrogen abstraction) that leads to conjugation. Subsequent addition of maleic anhydride is by Diels-Alder reaction, to furnish a dianhydride adduct (Aigbodion et al, 2003a, b, c), (Dutta et al, 2004), (Rheineck et al, 1969),. However, this is only if the diene is in the cisoid conformation (James et al, 1977). These reactions are, however, in addition to the conventional esterification taking place (Patton, 1962). These adducts formed, are capable of reacting with other chemical reactants to give unique polymers, for example, with polyol, it gives moderate molecular weight derivative that dry faster than the unmodified drying oil (Tark et al, 2003). Industrial application of maleic anhydride adducts in polymers_abounds in such coatings for concrete (Hart and Christenson, 1968), various vehicles, polymers used for electro-deposition (Weghorst and Battles, 1965), which have proved useful in coating hard to cover hidden areas of automobiles and other frames (Encyclopedia of Polymer Science Technology, 1964).

Work on the use of vegetal oil in the preparation of polyesteramide have been reported (Morrison and Boyd, 2004), (Urbanski et al, 1977), (Fan et al, 1997), (Sharif et al, 2003), (Sharif et al, 2001); typical approach for its synthesis involves the reaction of the triglyceride oil with diethanolamine to produce N,N^1-bis (2-hydroxyethyl) oil and subsequent reaction with a polyacid (e.g. phthalic acid) to produce the polyesteramide as shown below in scheme 1.

In the present study attempts have been made to prepare novel polyesteramide resin from maleic anhydride modified rubber seed oil that can be used for environment-friendly coatings. The proposed reaction sequence is shown in scheme 2 below.

2. Methods

Rubber seed oil (RSO) used was obtained by mechanical expression of rubber seed collected from the plantation of Rubber Research Institute of Nigeria, Iyanomo, without further purification. Its fatty acid composition is shown below in table 1. Maleic anhydride and diethanolamine both of analytical grade were obtained from Fluka Chemicals Ltd and were used as received.

2.1. Maleic anhydride modified rubber seed oil (MAMO)

Preparation of an intermediate maleic anhydride modified rubber seed oil (MAMO) from rubber seed oil was carried out according to the method earlier reported (Aigbodion et al, 2003a,b). Into a three necked-flask fitted with a reflux condenser, 200g of RSO and 40g of maleic anhydride was charged, and reacted at 220^{o}C for about 60 minutes, in the absence of a catalyst (see scheme 2). Samples were withdrawn and the physico-chemical properties determined using the standard method (Pacquot & Hauffene,1987).

2.2. Synthesis of rubber seed oil polyesteramide (RSOP)

The temperature of the reaction mixture was reduced to between 110-115^{o}C and diethanolamine (20g) was added over a period of two hours to obtain the polyesteramide (scheme 2). The physico-chemical properties of the resin and the maleinized intermediate were determined using standard methods. Films of polyesteramide were prepared with mixed cobalt and calcium naphthanates (0.5%) driers. Also, an emulsion of RSOP was prepared with a co-solvent (propan-2-ol) and water for low volatile organic content (VOC) coating. These were applied on thin glass slides air-dried and oven-baked (table 4). The chemical resistance and drying schedules of the films of the maleinised oil and the resin were determined according to the ASTM methods.

2.3. Measurement

Rubber seed oil fatty acid composition was determined by gas Chromatography. FTIR of rubber seed oil, its intermediate maleic anhydride modified oil and the polyesteramide were characterized using KBr cell on a Nicolet Avatar 330 FT-IR.

3. Results and discussion

Table 2 gives the physico-chemical properties of the brown colour RSO in comparison with those of the dark-brown coloured maleic anhydride modified oil (MAMO) and polyesteramide (RSOP). The marked reduction in the iodine values of MAMO and RSOP in comparison with the oil gives an indication of the extent of reaction and suggests a near quantitative conversion of the double bonds in the starting material.

The increase in the acid value of MAMO is due to the maleation of the oil. Subsequent reduction in acid value of the polyesteramide is due to the polyesterification reaction of the -OH and -COOH groups. There is an increase in saponification value from the oil to MAMO and through to that of the polymer.

3.1. FTIR

Table 3 shows FTIR spectra of characteristics absorption bands of rubber seed oil (RSO), the maleic anhydride modified oil (MAMO), and the derived polyestramide (RSOP). In the RSO spectrum the C-H stretching vibration absorption bands at 3009cm^{-1}, 2927cm^{-1}, and 2854cm^{-1} are shown.

The carbonyl C=O absorption bands is seen at 1744cm^{-1}, while the absorption at 1240cm^{-1} is the C-O band of ester.

The spectrum of malic anhydride modified oil (MAMO) in contrast to that of RSO, shows the broad O-H band of carboxylic acid at 3500-2500cm^{-1}; the presence of this band coupled with the absence of the anhydride absorption bands at 1850-1740cm^{-1} implies that rather than the anhydride adduct, the dicarboxylic acid adduct is formed: which also explain the presence of the O-H broad bands of carboxylic acids, and gives ample clue to the very high acid value of MAMO. The polyesteramide spectrum differs somewhat from that of the maleinised oil, and RSO. In addition to the Carbonyl group absorption bands at 1739cm^{-1}, it has the amide carbonyl C=O absorption bands at 1639cm^{-1}. This implies that in an addition to the esterification reaction there is also amidation reaction also taken place. The high acid value of the polyesteramide is due to the presence of some un-reacted carboxylic acid functionality in the polyesteramide chain: the O-H broad band between 3500-2500 cm^{-1}, which overlaps with the free O-H absorption band (3357cm^{-1}) of diethanolamine O-H group, also infers this.

3.2. Film properties

The drying schedule and chemical resistance of the films of polyesteramide resin are given in Table 4 in comparison with those of the maleic anhydride modified oil and earlier reported rubber seed oil-modified alkyd (Aigbodion et al, 2003b). The observed improvement in the measured properties of the polyesteramide in comparison with maleic anhydride modified oil is expected and is consistent with results of previous studies (Aigbodion et al, 2003b).

The chemical resistance of the polyesteramide, which is superior to that of the modified oil, is comparable to that of the alkyd resin; both samples showing similar susceptibility in alkaline medium, an observation that has been attributed to the chemical reactivity of ester and amide groups. It can be seen from the results in Table 4 that the chemical resistance and drying schedule of the polyesteramide resin are comparable to, but, somewhat inferior to those of reported for alkyd resin. Maleinisation of triglyceride affects the level of unsaturation in two ways; uncouples double bond in both the triglyceride oil substrate and the maleic anhydride moiety; converting the latter into a succinyl group (see scheme 2). The total impact of the reduced degree of unsaturation would be concomitant with increase in the drying schedule particularly the dry-through time of the polyesteramide.

4. Conclusion

Polyesteramide has been prepared from maleinised rubber seed oil by reaction with diethanolamine. The result of the physico-chemical properties, chemical resistances, and drying schedule of the resin suggest a potential for its application in high solid content, low volatile organic content (VOC), surface coating applications. Also the high acid value of the polymer obtained suggests that further reactions are feasible, which may likely improve or modify the polymer.

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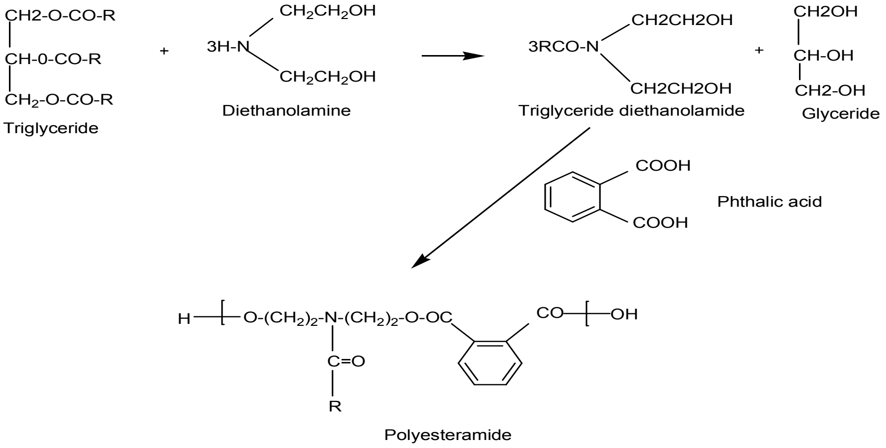
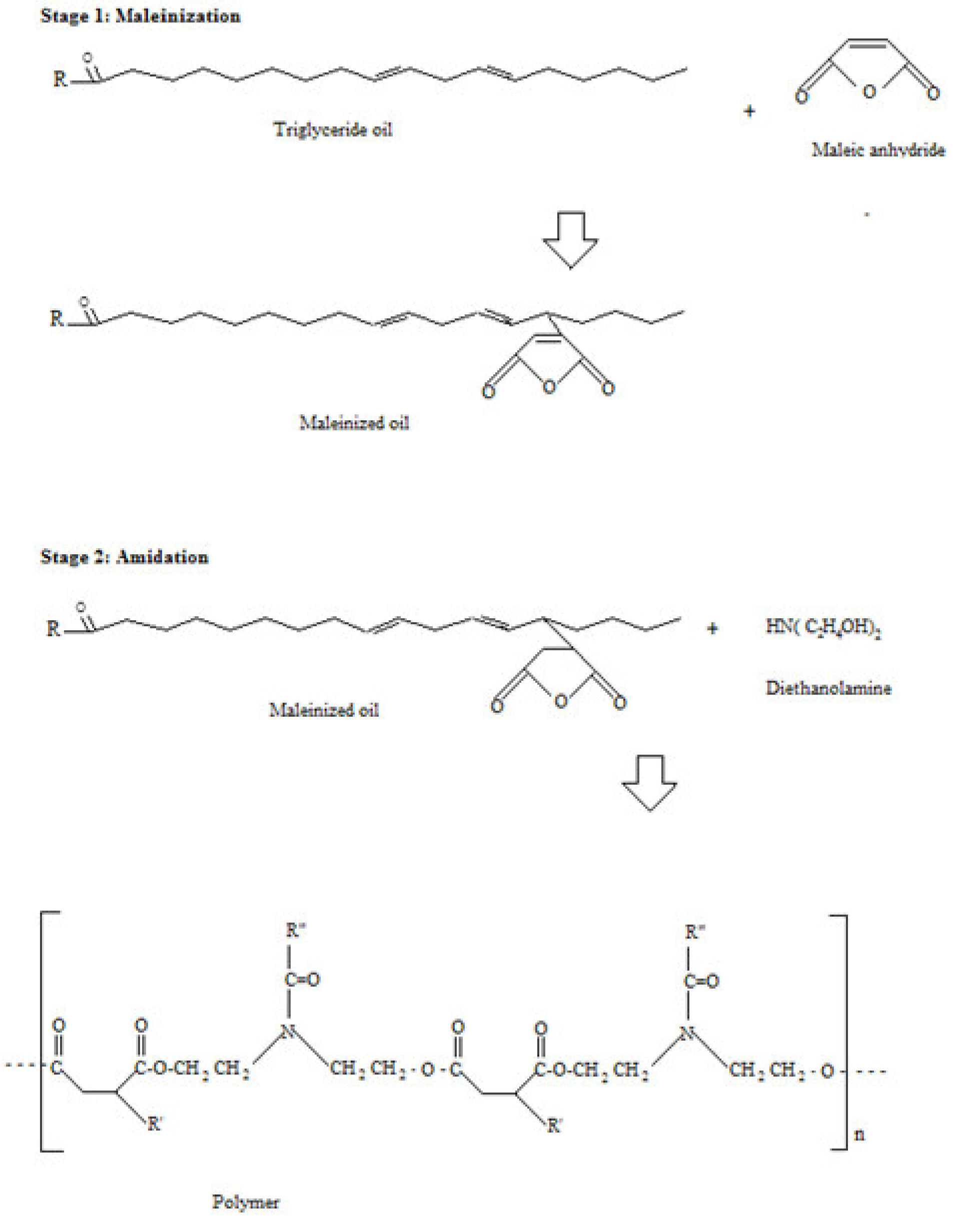


Scheme 1: Synthesis of Polyesteramide from triglyceride oil

Table 1: Fatty Acid Composition of Rubber Seed Oil

Fatty Acid	%
Saturated:	
C16:0 Palmitic acid	17.51
C18:0 Stearic acid	4.82
TOTAL	22.33
Unsaturated:	
C18:0 Oleic acid	25.33
C18:2 Linoleic acid	37.50
C18:3 Linolenic acid	14.21
TOTAL	77.04
Others	0.63



Scheme 2: formation of polysteramide.

Table 2: Some physico-chemical properties of rubber seed oil and its derivatives

Properties	RSO	MAMO	RSOP
Colour	Brown	Dark-brown	Dark-brown
Acid value	34.650	206.4	120.6
Iodine value	139.522	38.9	37.9
Saponification value	183.404	204.0	225.8
Specific gravity	0.931		

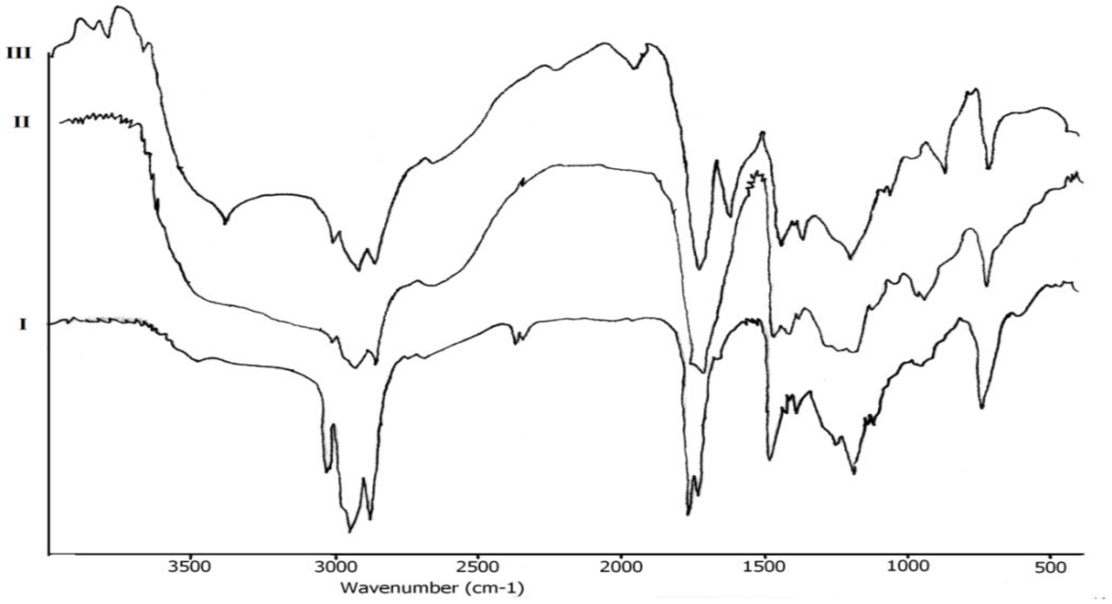


Fig. 1. FTIR spectra of **I** rubber seed oil **II** maleinised rubber seed oil and **III** rubber seed oil polyesteramide.

Table 3: Main peaks of FT-IR Spectra

Functional group	RSO	MO	RSOP
Free O-H band	-	-	3293
C-H str. Vib.	3009,2927,2854	2927, 2854	3001, 2924, 2846
O-H	-	3500-2500	3500-2500
C=O (ester)	1744	1712	1739
C=O (amide)	-	-	1639
C-O (ester)	1240	1177	1173

Table 4: Chemical resistance and drying time of polyesteramide film

Samples	Chemical Resistance / medium				drying schedule	
	Water	NaCl	NaOH	H_2SO_4	Set-to-touch	Dry-through
Maleinised Oil	3	3	4	2	4 days	>7days
RSOP (air-dried)	1	2	4	2	28 min	<48 hr
RSOP (oven-baked)	1	1	3	1		
Alkyd resin	1	1	4	1	30 min	<24 hr

1=not affected, 2= loss of gloss, 3=slightly wrinkled, 4=removed