International Journal of
Basic and Applied Sciences

(A peer reviewed International Journal)

Synthesis and Characterization of Polyesteramide Resin from Rubber Seed Oil for Surface Coating Application

International Journal of Basic and Applied Sciences, Vol. 1 No. 3. pp. 263-266 2277-1921. 2012

ISSN *2277 – 1921*

Article type *Full Length Research Article*

Submission date *24 May 2012*

Acceptance date *10 July 2012*

Publication date *15 July 2012*

Article URL *http://www.crdeep.com/category/ijbas*

Authors **Ikhayere Stephen, S.O. Ohikhena, Ekebafe L.O.,**

Center for Rural Development Ecology and Environment Protection

CRDEEP Head Office: 315/10, Kaulagarh Road, Rajendranagar, Indervihar, Dehradun, 248001, Uttrakhand, India.

International Journal of Basic and Applied Sciences Vol.1 No.3. 2012. Pp. 263- 266

Full Length Research Paper

Synthesis and Characterization of Polyesteramide Resin from Rubber Seed Oil for Surface Coating Application

Ikhayere Stephen[1]*, S.O. Ohikhena[2], Ekebafe[1] L.O.,
[1]Department of Polymer Technology, Auchi Polytechnic, Auchi, Edo State Nigeria
Department of Chemical Engineering Technology, Auchi Polytechnic, P.M.B. 13, Auchi, Nigeria

****Corresponding Author: khasteve019@yahoo.com***

Abstract
The polyesteramide resin was synthesized from adipic acid, N,N-bis-(2-hydroxyethyl) and Hevea brasiliensis. Fatty amide was obtained from methyl ester of the rubber seed oil by treatment with diethanol amine. The synthesized intermediates and resin were characterized in terms of acid value, iodine value, saponification value, drying time and specific gravity. The coating performance of the resins was tested by measurement of pencil hardness, adhesion and chemical resistance. The polyesteramide resin has lower saponification value than the oil. The lower iodine value of the polyesteramide resin is obviously due to the reduction of the molecular mass of the oil which accommodates the unsaturation present in the fatty acids of the oil. The resin has a short set to touch time but a considerably long dry through time of 5 hours, the oil is probably a semi drying oil rather than a none drying or drying oil.

Keywords: Rubber seed oil, Polyesteramide resin, Surface coating, triglycerides, curing

Introduction

Polyesteramide resins are products of poly-condensation reaction between polybasic acid polyhydric alcohols modified with fatty acid or drying oil. Oil modified polyhydric polyesteramide resin constitute a major group of resin used as blinders in surface coatings. It is estimated that polyester amide resins contribute about 70% to the conventional binders used in surface coating today[(1)] The popularity of polyesteramide as vehicle for coatings is largely due to their unique properties such as film hardness, durability, gloss and gloss retention, resistance to abrasion etc. impacted on them through modification with drying oils.[(2)] The oils that are mostly employed for polyesteramide resins synthesis are linseed, soybean, castor, tall oils.[(3)] These oils are largely imported to Nigeria for the formulation of coatings for metal cans used in packing of beverages, drugs, food etc. however, drying oils are available locally, which have remained untapped. These include rubber seed oil, soybean oil, walnut oil and tobacco oil.[(4)] Rubber seed is obtained in high yield as a by-product of (Heavea-Brasiliensis) rubber tree cultivated primarily for its latex.[(5)] Further, it was also found that the kernels comprises 50% of the whole seed and yield 42.39% oil, these reports have eventually generated a lot of interest in the rubber seed across the world.[(6)] However, research has shown it be a rich source of oil that is comparable in quality to try oils commonly used in surfacing[(7)].

Materials and Methods

Materials

Rubber Seed Oil was obtained from the Rubber Research Institute of Nigeria, Benin City, Xylene, Adipic Acid , Lead Mono-Oxide, Methyl-ethyl ketone Peroxide, Metallic Sodium, and Methanol , Anhydrous Sodium Sulfate, Ethanol, Potassium Hydroxide Sodium Thiosoulphate were supplied and are products of BDH, England. Styrene, and Diethanol Amine are products of Sigma-Aldrich, Germany

Preparation of methylester of the oil

Twenty five grams of oil in 50ml super dry methanol and 0.5% sodium methoxide (with respect to the oil) were refluxed for 3hrs in 250ml round bottom flask in air. The content of flask were then cooled to room temperature and kept overnight. The excess methanol was removed by distillation and the methyl esters were extracted by petroleum ester (b.p. 60-80^{o}c), washed with 15% aqueous NaCl solution and dried over anhydrous sodium sulfate. The methyl esters of the mixed fatty acids were purified from ester by distillation. Quantitative yield of the product was obtained.

Preparation of diethanol amide from the methylester of the oil

A three-necked round bottom flask equipped with a mechanical stirrer,and a dropping funnel were used for the preparation for the diethanol amide of the esters. 3.45g diethanol amine and 0.5% sodium methoxide (with respect to the ester) were taken in the flask with constant stirring under the presence of air and heated to 110-115^{o}C, then the methyl

esters of the oil were added into reaction mixture dropwise through the dropping funnel over a period of 1hr. The heating continued for another 3hr with constant stirring. Then the reaction mixture was cooled to room temperature, dissolved in petroleum ether, washed with 15% aqueous NaCl solution and dried over anhydrous sodium sulfate. The petroleum ester was removed by distillation to yield N,N'-bis(2-hydroxyethyl) rubber seed oil amide (diethanol amide of the fatty acids). The yield was ≈80%.

Preparation of polyesteramide from diethanol

Amide of the fatty acids and dibasic acid or its derivatives 0.08 mole (29.1g) of the amides of the fatty acids with 0.6% of PbO (with respect to the amide) were taken in a three-necked round bottom flask with the same arrangement as described earlier under the presence of air with constant stirring. The mixture was heated to 120-125^{o}C and 0.08 mole of diacid (11.68g adipic acid) was added into the mixture with 50mL xylene to facilitate the mixing of the reactants. Then it was heated to 180-190^{o}C for 2.5-3.5hrs and cooled to room temperature. The reaction was monitored by acid value determination of the viscous product. The yield was found to be very high (80-90%).

Curing of Resins

A homogenous mixture of resins with 30 phr of styrene as the reactive diluents, 4 phr of MEKP (methyl-ehtyl ketone peroxide) as initiator was prepared in a glass beaker at room temperature by hand stirring for 10min (phr=parts per hundred gram of resin). The plates (glass/mild steel) were uniformly coated by the respective resin into a thin film and heated in an oven at a definite temperature for specified period of time.

Characterization of polyesteramide resin

The physic-chemical properties of the polyesteramide resin samples (colour, specific gravity acide value sanponification value, iodine value) where determined according to ASTM standard methods [8, 9, 10]. The FTIR analysis was carried out to confirm changes in the structure of the rubber seed oil to the formation of the resin as shown in Figure 1.

RESULTS AND DISCUSSION

Rubber seed oil analysis

Table 1. Results of rubber seed oil analysis

Property	Rubber seed oil	Polyester amide resin
Specific Gravity (KG/m^3)	0.92992	0.9566
Acid Value (mol.dm^3)	27.300	25.90
Saponification Value (mg/g)	191.52	126.16
Iodine Value (mmol/kg)	145.8021	109.0470
Colour	Golden colour	Dark brown

The properties of rubber seed oil extracted and the polyesteramide resin produced from it are provided in table 1. As expected of any given oil, the rubber seed oil has a lower density than that of water (1g /cm^3). The high values of the saponification and iodine values of the oil can respectively be attributed to the presence of esters linkages and the level of unsaturated in the oil.

The polyesteramide resin has a much lower saponification value than the oil. The lower iodine value of the polyesteramide resin is most likely due to the reduction of the molecular mass of the oil which accommodates the unsaturation present in the fatty acids of the oil.

Polyesteramide resin analysis

Table 2. Result of polyesteramide analysis

Drying schedule	Time (mins)
Set to touch	16
Surface dry	45
Dry through	300
Property	**Resin observation**
Pencil hardness	HB pass
Adhesion	Fair
Solvent medium	Visual observation
Distilled water (cold)	Excellent
Salt (15% Nacl)	Excellent
Alkali (10% KOH)	Poor
Acids (0.5 Hcl)	Excellent

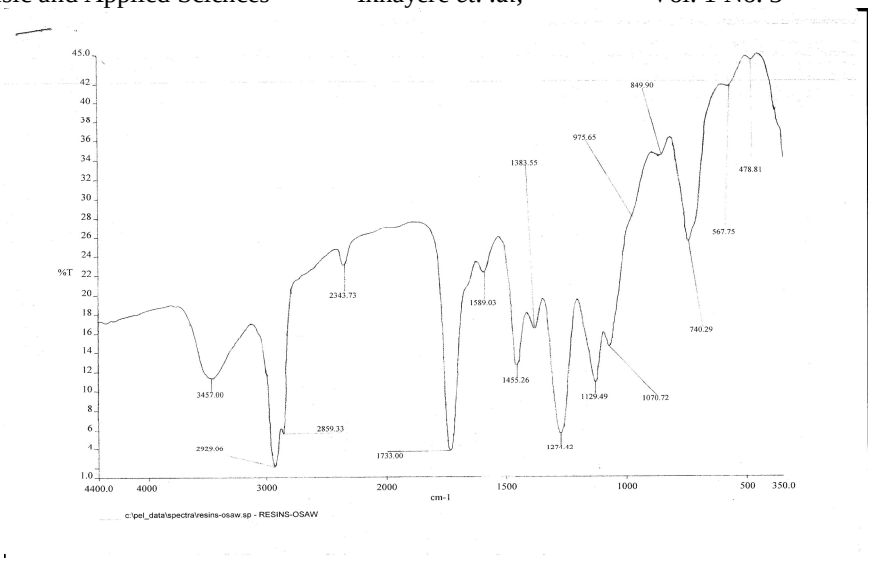

Figure 1: FTIR diagram of the polyesteramide resin

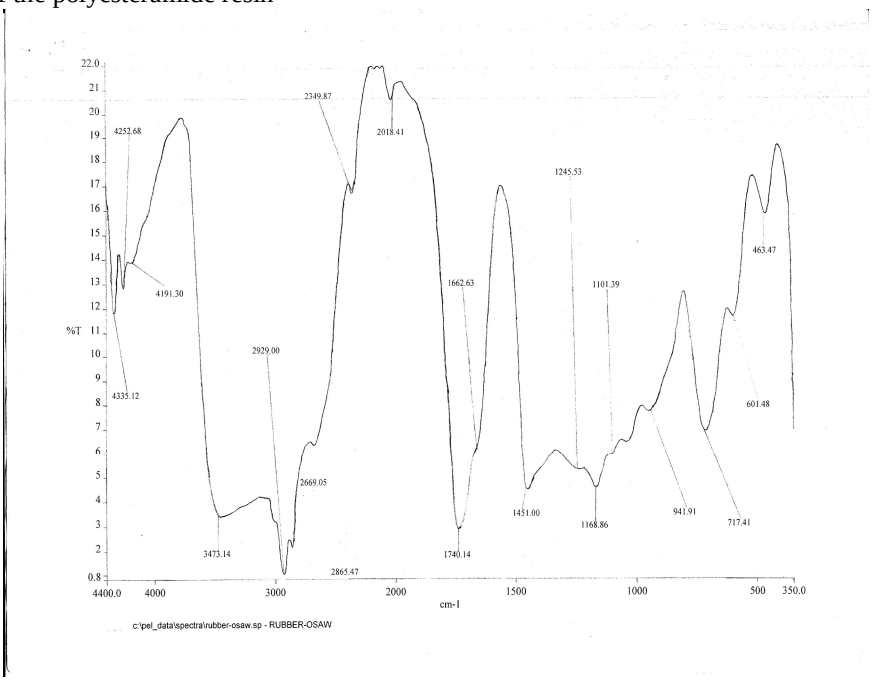

Figure 2: Structure of the FTIR for the rubber seed oil

The dry schedule of the polyesteramide resins are as presented in table.2. The resin has a short set to touch time but a considerably long dry through time of 5 hours, the oil is probably a semi drying oil rather than a none drying or drying oil.

The chemical resistances of polyesteramide resin as evaluated in different solvent medium are presented in Table 2. The polyesteramide resin film was found to resist water, salt and acid medium but poor. The poor observation when in alkali medium may be due to the susceptibility of polyesters to hydrolysis. Adhesion is relatively fair as film former retain some measurement of tackiness.

The FTIR analysis show remarkable changes in the functional group of the initial starting material, the rubber seed oil leading to the introduction of the ester and amide functional groups as seen in the resin FTIR spectrum in Fig 1

Conclusion

From this study,the renewable rubber seed oil has been utilized successfully for the synthesis of the industrial polyesteramide resins. The resins were successfully characterized by the determination of physical properties showing good adhesion, hardness and chemical resistance properties which make them

suitable for surface coating, and binder for composite,

References

1. M. BAJPAI, S. SETH. "Use of unconventional Oils Surface Coating: Blends of Alkyd Resin with Epoxy Ester. Pigment and Resins Technology; Second Edition Vol.29, 2000, pages 82-87
2. A.I, AIGBODION "Preliminary Studies on the preparation of Rubber Seed Oil". Indian J natur Rubber Res second Edition 1991,Vol. 4 page 144-70.
3. S. MAJUNDER. D. KUMAR,, Y.P.S NIRYAN, "Acrylate Grafted Dehydrated Castor Oil Alkyd. A Binder for Exterior Paints" Indian 1999, Vol. 60 page 57-65
4. Adefarati, FB "Development of Non-Edible Oils for use in the Nigeria Surface Coating Industry with particular Reference to Rubber (Hevea Brasillensis) Seed Oil for Manufacture of Air-Drying Oil" Modified Akyds 1986, Pages 27-38
5. H.B.KIM, N.A. WINNINK "Effect of surface acid Group Neutralization on Rubber Latex Films Macromolecules" 1994, Vol. 27 page 1007-12.
6. A.I.AIGBODION, PILLAICKS "Preparation Analysis and Applications of Rubber Seed Oil and its Derivatives in Surface Coating". Progress in organic 2000, Vol. 38 page 187-92.
7. F.E.OKEIMEN, C.O. OKIEIMEN "Utilization of Vegetable Oils as Alternative Diesel Fuel. A Review". Nigeria Journal applied science , 2002,Vol. 18 page 102-8.
8. ASTMD 1639-90, Standard Method for Acid Value of Organic Materials". Annual book of American society for testing and material standards Philadelphia, PA, 1994; 06.01:260-1.
9. ASTM D 1962-67 "Test for saponification value of drying oil, fats and polymerized fatty acids", annual book of American society for testing and material standards. Philadelphia, PA, (1979) 29:259-61.
10. ASTM D 1959-69, "Test for lodine value of drying Oils and their Derivatives", Annual book of American society for testing and material standards. Philadelphia, PA, 1979:29:265-7