International Journal of Advanced Research in Chemical Science (IJARCS)
Volume 2, Issue 1, January 2015, PP 1-5
ISSN 2349-039X (Print) & ISSN 2349-0403 (Online)
www.arcjournals.org

An Evaluation of the Impact of Epoxidized Neem Seed Oil *(Azadirachtaindica)* Modification on the Adhesive Properties of Soybean Glue

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Abstract: *Neem seed (Azadirachtaindica) oil was extracted from its oil seeds by cold maceration using petroleum ether (60-80%) as solvent. The oil obtained was characterized and the acid value, saponification value, iodine, refractive index, peroxide value and viscosity were found to be 17.40(mg/KOH), 213.18 (mg/KOH), 75.26 (Wij's), 1.462, 7.82 (mg/kg) and 88.43(cP) respectively. The oil was epoxidized at 40^{0}C using formic acid generated in situ. The epoxidized oil was characterized and the acid value, saponification value, iodine value and refractive index were found to be 29.6 (mg/KOH), 112.7 (mg/KOH), 7.1Wij's and 1.368 respectively. The epoxidized oil was used to cross-link prepared soybean adhesive. FTIR and Water Resistance analysis of the modified and unmodified soybean adhesive indicates that the modified soybean adhesive shows better performance in terms of bond strength and water resistance.*

Keywords: *Neem seed (Azadirachtaindica), Epoxidized oil and modified adhesive.*

1. Introduction

Soy-protein based adhesives were widely used in the production of plywood between 1930s and 1960s, because of their ease of use and low cost [1]. Soy-protein also present some disadvantages, however, such as low bond strength, low water resistance and high viscosity. After 1960, the low price of petrochemicals caused synthetic resin adhesives (formaldehyde-based adhesives) to take over the market because of their good water resistance and easy adaptability to a variety of their curing conditions [2].

Commercial adhesives for bonding wood are predominately urea-formaldehyde and phenol-formaldehyde resins which are derived from petroleum-based resources [3]. Wood products bonded with these resins based adhesives may release hazardous formaldehyde, which has been classified as a carcinogen by the World Health Organization [4]; therefore, recent researches are focused on the development of environmentally friendly wood adhesives from renewable bio-resources, such as soybean protein-based adhesive [5], and other renewable bio-resources. This research therefore seeks to develop a water resistant and environmentally safe soy-protein based adhesive using structure modification.

2. Experimental

Neem seed (Azadirachtaindica) were collected from Makurdi Local Government Area of Benue State. The seed were sun dried and then oven dried at 45^{o}C to constant weight and ground with porcelain mortar and piston to coarse particle size and stored in plastic containers for analysis.

The oil was extracted using petroleum ether (40-60^{o}C) on a soxhlet extractor for four hours [6]. The refractive index, acid value, saponification value, iodine value and the viscosity were determined using the method described by A.O.A.C. [7].

The epoxidation of Neem seed oil was carried out with the use of peracetic and performic acid, generated directly in the environment of the reaction as a result of the reaction of 30 wt % solution of hydrogen peroxide and acetic or performic acid respectively,[8].

Soybean glue was prepared by dispersing defatted, dried and pulverized soybean seed at room temperature in 10% NaOH solution with constant stirring.[9]

A portion of the soybean glue was modified by mixing 20% epoxidized Neem seed oil based on the weight of the glue, at 20^{o}C for 30 minutes to give the modified soybean glue.

The water resistance of the modified and unmodified adhesive was carried out using a three cycle soak test using interior plywood in accordance with the American National Standard for Hardwood and Decorative plywood [10].

FTIR spectra of the modified and unmodified soybean glue were recorded to indicative the effect of modification on the glue properties.

The viscosity of oil, the modified and unmodified adhesives were measured using a Brookfield viscometer with a spinning rate of 1 rpm and determined by averaging 5 measurements in 2 minutes at 20^{o}C.

The solid content of the adhesive was measured based on the oven dry method. About 5g (weight α) was placed into an oven at a temperature of 100 ± 2^{o}C until a constant weight (weight β) was obtained. The solid content was calculated using the following equation. An average of three replicates was used.

Solid content (%) = β (g) / α (g) × 100.

3. Results and Discussion

The physicochemical properties of Neem seed oil are shown in Table 1.0. From Table 1.0, the oil yield was found to be 59.42%. The yield shows it potential in the manufacture of oleochemicals. The iodine value of 75.26 indicated that the oil is non-drying oil, consisting predominantly of polysaturated fatty acids, with a potential is production of soap.[11]

The saponification value of the oil was found to be 213.18. Saponification value indicates the average molecular weight of the oil,[12]. A high saponification value indicates that the oil contained higher proportions of low molecular weight fatty acids.

Acid value was found to be 17.40. Acid value of oil measures the extent to which the glycerides had been decomposed by lipase action. The decomposition is usually accelerated by heat and light. The acids that are usually formed include free fatty acids, acid phosphate and amino acids. Free fatty acids are formed at a faster rate than the other acids,[13].

The peroxide value is the measure of oxidative rancidity of oil [14]. Oxidative rancidity is the addition of oxygen across the double bonds in unsaturated fatty acids in the presence of enzyme or certain chemical compounds. The odour and flavour associated with rancidity are due to liberation of short chain carboxylic acids. High peroxide values are associated with high rate of rancidity. Variation of peroxide value could be due to the number of unsaturated fatty acid content, since the rate of oxidation of fats and oils increases with increasing level of unsaturation. The low peroxide value of 7.82 indicates that it is less liable to oxidative rancidity at room temperature.

Table1.0. *Physicichemical Properties of Neem seed (Azadirachtaindica)*

Property	Value
Oil yield	59.42% ± 0.05
Iodine value	75.26 ± 0.013
Saponification (mg/KOH)	213.18 ± 0.46
Acid value (mg/KOH	17.40 ± 0.38
Peroxide value (mg/Kg)	7.82 ± 0.005
Viscosity (cP)	88.43 ± 0.06
Refractive index	1.462 ± 0.003

The viscosity of the oil was found to be 88.43 and the refractive of 1.462 all conforms to the values given by literature for other vegetable oils. This is an indication that the oil extracted was of high degree of purity.

The results for the epoxidation of *Neem (Azadirachtaindica)* seed oil are presented in Table 2.0. The refractive index of 1.368 of the epoxidized is lower than that of the extracted oil of 1.464, due to decrease in the degree of unsaturation occasioned by epoxidation, since refractive indices increase with degree of unsaturation. The acid value of epoxidized oil of 29.60 is higher than that of the extracted oil of 17.40. This could be due to structural residue formed during epoxidation, since acid value is found to increase with free fatty acid and structural residue.

The saponification value of the epoxidized oil of 112.70 is lower than that of the extracted oil of 213.18, due to increase in the molecular weight of epoxidized oil, since molecular weight decreases with increasing saponification value. The iodine value of 7.1 of the epoxidized oil is lower than that of the extracted oil of 92.46. This could be due to decrease in the degree of unsaturation, cause by epoxidation.

Table2.0. *Physicochemical Properties of Epoxidized Neem Seed Oil*

Property	**Value**
Refractive index	1.368 ± 0.13
Acid value (mg/KOH)	29.60 ± 0.005
Saponification (mg/KOH)	112.70 ± 0.55
Iodine value	7.10 ± 0.15

The results of the water resistance of plywood bonded by modified and unmodified adhesive formulations, the solid contents and the viscosities of both the modified and unmodified adhesives are shown in Table 3.0. All the specimens bonded with unmodified soybean adhesive delaminated after the third cycle, which could be attributed to low water resistance. Epoxidized oil denatured protein by cross-linking the free NH_2 and COOH of the protein, causing unfolding. This improves the hydrophobicity of the adhesive, thus improving the water resistance [15].

Table3.0. *Water Resistance of Plywood Specimens and Viscosities of modified and unmodified soybean Adhesives*

Adhesive	**1st Cycle**	**2nd Cycle**	**3rd Cycle**	**pass/ Fail**
Unmodified Soybean Glue	7/10	9/10	10/10	fail
Modified soybean Glue	0/10	2/10	3/10	pass
Viscosity of soybean Adhesive (cP)				**Value**
Unmodified				37,000 ± 0.33
Modified				68,000 ± 0.25
Solid content of soybean Adhesive (%)				**Value**
Unmodified				24.7
Modified				30.9

The operating viscosity limits of soy-protein based adhesives are very wide, ranging from 500 to 75,000 cP, depending on the application and the nature of the material to be glued [15]. A high viscosity usually after denaturing the protein is detrimental to the application and distribution of the adhesive. The higher viscosity in the modified adhesive can be reduced upon the incorporation of a disperser.

The modification of the soybean adhesive with epoxidized Neem seed oil increased the solid content of the adhesive from 24.7 to 30.9%. The elevated solid content could promote interlocking between wood and adhesive and reduce evaporation of water to enhance adhesion.

The FTIR spectra of the unmodified and modified soybean glue are shown in Fig 1 and Fig 2 respectively.

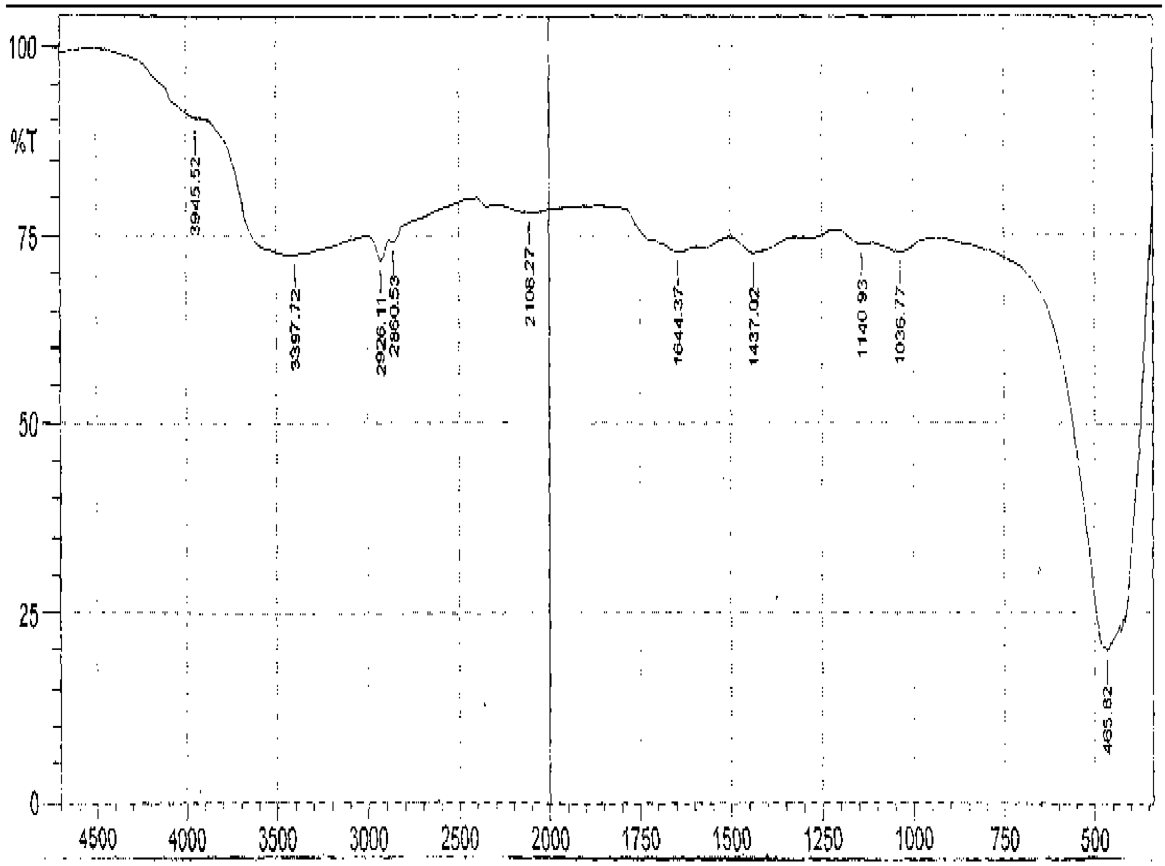

Fig1. *FTIR of Unmodified Soybean Adhesive*

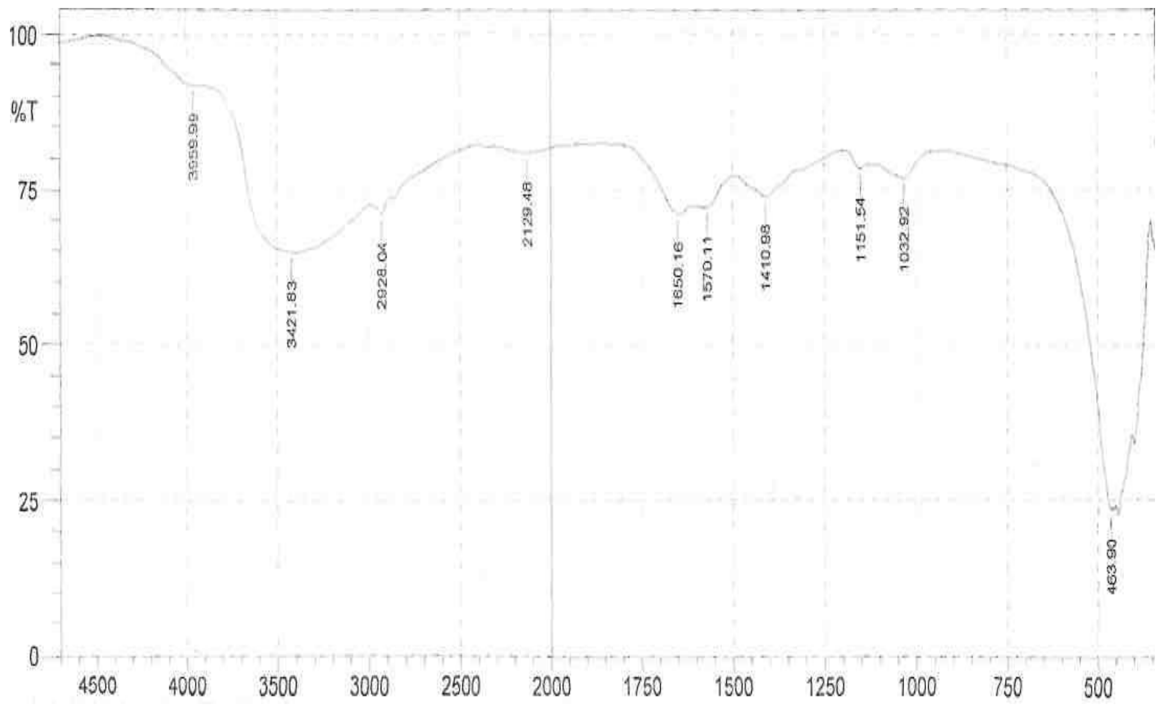

Fig2. *FTIR Spectrum of Modified Soybean Adhesive*

The most significant group frequencies of absorption in Fig 1 are the peaks between 3400-3380 cm^{-1} corresponding to aliphatic primary amine NH stretch, between 1190-1130 cm-1 corresponding to secondary amine CN stretch and that at 1437.05 cm^{-1} corresponding to carboxylate (carboxylic acid salt), which occur between 14200-1300 cm^{-1} in the infrared spectra. These peaks suggest the amino nature of the soy bean adhesive.

The FTIR spectrum of modified soybean adhesive shows similar peaks as that of the unmodified adhesive. The only significant difference is the peak at 2129.48 cm^{-1} corresponding to the oxirane ring absorption that is absent in the unmodified adhesive.

4. Conclusion

The physicochemical characteristics of Neem seed oil established that it has potential in the manufacture of oleochemicals. Modification of soybean adhesive with an epoxy moiety enhances the wet performance of the glue and hence the water resistance and the bond strength of the adhesive.

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