

FINAL REPORT

PROJECT TITLE: “Jathropha Oil Based Binders for Surface Coating Applications”.

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Final Report of the work done:

1. Introduction:

In the present work, jathropha oil was first converted into N, N-bis-(2-hydroxyethyl) Jathropha fatty amide (HEJFA) by condensation of jathropha oil with diethanolamine using zinc oxide as a catalyst. Different amounts of HEJFA was reacted with phthalic anhydride to obtain two different types of jathropha polyesteramides (JPEAs).

The prepared PEAs were than reacted with varying ratio of styrene and vinyl acetate. The resins were tested for different chemical, Mechanical and anticorrosive properties.

2. EXPERIMENTAL

2.1 Materials:

Jathropha seed oil, Diethanol amine, ether, phthalic anhydride toluene, styrene, Vinyl acetate, and all other chemicals used for the study were of laboratory grade.

2.2.1 Preparation of N, N –bis (2-hydroxyethyl) jathropha fatty amide.[HEJFA]:

HEJFA was synthesized as per the reported method. Jathropha oil (1.0 mole) was heated with diethanolamine (3.0 moles) under constant stirring at 200 °C for 15 minutes, using zinc oxide (0.02 moles) as a catalyst. The Reaction was carried out under the blanket of nitrogen. The progress of the reaction was monitored with the help of thin-layer chromatography (TLC) until the disappearance of jathropha oil spot was observed.

The HEJFA was purified from glycerol, excess diethanolamine and other water soluble impurities by washing the solution in diethyl ether with 15 percent aqueous sodium chloride solution followed by distilled water.

2.2.2 Preparation of Jathropha Oil Polyesteramides [JPEAs]from HEJFA:

Two polyesteramides were prepared by reacting HEJFA (1.25 mole, 1.40 mole) with phthalic anhydride (1.0 mole) as per the reported method. In actual experiments, the reactants were heated slowly with constant stirring under the blanket of nitrogen at the temperature of $175 \pm 5^{\circ}$ C for 3.5 hrs. Water of the

reaction was continuously removed by azeotropic distillation using xylene as a solvent in a Dean- Stark moisture trap. The samples of the reaction products were periodically checked for acid value to study the progress of the reaction. The condensation was carried out until low acid values were obtained.

2.2.3 Styrenation and Vinylation of Polyesteramide Resins)

Poststyrenation of the polyesteramide resins was carried out using benzoyl peroxide as a catalyst. The following general method was used for the purpose of polyesteramides in different PEA/ Styrene+ Vinyl acetate ratios.

Polyesteyramide resin (60% in xylene, 133 parts) was charged into a multi-necked flask, fitted with an efficient condenser, a mechanical stirrer, a thermometer and a means for purging dry nitrogen gas. The reaction mixture was heated and brought to reflux at 140⁰ C. Styrene and Vinyl acetate were added to the reaction flask from a separating funnel slowly over a period of 4 hrs. Benzoyl peroxide (2.5% by wt of polyesteramide) was previously dissolved in styrene. After the addition was complete, the reaction mass was stirred for further 4 hrs at 140 ± 5⁰ C. Samples were withdrawn periodically from the reaction flask and checked for viscosity and clarity. Reaction was stopped when no significant increase in viscosity was observed between two consecutive samples. The prepared resin was then thinned with xylene to 60% nonvolatile content.

3.0 Results and discussion

3.1 Spectral characteristic of Jathropa fattyamide (HEJFA) :

HEJFA was conformed by the following absorption bands . A broad band at 3350-3400cm⁻¹ may be due to free –OH group .A strong absorption in the region of 2850-2900 cm⁻¹ is due to C-H stretching .The presence of a strong band at 1739.15 cm⁻¹ is due to the amide carbonyl. Strong absorption bands at 163.94cm⁻¹ and 1463 cm⁻¹ can be attributed respectively to a 3⁰ amide and C-H bending. A very strong absorption band at 1095 cm⁻¹ is thought to be arising out of C-O stretching and C-O bending of primary alcohol .A strong absorption band at 722 cm⁻¹ and a weak absorption band at 938 cm⁻¹ can be attributed to C-H bending arising from polymethylene groups respectively which are present in the fatty acid moiety of the amide.

3.1.2 Spectral Characteristics of Polyesteramide of Jatropha:

The IR spectrum of polyesteramide of jatropha [JPEA] has strong absorption band at 3400 cm^{-1} suggests the presence of residual hydroxyl group in the resin. A strong band at 2854 cm^{-1} is due to the C-H stretching of the methylene group present in the fatty acid. A strong absorption band at 1738 cm^{-1} is due to the ester carbonyls present in the polymeric chain. A weak band at 1651 cm^{-1} is attributed to the C-H stretching and to amide carbonyl group respectively. The strong band at 780 cm^{-1} and weak band at 790 cm^{-1} and 1070 cm^{-1} each can be attributed to the aromatic moiety present in the structure.

3.2 Characteristics of Styrenated Polyesteramides

The various properties of polyesteramides and styrenated vinylated polyesteramide resins derived from Jatropha are compared. A comparison of the results indicate that under the conditions of the experiment, Jatropha based polyesteramides undergo significant degree of copolymerization as evidenced from increase in viscosity and good clarity of the product. It has been found that with decrease in PEA/ Styrene Vinyl ratio, viscosities of resins increases. This follows that by decreasing PEA/Styrene Vinyl ratio, degree of styrenation increases. However, by the comparison of the trend of viscosity it is found that at equal amount of Styrene and Vinyl acetate ratio, the viscosity of the resin higher. This might be attributed to the higher degree of polymerization by virtue of the presence of higher unsaturation, which is known to facilitate.

From the results it is found that as the PEA/Styrene Vinyl ratio is decreased, the trend for color and percent nitrogen content is similar for all the families of resins. It, therefore, follows that these two characteristics are functions of degree of styrenation. The decrease in color with decrease in PEA/styrene vinyl ratio can be accounted for the fact that out of the two components in styrenation, the PEA is responsible for darker color and therefore with decrease in PEA/ Styrene vinyl ratio, color decreases.

3.3 Film Properties

The film properties of air-dried and baked films of various resins are discussed in the following paragraphs.

From the results it is apparent that styrenation and vinylation of polyesteramide results into significant reduction in air drying time of the films, particularly the surface-drying (dry-to-touch) time, in all the families of the resins. Further all the resins showed decrease in drying time with decrease in PEA/Styrene Vinylation ratio. This can be attributed to the thermoplastic nature of polystyrene moiety in the resin structure. A comparison of drying time among the resins reveals that the resin with styrene to vinyl ratio 2:1 resin dry in shorter time than their counterparts.

All the samples, both air dried and baked, passed the flexibility test on ¼” conical mandrel. All these samples also passed stripping test for adhesion. These results indicate that even upon styrenation up to about 33% by wt. of PEA, no substantial compromise in the two properties has been observed.

Considerable variations in scratch hardness and impact resistance have been observed in all the families of the resins with decrease in PEA / Styrene Vinyl ratio. In general, styrenated and vinylated polyestramide showed improved resistance to impact and greater scratch hardness when compared with the unstyrenated counterparts. Further, between the air dried and baked films, the later showed improved properties as compared to their air dried counterparts. The scratch hardness of the air dried and baked films of all the families of the resins showed an improvement with decrease in PEA/Styrene ratio. This may be due to the higher percentage of polystyrene moiety in the resins structure, which is responsible for film hardness.

In all the families of the resins, the impact resistance of air dried films are comparable and no much variation in this property is observed with decreasing PEA/Styrene ratio. However, decrease in impact resistance was observed when PEA/Styrene Vinyl ratio was 2:1 in baked films. This may be due to film embrittlement caused by the presence of higher amount of polystyrene residue.

In baked films, however impact resistance increased with decrease in PEA/ Styrene ratio to 3:1. Thereafter, further decrease in the ratio to 2:1 had resulted into decrease in impact resistance. It therefore, follows that for a given polyesteramide, there is an optimum degree of styrenation and vinylation upto which impact resistance of the films could be increased by decreasing PEA/Styrene ratio. Reduction of this ratio below this optimum level significantly detracts the film from impact resistance properties. The comparison of scratch hardness and impact resistance of styrenated polyesteramide and polyesteramide indicates that the film properties of styrenated and vinylated polyesteramide were better. The resulting high value of scratch hardness and impact resistance may be due to the presence of polystyrene moiety which is responsible for film hardness i.e. higher value of scratch hardness and impact resistance.

AIR DRIED FILM PROPERTIES OF VARIOUS POLYESTERAMIDE :

The result indicates that styrenation and vinylation of polyesteramides considerably improves water, acid and alkali resistance properties in both the air dried and baked films. In general, acid, alkali and water resistance properties have been found to improve with decrease in the PEA/Styrene ratio among both the family of the resins. Alkali resistance of baked films is superior to their air drying counterparts. There is slight improvement in acid and water resistance of baked films as compared to their air drying counterparts. These observations can be explained by the fact that with increase in styrene content, there is corresponding decrease in hydrolysable ester linkages in the matrix of the film, rendering it improved alkali, acid and water resistant. Styrenation and vinylation is also thought to impart more non polar character to polyesteamides, making them more hydrophobic and consequently improve water resistance of the films. This can also explain the increased water resistance with decrease in PEA/ Styrene ratio. Moreover, the amount of oxygen taken by styrenated polyesteramides for autoxidation is considerably less than the unstyrenated counterparts .The reduced oxygen uptake may be advantageous in minimizing the number of groups sensitive to chemical attack.

The reduced value of xylene resistance of styrenated polyesteramides compared to that of the polyesteramides may be due to the reduction in the number of crosslinkings and complexity of film as crosslinking involves at unsaturated sites.

4.0 Conclusion

Styrenation a useful modification of PEAs has been discussed .All the PEAs from have been styrenated and vinylated by poststyrenation method.

From the results of the study of styrenation and vinylation of polyesteramide resins, it can be concluded that polyesteramides can be styrenatedand vinylated by post styrenation technique, using benzoyl peroxide as a catalyst under given experimental conditions. The study of the film properties of these resins reveals that the films of styrenated vinylated polyesteramides can be cured satisfactorily by air drying and by baking methods.

In general, most of the mechanical and chemical properties of the films cured by baking method are superior to their air drying counterparts. In all the families of the resins and for a given method of curing, chemical, water resistance and scratch hardness of the film improve with increase in degree of styrenation and vinylation , while the trend for xylene resistance is exactly opposite. Impact resistance of a given styrenated vinylated polyesteramide is maximum at certain optimum level of styrenation and vinylation.

5. Acnowledgement:

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