

# Development of eco-friendly polyurethane coatings based on neem oil polyetheramide



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## ABSTRACT

Renewable sources like vegetable oils have been used to prepare many polymeric resins and the topic is gaining more importance due to the functional attributes to structure of oils. In the regard, renewable source based polyurethane coatings have been prepared from polyetheramide of neem oil in the laboratory. In the preparation of polyetheramide, first neem oil was allowed to react with diethanol amine. Obtained fatty amide was modified to the polyetheramide by reacting it with bisphenol-A. Spectroscopic techniques such as FT-IR and <sup>1</sup>H NMR confirmed the structures of fatty amide and polyetheramide. Polyurethane coatings were prepared from the polyetheramide by treating it with methylene diphenyl diisocyanate.

Coating properties such as gloss, scratch hardness, adhesion, flexibility, thermal stability, impact and chemical resistances were evaluated using standard methods. The influence of surface modified TiO<sub>2</sub> nano particles on the properties of the neem oil based polyurethane coatings was examined by loading nano TiO<sub>2</sub> from 0 to 4%. The overall performance of coatings revealed that neem oil based polymeric coatings can be successfully used as coatings in industrial applications.

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## 1. Introduction

The demand for polymers prepared from renewable sources is on the increase because of a number of reasons notably environmental concern, abundant availability and low price of renewable sources (Anand et al., 2012; Guner et al., 2006; Lligadas et al., 2012). Cellulose and vegetable oils are two major renewable sources present on the earth in large quantities. Applications of cellulose in polymeric coatings is limited while vegetable oils have been used most of the time to prepare polymeric binders for coatings formulations, flooring materials and resin applications (Gu et al., 2012; Opera, 2010). Vegetable oils obtained from different sources have also been widely used in preparation of inks, diluents, plasticizers, lubricants, agrochemicals, food industries, composite materials, etc. (Derksen et al., 1996; Kashif et al., 2011; Khot et al., 2001; Sharmin et al., 2006). Vegetable oils can be commonly converted

into derivatives such as alkyd resins and polyols based on alkyds (Nimbalkar and Athawale, 2010). Polyols are low molecular weight polymers that may be reacted with different diisocyanates such as isophorone diisocyanate (IPDI), methylene diphenyl diisocyanate (MDI) or others, to obtain polyurethane (PU) coatings (Gite et al., 2010). A number of reports have described the preparation of polyols from different vegetable oils such as jatropha, soya, cottonseed, linseed, neem oils and their subsequent use in the preparation of PU (Chaudhari et al., 2013a,b; Gite et al., 2006; Jaliliana et al., 2010; Meshram et al., 2013a,b; Zlantic et al., 2004). PU of the kind of interpenetrating polymer networks have also been prepared using castor oil with styrenic-acrylic polymers and these have gained much attention due to their interesting properties (Meier et al., 2007). Epoxidized soybean oil has been studied by curing with various cyclic acid anhydrides in presence of tertiary amines (Gerbase et al., 2002). Recent routes explored utilization of vegetable oils in coatings by preparing polyetheramides (PEthA) (Akintayo and Akintayo, 2010; Alam et al., 2004) and polyesteramides (PEA) (Dutta and Karak, 2005; Shende et al., 2004; Zafar et al., 2004).

*Azadirachta indica juss* can be said to be underutilized when its available production potential is compared to its present limited applications in pharmaceuticals (Biswas et al., 2002) and agrochemicals sector as medicinal compound and bio pesticide (Bagle et al., 2013) respectively. Neem seed oil contains three

Abbreviations: IPDI, Isophorone diisocyanate; MDI, Methylene diphenyl diisocyanate; PEthA, Polyetheramide; PEA, Polyesteramide; TTIP, Titanium isopropoxide; THF, Tetrahydrofuran; TEVS, Vinyltriethoxysilane; DBTDL, Dibutyltin dilaurate; MS, Mild steel; AIJFA, *Azadirachta indica juss* fattyamide; PU, Polyurethane.

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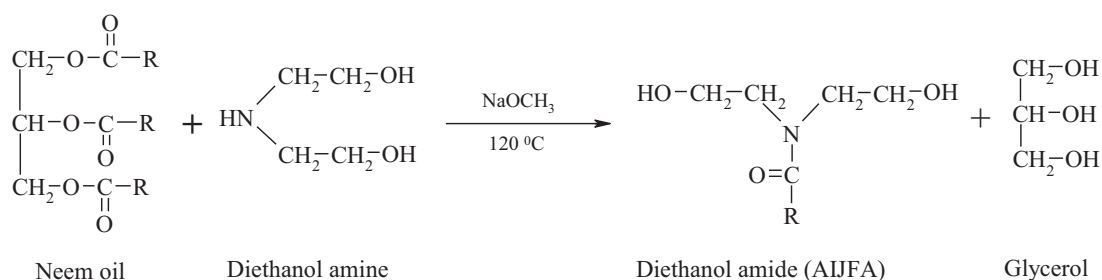


Fig. 1. Synthesis of AIJFA.

saturated fatty acids including palmitic (11.90%), stearic (29.96%) and arachidic (2.94%) acids. It also contains two unsaturated fatty acids viz. oleic (50.04%) and linoleic (5.15%) acids (Chaudhari et al., 2013a). Although neem plant is widely cultivated in arid zones of India with annual neem oil production rate of 18,000 ton, the utilization of the seed oil in the development of polymeric resins has not been investigated except our earlier report (Chaudhari et al., 2013a). Our previous report claims preparation of PU coatings from neem oil fatty amide using diisocyanate.

In the present work, further chemical modification of fatty amide (AIJFA) prepared from neem oil has been carried to obtain polyetheramide (PEthA). The synthesized PEthA was treated with diisocyanate at room temperature to prepare the PU coatings. Effects of percent loading of silane modified nano TiO<sub>2</sub> on the performance of pristine neem oil PEthA based PU coatings have been investigated first time. Performance of PU coatings was evaluated using standard methods.

## 2. Experimental

### 2.1. Chemicals and materials

Neem seed oil was purchased from local supplier and used as it is. MDI, bisphenol-A, titanium isopropoxide (TTIP), vinyltriethoxysilane (TEVS) and dibutyltin dilaurate (DBTDL) (Aldrich Chemicals, UK) were of laboratory grade. Cyclohexanone, tetrahydrofuran and diethanolamine of analytical grade were obtained from s.d. fine-chemicals Ltd., India.

### 2.2. Synthesis of *A. indica* juss fatty amide (AIJFA)

AIJFA was synthesized (Fig. 1) according to our earlier report (Chaudhari et al., 2013a).

### 2.3. Synthesis of polyetheramide (PEthA)

Mixture of AIJFA (20 g, 0.10 M) and bisphenol-A (16.65 g, 0.073 M) were reacted (Fig. 2) in round bottom flask equipped with Dean and Stark trap, nitrogen inlet tube, thermometer and rotational. The mixture was allowed to react by dissolving it in a mixture of solvents (80:20 parts of xylene and n-butanone) in presence of dilute sulfuric acid as a catalyst. The reaction mixture was heated at 175 ± 5 °C and refluxed until the theoretical amount of water was collected in Dean and Stark trap. Once the theoretical amount of water removed, reaction was allowed to stop. After the completion of reaction, solvent was evaporated in a rotary vacuum evaporator under reduced pressure to obtain PEthA.

### 2.4. Synthesis of nano TiO<sub>2</sub> and their modification by silane coupling agent

Nano TiO<sub>2</sub> was synthesized (Mahshid et al., 2006) and modified by using vinyltriethoxysilane (TEVS) coupling agent as reported in the literature (Chaudhari et al., 2013b; Sabzi et al., 2009).

### 2.5. Preparation of PU coatings based on PEthA

PU coatings were obtained (Fig. 3) by reacting PEthA at room temperature with MDI using NCO/OH ratio 1.1:1 in the presence of a catalyst DBTDL (0.5%). In a typical process 50% solid content solution of PEthA was prepared in cyclohexanone and THF (80:20) mixture. PU were coded as PU0, PU1, PU2, PU3 and PU4 where suffix 0–4 indicated the percentage of modified nano TiO<sub>2</sub> ranging from 0 to 4% (based on amount of PEthA) in PU coatings.

After addition of nano TiO<sub>2</sub>, reaction mixtures were sonicated on a sonicator for the proper dispersion of modified nano TiO<sub>2</sub> and then mixture was treated with MDI. The entire reaction mixture was stirred for next 5 min at room temperature to attain pourable viscosity. This mixture was applied as a coating by using bar applicator on MS steel panels of 4 × 6 in. dimensions. The prepared coating panels were allowed curing at room temperature under visual examination. Prior to application of the coatings, the steel panels were pretreated by sand paper and washed with acetone.

## 3. Characterization

### 3.1. Chemical analysis

Neem oil, AIJFA and PEthA were characterized for specific gravity (ASTM D5355 - 95), refractive index (ASTM D1747 - 09), saponification (ASTM D464 - 05), acid (ASTM D5768 - 02), hydroxyl (ASTM D1957-86) and iodine values (ASTM D5768-02).

### 3.2. Spectroscopic analysis

The FT-IR spectra of the prepared resins were recorded on FTIR spectrophotometer (Shimadzu, Japan, Model No. 8400) from the range of 4000–500 cm<sup>-1</sup> as KBr pellets. Homogenous mixture of sample in KBr was prepared by grinding in mortar and by the action of 12 ton lab press to diminish moisture present in the sample. <sup>1</sup>H NMR spectra of samples were recorded on Varian Mercury 300 MHz spectrometer using TMS as an internal standard in presence of CDCl<sub>3</sub> as a solvent.

### 3.3. Transmission electron microscopy (TEM)

The synthesized nano titanium dioxide particles were studied for their size by using TEM (TEM, Philips, CM-200, Holland). The analysis was carried out by accelerating voltage in the range of

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