

## ABSTRACT

Recently the significant emphasis on environmental issues, limitation of non-renewable resources, climate change, green house gas emissions and concern about waste disposal have led to substitute the petroleum based materials with their bio-based counter parts on the basis of cost performance. Bio-based polymers derived from renewable resources have become increasingly important as sustainable and eco-efficient products which can replace the products from the petrochemical-derived stocks. Among the different types of petroleum based polymers, epoxy resins are converted to thermoset polymers that are well known due to their greater properties such as high mechanical strength, adhesive strength, stiffness, electrical, heat and chemical resistance. One of the main drawbacks of epoxy resin is its brittleness. This brittleness of epoxy resin has been overcome by the addition of some functional vegetable oils such as epoxidized vegetable oils which improved the toughness of epoxy resin.

In the recent years, wide range of innovative monomers and prepolymers starting from cardanol, vegetable oils and low cost industrial grade oil obtained by vacuum distillation of Cashew Nut Shell Liquid (CNSL), were developed. CNSL is a by product of the cashew industry. The nut has a shell of about 3.2 mm thickness inside which is a soft honeycomb structure containing a dark reddish brown viscous liquid. In the search for the cost effective modern materials, CNSL and its products have a significant role to play. Being renewable, it offers many advantages over synthetics. Recent research has shown that the constituents of CNSL possess special structural features for transformation into specialty chemicals and high value

polymers. Thus, CNSL offers wide scope and opportunities for the production of specialty chemicals, high value products and polymers.

The main component of technical grade Cashew Nut Shell Liquid (CNSL) is cardanol. The purity of the cardanol was analyzed by thin layer chromatography and high performance liquid chromatography technique. Cardanol differs from phenol only in the alkyl side chain present in the meta position. It undergoes the well known formaldehyde condensation reaction of phenols that gives rise to phenolic resins. Moreover, it can be polymerized through the unsaturation in the side chain although the bulky nature of the side chain restricts the molecular weight attainable to oligomers. The significant advantage of the cardanol is its amenability to chemical modification to effect suitable structural changes so as to get specific properties for making tailor made polymers of high value. Thus, structural changes could be effected at the hydroxyl group, on the aromatic ring and on the side chain.

The main objectives of the present investigation deals with the development of bio-based epoxy resins from cardanol and study their application in composite fields for partial replacement of conventional diglycidyl ether of bisphenol-A (DGEBA). The prepared bio-based epoxy resins were modified with the commercial DGEBA epoxy at various weight ratios and were cured with amine hardener. These bio-based composites were reinforced with glass fiber and nanoclay fillers. The thermal, mechanical, morphological, water absorption and flammability properties of the prepared composites were evaluated.

Two types of bio-based epoxy resins, ECF and EC, were prepared by the step-growth polymerization. Novolac resins were prepared with excess of cardanol and formaldehyde under acidic conditions. The

formylation reaction between cardanol and formaldehyde occurs by electrophilic aromatic substitution.

Epoxidized cardanol formaldehyde novolac resin was synthesized from the reaction of novolac oligomers with excess of epichlorohydrin (ECH). The epoxide group of ECH react with hydroxyl groups that are present in the cardanol moiety under an alkaline catalytic influence to form chlorohydrin. This would undergo dehydrochlorination reaction involving stoichiometric amounts of alkali, resulting in the formation of glycidyl ether together with sodium chloride and water. Epoxidised cardanol (EC) was also synthesized from cardanol in the same manner. All the resins were synthesized with more than 85% yield and the molecular structure was confirmed by UV-Visible, FTIR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopic analyses. The above synthesized resins were modified with conventional DGEBA with various weight ratios.

The synthesized and modified products have been analysed for physico-chemical properties. The specific gravity of the resin increased as the formaldehyde content increased in C: F (Cardanol:Formaldehyde) molar ratio. The increases in the methylene groups with increase in the amount of formaldehyde causes the cross-linking reaction to take place at faster rate. These results in the increase in the average molecular weight of the resins with C: F molar ratio and enhancement of specific gravity.

Brookfield viscosity was obtained for all resins. In the resins, a Newtonian behavior was observed in the range of 100rpm shear measurements. The gel time of the CFR resins decreased with increase in C: F molar ratio. This is due to the progressive increase in the methylene groups as the amount of formaldehyde increases. The increase in the number of methylene groups speeded up the cross-linking reaction and resulted in an

early attainment of gel time. Epoxy equivalent weight (EEW) of all the bio-based epoxy resins was determined by pyridinium hydrochloride method. The EEW of the epoxy resin increased as the ECH content increased. The molecular weight of synthesized bio-based resins was determined by GPC analysis.

The amount of bio-based epoxy resin (ECF, EC) that replaced the primary resin component (DGEBA) was varied from 0-40 wt% in increments of 20wt%. A total of five neat resin (without clay) systems were obtained. Each of these resin systems were reinforced with nanoclay inclusions at a loading of 1, 3 and 5wt%. Similarly, a measured amount (1, 3 and 5wt %) of 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was mixed with modified bio-based epoxy resins.

The thermal stability and thermal degradation kinetics of the synthesized epoxy resins were determined by TGA, heated from 30 to 700°C with heating rate of 10°C/min under nitrogen atmosphere. Most of the fabricated specimens were stable up to 350°C. The glass transition temperature and curing kinetics data were obtained from DSC, heated from 30 to 300°C with different heating rates (5, 10, 15, 20°C/min) under nitrogen atmosphere.

The mechanical properties (Tensile, Flexural and Impact) of the fabricated composites and thermosets were studied on universal testing machine. It was noticed that the incorporation of 40% bio-based epoxy resin showed the maximum mechanical strength. Mechanical properties of the ECF based composites are higher than EC based composites.

Fractured surfaces of composites systems were observed on Scanning electron microscope. Dispersion of the clay particles into bio-based

modified resins was viewed by transmission electron microscopy and X-ray diffraction.

Flammability property of composite was studied with the help of LOI analyzer and UL-94 vertical burning test. The presence of aromatic ring in the bio-resin content imparts higher thermal stability and the presence of phosphorous acts as flame retardant group diluting the concentration of flammable gas produced during the combustion process and decreased the heat release from the samples.

Water absorption property of the fabricated composite was studied and compared. As the weight percentage of bio - resin content increased water absorption percentage also increased in the composites.

The results of this investigation indicated that the bio - based epoxy resins from cardanol can be used for composite applications. Among the modified epoxy resins, 40wt % modified resin has superior property than the other modified resins.