

ABSTRACT

The current global economy is focused on the petrochemical industry, which has created a network of fossil energy and materials reliance. The search for low-cost, environment friendly, and innovative biodegradable materials has paved the way for the use of natural resources like biomass, which provides both energy and a broad range of new material opportunities. Bio-derived polymers have recently become more popular as a replacement for non-recyclable thermosetting polymers. Replacing toxic and expensive petroleum-based products with materials that have superior thermal and mechanical properties is the most difficult aspect of developing renewable resins and polymeric materials. The thermosetting epoxy resins are widely used among polymeric materials, and their production is dependent on the petroleum industries. Diglycidyl ether of Bisphenol-A (DGEBA), a commercially available epoxy resin, has superior mechanical, thermal, and chemical resistance. They are more flammable due to their petroleum origin. The disadvantage of DGEBA resin is its brittleness as well as the health risks posed by the chemical constituent bisphenol-A. As a result, an eco-friendly epoxy resin must be used to replace the hazardous epoxy resin.

Cashew nut shell liquid (CNSL), a renewable byproduct of the cashew nut industry, contains naturally occurring phenols and is a good substitute for petroleum-based phenols. Cardanol, a major constituent of CNSL, is a phenol with a meta substituted unsaturated side chain that can be used to produce polymers and composites. Cardanol's phenolic -OH undergoes a condensation reaction similar to that of phenol, and the side chain promotes the plasticizing effect. The flame retardancy of the resin can be imparted by introducing flame retardant additives, and the mechanical properties can be enhanced by utilizing fibres. Natural fibres are an excellent alternative to synthetic fibres due to their low cost, ease of availability, and biodegradability. However, replacing synthetic fibres and petroleum resins entirely with bio-based ones is not a viable option.

Meanwhile, partially replacing petroleum-based materials and synthetic fibres with bio- The primary goal of the present research is to develop bio-based epoxy composites from cardanol, a renewable source, with progressive thermal stability and flame retardancy properties without sacrificing mechanical strength. The cardanol-based epoxy resins were produced through the alkali-catalyzed direct epoxidation of cardanol (ECR) with epichlorohydrin and novolac resin was created by condensation with formaldehyde and epoxidized with epichlorohydrin (ENR). These two cardanol based epoxy resins were mixed in various proportions with the commercial epoxy resin DGEBA. Blended resins' physic-chemical properties were investigated. The curing behaviour of ECR and ENR blended resins with triethylenetetramine hardener was investigated using DSC and was observed to occur between 50 and 140°C. The thermal and mechanical properties of both the blended resins were perceived to decrease as the bio-resin content increased. Since DGEBA resin is derived from petroleum, the flammability of blended resins was high. Among the blended resins, ECR15 resin with 15% ECR content and ENR25 resin with 25% ENR content were chosen for all study.

In an attempt to improve the flame retardancy and thermal stability of the bio-based resins, flame retardants were incorporated. An agro-waste rice husk (RH), which is also a bio-silica source with 17% of silica was used as filler. The RH was added in various weight percentage (3, 7, 11 wt %) to the bio-based ECR15 and ENR25 resins. The composites formed were characterized using Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). The thermal stability of both bio-based resins increased with the increment of RH. RH composites of ECR15 and ENR25 resin with 11 wt % RH exhibited higher degradation temperature and char yield of about 40.47% and 75.16% in char yield. Thermal degradation kinetics were studied using Broido, Horowitz-Merzger, and Arrhenius models. The flame retardancy of RH composites was investigated using the Limiting Oxygen Index (LOI) and the Underwriters Laboratory -94 (UL-94) test, and it was realised that incorporation of RH had greatly improved the flame retardancy. The silica in RH forms a carbonaceous char

layer over the burning polymer surface, limiting heat and mass transfer and thus increasing the composites' flame retardancy. Scanning Electron Microscopy (SEM) and ATR-FTIR were used to examine the char formed after burning of the specimen. The Elemental Dispersive spectroscopy (EDS) confirmed the presence of silica in the char that accounts for the flame retardancy of the composites. The mechanical properties of ECR & ENR, RH composite decreased slightly with increase in RH, but was higher than DG/RH composites. Water absorption of the RH composites was studied and RH being hydrophilic increased the water absorption of the composites.

Further, phosphorous containing flame retardant additives were added to the bio-based composites and their properties were analysed. Vanillin, a phenolic aldehyde, based phosphonate co-polymer (PCP) was synthesized and characterized using ATR-FTIR and Ultraviolet-Visible (UV) spectroscopy. The TGA and DSC analysis of PCP indicates the decomposition of polymer above 170°C. The PCP and commercially available phosphorous flame retardant, 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DP), were added to epoxy resins in various ratios (1, 3, 5 wt %). The thermosets of bio-based epoxy resins with PCP and DP were analysed for the mechanical, thermal and flame retardancy properties. The PCP added thermosets exhibited higher thermal stability than the DP incorporated thermosets. The ENR25 resin with 5 wt% PCP exhibited higher LOI value of about 37.8%. DP added thermosets exhibited higher tensile strength than the PCP added thermosets.

In addition, fiber reinforced bio-based epoxy composites were developed using kenaf fiber as reinforcement. The untreated kenaf fiber reinforced composites showed low thermal and mechanical properties due to the poor fiber-matrix interaction. To overcome this, kenaf fiber was treated with 6 wt% NaOH. The untreated and treated fibers were examined using ATR-FTIR and DSC. Besides the treated kenaf fiber reinforced composites, hybrid composites were developed by incorporating RH (11 wt %), PCP (5 wt %) and DP (5 wt %). The TGA analysis of hybrid composites revealed

that the composites with treated kenaf/RH/ECR15 (KRC) possess higher thermal degradation temperature and produced higher percentage of char residue. The kenaf/RH composites outperformed the kenaf/PCP and kenaf/DP incorporated epoxy composites in terms of thermal stability, mechanical properties, and flame retardancy. The activation energy of kenaf/RH/ECR15 and kenaf/RH/ENR25 composites was found to be higher than the remaining hybrid composites based on thermal degradation kinetics and validating their thermal stability. The kinetics of water absorption of thermosets and composites were also investigated.

The present investigation found that the synthesized bio-based epoxy resins and their composites outperformed DGEBA composites in terms of thermal, mechanical, and flame retardancy properties, and that they can find application in various industries.

