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Self-Healing and Thermomechanical Properties of Activated Carbon Pyrochar Derived from Municipal Mixed Plastic Waste Pyrolysis with Self-Healing Epoxy Vitrimer Composites

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ABSTRACT

An ecological vitrimer is being developed using activated carbon pyrochar from municipal mixed plastic waste pyrolysis into an epoxy composite. Durable vitrimeric materials may be created by adding pyrochar to polymeric composites. Due to their ductility, reusability, and recyclability, vitrimeric materials have become popular and reliable materials. As a result, the self-healing temperature of composite vitrimers is lower via disulfide exchanges than that of virgin epoxy vitrimers. Additionally, compressive studies have been used to study self-healing capacities, and modulus variations have been used to highlight changes in the healing efficiency of the materials.

INTRODUCTION

Plastics are made from hydrocarbon-based petroleum products. At the same time, they contain several additives that are not necessarily good for the environment, such as antioxidants, colorants, and stabilizers (Brems et al. 2012). Char is a solid substance made up of tiny particles high in carbon and contains some oxygen and hydrogen (Xu et al. 2020). These particles have a large surface area and porosity, are chemically stable, are inexpensive, and may be prepared at temperatures between 500 and 700 degrees Celsius (Ahmed & Hameed 2020). To attain the desired material properties, plastics often incorporate additives such as color pigments, reinforcing fillers, plasticizers, flame retardants, antioxidants, and UV stabilizers (around 5 percent of total weight) (Beach et al. 2013). However, there has been little research on the use of char in composite manufacturing, and none of these composites used epoxy resin (ER) as a matrix. For example, coconut shell char was used in aluminum alloy matrix composites (Murali et al. 1982, Moorthy Rajendran et al. 2020)

White et al. (2001) recently proposed one of the autonomic self-healing systems adapted to fulfill specific objectives in the realm of aeronautic applications (White et al. 2001, Krishnakumar et al. 2020). As a result, the mending mechanisms of animated bodies are imitated. High chain mobility permits multiple possible self-healing methods in soft materials with low glass transition temperatures (lower than the material's service temperature). There are substantial limitations in selecting self-healing methods for load-bearing materials with high stiffness and little chain mobility, resulting in limited chances of success. Hollow fibers and microvascular networks have lately been presented as alternatives to microencapsulated systems.(Patrick et al. 2016, White et al. 2014). Although several chemistries for vitrimer materials have been investigated, the reported materials are fairly limited in scope. Their mechanical properties are frequently not equivalent to commercial resins or conventional engineering polymers (Brutman et al. 2014).

Epoxy resins are used to make epoxy composite materials. Epoxy resins comprise a matrix and particles as a filler material (Kang et al. 2001, Verma et al. 2017, 2018). Talc, calcium carbonate, and synthetic additives like carbon black are used to make these particles (Kang et al. 2001, Verma et al. 2017, 2019, 2018). Because of its copious resources from maize and its high stiffness and thermal stability, isosorbide was chosen as a natural building block for renewable polymers with high glass transition temperatures (Tg). The thermal reprocessing of epoxy vitrimers was helped by the relatively high thermal stability of isosorbide. Meanwhile, the dynamic disulfide bond reaction comprises several mechanisms influenced by reaction conditions. Disulfide connections broke mechanically due to external stressors, releasing thiol radicals that might swiftly exchange with other disulfide bonds, resulting in self-healing or reprocessing of crosslinked networks (Fenouillot et al. 2010, Duan et al. 2015, Martin et al. 2016, Yang et al. 2015, Black et al. 2014).

In developing bio-based vitrimers based on this technique, some bio-based compounds with multiple epoxy groups have been investigated by curing sebacic acid poxy with ozonized Kraft lignin, a bio-based vitrimer with shape memory, mending properties, and potential adhesive usage was produced. A vitrimer with similar strength and modulus to cured bisphenol A epoxy was created by curing another bio-based triepoxy (TEP) with an anhydride monomer (Zhang et al. 2018, Liu et al. 2018). Furthermore, because of the new trend in composite material manufacturing, Out of autoclave, a significant amount of study has been committed to understanding the nature of thermoplastic composite materials (Yassin & Hojjati 2017).

To further understand the impact of the inorganic filler, we used epoxy resins cured at moderate temperatures of less than 120°C in the first study. We used tertiary amines as curing catalysts to do this. Anionic polymerization occurs when Lewis bases, such as tertiary amines, are present. Due to the lengthy cure cycles required and the low heat-distortion point of the resultant resins, anionic initiator polymerization of epoxy resins has not yet received widespread commercial use. However, the most recent discoveries described in this paper provide strong potential for reducing earlier concerns and boosting the adoption of this class of catalytic curing agents in the future. Only a small amount of literature on diepoxide (or polyepoxide) resins using anionic initiators as curing agents. However, in recent years, these curative agents have become more popular among researchers working on aeronautical functional applications worldwide (Brown et al. 2002, 2004, Kessler & White 2002, Kessler et al. White et al. 2001, Krishnakumar et al. 2020). Peng et al. (2016) employed a similar process to create rGO/epoxy polymer nanocomposites with good rGO nanosheet dispersion, which they found to be quite beneficial. The GO was reduced by suspending it in an epoxy resin (triglycidyl paraaminophenol) for 5 min at 200°C, followed by curing the epoxy resin with the addition of 3,5-dimethylthio-2,4-toluenediamine and curing the epoxy resin (Peng et al. 2016).

The exchangeable link concept can also be used to create materials that are hard at room temperature yet flexible but insoluble at higher temperatures. Hydroxy groups and ester linkages are found in used epoxy-anhydride resins (Tesoro 1988). Within that work, we investigate a reliable method for creating self-healing epoxy vitrimer nanocomposites that are encouraged by graphene oxide without needing a catalyst. The capacity of the self-healing nanocomposites is attributed to disulfide exchange-based covalent adaptive network activity, in which aromatic disulfide hardeners stimulate radical-mediated exchanges to affect bond exchange in such vitrimers (Krishnakumar et al. 2020, Luzuriaga et al. 2016a, 2016b)

Altuna et al. (2016) investigated an epoxy vitrimer cured with carboxylic acids and imidazole as a catalyst to improve its performance. After 1 h of heating at 160°C, the BERs of esterification and transesterification were utilized to analyze the properties of the epoxy vitrimer's reconfigurable forms. The samples' shape fixities and shape recovery ratios were 99 percent accurate. During partial stress relaxation, the characteristics of vitrimers can be identified to a limited extent (Altuna et al. 2016).

Zako et al. devised a method for incorporating small thermoplastic adhesive particles into glass/epoxy composite laminates (50m). The epoxy resin matrix was cured at a temperature of 100-110°C. When damaged composites were heated to 120°C for 10 min on a hot plate, the thermoplastic particles implanted in them melted. The percentage of curing was documented in the subsequent three-point bend test based on the measurement of the flexural strength of the repaired specimen, and the load-displacement curve revealed that stiffness was recovered in the repaired specimen (Zako & Takano 2016).

Thermal activation is some of the most prominent approaches for developing self-healing characteristics in biological systems. As a result, raising the heat conductivities of polymers would assist in enhancing the self-healing efficiency and effect of the polymers (Yang et al. 2018, Burger et al. 2016). The self-healing properties of the synthesized nanocomposites are attributed to covalent adaptive network activity based on disulfide exchange, in which aromatic disulfide hardeners strengthen radical-mediated exchanges to conduct the link change in such vitrimers (Krishnakumar et al. 2020, Luzuriaga et al. 2016a, 2016b)

To create a low-temperature self-healing material, activated carbon pyrochar derived from municipal mixed plastic waste pyrolysis was combined with an epoxy vitrimer system to create more environmentally friendly composites. As a result, a composite vitrimer with aromatic disulfide crosslink-assisted self-healing has been developed. Various aromatic disulfide concentrations are also used to improve the chemical and mechanical properties of epoxy vitrimer composites. The thermomechanical and self-healing properties of plastic pyrochar-derived activated carbon epoxy vitrimer composites have yet to be thoroughly explored. The issues highlighted in this paper have been dealt with succinctly.

MATERIALS AND METHODS

Materials

A lab-scale pyrolysis setup was developed @ UPES. Fig. 1 presents an illustration of the manufacturing flow process that converts waste plastic into an alternative fuel with activated carbon char.

Two components of the epoxy resins were acquired from Sigma-Aldrich: 2- Aminophenyl disulfide (AFD) (248.37 $g.mol^{-1}$)/diethylenetriamine (DETA) (103.17 $g.mol^{-1}$) and bisphenol A diglicidyl ether (BADGE) (340.41 $g.mol^{-1}$). This paper describes the preparation of the activated carbon (AC) pyrochar produced from municipal mixed plastic waste pyrolysis (Krishnakumar et al. 2021).

Calculation for Epoxy and Amine Hardener Ratio

Parts by weight of amine to be used with 100 parts by weight of BADGE resin (phr)

$$= \left(\frac{\text{amine hardener molecular weight} / \text{number of hydrogens per molecule}}{\text{BADGE equivalent weight}} \right) \times 100\%$$

BADGE resin has an equivalent weight of 176 g/mole (as stated by the manufacturer), and active hydrogen in 2-AFD is four.=> $\left(\frac{248/4}{176}\right) \times 100\% = 35.6\%$

To cure 100 g of BADGE resin, 35.6 g of AFD is required.

Preparation of Epoxy Nanocomposite

The synthesized AC (300 mg) was diffused in 20 mL ethanol and ultrasonicated for 30 min to obtain a homogeneous suspension. The AC solution was immediately added to the Bisphenol A diglicidyl ether resin and stirred vigorously until entirely dissolved (EP- x percent; x: 0,0.1,0.2,0.5,1,2), where ‘x’ is the amount of AC added to the epoxy resin mixture in weight percentages. The mixture was also heated to 80°C and vacuum degassed until the ethanol was completely gone. The hardener (2-aminophenyl disulfide (APD)) was then added and mixed at the same temperature for 15 min. The degassed liquid was put into a silicon mold to set the color and baked for 5 h at 150°C. Bisphenol A diglicidyl ether resin-based reference specimens were also created, with diethylenetriamine (DETA) functioning as a hardener, to study the influence of APD on self-healing in accordance with previously reported procedures. To study the activated carbon impacts, reference clean (R-epoxy) and AC-impregnated epoxy (R-Epoxy-1 percent) nanocomposites were constructed (Hummers & Richard 1958, Nia et al. 2014, Rana et al. 2016, Park et al. 2019, Krishnakumar et al. 2020).

Material Characterization Methods

The D8 ADVANCE ECO-Bruker was used to conduct

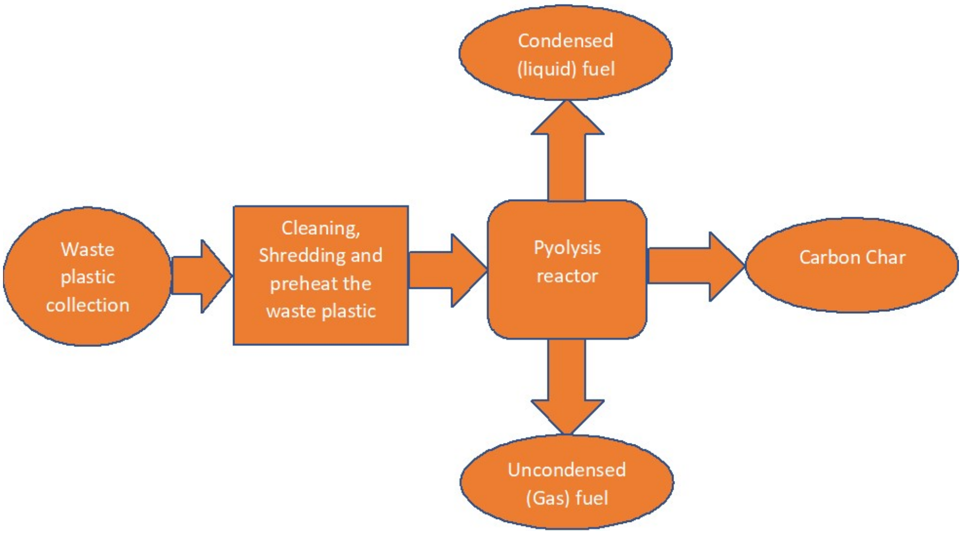

Fig. 1: Schematic flow process diagram of domestic plastic waste to alternate fuel.

an X-Ray Diffraction spectroscopy analysis to detect the activated carbon. Epoxy's activated carbon was studied using the spectroscopic UV-Visimeter (LAMDA 35, Perkin Elmer). The curing process was studied by FT-IR spectra analysis (Frontier FT-IR/FIR, Perkin Elmer). The effects of activated carbon dispersion in the epoxy matrix were investigated using an HR-TEM, JEM 2100F, from JEOL. The glass transition temperature was determined using differential scanning calorimetry (DSC) tests and TA-Q400em dimensional change studies. At temperatures ranging from 30 to 220 degrees Celsius, Perkin Elmer differential scanning calorimetry (DSC-7) was used with a nitrogen purge gas flow rate of 19.8 mL per minute and a pressure of 3 bars. Three-point bending tests were performed on rectangular specimens (15×5×0.5 mm) in the TA-Q400em to evaluate their mechanical properties. All mechanical characteristics tests were carried out at temperatures ranging from 40 to 120 degrees Celsius, with heating rates of 10 degrees Celsius per minute, a nitrogen purge gas flow of 50 ml per minute, and a force of 0.02 Newton. To straighten the specimen in the stress relaxation experiment, a preloaded force of 1×10^{-3} N was applied. After determining the temperature and strain, testing consisted of applying 1% strain at the proper temperature and measuring the relaxation modulus with respect to time. Stress-strain experiments were conducted in strain ramp mode with a force of 0.02 N, and the strain was measured at an isothermal temperature of 40°C.

RESULTS AND DISCUSSION

Material Characterization

Activated carbon in an epoxy vitrimer composite was detected using ultraviolet spectroscopy (UV). The material was characterized by a fine-grinded matrix efficiently diffused in ethanol using ultrasonication. The absorbance peak revealed the presence of activated carbon in the epoxy composite at 237 nm. In Fig. 2a, the obtained UV data for epoxy-activated carbon and epoxy-AC composites were plotted together.

The x-ray diffraction spectroscopy (XRD) analysis of the activated carbon synthesized from pyrochar (Fig. 2b) shows that the peak at 27.23°C marks their formation. The lack of distinct peaks indicated the amorphous nature because of the hexagonal shape resembling a graphite flake peak found at 27.23°C. AC might be considered assemblages of imperfect graphene.

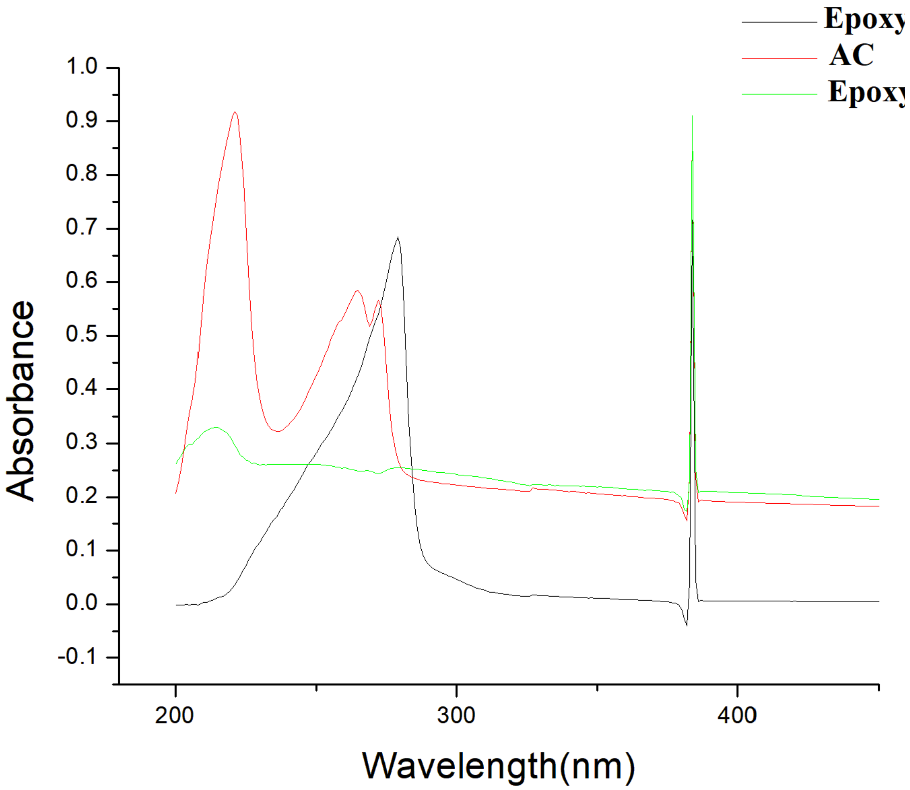

Fig. 2a: UV spectrum for epoxy, activated carbon, and epoxy-activated carbon composite.

The curing and uncuring of epoxy vitrimer composites were determined using FT-IR analysis. The disappearance of the oxirane rings of the oxirane ring (917 cm^{-1}) was noticed, which indicated that the epoxy had completed its curing process (Fig. 2c). The curing of the epoxy was monitored using FT-IR analysis at intervals of 1 h. It was discovered that the curing process was complete after 5 h of observation.

SEM analysis shows that carbon pyrochar is generated from municipal mixed plastic waste pyrolysis and activated carbon surface, in which the chemically activated carbon reveals pores on its surface (Fig. 2d, 2e). Because of their modest volume, these pores allow activated carbon to increase the surface area for chemical reactions.

Mechanical and Thermo-Mechanical Properties

A thermomechanical analyzer was used to determine the Tg and dynamic mechanical performance of activated carbon-epoxy vitrimer composites. The thermal characteristics of pristine epoxy composites have been investigated. The TA Q-400em is effective in finding Tg from temperature-influenced aspect variations.

Tg values for virgin epoxy vitrimer and activated carbon-epoxy vitrimer composites with different quantities of activated carbon filler are shown in Table 1. Among the studied epoxy samples, EP-1 had the lowest Tg.

Furthermore, the lack of reactivity between epoxy and activated carbon improves chain mobility, allowing for more free space between the filler and matrix. As a result, chains near the interface easily flow into the free volume, boosting mobility and lowering Tg (Grady 2012). The free volume space between matrix and nanofillers (Sun et al. 2004) may have reduced Tg for all composites, enhancing chain mobility and achieving low-temperature self-healing characteristics. However, adding 1 wt% activated carbon filler increases Tg somewhat, perhaps owing to the amalgamation of activated carbon in the epoxy matrix (Landel & Nielsen 1994, Krishnakumar et al. 2020).

The lower Tg aids low-temperature self-healing and shape memory. As a result, more study was conducted on composites containing up to 1% activated carbon in the matrix. A dynamic three-point bending test was used to investigate the effects of activated carbon filler on the

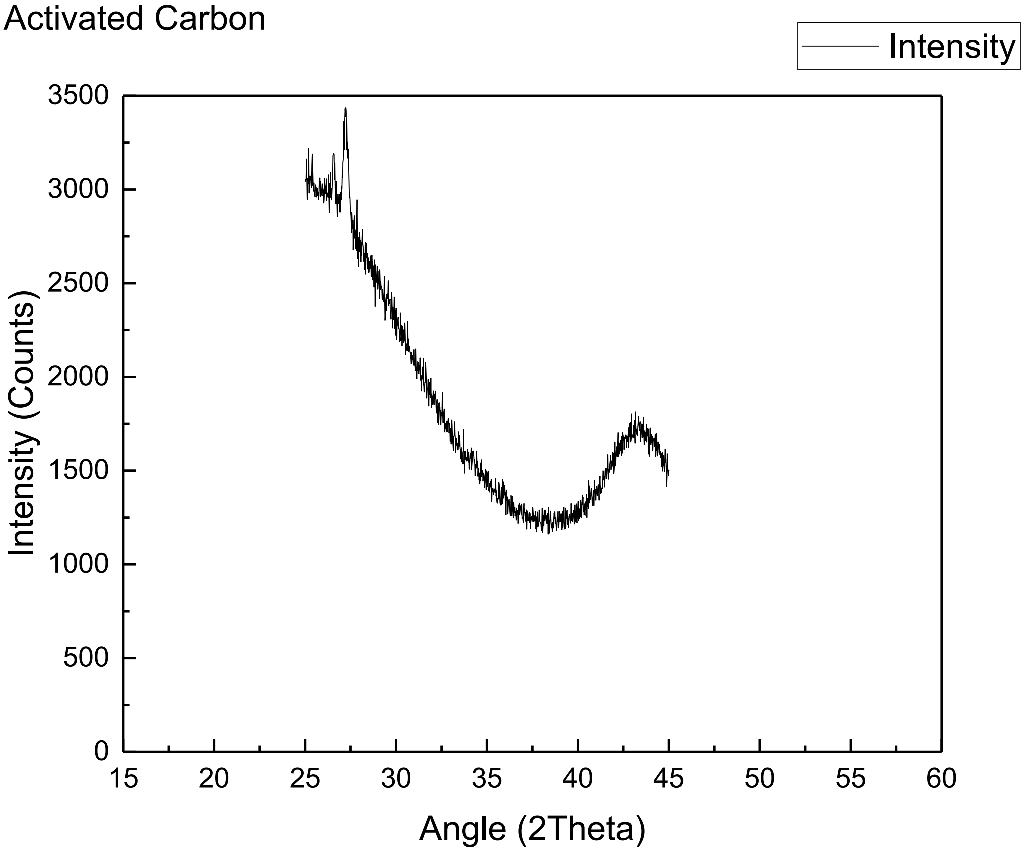

Fig. 2b: XRD spectrum for activated carbon.

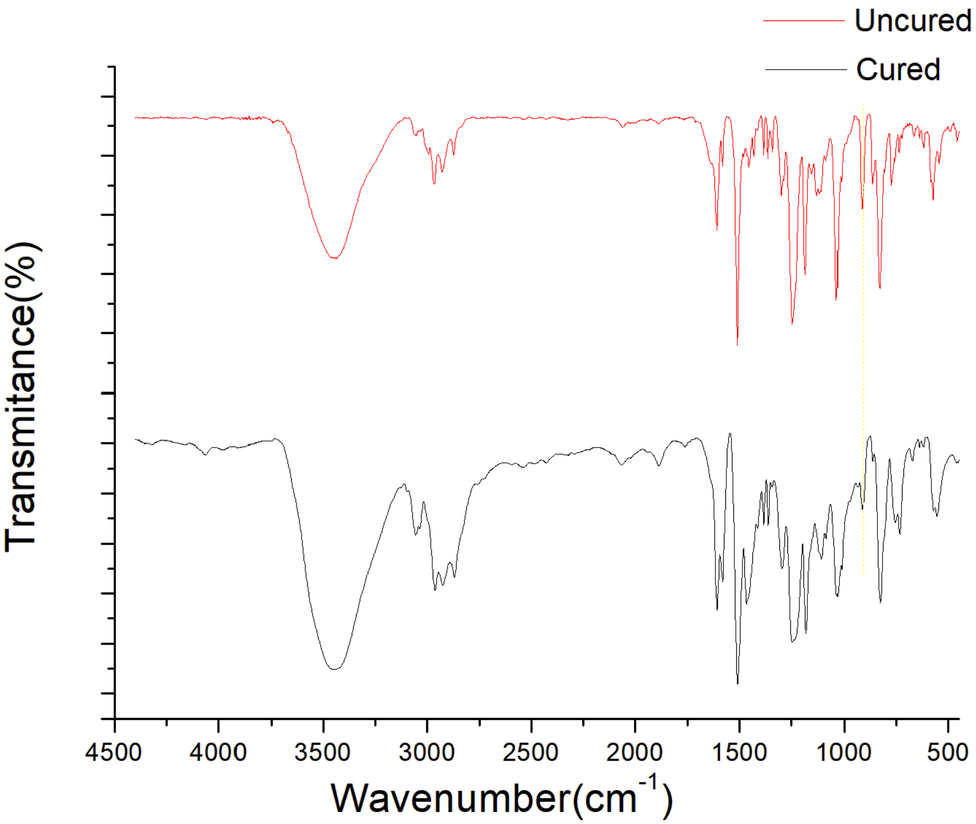

Fig. 2c: UV spectrum for cured and uncured epoxy composite.

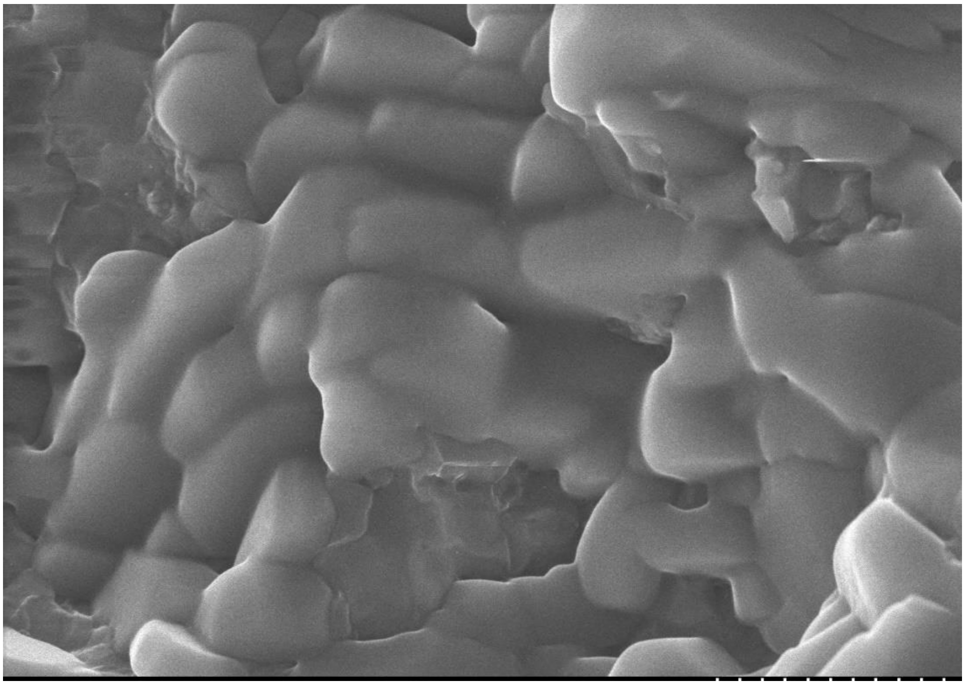

Fig. 2d: SEM images for pyrochar carbon.

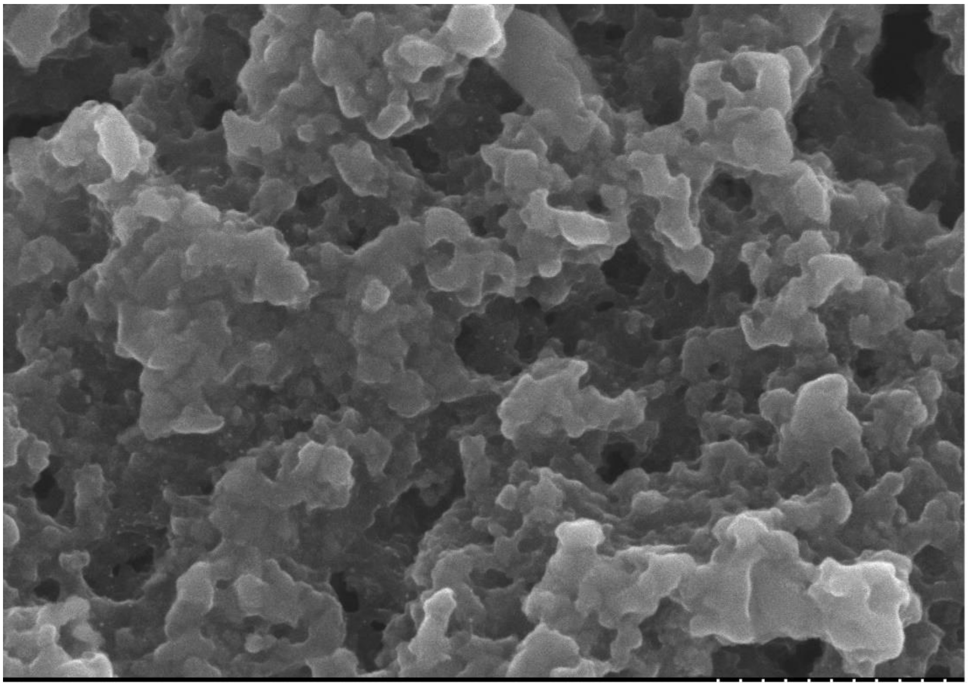

Fig. 2e: SEM images for activated carbon.

mechanical behavior of epoxy vitrimer. Table 2 shows the changes in mechanical parameters of vitrimer epoxy when utilizing cured pristine and activated carbon epoxy. The viscoelasticity of pristine epoxy vitrimer and activated carbon-epoxy vitrimer composites was investigated at different temperatures (Fig. 3a and 3b). The storage (E') and loss (E) modulus of the epoxy vitrimer material were addressed. In the high activated carbon sample, the storage modulus (52.2 GPa) (EP-1%). Fig. 3a shows a steady rise in storage modulus with nanofiller, and Table 2 shows the achieved values.

The wavy structure of activated carbon may aid in achieving effective intercalate interlocking with polymer matrix, thereby increasing modulus. The loss modulus (E) (Fig. 3b) also shows the material's viscoelasticity (E'>E). The shoulder peak (Fig. 3a) represents the rubbery area of the vitrimer materials following Tg. The glass transition temperature (Tg) of the epoxy vitrimer was decreased by adding 1% activated carbon to EP-1. With the addition of fillers, Tg decreases, resulting in a low-temperature rubbery zone in vitrimeric composites (Landel & Nielsen 1994)

Table 1: The glass transition temperature of epoxy composites.

Material	T_g (TMA) (^oC)
EP-pristine	83
EP-0.1%	62
EP-0.2%	58
EP-0.5%	56
EP-1%	53

As a result, the solid-to-rubbery phase shift temperature completely depended on material viscoelasticity (storage and loss modulus) (Guadagno et al. 2011).

The stress-strain relationship of developed vitrimer composites was determined using three-point bending tests at 40°C. According to Fig. 3c, EP-1 % has greater flexural strength than EP-Pristine, and EP-1 % has higher flexural strengths than EP-pristine samples (Table 2). Combining activated carbon with epoxy composites gains stiffness and bending resistance while reducing strain-at-break (Bortz et al. 2012). Using activated carbon fillers enhanced the flexural modulus from 0–9.4% to 0–9.4%.

The pure epoxy sample has a lower flexural modulus than EP-P and EP-1%. Fig. 3b shows the nanofiller-based variation in flexural strength and modulus. The flexural values (strength and strain at break) of conventional and vitrimer epoxy networks are listed in Table 2 (Ebnesajjad & Arthur 2015).T

Dynamic Properties

Stress relaxation: By performing stress relaxation analysis on the epoxy composites, which is designed to determine the relaxation modulus of malleable materials, it has been

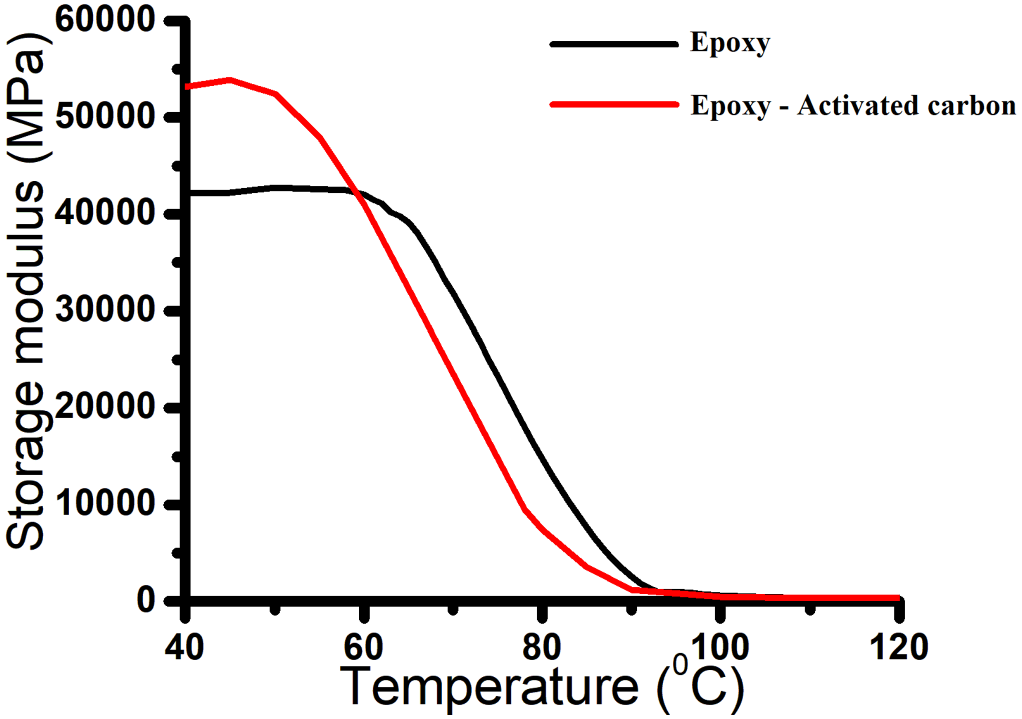

Fig. 3a: Storage modulus for epoxy vitrimer.

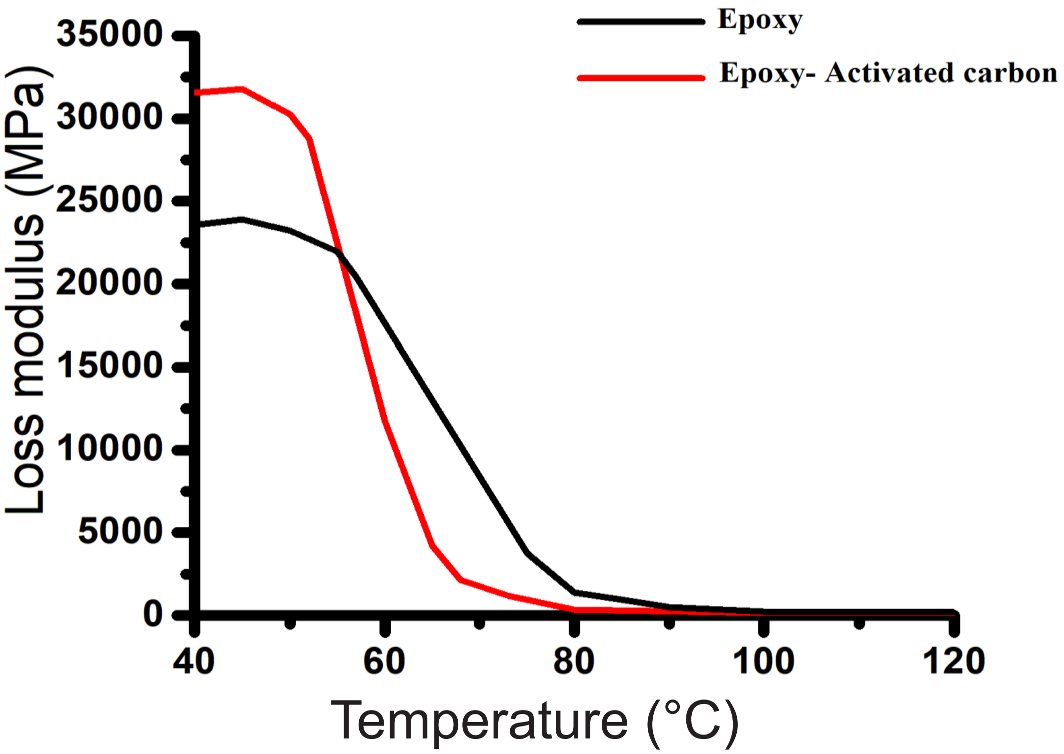

Fig. 3b: Loss modulus for epoxy vitrimer.

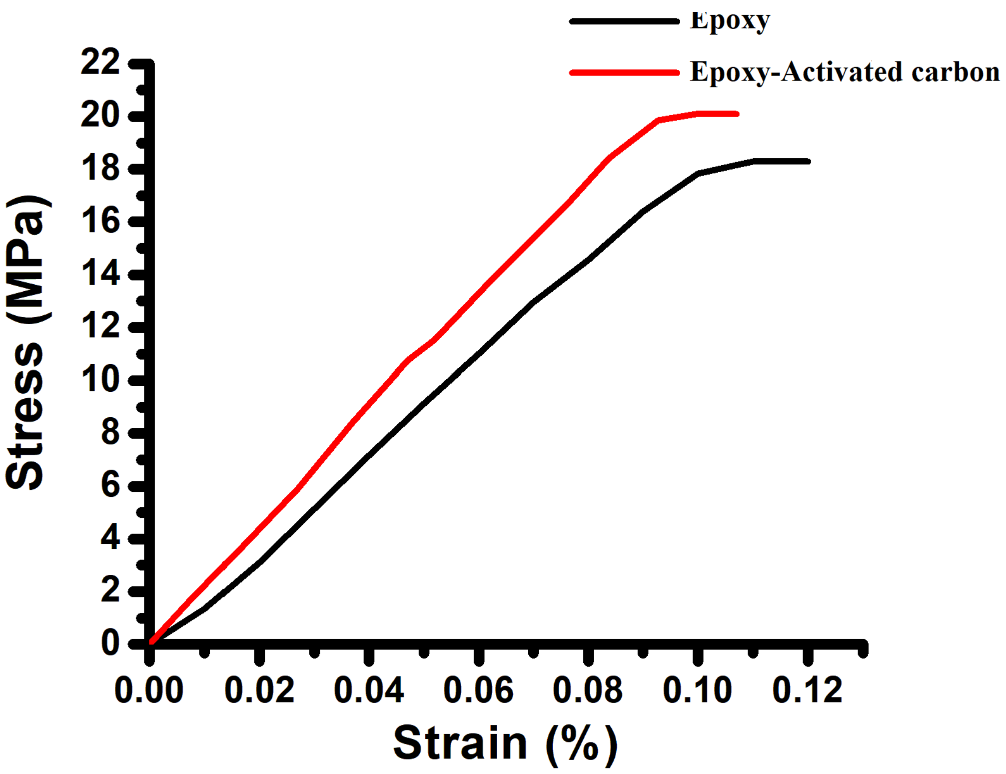

Fig. 3c: Stress-strain curve for epoxy vitrimer.

verified that they exhibit vitrimer behavior (Ogden & Guan 2018). In this study, an EP-pristine stress relaxation investigation was carried out, and the resulting time-dependent relaxation modulus was plotted in accordance with the data received from their temperature measurements. The high relaxation rates reported in the material suggest a fast disulfide exchange in the substance. Because of the relationship between temperature and relaxation time, a shorter relaxation period corresponds to a quicker disulfide exchange rate. The temperatures of 60°C, 70°C, and 80°C used in the experiments resulted in relaxation durations of 112.8 s, 40.8 s, and 34 s, respectively. The obtained findings indicate a quick exchange response after Tg and that the imposed tension is rapidly relaxed. By using an Arrhenius equation (1), the acquired data were displayed, which allowed for the calculation of a low activation energy (Ea = 59/KJ.mol^{-1}) (Jousseaume et al. 2002).

$$\tau^* = \tau_0 \exp (E_a/RT) \qquad \ldots(1)$$

According to some theories, this is due to activated carbon, which has lower epoxy vitrimer crosslinking density and increased viscosity. However, it was discovered that the development of free volume between the filler and the matrix was the most important factor in the diminution of the glass transition temperature (Sun et al. 2004). Generally, when viscosity exceeds 10^{12} Pa.s, it is necessary to consider the temperature of the material topology transition shift (Dyre 2006). Using Maxwell's and Arrhenius' equations, the projected topological freezing transition temperature (Tv) was calculated to be 19°C due to this typical study.

Self-healing: A temperature value of 75°C was used to study the produced samples' self-healing behavior. The findings indicate that the samples had considerable self-healing effects. It is anticipated that a lower temperature self-healing will be associated, which will be beneficial in lowering the Tg, where the S-S bonds will be able to reorganize more quickly at the lower Tg. As a result of the inclusion of the filler, the self-healing capability has been enhanced, which is beneficial in accelerating and constraining the flow constraints for the disulfide groups. For the sample, EP-1 %, a low-temperature self-healing (75°C for 5 min) was achieved, which was beneficial in lowering the Tg. A razor

Table 2: Mechanical properties of epoxy AC nanocomposites.

Epoxy material	Storage modulus [GPa]	Flexural strength [MPa]	Flexural strain%	Flexural modulus [GPa]
EP-P	39.9	19.4	0.05	32.5
EP-1%	53.5	19.2	0.11	15.7

blade was used to split the test specimen in half, and the parts were instantly assembled at 75°C for 5 min with the use of a tweezer to assess their bond strength (Olowojoba et al. 2017). The effectiveness of the healed samples was determined using flexural testing, and the stress-strain correlations of the healed samples were presented in Fig. 4a for two different healed samples.

No changes in flexural strength were seen after healing. However, the flexural modulus was significantly reduced due to the increased strain, as shown in Table 3. Specifically, this decrease establishes the upper limit for crosslinked chains and is related to the drop in crosslink density (Guadagno et al. 2018, Florea et al. 2015). After healing, EP-pristine and EP-1 percent returned 72% and 83% of their flexural modulus, respectively, and the second healing cycle demonstrated a 60% and 75% increase in flexural modulus, respectively (Fig. 4b). So, the reported values proved to be useful in determining the healing efficiency that had prevailed. It was identified that Carbon pyrochar generated from municipal mixed plastic waste pyrolysis was good in achieving effective healing.

CONCLUSION

According to this study, activated carbon from municipal mixed plastic waste pyrolysis could be employed as a filler in an epoxy vitrimer biocomposite. The enormous surface area of activated carbon in the AC-epoxy vitrimer biocomposite allows for chain exchanges. Self-healing was observed in virgin epoxy vitrimer at 80°C for 5 min; however, when activated carbon was added, the material showed a lower self-healing temperature at 75°C for 5 min. Comparing the composite EP-1 % (which contains 1 wt % AC) to virgin epoxy vitrimers, the EP-1 % composite exhibits 17% greater flexural strength and modulus and a 16.9% increase in modulus. Vitrimer composites with 1 wt% AC (EP-1) exhibited 83 and 75 % recovery efficiency after two successive healings in flexural trials. Composite vitrimer research will be useful in the future to witness ecologically sound vitrimer composite materials for practical uses.

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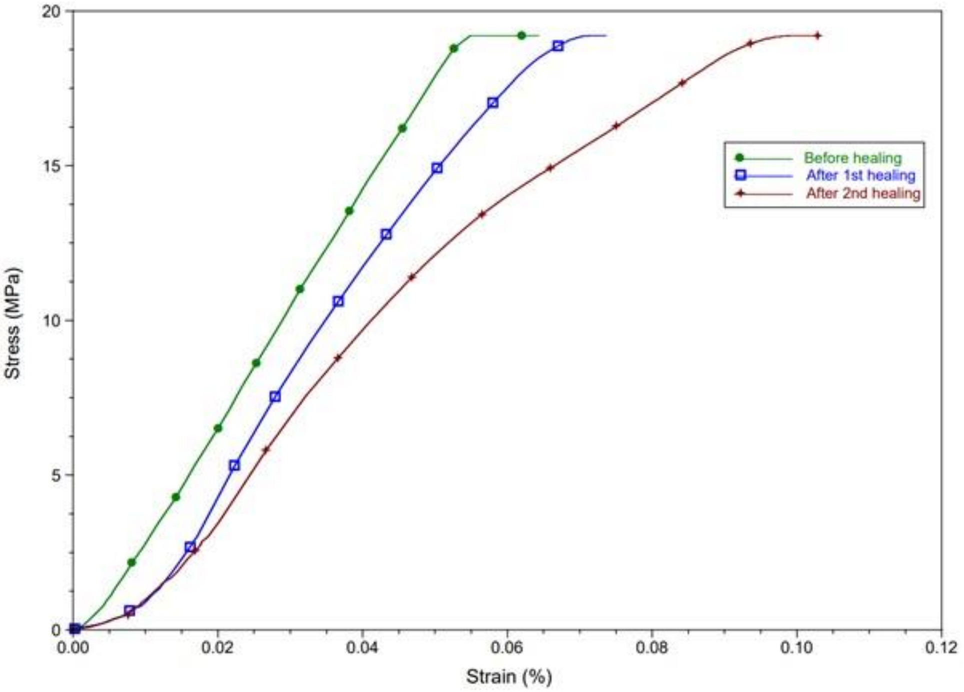

Fig. 4a: EP-pristine healing represented stress-strain curve.

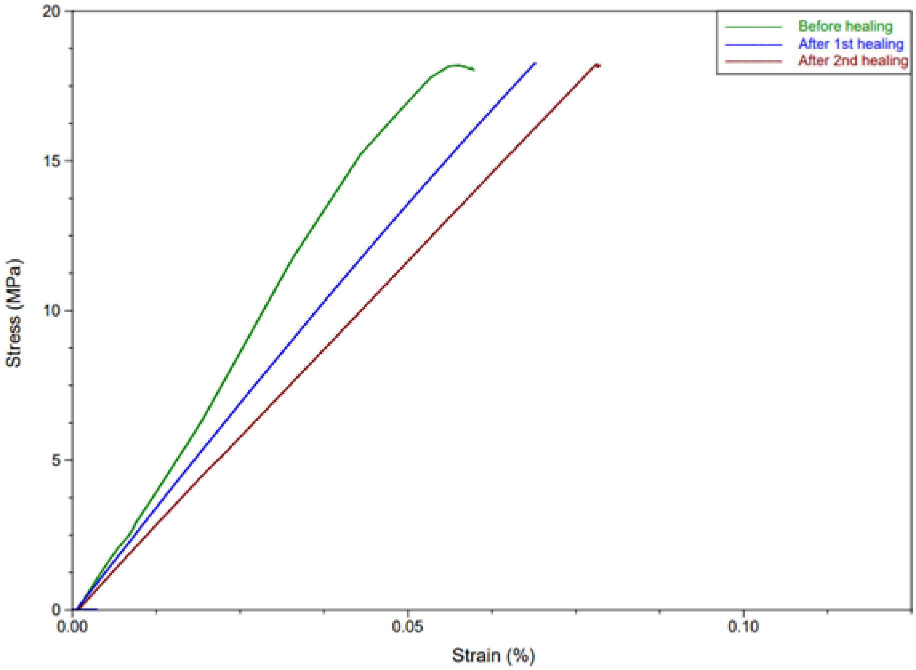

Fig. 4b: EP-1% healing represented stress-strain curve.

Table 3: Flexural modulus changes after healing.

Sample EP-x%	Before healing [GPa]	After healing [GPa]	
		1^{st}	2nd
EP-pristine	34.2	28.7	20.9
EP-1	39.8	34.6	32.3

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