Effect of Chemical Treatment on Decomposition Profiles of Carbon Fiber Reinforced Polymer Composites and Its Recycling

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1 Introduction

The composite industry is marked a global market size of USD 86.4 billion in 2021, and in the coming years (2021–2028), a 6.6% of compound annual growth is expected [1]. The growth is driven by its huge applicability in various industries like aerospace, construction, aviation, marine, wind energy, oil and gas, sporting goods, etc. [2, 3]. The remarkable material properties of composite materials like high strength-to-weight ratio, thermal and electrical properties, and corrosion resistance account for its thriving demand [4]. The fibrous composites, especially carbon fiber reinforced polymer (CFRP) composites, are one of the leading contributors to the growth considering their properties and applications. However, carbon fiber production is high energy demanding process achieved at high temperatures ranging from 1000 to 2000 °C [4]. On the other hand, the thriving nature of the CFRP composite industry in both production and consumption now leads to a large number of "End-of-Life" (EOL) materials that need to be recycled sustainably. It is estimated that 102. 4 Mt and 148.7 Mt CFRP waste materials will be accumulated from aviation and wind turbine, respectively, in the Asian region alone by 2050 [5, 6]. Therefore, the environmental problems related to the disposal of this composite waste and the cost of virgin

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fibers demand that researchers find a sustainable recycling technique to recover the fibers from the EOL composites.

Mechanical, thermal, and chemical recycling are the major methods adopted to recycle CFRP composites. The mechanical recycling methods are limited, in that it does not recover the structure of the fiber; instead, the FRP composites are milled into small pieces called recyclate, which can be used as filling or aggregate replacement [2]. The chemical recycling methods ensure the recovery of fibers with better mechanical properties, but the disposal of the solvent and its impact on human health and the environment makes it challenging [2, 7]. In thermal recycling, pyrolysis stands out against incineration in end product usability. The gas and liquid coming out of the pyrolysis reactor can be used as chemical feedstock. However, the char formation on the surface of the recycled fibers and mechanical property deterioration at higher operating temperatures are the major limitations of the pyrolysis process [2, 3]. By understanding the advantages and drawbacks of each method, a complementary approach for recycling the CFRP can lead to a process with promising results. The present work examines the effect of chemical treatment before the thermal recycling method by pre-treating the CFRP composites with $ZnCl_2$-Ethanol solution.

2 Materials and Method

All the chemicals used in this study were reagent grade. The ethanol (99.5%) was supplied by Tedia company Inc., Fairfield, USA, and $ZnCl_2$ was by Merck Life Scientific Pvt. Ltd., Mumbai, India. The method followed for pre-treatment is shown in Fig. 1. The cured CFRP coupon was cut into 2 cm × 2 cm pieces. Different concentration (w/v) of $ZnCl_2$-Ethanol solution (5–40%) was prepared. The sized CFRP was treated with $ZnCl_2$-Ethanol solution in a stoppered flask under magnetic stirring at 80 °C for 2 h. The solid-to-solvent ratio was kept at 60. After the treatment, the CFRP pieces were filtered out from the solvent, washed, and dried. The samples were named CFRP_ZnXX, where XX represents the concentration of $ZnCl_2$ in an ethanol solution, i.e., CFRP_Zn10 represents the CFRP samples treated with 10% of $ZnCl_2$-Ethanol solution. The effect of chemical treatment on the decomposition of the matrix in the CFRP was analyzed using the thermogravimetric analyzer (TGA), TG 209 F1 Libra, M/s Netzsch, Germany. The samples were placed in a crucible, and TGA studies were conducted from room temperature to 1000 °C at a rate of 10 °C/min. Both TGA curve and derivative thermogravimetric (DTG) curves were obtained from the study. Further, the filtrate collected was characterized with Fourier transform infrared (FTIR) spectroscopy from 500 to 4000 cm^{-1} and compared with the fresh solvent before treatment.

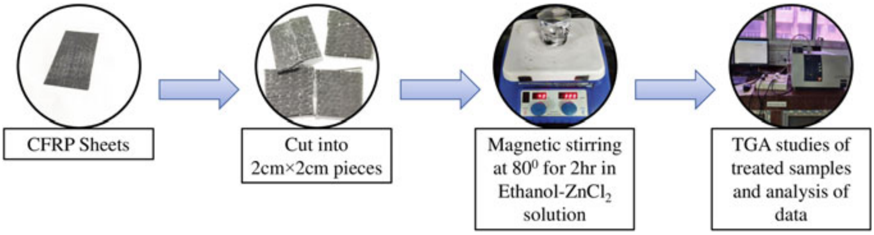

Fig. 1 Process flow diagram of the chemical treatment process of CFRP

3 Result and Discussions

The TGA curves of both raw and pre-treated CFRP composite were found to be similar and show only one sharp drop corresponding to the decomposition of the epoxy resin, as shown in Fig. 2. However, the range of temperature at which the mass loss happens varies with the concentration of $ZnCl_2$. Moreover, the peak of the DTG curve (Fig. 2) shifted to the left due to the effect of $ZnCl_2$, and the largest shift was at 10% $ZnCl_2$-Ethanol solution. The peak, onset, and end temperatures and maximum mass loss are shown in Table 1. At 10% of $ZnCl_2$, the peak temperature shifted to 32 °C left from 373.1 °C of the raw CFRP. The overall mass loss temperature range without pre-treatment was found to be between 336.8 and 442.7 °C, and that of 10% $ZnCl_2$ treatment is 307.6 and 355.7 °C. Therefore, the pyrolysis temperature of the CFRP composite can be reduced by 87 °C with the help of pre-treatment. The ethanol in the pre-treating solution acts as a swelling agent for epoxy resins and enables the penetration of the Zn^{2+} ion into it [8]. The penetrated Zn^{2+} ions then form organo-metallic bonds with the carbon–nitrogen bonds in epoxy resin and promote the catalytic decomposition of epoxy resins [9]. The C–N bonds in the epoxy resins are likely to break first during pyrolysis since it possesses lower bond energies throughout the cross-linked structure of epoxy resin [9]. The chemical action of Zn^{2+} ions accelerate the breakage of the C–N bond and lowers the temperature of the breakdown.

The peak temperature of decomposition of epoxy resins decreases first and reaches a minimum value (341.7 °C) at 10% $ZnCl_2$ solution and then increases with concentration (Table 1). The temperature range of mass loss also follows the same pattern. Initially, more Zn^{2+} ions are available for bond formation when the concentration increases from 5 to 10%. After 10%, the density and viscosity of the solution increase along with the increase in the number of Zn^{2+} ions. The higher density and viscosity of the solution decrease the swelling efficiency of ethanol and hence the penetration of Zn^{2+} ions [10].

The FTIR spectra of the 10% $ZnCl_2$-Ethanol solution before and after pre-treatment is shown in Fig. 3. Both samples gave a similar spectrum with a slight change in transmittance value, and it is comparable to one given in the literature [11]. The broad band (3598–3032 cm^{-1}) centered at 3302 cm^{-1} is assigned to the stretching vibration of the O–H bond in ethanol [11]. The stretching and bending

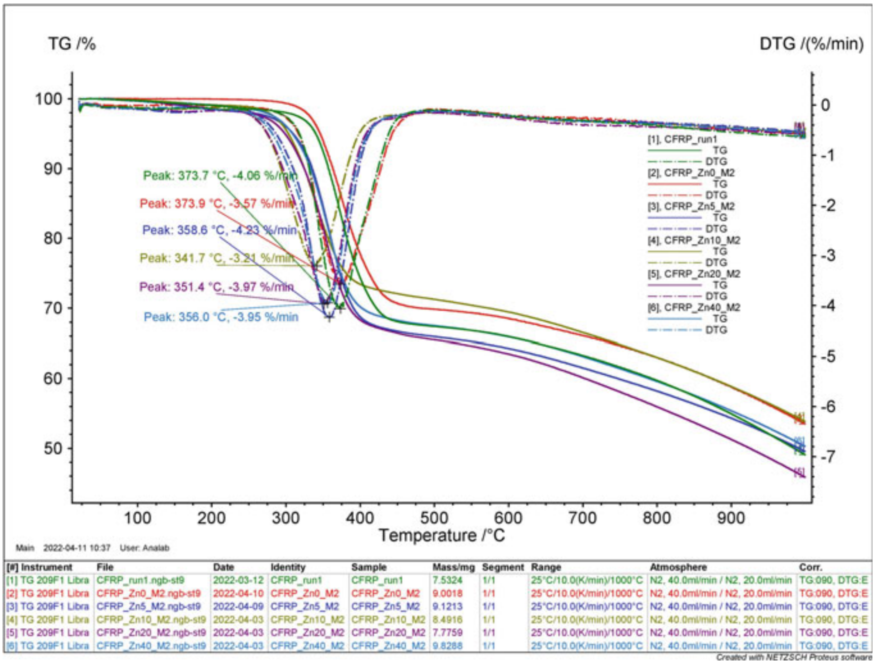

Fig. 2 TGA and DTG curves of CFRP (raw and pre-treated)

Table 1 Temperature profile of resin decomposition zone

Sample	Concentration (%)	Resin decomposition zone		
		Onset Temp. (°C)	Max. Decomp. Temp. (°C)	Offset Temp. (°C)
CFRP	–	336.8	373.7	442.7
CFRP_Zn5	5	314.6	358.6	414.5
CFRP_Zn10	10	**307.6**	**341.7**	**355.7**
CFRP_Zn20	20	317.4	351.4	404.4
CFRP_Zn40	40	311.6	356.0	412.2

The best results of pre-treatment studies were obtained at 10% $ZnCl_2$-Ethanol solution and the particular values are given in 'bold'

vibrations of the –C–H bond of the $–CH_3$ group are shown by the peaks at 2974 cm^{-1} and 1383 cm^{-1}, respectively [12]. Compared to the peaks of pure, the peaks of $ZnCl_2$-Ethanol solution are shifted to the right due to the effect of $ZnCl_2$ in the ethanol [11]. Also, the peaks of the $ZnCl_2$-Ethanol solution collected after treatment show a slight shift due to the concentration difference compared to the freshly prepared solution. Furthermore, there are no new peaks identified after treatment which indicates that the ethanol only acts as a swelling agent rather than dissolving the epoxy material

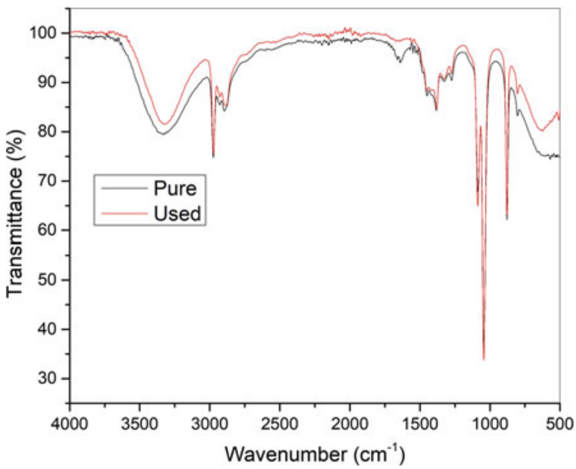

Fig. 3 FTIR spectrum of pure and used $ZnCl_2$-Ethanol solution

in the CFRP. Thus, the solution can be reused in the process effectively without any treatment.

4 Conclusions

The effect of Ethanol-$ZnCl_2$ solution on the decomposition of epoxy in CFRP was studied at different concentrations of the solution. It was found that both the swelling property of ethanol and the catalytic activity of Zn^{2+} ions help in reducing the decomposition temperature profile of the epoxy resin. A 10% of solution shows a higher effect with a reduction of 87 °C in the temperature range at which the major mass loss happens. The study can be extended to optimize the process parameters like temperature, time of the pre-treatment, and also the pyrolysis at the reduced temperature of CFRP to check the quality of recycled fibers.

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