Applied Composite Materials (2020) 27:357–373
https://doi.org/10.1007/s10443-020-09821-7

Zero-Waste Recycling of Shelf-Cured Pre-Impregnated Carbon Fiber Reinforced Epoxy Laminae

Alaa Ajam[1] · **Ali Tehrani-Bagha**[2] · **Samir Mustapha**[1] · **Mohammad Harb**[1]

Received: 24 March 2020 / Accepted: 8 June 2020 / Published online: 13 June 2020

Abstract

The main objective of this study was to investigate a zero-waste restoration and reprocessing method of carbon/epoxy prepreg. We studied a series of chemical and thermal treatments to reshape and re-strengthen pre-impregnated (prepreg) carbon fiber-reinforced polymer (CFRP) composite rolls that were cured over the shelf, never been used, and would otherwise be discarded. The proposed treatment method is of high interest in minimizing solid waste and reducing the environmental footprint of polymer composites. We used a series of solvents (water, ethanol, N, N- Dimethylformamide (DMF) and Sulfuric Acid) to induce ductility in the scrap already rigid self-cured specimens. The chemical treatments of the scraps using mixtures of DMF-Water or DMF-Ethanol enhanced the ductility of the samples without any negative impact on the mechanical properties. However, the chemical treatment of scarps using a mixture of sulfuric acid with other solvents, could not improve the ductility of the samples. Heat pressing the chemically treated samples further enhanced the ductility of the samples and flattened the scrap composites. The recovered strength and modulus of the recycled prepreg CFRP reached a promising value of over 65% of the original properties, where the samples treated with a mixture of DMF-ethanol preserved their mechanical properties better than other treated samples. The simple, safe, and zero-waste recycling technique presented in this study has proven to be effective for closing the life cycle of a thermoset polymer composite.

Keywords Composites · Carbon fibers · Thermoset polymers · Recycling · Mechanical properties · Chemical analysis

---

✉ Mohammad Harb
mh243@aub.edu.lb

[1] Smart Structures and Structural Integrity Laboratory, Department of Mechanical Engineering, American University of Beirut (AUB), Beirut 1107-2020, Lebanon

[2] B.&W. Bassatne Department of Chemical Engineering and Advanced Energy, American University of Beirut (AUB), Beirut 1107-2020, Lebanon

1 Introduction

Light-weight, strong, durable, and corrosion-resistant polymer composites have the potential to offer significant structural advantages for different applications. Resin pre-impregnated composite fabrics (Prepreg) have been used in a wide range of applications without the need to add resin during manufacturing since it is already infused in the material [1, 2]. Such materials are ideal for manufacturing composite parts resulting in a cleaner process and optimal product quality. Despite their promising properties and advantages, many unused prepreg rolls are cured overtime after the expiry of their shelf-life. As a result, such expensive, expired, and non-biodegradable composites are often discarded in landfills.

In the past two decades and since prepreg fabrics have found their way to almost every aerospace and automotive company, many efforts have been focusing on recycling such quality material or reclaiming the fibers within [3]. Prepreg based on carbon fiber reinforced polymer (CFRP) laminates are ordinarily enriched with thermoplastic or thermosetting resins. While thermoplastics are relatively easy to recycle [4, 5], thermosets form a strong crosslinked network when cured and thus creates a challenge in recycling such materials [6].

Mechanical Recycling (MR), Thermal Recycling (TR), and Chemical Recycling (CR) and their combinations are among the most common ways for recycling thermoset polymeric composites [7–9]. MR reuses the cured material by mechanically crushing the composite as a whole, including matrix and reinforcement, while TR and CR reclaim the reinforcements (fibers) only from the scrap materials. MR techniques mechanically reduce the size of scrap composite components into millimeter-sized pieces, known as recyclates, and use them as reinforcing fillers in different products. Researchers have found that the size of the obtained recyclates affects the properties of the new product manufactured using the recycled materials, where the smaller particles contain greater percentages of filler and resin and the larger particles contain more fibers [8–10]. Such recyclates can be embedded in a specific type of application with the appropriate content percentage and induce high retention in the mechanical properties [11].

CR, industrially known as Solvolysis, is a technique used to decompose the matrix polymer and reclaim only the fibers [12, 13]. The thermoset matrix is often decomposed into monomers by using the appropriate reactive solvent chosen depending on the type of matrix polymer under specific pressure and temperature. The recycling of composites was investigated by researchers using this chemical process, where water and ethanol are the typical and most practical solvents used [14]. The main parameters that affect the obtained recyclates by this chemical process are the concentration of the solution used and the agitation time. To improve the decomposition process of the matrix, catalysts were used to optimize the solvent properties [13]. Hernanz et al. [15] used De-ionized water in the dissolution of epoxy resin at 270–400 bars and 250–400 °C and found that the amount of epoxy resin that was eliminated is small since they lost only about 20.7 wt% from the resin. To improve this process, they added potassium hydroxide to the solution and found that the elimination rate of resin increased to 95.4 wt% while improved the duration of decomposition, which decreased from 30 to 15.5 min. Feraboli et al. [16] used a sulfuric acid solution with hydrogen peroxide as a catalyst to oxidize the epoxy resin at 110 °C for several hours. Pinglai et al. [17] examined a mixture of the two solvents nitric acid and N, N-Dimethylformamide (DMF) with hydrogen peroxide catalyst to decompose epoxy polymer using several heating temperatures, where the decomposition ratio is the highest when the temperature is above 90 °C.

TR process, which recovers the fibers only while scraping the matrix, contains three techniques: combustion, fluidized bed, and pyrolysis processes. Burning the scrap composites is a combustion process used for energy recovery [17]. The two other techniques recover the fibers only while scraping the matrix. The fluidized bed process is useful for any kind of material even to that of complex structures since they could be shredded into pieces of different sizes before they are fed into the bed. It can be also used on any polymer type since the matrix will be degraded due to the high steam temperature, producing a fluffy form of fiber filament [18]. Pyrolysis is used to recycle composites by the decomposition of polymer without the presence of oxygen in an environment between $350°C$ and $800°C$. Plenty of optimization techniques were developed by researchers to improve this process and the recovered material [9]. It was also found that the mechanical properties of the recycled fibers are affected by the high temperature during pyrolysis [13].

Recently, researchers have been working on optimizing the recycling processes of thermoset composites using quick no-waste recovery methods that require low energy usage. Asmatulu et al. used *as-is* samples of different shapes from end-of-life products (airplanes and cars) in manufacturing new smaller parts like doors, rackets, and tables [19]. Englund et al.prepared larger pieces in the 6–7 m^2 range from whole wind turbine blades, representing a mix of the various microstructures present in the thermoset product. The pieces were loaded into virgin epoxy resin at high levels (85–90 wt.%) and the mixture was then thermoformed into sheet products. As a result, the scrap composites were fully recovered and used in new applications [20].

As the recycling of composite end products is desperately needed for environmental safety, recycling of uncured prepreg manufacturing waste has been also investigated to reduce if not eliminate any production line waste. Souza et al. [21] used uncured carbon fiber/epoxy resin pieces of different sizes, that were produced during a ply cutting manufacturing process, to form panels that were cured at 180 °C. The obtained composite material proved its applicability with high mechanical properties. Nilakantan and Nutt [22, 23] produced laminates from chopped uncured scraps that could be used in automotive and aerospace fields.

None of the technologies mentioned before have focused on fully recycling shelf-cured prepreg CFRP laminae, which presents two challenges, especially when cured in its original storage roll shape. The first challenge is to induce flexibility into the composite lamina to enable remolding and shape preservation. The second challenge is to strengthen and retain the mechanical properties of the recycled composites. Adams et al. [24] showed that thermoset resins have exhibited some ductile behavior when exposed to an elevated temperature in the range of their Glass Transition Temperature (T_g).

In this study, we have introduced a recycling technique using a chemical-treatment process followed by a thermal treatment process. The chemical-treatment process was characterized by soaking the scrap composites into different solvent mixtures of Sulfuric Acid, N, N- Dimethylformamide (DMF), water, and Ethanol at room temperature. This process did not viciously decompose the crosslinked polymers, instead, it loosened some of the polymeric chain entanglements formed by the cross-linking points produced in the polymer chain network structure. The induced flexibility in the recycled material was monitored by studying the flattening enhancement of the treated specimens in comparison to a scrap specimen. The thermal-treatment process was investigated using several curing cycles, where the non-crosslinked polymers cured and the lamina thermoformed into a new desired shape. The tensile strength and elastic modulus were analyzed to monitor the effect of the recycling technique on the mechanical properties of the recyclates. Additionally, chemical analysis was performed to study the effect of the recycling process on the composition of the polymer matrix. Finally, we have summarized the recycling technique and presented the feasibility of the proposed technique in recycling already-cured composite laminae.

2 Experimental Approach

2.1 Materials

The base (virgin) and scrap (already-cured) material used in this study were XPREG® XC130 Prepreg CFRP composite (12 K, 450 g, 2/2 Twill) by *easy composites*. XPREG® XC130 is an epoxy-based component autoclave prepreg carbon fiber system with a 130 °C maximum service temperature developed for autoclave or other positive pressure cure. When not in use, XPREG® prepregs should be kept frozen at −18 °C (0 °F) in sealed plastic packaging. The scrap prepreg material roll used in this study was left at room temperature for three years beyond its recommended out-of-freezer storage life. The ten meters long and one meter in width rolled prepreg has cured as a single lamina due to the backing paper covering the fabric, which kept it from adhering to itself. The prepreg lamina was cut along the roll length into pieces of width 14 cm using a metal cutter and the backing film was then manually but easily removed. The large pieces obtained were then cut into smaller pieces (14 × 1 × 0.06 cm) that were used in our study as seen in Fig. 1. On the other hand, the solvents used were Ethanol absolute ≥99.8%, N, N-Dimethylformamide≥99.8%, and Sulfuric Acid with 95% purity obtained from Sigma-Aldrich Corp.

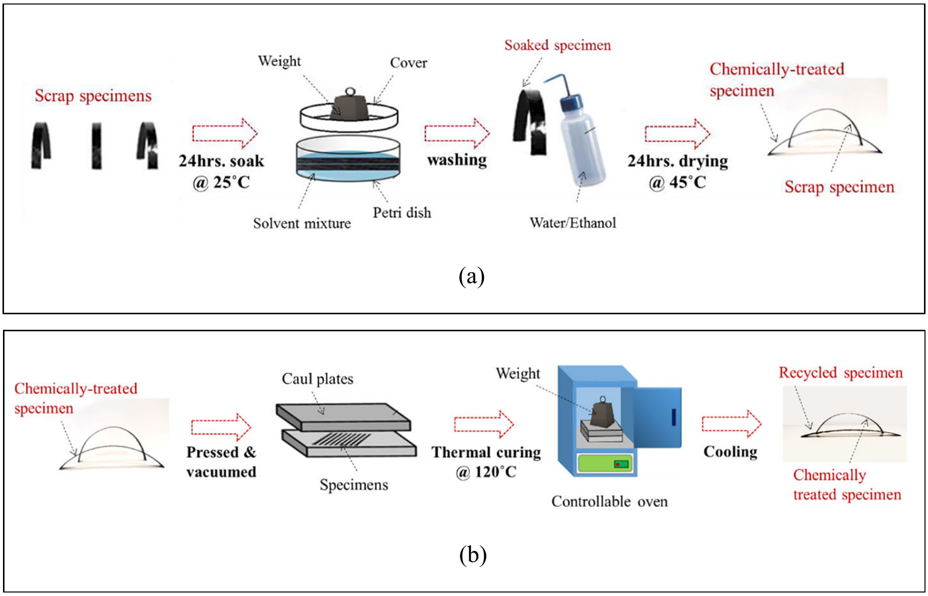


Fig. 1 Schematic for (**a**) chemical-treatment (CT) process and (**b**) thermal-treatment (TT) process

2.2 Recycling Method

The recycling technique has been investigated by the implementation of a two-step recycling process. The first step involves a chemical treatment process while the second is based on a thermal treatment process.

2.2.1 Chemical Treatment

A chemical treatment process was first investigated to induce flexibility into the already cured/stiffened prepreg CFRP composites. The effect of several chemicals (water, ethanol, H_2SO_4, and DMF) on the mechanical and physical-chemical properties of the scrap composites were examined. Scrap composite specimens were placed into a large covered petri dish filled with 80 mL after the backing films were removed. The specimens were soaked in the solvent by applying a pressure of ~2 kPa to ensure complete immersion. The petri dish was placed in a closed Pyrex pot to prevent the solvents from evaporation during the chemical treatment.

The scrap specimens were treated in a mixture of solvents at different time intervals, as can be seen in Table 1. In each of the fourteen solvent mixtures, four sets of three specimens were soaked for 1, 2, 4, and 24 h. A total of 168 specimens were chemically treated and studied to determine the desired mixture. After removing the specimens from the solvent, they were rinsed thoroughly with water or ethanol. Then, they were dried at low heat while sandwiched between two flat metallic plates at 45 °C for 24 h. The chemical treatment technique is configured in the sketch in Fig. 1a.

2.2.2 Thermal Treatment

A press heating process was then implemented to remold the chemically treated specimens into a new shape and re-strengthen the composite. This ensures the curing of any non-crosslinked polymers and post-cure the already cured polymers that were crosslinked at room temperature which is discussed in detail in a later section. The experimental setup is detailed in Fig. 1b. The specimens were cured using the original curing cycle of the virgin XPREG XC130® recommended by the manufacturer.

Table 1 The solvent mixtures used for chemical treatment

Code	Mixtures
100D	100% DMF
25D75W	25% DMF - 75% Water
50D50W	50% DMF - 50% Water
75D25W	75% DMF - 25% Water
25D75E	25% DMF - 75% Ethanol
50D50E	50% DMF - 50% Ethanol
75D25E	75% DMF - 25% Ethanol
100A	100% H_2SO_4
30A70W	30% H_2SO_4–70% Water
50A50W	50% H_2SO_4–50% Water
70A30W	70% H_2SO_4–30% Water
30A70E	30% H_2SO_4–70% Ethanol
50A50E	50% H_2SO_4–50% Ethanol
70A30E	70% H_2SO_4–30% Ethanol

2.3 Characterization Approaches

In our study, Fourier Transform Infrared Spectroscopy (FTIR) was done using Cary 630 spectrometer (Agilent Technologies, USA) to compare the absorbance spectrums of the scrap and the recycled specimens to monitor the change in the structure of the polymer at the surface. FTIR spectra were obtained using Agilent Cary 630 FTIR spectrometer in the wavenumber range of 650–4000 cm^{-1}.

Differential Scanning Calorimetry (DSC) was performed using Q2000 DSC (TA Instruments, USA) to determine the glass transition temperature of the virgin, scrap, and recycled composites. Three thermal cycles Heat/Cool/Heat were adopted, with a heating rate of 10 °C/min and a cooling rate of 20 °C/*min*, in a nitrogen atmosphere. DSC data analysis was always carried out with a reference empty-cell from 25 up to 250 °C. The degree of cure (α) of the tested specimens was calculated using the following equation [25]:

$$\alpha = \frac{H_0 - H_t}{H_0} \tag{1}$$

Where, H_0 is the heat of reaction measured for the virgin composite, obtained from the first heating cycle, and H_t is the obtained residual heat of reaction for the recycled composite.

Thermogravimetric analysis (TGA) was performed using Q500 TGA (TA Instruments, USA) to study the thermal stability of the scrap and recycled specimens by monitoring the change in their mass. The analysis was done using a TA Instrument in a nitrogen atmosphere with a heating rate of 10 °C/min from 30 °C to 1000 °C. Each specimen used from the recycled composite had a mass of about 8 mg. The initial degradation temperature (IDT), the temperature at the maximum rate of weight loss (T_{max}), and the maximum weight loss rate (R_{max}) for the treated specimens were calculated using derivative thermogravimetry (DTG). The activation energy (E_a) for epoxy degradation within the specimens was also calculated using Horowitz and Metzger method [26]. Additionally, the degree of flexibility of the recycled composite was referred to as the flattening enhancement (*FE*) which was obtained using the following equation:

$$FE = \frac{h_1 - h_2}{h_1} \tag{2}$$

where h_1 is the original height of the scrap specimen, and h_2 is the height of the treated specimen.

The fundamental mechanical properties of the recycled composite were analyzed under tensile tests using the H100KS UTM (Hounsfield). The setup had a 10 kN load cell and a crosshead speed of 2 *mm/min,* according to the D3039 ASTM standard [27]. Five specimens for each of the virgin, scrap, and each type of chemically and thermally treated specimens were cut, shaped, and tested.

3 Results and Discussion

As was mentioned previously, all scrap specimens to be recycled had adapted a curved shape, as shown in Fig. 1. To evaluate the softening/flexibility and reshaping effect of the recycled material, the flattening enhancement (*FE*) of each specimen after chemical soaking and treatment was investigated. This was the first factor that was taken into consideration to choose among the different mixtures tried for the chemical treatment. An inconsistency was noticed in the softness of the specimens treated using the time intervals 1, 2, 3, and 4 h, which proved the necessity for a long chemical soak. With 24 h immersion in all the solvent mixtures shown in Table 1, the following observations were concluded: 100D, 75D25E, and 100A solvent mixtures caused the polymers within the specimens to fully loosen and degrade as shown in Fig. 2. These solvents were excluded from the chosen solvent mixtures, as our objective was to reshape and reuse the material and not decompose the matrix to reclaim embedded fibers. The other DMF mixtures (25D75W, 50D50W, 50D50E) and H_2SO_4 mixtures (50A50W, 50A50E, 70A30W, and 70A30E) did not degrade the resin but had an insignificant effect on the flexibility of the scrap specimens with 5 to 15% *FE*. Meanwhile, 25D75E, 75D25W, 70A30W, and 70A30E introduced very ductile and flexible scrap composites with FE ranging between 26 and 42%, as shown in Fig. 3a.

Figure 3b shows the percentage of flattening enhancement of the re-cured chemically treated specimens. The percentage mentioned for each type is the average enhancement of the specimens cured using the manufacturer's recommended curing cycle. It was noticed from the error bars that the flattening enhancement is almost the same using any of the heating cycles for each type. The flattening of the specimens enhanced by about 80% for all types revealing a promising recycling method for reshaping and recuring thermoset polymeric composites. The thermal treatment process implemented in this study followed the manufacturer's recommended curing cycle for virgin XPREG® XC130. Further studies will be investigated at a later stage to optimize the re-curing cycle.

3.1 Physical and Chemical Properties

3.1.1 Differential Scanning Calorimetry (DSC)

DSC testing and analysis was implemented to determine the effect of the chemical and thermal treatment processes on the recycled composites. From the DSC thermograms of un-cured, well-cured, and scrap specimens shown in Fig. 4a, a curing exothermic peak at 150 °C was very well noticed for the un-cured specimen. At the same temperature, a smaller peak was observed for the scrap composite specimen confirming incomplete curing of the epoxy networks in the scrap composites and reassured with the disappearance of this peak for the well-cured composite specimen.

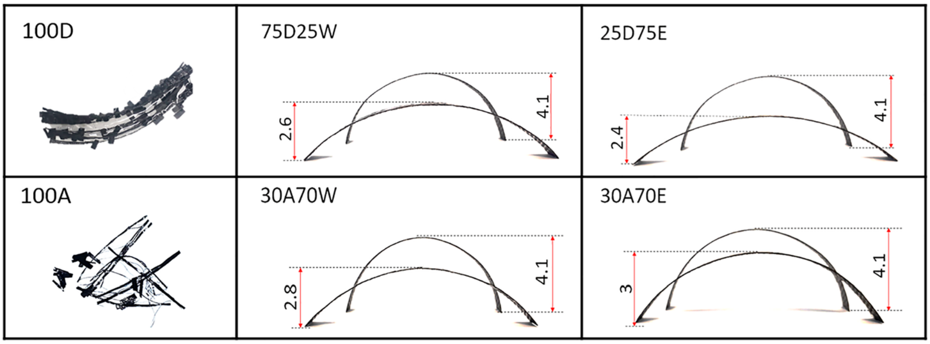


Fig. 2 The effect of solvent mixtures on the scrap specimens (dimensions in cm)

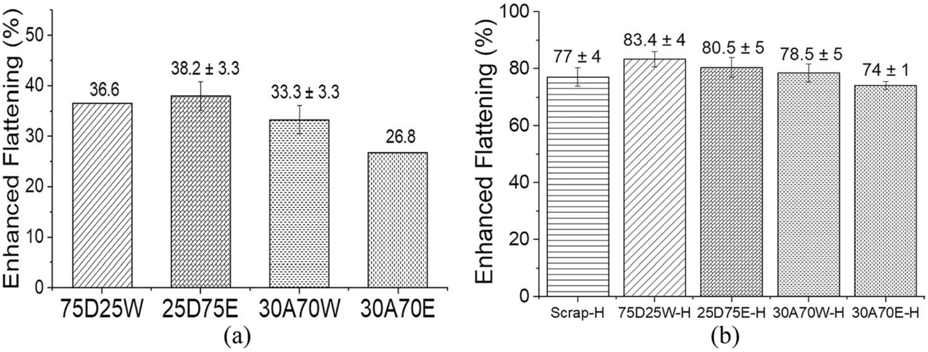


Fig. 3 Percentage of flattening enhancement after (**a**) chemical treatment and (**b**) thermal treatment

The glass transition (T_g) temperatures were then obtained by taking the middle point on the slope of shifting on each thermogram and reported in Table 2. The T_g for the well-cured and scrap composite was found to be 121 and 60.2 °C, respectively. The considerable variation in the transition temperatures was the result of the curing temperature. Thus, the incomplete curing of the scrap composite at room temperature resulted in a dramatic decrease in its T_g. The calculated data of the degree of cure (α) using eq. (1) showed that the scrap composite was

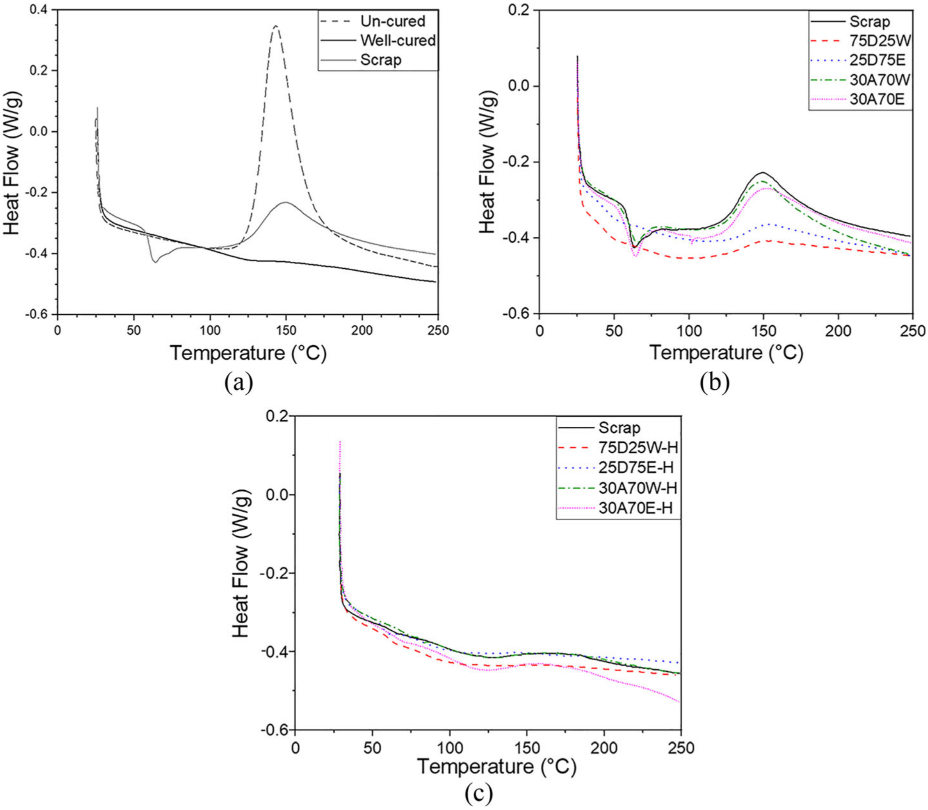


Fig. 4 DSC thermograms of the composites: (**a**) un-cured, well-cured and scrap, (**b**) chemically-treated and (**c**) thermally-treated

only 68% cured when H_0 was found to be 115.5 W/g and H_t was 37.05 J/g. Hence, at least a third of the polymers (~32%) present in the scrap material were still un-cured.

Figure 4b shows the DSC thermograms for the chemically treated composites compared to the scrap composite. It was noticed that the relaxation enthalpy disappeared in the thermograms of the DMF treated specimens; also the exothermic peaks had significantly decreased in the two types 75D25W and 25D75E. The decrease was also reported by a 27% (43.84 °C) and 22% (46.37 °C) reduction in the T_g and a rise in the degree of cure (α) of the chemically treated scrap specimen with 75D25W and 25D75E, respectively. However, no significant change was reported for the specimen treated with 30A70W and 30A70E mixtures with a slight increase in the degree of cure which presented the week effect of these solvents on the scrap specimens. The increase in the degree of cure (α) for the specimens treated with 75D25W and 25D75E mixtures led to our understanding that DMF infiltrated into the specimens and caused some swelling and relaxation which helped in leaching-out part of the non-crosslinked polymers. On the other hand, the glass transition temperatures of these specimens were depressed due to the penetration of the diffused solvents into the polymer matrix.

As evidence of this phenomenon, the 75D25W and 25D75E solvents that were used for chemical treatment were taken out and heated for 1 h at 155 °C; above the boiling point of DMF, water, and ethanol. A layer of cured epoxy (Bisphenol A) was noticed on the bottom of the petri dish which was characterized using FTIR. This was also confirmed from the weight reduction of the specimens after chemical treatment and drying.

Another set of chemically treated specimens were then thermally treated using the manufacturer's recommended curing cycle. DSC was used also to monitor the change and the effect of the treatment on the T_g of the composites and the thermograms were then plotted in Fig. 4c. As could be noticed, an exothermic hump was still present for all treated specimens with almost a 25% increase in the T_g of DMF treated specimens and less than 10% in the H_2SO treated specimens as reported in Table 2.

The increase in T_g for the specimens treated with 75D25W and 25D75E mixtures resulted from the increase in the degree of cure of the specimens after the chemical treatment. This was realized after the thermal treatment due to the evaporation of the penetrated solvents (DMF). However, the slight increase in the transition temperature for the specimens treated with 30A70W and 30A70E mixtures could be due to the curing of the presented non-crosslinked polymers found in the scrap specimens.

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra for a virgin well-cured and a scrap sample were plotted in Fig. 5a. A band was shown at 910 cm^{-1} in the scrap material spectrum when compared to the well-cured

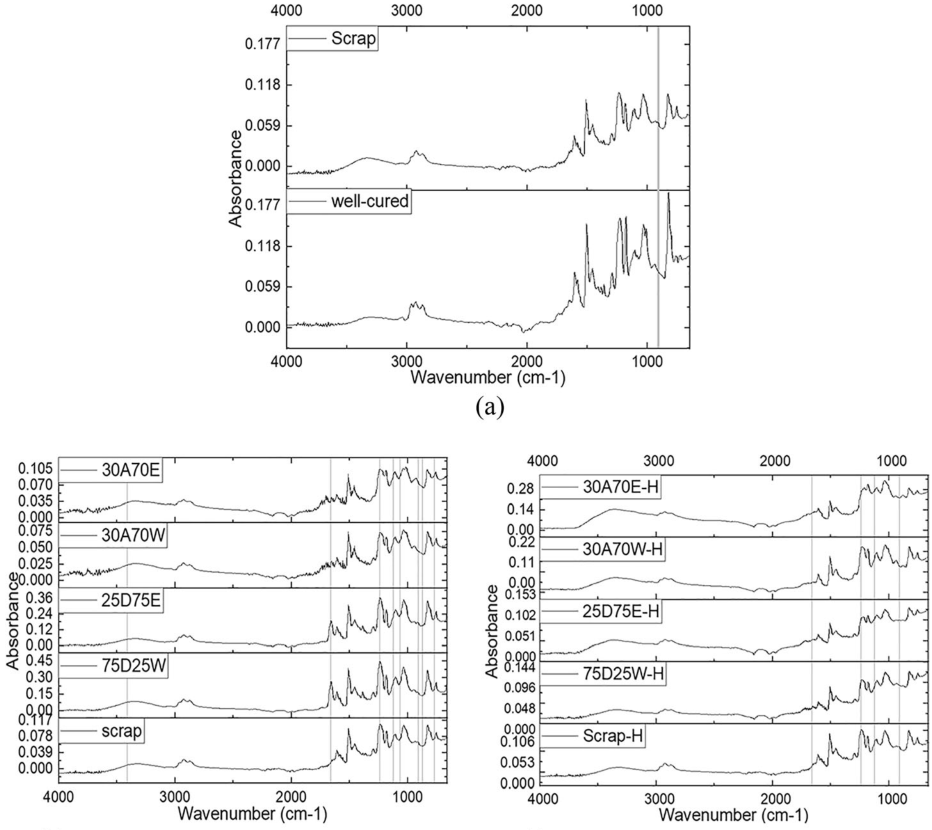
Table 2 Glass transition temperatures (T_g) and degree of cure (α) of well-cured, scrap, and treated composites

Specimens	T_g (°C)	Degree of Cure α (%)	Specimens	T_g (°C)
Well-Cured	121	100	–	–
Scrap	60.2	68	Scrap-H	61.1
75D25W	43.84	90	75D25W-H	59.04
25D75E	46.37	87.5	25D75E-H	54.11
30A70W	60.57	72.7	30A70W-H	67.41
30A70E	60.27	76	30A70E-H	63.61

material spectrum. This band corresponded to an epoxy ring absorption, as stated by Kong [28] which gave a clear indication of the presence of non-crosslinked monomers in the scrap composites.

Figure 5b shows the FTIR spectra of the chemically treated composites compared to the spectrum of the scrap composite. The spectra of the chemically treated specimens in different mixtures showed that the absorbance value of the bands at 769, 910, 1122, and 1241 cm^{-1} decreased in comparison to that of the scrap specimen. This decrease ensures that during the chemical treatment, the number of non-crosslinked polymers has reduced. It was noticed that sulfuric acid had a higher effect on decreasing the intensity of the bands at 1122 and 1241 cm^{-1} which are attributed to the C–O stretching vibration band [29]. However, DMF had more effect on decreasing the intensity of the band at 769 and 910 cm^{-1} due to the C–H bending vibration bands of the substituted benzene cycle of epoxy resin [30].

A new band at 1662 cm^{-1} appeared when using the DMF solvent mixtures that corresponded to carbonyl group C=O [31]. This assured the presence of DMF in the specimen even after washing and drying, which could be replacing the non-crosslinked polymers. Additionally, new bands at 872 and 1066 cm^{-1} appeared in the specimens that were treated with sulfuric acid solvent mixtures. These bands were due to asymmetric S-O-C stretching



(a)

(b)

(c)

Fig. 5 FTIR spectra of (**a**) well-cured and scrap composite, (**b**) chemically-treated, and (**c**) thermally-treated specimens vibration at 872 cm^{-1} and to the SO_2 symmetric stretch band at 1066 cm^{-1} [32]. The presence of new bands could be explained either by the fact that the acid had broken down some of the crosslinked chains or it had reacted with the non-crosslinked monomers. Additionally, an increase in the absorbance value of the band at 3411 cm^{-1} representing a hydroxyl group was due to the absorbance of water and ethanol [29]. As a result, we can conclude that the treatment with the acid and DMF are surface and bulk treatments, respectively.

After the chemical treatment process, the specimens were then thermally cured and their FTIR spectra plotted in Fig. 5c. The absorbance values of the bands at 910, 1122 and 1241 cm^{-1} have decreased slightly for all the specimens treated with H_2SO_4 which ensures that the acid has hindered the curing during thermal treatment. On the other hand, the specimens treated with DMF showed a decrease in the absorbance value of the band 1662 cm^{-1} related to carbonyl group which happened with a decrease in the value of absorbance bands at 910, 1122, and 1241 cm^{-1}. The decrease of the carbonyl group was related to the evaporation of some of the DMF compounds after heating to 120 °C noting that the boiling point of DMF is 154 °C. The noticeable decrease in the other bands highlighted a high degree of curing of the remaining non-crosslinked polymers.

3.1.3 Thermogravimetric Analysis (TGA)

The TGA thermograms used to study the thermal stability of all specimens were plotted in Fig. 6. Based on the thermograms of the well-cured and scrap specimens in Fig. 6a, their decomposition was considered as a single stage in the 270–500 °C region which is associated with epoxy degradation. For the scrap specimen, it was noticed that part of the matrix had started decomposing before the epoxy degradation started at an IDT of 282 °C. This indicates the presence of non-crosslinked monomers in the scrap material corresponds to about 2% by weight of the material. The well-cured material remained stable without degradation until an IDT of 292 °C, which was evidence of the high cross-linking density. Additionally, the temperature at the maximum rate of weight loss (T_{max}) has decreased from 444 °C for the well-cured specimen to 432 °C for the scrap specimen. Lower thermal stability in the scrap material is deduced due to the weight loss/epoxy decomposition at lower IDT and T_{max} values.

TGA thermograms for chemically treated specimens were plotted in Fig. 6b. The curves for DMF treated specimens featured two decomposition stages. The first stage (50–250 °C) due to the decomposition of some chemical residuals inside the specimens; that did not evaporate during the drying stage [32]. The second stage (270–500 °C) related to the decomposition of epoxy started at the same IDT as the scrap material and had the same T_{max}. On the other hand, the thermograms of the H_2SO_4 treated specimens showed one decomposition stage as the scrap material with a negligible difference for the 30A70W treated specimen. However, the 30A70E treated specimen had a 3% weight reduction before the degradation stage of epoxy. This decrease could be explained by the evaporation of some solvents that were still present in the chemically treated specimens after rinsing and drying or other compounds that formed from the reaction of the acid with epoxy in the scrap material.

The maximum weight loss rates (R_{max}) of the DMF and H_2SO_4 mixtures treated specimens had decreased in the range of 10–20% when compared to the scrap specimens as shown in Table 3a. Similarly, the activation energy (E_a) values also decreased in the range of 20–26%. This change might have been attributed to the relaxation of the material after chemical treatment. The higher drop in the 30A70E treated specimen could be explicated that the acid broke down some of the crosslinked chains.

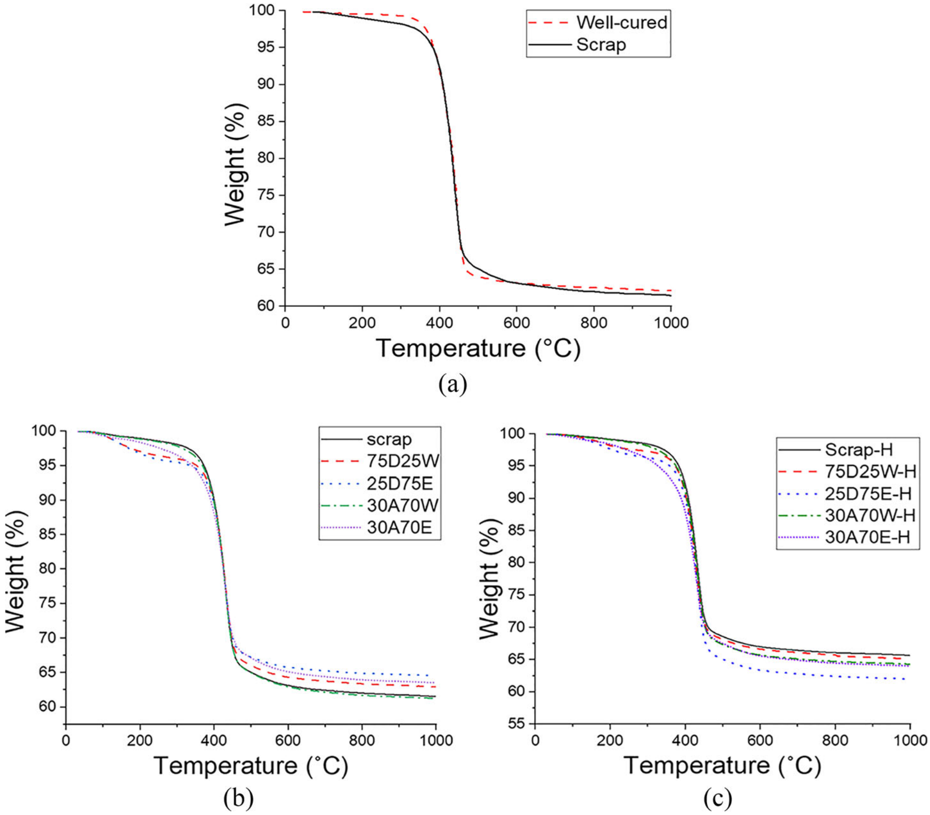


Fig. 6 TGA of (**a**) well-cured and scrap, (**b**) chemically-treated, and (**c**) thermally-treated composites

Figure 6c shows the TGA thermograms for the thermally treated composites after the chemical treatment according to the manufacturer's curing cycle. All the thermograms are

Table 3 Thermal stability and degradation parameters for (a) the chemically-treated and (b) chemically then thermally-treated composites

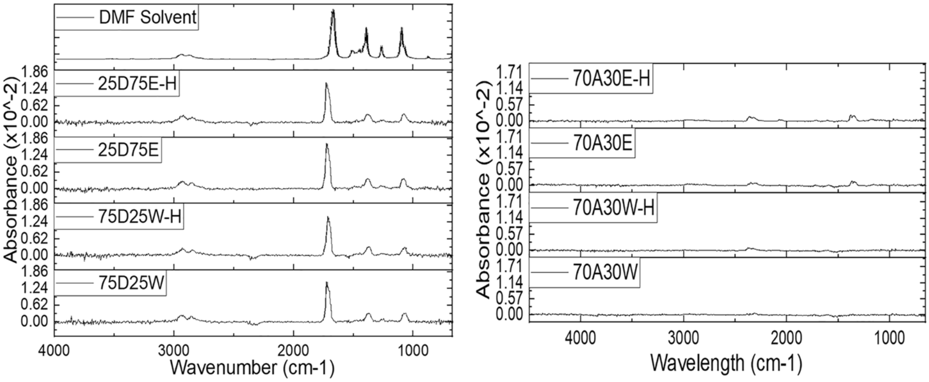
	IDT (°C)		T_{max} (°C)		R_{max} (%/°C)		E_a (KJ/mol)
Specimens	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 2
a							
Well-cured	–	292	–	444	–	56	50.8
Scrap	–	282	–	432	–	55	45.7
75D25W	47	282	132	432	3	53	41.7
25D75E	47	282	132	432	3.2	52	40.08
30A70W	–	282	–	432	–	54	44.5
30A70E	–	282	–	432	–	45	37
b							
Scrap-H	–	277	–	432	–	54	48.4
75D25W-H	47	277	167	432	2	53	45.5
25D75E-H	47	277	167	432	2.5	57	43.8
30A70W-H	–	277	–	432	–	54	46
30A70E-H	–	277	–	432	–	45	37.4

identical to those obtained from the chemical treatment alone. However, an increase in E_a for all specimens was noticed confirming the curing of any non-crosslinked (un-cured) polymers in the materials. Additionally, thermal treatment had increased the T_{max} of the first stage of decomposition for DMF treated samples as reported in Table 3b and thus improved its thermal stability. Finally, a decrease in R_{max} for the first stage could be explained by the evaporation of residual mixtures during thermal treatment.

The TGA analysis in this study was coupled with FTIR to further investigate the weight loss before the decomposition of the epoxy at specific temperatures for different solvent mixtures. The DMF chemically and then thermally treated specimens were analyzed at 167 °C; T_{max} at the first decomposition stage reported in Table 3b. The FTIR spectra for these cases plotted in Fig. 7a showed several peaks that were related to DMF solvent peaks [26]. This proofs that no reaction took place between DMF and the scrap composite material.

On the other hand, the FTIR spectra for H_2SO_4 treated samples plotted in Fig. 7b featured only one peak for the specimens treated with 30A70W at 2300-2370 cm^{-1} wavenumber range and two peaks for the specimens treated with 30A70E at 1330-1395 cm^{-1} and 2300-2370 cm^{-1} wavenumber ranges. The 1330-1395 cm^{-1} wavenumber range attributed to CH_3 was an indication of the decomposition of the crosslinked bonds [33] and thus clarifying the weight loss before the degradation of epoxy. The band range at 2300-2370 cm^{-1} attributed to CO_2 confirmed the oxidation of the surface [34].

The FTIR analysis had demonstrated the bulk and surface treatment mechanisms that DMF and H_2SO_4 solvent mixtures were undertaken inside the polymer, respectively. Where DMF solvent mixtures were leaching-out the non-crosslinked polymers and penetrated inside the matrix which produced flexible specimens. While H_2SO_4 solvent mixtures had broken down some of the crosslinked chains only. Moreover, TGA analysis confirmed the diffusion of DMF solvent mixtures inside the matrix and the surface oxidation of H_2SO_4 solvent mixtures. Thus, DMF has proved its validity to recycle the scrap prepreg composites. It should be noted also that DMF mixtures were much safer and cheaper to use and dispose of, than any of the acidic mixtures. However, DMF is still a hazardous solvent and should be recycled to lower the cost of the treatment and protect the environment. Also, more studies are required to find a way to get rid of the diffused solvents inside the recycled specimens for safer artifacts usage.



(a) (b)

Fig. 7 TGA-FTIR spectra of gases released from (**a**) the samples treated with a mixture of DMF and other solvents at 167 °C and (**b**) the samples treated with a mixture of H_2SO_4 and other solvents at 250 °C

3.1.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) performed on Tescan MIRA$_3$ LMU (Tescan, Czech Republic) was used to determine the surface and cross-sectional topography of the chemically treated specimens and monitor the effect of different solvent mixtures on the network structures of the carbon fiber reinforced thermoset polymer material. All specimens were sputter-coated with a 20 *nm* layer of platinum before scanning. SEM images of the outer-surfaces and cross-sections of scrap and treated specimens were presented in Fig. 8. Internal and surface cracks were visible in both DMF treated samples due to internal stresses. The internal-outward stresses were induced by the swelling of the specimens due to the diffusion of DMF and water/ethanol and leaching-out the non-crosslinked polymers and consequently replacing them. Acid solvent mixtures had a minor effect on the treated specimens. However, some voids have appeared on the surface of the 30A70E treated specimens which could have resulted from the oxidation of the outer-surface with no visible change to the interior of the specimens. Thus, the SEM analysis agrees with the treatment mechanisms that were concluded from the chemical analysis. Where the diffusion of DMF solvent mixtures produced some cracks in the treated specimens and the oxidation of H_2SO_4 solvent mixtures produced some voids on the surface.

3.2 Mechanical Properties

The tensile strengths and elastic moduli results obtained for chemically and thermally treated specimens were plotted in Fig. 9. The data is used to study the effect of each chemical mixture on the mechanical strength of the treated specimens while using the curing cycle of the virgin composite material. It was clear that the tensile strength and elastic modulus of the scrap material were about 65% of the virgin well-cured material. After chemical treatment, the material lost some of its strength but not exceeding 23% in any of the used solvent mixtures. The highest tensile strength drop was recorded for the specimens treated with 75D25W and 30A70W, where the specimen's strength decreased by 15% and 23%, respectively. This decrease was accompanied by a drop in the elastic modulus by half. The tensile strength of the specimens treated with 30A70E dropped by 15% and its elastic modulus by 25%. However, the properties of the specimens treated with 25D75E were not noticeably affected,

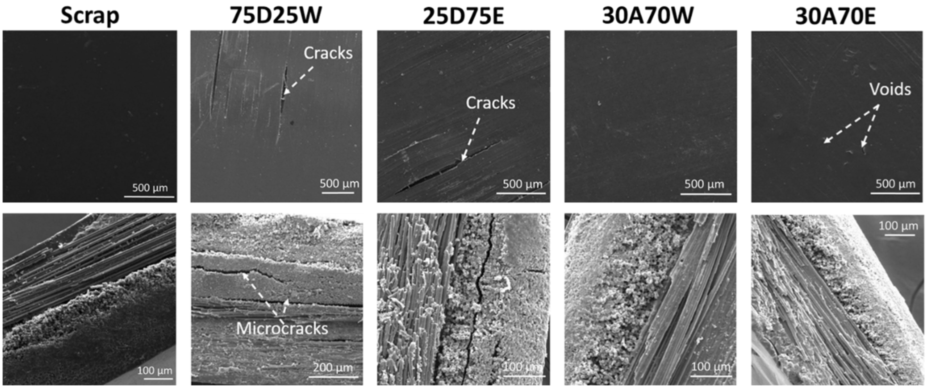


Fig. 8 SEM images for the surface (top) and cross-section (bottom) of scrap, 75D25W, 25D75E, and 30A70W treated specimens

where the tensile strength has dropped by 5% and its elastic modulus by 3%. This showed that the 25D75E mixture which gave the highest flexibility for the scrap material would also preserve its mechanical properties.

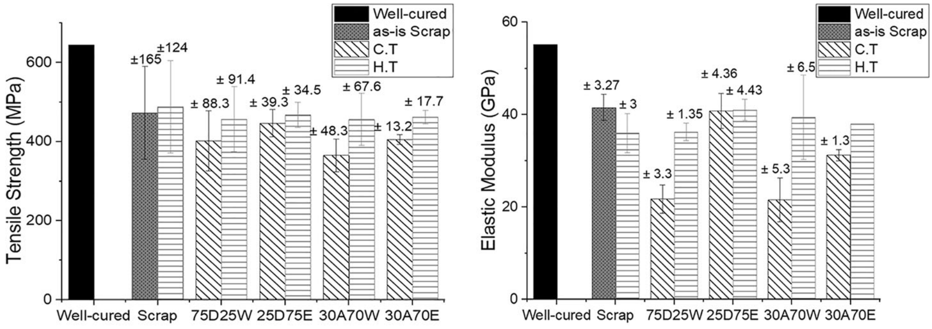
After thermal treatment, the tensile strengths and elastic moduli of all the specimens increased to reach nearly the same values as the scrap material. Consequently, it was concluded that thermal re-curing of any chemically treated specimen would preserve the scrap material's mechanical properties which hold 65% of the well-cured virgin composite properties. It was also noticed that none of the treated samples regained any of the virgin composite properties.

When combining the flexibility, strength, and elastic modulus, it could be concluded that all four solvent mixtures (75D25W, 25D75E, 30A70W, and 30A70E) are good candidates to reshape and recycle shelf-cured prepreg laminae. However, the 25D75E solvent mixture was the most effective in enhancing (up to 83%) the flexibility and reshaping of the stiffened scrap specimens while preserving 96% of its mechanical properties.

4 Conclusion

This work investigated a recycling technique for scrap composite rolls that were cured in a rigid cylindrical shape over the shelf. Two processes, chemical and thermal, were examined to induce flexibility and ductility into the scrap specimens to enable its reshaping while preserving their mechanical properties. The influence of different solvent mixtures on the scrap composites was studied to obtain flexible specimens. The treated specimens were then thermally cured under vacuum using the curing cycle of the virgin composite to obtain final strengthened recyclates.

From all fourteen different DMF and sulfuric acid-based mixtures that were tested, four mixtures (25D75E, 75D25W, 70A30W, and 70A30E) have provided excellent flexibility (26 and 42%) and flattening improvement (74 and 83%) after curing. The same mixtures have also preserved at least 55% of the tensile strength and elastic modulus of the scrap material after chemical treatment and retained almost 96% of the properties when thermally re-cured. However, the 25D75E had shown the most consistent and promising results with 83% flattening enhancement and 96% preservation for the mechanical properties of the scrap material equivalent to almost 65% of the original virgin used composite. Furthermore, no



(a) (b)

Fig. 9 **a** Tensile strength and (**b**) elastic modulus obtained after chemical and thermal treatments additional residues or waste was found from the chemical treatment process using DMF mixtures since no chemical reactions were observed.

Different characterization techniques (FTIR, DSC, TGA, and SEM) were used to observe and analyze the chemical treatment method and the interaction of the four solvents mixtures with the composite. With all the results and analyses that were done, it was feasible to conclude that DMF mixtures diffused into the material causing the specimens to swell and leash-out any untangled polymer chains. The swelling and loosening of the entanglements provided better flexibility but then re-cured after thermal treatment. Sulfuric acid mixtures did not diffuse much into the material but loosen and broke some polymer network entanglements at the surface of the specimens.

Acknowledgements The authors would like to acknowledge the financial support of the National Council for Scientific Research – Lebanon (CNRS-L) and the University Research Board (URB) at the American University of Beirut.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

References

1. Mangalgiri, P.D.: Composite materials for aerospace applications. Bull. Mater. Sci. **22**, 657–664 (1999)
2. Adam, H.: Carbon fibre in automotive applications. Mater. Des. **18**, 349–355 (1997)
3. Pimenta, S., Pinho, S.T.: Pinho. Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook. Waste Manag. **31**, 378–392 (2011)
4. Schinner, G., Brandt, J., Richter, H.: Recycling carbon-fiber-reinforced thermoplastic composites. J. Thermoplast. Compos. Mater. **9**(3), 239–245 (1996)
5. Li, H., Englund, K.: Recycling of carbon fiber reinforced thermoplastic composite wastes from the aerospace industry. J. Compos. Mater. **51**(9), 1265–1273 (2017)
6. Fried, J.R.: Polymer Science & Technology. Pearson Education, United States of America: Hoboken, (2003)
7. Palmer, J., Ghita, O.R., Savage, L., Evans, K.E.: Successful closed-loop recycling of thermoset composites. Composites Part A. **40**, 490–498 (2009)
8. Oliveux, G., Dandy, L., Leeke, G.: Current status of recycling of fibre reinforced polymers: review of technologies, reuse and resulting properties. Prog. Mater. Sci. **72**, 61–99 (2015)
9. Liu, Y., Farnsworth, M., Tiwari, A.: A review of optimization techniques used in the composite recycling area: state-of-the-art and steps towards a research agenda. Clean. Prod. **140**, 1775–1781 (2017)
10. Thomas, C., Borges, P.H.R., Panzera, T.H., Cimentada, A., Lombillo, I.: Epoxy composites containing CFRP powder wastes. Composites Part B. **59**, 260–268 (2014)
11. Ogi, K., Shinoda, T., Mizui, M.: Strength in concrete reinforced with recycled CFRP pieces. Composites Part A. **36**, 893–902 (2005)
12. Wong, K., Rudd, C., Pickering, S., Liu, X.L.: Composites recycling solutions for the aviation industry. Sci. China Technol. Sci. **60**, 1291–1300 (2017)
13. Meyer, L.O., Schulte, K.: CFRP-recycling following a pyrolysis route: process optimization and potentials. Compos. Mater. **43**, 1121–1132 (2009)
14. Pickering, S.J., Liu, Z., Turner, T.A., Wong, K.H.: Applications for carbon fibre recovered from composites. IOP Conf Ser Mater Sci Eng. **139**, 012005 (2016)
15. Piñero-Hernanz, R., Dodds, C., Hyde, J., García-Serna, J., Poliakoff, M., Lester, E., Cocero, M.J., Kingman, S., Pickering, S., Wong, K.H.: Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water. Composites Part A. **39**, 454–461 (2008)
16. Feraboli, P., Kawakami, H., Wade, B., Gasco, F., DeOto, L., Masini, A.: Recyclability and reutilization of carbon fiber fabric/epoxy composites. J. Compos. Mater. **46**(12), 1459–1473 (2011)
17. Xu, P., Li, J., Ding, J.: Chemical recycling of carbon fibre/epoxy composites in a mixed solution of peroxide hydrogen and N, N-dimethylformamide. Compos. Sci. Technol. **82**, 54–59 (2013)

18. Mastali, M., et al.: The impact resistance and mechanical properties of self-compacting concrete reinforced with recycled CFRP pieces. Composites Part B. **92**, 360–376 (2016)
19. Asmatulu, E., Twomey, J., Overcash, M.: Recycling of fiber-reinforced composites and direct structural composite recycling concept. Compos Mater. **48**, 593–608 (2014)
20. Mamanpush, S.H., Li, H., Englund, K., Tabatabaei, A.T.: Dataset demonstrating physical properties of recycled wind turbine blade composites. Data Brief. **20**, 658–661 (2018)
21. Souza, C., Opelt, C., Candido, G., Souza, S.D.B., Botelho, E., Marlet, J.M., Rezende, M.: Reuse of uncured carbon fibre/epoxy resin Prepreg scraps: mechanical behavior & environmental response. ACS Sustain. Chem. Eng. **7**(2), 2200–2206 (2019)
22. Nilakantan, G., Nutt, S.: Reuse and upcycling of thermoset prepreg scrap: case study with out-of-autoclave carbon fiber/epoxy prepreg. J. Compos. Mater. **52**(3), 341–360 (2018)
23. Nilakantan, G., Nutt, S.: Reuse and upcycling of aerospace prepreg scrap and waste. Reinf. Plast. **59**(1), 44–51 (2015)
24. Adams, R.D., Collins, A., Cooper, D., Wingfield-Digby, M., Watts-Farmer, A., Laurence, A., Patel, K., Stevens, M., Watkins, R.: Recycling of reinforced plastics. Appl. Compos. Mater. **21**, 263–284. Aug 2019 (2014)
25. Corcione, C.E., Freuli, F., Frigione, M.: Cold curing structural epoxy resins: analysis of the curing reaction as a function of curing time and thickness. Mater. **7**, 6832–6842 (2017)
26. Gul, S., Shah, A.A., Bilal, S.: Calculation of activation energy of degradation of polyaniline-dodecylbenzene sulfonic acid salts via TGA. J Sci Innov Res. **2**(3), 673–684 (2013)
27. ASTM: D3039 / D3039M-17, Standard test method for tensile properties of polymer matrix composite materials. ASTM International, West Conshohocken (2017) www.astm.org
28. Kong, E.S.: Physical aging in epoxy matrices and composites. In: Dusek, K. (ed.) Epoxy Resins and Composites IV, pp. 125–171 (2005)
29. Hepburn, D.M., Kemp, I.J., Shields, A.J., Cooper, J.: Degradation of epoxy resin by partial discharges. IEEE Proc. Sci. Meas. Technol. **147**, 97–104 (2000)
30. Huang, Y., Ge, Z., Zhao, C., Dong, J., Shitian, M., Ma, W., Wang, G., Qian, X.: Solvothermal recovery of carbon fibers from thermoset polymer-based carbon fiber reinforced polymers. J. Reinf. Plast. Compos. **34**(20), 1673–1683 (2015)
31. Sun, J., Li, H., Wang, C., Yuan, D., Stubbs, L.P., He, C.: The effect of residual solvent N, N′-Dimethylformamide on the curing reaction and mechanical properties of epoxy and lignin epoxy Composites. Macromol. Chem. Phys. **217**, 1065–1073 (2016)
32. Lau, K., Lu, M., Lam, C., Cheung, H., Sheng, F., Li, H.: Thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion. Compos. Sci. Technol. **65**, 719–725 (2005)
33. Ren, Y.K., Liu, S.D., Duan, B., Xu, Y.F., Li, Z.Q., Huang, Y., Hu, L.H., Zhu, J., Dai, S.Y.: Controllable intermediates by molecular self-assembly for optimizing the fabrication of large-grain perovskite films via one-step spin coating. J. Alloys Compd. **705**, 205–210 (2017)
34. Rodríguez-González, J.A., Rubio-González, C., Meneses-Nochebuena, C.A., González-García, P., Licea-Jiménez, L.: Enhanced interlaminar fracture toughness of unidirectional carbon fiber/epoxy composites modified with sprayed multi-walled carbon nanotubes. Compos Interface. **24**, 883–896 (2017)