

AMERICAN UNIVERSITY OF BEIRUT

RECYCLING OF SHELF-CURED PRE-IMPREGNATED
CARBON FIBER LAMINATES

by

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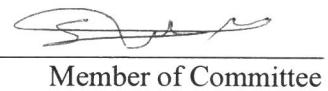
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AN ABSTRACT OF THE THESIS OF

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Composites are light, strong, durable, and corrosion resistant materials that have the potential to offer significant structural and aerodynamic advantages for different applications. One of the most commonly used and reliable composites is the carbon fiber reinforced polymer pre-impregnated with an epoxy resin system, which includes the proper curing agent with a limited shelf life. This composite offers a near-perfect epoxy resin content that maximizes the strength properties of the fabric. This research work investigated a technology that will utilize pre-impregnated composites that were cured over the shelf and never-used, that would otherwise be discarded, which will help in managing the composites wastes. Also, it will reduce the cost of production of new materials when using the recovered end-of-life composites in different applications. Chemical treatment process was used to induce ductility in the scrap specimens to enable its reshaping by soaking them in different solvent mixtures of Sulfuric Acid (H_2SO_4), N, N-Dimethylformamide (DMF), Water and Ethanol. Heat treatment process was conducted to flatten and reshape the scrap composites and to improve its final mechanical properties. This study characterized the mechanical properties of the recycled material and the percentage of the original properties that could be retained. Moreover, the chemical properties were analyzed using Fourier-Transform Infrared Spectroscopy (FTIR) technique, Differential Scanning Calorimetry (DSC) instrument and Thermogravimetric Analysis (TGA). Also, the surface properties were characterized using Scanning Electron Microscope (SEM) and by determining the surface energy of the scrap and the treated specimens. Finally, the adhesion and reshaping of the recycled composites were illustrated to validate the applicability of the proposed recycling technique.

Keywords: Prepregs, Recycling, Mechanical Properties, Chemical Analysis, Surface Properties, Adhesion.

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CHAPTER I

INTRODUCTION

Composite materials are the first among plenty of other materials used in the advanced technology. Resin pre-impregnated fabric (Prepreg) has been used in a wide range of applications without the need to add resin during manufacturing, since it is mainly included in the material [1-2]. It contains the ideal percentage of resin content which is difficult to control in normal hand lamination and thus giving the material its maximum properties. Such materials are easy to use while making the process cleaner with better product quality. However, due to the growth in the production of fiber reinforced polymers many prepreg fabric rolls are left unused and either cure over the shelf or expire before being used.

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 carbon fiber reinforced polymer (CFRP) laminates are ordinarily enriched with thermoplastic or thermosetting resins. While thermoplastics are relatively easy to recycle [4-5-6], thermosetting resins form exceptionally strong crosslinked networks when cured and thus creates a challenge in recycling such materials [7]. All the recycling processes investigated until now fall into one of three processing families [8-9-10]: Mechanical Recycling (MR), Thermal Recycling (TR) and Chemical Recycling (CR) (Figure 1). 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.

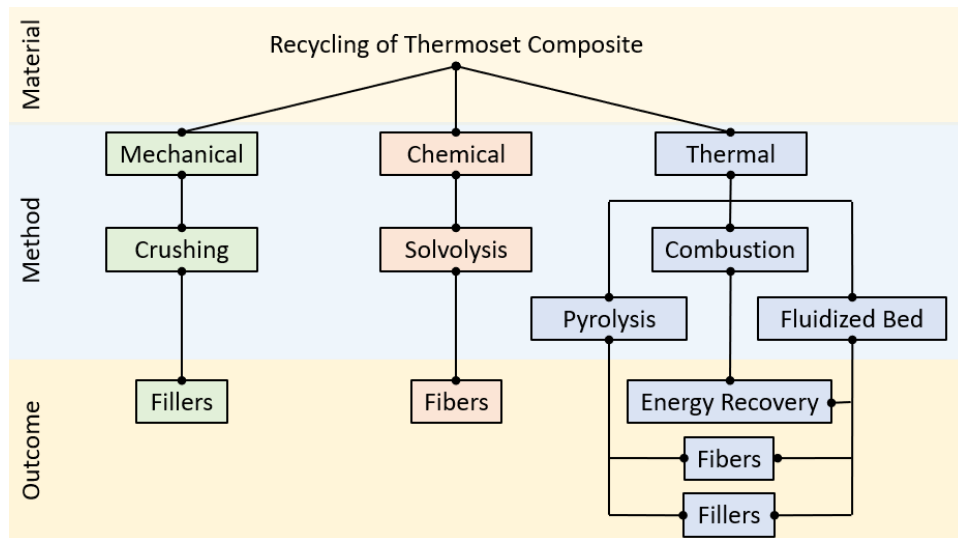


Figure 1: Thermoset fiber composites recycling processes and recyclates.

A. Mechanical Recycling

The initial attempt of recycling thermosetting cured fabrics was to mechanically reduce the size of scrap composite components into millimeter-sized pieces and use them as reinforcing fillers in different products. Researchers have found that the size of the obtained recyclates was affecting 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 [9-11]. The recyclates can be separated into different sizes, each size category can be embedded in specific type of application with the appropriate content percentage and induce a high retention in the mechanical properties [12]. The use of carbon powder recyclate (CPR) in new product can improve the mechanical properties of the

material. Thomas et al. found that the incorporation of 10wt% of CPR in epoxy resin can give the material compressive and flexural strength higher values than that of virgin epoxy resin, also increasing the percentage of the content weight of the CPR can improve more the mechanical properties [13]. For other applications DeRosa et al. found that the recyclate can replace short fibers in Bulk Molding Compounds (BMC), where the remaining long fibers are used as virgin ones, this investigation improves the BMC mechanical properties [14].

Ogi et al. studied the effect of the two parameters (size and content percentage) in the same experiment. They tested the incorporation of three sizes (S(3mm), M(10mm) and L(20mm) specimen length) of carbon fiber reinforced plastic (CFRP) recyclates using different content percentages in new material. The results showed an increase in the compressive strength for the three types with the increase of the content of the recyclate in the CFRP concrete material (Table 1). On the other hand, the flexural strength of specimen increased by the use of the largest volume recyclate, but it decreased with the use of the other smaller two types with the increase of the recyclate content. In addition, the excessive increase in the recyclate content will drop the performance of the material [12]. Similar results were reported by Mastali et al. concerning the compressive strength of 20 coupons of concrete specimens enriched with recyclates, but in this study they found that the flexural strength was improved for all the coupons as they increased the recyclate content in the concrete material [15].

Beside all the advantages of this process, it has its drawbacks which are presented in creating a lack of bonding in the structure and thus producing a weak material by incorporating large pieces in new materials. Also, the use of large recyclates could produce stress concentration in the product and may not give the desired mechanical properties of the virgin material. As

we can see, all of the obtained recyclates from the mechanical process are embedded in new polymer and none of the previous researchers investigated the direct use of recyclates, which is one of our aims in this research.

CFRP size		A (0%)		B (5%)		C (7.5%)		D (10%)	
		Large	Small	Large	Small	Large	Small	Large	Small
Nothing (MPa)	Compressive	1.59	2.48	-	-	-	-	-	-
	flexural	0.26	0.22						
L (MPa)	Compressive	-	-	0.58	0.85	0.86	1.38	1.02	1.02
	flexural			0.06	0.65	0.19	0.69	0.17	0.27
M (MPa)	Compressive	-	-	0.49	1.29	0.69	1.92	0.05	1.27
	flexural			0.26	0.26	0.07	0.83	0.44	1.38
S (MPa)	Compressive	-	-	0.71	1.78	0.94	0.95	1.93	1.84
	flexural			0.28	0.18	0.19	0.32	0.04	0.36

Table 1: Variation of the compressive and flexural strengths with the change of recyclates size and content in mechanical recycling technique [12].

B. Chemical Recycling

Chemical recycling or industrially known as Solvolysis is a technique used to decompose the matrix polymer and reclaim only the fibers [16-17]. The main concept of this process is decomposing thermoset matrix 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 simple chemical process where water and ethanol are the typical and most practical solvents used [18]. The main parameters that affect the obtained recyclates by this chemical process are the concentration of the solution used and the agitation time. And to improve the decomposition process of the matrix, catalysts were used to optimize the solvent properties [17]. Hernanz et al. [19] 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 20.7wt% from the resin. In order to improve the process, they added potassium

hydroxide to the solution and found that the elimination rate of resin increased to 95.4wt%, it also improved the duration of decomposition which decreased from 30 to 15.5 min. Feraboli et al. [20] used sulfuric acid solution with hydrogen peroxide as catalyst to oxidize the epoxy resin at 110°C for several hours. Pinglai et al. [21] 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.

Chemical recycling process mostly requires knowing the type of the matrix polymer in the scrap composite before applying the recycling process. The best decomposing properties and the lowest cost are the two factors that help in choosing the appropriate solvent to be used, since cost saving is a major factor that must be taken into consideration before applying the recycling technique.

C. Thermal Recycling

Reclaiming the high strength fibers from waste resin pre-impregnated fabric has been investigated by many researchers by applying thermal processes to decompose the thermoset matrix [9-10]. Thermal recycling process contains three techniques: combustion, fluidised bed and pyrolysis processes.

Burning the scrap composites is a combustion process used for successful energy recovery. The reinforcements and fillers that are found in composites produce minerals, when burned in cement kilns, can be fused in the cement mixture to improve its properties [22]. However, this procedure has a problem of emitting boron from recycled E-glass fibers, which affects

the cement forming duration in the kiln. On the other hand, other studies found that the incorporation of waste composites containing calcium carbonate filler in the co-combustion of coal decreases the Sulphur emission resulted from the combustion [23]. Beside the advantage of burning the waste composites by getting rid of it, there is a benefit from incorporating the resulting minerals from the combustion of the waste composites in different processes.

Fluidised bed process (Figure 2) which is the second thermal technique for recycling composites produces a fluffy form fiber filaments (Figure 3). This 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 and the gas steam that pulls up the fibers out of the bed. At the end, the recyclates are limited to the fibers only but with high retention in its mechanical properties, which make its incorporation in new matrix valuable.

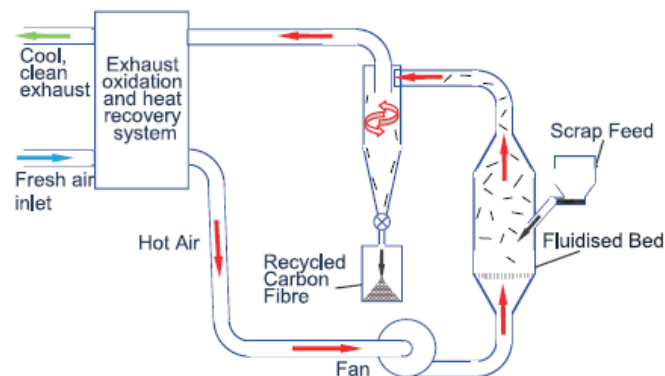


Figure 2: Fluidised bed recycling process scheme [13].

Pickering et al. [24] tested the recovered unstructured fibers obtained from fluidised bed process conducted at different temperatures, the results showed that the tensile strength of the fibers decreases with the increase in the process temperature (Figure 4), noting that working at low temperature slows down the time of the decomposition of composite matrix. A compromise between the tensile strength and the decomposition time should be taken into consideration to choose the appropriate temperature of the process.



Figure 3: Fluffy form fiber filaments [15].

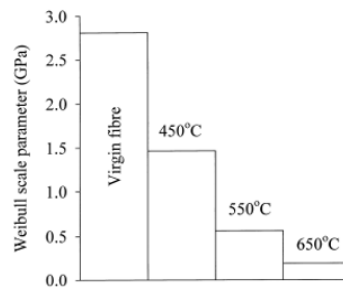


Figure 4: Effect of fluidised bed recycling process temperature on the strength of fibers [14].

Pyrolysis (Figure 5) is another heating process 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 [10]. The properties of fibers recovered by pyrolysis process are affected by the process temperature. Meyer et al. [17] found that working at low pyrolysis temperature

(below 500°C) in air atmosphere produces dirty fibers, although increasing the temperature will decompose the resin residues remained during the process and gives cleaner fibers. They also found that the mechanical properties of the fibers were reduced compared to that obtained at lower temperature. Pickering et al. [24] made a compromise between the pyrolysis temperature and the mechanical properties of the recovered fibers from carbon fiber composites and ends up with a temperature range of 500-550°C for the process to obtain the best results. Recycled fibers can be used as short fibers embedded in new matrix but cannot replace long fibers because of the discontinuity in its structures. We can conclude from what had been researched about this process that the recycle products are limited to the fibers while scraping the matrix.

Recently, researchers have been working on the evolution of thermoset (TS) composite recycling as direct recovery where the scrap materials were used without applying any recycling technique [25], which is the case that matches our aims in this research. Asmatulu et al. used specimens of different shapes from end-of-life (EOL) products such as airplane, cars, ships or other products *as-is* in manufacturing new specimens with smaller volumes like doors, racket, tables, etc. [25]. Englund [26] prepared larger pieces in the 6–7 cm² range from whole wind turbine blades, representing a mix of the various microstructures present in the TS product. The pieces were loaded into virgin epoxy resin at high levels (85–90 wt.%) and the mixture was then thermoformed into sheet products.

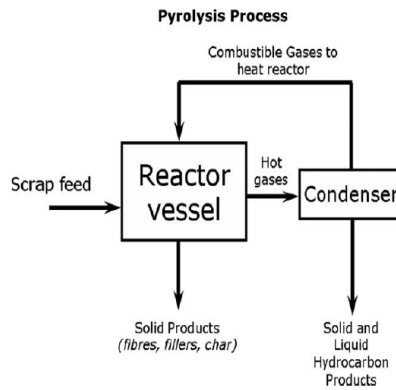


Figure 5: Pyrolysis process scheme [19].

D. Work Needed

None of the technologies mentioned before have focused on fully recycling prepreg CFRP laminates that have cured over the shelf, which presents many challenges specially when cured in its original shipment roll shape. The first challenge is how to induce ductility in the composite laminate to enable remolding, by considering the chemical recycling technique without losing the crosslinked polymer or in such a way recovering as much as possible from it. The second challenge is to improve the mechanical properties of the recycled composites by heat treatment, where the non-crosslinked polymers would be cured and the laminate thermoformed into the desired shape. Highly networked thermosetting polymers, where up to 50% of the chain repeat units are crosslinked, become permanently stiff during their formation and curing process and would not soften upon heating. However, it was shown by Adams et al. [27] that thermoset resins have exhibited some ductile behavior when exposed to an elevated temperature in the range of their Glass Transition Temperature (T_g).

Carbon fiber pre-impregnated composites are considered among advanced composites with excellent mechanical and thermal properties but high manufacturing and processing costs.

The area of optimization of recycled composites is in its climax state and requires a lot of new inventions that should be reached by researchers to develop this domain of optimization [10]. In the future, new recycled composite materials will be developed which will lead to cost and energy savings as a result from the evolution in the design and manufacturing sectors and the invention of new recycling technologies [28]. Manufacturers from different industries have been increasingly focused on cost and environmental consciousness to offer customers low cost services and products and reduce environmental footprint. Recycling pre-impregnated carbon fibers will vastly reduce the amount of waste produced by the consumed industry which will in return cut down the cost of production. This work will solve a waste material challenge before it adds additional burden on the Lebanese garbage crisis and our green environment. It will focus on the type of materials that were cured before being used.

E. Aim

In this study the recycling of shelf-cured pre-impregnated carbon fiber laminates have been investigated by applying different treatment mechanisms using different solvent mixtures of Sulfuric Acid (H_2SO_4), N, N-Dimethylformamide (DMF), Water and Ethanol at room temperature. Several curing cycles were examined to ensure the highest mechanical properties beside obtaining the desired shape. The mechanical properties of the recycled materials were analyzed using Universal Testing Machine (UTM) for tensile strength testing and by measuring the flattening enhancement (%) for flexibility determination. The changing in the composition of the polymer matrix were studied using fourier-transform infrared spectroscopy (FTIR) technique, differential scanning calorimetry (DSC) instrument,

thermogravimetric analysis (TGA) and scanning electron microscope (SEM). Moreover, some applications may require more than one layer of composites or even the bonding of composite to another material. Then, the surface free energy of the recycled materials was calculated using Owens, Wendt, Rabel and Kaelble (OWRK) method after measuring the contact angle using Contact Angle Goniometer (CAG).

CHAPTER II

EXPERIMENTAL APPROACH

A. Materials

Prepreg Carbon Fiber rolls (Figure 6-a) used in this study were provided by *easy-composites* supplier (XPREG XC130 Prepreg Carbon Fiber 12K, 450g, 2/2 Twill,), based on available material at the Laboratory of Smart Structures and Structural Integrity at the American University of Beirut. They were epoxy-based prepreg rolls with a balanced carbon fiber 12K fabric, with service temperature between 90 and 140°C. The rolls were left at room temperature for three years beyond the recommended three weeks out-of-freezer storage life, where they adopted a stiffened cylindrical shape as shown in Figure 6. However, it has an advantage of being cured as a single ply of fabric because of the backing paper covering the fabric, which keeps it from adhering to itself.

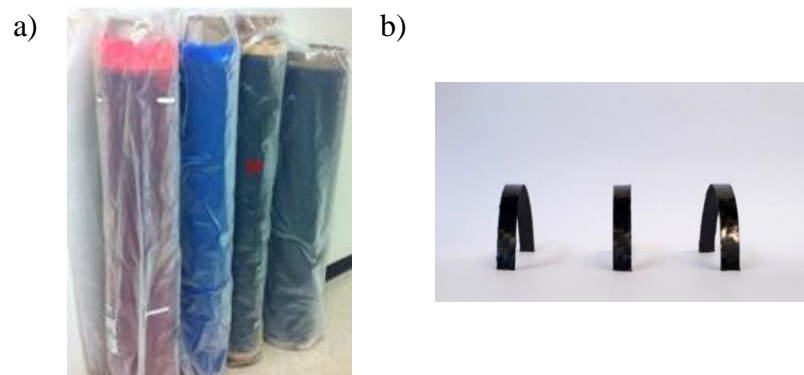


Figure 6: a) Pre-impregnated self-cured rolls and b) Prepared scrap specimens.

The prepreg plies were cut along the roll length into pieces of width 140 mm using a metal cutter. Then, the large pieces obtained were cut into smaller pieces of width 10 mm to obtain the specimens that were used in our study (Figure 6-b).

The solvents used for chemical treatment were Distilled water (H_2O), Ethanol absolute (C_2H_5OH) $\geq 99.8\%$, N, N-Dimethylformamide ($(CH_3)_2NC(O)H$) $\geq 99.8\%$ and Sulfuric Acid (H_2SO_4) with purity 95%.

B. Recycling Technique

The recycling technique have been investigated by the use of two step recycling processes. The first step was a chemical treatment process, where the scrap composites were soaked into solvent mixtures at room temperature. The second step was a heat treatment process, where the chemical treated composites were re-cured in the oven, to obtain a recycled composite that can be used as-is in several applications.

1. Chemical Treatment

Chemical treatment process was used to induce ductility in the scrap specimens to enable its reshaping from its already cured form. The effect of different chemicals on the polymer network of the scrap composites were examined. The chemical treatment technique is shown in Figure 7-a. An experiment was designed by putting the scrap composite specimens into 150mm petri dish filled with 80mL of solvent and covered. All the specimens used in this study were 140 x 10 x 0.6 mm (length x width x thickness). The application of chemical treatment process is shown in Figure 7-b. The samples were soaked in the solvent by applying

a pressure of 1840 Pa to ensure complete immersion and flattening. Then, the whole setup was placed into large Pyrex pot and closed to prevent the solvent from evaporation.

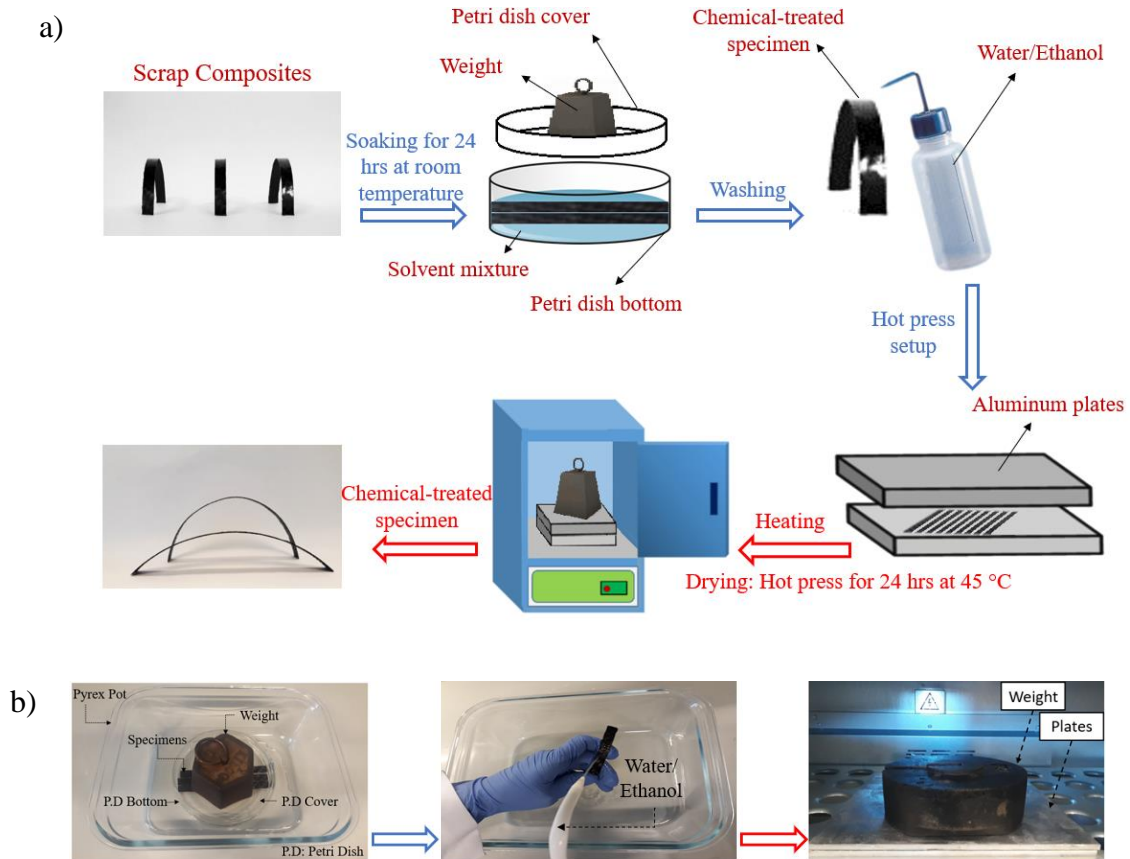


Figure 7: a) Chemical treatment process and b) chemical treatment application.

In order to reshape without damaging the composite structure, a series of solvent mixtures with various compositions were tried using water, ethanol, H_2SO_4 and DMF (Table 2). The influence of solvents on the specimens was evaluated using different time intervals: 1 hr, 2 hrs, 3hrs and 4 hrs. After removing the specimens from the solvent, an inconsistency in the flexibility and in the strength of the specimens were noticed. So, a time interval of 24hrs was adopted to ensure the full treatment of the specimens. For each solvent mixture three

specimens were treated. After removing the specimens from the solvent, they were rinsed thoroughly with water or ethanol depending on the solvent used for treatment. Then, they were dried by heat press, which consists of two flat metallic plates pressing the specimens that were covered with release films and placed inside a vacuum bag while applying a vacuum pressure of 1110 Pa in the oven at 45°C for 24hrs.

Type	Solvents mixture	Type	Solvents mixture
100D	100% DMF	100A	100% H ₂ SO ₄
25D75W	25% DMF - 75% Water	30A70W	30% H ₂ SO ₄ - 70% Water
50D50W	50% DMF - 50% Water	50A50W	50% H ₂ SO ₄ - 50% Water
75D25W	75% DMF - 25% Water	70A30W	70% H ₂ SO ₄ - 30% Water
25D75E	25% DMF - 75% Ethanol	30A70E	30% H ₂ SO ₄ - 70% Ethanol
50D50E	50% DMF - 50% Ethanol	50A50E	50% H ₂ SO ₄ - 50% Ethanol
75D25E	75% DMF - 25% Ethanol	70A30E	70% H ₂ SO ₄ - 30% Ethanol

Table 2: The solvent mixtures used for chemical treatment.

2. Heat Treatment

Press heating process was performed to flatten the cured composites and increase its strength. After performing the chemical treatment process, the heat treatment process (Figure 8) was followed to cure the remaining non-crosslinked polymers and to post-cure the already cured polymers that were crosslinked at room temperature. The experimental setup is the same as the drying process. However, the specimens were heated using different heating cycles shown in Table 3 to investigate the dependency of the flexibility, tensile strength, and polymer composition of the specimens on the re-curing cycle. The heating cycles were

chosen in a way to minimize the original curing cycle (C4) of the virgin prepreg carbon fiber by *easy-composites*, since part of the polymer network was crosslinked during its room temperature self-curing.

Name	Heating Cycle
C1	1 hr at 70 °C-1 hr at 120 °C
C2	2 hr at 70 °C- 1 hr at 120 °C
C3	3 hr at 70 °C- 1 hr at 120 °C
C4	4 hrs at 70 °C- 1 hr at 120 °C
C5	1 hr at 120 °C

Table 3: Heating cycles for heat treatment.

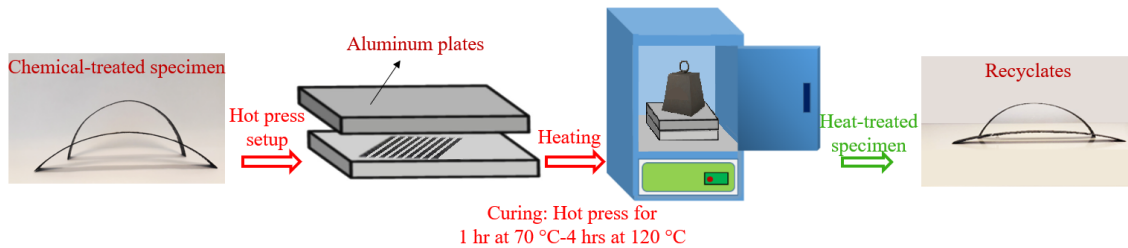


Figure 8: Heat treatment process.

CHAPTER III

CHARACTERIZATION AND RESULTS

A. Mechanical Properties

1. Flexibility

As it was mentioned in the previous chapter, all specimens to be tested have adapted a curved shape as shown in Figure 6b. To evaluate the flexibility of the recycled material, percentage of flattening enhancement of each specimen after treatment was investigated. It was the first factor that was taken into consideration to choose among the different mixtures tried for chemical treatment. Pure DMF (100D) and pure acid (100A) solvents were found to be the most effective solvent on the epoxy thermoset structure. 100D solvent caused the specimens to swell and fully loosen the entanglement in its network after a short time of soaking the scrap specimens in the solvent (Figure 9-a). While, Figure 9-b shows the effect of 100D on well-cured material, where no changes were recorded since all the polymeric chains are fully crosslinked. On the other hand, 100A fully degraded the matrix of scrap material and well-cured as well and only the fibers were remained (Figure 9-c). It was also noticed that 75% DMF - 25% Water mixture (75D25E) had the same effect as 100D (Figure 10-a). Other solvent mixtures 25D75W, 50D50W, and 50D50E did not degrade the resin but had small effect on the flexibility of the scrap specimens with 5% to 15% flattening enhancement, respectively (Figure 10-b, c, d). Meanwhile, 75D25W and 25D75E introduced very ductile and flexible scrap composites, and the height of the scrap specimens improved by 36.6% and 41.5% after the chemical treatment which can be seen in Figures 10-e and 10-f.

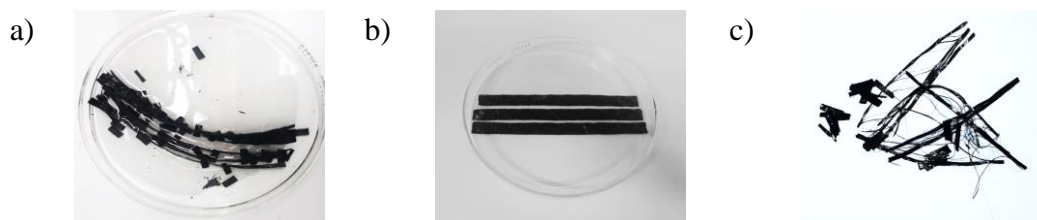


Figure 9: The effect of 100D on a) the scrap material and b) well-cured material and c) the effect of 100A on scrap material.

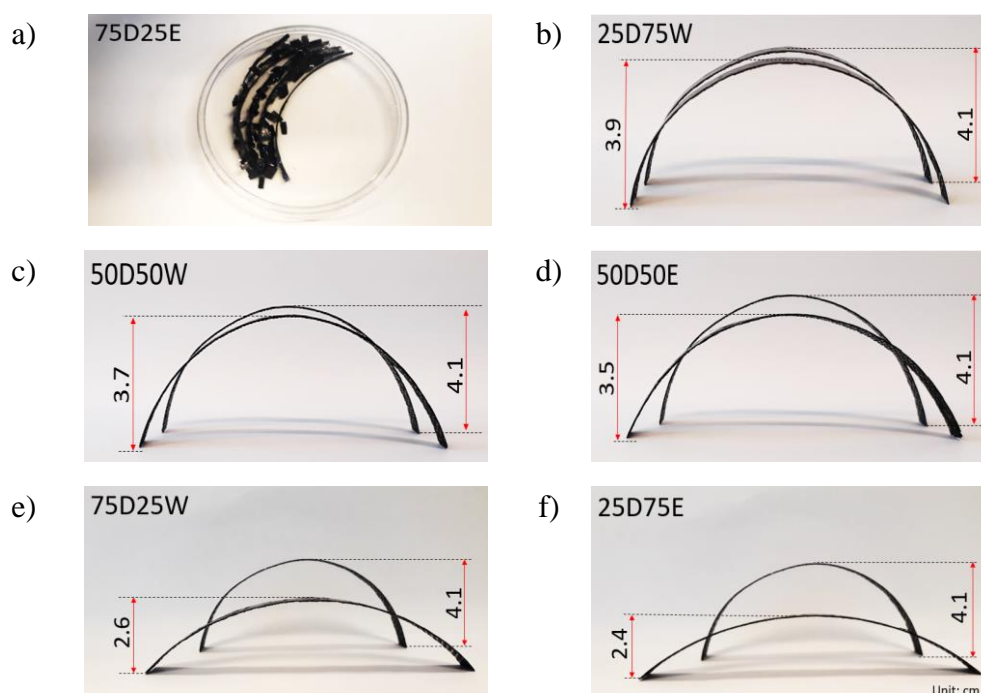


Figure 10: Comparison of the height of the scrap and chemical-treated composites with DMF solvent mixtures: a) 75D25E, b) 25D75W, c) 50D50W, d) 50D50E, e) 75D25W and f) 25D75E.

On the other hand, the flexibility of the specimens that were treated with acid were not affected evidently, where the highest reduction recorded by 30A70W and 30A70E were 32% and 27% flattening enhancement, respectively (Figure 11-a, b). Moreover, 70A30W,

70A30E, and 50A50W had similar flattening enhancement around 12% (Figure 11-c, d, e). Whereas, the lowest flattening enhancement of 5% was recorded by 50A50E (Figure 11-f).

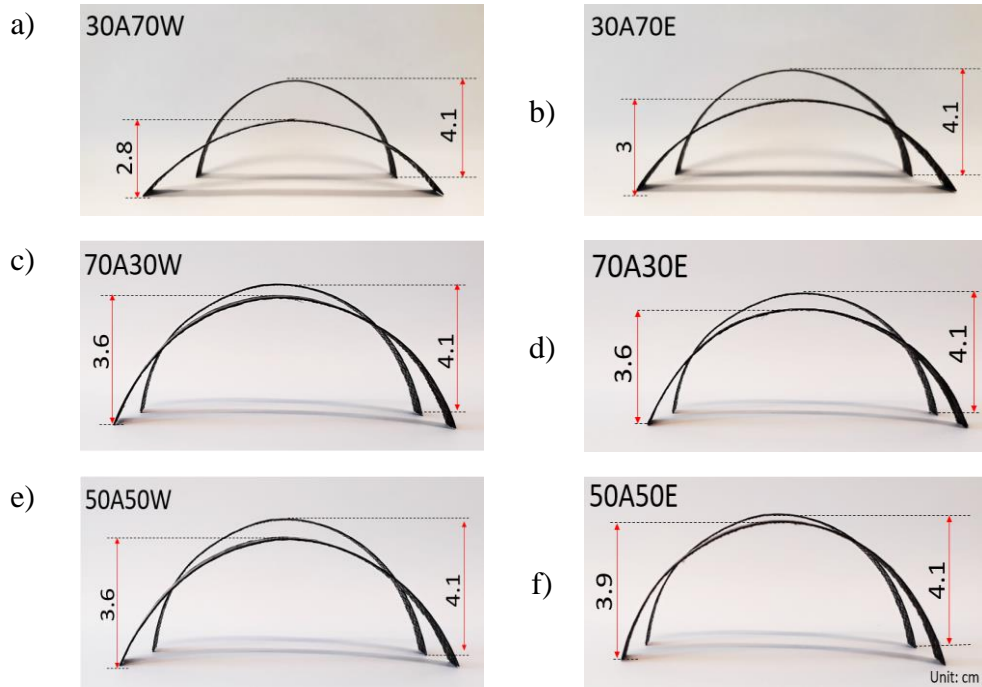


Figure 11: Comparison of the height of the scrap and chemical-treated composites with H₂SO₄ solvent mixtures: a) 30A70W, b) 30A70E, c) 70A30W, d) 70A30E, e) 50A50W and f) 50A50E.

Figure 12 shows the flattening enhancement in (%) for the scrap specimens treated with the solvent mixtures that were chosen according to their best effect on the flexibility. 25D75E has the highest flattening enhancement with 38.2% followed by 75D25W with 36.6% and 30A70W with 32% and the lowest flattening enhancement was for 30A70E with 27% only.

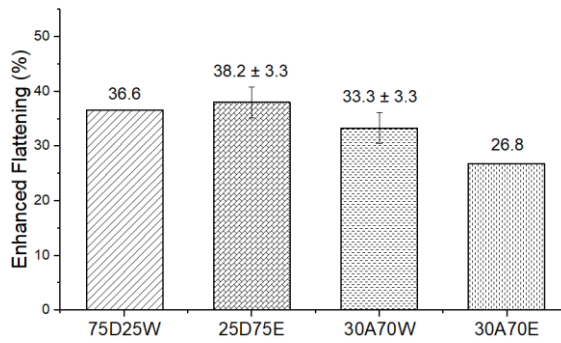


Figure 12: Enhanced flattening (%) after chemical treatment.

Figure 13a compares the height of the scrap specimens with the re-cured chemical-treated specimens (heat-treated specimens). The value mentioned for each type is the average height of the specimens cured using different heating cycles (Table 3). 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% which revealed a great improvement (Figure 13b).

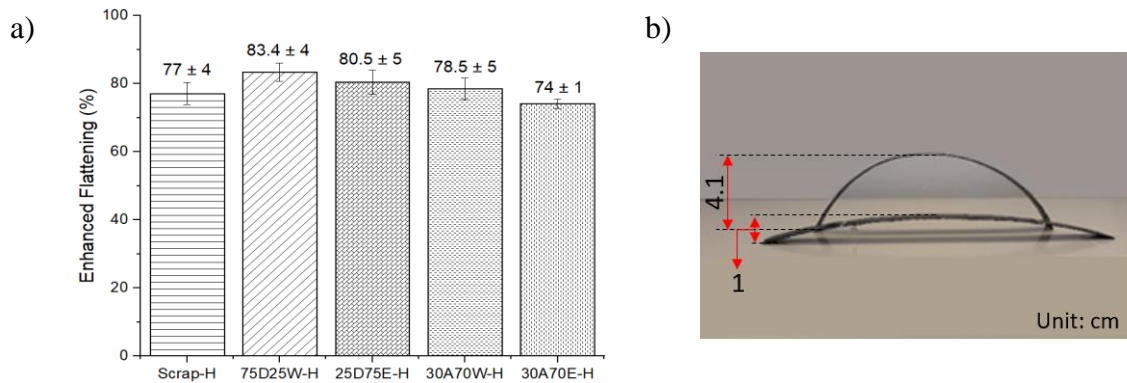


Figure 13: a) Flattening enhancement (mm) after heat treatment for all chemical treated types, b) Average flattening enhancement after heat treatment.

2. Tensile Strength

Universal Testing Machine (UTM) was used to conduct a tensile test on the treated specimens using 10 KN load cell and crosshead speed of 2 mm/min according to ASTM D3039 standard [29] (Figure 14). Three specimens for each type of chemical and heat treatment in addition to non-treated scrap was cut, shaped, and tested. Where, the composite specimen of dimension 14 x 1 cm was held by the two grips with a gage length equal to 8 cm confined by two reflective tapes used to monitor the strain elongation by the extensometer laser.

First the chemically treated samples with the four chosen mixtures (75D25W, 25D75E, 30A70W and 30A70E) were tested to investigate the effect of each mixture on the mechanical strength of the treated specimens. The obtained results were compared to the tensile strength of the well-cured material, given in the datasheet of the virgin material (Figure 15) (Appendix A). As seen from figure 15, the raw data of the scrap material shows a decrease of about 25% in tensile strength and elastic modulus of the virgin material and thus preserving about 75% of these mechanical properties. After chemical treatment, the material lost some of its strength but not more than 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% to 23%, respectively. This decrease is accompanied with a drop in the elastic modulus by half. This drop in the mechanical properties may be attributed to the wetting of the specimens due to the presence of water. However, the mechanical properties for the specimens treated with 25D75E was not noticeably affected, where the tensile strength has dropped by 5% and its elastic modulus by 3%. The tensile strength of the specimens treated with 30A70E dropped by 15% and its elastic modulus by

25%. Here, the drop in the mechanical properties may be attributed to the breakage in some of the crosslinked chains.

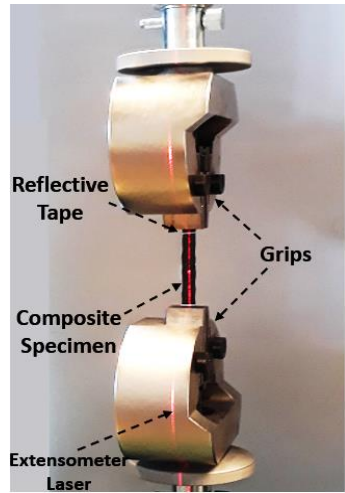


Figure 14: Actual setup for tensile testing.

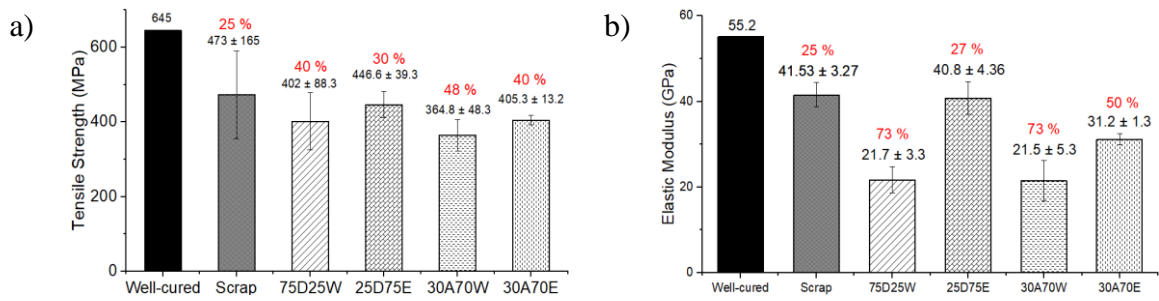


Figure 15: a) Tensile strength and b) Elastic modulus of well-cured, scrap and chemically-treated specimens.

The tensile strengths of heat-treated specimens at different re-curing cycles (Table 3), after chemical treatment, are shown in Figure 16 with further detailed data in Appendix B. As shown, the tensile strength was highest when using cycle C4 for all the treated specimens which is the required curing cycle of the virgin composite material used. Knowing that the

flattening enhancement of the specimens was the same among all cycles, and since C4 has given the highest tensile strength, it was chosen as the ultimate heat treatment cycle to obtain the strongest and most flexible recycle.

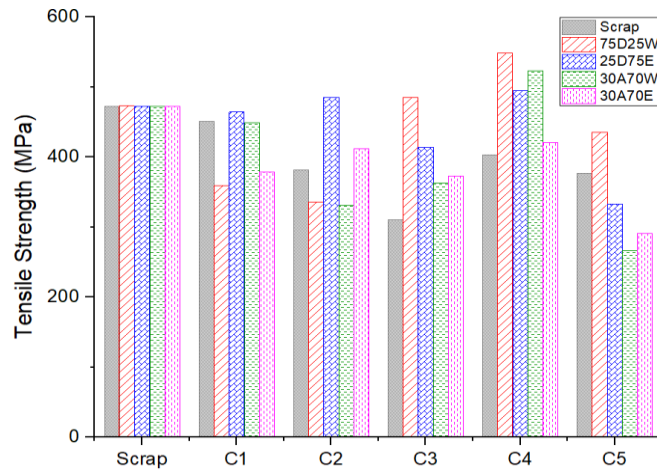


Figure 16: Tensile strength of heat-treated specimens.

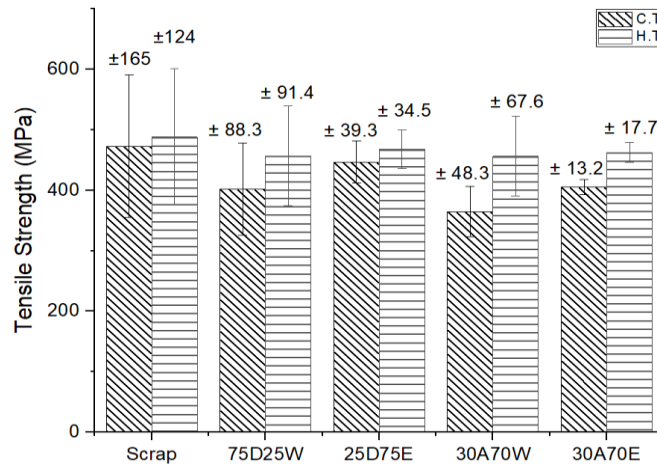


Figure 17: Comparison of the tensile strength obtained after chemical (C.T) and heat treatment (H.T) processes.

Figure 17 shows a comparison of the tensile strength obtained after chemical and heat treatment techniques. The tensile strength of the scrap heated specimens increased compared

to the scrap specimens, which explained that the non-crosslinked polymers found in the scrap composites had been cured during heating or/and the cured polymers at room temperature may be undergoes post curing. The tensile strength of the treated specimens was increased after heat treatment for all the types to reach nearly the same strength which is slightly lower than that of the scrap heated specimens, however heat treatment had increased more the tensile strength of the specimens treated with acid solvent mixtures.

B. Chemical Properties

1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) technique is widely used in polymer science. It was used in this study to compare the absorbance spectrums of the scrap and the treated specimens to monitor the change in the structure of the polymer at the surface and to understand more the treatment and degradation mechanisms. Figures 18, 19 and 20 shows the FTIR spectrums of well-cured, scrap, chemical-treated and heat-treated specimens. The changes in the functional groups appeared mainly in the wavenumber range $650\text{-}1600\text{ cm}^{-1}$ and at 3340 cm^{-1} .

First, if we compare the spectrum of well-cured and scrap composites (Figure 18), we can see that there is a band appeared at 910 cm^{-1} in the scrap spectrum while it is not found in the well-cured spectrum. The appearance of this band which corresponded to the epoxy ring absorption band [30] is a direct explanation of the presence of non-crosslinked monomers in the scrap composites.

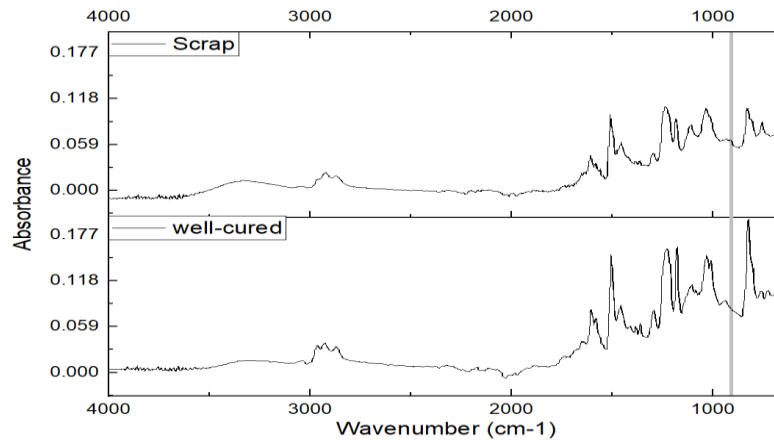


Figure 18: FTIR spectrums of well-cured and scrap composites.

Figure 19 shows the spectrums of the chemical-treated composites compared to the spectrum of scrap composite. After the chemical treatment of the scrap composites using different solvent mixtures, the absorbance value of the bands 769, 910, 1122 and 1241 cm^{-1} decreased comparing it to the absorbance values of the scrap specimen. This decrease ensures that during the chemical treatment we had getting rid of some of the non-crosslinked polymers. Acid had more effect on decreasing the intensity of the bands 1122 and 1241 cm^{-1} attributed to C-O stretching vibration band [31] and DMF had more effect on decreasing the intensity of band 769 cm^{-1} attributed to C-H bending vibration bands of substituted benzene cycle of epoxy resin [32] and of the band at 910 cm^{-1} .

On the other hand, new band at 1662 cm^{-1} appeared when using the solvent mixtures that contain DMF corresponded to carbonyl group C=O [33]. This enlightened the presence of DMF in the specimen even after washing and drying it, and the replacing of the non-crosslinked polymers which appeared in the decreasing of the intensity of the bands at 769 and 910 cm^{-1} related to epoxy resin. Moreover, new bands at 872 and 1066 cm^{-1} appeared

after using the solvent mixtures that contain sulfuric acid. These bands attributed to asymmetric S-O-C stretching vibration (872 cm^{-1}) [34] and to SO_2 symmetric stretch band (1066 cm^{-1}) [34]. The presence of new bands can be explained either by the theory that H_2SO_4 had broken down some of the crosslinked chains, or that H_2SO_4 had been reacted with the non-crosslinked monomers. As a result, we can conclude that sulfuric acid oxidized the surface but DMF only penetrated inside the material. The increase in the absorbance value of the band at 3411 cm^{-1} which represent the hydroxyl group is attributed to the absorbance of water, ethanol and moisture .. [31].

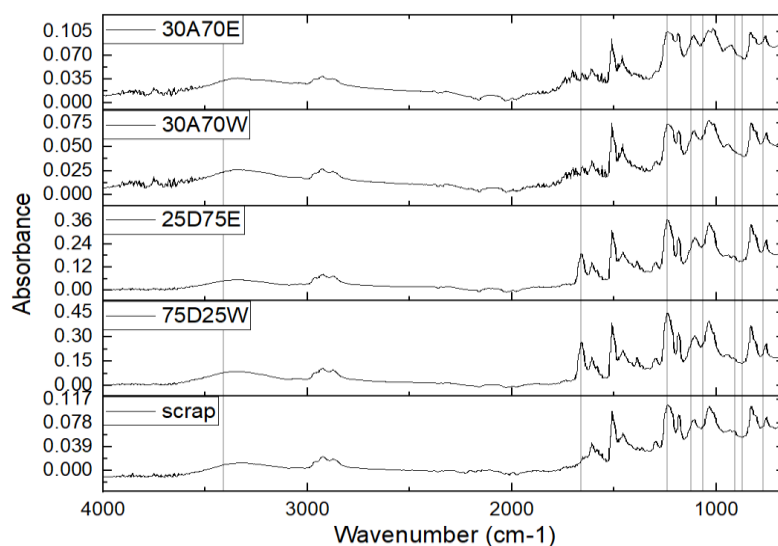


Figure 19: FTIR spectrums of scrap and chemical-treated specimens.

Heat treatment had slight effect on the chemical-treated specimens (Figure 20). The absorbance values of the bands at 910 , 1122 and 1241 cm^{-1} were decreased slightly for all the specimens treated with H_2SO_4 which ensures that acid limited the curing during heat treatment. On the other hand, the specimens treated with DMF showed an extensive decrease

in the absorbance value of the band 1662 cm^{-1} related to carbonyl group which happened with an extensive decrease in the value of absorbance bands at 910 , 1122 and 1241 cm^{-1} . The decrease of carbonyl group is related to the evaporation of some of DMF compound after heating to $120\text{ }^{\circ}\text{C}$ noting that the boiling point of DMF is $154\text{ }^{\circ}\text{C}$. The noticeable decrease in the other bands shows high degree of curing of the remained non-crosslinked polymers.

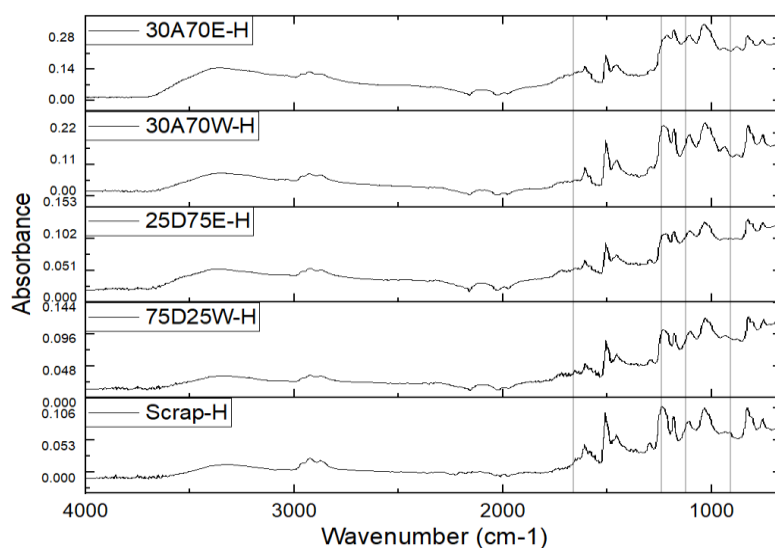


Figure 20: FTIR spectrums of heat-treated specimens.

2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature of the scrap and treated composites. Specimens were added to aluminum pans and analyzed using three thermal cycles Heat/Cool/Heat respectively, with heating rate of $10^{\circ}\text{C}/\text{min}$ and cooling rate of $20^{\circ}\text{C}/\text{min}$, in a nitrogen atmosphere. Analysis were always carried out with a reference empty cell from room temperature up to $250\text{ }^{\circ}\text{C}$.

From the DSC thermograms of un-cured, well-cured and scrap specimens (Figure 21), curing exothermic peak was not observed using well-cured composite in the first heating cycle, whereas it was noticed in the scrap composite confirming the incomplete curing of epoxy networks. The glass transition temperatures (Table 4), obtained by the method of the middle point of the slope on shifting, for the well-cured composite is 121°C and for the scrap composite is 60.2 °C appeared in the first heating cycle. The endothermic peak appeared near the glass transition temperature of the scrap composite is the relaxation enthalpy of the molecules due to the thermal stresses induced in the material during room temperature curing. The huge variation in the transition temperatures is the result of the curing temperature adopted. The well-cured composites were cured at 120 °C for 1 hour resulted a transition temperature 121°C, whereas the scrap composites were cured at room temperature for 3 years resulted a transition temperature 60.2 °C. Also, the decrease in transition temperature can be affected by the incomplete curing of the scrap composite at room temperature. In order to measure the degree of curing (α) of the scrap composite, Eq. 1 [35] was used as follows:

$$\alpha = \frac{H_0 - H_t}{H_0} \quad (1)$$

Where, H_0 is the heat of reaction measured for the un-cured composite obtained from the first heating cycle (Figure 21-a) and it is found to be (about 115.5 W/g) and H_t is the residual heat of reaction for the scrap composite obtained also from the first heating cycle and it is (about 37.05 J/g). The calculation showed that the degree of curing of scrap composite is 68%. So, 32% of un-cured polymers were still present in the scrap material. On the other hand, if we take a look on Figure 21-b for the second heating cycle of un-cured and scrap composites,

we can find that there are no exothermic peaks which ensures the complete curing of it to validate the previous calculation.

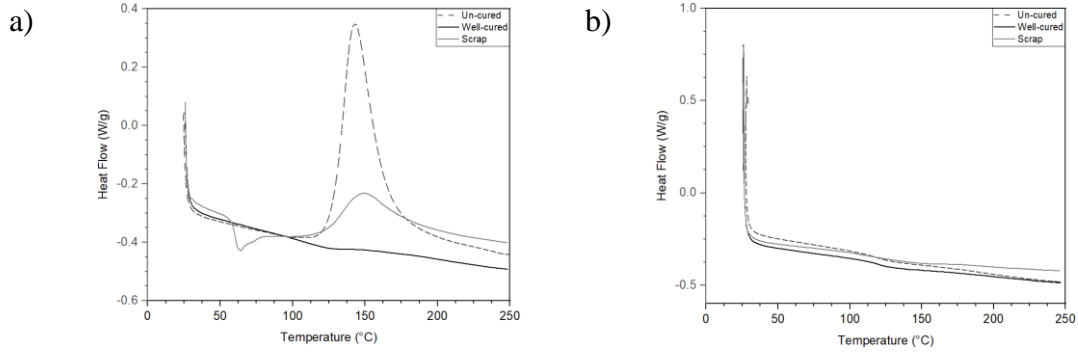


Figure 21: DSC thermograms of Un-cured, Well-Cured and Scrap composites a) First and b) Second heating cycle.

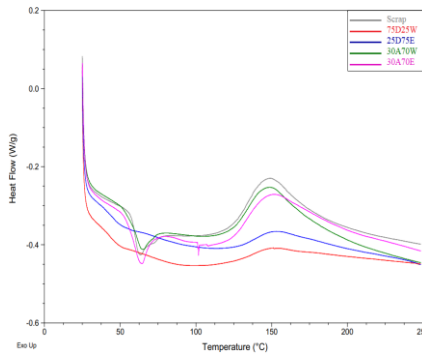


Figure 22: DSC thermograms of chemical-treated composites.

Figure 22 shows DSC thermograms for the chemical-treated composites compared to the scrap composite. We can notice that the relaxation enthalpy tended to disappear in the thermograms of the specimens treated with DMF, also the exothermic peaks were significantly decreased for the two types 75D25W and 25D75E. The transition temperatures shifted 16 °C when treated with 75D25W and 14 °C when treated with 25D75E lower than the scrap Tg. This explained that DMF encouraged the specimens to swell and relax and leached-out of the material some of the non-crosslinked polymers.

As an evidence of the role of DMF solvent mixtures in leaching-out the non-crosslinked polymer, the solvents that were used for chemical treatment were heated for 1 hour at 155 °C (above the boiling point of DMF, water and ethanol) (Figure 23-a). A layer of cured epoxy was formed in the bottom of the petri dish where it was characterized using FTIR and the results showed that it is epoxy Bisphenol A (Figure 24). The percentage of the non-crosslinked polymers that were leached-out the material was calculated using Eq. 1. where, H_0 is the residual heat of reaction for the scrap composite (37.05 J/g) and H_t is the residual heat of reaction for treated composite (about 11 J/g for 75D25W and 14.5 J/g for 25D75E) obtained from the thermogram curves of Figure 22. The calculations showed that the remaining non-crosslinked polymers in the material were (30% for 75D25W and 39% for 25D75E). As a result, we were losing more than 60% of the non-crosslinked polymers in the solvent mixtures. This can be seen also from the loss in the weight of the specimens after chemical treatment (Figure 25)

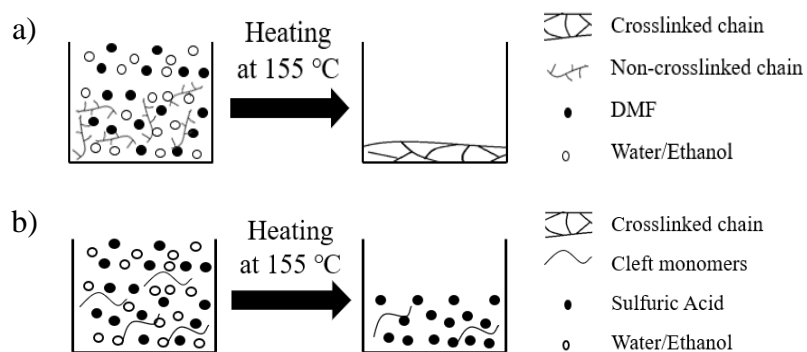


Figure 23: Heating a) the DMF and b) the sulfuric acid solvent mixtures used for chemical treatment.

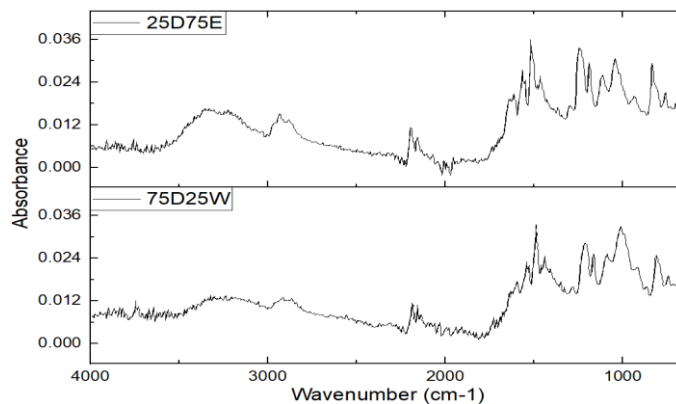


Figure 24: FTIR spectrums of the epoxy cured at the bottom of petri dishes after heating the DMF solvent mixtures used for chemical treatment.

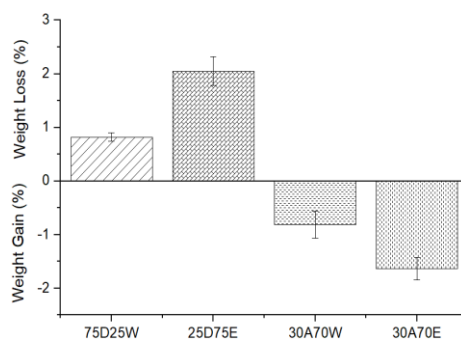


Figure 25: Specimens weight change after chemical treatment.

On the other hand, no obvious changes in the relaxation enthalpies of the specimens treated with acid. And, the exothermic peaks were slightly decreased for the two types 30A70W and 30A70E with higher percentage for the latest with no effect at all on the transition temperature. The acid solvent mixtures used for treatment were heated also at 155 °C (above the curing temperature of epoxy) for 1 hr (Figure 23-b), to deduce whether a layer of epoxy will be formed at the bottom of the petri dish. Knowing that the solvent will not evaporate since the boiling point for acid is 337 °C, we avoided heating to this temperature since it is near the degradation temperature of epoxy \approx 400 °C. As a result, no cured epoxy layer formed in the petri dish which confirmed that acid didn't penetrated in the specimens and the non-

crosslinked monomers were not leached out of the material. Also, we can see a weight gain in the specimens after treatment (Figure 25), which can be attributed to the presence of some residuals even after drying.

After the heat treatment, DSC was used also to monitor the change and the effect of the treatment on the transition temperatures of the composites. Figure 26 shows the DSC thermograms of the heat-treated composites. We can notice even after the use of heating cycle given by the company; the full curing wasn't achieved since a small exothermic peak is still appearing in the DSC thermograms for all the types (Figure 26-a) with a very slight increase in the transition temperature (Table 4). This can be explained by the presence of penetrated solvents in the treated specimens, which affected the curing process. However, if we take a look on the DSC thermograms of the second heating cycle (Figure 26-b), we can see that the transition temperatures were obviously increased in the range 100-120 °C for all the types. So, a post curing cycle is recommended to obtain a higher transition temperature.

Type	T _g (°C)	Type	T _g (°C)
Well-Cured	121	-	-
Scrap	60.2	Scrap-H	61.1
75D25W	43.84	75D25W-H	59.04
25D75E	46.37	25D75E-H	54.11
30A70W	60.57	30A70W-H	67.41
30A70E	60.27	30A70E-H	63.61

Table 4: Transition temperatures (T_g) of well-cured, scrap and treated composites.

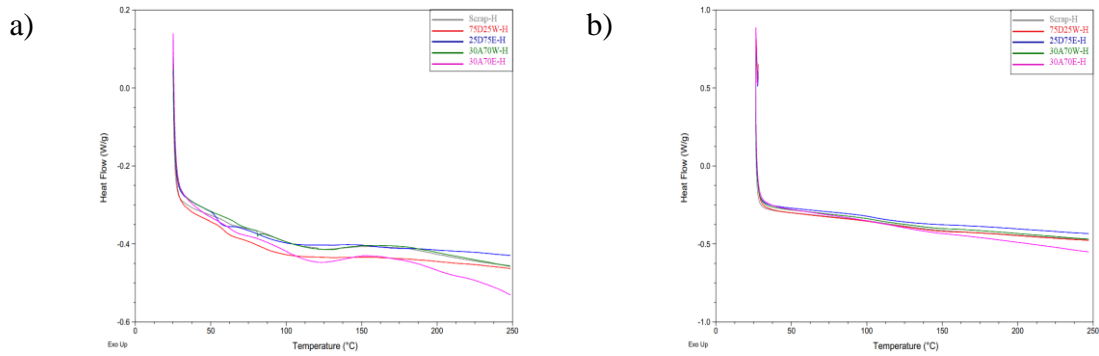


Figure 26: DSC thermograms of heat-treated composites a) First and b) Second heating cycle.

3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to study the thermal stability of the scrap and treated specimens by monitoring the change in the mass of the specimens as a function of temperature in nitrogen atmosphere with a heating rate 10 °C/min from 30 °C to 1000 °C. A specimen mass of about 8 mg was used. The initial degradation temperature (IDT), the maximum weight loss rate (R_{max}) and the temperature at maximum rate of weight loss (T_{max}) were taken from the differential thermogravimetric (DTG) thermograms (Figures 27-b, 28-b and 29-b) and summarized in Tables 5 and 6. The activation energy E_a (Tables 5 and 6) for epoxy degradation was also calculated using Horowitz and Metzger method. The activation energy was obtained from the slope of the plot (Figure 30) of double logarithm of the reciprocal of the weight fraction versus temperature using the equation as follows [36]:

$$\ln\left[\ln\left(\frac{W_0 - W_f}{W_t - W_f}\right)\right] = \frac{E_a}{RT_s^2} \theta \quad (2)$$

Where,

W_0 : The initial weight of the sample

W_f : The final weight of the sample

W_t : The weight of the sample at temperature t

E_a : Activation energy

R : Gas constant

T_s : Reference temperature

$$\theta = T - T_s$$

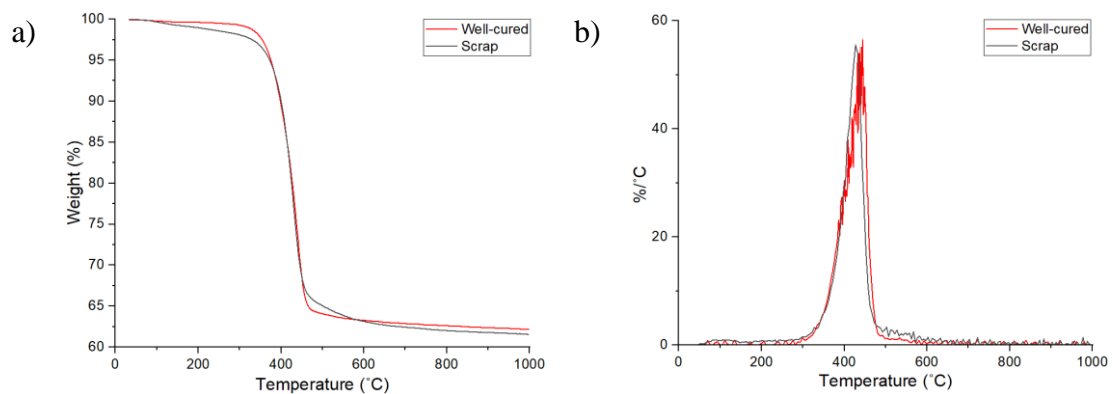


Figure 27: a) TGA and b) DTG curves of well-cured and scrap composites.

The thermograms of well-cured and scrap composites are shown in Figure 27-a. Based on the TGA thermograms, the decomposition of scrap and well-cured materials was considered as single stage in the region 270-500 °C, which is related to epoxy degradation. Some of the scrap material was decomposed before the epoxy degradation started at 282 °C which explained the presence of non-crosslinked monomers in the scrap material corresponds to about 2% of the weight of the material. Unlike the well-cured material that remained stable

without degradation before the starting of its decomposition at 292 °C, which is an evidence of the high cross-linking density. The weight loss attributed to epoxy decomposition had shifted to lower temperature T_{max} and the IDT also decreased (Table 5) which clarified a lower thermal stability in the scrap material. However, no big difference in the weight loss rate R_{max} , and the activation energy for scrap material decreased by 5 KJ/mol.

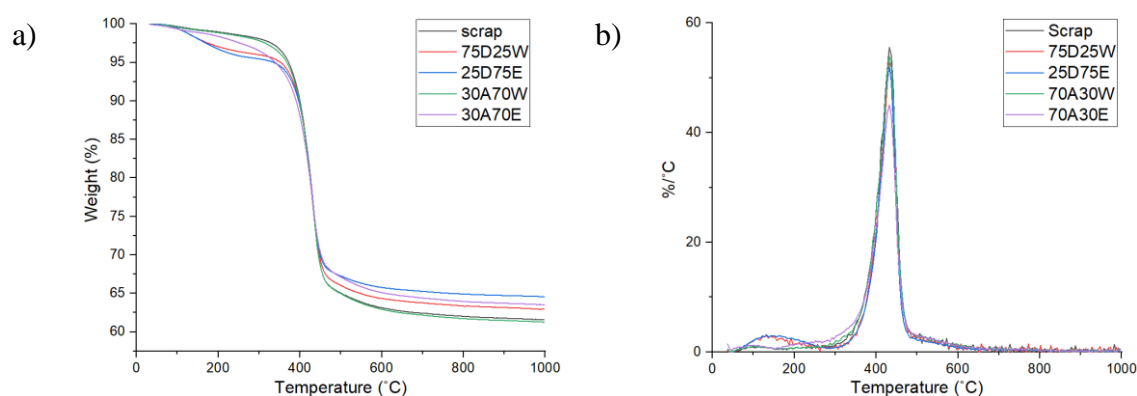


Figure 28: a) TGA and b) DTG curves for chemical-treated composites.

	IDT (°C)		T_{max} (°C)		R_{max} (%/°C)		E_a (KJ/mol)	Char Yield (%)
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 2	
Well-Cured	-	292	-	444	-	56	50.8	62
Scrap	-	282	-	432	-	55	45.7	61
75D25W	47	282	132	432	3	53	41.7	63
25D75E	47	282	132	432	3.2	52	40.8	64.5
30A70W	-	282	-	432	-	54	44.5	61
30A70E	-	282	-	432	-	45	37	63.5

Table 5: Thermal stability and degradation parameters of the chemical-treated composites.

Figure 28-a shows the TGA curves for chemical-treated composites. The thermogram curves of the specimens treated with solvent mixtures that contain DMF were divided into two stages of decomposition. The first stage is in the region 50-250 °C, which may be related to some residuals that were not evaporated like DMF [34]. The IDT is 47 °C and T_{max} is 132 °C for the two solvent mixtures 25D75W and 75D25E (Table 5). The second stage for the same specimens is in the region 270-500 °C is related to the decomposition of epoxy started at the same initial decomposition temperature (IDT) as scrap material and have the same T_{max} also. The maximum weight loss rate (R_{max}) of the specimens treated with DMF were close to that of scrap with a slight decrease, and the activation energy also decreased by about 4-5 KJ/mol comparing it to the scrap composite. This change may be attributed to the relaxation of the material after chemical treatment.

The thermogram curves of the specimens treated with H_2SO_4 solvent mixture have only a single stage decomposition that represent the epoxy degradation. The IDT and T_{max} are the same as the scrap material in the curves of the two types. Whereas, R_{max} and E_a values for the specimens treated with 70A30W solvent mixture is close to that of the scrap material with a decrease of only 1 %/°C and 1 KJ/mol, respectively. This explains that 70A30W has a very weak effect on the scrap material. However, the decomposition of the specimens treated with 30A70E started before the degradation of epoxy by 3% of its weight. This decrease may be also related to some solvents that were not evaporated like H_2SO_4 that was used for treatment or other compounds that were appeared from the reaction of acid with the scrap material. The maximum weight rate loss (R_{max}) of epoxy decreased to 45 %/°C and the activation energy

to 37 KJ/mol, this obvious drop explicated that the acid broke down some of the crosslinked chains.

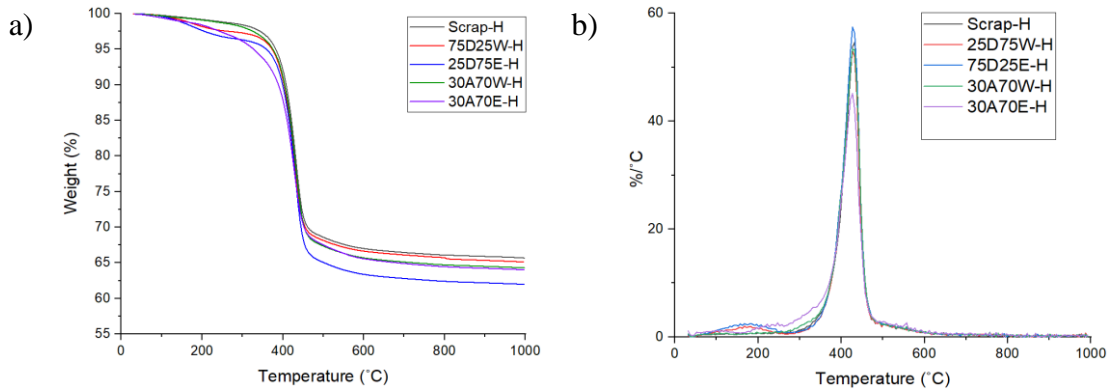


Figure 29: a) TGA and b) DTG curves for heat-treated composites.

Figure 29-a shows the TGA curves for the heat-treated composites. All the thermograms are identical to that obtained from the chemical treatment alone. The main difference can be observed in the activation energy where it was increased for all the types confirming the curing of new polymers (non-crosslinked polymers) in the materials. Moreover, as we can see in Figure 29-a, the decomposition of the materials treated with 75D25W and 25D75E happened also at two stages even after heating which illustrated the presence of a compound that has a boiling point above 120 °C. However, the heat treatment shifted the T_{max} of the first stage of decomposition using DMF into higher values (Table 6), which gives the material more thermal stability. The maximum weight rate loss (R_{max}) for the first stage was decreased (Table 6) which proof the evaporation of some compounds after heating. The char yield (%) at 1000 °C which represent the carbon fibers that were remained differ among all the

specimens, since each specimen has different percentages of epoxy and carbon fibers depending on the cut.

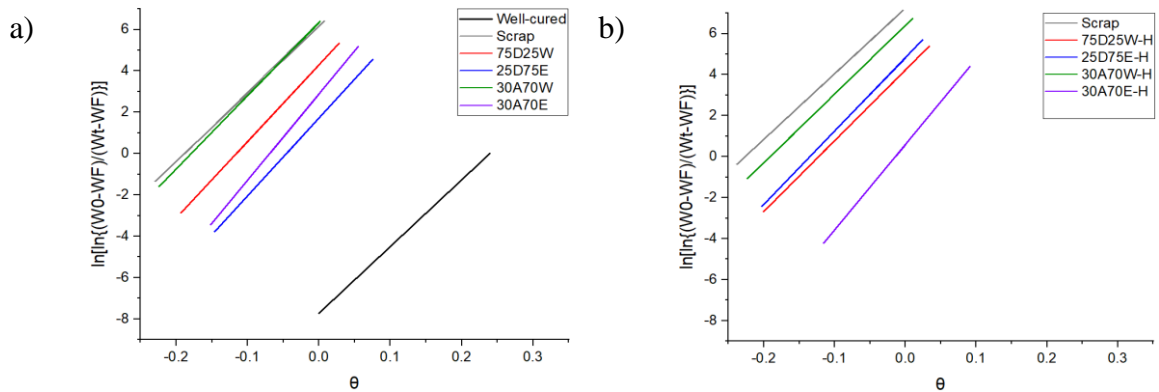


Figure 30: Calculation of Activation Energy for epoxy degradation for a) Chemical-treated and b) heat-treated composites.

	IDT (°C)		T _{max} (°C)		R _{max} (%/°C)		E _a (KJ/mol)	Char Yield (%)
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 2	
Scrap-H	-	277	-	432	-	54	48.4	66
75D25W-H	47	277	167	432	2	53	45.5	65
25D75E-H	47	277	167	432	2.5	57	43.8	62
30A70W-H	-	277	-	432	-	54	46	64.5
30A70E-H	-	277	-	432	-	45	37.4	64

Table 6: Thermal stability and degradation parameters of the heat-treated composites.

The TGA in this study was coupled to FTIR spectroscopy to analyze the gas emitted during the decomposition of the material at specific temperatures to understand more the reaction mechanisms using different solvent mixtures. The specimens treated with DMF were

analyzed at the temperature at maximum rate of weight loss in the first stage (167 °C) for the two types. Moreover, the specimens treated with H₂SO₄ were analyzed at temperature 250 °C to know more about the weight loss happened before the decomposition of epoxy. Figure 31 shows the FTIR spectrums of Scrap composites at 167 and 250 °C and well-cured composites before the decomposition of epoxy, which were taken as a reference to compare with the treated specimens. As we can see that there are no peaks appeared in the spectrums except a small peak at the band 1671 cm⁻¹ related to carbonyl group [37] in the scrap spectrum at 167 °C.

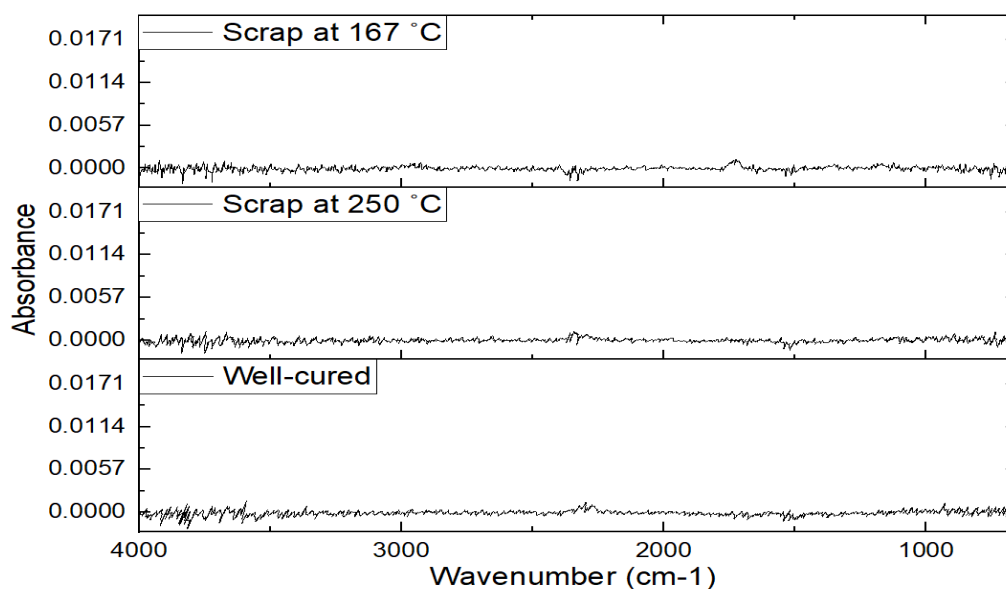


Figure 31: FTIR spectrums of Scrap composites at 167 and 250 °C, and well-cured composites before the decomposition of epoxy.

Figure 32 shows the FTIR spectrums for the first decomposition stage at 167 °C, the temperature at maximum rate of weight loss, of specimens treated with DMF. All the peaks appeared in the spectrums are related to DMF solvent peaks (Figure 32) [36]. This proof that there is no reaction between DMF and the scrap composite material. On the other hand,

Figure 33 shows the FTIR spectrums at 250 °C before the decomposition of epoxy of specimens treated with H₂SO₄. We can notice that there is only one peak for the specimens treated with 30A70W at 2300-2370 cm⁻¹ wavenumber range, whereas two peaks appeared in the spectrums of the specimens treated with 30A70E at 1330-1395 cm⁻¹ and 2300-2370 cm⁻¹ wavenumber ranges. The 1330-1395 cm⁻¹ wavenumber range is attributed to CH₃ [37] is an evidence of cleavage of the crosslinked bonds. This explains the weight loss before the degradation of epoxy in the TGA curves of the specimens treated with 30A70E. The band range 2300-2370 cm⁻¹ is attributed to CO₂ which confirmed the oxidation of the surface [38].

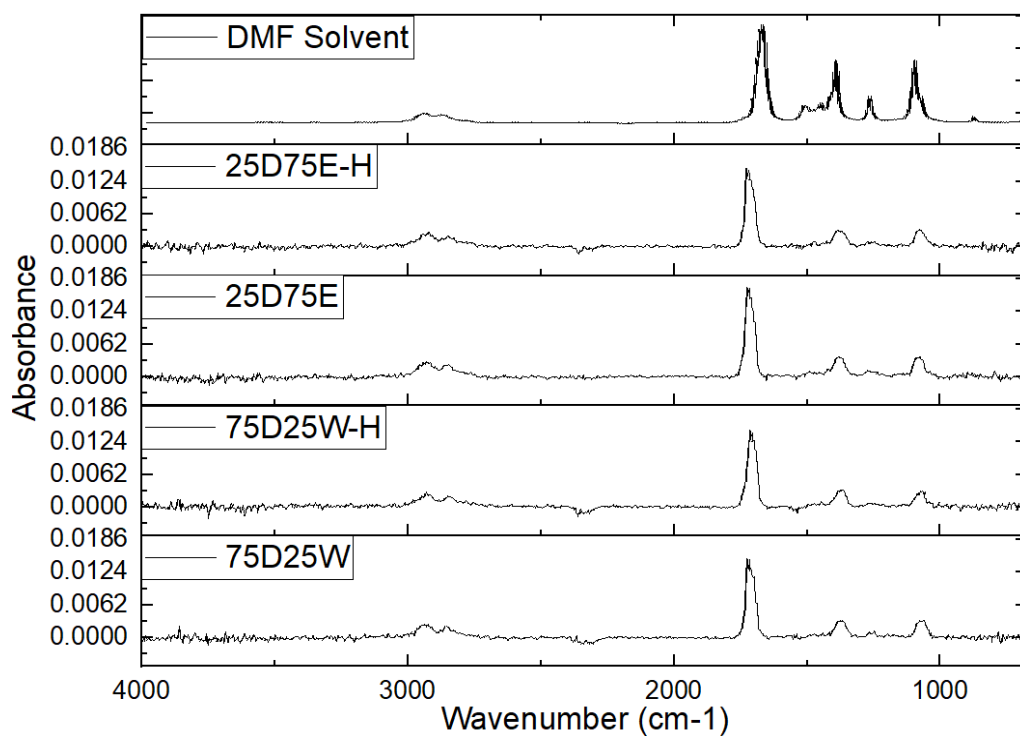


Figure 32: FTIR spectrums at 167 °C of specimens treated with DMF vs FTIR spectrum of DMF solvent.

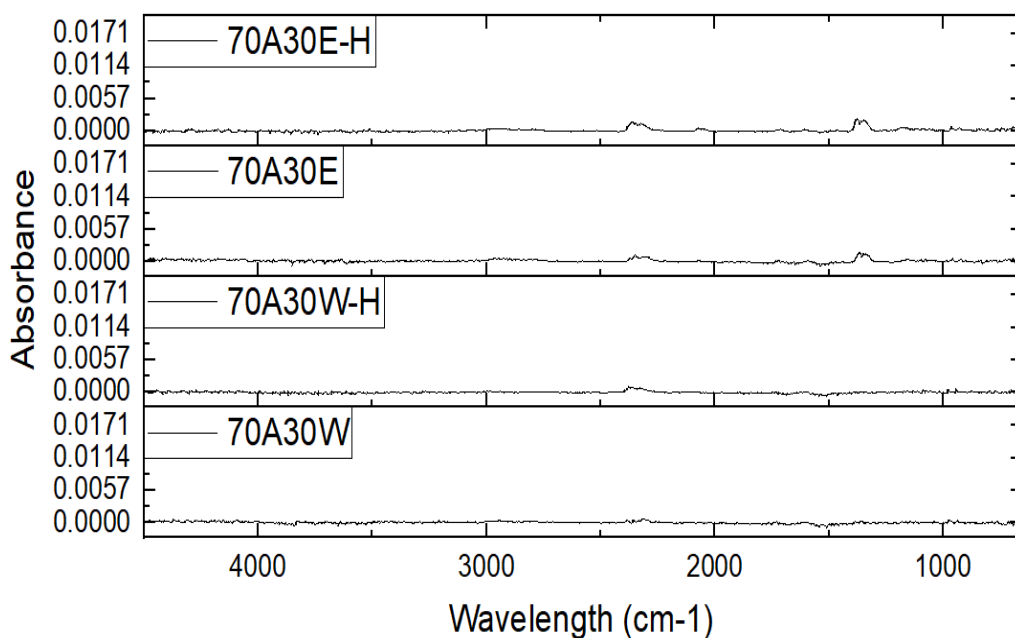


Figure 33: FTIR spectrums at 250 °C of specimens treated with H₂SO₄.

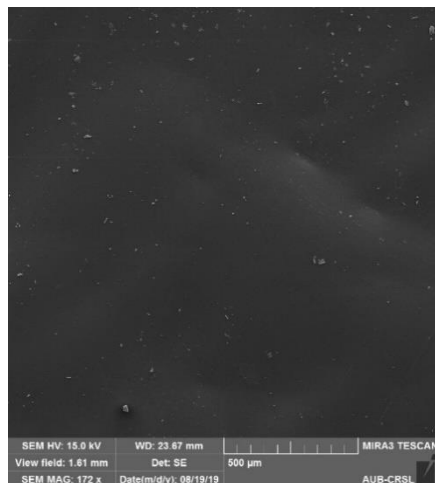
4. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to determine the surface and cross-sectional topography of the chemical treated specimens and to monitor deeply the effect of the chemical reactions on the network structures of thermoset materials. All the specimens were sputter coated with a 20 nm layer of platinum before the scanning. Figure 34 shows the SEM images at the surface and cross sections of scrap, well-cured and treated specimens. The surface of the untreated specimens, well-cured and scrap, are very smooth without any defects appeared (Figure 34-a, c). Also, it is obvious that there are no changes in the cross-sectional topography of the scrap specimens (Figure 34-c) compared to the well-cured specimens (Figure 34-b). On the other hand, the diffusion of DMF and water/ethanol caused the specimens to swell and the fibers to be more visible by the naked eye near the surface (Figure 34-e, h). Moreover, the swelling phenomena induced stresses in some spots on the

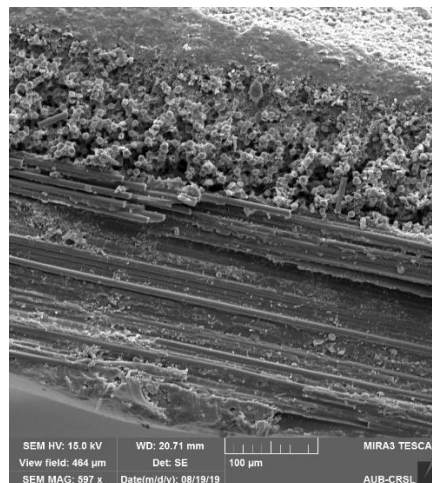
surface which produced some cracks (Figures 34-g and 34-j), when applying weights on the specimens and enforcing them to took a flat shape during chemical treatment process. We can notice also that the diffusion of DMF solvent mixtures produced some microcracks inside the specimens (Figures 34-f and 34-i) by penetrating into the specimens and leaching-out the non-crosslinked polymers and consequently replacing them.

Acid solvent mixtures have a minor effect onto the treated specimens. No obvious changes were recorded for the surface and cross section of the specimens treated with 30A70W (Figure 34-k, l). Some pits were appeared onto the surface of the specimens treated with 30A70E (Figure 34-m) which resulted from the corrosion of the surface with no change inside the specimens (Figure 34-n).

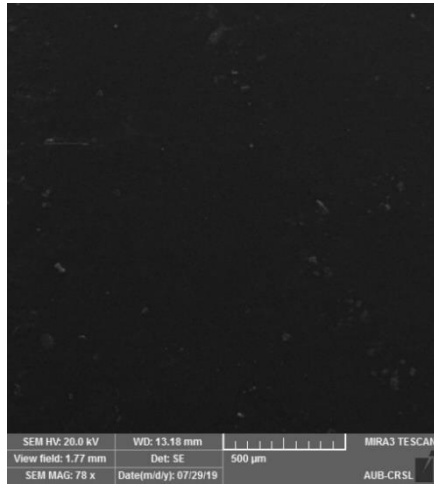
a)



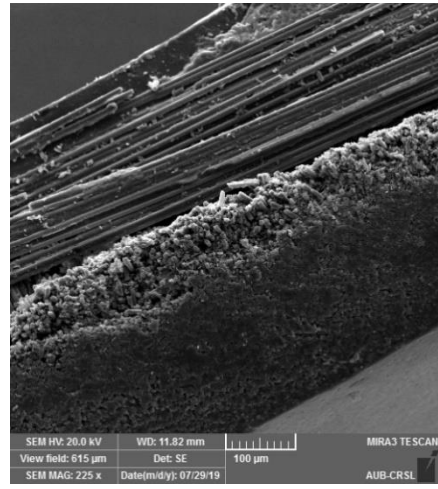
b)



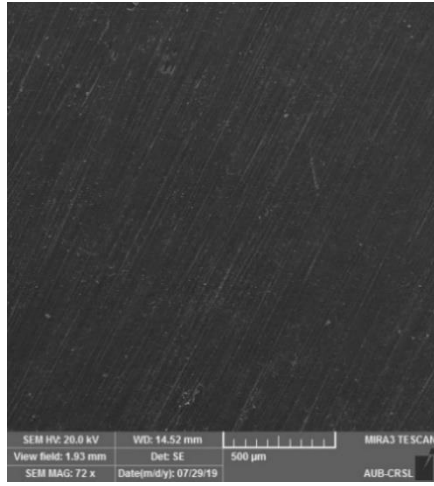
c)



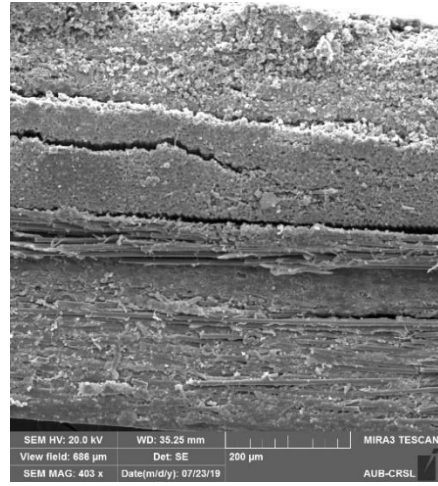
d)



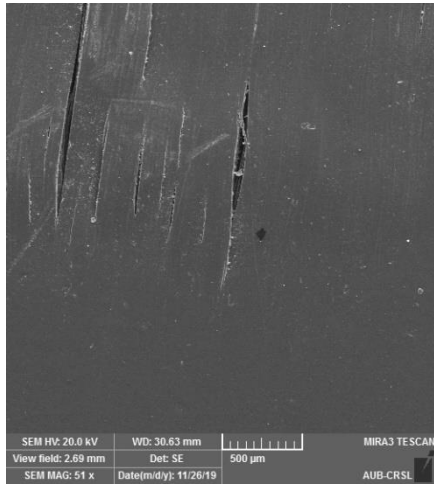
e)



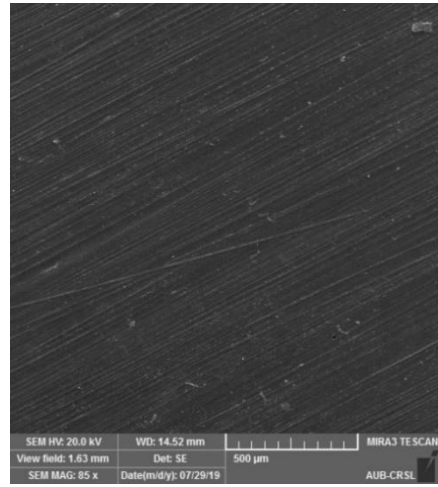
f)



g)



h)



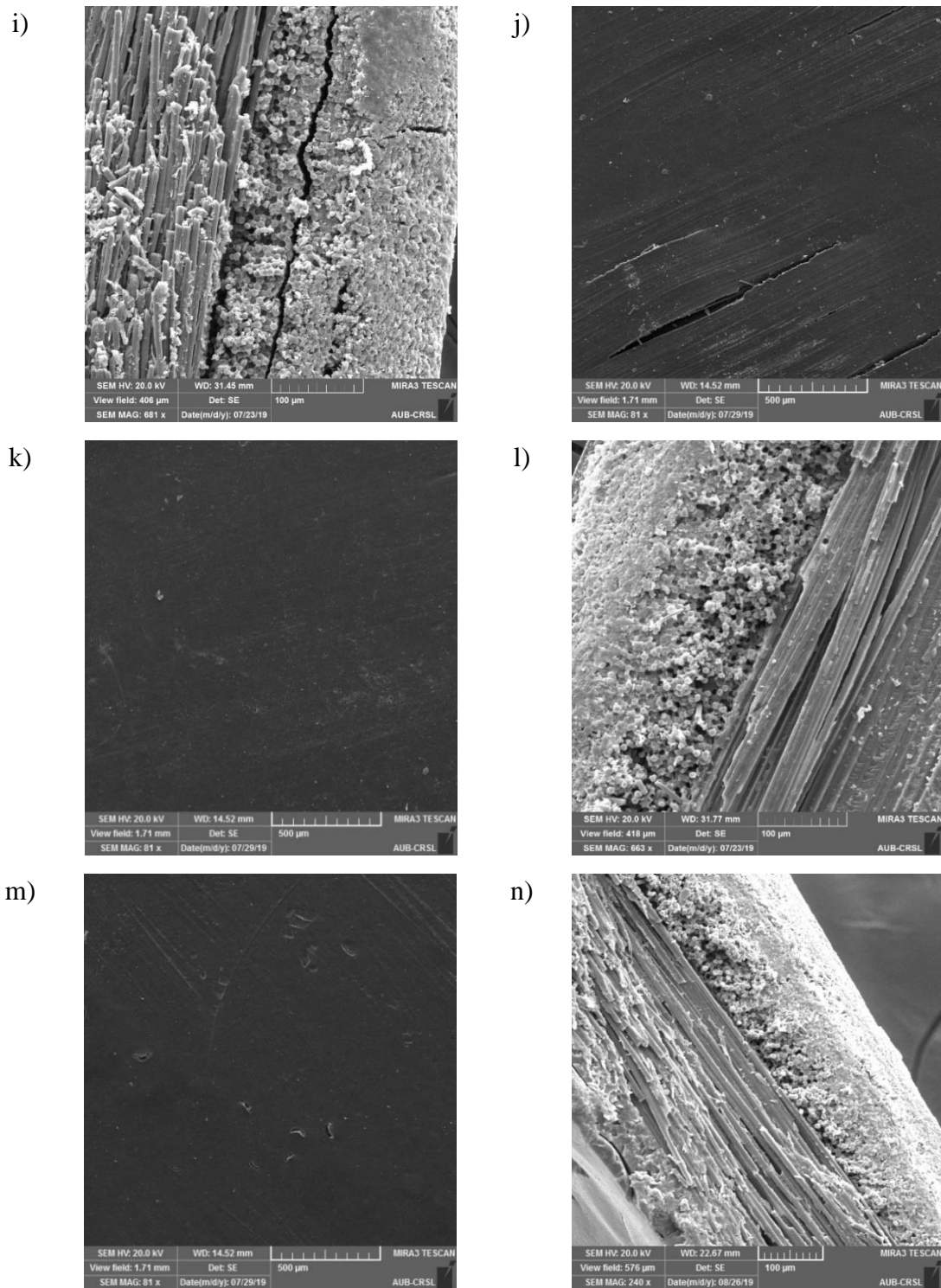


Figure 34: SEM images for the surface and cross section, respectively, of : a-b) well-cured, c-d) scrap and e-f) 75D25W, h-i) 25D75E, k-l) 30A70W and m-n) 30A70E chemical treated composites.

C. Treatment Mechanisms

The chemical composition and the structure of the non-fully cured epoxy composites, immersed in DMF and sulfuric acid solvent mixtures, gave the treatment processes two unrelated mechanisms. The first mechanism (Figure 35) contributed to the diffusion of DMF into the scrap specimens after immersing it in the DMF solvent mixtures for 24 hrs (1st step). The DMF penetrated inside the material without any reaction with the polymer and leached-out the non-crosslinked monomers to the solution which decreased the exothermic peak in the DSC thermograms. On the other hand, the diffusion of DMF solvent mixtures enforced the specimens to swell and fully loosen the entanglement in its network which explained the decrease in the endothermic peak in the DSC thermograms (2nd step). That's why the penetration of DMF solvent mixtures produced flexible specimens and decreased the tensile strength due to the production of stress concentration points, and produced some microcracks in the specimens that can be seen in the SEM images.

After removing the specimens from the solution, they were washed with water/ethanol to homogenize DMF since it is miscible in them, but the FTIR spectrums and TGA thermograms showed that DMF remained inside the material and on the surface (3rd step). Noting that after heating the chemical-treated specimens, the mechanical properties of the specimens treated with 75D25W increased more than that treated with 25D75E where the evaporation of the residual sorbed moisture reduced the stress concentration points. So, we can conclude that water has higher diffusion factor than ethanol, also it can be seen from the percentage of the leached-out non-crosslinked polymers where it was higher when using 75D25W.

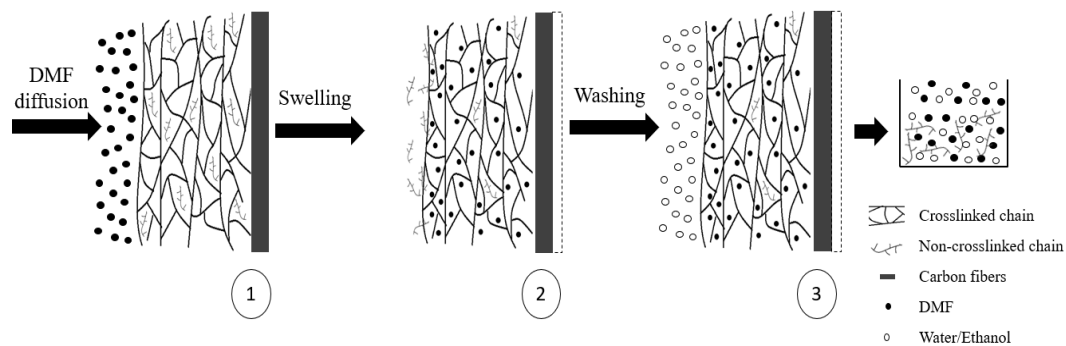


Figure 35: Treatment mechanism of DMF.

The second treatment mechanism (Figure 36) contributed to the chemical reaction of sulfuric acid with the scrap material (1st step). The reaction was limited only on the surface of the scrap composite without penetrating inside the material, leaving behind it a corroded layer represented by a green color appeared on the surface (Figure 37). The acid had break down some of the polymer chains on the surface which appeared in the FTIR spectrums and TGA thermograms and can be noticed also from the pits that appeared in the SEM images.

Moreover, acid had reacted with some of the non-crosslinked polymers on the surface which reduced slightly the exothermic peaks in the DSC thermograms or/and leached-out of the material some of the non-crosslinked polymers (2nd step). The flexibility of the specimens treated with acid had not changed obviously like when using DMF, which explained that there is no diffusion of the acid solvent mixtures inside the material or may be the existence of a weak diffusion mechanism. And, the decrease in the tensile strength after chemical treatment resulted from the breaking of some crosslinked chains. These values increased obviously after heat treatment which can be attributed to the fact that acid didn't affect the

non-crosslinked polymers which remained after chemical treatment and cured during heat treatment. After removing the specimens from the solution, they were washed with water/ethanol to homogenize H_2SO_4 since it is miscible in them (3rd step), where the non-reacted acid and the cleft monomers fused in water/ethanol solution.

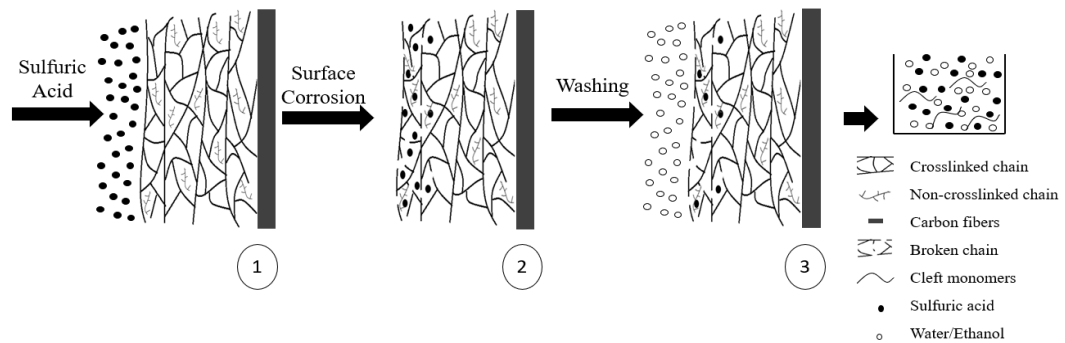


Figure 36: Treatment mechanism of sulfuric acid.

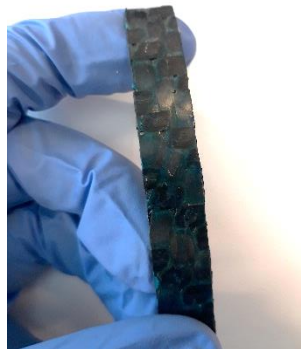


Figure 37: Green corroded layer of acid treated specimen.

CHAPTER IV

SURFACE PHYSICS AND ADHESION PROPERTIES

A. Contact Angle and Surface Free Energy

Knowing that the surface energy of the specimens was affected upon treatment depending on the solvent mixtures that were used. Therefore, the contact angle for all the specimen types was measured using Contact Angle Goniometer at the interface between the liquids used, Water and Glycerol in this case, and the specimen's surface. Then, the surface energy was calculated using Owens, Wendt, Rabel and Kaelble (OWRK) method. Two fundamental equations [39], shown below, are the basic of this method, which explain the interactions between solid surfaces and liquids.

Good's Equation [39]:

$$\sigma_{SL} = \sigma_S + \sigma_L - 2(\sigma_L^D \sigma_S^D)^{1/2} - 2(\sigma_L^P \sigma_S^P)^{1/2} \quad (3)$$

Young's Equation [39]:

$$\sigma_S = \sigma_{SL} + \sigma_L \cos \theta \quad (4)$$

σ_L : Surface tension of liquid

σ_L^D : Dispersive component of the surface tension of the liquid

σ_L^P : Polar component of the surface tension of the liquid

σ_S : Surface energy of the solid

σ_S^D : Dispersive component of the surface energy of the solid

σ_S^P : Polar component of the surface energy of the solid

σ_{SL} : The interfacial tension between the solid and the liquid

θ : The contact angle between the liquid and the solid.

The surface tension components of water and glycerol are given in Table 7. After measuring the contact angle for all the specimen types (Table 8), the surface energy was calculated using Eq. 3 and Eq. 4. We can notice that the surface energy of scrap composites had a slight decrease by about 4 mN/m than that of well-cured composites. On the other hand, chemical treatment had improved the surface energy of the scrap composites. The two DMF solvent mixtures had the same effect on the surface, where the surface energy of the scrap composites increased by about 9 mN/m after treatment. This increase can be attributed to the increase in the hydroxyl group on the surface after treatment that was shown in the FTIR spectrums.

Liquid	σ_L (mN/m)	σ_L^D (mN/m)	σ_L^P (mN/m)
Water	72.8	26.4	46.4
Glycerol	63.4	37	26.4

Table 7: Surface tension components of liquids [39].

However, the surface energy for the specimens treated with sulfuric acid showed an obvious variation in the values. Where, the surface energy of the specimens treated with 30A70W increased by about 12 mN/m, while the value increased extensively to 79.14 mN/m for the specimens treated with 30A70E. This ensures that ethanol has higher oxidation effect on epoxy than water, which appeared in the FTIR spectrums as well.

	Contact angle θ ($^{\circ}$)		σ_s (mN/m)
	Water	Glycerol	
Well-cured	69	73	34.22
Scrap	74	79	30.74
75D25W	62.31	64.3	39.05
25D75E	61.79	63.63	39.44
30A70W	58.72	62.1	42.3
30A70E	26.05	52.82	79.14

Table 8: Contact angle and surface energy of scrap and treated composites.

B. Lap Shear Test

The lap shear test was performed on the scrap and chemical-treated specimens of dimension 7x1 cm (Figure 38-a) to characterize the adhesion property of the surface using the ASTM standard D5868 [40]. Two dried samples were connected to each other by 1 layer of film adhesives (Xpreg XA120, *easy-composites*) of 1 x 1 cm (Figure 38-b). The same setup of the press heating process was applied with heating cycle C4 (Table 3). The obtained new specimens are shown in Figure 38-c, where the produced specimen was almost flat. Then, the lap shear strength of the prepared specimens was tested and the results are shown in Figure 39 (Appendix D). As we can see, the lap shear strength of the specimens treated with DMF solvent mixtures have increased compared to that of the scrap specimens due to the improvement in the surface energy of the treated specimens after treatment (Table 8), which improved the adhesion properties of the surface. However, the specimens treated with acid solvent mixtures recorded a very low lap shear strength in contradiction to the results of the surface energy which showed a very high surface tension for these types of specimens. This

can be attributed to the lack of bonding between the specimens and the adhesive layer due to the presence of residual solvents after treatment, especially for the specimens treated with 30A70E where the reaction mechanism is higher.



Figure 38: a) Specimens for lap shear test, b) Connected specimen and c) Obtained specimen after press heating.

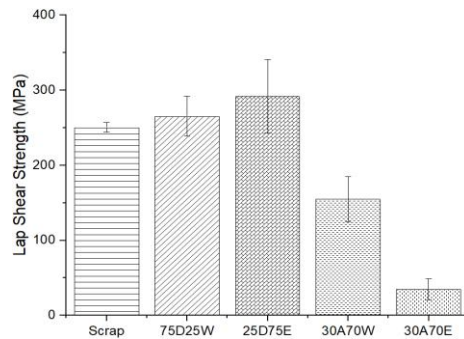


Figure 39: Lap shear strength of scrap and treated specimens.

C. Composite Sheets

The scrap composite roll was being cured as a single ply and some applications require more than one ply or need to adhere to another material. Two layers of dimension 14x14 cm were adhered together using one layer of adhesive between them (Figure 40-a) and form a composite sheet of two layers. The composite sheets were cured in the oven by applying vacuum using the heating cycle C4 (Table 3) (Figure 40-b). The adhesion of several sample layers (Table 9) were studied and the prepared composite sheets are shown in Figure 41.

Knowing that after heat treatment for single ply specimens the specimen shape wasn't 100% flat (Figure 13), we can notice that the obtained sheets were fully flat which confirmed that the adhesive layer after curing was taken a flat shape and enforced the composite layers to take the same form after adhesion.

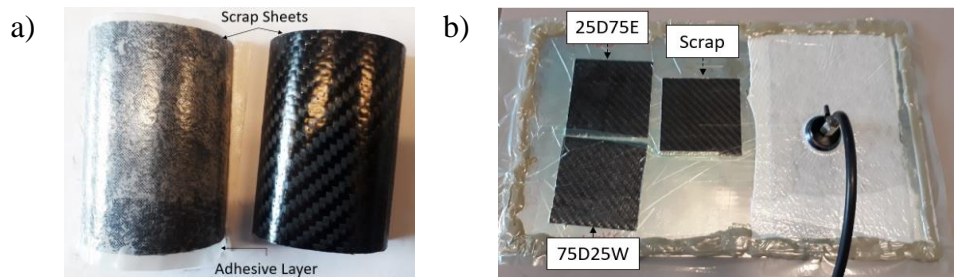


Figure 40: a) Preparation of 2 layers composite sheets and b) vacuum curing of the composite sheets.

Name	1 st Sheet Layer	2 nd Sheet Layer
Scrap	Scrap	Scrap
wD-wD	75D25W	75D25W
eD-eD	25D75E	25D75E
W-W	Well-cured	Well-cured
S-W	Scrap	Well-cured
wD-W	75D25W	Well-cured
eD-W	25D75E	Well-cured

Table 9: Samples layers used for preparing the composite sheets.



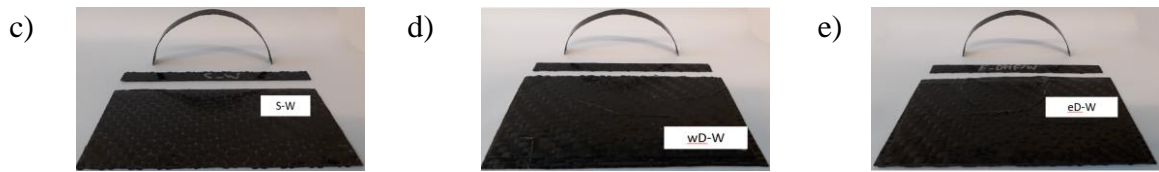


Figure 41: composite sheets.

Specimens of dimension 14 x 1 cm were prepared in the machine shops from the composite sheets to test their tensile strength, the results are shown in Figure 41. The tensile strength of S-S had dropped by 36% comparing it to W-W and that decrease is obvious, since the scrap composite strength is 25% lower than that of well-cured material (Figure 15). The composite sheets formed from two treated layers had a tensile strength near that of S-S with a slight drop for wD-wD, also these results can be contributed to the strength of single ply (Figure 15) (Appendix E). On the other hand, the use of well-cured sample layer with scrap layer improved slightly its strength by 5%, whereas the use of well-cured layer with the treated sample layers improved apparently the strength of the composite sheets by 22% (Figure 42). This increase can be attributed to the better bonding of well-cured layer with the treated layers than with scrap layers, since the treated layers had higher surface energy (Table 8).

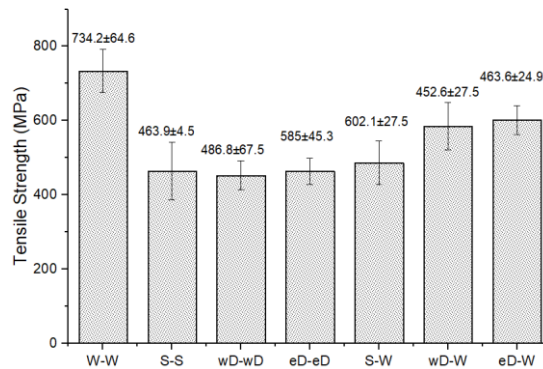


Figure 42: Tensile strength of the composite sheets.

CHAPTER V

CONCLUSION

This work investigated a recycling technique for scrap composite rolls that were cured over the shelf before being used adopting a stiffened cylindrical shape. Two processes, chemical and mechanical, were examined to induce ductility into the scrap specimens and enable its reshaping and to improve the mechanical and thermal properties of the recyclates. The influence of different solvent mixtures on the scrap composites was studied to obtain flexible chemical treated specimens that were heated at the next step using the original curing cycle of composites to obtain the final recyclates.

It may be concluded from the chemical characterization of the treated specimens that N, N-Dimethylformamide had a high diffusion mechanism, with higher rate for water-DMF solvent mixture, where it was diffused and penetrated inside the specimens, which can be noticed by the presence of DMF peaks in the FTIR spectrums of the treated specimens and from the appearance of the cracks in the SEM images. Moreover, the diffusion of the DMF solvent mixture inside the material leached-out the non-crosslinked polymers which produced ductile specimens with lower strength that increased after the re-curing of the specimens. The leaching mechanism can be concluded from the loss in the weight of the specimens after chemical treatment and from the decrease in the exothermic peak in the DSC thermograms, also it can be seen in the FTIR spectrums where the decrease in the absorbance bands related to the epoxy resin ensures the losing of some of the non-crosslinked polymers.

Furthermore, the chemical treatment using DMF solvent mixtures improved slightly the surface properties of the scrap composites by increasing the surface energy.

On the other hand, sulfuric acid had a surface treatment effect, where it oxidized the surface with slight effect on the mechanical and chemical properties. The oxidation effect appeared obviously in the SEM images where some pits appeared on the surface, and it was noticed in the FTIR spectrums where carbon dioxide band was appeared. Also, sulfuric acid had broken some of the crosslinked chains which noticed in the FTIR spectrums and can be concluded from the decrease in the tensile strength of the treated specimens. The oxidation of the surface improved considerably the surface and adhesion properties of the specimens treated with acid with higher effect to acid-ethanol solvent mixture.

At the end, the recycling of the scrap composites using the proposed recycling technique enables the reuse of the scrap materials as-is with the ability of reshaping, reclaiming more than 60% of its origin mechanical properties.

CHAPTER VI

FUTURE WORK

After the treatment of the scrap composites with DMF solvent mixtures, some of the non-crosslinked polymers were leached-out from the material which represent the un-cured epoxy found in the scrap material. So, it is important to investigate how to reuse this epoxy resin, whether directly in the treated samples or in different application. Also, the DMF that was penetrated inside the treated specimens required a process to remove it, since it may affect the properties of the recyclates.

After the treatment of the scrap composites with Sulfuric Acid solvent mixtures, some residuals penetrated inside the material and didn't evaporate even after the heat treatment, which affected the adhesion properties of the recyclates. So, it is important to investigate how to fully remove the residual solvents after surface treatment.

Furthermore, the mechanical properties of the recycled material were reduced after treatment. So, several mechanical tests are required, like short-beam strength test (D2344), to develop a property database that will define the mechanical properties of the recyclates.

Finally, the application of the recycled material in a real composite manufacturing scenario should be investigated to evaluate the feasibility of using the reclaimed material.

APPENDIX A

CHEMICAL TREATMENT RESULTS

Solvents	Height before treatment (cm)	Height after treatment (cm)	Height loss (%)	Average Height loss (%)	Tensile (MPa)	Average Tensile (MPa)	STDEV Height	STDEV Tensile
-	-	-	-	-	645.00	-	-	-
Scrap	-	-	-	-	550.60	472.98	-	117.43
					635.00			
					398.80			
					433.20			
75D25W	4.10	2.60	36.59	36.59	444.00	402.03	0.00	76.53
		2.60	36.59		448.40			
		2.60	36.59		313.70			
25D75E	4.10	2.60	36.59	38.21	459.40	446.60	2.82	34.72
		2.40	41.46		407.30			
		2.60	36.59		473.10			
30A70W	4.10	2.80	31.71	33.33	384.10	364.77	2.82	42.07
		2.80	31.71		316.50			
		2.60	36.59		393.70			
30A70E	4.10	3.00	26.83	26.83	416.90	405.27	0.00	12.47
		3.00	26.83		392.10			
		3.00	26.83		406.80			

APPENDIX B

HEAT TREATMENT RESULTS

Solvents	Heating Cycle	Height before treatment (cm)	Height after treatment (cm)	Height loss (%)	Tensile (MPa)
Scrap	1 hr at 70 °C-1 hr at 120 °C	3.80	1.00	73.68	451.50
	2 hr at 70 °C-1 hr at 120 °C	4.20	1.10	73.81	381.30
	3 hr at 70 °C-1 hr at 120 °C	3.80	1.00	73.68	310.00
	4 hr at 70 °C-1 hr at 120 °C	4.20	0.80	80.95	403.50
	1 hr at 120 °C	3.80	0.80	78.95	376.80
75D25W	1 hr at 70 °C-1 hr at 120 °C	4.00	0.80	80.00	358.70
	2 hr at 70 °C-1 hr at 120 °C	3.30	0.70	78.79	335.90
	3 hr at 70 °C-1 hr at 120 °C	4.00	0.50	87.50	484.40
	4 hr at 70 °C-1 hr at 120 °C	3.10	0.70	77.42	548.40
	1 hr at 120 °C	4.00	0.70	82.50	435.60
25D75E	1 hr at 70 °C-1 hr at 120 °C	3.20	0.90	71.88	464.50
	2 hr at 70 °C-1 hr at 120 °C	3.10	0.70	77.42	485.50
	3 hr at 70 °C-1 hr at 120 °C	3.20	0.70	78.13	414.10
	4 hr at 70 °C-1 hr at 120 °C	3.20	0.70	78.13	495.40
	1 hr at 120 °C	3.20	1.00	68.75	332.50
30A70W	1 hr at 70 °C-1 hr at 120 °C	2.20	0.80	63.64	449.80
	2 hr at 70 °C-1 hr at 120 °C	3.10	1.10	64.52	330.80
	3 hr at 70 °C-1 hr at 120 °C	2.00	0.80	60.00	363.10
	4 hr at 70 °C-1 hr at 120 °C	2.80	0.90	67.86	524.00
	1 hr at 120 °C	3.20	0.80	75.00	266.30
30A70E	1 hr at 70 °C-1 hr at 120 °C	3.50	1.10	68.57	378.60
	2 hr at 70 °C-1 hr at 120 °C	3.30	1.10	66.67	411.90
	3 hr at 70 °C-1 hr at 120 °C	3.50	1.10	68.57	372.80
	4 hr at 70 °C-1 hr at 120 °C	3.30	1.00	69.70	421.40
	1 hr at 120 °C	3.50	1.00	71.43	290.60

APPENDIX C

HEAT TREATMENT RESULTS USING CURING CYCLE

Solvents	Tensile (MPa)	Average Tensile (MPa)	STDEV Tensile
Scrap	612.00	488.07	112.62
	392.00		
	460.20		
75D25W	388.60	457.00	82.35
	434.00		
	548.40		
25D75E	474.80	467.87	31.58
	495.40		
	433.40		
30A70W	392.70	456.43	65.73
	452.60		
	524.00		
30A70E	446.40	462.70	17.04
	461.30		
	480.40		

APPENDIX D

LAP SHEAR STRENGTH RESULTS

Solvents	Tensile (MPa)	Average Tensile (MPa)	STDEV Tensile
Scrap	245.90	250.70	6.79
	255.50		
75D25W	247.00	265.70	26.45
	284.40		
25D75E	326.90	292.35	48.86
	257.80		
30A70W	134.00	155.00	29.70
	176.00		
30A70E	25.00	35.00	14.14
	45.00		

APPENDIX E

TENSILE STRENGTH OF COMPOSITE SHEETS

Specimens	Tensile (MPa)	Average Tensile (MPa)	STDEV Tensile
W-W	714.00	734.17	57.28
	798.80		
	689.70		
S-S	468.30	463.85	6.29
	459.40		
S-W	454.90	486.80	58.49
	451.20		
	554.30		
wD-W	539.70	585.00	64.06
	630.30		
eD-W	629.50	602.05	38.82
	574.60		
wD-wD	425.10	452.60	38.89
	480.10		
eD-eD	438.70	463.55	35.14
	488.40		

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