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Recovery of Undamaged Carbon Fabric from Carbon Fiber-Reinforced Epoxy Polymers Through Subcritical Solvolysis Route: Effect of Flame Retardant Presence

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Abstract

The recycling of carbon fiber-reinforced polymers (CFRPs), particularly carbon fiber-reinforced epoxy polymers (CFREPs), is a challenging problem because of their broad application spectrum, the amount of laminates produced per year, and the cost per kg of the carbon fiber fabric. Recently, several papers were published on the recycling of CFREPs through solvothermal methods that allow the recovery of the carbon fiber fabrics with a relatively low environmental impact. In the present paper, for the first time, the effect of the presence of flame retardants is discussed. A carbon fiber-reinforced epoxy polymer (CFREP) charged with P-, Zn-, B- and Al-based flame retardants, supplied by the aerospace industry, was subjected to a double-step solvothermal treatment. The epoxy matrix was successfully dissolved in monoethanolammine after a preswelling step in acetic acid. The experimental results show that the proposed process allows the full recovery of the carbon fabric with its original sizing layer without injury to the fiber. As confirmation, CFREP laminates produced with the recycled carbon fiber fabrics exhibited mechanical properties close to that of laminates obtained from the virgin epoxy/carbon prepreg. Contrary to what is reported in the literature, the present paper also shows that, in the studied case, whilst acetic acid treatment promotes swelling, it also causes the formation of a degraded surface layer that would impede complete removal of the polymeric matrix and full recovery of the carbon fabric if only acetic acid was used. On the basis of the known mechanism of flame retardancy of phosphates and borates, the degraded layer formation is attributed to the acidic character of the acetic acid. It is worth pointing out that the paper suggests, therefore, that the presence of flame retardants may strongly affect the solvothermal processes.

Keywords: solvolytic chemical recycling; subcritical acetic acid; subcritical monoethanolamine; carbon fiber-reinforced epoxy; flame retardant

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1. Introduction

Carbon fiber-reinforced polymers (CFRPs), particularly epoxy ones (CFREPs), are largely used, nowadays, for structural applications in the transport industry (aircraft, boats, motor vehicles) as well as in sport equipment, wind turbine blades, etc. This wide spectrum of applications is justified by their good specific mechanical properties as well as noteworthy corrosion, moisture and chemical resistance [1–4]. In the above-cited fields thermosetting matrices are employed, particularly epoxy ones. It is estimated, in fact, that the epoxy

market accounts for 70% of the total thermosetting one [3]. Their disposal raises great problems based on their noteworthy corrosion, moisture and chemical resistance alone. It is worth pointing out, however, that the cost itself of the raw materials, together with their increasing demand [2], makes the application of proper strategies for their recovery very attractive. The cost per kg of carbon fiber, in fact, may be as great as 160 or 40 times greater than the cost per kg of carbon steel and aluminum materials, respectively [1].

Three recycling strategies were proposed: mechanical, thermal and chemical [1–5]. The latter raised significant interest for its potential to recover both valuable carbon fibers and chemicals. Thermal recycling is a process that requires elevated temperatures (450–700 °C) at which the degraded polymeric matrices cannot be used, becoming, generally, secondary waste; moreover, the thermally recycled carbon fibers easily suffer decline [1–5]. Chemical recycling includes acid digestion and solvolysis in supercritical or subcritical fluids [1]. In the recent decade, a number of chemical recycling technologies have been reported using relatively environmentally friendly solvents (i.e., alcohol, water…) at subcritical temperatures (<230 °C) [1]. The papers reported in the literature, however, all deal with the recycling of neat polymers or fiber-reinforced polymers, not with the flame-retardant ones, which represents the case of interest in the applications. In fact, as is well known, the need for proper flame-retardant polymeric materials has recently enormously increased [6–10]. In some fields, like the aeronautical one, it is a must in order to allow the materials to satisfy the strict fire safety requirements, as defined by the Federal Aviation Regulations (FAR 25.853) [10].

Recently, new recyclable flame-retardant thermosets characterized by specific bonds that can be broken and reconnected reversibly when subjected to external stimuli were proposed [3]. However, complicated synthesis strategies and proper optimization of the number of "adaptable bonds" are needed to assure good thermomechanical recycling yield, as well as satisfactory thermal stability, degradation behavior, and mechanical performance of the recycled material [3]. The strategy most commonly adopted to assure good flame-retardant properties is still the inclusion of inorganic and/or organic additives through physical doping [2–8,11,12].

The present paper deals with the solvothermal chemical recycling of a carbon fiber-reinforced epoxy polymer (CFREP), containing P-, Zn-, B- and Al-based flame retardants, supplied by the aerospace industry. To the authors' knowledge, this is the first attempt to investigate the effect of the presence of flame retardants within the epoxy matrix on the solvothermal process.

It is worth noting that acetic acid has been used for pre-swelling studies of carbon fiber-reinforced polymer (CFRP) boards [1]. In fact, solvothermal chemical recycling occurs in two steps: diffusion into the CFRP board and cleavage of the covalent bonds to form soluble molecules. Pre-swelling may therefore facilitate the process. Acetic acid is considered the best choice for CFREP pre-swelling [1]. It is also important to note that both valuable carbon fibers and oligomers were recently recovered in a solvothermal process using the $AlCl_3/CH_3COOH$ degradation system [13]. Furthermore, it was proven that acetic acid allowed the swelling and slight degradation of CFREP, even in the absence of the catalyst, becoming soft and delaminated at low treatment temperatures, such as 140–160 °C [14].

In the present study, the flame-retardant CFREP samples were subjected to a double-step solvothermal treatment. The epoxy matrix was successfully dissolved in monoethanolammine after a presweling step in acetic acid. The experimental results show that the proposed process does allow the full recovery of the carbon fabric with its original sizing layer without fiber injury. As confirmation, CFREP laminates produced with recycled carbon fiber fabrics exhibit mechanical properties similar to those of laminates obtained from the virgin epoxy/carbon prepreg.

Contrary to what is reported in the literature, the present paper also shows that, in the case studied, although assuring swelling, the acetic acid treatment causes formation of a surface degraded layer, that would impede complete removal of the polymeric matrix and full recovery of the carbon fabric if only acetic acid would be used. Based on the known flame retardancy mechanism of phosphates and borates [6–10,15], the degraded layer formation may be attributed to the acidic character of the acetic acid.

2. Experimental

2.1. Materials

The epoxy/carbon prepreg was supplied by Geven S.p.A., Nola (Napoli), Italy [https://www.geven.com (accessed on 10 February 2026)], an aerospace industry of aircraft interiors, together with the cure schedule.

Acetic acid, monoethanolamine (MEA) and KOH were purchased from Sigma Aldrich (Milan, Italy) and were used as received without further purification treatment.

2.2. The Solvothermal Treatment

The solvothermal process was performed in a stainless-steel autoclave lined with Teflon, as shown in Figure S1. This is a steel tube with an internal Teflon lining able to resist temperatures and pressures up to 200 °C and 10 bars in aggressive environments. The investigation was carried out on the epoxy/carbon prepreg plies supplied by Geven S.p.A., which were cured according to their cure schedule. In a typical experimental set-up, the reactor internal volume of 50 cm^3 is filled (by 75%) with 37.5 mL of either acetic acid or a MEA/KOH (14% KOH) solution. One cured carbon fiber-reinforced epoxy polymer (CFREP) ply, 4 cm wide and 4 cm long (712 ± 50 mg), is soaked completely in the solvent before sealing the reactor. Consequently, the CFREP mass/solvent volume ratio is 19 mg/cm^3. The reactor is then put in a muffle furnace with an internal volume of 125 dm^3 that has been preheated to the solvothermal treatment temperature. No stirring is performed during the solvothermal treatments. Once the treatment is completed, the reactor is extracted from the furnace and left to naturally cool down.

The samples were washed with acetone. The samples are dried at 100 °C for 24 h before any use or characterization.

2.3. Preparation of CFREP Laminates

Virgin and recycled CFREP laminates were produced for the three-point bending tests, as described below.

The virgin CFREP laminates were produced using the epoxy/carbon prepreg supplied by Geven S.p.A. [https://www.geven.com/ (accessed on 10 February 2026)] together with the cure schedule. The used prepreg material is in the form of twill wave fabric characterized by an areal density of 250 g/m^2 and a thickness of almost 0.25 mm resulting in a fiber volume fraction of almost 70%. Therefore, for the production of the CFREP virgin samples, a total of 6 layers were stacked in a $[0/90]_S$ configuration to produce a composite laminate 200 mm × 200 mm in dimension. The virgin CFRP (vCFREP) laminates were produced adopting the compression molding technique where the prepreg layers were stacked on a mold plate. At the end of the stratification phase, the composite laminate was placed under a hydraulic press to allow for the cure at a pressure of 0.8 MPa at a temperature of 150 °C for 2 h.

The same manufacturing process was adopted for producing the recycled laminates derived from the solvolysis process. After investigating the feasibility and the efficiency of the solvothermal treatment, part of the treated fabric was used to manufacture recycled composite samples. In that case, the carbon fabric was impregnated using epoxy resin film

supplied by Mates s.r.l., Cisliano (Milano), Italy. This film has an areal density of 350 g/m^2. Therefore, to produce a recycled composite material (rCFREP) comparable to the vCFREP, the same number of recycled layers (equal to 6) was used. During the manufacturing phases, the 6 recycled layers were impregnated with 2 layers of resin film, placing them between two pairs of recycled fabric layers in a [$C_2MC_2MC_2$] configuration. By adopting this stacking strategy, it was possible to achieve a recycled fiber volumetric fraction of almost 60% at the end of the manufacturing process. Then, the uncured recycled composite was placed in a hydraulic press to allow for the polymerization of the resin film, adopting a pressure of 0.8 MPa and a cure temperature of 150 °C for 2 h. In Figure S2 is represented the schematization of the stacking strategies adopted to produce both the virgin and the recycled CFRP laminates.

2.4. Characterization Techniques

The samples submitted to the solvothermal treatments were weighed before and after the treatment. The swelling ratio (S%) and the mass loss ratio (D%) were calculated through the following equations:

$$S\% = ((M_1 - M_2)/M_0) \times 100 \quad (1)$$

$$D\% = ((M_0 - M_2)/M_0) \times 100 \quad (2)$$

where M_0 is the mass of the board submitted to the treatment, M_1 is the mass of the "wet" treated sample (including the absorbed acetic acid), M_2 is the mass of the dried treated sample. The samples were weighed using a 4-digit analytical balance. The experiments were repeated twice and the mean values were plotted. Scanning Electron Microscopy (SEM) analysis of the sample surfaces was performed to investigate the resin degradation on boards by using a FEI Quanta 200 FEG Microscope (Hillsboro, OR, USA) in combination with An Ultim Max 40 energy-dispersive X-ray (EDX) micro-analyzer coupled with the microscope (Oxford, UK), integrated with AZtecLive software 6.2 released by Oxford Instruments (High Wycombe, UK). A piece of sample was adapted on the surface of an aluminum stub and sputtered in a Cressington sputter-coated 208HR (Watford, Hertfordshire, UK) with an Au layer to prevent surface charge accumulation, reduce thermal damage, minimize sample outgassing, and improve secondary electron signal emission, resulting in higher-resolution imaging.

Fourier-Transform Infrared Spectroscopy (FT-IR) in the attenuated total reflection (ATR) mode was carried out to assess the chemical composition of samples by utilizing a Nexus FTIR Spectrometer (Thermo Nicolet, Madison, WI, USA). ATR absorption spectra were recorded in the 4000–400 cm^{-1} range and with 8 cm^{-1} spectral resolution by using DuraSam-plIR II accessory equipped with a ZnSe Crystal (Thermo Nicolet, Madison, WI, USA).

The thermal properties of samples were investigated through Thermogravimetric Analysis (TGA) by using a TA Instrument Simultaneous Thermoanalyser SDT Q600 (TA Instrument, New Castle, DE, USA). Each sample weighing 10 mg was placed into a platinum pan and evaluated under inert atmosphere conditions within a temperature range of 25–800 °C and a heating rate of 10 °C/min.

The flexural properties of both the virgin and the recycled composite samples were investigated by performing three-point bending tests according to the D790 ASTM standard [16]. The mechanical tests were carried out using a universal testing machine Instron 5565 equipped with a 5 kN piezoelectric load cell (Instron Corporation, Norwood, MA, USA). To investigate the mechanical performance of the recycled CFRP material, a total number of 4 specimens for each configuration were used. Both the virgin and the recycled composite laminates were 100 mm in length and 12.7 mm in width as established by the

ASTM standard, as well as for the geometry of the fixture where the loading nose and the supports are characterized by a circular section 10 mm in diameter. As for the specimen's dimension and the fixture geometry, both the testing speed and the span length were defined according to the standard.

3. Results and Discussion

3.1. The Solvothermal Process

The CFREP samples were submitted to a double-step solvothermal treatment: a first preswelling step in acetic acid and a second dissolution step in monoethanolamine.

In order to choose the duration of the preswelling step, the CFREPs were submitted to solvothermal treatments in acetic acid at 200 °C for different times up to 16 h. Figure 1a,b show the plots of swelling (S%) and mass loss (D%) ratios (calculated with the above reported Formulas (1) and (2)) as a function of the solvothermal treatment duration in acetic acid. As can be seen, in both cases, a maximum is rapidly reached that remains constant for longer treatments.

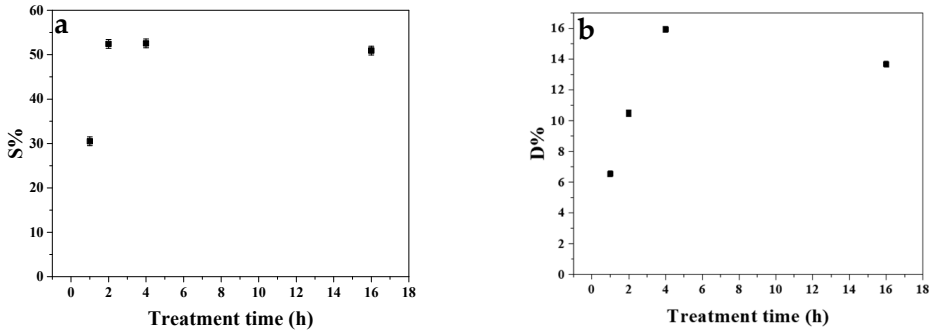


Figure 1. Plots of S% (**a**) and D% (**b**) calculated with Formulas (1) and (2) as a function of duration of the solvothermal treatment at 200 °C in acetic acid.

CFREP samples were submitted to thermogravimetric analysis (TGA). The TGA curve is reported in Figure 2 together with its derivative one (DTGA). It is the typical TGA curve of CFREP boards [17]. Weight loss is due to thermal degradation of the polymeric matrix. The DTGA peak at 550 °C underlines that there is also important weight loss above 500 °C, usually not present in the epoxy resin TGA curves, that will be discussed later.

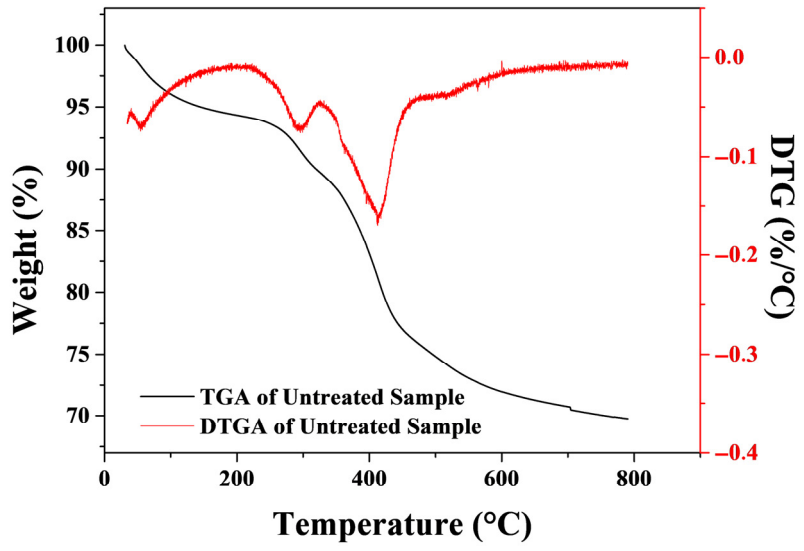


Figure 2. TGA and its derivative (DTGA) curves of untreated sample.

It is worth pointing out that the maximum D% value in Figure 1 is 15 ± 1%. It is much lower than the total weight loss recorded by TGA (30%). Otherwise, the CFREP surface acquires a whiter and more opaque aspect the longer the solvothermal treatment is. All this means that the stabilization of D% after 4 h is not due to matrix removal completion but to the formation of a degraded layer that impedes complete removal of the polymeric matrix and full recovery of the carbon fiber fabric. Therefore, the preswelling step duration was fixed at 4 h.

CFREP samples solvothermally treated for 4 h at 200 °C in acetic acid were, therefore, submitted to a solvothermal treatment in MEA at the same temperature (200 °C) with a similar procedure, as described in the experimental section. It was found that, after 4 h solvothermal treatment in MEA, matrix dissolution occurred, and the carbon fabric could be recovered in its original warp and weft structure.

Figure 3 shows the TGA curves of CFREP before and after the double solvothermal treatment (4 h at 200 °C in acetic acid +4 h at 200 °C in MEA). After the two-step solvothermal treatment, the strong weight loss up to 450 °C almost disappears, confirming epoxy matrix dissolution during solvothermal treatment. Only the slight weight loss at higher temperature is preserved.

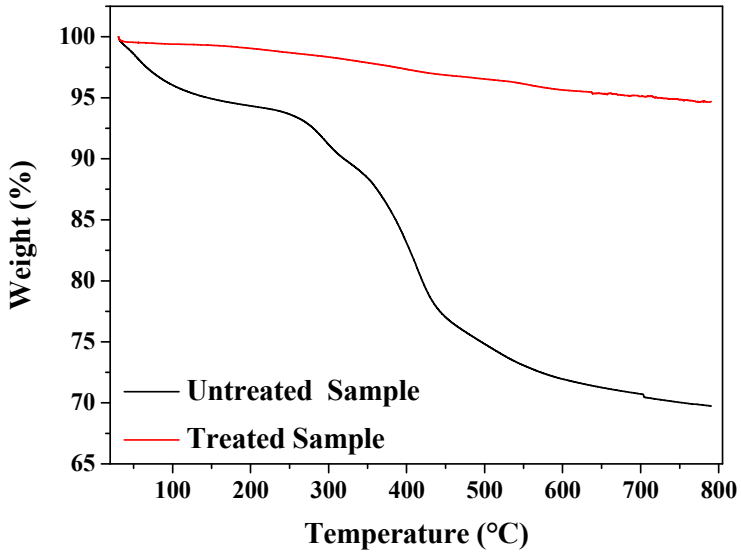


Figure 3. TGA curves of CFREP before and after 4 h at 200 °C in acetic acid +4 h at 200 °C in MEA.

Figure 4 shows the SEM and EDX spectrum recorded for the untreated sample. The peak at 2.1 keV is due to the gold used for the metallization. Carbon and oxygen are obviously present because they are components of the epoxy resin and reinforcing fabric. Zn, Al and P are components of flame retardants [6–10]. It is also known that silanes, particularly aminopropyltriethoxysilane ($Si(OC_2H_5)_3CH_2CH_2CH_2NH_2$), have been proposed in the literature as coupling agents for a better epoxy/carbon fiber interface, as well as the interface between epoxy and other carbon-based reinforcing fillers: carbon fibers [18–20], carbon nanofibers [21], graphene [22], graphene and graphene oxide powders [23], carbon nanotubes [24,25]. The presence of Si is just due to the presence of a sizing layer, increasing the adhesion between the fibers and the matrix.

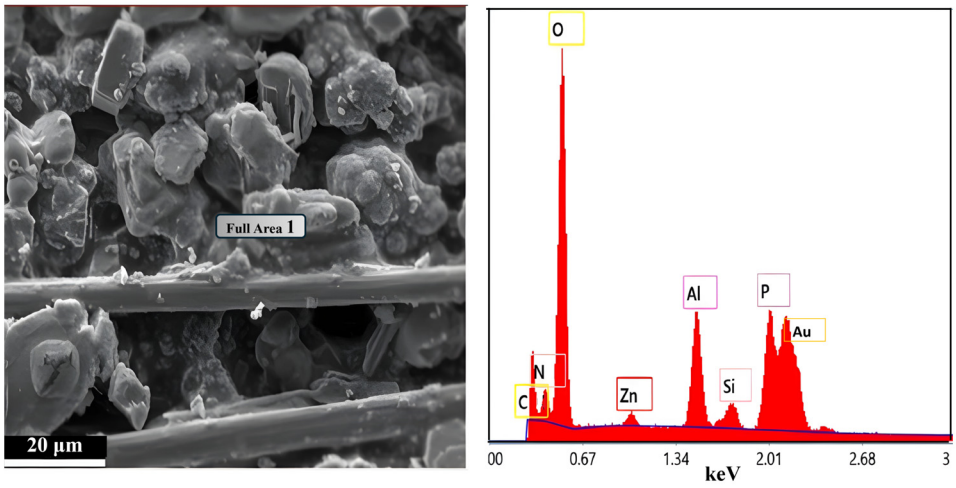


Figure 4. SEM and EDX spectrum of the untreated sample.

Figure 5 shows the SEM micrographs and EDX spectra of three samples submitted to the double solvothermal treatment (4 h at 200 °C in acetic acid +4 h at 200 °C in MEA): the one recovered from solvothermal treatment (a); the one after TGA run up to 450 °C (b); the one after TGA run up to 800 °C (c). Figure 5a confirms the almost full dissolution of the matrix during solvothermal treatment. In fact, the EDX peaks of O, N, Zn, P, Al, present in the EDX spectra of Figure 4, almost disappear. It is worth noting that, instead, the peak of silicon remains present. This suggests that the fiber sizing is preserved and suggests, more generally, that the fibers are not damaged by the solvothermal treatment, contrary to what is reported in the case of pyrolytic processes [1–5]. The exceptional mechanical properties of carbon fabric are expected, therefore, to be preserved, as proved in the following paragraph. The Si EDX peak is also preserved after the TGA run up to 450 °C, as shown by Figure 5b. It disappears in the case of the full TGA run up to 800 °C. This suggests that the weight loss at higher temperatures shown by the TGA curve of the treated sample in Figure 3 is linked to destruction of the sizing layer. This suggests also that the sizing layer recovery is linked to the lower temperatures of the solvothermal processes with respect to the pyrolytic processes.

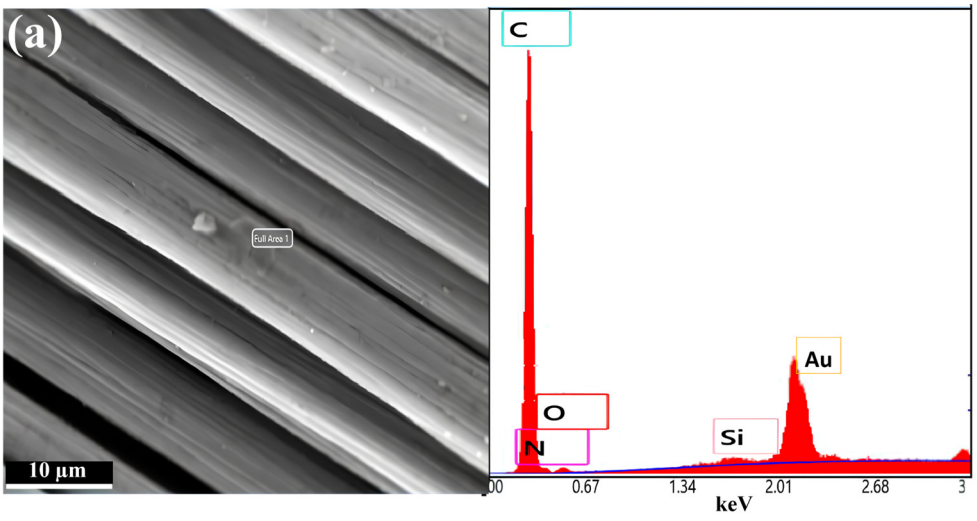


Figure 5. *Cont.*

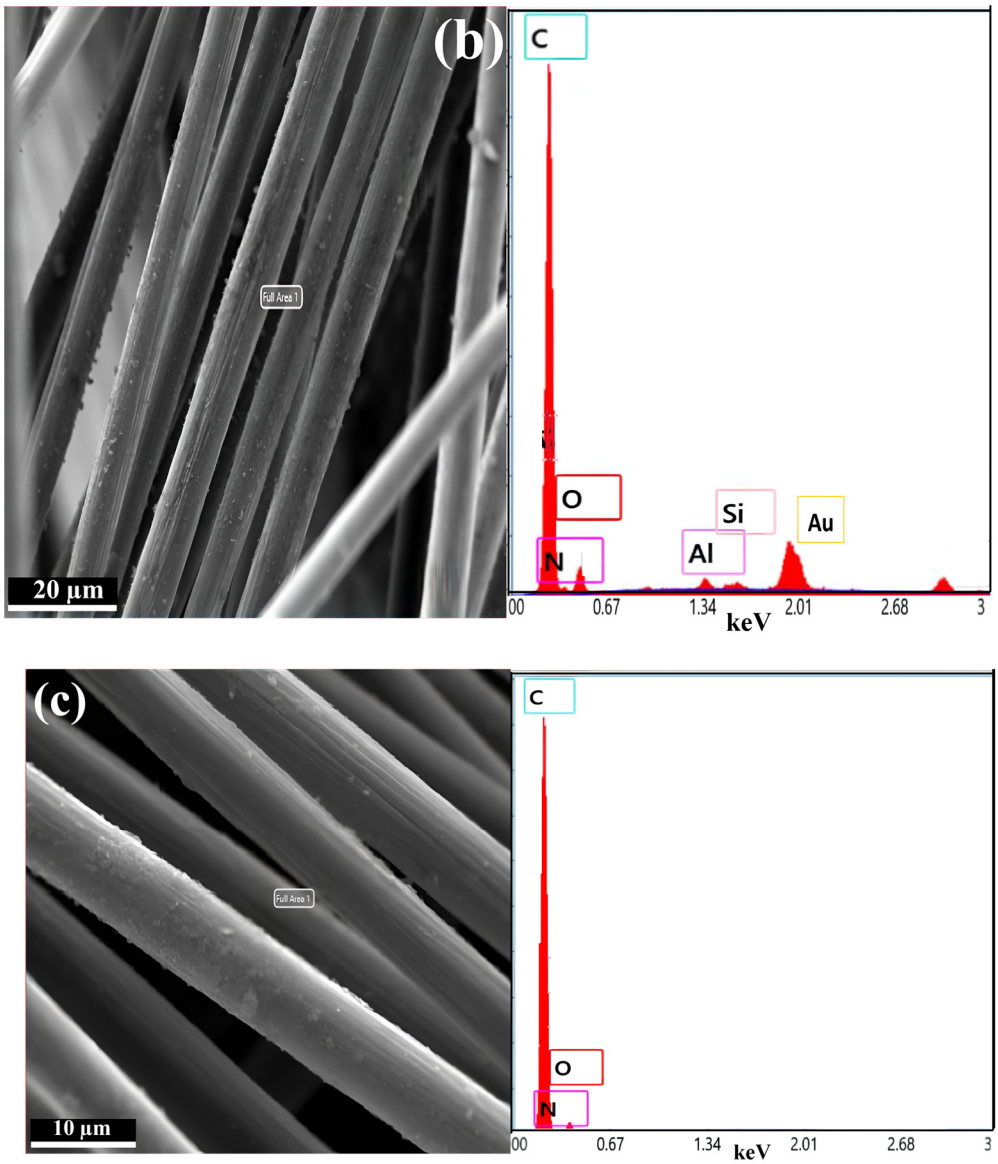
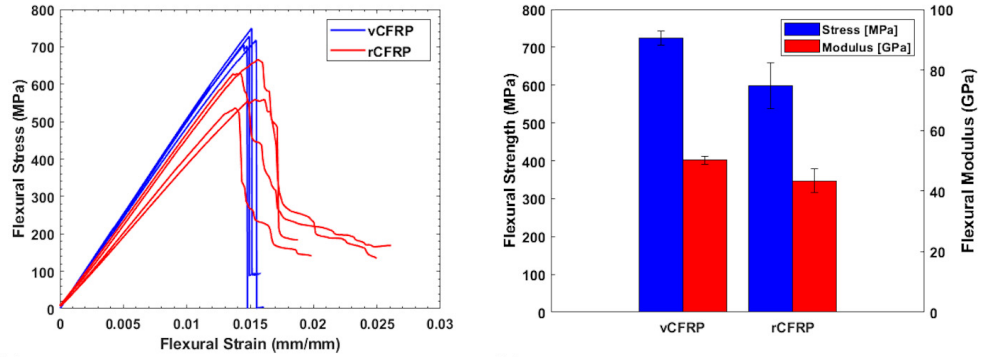


Figure 5. SEM micrographs and EDX spectra of samples after the double solvothermal treatment (4 h at 200 °C in acetic acid +4 h at 200 °C in MEA): as recovered from treatment (**a**); after TGA run up to 450 °C (**b**); after TGA run up to 800 °C (**c**).

3.2. Flexural Tests

Flexural tests were performed on virgin and recycled CFREP (vCFREP and rCFREP) laminates, produced as described in the experimental section. The stress–strain curves and the mean values of the flexural characteristics of the two sample typologies under inspection are reported in Figure 6. The curves highlight that the mean value of the flexural stress that characterizes the recycled sample (rCFREP) is comparable to that of the vCFREP laminate, revealing a reduction in the flexural strength of only 17.52%.

Table 1 summarizes the main results in terms of flexural strength and modulus of elasticity of both sample typologies at the end of the flexural tests.



(a) **(b)**

Figure 6. Stress–curves of virgin and recycled CFRP samples (**a**) and their flexural strength and modulus (**b**).

Table 1. Mean value and standard deviation of the flexural strength and modulus of elasticity of virgin and recycled CFRP laminates.

Label	Flexural Strength		Flexural Modulus	
	Average [MPa]	St.Dev.	Average [GPa]	St.Dev.
vCFRP	725.22	18.685	50.15	1.289
rCFRP	598.14	60.754	43.44	3.957

Further differences between the two samples can be seen by looking at the modulus of elasticity and the flexural strength. In detail, while the solvothermal recycling process preserves the fabric geometry and then the fiber's orientation, it is not possible to ensure perfect fiber bundle alignment during the production process. Therefore, this aspect, coupled with the lower fiber volume fraction of the rCFREP (see Section 2.2), results in a 13.38% reduction in the mean elastic modulus compared to the vCFREP. The same observation can be drawn for the flexural strength, since the mean value is only 17.52% lower than that of the virgin material. It is further worth noting that the standard deviation of the rCFREP sample is more than three times higher than that of the vCFRP; the higher value is typical of the recycled composite materials since the fibers are not perfectly oriented along the direction of the applied load. A reduction in the reinforcement fraction leads to a proportional decrease in the mechanical properties, in particular for Young's modulus in accordance with the role of the mixture. Therefore, the observed degradation in mechanical performance of the rCFRP with respect to vCFRP can be attributed not only to the imperfect row alignment along the loading direction, but also to the lower fiber content within the composite. The very good performance of the recycled carbon fabrics is of course to be attributed to the fact that the proposed solvothermal process allows one to obtain undamaged fibers with their original sizing layer.

3.3. Effect of the Presence of Flame Retardants on the Solvothermal Process

As mentioned in the introduction, the use of acetic acid in solvothermal processes has been widely studied both for the preswelling of CFREP [1] and for the full recovery of both carbon fibers and oligomers to add to new epoxy [1,13,14]. To investigate the origin of the observed unexpected formation of a protective degraded layer in the course of the preswelling step in acetic acid, CFREP samples recovered from the preswelling step were submitted to SEM observation and EDX and FTIR analysis. Figure 7 shows the SEM micrographs of the untreated sample (Figure 7A,C) and the sample treated for 4 h at 200 °C (Figure 7B,D) in acetic acid at different enlargements. As can be seen, the surface of the untreated sample is covered with a granular deposit whose aspect dramatically

changes after the solvothermal treatment. However, the micrographs at greater enlargement show that the adhesion of the deposit to the fibers is also very good after the preswelling solvothermal treatment.

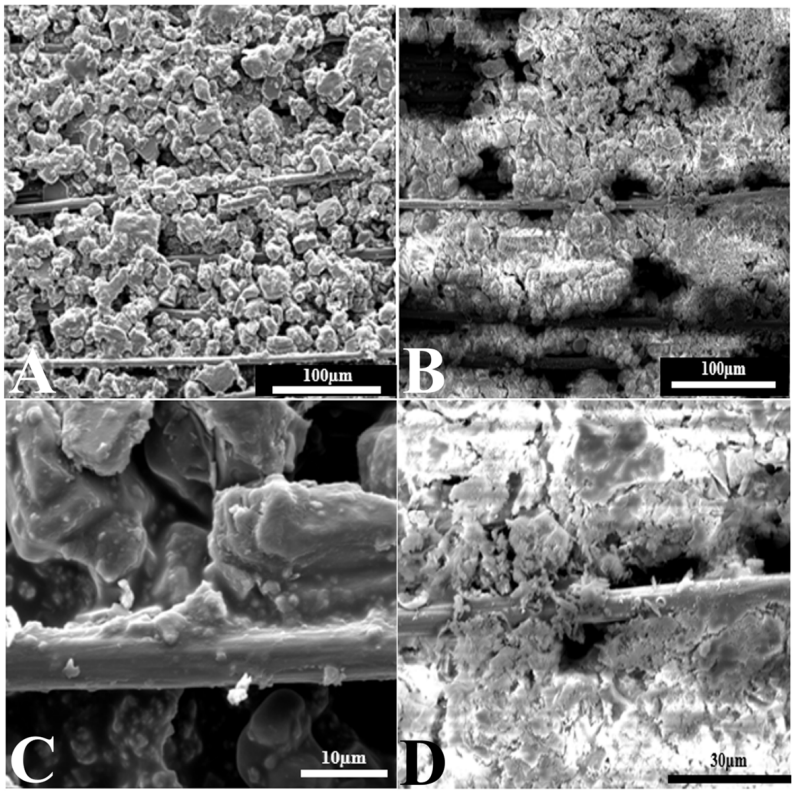


Figure 7. SEM micrographs of untreated sample (**A**,**C**) and of sample treated 4 h at 200 °C (**B**,**D**) in acetic acid at different enlargements.

Figure 8 shows the EDX spectrum recorded after the solvothermal treatment of 4 h at 200 °C in acetic acid. The EDX spectrum of Figure 8 is very similar to that recorded for the untreated sample reported in Figure 4, indicating that the flame retardants are not removed during the solvothermal treatment and suggesting possible involvement in forming the degraded layer.

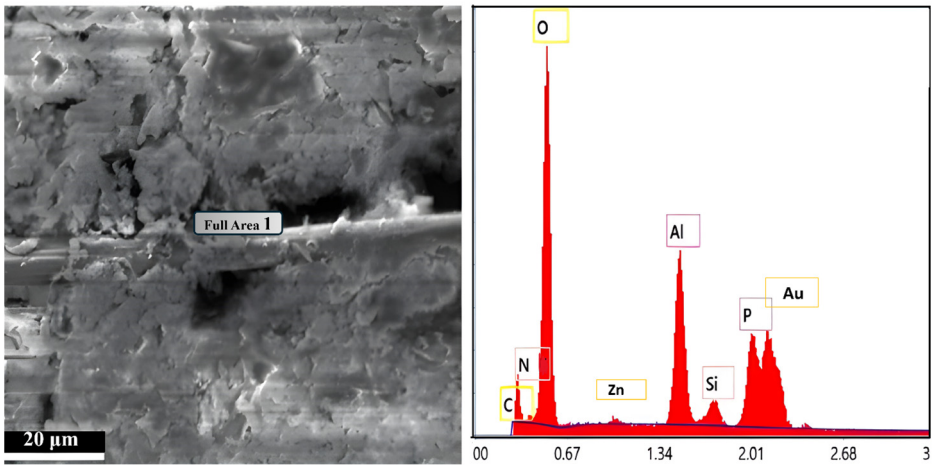


Figure 8. SEM and EDX spectrum recorded after the solvothermal treatment of 4 h at 200 °C in acetic acid.

Figure 9 shows the FTIR spectra of samples submitted to solvothermal treatments at 200 °C in acetic acid for different times, altogether with the untreated sample. The bands at 1608, 1508, 1450, 1238 and 1010 cm^{-1} that appear in the spectrum of the untreated sample are the typical bands [13] present in the spectra of all epoxy resins [1]. The first three ones may be attributed to the benzene ring. The band at 1238 cm^{-1} is due to aryl alkyl ethers (C−O−C) group. The band at 1010 cm^{-1} may be attributed to the presence of C−OH groups formed during the cure.

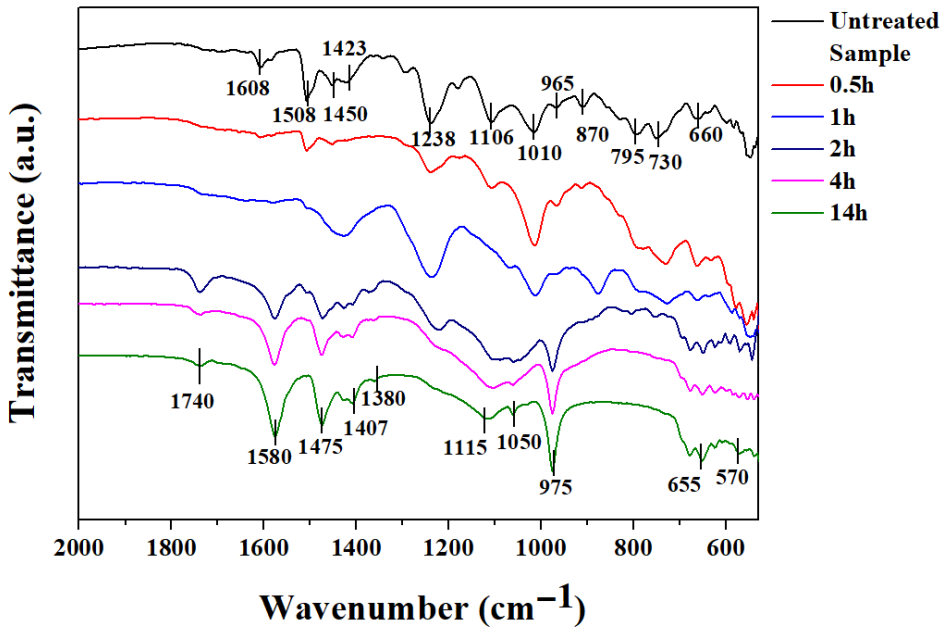


Figure 9. FTIR spectra of samples after solvothermal treatments at 200 °C in acetic acid at different treatment times.

The spectrum changes progressively during the first 2 h. The spectra for longer durations are, instead, very similar to each other. As can be seen, the epoxy bands are hardly distinguished after the 2 h solvothermal process. Starting from 2 h the spectrum is dominated by the bands attributable to acetate ion: 1580, 1475, 975 and 600–700 cm^{-1} [13,26]. This is consistent with results from the literature. The presence of these bands, as well as the ester bond band at 1740 cm^{-1}, may be explained by the esterification reaction of acetic acid with C-OH groups formed during the epoxy cure and/or formation of aluminum acetate from aluminum hydroxide [13].

The spectra also show bands attributable to the P, B and Al flame retardant phases, which appear to undergo relevant modifications during the solvothermal treatment. The bands at 1423, 1106, 795 and 730 cm^{-1} present in the untreated sample may be attributed to vibration of borate structures [27]. The presence of the FTIR bands of borate structural units, together with Zn in the EDX spectra, indicates the presence, in the CFREP boards, of the well-known flame-retardant zinc borate [8,15,28]. In this case the FTIR spectra are more difficult to interpret due to the occurrence of different structural units with boron possibly engaged with oxygen in trigonal but also tetrahedral structures. Many papers, in fact, deal with hydrated zinc borate phases differing in ZnO, B_2O_3 and H_2O content and possessing quite different FTIR spectra [29–33]. It is also worth remembering that the band at a wavenumber at about 1100 cm^{-1} present in all the spectra may be also attributed to the stretching vibrations of PO_4 tetrahedra or Al-O bonds other than to the B-based tetrahedral units [32,33].

It is worth pointing out that two of the borate bands (795 and 730 cm^{-1}) disappear during the solvothermal treatment. This strongly suggests that the borate phase present in

the untreated samples reacts during solvothermal treatment, possibly transforming into a phase in which boron is more engaged with the oxygen in tetrahedral structures. Zinc borate is, otherwise, known to develop a synergistic flame-retardant action with phosphate-based flame retardants [8,15] giving a boron-aluminum phosphate layer, which may exert an even better protection against fire [8,15]. The changes of the borate FTIR bands during the solvothermal treatment may thus be justified.

The unexpected surface insoluble layer formation during the preswelling step may, therefore, admit a simple explanation. It is worth remembering, in fact, that phosphate and borate-based flame retardants are able, when the temperature is raised, to play their flame retardancy role by promoting the formation of a carbonaceous char at the polymer surface [6–10]. The phosphate-based flame retardants generate (poly)phosphoric acid species that, owing to its acidity, promote the carbonization of the epoxy matrix by dehydration reactions [6–10]. The experimental results suggest, therefore, that the surface insoluble layer formed during the studied solvothermal process, having an organic/inorganic hybrid nature, is the result of the intersection of two reaction paths: degradation of epoxy in the presence of acetic acid and carbonaceous char formation caused by the presence of Al-, P-, Zn- and B-based flame retardants. Considering the abovementioned mechanism of action of phosphate and borate flame retardants, one may also speculate, as also proved by successive dissolution in the monoethanolamine, that the protective degraded layer formation may be favored by the acidic nature of acetic acid.

4. Conclusions

The recycling of CFRP, particularly the CFREP, is a challenging problem due to the wide range of applications, the amount of laminates produced per year, and the high cost per kg of the carbon fiber fabric, which is 160 or 40 times the cost per kg of carbon steel and aluminum materials, respectively.

Recently, many papers have been published on the recycling of carbon fiber-reinforced epoxy polymers (CFREPs) through solvothermal methods, which allow one to recover the carbon fiber fabrics with a relatively low environmental impact, owing to the mildness of the process conditions and the use of relatively less aggressive chemicals. These papers deal with neat or fiber-reinforced polymers. This current work shows the results obtained in the case of a CFREP obtained using a flame-retardant epoxy/carbon weave fabric prepreg supplied by the aerospace industry of aircraft interiors, in which the use of flame retardants is essential. To the authors' knowledge, this is the first attempt to investigate and discuss the effect of the presence of flame retardants on the solvothermal process of CFREP.

In the present case the studied samples of the flame-retardant CFREP had to undergo a two-step solvothermal treatment. The epoxy matrix was successfully dissolved in monoethanolammine after a preswelling step in acetic acid. The experimental results show that the proposed process does allow the full recovery of the carbon fabric with its original sizing layer without fiber injury. As confirmation, CFREP laminates produced with recycled carbon fiber fabrics exhibit mechanical properties close to that of laminates obtained from the virgin epoxy/carbon prepreg.

Contrary to what has been reported in the literature, the solvothermal treatment in acetic acid does not allow, in the studied case, complete dissolution of the epoxy matrix. In fact, a maximum mass loss ratio of 15% is rapidly reached, remaining constant for longer times. This value is much lower than the 30% matrix content evaluated through thermogravimetric analysis. This means that, although assuring swelling, the acetic acid pretreatment causes the formation of a surface degraded layer, which impedes complete removal of the polymeric matrix and full recovery of the carbon fabric if only acetic acid

is used. The SEM-EDX and FTIR results indicate that the surface insoluble layer has an organic/inorganic hybrid nature and suggest that it is the result of the intersection of two reaction paths: solvothermal degradation of epoxy and char formation caused by the presence of Al-, P-, Zn- and B-based flame retardants. Based on the known mechanism of flame retardancy of phosphates and borates, the degraded layer formation is attributed to the acidic character of the acetic acid. It is worth pointing out that the paper suggests, therefore, that the presence of flame retardants may strongly affect the solvothermal processes.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/solids7020017/s1, Additional experimental details, including photographs of experimental setup (Figure S1. Photo of the solvothermal reactor and Figure S2. Schematization of the stacking sequence of the vCFRP (a) and rCFRP (b) samples.).

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Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

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