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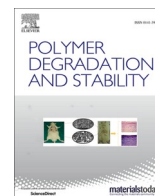
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Recovery of chemical recyclates from fibre-reinforced composites: A review of progress

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ABSTRACT

In this critical review article, the current state-of-the-art in composite solvolysis is reviewed against the backdrop of a growing need for recycling in the composites industry. The scope of the review includes all fibre types in any polymer matrix but focuses on articles since 2015. Given the unique position of solvolysis for recovering products from matrix recyclates, it is noteworthy that relatively few studies have examined this aspect of solvolysis in detail, although particular attention is given herein to the works that do consider matrix recyclates. An additional emphasis is placed on critiquing the potential for scalability/industrialisation of the different technologies and the associated blockers. After the state-of-the-art review, a ‘cheat sheet’ of a typical solvolysis process is given, describing the workflow of the recycling treatment, the common metrics by which its success is measured, what substrates solvolysis is most suitable for, finally culminating in a technology readiness level (TRL) assessment of solvolysis in the UK and worldwide.

1. Introduction

Fibre-reinforced polymer composites (FRPs) are ubiquitous in high-performance modern structures, from concrete rebar to wind turbines, marine vessels to aircraft, and tennis racquets to bicycles; composite use is widespread and growing. The UK composites industry alone (materials and parts) was valued by Lucintel at £4.0 billion in 2019 with a forecast of growth to £6.3 billion by 2035 [1]. Despite the *in service* benefits from their high performance-to-weight ratio, there is growing concern about the sustainability of composites, notably at end-of-life (EOL). In the 2021 JEC Observer report, it was revealed that only 2% of EOL FRP is currently recycled worldwide [2]. The variety of materials used in FRPs is one of the major recycling challenges, since different polymers and different fibres require different treatments, which is both a product of the intrinsic material properties and their relative market value. The majority of the academic literature focuses on carbon fibre reinforced thermosets and for good reason; carbon fibres are highly valuable and are typically used with thermoset resins in high-end applications and make up approximately 80% of the carbon FRP market [3]. However, in 2018 carbon fibre composites represented only 1% of the *global* composites market by volume. Conversely, GFRP (glass fibre reinforced polymer) composites account for ~99% of the market, of this there is a roughly even divide between thermoset and thermoplastic matrices [4]. In summary, there is a large volume of relatively low value GFRP in our built environment and a small but significant volume of

highly valuable CFRP (carbon fibre reinforced polymer). Both types of FRP require attention to overcome their EOL recycling challenges.

Composite solvolysis is one of a range of techniques that falls under the umbrella of so-called ‘advanced recycling’ processes. Simply put, advanced recycling is any non-mechanical recycling process and includes other techniques such as pyrolysis, steam thermolysis, fluidised bed thermolysis, and electrofragmentation. Mechanical recycling was the first method of composite recycling to be commercialised courtesy of its low cost; however, the recyclates it generates generally have very low value. In theory, advanced recycling techniques enable the recovery of higher value recyclates, such as intact fibres and sometimes matrix degradation products. The term solvolysis is often used synonymously with ‘chemical recycling’. Strictly, chemical recycling refers to the use of a chemical agent or process to facilitate recycling either as reactant or solvent. However, this can leave some ambiguity with certain thermolysis processes, which some authors refer to as a sub-category of chemical recycling. More commonly, chemical recycling is used to refer to dissolution (the physical processes of solubilising a solid) or solvolytic processes, which strictly describe bond-breaking that occurs by the action of a solvent medium. Although there are some examples of dissolution-based recycling of specific thermoplastic composites, the majority of the literature concerns some degree of bond breaking in solution and thereby constitutes solvolysis.

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1.1. Pre-2015

Oliveux et al. [5] reviewed FRP recycling in 2015 with a thorough examination of solvolysis techniques including commercial examples. It is that article that forms the baseline and boundary for the rest of this review. The authors divided their solvolysis review into high temperature/pressure systems (temperatures >200 °C) and low temperature/pressure systems (<200 °C and usually atmospheric pressure). Amongst the advantages the authors cite for solvolysis over thermolytic treatments, is the lower temperatures required to separate the fibres from the matrix. Crucially, this means that there is less likelihood of damage to the fibres, which is particularly true in the case of glass fibres, which are highly thermally sensitive. Although theoretically the use of lower temperatures (in solvolysis vs. thermolysis) would be associated with lower energy costs, in reality several LCA (life cycle assessment) studies have indicated that high temperature thermolytic treatments are associated with significantly lower energy intensities than solvolysis treatments (with supercritical fluids) [6,7]. The origin of this energy intensity is likely due to a combination of heating large volumes of solvent (in contrast to the gases of thermolytic processes) and the energy required to synthesise the solvent in the first place.

The commonly used solvents are water, organic solvents including alcohols (ethanol, propanol, butanol, ethylene glycol etc.), phenol, acetone, amines, and the mixture of any of these with water as a co-solvent. Of the non-aqueous media, alcohols, glycols, and acetone are most common, in part due to their status as broadly 'non-harmful'. The solvolysis processes are often enhanced with additive acids or bases, which may or may not constitute catalysts dependant on if they are consumed by the degradation reactions or not. In general, degradation rate is intimately related to the temperature, where a high temperature accelerates degradation. Another important factor affecting rate is substrate scale, larger substrates can introduce diffusion concerns. Much research has focused on the use of supercritical fluids as the solvolysis media due to their tuneable properties (pressure dependant solvent power), their very high diffusivity and mass transfer. The authors noted that supercritical water (SCW) is often used but that supercritical alcohols generally necessitate lower pressures to surpass the critical point. Aside from the increased energy costs, high temperatures can also be disfavoured due to the prevalence of side reactions. In some cases, higher temperatures decrease degradation efficiency by producing an insoluble char on the fibres [8]. Achieving degradation efficiency of near 100% is generally very important, because any residual matrix can hinder adhesion when the fibres are processed into new composites. Although this is more of a problem with thermolytic processes, it can also be true of solvolysis. As such, solvolysed composites are usually washed, which adds processing time and effort, although this step may not be required in (semi-) continuous reactors. In some circumstances residual matrix can *improve* the mechanical performance of single fibres but hinder adhesion in new composites; consequently, recycled fibres require thorough qualification.

The substrates that feature in this literature include both carbon and glass reinforced polymer, with matrices including amine-epoxy, anhydride-epoxy, unsaturated polyester (UP) and PEEK (polyether ether ketone). Of these examples, UP is the easiest to degrade and PEEK the hardest, with the two categories of epoxy somewhere in between. This tends to manifest in terms of the temperatures required to effect complete degradation over the chosen timescale. Furthermore, the authors also highlight that not all polymers of the same class degrade at the same rate. The different molecular structures, the crosslink density (and by extension, T_g), the fibre volume fraction and the reinforcement format (woven vs. non-woven) all have a large impact on degradation rate. Both carbon and glass fibres can be deteriorated by harsh solvolysis conditions, though this is most significant with glass and most significant with strongly acidic/basic conditions. Any appreciable level of fibre degradation compromises the value of solvolysis over cheaper recycling processes.

1.2. 2015–2022

This section is primarily organised by matrix type, with a secondary sorting by chronology of publication year. A few solvolysis-related reviews have been published since the Oliveux article: Kumar and Krishnan [9], which focuses on chemical recycling of CFRP; Scaffaro et al. [10], which focuses on the limited articles in which both fibres and matrix products are recovered; and Xue et al. [11], which examines all recycling methods for *thermoset* FRPs. Crucially, what is absent from these reviews and what this article aims to address, is a joined-up approach between industrial need and academic research; with a realistic assessment of what materials solvolysis is well positioned for (and what materials it is not) and what research is required to develop solvolysis into a viable proposition for composite EOL.

1.2.1. Amine-epoxy

Amine-cured epoxies (Fig. 1) are the most researched substrate in the composite solvolysis literature, which is unsurprising given the ubiquity of epoxy FRPs. Given their structural differences from anhydride-cured epoxies, the literature concerning these materials will be reviewed separately. In 2015, Oliveux and co-workers [12] explored a variety of different solvolysis (hydrolysis) conditions to degrade a DDS (diaminodiphenylsulfone)–DGEBA (diglycidyl ether bisphenol A) CFRP within a 115 ml batch reactor. Pure solvent, biphasic solvent or CO₂-expanded solvent was used. Several interesting trends emerged from this work; (i) counterintuitively, stirring was observed to decrease degradation rate. (ii) CO₂ in water enhances its fluidity and thereby accelerates degradation but only up to a point before the higher pressure inhibits degradation. (iii) in binary solvent systems a blend of 80% organic solvent to 20% water was most effective. This was true of propanol, acetone and ethanol, such systems at 350 °C can double the degradation rate relative to reactions in pure solvent. Analysis of the liquid fractions indicated that some valuable small molecules may be recoverable. The high temperatures and pressures used in this study were not required in the work of Wang et al. [13], though it should be noted that the residency times used by Oliveux et al. are significantly shorter (<60 min). In their study, Wang and co-workers solvolysed a DGEBA-based amine-epoxy CFRP using an acetic acid/AlCl₃ system under relatively mild conditions (180 °C, 3 bar, 6 h). Several different salts (including other Lewis acids) were tested for catalytic activity, in a range of different solvents, though AlCl₃/acetic acid was by far the best system under these conditions. In addition to the long residency time, another drawback of this process was very high catalyst loading (15 wt %). However, the catalyst does precipitate out from the acetone wash (post-processing of the fibres) such that it can be effectively recycled itself. Unsurprisingly given the mild conditions, the rCFs exhibited excellent mechanical performance, maintaining 98% of their tensile strength and stiffness when compared to virgin CF (vCF). There is minimal discussion concerning the matrix recyclates, though the implication is that these are primarily low-value oligomers.

Henry et al. [14] employed a semi-continuous flow HTP (high temperature and pressure) system to solvolyse aerospace grade, tetrafunctional epoxy-amine CFRP in both near- and supercritical conditions. Both water and water-ethanol mixtures were tested as the solvolysis medium with a flow rate of 1 L/h, temperatures in the region of 350–400 °C, with a pressure of 25 MPa for up to 2 h (excluding ramp and cool down). These authors examined both the fibres, which were observed to be matrix-free by SEM and mechanically robust by tensile testing, and the matrix recyclates. The degraded matrix products were characterised, and it was noted that the ethanol-water mixtures were more effective at producing small molecules. This implicitly suggests that without organic solvent, oligomers are more dominant. This has important implications for the recycle value since at present, there seems to be little market for oligomeric recycle.

In a 2017 article by Oliveux et al. [15], discontinuous rCF produced by the HTP acetone-water solvolysis discussed previously [12] was used

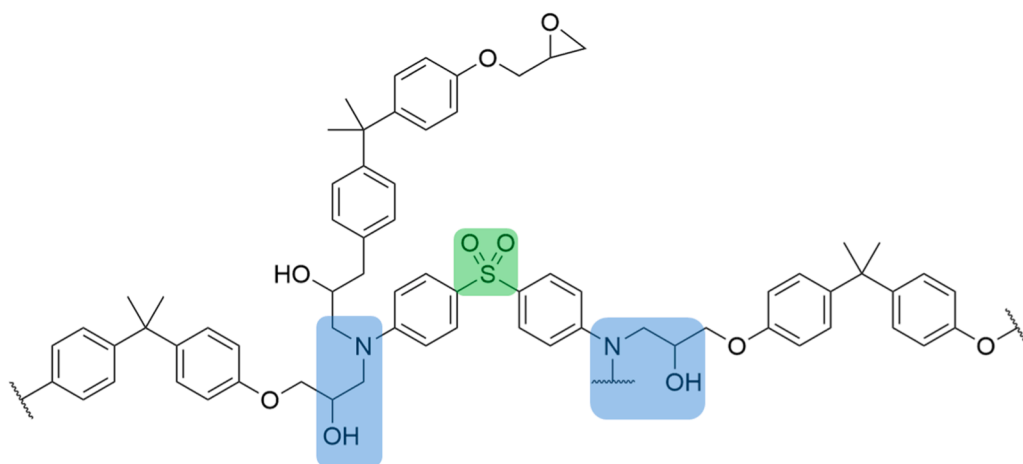


Fig. 1. The molecular structure of a common amine-epoxy system, the product of DGEBA and DDS cross-linking. The representative unit of epoxy-amine adducts is highlighted in blue, where a secondary or tertiary (both tertiary in this case) amine is beta to a hydroxyl unit. This is a relatively stable structure but under harsh conditions can be cleaved, *vide infra*. In the particular case of DDS-hardened epoxies, the sulfone unit (highlighted green) represents an additional position for chain scission.

in the manufacture of new composites. Importantly, the authors used a fibre alignment system developed by the University of Bordeaux to improve the properties of the rCFRP laminates. A ‘light’ acetone wash was the only post treatment required prior to implementation of the alignment process; this was important as it reduced mass fraction of residual resin from 3 wt% to 1 wt%. The authors speculate that a continuous system would be more effective and as such might not necessitate a washing phase. Overall, excellent mechanical performance was observed, although the authors observed some differences in failure mode when comparing rCF and vCF composites, which they attribute to the 1 wt% residue interfering with the adhesion to the new matrix.

Ma and co-workers [16] explored the use of two different solvolysis systems to degrade various epoxy-amines. The first system comprises benzyl alcohol and K_3PO_4 (at 200 °C, ambient pressure), which has previously been demonstrated to solvolyse anhydride-cured epoxies, *vide infra*. The second system the authors described as acid digestion, which employs a hydrogen peroxide/acetic acid mixture at 110 °C. A pre-processing stage was employed in both processes in which the polymer substrate was soaked in benzyl alcohol for 3 h at 200 °C. The acid digestion process was considerably faster, but the authors concede in a later study that the use of peroxide makes it non-viable on an industrial scale [17]. Moreover, in the subsequent study, in which the same processes were applied to composites (instead of neat epoxy), the authors found that peroxide-acetic acid solutions significantly damage glass fibres. Furthermore, unlike the benzyl alcohol solvolysis, the peroxide treatment does not yield any matrix recyclate. One particularly valuable insight from this work was that due to the higher crosslink density and T_g , tri- and tetra-functional epoxies (that are common in aerospace grade CFRP) can degrade an order of magnitude slower by these solvolysis conditions—the unreinforced tetrafunctional epoxy required 50 h for complete degradation by the benzyl alcohol (200 °C) route.

A similar peroxide-based solvolysis medium was employed to degrade a DDS-DGEBA CFRP by Navarro et al. [18], this time using hydrogen peroxide in combination with scandium trichloride. It was reported that the peroxide ‘‘catalyses’’ the oxygen transfer step and the scandium trichloride acts as a catalyst for imine hydrolysis in the latter part of the degradation mechanism. The authors used GCMS and MALDI-MS to analyse recyclates but determined that the conditions were too harsh (peroxide, 110 °C, 12 h) for the isolation of monomer. Although the fibres appeared pristine, no significant quantity of monomer or other small molecules were observed. Due to the hazards associated with industrial peroxide use *and* the complete destruction of the matrix, these conditions are not appropriate for industrialisation.

In 2019, Keith and co-workers [19] examined the efficacy of the sub-/ supercritical 80:20 acetone:water system (examined previously [15]) in more detail. In this study a composite of T700 CFs and RTM6

resin was prepared and tested ($T_g > 210$ °C), with HTP screening between 300 and 380 °C and 16–30 MPa. The authors determined that 2 h was the minimum duration required to produce clean fibres after processing at 320 °C. Clean fibres were defined as 95 wt% matrix removal (determined by TGA) after post-solvolytic washing with acetone. Below 320 °C it was not possible to fully degrade the resin even after 2 h, this was attributed to the very high crosslink density and associated T_g , which is representative of high-performance epoxy composites. Higher temperatures of 340 and 360 °C resulted in complete resin decomposition in 45 and 15 min respectively. In this case, the substrate was cut into $10 \times 10 \times 6$ mm cuboids, and there was significantly higher degradation in the xy plane than through the thickness (z-axis) of the composite. This was attributed to the lower fibre density between plies. XRCT imaging demonstrated that the solvent appeared to reach the centre of these sized substrates rapidly, hence the authors inferred that the degradation reaction was under kinetic control. As such, the degradation was modelled by two methods: Arrhenius and shrinking core. Although both models predicted degradation to within 5% accuracy of experiment, the first-order Arrhenius model appeared to give a better fit. In another article, Keith et al. [20] examined different methods of catalysing the 80:20 acetone:water system, to enhance reactivity. Once more, the authors used RTM6-T700 composite, but this time managed to effect efficient solvolysis under milder conditions (280–320 °C and 13–20 MPa). In this case, the catalysts were a range of salts (carbonates, chlorides and hydroxides), used in concentrations of 0.1–0.4 M, although NaOH, KOH, $CaCl_2$, $CsCO_3$ and several other salts were ineffective, the Lewis acids $ZnCl_2$, $MgCl_2$ and $AlCl_3$ enabled recovery of clean fibres under the above conditions. This is in contrast to the findings of Sokoli. In addition, these catalysts also reduced the reaction time (as well as the temperature and pressure), when compared to the uncatalysed system that was previously discussed. The minimum requirements for complete matrix degradation (of all three catalysts) were 290 °C for 1.5 h or 300 °C for 0.75 h. The authors examined the matrix degradation products and the ‘organic liquid fraction’ more generally, in some detail. Interestingly, the products of the Lewis acid-catalysed experiments are very different from those that were base catalysed, indicating that there are lesser amounts of acetone-derived products. Accordingly, if these products were separated for further use it would constitute value recovered from the matrix. In this case, GCMS and FTIR were used, as such there is minimal information concerning the proportion of oligomeric products in the liquid fraction, which would be valuable information. The primary limitations of this work are the small size of substrate ($10 \times 10 \times 6$ mm), which necessitates significant machining and the lack of fibre characterisation—it is conceivable that the catalysts could lead to fibre damage.

Okajima and Sako [21] used HTP acetone to degrade CFRP (amine-epoxy) substrate of $50 \times 5 \times 1$ mm size, without water or catalyst.

High temperature (350 °C) and pressure (10–14 MPa) were effective, leading to 95.6% matrix degradation within 1 h. Interestingly, the authors noted that higher temperatures and longer durations decreased degradation efficiency due to carbonisation of the polymer. Neither the fibre nor matrix recyclates were characterised, as such there does not appear to be any advantage over the milder conditions of the prior literature. In 2020, Faisal and co-workers [22] used concentrated sulfuric acid (15–18 M) to solvolyse expired CFRP prepreg. Above 15 M concentrations, good levels of degradation were achieved at room temperature and pressure, such that rCF of >99% original tensile strength are recovered with only 30 min of reaction (followed by acetone/water washes). The major limitations of this study are threefold, (i) the composite prepreg does not appear to be well consolidated and will have low T_g since it was cured at room temperature, (ii) the matrix recyclates were not analysed, (iii) 18 M sulfuric acid is essentially neat and is extremely corrosive. Accordingly, these conditions may not be practicable on an industrial scale.

Zhao and co-workers [23] developed a two-step solvolysis system for degrading amine-epoxy composites that consists of (i) swelling in acetic acid and (ii) solvolysis with KOH in ethanolamine. Up to 99% resin degradation was achievable with a 40 min, 90 °C (i) pre-treatment followed by a 90 min, 160 °C treatment with 10 wt% KOH in ethanolamine. rCFs recovered from this treatment maintained 93.5% of their original tensile strength. This minor decrease in strength may originate from the observed increase in surface amorphous carbon. The matrix recyclates were not examined. Liu et al. [24] used supercritical n-butanol with KOH catalyst (0.05 M) to degrade UD CFRP with a DGEBA-dicyandiamide matrix, it is not evident how well consolidated this composite was. With 1 h at 330 °C and 6.5 MPa it was possible to completely degrade the matrix. The matrix recyclates were not studied. Much of this article focused on the reuse of the rCFs as short fibre reinforcement for PP composites. The lack of sizing on the rCFs and the associated quality of the interfaces of their composites was highlighted as a problem, although de-sized virgin CF generally performed worse in the PP matrices than the rCFs. Liu et al. [25] also performed an LCA for the purpose of comparing this solvolysis technique with incineration and steam thermolysis, performing favourably against both.

Zabihi and co-workers [26] employed a microwave-assisted approach to effect rapid solvolysis of a VARI-prepared CFRP laminate cut into 70×10×2.5 mm pieces (with a Hexion proprietary epoxy formulation). In this study the solvolysis medium was a combination of hydrogen peroxide (50 wt% in water) and tartaric acid in a 3:1 ratio. In a typical experiment, the solvolysis medium was microwaved (in a conventional 800 W microwave on full power) for 2 min, reaching a maximum temperature of 120 °C. The degraded composite was then sonicated in acetone for 5 min and finally dried at 60 °C. Conventional heating was at least 100x slower to reach a similar level of degradation. An extensive programme of testing was used to characterise the rCFs, including single-fibre and flexural testing of composites prepared from recycled and re-sized composites. A small amount of residue was generally observed, which was consistent with the incomplete degradation yield given by TGA (typically 92–95%). The best-case sample of fibres were associated with an 8% reduction in strength and the single fibre experiments have a high degree of scatter; this may be due to defects formed on the surface (which becomes significantly oxidised). The oxidised fibre surfaces seem to improve adhesion in product composites. Overall, it seems like these conditions are too harsh—hydrogen peroxide is an aggressive reagent. The matrix recyclates were not thoroughly characterised; however, the degraded epoxy was tested as a partial replacement/filler in low performance epoxies. Replacement levels as high as 10 wt% lead to significant mechanical degradation (14% lower tensile strength). This suggests that the value of this material in this type of application is minimal, such that the matrix recycle may be more valuable as a fuel. Lebedeva et al. [27] also used hydrogen peroxide (in conjunction with water and sulfuric acid) to solvolyse amine-epoxy CFRP, which was capable of yielding clean fibres, though the fibres

were not mechanically characterised and the matrix recyclates were not examined at all.

In 2021, Schamel and co-workers [28] employed another peroxide based approach to degrade amine-epoxy (isophorone diamine–DGEBA) CFRP. In this study an initial swelling phase was employed using NMP (N-methyl-2-pyrrolidone) at 195 °C, after which the composite was washed and then treated with hydrogen peroxide up to 200 °C. Excellent resin degradation was reported (up to 99%). However, there are several limitations with this work including (i) an inert atmosphere was employed to prevent oxidation of the solvent (this adds an additional cost), (ii) single fibre data was not reported ‘due to high scatter’, which indicates there may be significant fibre damage, (iii) there is no analysis of the matrix recycle. Navarro et al. [29] presented an alternative to the use of hydrogen peroxide in the form of epoxy-degradation based on the use of oxygen gas. Using acetic acid as the solvent, a Lewis acid catalyst (5 wt%) and 10 atmospheres of oxygen at 180 °C for 43 h, the researchers produced both clean rCFs and useful matrix recyclates from amine-epoxy ($T_g \sim 180$ °C) CFRP. The authors speculated that atmospheric oxygen might play a role in much of the solvolysis literature. A screening of several catalysts revealed that a combination of $MnCl_2$ (as the oxidation catalyst) and $AlCl_3$ (as the solvolytic catalyst) worked best. A variety of alternatives to Mn were similarly effective but Mn was chosen due to its lower cost and toxicity. The authors also used a benzyl alcohol pre-treatment to swell the composite (4 h, 200 °C). The fibres were not thoroughly characterised, although appeared to be clean and undamaged by microscopy. Although only 25% of the total matrix mass is recovered as matrix recycle, some of these products have been demonstrated to have utility: both materials from bisphenol A and DDS can be recovered. The oxidised oligomer of DDS can be used as an accelerator in preparing new anhydride-hardened epoxy. A small fraction of the matrix recycle can be transformed into bisphenol A in a single step. Nevertheless, the long residency times, high pressure of oxygen and two-pot nature of this process may make it difficult to scale-up. A spin-out company ‘Closed Composites LLC’ is attempting to do just this.

In 2022, Rani et al. [8] reported a microwave-assisted solvolysis of epoxy-GFRP (DGEBA-polyamine), citing that conventional heating methods for chemically recycling GFRP are not feasible due the high energy costs and low value of the glass. The solvolysis medium is a mixture of hydrogen peroxide and acetic acid. Analogously to several earlier works, a swelling step is employed prior to the solvolytic step, although the swelling medium was the same as the solvolysis medium in this case. Crucially, a total microwave irradiation of 180 s (700 W, up to 183 °C) facilitates ~97% resin degradation and can lead to fibres of 93–99% of virgin performance (tensile strength is retained but there is some loss of strain to failure and modulus). By separating the microwave exposure into a 2 min on, 15 min off and 1 min on configuration, charring is not observed (which reduces degradation efficiency). No investigation of the matrix recyclates were discussed. The use of hydrogen peroxide may prevent this process from being adopted on an industrial scale, particularly given the use of acetone in the post-solvolysis (washing) step; the use of peroxide and acetone together presents a small risk of forming triacetone triperoxide, a potent explosive.

Ballout et al. [30] used formic acid to degrade RTM6 epoxy CFRP that was prepared by RTM. Formic acid was chosen as strong and relatively green acid that can be produced by CO₂ capture. A room temperature and pressure treatment in this acid for 48 h, followed by washing and drying, led to 90% resin degradation. The residual 10 wt% of resin significantly impaired the mechanical performance (ILSS and compression after impact) of new composites prepared from the rCF. Due to not requiring either heat or pressure, large volume vats can be used such that minimal machining is required. Accordingly, large substrates can be used with minimal degradation to the fibre architecture. The matrix recyclates were not analysed.

A recent article by Skrydstrup et al. [31] used a Ru[II] catalyst to

solvolysed various epoxy polymers and composites (predominantly amine-hardened epoxies), under mild conditions. In these reactions 6 wt% of the Ru catalyst (relative to the composite substrate) was heated to 160 °C in toluene, with a small amount (8 vol%) of isopropanol used as a cosolvent and hydrogen donor. Since the reaction was performed in a sealed autoclave above the boiling point of the solvent, it is probable that there was significant pressurisation; however, this detail was not reported. This research was focused specifically on the recovery of matrix recyclates, specifically bisphenol A, which is rightly cited as an important feedstock chemical. Indeed, the authors managed to isolate good yields of bisphenol A from various experiments, often in the region of 20 wt% or more. Unfortunately, long durations (up to 6 days) were required to complete the degradation reaction when it was applied to composites. Fibre quality was not characterised in detail. This research highlights an important point concerning scalability that should be considered in any proposed solvolysis process. With a catalyst loading of 6 wt% relative to the composite substrate (and 2.7 wt% relative to the quantity of epoxy), when scaled up to the size of a 15 MW wind turbine blade, 2.7% of the total mass of epoxy is a very large volume of material. At 75 tonnes total, there could be as much as 19 tonnes of epoxy in a single wind blade. 2.7% of this is ~2.5 tonnes of expensive, Ru[III] catalyst. Accordingly, for a process to be industrially relevant it needs to have low cost, efficient reactions—either the reactants need to be cheap, or the expensive ones need to be used at low concentrations—unless an efficient process for recycling the reactants is in place. Unfortunately, in the case of this Ru[III] catalyst it has a major deactivation pathway that forms a highly stable hydride-bridged dimer, reported elsewhere [32]. It seems likely that this dimeric structure will significantly hinder the recycling of the catalyst in this case.

The data of this section is summarised in Table 1.

1.2.2. Anhydride-epoxy

Anhydride-cured epoxies are structurally different to amine-cured epoxies (Fig. 2), with the anhydrides generally believed to form carboxylic acids *in situ*, which themselves react with the epoxide moieties to generate ester linkages. These ester groups are typically less stable than the amino linkages formed in amine-epoxies and as such, anhydride epoxies are generally slightly easier to solvolysed. To the best of our knowledge, information regarding the market share of anhydride vs. amine epoxy is not publicly available. This may be in part due to commercial sensitivity and in part due to a lack of awareness from users—ultimately designers are more interested in performance characteristics and cost, than the underlying chemistry. Anecdotally, it appears amine-epoxies are more prevalent than anhydride-epoxies, but anhydride-epoxies represent a still significant fraction. This seems to be substantiated by the relative number of articles in the recent research literature concerning solvolysis of epoxies, there are less than half the number of articles concerning anhydride systems, despite their more facile solvolysis.

Many companies worldwide are reportedly investigating and attempting to commercialise anhydride-epoxy composite solvolysis; however, there is very little information on these projects within the public domain. One such example that is publicly available is Hitachi Chemical's study concerning the solvolysis of CFRP tennis racquets [33]. In this work, Nakagawa and co-workers demonstrated the recycling of intact, (unshredded) tennis racquets under ambient pressure using 200 L baths of benzyl alcohol and tripotassium phosphate as the catalyst. When exposed to this solvolysis medium at 200 °C, the anhydride-cured epoxy of the tennis racquets is fully degraded, and the recovered CF has mechanical performance in the region of virgin non-woven CF. The authors examined the energy intensity of this treatment and found that, per kg of rCF, the energy burden was 60–95 MJ, although this was dependant on the volume of tennis racquets. Distillation of the solvolysis medium contributed to a large proportion of the total energy intensity. However, the authors did not examine the matrix recyclate in any detail.

In 2017, Liu et al. [34] used aqueous solutions of phosphotungstic

acid to degrade an anhydride-cured epoxy under mild conditions (190 °C, ambient pressure, 5 h). The authors examined several other catalysts, including different polyacids (to phosphotungstic acid) and ZnCl₂, which has been demonstrated to be an effective catalyst for amine-epoxy solvolysis. Interestingly, ZnCl₂ was ineffective with the anhydride-epoxy in this study. Generally, a 5 wt% catalyst loading was used in the study but loadings as low as 1 wt% are purportedly effective. No fibres were used in this study, so it is not clear if the solvolysis conditions are CF/GF benign. However, some further testing on the polymer recyclate was performed, whereby the recyclate was included as a partial replacement in new epoxy blends. Unfortunately, increasing content of recyclate was associated with a significant drop in T_g. Nevertheless, low replacement levels (up to 10 wt%) were observed to increase both impact and flexural strengths, although the gains were marginal.

Sokoli et al. [35] used acetone to solvolysed real wind blade GFRP based on DGEBA (epoxy); analysis of the matrix recyclates indicated that the hardener was anhydride-based. The authors demonstrated that repeated cycles of solvolysis eventually led to increased levels of matrix degradation—the authors deliberately chose ineffective solvolysis conditions to test this. The majority of the post-solvolysis liquid phase was acetone-derived products, which could suggest that little value is being recovered from the matrix itself. Interestingly, the authors speculated that the degradation products from one solvolysis cycle enhanced the degradation efficiency in the next cycle.

In 2018, Kuang et al. [36] examined the solvolysis of epoxy-anhydride CFRP using an organic guanidine base (TBD) as a catalyst in NMP–ethylene glycol blends. The authors noted that degradation is sluggish below T_g but was effective at 170 °C (1.5 h). The catalyst was much more effective than alternatives (zinc acetate, triphenylphosphine and NaOH). However, TBD is both very expensive and is seemingly difficult to recycle. It is also worth noting that the composite prepared in this study was also not consolidated, so is likely to be relatively low V_f and high porosity. Accordingly, conventionally prepared composites would be expected to degrade more slowly under these conditions. Zhang and co-workers [37] also used organic base catalysts in ethylene glycol solutions to solvolysed anhydride-epoxies. N-methyl-4-piperidinol was found to be the most effective transesterification catalyst in this case (the reaction by which the polymer degradation occurred) and was tested in temperatures up to 200 °C. In this study, no fibre reinforcement was used, and the authors focused on the analysis of matrix products and the reusability of the solvent system. N-4-piperidinol was not the most effective catalyst but was chosen for its similarity of boiling point with the solvent (EG), such that both catalyst and solvent could be recovered simultaneously by distillation. The process was proven to be reasonably effective (up to 90 wt% resin removal) in each of three successive cycles. Although the matrix products were examined, they were not investigated for further utility.

The recent article of Kim et al. [38] investigated the conditions required to effect solvolysis of anhydride-epoxy CFRP using non-catalysed supercritical water. 2 h at 405 °C and 280 bar was sufficient to degrade 99% of the matrix mass, where the composite substrate in this case was cut into 1 cm cubes. This high surface area to volume ratio suggests that on a large scale, intact (uncut) parts might require a significantly longer residency time. Although this degradation efficiency is impressive, the energy required to maintain these conditions may make such a process less feasible than catalysed solvolysis, particularly if no value is gained from matrix recyclates—which were not examined in this article. Moreover, these harsh conditions had a deleterious effect on fibre performance, with tensile strength reduced by up to 20% and young's modulus by up to 36%. Zhao and co-workers [39] recently reported a mild solvolysis system comprised of ethanolamine / KOH solutions, which in concentrations of 0.4–0.7 M were found to be effective at degrading anhydride-cured DGEBA (methyl terephthalic anhydride and an imidazole catalyst) at temperatures as low as 160 °C (atmospheric pressure). Within 60 min, complete matrix decomposition was

Table 1
2015–2022 literature concerning the solvolysis of amine-epoxy.

| Entry | Reference | Substrate | Substrate size | Solvent | Substrate-solvent ratio | Additive | Additional process | Temperature | Pressure | Duration | Degradation yield ^a | Fibre quality ^b | Matrix recyclates | Notes |
|-------|------------------|---|----------------|---|------------------------------|--|--|-------------|-------------|----------|--------------------------------|------------------------------|---|--|
| 1 | Oliveux et al. | DGEBA-DDS, ^f unreinforced | Unknown | 80:20 v/v Acetone:water | 30 mg / ml | N/A | Acetone wash | 350 °C | 235 bar | 0.5 h | 93–99% ^c | N/A | Some valuable small molecules | Option of additional CO ₂ pressure |
| 2 | Oliveux et al. | DGEBA-DDS, unreinforced | Unknown | Water | 10 mg / ml | N/A | Acetone wash | 350 °C | 155 bar | 1 h | 84% | N/A | Some valuable small molecules | |
| 3 | Wang et al. | DGEBA-DMDC, ^f CF | 1 small piece | Acetic acid | 1.5 g / 5 g | 15 wt% AlCl ₃ | Acetone wash | 180 °C | 3 bar | 6 h | 100% | 98% virgin tensile strength | Oligomers, undetermined | N/A |
| 4 | Wang et al. | DGEBA-DMDC, CF | 1 small piece | Acetic acid | 1.5 g / 5 g | 10 wt% AlCl ₃ | Acetone wash | 180 °C | 3 bar | 6 h | 84% | 98% virgin tensile strength | Oligomers, undetermined | N/A |
| 5 | Henry et al. | RTM6 [tetrafunctional], plain weave CF | 50×20×2.2 mm | 50:50 v/v Ethanol:water | 3 g [1 L/h flow] | N/A | N/A | 375 °C | 250 bar | 2 h | 96% | >94% virgin tensile strength | Some small molecules, oligomers | Semi-continuous reactor, in some cases degradation is nearly complete during ramp, durations are unclear |
| 6 | Henry et al. | RTM6 [tetrafunctional], plain weave CF | 50×20×2.2 mm | Water | 3 g [1 L/h flow] | N/A | N/A | 375 °C | 250 bar | 2 h | 98% | >94% virgin tensile strength | Oligomers | Inert atmosphere (Nitrogen) |
| 7 | Ma et al. | DGEBA-DDS, unreinforced | 1 g | Benzyl alcohol | 1 g / 100 ml | K ₃ PO ₄ | Benzyl alcohol 3 h, 200 °C soak; acetone wash | 200 °C | 1 bar | 2 h | ~100% | N/A | Oligomers, some small molecules | Inert atmosphere (Nitrogen) |
| 8 | Ma et al. | 4,4'-Methylenebis (N,N-diglycidylaniline), unreinforced | 1 g | Benzyl alcohol | 1 g / 100 ml | K ₃ PO ₄ | | 200 °C | 1 bar | 32 h | ~100% | N/A | Oligomers, some small molecules | Inert atmosphere (Nitrogen) |
| 9 | Ma et al. | Cycom 5320-1/8HS prepreg | 100×20×2 mm | 6:1 v/v Acetic acid:H ₂ O ₂ (aq.) (30% w/w) | 6.5 g / 110+ ml ^d | N/A | Benzyl alcohol 3 h, 220 °C soak 5 bar; DMSO wash | 110 °C | 1 bar | 48 h | ~100% | N/A | None | Unsuitable for GFRP due to fibre damage |
| 10 | Navarro et al. | DGEBA-DDS, woven CF | 100×20×2 mm | 6:1 v/v Acetic acid:H ₂ O ₂ (aq.) (30% w/w) | 5 g / 70+ ml ^d | ScCl ₃ | N/A | 110 °C | 1 bar | 6 h | ~100% | N/A | None | N/A |
| 11 | Keith et al. | RTM6, T700 | 10×10×6 mm | 80:20 v/v Acetone:water | 30 g/L | ZnCl ₂ , AlCl ₃ , MgCl ₂ (dilute) | Acetone wash | 290 °C | 145 bar | 1.5 h | 95% | N/A | Some valuable small molecules | N/A |
| 12 | Okajima and Sako | Amine-epoxy CFRP | 50×5 × 1 mm | Acetone | 0.4 g / 2.5 ml | N/A | Acetone wash | 350 °C | 100–150 bar | 1 h | 96% | N/A | Undetermined | N/A |
| 13 | Faisal et al. | Expired CFRP prepreg | 50×25×0.5 mm | 15–18 M H ₂ SO ₄ | 1 g / 50 ml | N/A | Acetone wash, water wash | 25 °C | 1 bar | 0.5 h | 98% | 99% virgin tensile strength | Undetermined | N/A |
| 14 | Zhao et al. | Amine-DGEBA, T700 woven | 25×15×3 mm | Ethanolamine | 3 g / 90 ml | 10 wt% KOH | Acetic acid soak 40 min, 90 °C | 160 °C | 1 bar | 1.5 h | 99% | 94% virgin tensile strength | Undetermined | N/A |
| 15 | Liu et al. | DGEBA-dicyandiamide, CF | Unknown | N-butanol | 0.1 g / ml | 0.05 M KOH | Acetone wash | 330 °C | 65 bar | 1 h | ~100% | 95% virgin tensile strength | Undetermined | High Weibull mod. indicates high scatter in mech. testing, defects. 93% Young's mod. retention |
| 16 | Zabihi et al. | Hexion epoxy, Hexcel UD CF | 70×10×2.5 mm | H ₂ O ₂ (aq) / tartaric acid | 1 g / 20 g | N/A | Microwave-assisted solv. Post-process: sonication in acetone | 120 °C | 1 bar | 0.1 h | 92–95% | 92% virgin tensile strength | Some oligomers, not fully characterised | Conventional heating ~100 x slower. Tensile results associated |

(continued on next page)

Table 1 (continued)

| Entry | Reference | Substrate | Substrate size | Solvent | Substrate-solvent ratio | Additive | Additional process | Temperature | Pressure | Duration | Degradation yield ^a | Fibre quality ^b | Matrix recyclates | Notes |
|-------|-------------------|---------------------------------|-------------------------|--|-------------------------|--|--|-------------|----------|-------------------------------|--------------------------------|--|---|---|
| 17 | Schamel et al. | DGEBA-isophorone diamine, CF | 18×10×5 mm | 30% (v/v) H ₂ O ₂ (aq) | Unknown | N/A | Pre-swell: 195 °C in NMP for 5 h. | 195 °C | 1 bar | 19 h | ~100% | N/A | Uncharacterised oligomers | with significant scatter Mechanical tests performed but not reported due to high scatter |
| 18 | Navarro et al. | DGEBA-DDS, woven CF | 1 small piece | Acetic acid | 1 g / 80 ml | 5 wt% MnCl ₂ or AlCl ₃ | Benzyl alcohol soak, 4 h 200 °C. O ₂ atmos. during solv., DMSO wash | 180 °C | 10 bar | 43 h | ~100% | N/A | Small molecules (incl. monomers) and oligomers isolated | Closed Composites LLC are attempting to commercialise this |
| 19 | Rani et al. | DGEBA-polyamine, E-GF | 40×40×4 mm | 7:3 v/v Acetic acid:H ₂ O ₂ (neat) | 1 g / 16 ml | N/A | 0.5 h pre-swell in solv. medium, microwave-assisted, acetone wash | 183 °C | 1 bar | <1 h ^c [<0.1 h] | 97% | 99% virgin tensile strength | Undetermined | 93% virgin modulus [glass fibres] |
| 20 | Ballout et al. | RTM6, (satin weave) CF | 420×300×3.5 mm | Formic acid | Unknown | N/A | Water wash | 25 °C | 1 bar | 48 h | 90% | Composite: 88% virgin ILSS, 75% virgin CAI | Undetermined | Relatively low level of resin degradation under reported conditions |
| 21 | Skrydstrup et al. | Various DGEBA-amine epoxies, GF | 5 g piece of wind blade | Toluene (8 vol % ¹ PrOH) | 5 g / 54 ml | 6 wt% homogeneous Ru[II] catalyst | Column chromatography to purify matrix products | 160 °C | Unknown | 144 h | ~100% | N/A | Bisphenol A | Very expensive catalyst |

^a yields of ~100% are inferred from description.

^b only mechanical characterisation data is considered in this table.

^c 1 wt% residual matrix reported in a later study.

^d further aliquots of peroxide added every hour.

^e swelling step and microwave downtime added to microwave *on* time (only 3 min of microwave heating).

^f DGEBA = diglycidyl ether bisphenol A, DMDC = 4,4'-methylenebis(2-methylcyclohexylamine), DDS = diaminodiphenylsulfone.

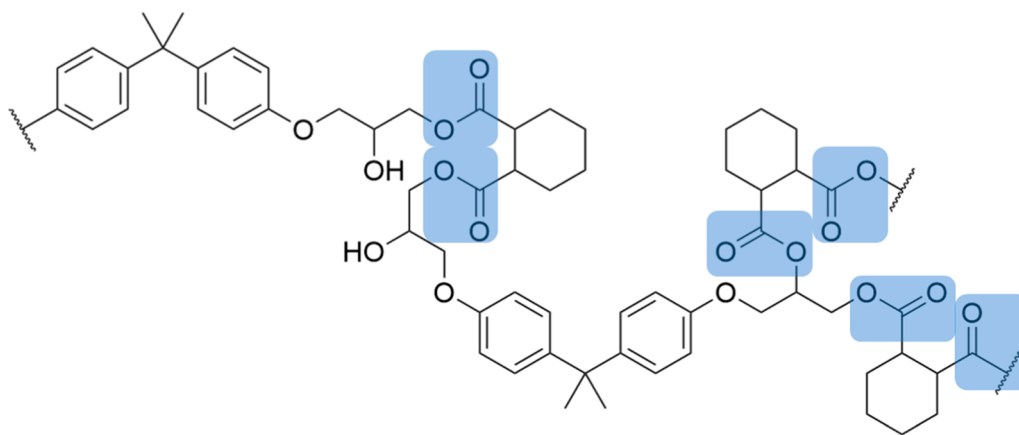


Fig. 2. The molecular structure of a representative anhydride-epoxy, DGEBA hardened with 1,2-cyclohexanedicarboxylic anhydride. The ester linkages highlighted in blue represent the weak points in the polymer chain that are susceptible to cleavage.

observed. As is typical, the recovered fibres were washed with acetone and water prior to an extended period of drying at elevated temperature (~20 h). In this study, both the matrix and fibre recyclates were examined, although fibre characterisation was limited to electron microscopy and Raman spectroscopy, which both suggested that the carbon fibres are undamaged. The process of isolating the matrix recyclates was detailed, accounting for recycling of the solvolysis medium. The matrix recyclates themselves were used in the partial replacement in new epoxy adhesives. However, only modest replacement levels can be reached before mechanical performance is significantly compromised. This highlights the problem of reutilising epoxy oligomers. The presence of amides in the liquid fraction was used to evidence an aminolysis mechanism.

Zhao et al. [40] explored a range of different solvolysis conditions for the degradation of methylterephthalic anhydride-hardened DGEBA. Negligible degradation was observed with aqueous HCl, which the authors attribute to the hydrophobicity of the polymer. Of all tested additives, K_3PO_4 was found to be most effective. The authors presented a process that follows: substrate crushing/cutting down to size, then alcoholysis with K_3PO_4 , before hydrolysis and then drying. One of the major advantages of this process is the very low temperature (120 °C, 3 h). The fact that the catalyst is completely insoluble in ethanol at room temperature (but not under solvolysis conditions) also makes catalyst separation for reuse straightforward. No fibre reinforcement was tested in this case. Analysis of the resin recyclate suggested that it was rich in carboxylic acid groups, which are believed to be the active functionality in anhydride hardening reactions. Accordingly, the authors investigated the use of this recyclate as a partial replacement for anhydrides in new epoxies. Anhydride can be replaced with up to 30 wt% of this recyclate without significant compromise to the baseline mechanical performance. This relatively valuable use of the matrix recyclate is a significant achievement. Nonetheless, it is worth noting that the substrate particle size in this solvolysis was ~1 mm and as such these process conditions are not directly applicable to composites. With larger sections of substrate, the degradation rate would probably be much lower.

The data of this section is summarised in Table 2.

1.2.3. Unsaturated polyester

Unsaturated polyesters (UP) (Fig. 3) are the most used thermosets in GFRP composites. Accordingly, there has been significant research investment into UP solvolysis in recent years. By virtue of the lower value of rGF than rCF, most authors pay greater attention to the matrix recyclates in these studies than with epoxy solvolyses. In 2015, Sokoli et al. [41] explored both acid and base-catalysed degradation of UP GFRP in microwave-assisted processes. The aqueous nitric acid solvolysis medium was found to be considerably more effective than the KOH

treatment, such that it was capable of complete (100%) matrix removal within 30 min at 208 °C (ambient pressure) and recovery of monomers. The KOH treatment did not allow monomer recovery. Wang and co-workers [42] explored the degradation of UP composites using different Lewis acid catalysts in acetic acid (180 °C, 6 h, ambient pressure). Both $AlCl_3$ and $FeCl_3$ were effective agents, leading to complete degradation of the matrix. The treatments also did not lead to significant fibre damage, which is particularly unusual with glass reinforcement—tensile strengths of rGF were reportedly 96% of vGF. Interestingly, the $AlCl_3$ system was also used by the same authors to effectively solvolyse epoxy composites. The authors noted that although $FeCl_3$ was an effective solvolysis catalyst for UP, its solubility in room temperature acetic acid makes its recycling considerably more challenging than $AlCl_3$, hence this catalyst is preferred. A combination of oligomers and monomers were identified in the matrix recyclate.

In 2016, Sokoli and co-workers [43] used a 50:50 mixture of acetone/water with a KOH catalyst to convert UP GFRP (based on maleic anhydride, phthalic anhydride, propylene glycol and styrene crosslinks) into a high heating value oil. At high pressure and temperature (325 °C and 300 bar) full matrix removal is possible. However, analysis of the liquid products revealed that most of the oil originated from acetone adducts (products of base catalysed aldol reactions), which indicates that little value is recovered from the matrix itself—which is supposed to be an advantage of solvolysis over other recycling processes. Moreover, these relatively harsh reaction conditions are likely to have damaged the rGF, which was not quantified in the article. This work was expanded in 2018 in the article of Arturi et al. [44] in which the liquid phase was more thoroughly analysed by LCMS-MS. Many monomers and related compounds were identified; however, acetone-derived products dominated the mixture. The authors claimed that these were value-added chemicals but did not specify how they may be separated or what market they would be useful for. In a related study, Sokoli and co-workers [45] examined the solvolysis of the same UP blend in sub-critical water (30 min, up to 300 bar and 325 °C), with either no catalyst, KOH or KOH/phenol used as the catalyst. Without the catalyst, subcritical water was reasonably effective at degrading the matrix; however, KOH facilitated breakdown into smaller constituent parts, such that greater monomer recovery was possible. The oligomers produced from all experiments, but in greater quantity in the uncatalysed experiments, are probably less valuable than monomers. The authors highlighted that the specific monomers that were recovered were highly sensitive to the catalyst and reaction conditions, some monomers decomposed or reacted further at higher temperatures (such that they could not be isolated). For example, phthalic anhydride could only be recovered without KOH. Acetone washes were also very important to remove matrix residues and isolate good yields of matrix degradation

Table 2
2015–2022 literature concerning the solvolysis of anhydride-epoxy.

| Entry | Reference | Substrate | Substrate size | Solvent | Substrate-solvent ratio | Additive | Additional process | Temperature | Pressure | Duration | Degradation yield ^a | Fibre quality ^b | Matrix recycles | Notes |
|-------|-----------------|---|-----------------|-----------------------------|-------------------------|--|--------------------------|-------------|----------|----------|--------------------------------|--|---|-----------------------------------|
| 1 | Nakagawa et al. | Epoxy-anhydride tennis racquet (CF) | Intact racquets | Benzyl alcohol | Unknown | K ₃ PO ₄ | N/A | 200 °C | 1 bar | 10 h | ~100% | Unknown | Undetermined | 60–95 MJ / kg of rCF |
| 2 | Liu et al. | DER 331 epoxy, NMA (anhydride) ^c | 6.35 mm sieved | Water | 6 g / 20 g | 1–5 wt% Phosphotungstic acid | Acetone wash | 190 °C | 1 bar | 5 h | 91% | N/A | Oligomers, some characterisation | N/A |
| 3 | Sokoli et al. | DGEBA-anhydride, GF | 60×20×15 mm | Acetone | 33 g / 140 ml | KOH | N/A | 260 °C | 80 bar | 0.5 h | ~100% | Unknown | Mostly acetone-derived products | N/A |
| 4 | Kuang et al. | DGEBA-anhydride, CF | 75×55×30 mm | 9:1 v/v NMP–ethylene glycol | 13.9 g / 150 | TBD ^d (organic base) | Acetone wash | 170 °C | 1 bar | 1.5 h | ~100% | Composite: ~100% virgin tensile strength and modulus | Oligomers, some characterisation | N/A |
| 5 | Zhang et al. | DGEBA-methylcyclohexen-1,2-dicarboxylic anhydride | 40×10×4 mm | Ethylene glycol | 1 g / 7.7 ml | 0.2 M N-methyl-4-piperidinol (and other organic bases) | Acetone wash | 180 °C | 1 bar | 3 h | ~100% | N/A | Small molecules and oligomers, some characterisation | Inert atmosphere (Argon) |
| 6 | Kim et al. | epoxy-anhydride, T700 CF | 10×10×10 mm | Water | ~1.7 g / 80 ml | N/A | N/A | 405 °C | 280 bar | 2 h | 99% | Unknown | Undetermined | N/A |
| 7 | Q. Zhao et al. | DGEBA-methylterephthalic anhydride, woven T700 CF | 30×15×3 mm | Ethanolamine | 1 g / 9 ml | 0.4–0.7 M KOH | Acetone and water washes | 160 °C | 1 bar | 1 h | ~100% | Unknown | Oligomers | Extensive drying after isolation |
| 8 | X. Zhao et al. | Epoxy-methylterephthalic anhydride | 1 mm particles | Ethanol | 1.5 g / 15 g | 0.033 wt% K ₃ PO ₄ | Hydrolysis second stage | 120 °C | 1 bar | 3 h | 95% | N/A | Partially characterised, carboxylic acid functionalised species | Reasonably useful matrix recycles |

^a yields of ~100% are inferred from description.

^b only mechanical characterisation data is considered in this table.

^d nadic methyl anhydride.

^c triazabicyclodecene.

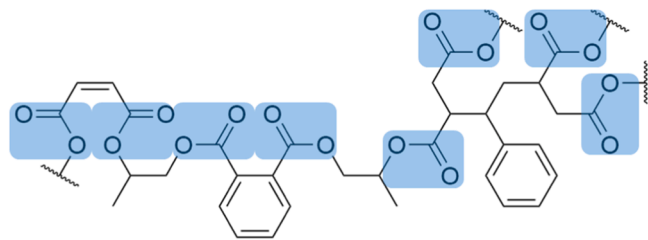


Fig. 3. The molecular structure of the product of maleic anhydride, propylene glycol, phthalic anhydride, and styrene polymerisation. As with anhydride-epoxies, the potential points of chain scission are ester groups, highlighted in blue.

products. This study highlights how important it is that the chemical output of each set of solvolysis conditions be thoroughly characterised if value is sought from the matrix degradation products.

In 2020, Mattsson et al. [46] used a variety of sub and supercritical solvent systems to solvolyse a mixed waste stream of EOL wind blade composites. The authors cite that the main driving force for blade recycling is environmental impact, rather than economic profitability, which is putting off research. The major novelty of this study was the use of real composite components of unknown provenance. In the study, the authors examined a range of temperatures (250–370 °C) and pressures (100–170 bar) within a very small, 7 ml reactor. They found that subcritical water treatment (300 °C) could generate a calorific solvolysis oil (that could be burnt for energy recovery) and rGF of between 80 and 90% of the vGF tensile strength. Of the tested solvent conditions, ethylene glycol, propylene glycol or water-alcohol plus base mixtures seem to be the best. In some cases, very long residency times of 16 h and long acetone soaks (5 days) were used to yield clean fibres. This study highlights just how much more challenging it can be to recycle real EOL composite waste (with complex mixtures of components) than model composite systems. The most effective procedures coupled to different solvolyses conditions: 16 h in ethylene glycol at 270 °C, followed by 3 h in a ternary blend of KOH, propanol and water for 3 h at 330 °C.

The more recent study of Zhang and co-workers [47] used an organic acid catalyst (*p*-toluenesulfonic acid *p*-TsA, at 180 °C) in mixtures of acetic acid and water to degrade UP, citing the value of the catalyst as an amphiphile: the non-polar end helping to penetrate the polymer network and the polar end helping to draw water into the network with it. Limitations of this study are that the UP was not fibre reinforced, which could limit the degradation efficiency, and although the relatively mild conditions might be expected to leave GFs undamaged, it is still important to quantify their performance post solvolysis. In addition, a catalyst loading of 25 wt% is very high and would be expected to make this an expensive process. One of the more valuable sections of this article is the flow chart that details the separation of the polymer recyclates into three different streams for further use. In the first step, the authors performed a distillation (by rotary evaporator) to remove the solvent (acetic acid and water). After addition of cold (0 °C) water to the remaining degradation products, a precipitate and supernatant were formed and separated by filtration. The aqueous supernatant was then subjected to liquid-liquid extraction with chloroform. The major fraction of the organic phase was isolated by evaporation yielding mostly ethylene glycol diacetate. The aqueous phase was also evaporated. This led to formation of a further solid product and a liquid phase, from which the catalyst *p*-TsA was eventually separated. However, it should be noted that recovered catalyst was only 64.3% pure, and the yield of this and other species is unclear. This protocol highlights the complexity that can be associated with catalyst/solvent recovery, which also extends to matrix degradation product valorisation.

The data of the section is summarised in Table 3.

1.2.4. Other thermosets

Unsaturated polyesters dominate the landscape of TS GFRP and unsurprisingly form a large part of the literature concerning FRP solvolysis. Similarly, although CFRP has a much smaller share of the overall volume of composite production worldwide, since rCF is valuable and much cheaper than vCF, there is significant research into CF-epoxy, because epoxies are the most-commonly used TS CFRP matrices. However, an enormous variety of other thermoset resins are used in FRPs including phenolics, polyimides and bismaleimides, benzoxazines, cyanate esters and polyurethanes; however, these are barely represented in the recent literature. Knappich et al. [48] successfully solvolysed PU FRPs with a proprietary solvent system but did not characterise the matrix recyclates. Similarly, Kulikova and co-workers [49] successfully solvolysed phenol-formaldehyde CFRP with strong oxidant-acid solutions but did not examine the matrix recyclates. Likewise, Lo et al. [50] solvolysed a commercial epoxy-benzoxazine blend with a Ru-catalysed oxidation, which appeared to be successful at temperatures as low as 80 °C; however, in this case neither the fibre or matrix recyclates were properly characterised.

Non-composite thermoset solvolysis. Wu et al. [51] examined the degradation of melamine-formaldehyde resins in a THF-H₂O binary solvent system, employing methanesulfonic acid as the catalyst. The authors reported the recovery of valuable chemical recyclates. However, melamine-formaldehyde resins are not commonly used as composite matrices.

1.2.5. Thermoplastics

Bernatas et al. [52] reviewed the recycling methods available for TP FRP including solvolysis and dissolution. Surprisingly, given that there is a widely held belief that TP composites are more recyclable than TS composites (due to their lack of crosslinks), there is a relatively limited pool of literature to support this, particularly in terms of solvolytic recycling. Two examples, however, are the works of Tapper et al. [53] and Liu et al. [54], both performed at relatively low temperature (160 and 60 °C, respectively), which lend some credibility to this hypothesis. Leading methods of TP FRP recycling are cited as solvolysis and dissolution, electrofragmentation and steam thermolysis. The authors highlight the steam thermolysis system that Alpha Recyclage Composites are in the process of commercialising. Amongst the more interesting topics covered is the recovery of acrylate TP resins (Elium).

Elium/acrylate recycling. Several recent studies have explored the recycling of Elium (a liquid infusible resin that forms thermoplastic polyacrylates). Allagui et al. [55] reported that short-fibre NFRPs with an Elium matrix can be mechanically recycled with very little degradation of performance (both mechanical and damping). Meyer zu Reckendorf et al. [56] used acetone to dissolve the matrix away from VARI basalt-Elium composites and compared the influence of stirring and ultrasound, with ultrasound found to significantly improve dissolution. Since the solvent is not breaking matrix bonds this does not strictly constitute solvolysis. Gerbhardt and co-workers [57], performed a similar study confirming that chemically recycled (dissolved by acetone) Elium can partially replace acrylate monomers in the processing of new Elium composites without compromising performance.

Polyamide recycling. Several authors have tested the solvolysis of polyamide FRPs (Nylons), particularly PA6 [48,58,59]. Chaabani et al. [58] found that both sub- and supercritical water were very effective at depolymerising Nylon 6 CFRP (39 wt% matrix), with complete matrix removal within 30 min at 350 °C or 15 min at 400 °C. Importantly, this process produces large quantities of the monomer ϵ -caprolactam and recovery of good quality rCFs, demonstrating value from both recycle streams. Knappich and co-workers [48] used a series of proprietary solvent systems developed by CreaSolv to both solubilise PA6 CFRP and solvolyse TS CFRP (epoxy and PU). The authors reported effective resin removal even in the case of the thermoset composites (when sufficiently high temperatures were employed, such as 280 °C). However, in some cases there was significant fibre damage. Moreover, no effort was made

Table 3
2015–2022 literature concerning the solvolysis of unsaturated polyester (UP).

| Entry | Reference | Substrate | Substrate size | Solvent | Substrate-solvent ratio | Additive | Additional process | Temperature | Pressure | Duration | Degradation yield ^a | Fibre quality ^b | Matrix recycles | Notes |
|-------|-----------------|--|--------------------|--------------------------------|-------------------------|---|--|-------------|-------------|----------|--------------------------------|---|---|---|
| 1 | Sokoli et al. | M/P anhydride, ^c PG and styrene, GF | Unknown | Water | ~4 g / 30 ml | 1–7 M Nitric acid | Microwave-assisted, acetone and water washes | 173–239 °C | 60 bar | 0.5 h | 84–100% | Unknown | Monomers, other small molecules and oligomers | N/A |
| 2 | Sokoli et al. | M/P anhydride, ^c PG and styrene, GF | Unknown | Water | ~2.5 g / 10 ml | 1 M KOH | Microwave-assisted, acetone and water washes | 230 °C | 60 bar | 0.5 h | 63% | Unknown | Some oligomers and small molecules | N/A |
| 3 | Wang et al. | M/P anhydride, ^c PG and styrene, GF | Small piece | Acetic acid | 1.5 g / 4.5 g | 10 wt% Lewis acids (AlCl ₃ , FeCl ₃) | THF washes, dilute HCl washes | 180 °C | 1 bar | 12 h | ~100% | 96% virgin tensile strength GF | Monomers, other small molecules and oligomers | N/A |
| 4 | Sokoli et al. | M/P anhydride, ^c PG and styrene, GF | 50–100×20–40×10 mm | 50:50 v/v Acetone-water | 0.33 g / ml | ~0.6 M KOH | Acetone and water washes | 325 °C | 300 bar | 0.5 h | >90% | Unknown | Mostly acetone-products, some monomers | Extensive drying (80 °C, 24 h); likely fibre damage |
| 5 | Sokoli et al. | M/P anhydride, ^c PG and styrene, GF | 100×40×10 mm | Water | 0.3 g / ml | None, KOH or KOH/phenol | Acetone wash | 325 °C | 300 bar | 0.5 h | 92% | Unknown | More small molecules when catalysed with KOH | Some monomers unstable in KOH; likely fibre damage |
| 6 | Mattsson et al. | Mixed wind blade waste | Unknown | Ethylene glycol | ~0.4 g / 5 ml | N/A | Acetone soaks (5 days) | 270 °C | 100–170 bar | 16 h | 50–90+% | 80–90% virgin tensile strength GF cited, not actually tested in this work | Calorific solvolysis oil | Degradation yield varied significantly dependant on the section of GFRP waste |
| 7 | Mattsson et al. | Mixed wind blade waste | Unknown | Propylene glycol | ~0.4 g / 5 ml | N/A | Acetone soaks (5 days) | 270 °C | 100–170 bar | 16 h | 40–90% | 80–90% virgin tensile strength GF cited, not actually tested in this work | Calorific solvolysis oil | Degradation yield varied significantly dependant on the section of GFRP waste |
| 8 | Mattsson et al. | Mixed wind blade waste | Unknown | 7:2:1 w/w Water, propanol, KOH | ~0.4 g / 5 ml | N/A | Acetone soaks (5 days) | 330 °C | 100–170 bar | 4–16 h | 10–88% | 80–90% virgin tensile strength GF cited, not actually tested in this work | Calorific solvolysis oil | Degradation yield varied significantly dependant on the section of GFRP waste |
| 9 | Zhang et al. | Mixed waste: M/P anhydride, ^c EG, water and styrene | Unknown | Acetic acid-water | 0.1 g / ml | 25 wt% <i>p</i> -toluenesulfonic acid | THF washes | 180 °C | 1 bar | 12 h | 100% | N/A | Monomers and oligomers isolated | Complex separation process for different matrix recycles |

^a yields of ~100% are inferred from description.

^b only mechanical characterisation data is considered in this table.

^c M = Maleic anhydride, P = phthalic anhydride, PG = propylene glycol, EG = ethylene glycol.

to characterise matrix degradation products. Cesarek et al. [59] demonstrated a very efficient hydrolysis of polyamide composites within 20 min at 200 °C by using energy-efficient microwave heating and HCl as a catalyst. A high yield of monomers was recovered as matrix degradation products along with some oligomers. However, the rCF and GF recyclates were not characterised.

Commodity thermoplastic recycling. Several recent articles have explored solvolysis and solvolysis adjacent methods of recycling commodity thermoplastics [60–63]. In general, TP polyesters such as PET are most easy to degrade and fully aliphatic polymers such as HDPE and PP are much more challenging. Although there are some parallels between commodity thermoplastics and the engineering thermoplastics used as composite matrices, the lack of fibres and low T_g of these materials makes their solvolysis much easier, so these articles are not reviewed herein.

1.2.6. Solvolysis-adjacent techniques

Several chemical recycling treatments share commonalities with solvolysis and as such the most pertinent solvolysis-adjacent literature since 2015 is reviewed hereafter.

Superheated steam (SHS) recycling is an example of a chemical recycling process that straddles the boundary between thermolysis and solvolysis. Since there is no liquid medium, SHS is better characterised as thermolysis; however, the penetration and reaction of water molecules within the composite substrate is similar in principle to conventional hydrolysis. One limitation of SHS vs. hydrolysis is that the steam flowthrough leads to significant loss of the matrix in the gas phase, such that minimal value is recovered from it. This was exemplified by the recent study of Chan et al. [64], in which less than half of the matrix mass was recovered in terms of recyclates under their optimised conditions (350 °C). Boulanghien et al. [65] performed a similar study using SHS at 700 °C and found that single fibre mechanical tests were observed to exhibit too much scatter to provide meaningful information. However, fibre bundle mechanical tests were used to successfully demonstrate near ~100% performance retention of rCF. The environmental credentials of this type of composite recycling were examined in an LCA by Nunes et al. [66] The authors found that CFRP waste treated by this process presented a 25–30% reduction in environmental impact relative to the current mix of landfill and incineration. A similar superheated steam process has been recently used by a consortium in the UK including the National Composite Centre, B&M Longworth Ltd and Cygnet Texkimp to recycle a filament wound CFRP (epoxy-anhydride); however, few details are shared in the public domain [67].

By convention, ionic liquids (ILs) are generally defined as melts of cations and ions that are liquid in the region of 100 °C or below. ILs offer unique properties compared to many conventional organic solvents (including very low volatility and tunability) and crucially can be potent solvents. A review of the recent solvolysis literature indicated that conventional ILs have not recently be used to degrade FRPs. However, two studies by Wu and co-workers [68,69] employed ionic melts as the solvolysis medium, in both cases using molten $ZnCl_2$ to great effect. These authors describe the process as pyrolysis and, in truth, it blurs the boundary between solvolysis and pyrolysis. Like pyrolysis, the matrix is seemingly destroyed, such that there is no discussion in either study concerning the recovery of matrix recyclates. However, akin to conventional solvolysis processes, high quality rCFs are produced, with mechanical properties approaching vCFs (~95% tensile strength). An embedded energy assessment of this type of CFRP recycling does not seem to have been reported, although it seems likely that the large volumes of liquid are energetically expensive to maintain at such high temperatures (>350 °C), so this does not present an advantage over conventional solvolysis processes. Moreover, like conventional pyrolysis, these processes produce char that is left as residue on the recycled fibres, which necessitates a second thermal treatment to remove.

Electrical recycling of composites generally takes the form of high voltage fragmentation, where a composite substrate is immersed in a

dielectric liquid (e.g. water) between two electrodes and subject to electrical pulses. In theory, the discharge creates a spark which then travels between material boundaries, creating shockwaves of high pressure and temperature that can cause the material to fragment [70]. The recent study of Oshima et al. [71] explored the use of different salt solutions and different voltages to recycle carbon fibre reinforced epoxy. The authors noted that gas generation seemed to lead to resin peeling off the fibres. However, fibre-matrix separation was limited compared to traditional solvolytic processes and the recyclates were not properly characterised.

1.2.7. Unconventional polymers

Numerous studies in recent years have employed solvolysis to recycle FRPs comprising non-conventional thermosets, namely those polymers that contain degradable bonds or functional groups (e.g. acetals [72–74], imines [75,76], disulfides [77–79], Diels-Alder adducts [80,81], boronic esters [82], and others [83–86]). These polymers and their composites are designed to be intrinsically susceptible to solvolysis and as such can generally be degraded much more efficiently than conventional polymer composites and crucially, often generate more valuable matrix recyclates. These matrix recyclates can often be used in their original format with minimal performance loss. The most pertinent of these works to this review is the article by La Rosa et al. [87], in which the solvolysis of a Recyclamine-epoxy CFRP was tested. With this technology, the recyclability of epoxies is improved by incorporating acetal groups within the polyamine hardener. By treatment with 25% aqueous acetic acid at 80 °C, the authors were able to fully degrade the matrix from their CFRP substrate (6.6 g in 300 ml of solvent) within 1.5 h. The authors examined the matrix recycle, which they determined to be polyaromatic thermoplastic, though the value of this is yet to be determined. Only SEM and EDX were used to characterise the rCFs, which revealed no differences with vCF. Although these polymers are of fundamental importance to solvolysis and may form a part of the future composite landscape, their current utilisation is minimal and as such they will not be reviewed further herein. However, the interested reader is directed to these reviews [88–90].

2. LCA of solvolysis

Koovavalli et al. [7] demonstrated that the embodied energy (EE) of the solvent and heating up the solvent are the major contributors to the overall energy burden of solvolysis. Accordingly, solvolysis is much more energy intensive than pyrolysis, though by modelling supercritical solvolysis this represents a worst-case scenario, since lower temperatures and shorter residency times are possible. The results of this study indicate an enormous EE associated with solvolysis, in excess of 250 MJ per kg of rCF, with the majority of this energy from heating the solvent. This would suggest that solvolysis is completely non-competitive with pyrolysis, which the authors' model suggested has an EE or less than 50 MJ/kg rCF. However, these results are in stark contrast with data from the University of Birmingham, which suggests only 21 MJ/kg rCF is required (of heating energy) for their acetone-water solvolysis [91], see Table 1, Entries 1 and 11. In this case the resin to solvent loading was optimised, however the energy integration was not considered, which would further reduce the energy requirement.

Khalil's LCAs explored the impact of different supercritical solvents on human and environmental health [6] and compared solvolysis with pyrolysis [92]. Even the most benign supercritical solvent (water) was associated with greater human and environmental health impact than the modelled thermolytic process (pyrolysis). Liu et al. [25] performed an LCA for the purpose of comparing their supercritical n-butanol solvolysis with incineration/landfill and with steam thermolysis. Generally, this solvolysis performs well compared to steam thermolysis, but performs less well in terms of global warming potential. This is partially due to the burning of the matrix recycle (along with the solvolysis medium), which was the method that the authors chose to derive value

from this material. Solvolysis is generally better than land-fill/incineration in most metrics excluding ozone depletion, human toxicity and terrestrial ecotoxicity. Indeed, Pillain and co-workers [93] reported a similar result: the environmental impact of hydrolysis, pyrolysis and electrodynamic fragmentation are all worse than land-fill/incineration when reuse benefits are not considered. Interestingly, Liu found that when some energy recovery from burning the matrix recyclates was considered, the energy burden of solvolysis is 40% lower than steam thermolysis. It is also worth noting that Liu et al. chose to model the energy intensity of the solvent using data for supercritical water, instead of supercritical butanol, since this information was unavailable. This study also highlights an extreme sensitivity to the manufacturing energy of vCF. It may be prudent to calculate the energy value associated with the incineration of matrix recyclate and use this energy as a benchmark of energy available to separate/purify matrix recyclates into more valuable products (e.g. for petrochemical feedstocks). Sommer et al. [94] investigated environmental and economic factors simultaneously in their study, finding that the favoured end of life treatment for CFRP is chemical recycling and for GFRP, mechanical recycling. Where chemical recycling is either solvolysis, thermolysis or electrofragmentation dependant on the specific circumstances.

3. Literature summary

3.1. Substrate selection: fibres and matrix

Polymer matrix. The FRP matrix is the single most important feature determining solvolysis conditions, given the intrinsic relationship between the polymer chemistry and degradation mechanism. As the most popular matrix for carbon fibre composites, epoxies (particularly amine-epoxies) have unsurprisingly dominated the research literature in recent years. The most popular thermosetting matrix for GFRP is UP and thus it is also no surprise that UP GFRP is the next most researched solvolysis substrate. Other matrices have only sparsely featured in the recent literature, this likely reflects the market position for other thermosets—they are not produced in sufficient volume, particularly in CFRP, to make their solvolysis feasible at an industrial scale, since in most cases they would likely require a specialist treatment. One perhaps surprising omission from the literature is vinyl ester solvolysis, since it is the major competitor of polyester matrices in moderate-low performance composites. One major limitation of the thermoset solvolysis literature, is that these studies invariably examine untoughened systems, although higher performance CFRP is often toughened with the incorporation of one or more additional materials (often thermoplastics). These additives could significantly affect solvolysis performance, but toughened composites are conspicuous by their absence in the literature.

Thermoplastic composites have also received relatively little attention in recent years, which is surprising given that TP GFRP reportedly represented almost 50% of the global volume of composite materials produced in 2016 [4]. In the UK, according to Lucintel analysis, the two major TP matrices are polypropylene (PP) and polyamides (e.g. Nylons), although together these TP composites represent only ~14% of the composites value produced in the UK [1]. Of the composites-specific literature reviewed, several articles concerned 'solvolysis-adjacent' processing of acrylate matrices (Elium) and a few articles examined polyamide solvolysis. Importantly, the solvolysis of both these matrix types has produced useful matrix recyclates, which is not true of the wider solvolysis literature.

Fibre reinforcement. Although the fibre type does not substantially influence solvolysis directly, the compatibility of particular fibres with different solvolysis conditions means that the choice of reinforcement is important. To justify the higher cost and environmental burden of solvolysis over thermolytic processes, solvolysis must not lead to significant fibre degradation. In the literature where rCF mechanical testing has been performed, rCF mechanical performance is not generally degraded by even HTP solvolysis conditions. However, strongly oxidant

conditions may adversely affect rCF surfaces. Other fibre types are not so tolerant.

Glass fibres. Thermal treatments as low as 200 °C begin to degrade the tensile strength of glass fibres (both E and S as well as basalt). This effect becomes more pronounced above 300 °C such that by 500–650 °C more than 50% of the original strength is lost. The exact mechanism for this strength loss is unknown but has been the subject of much research [95]. Three of the most important factors behind this are (1) sizing degradation, (2) surface dehydration/dehydroxylation and (3) thermal contraction. (1) In addition to enhancing fibre-matrix adhesion, glass sizings are also thought to compensate for (or heal) surface defects on glass fibres, this in itself makes sized fibres stronger than unsized fibres. However, sizing degradation can also lead to additional strength loss by two further mechanisms (i) by creating new surface defects/inclusions during decomposition and (ii) by loss of the abrasion protection—fibre-fibre contact without sizing is known to lead to scratching (surface defects). (2) Glass fibres contain a significant quantity of water and have a significant quantity of surface-adsorbed water. Above 200 °C, the adsorbed water is removed, altering the surface morphology, and at higher temperatures still, the surface can become dehydroxylated leading to further changes and greater defect formation. (3) The former two phenomena have primarily concerned surface defects; however, thermal treatment is also known to affect the bulk structure of glass fibres, an example of this is contraction. Above 300 °C fibre contraction and densification can occur, which might be expected to lead to defect formation in the bulk [95].

In summary, glass fibres are highly thermally sensitive, particularly above 300 °C and as such, high temperature recycling treatments are unlikely to be viable for recycling GFRP, particularly considering that thermolytic processes do not usually recover much in the way of matrix products. Accordingly, lower temperature treatments, e.g. LTP (low temperature and pressure) solvolysis are more appropriate. Nonetheless, the low value of virgin glass fibre means that even with effective solvolytic recovery of glass fibres and matrix recyclates, GFRP solvolysis is unlikely to be economically viable without subsidisation. Given that the vast majority of composite waste is GFRP (~99% volume, 2016) [4] and that there are currently not any existing methods of producing valuable recyclates from GFRP, GFRP solvolysis may warrant further study, if only to determine the level of subsidisation required to make it viable. A new field of research that might enhance GFRP recycling more generally is strength restoration of damaged rGFs [96].

Basalt fibres exhibit a similar thermal sensitivity to glass [97]. Accordingly, low-moderate temperature solvolysis may be appropriate for basalt fibre composite EOL treatment.

Natural fibres. Very limited research has been published concerning the solvolysis of natural fibre (NF) composites [55,98]. Crucially, NFs are not very tolerant of high temperatures. For example, flax can only be exposed to 200 °C for 5 min or 160 °C for 30 min without showing signs of degradation. Accordingly, mechanical recycling and incineration for energy recovery may be more feasible EOL treatments for NFRPs. As such, the use of TP matrices, which retain some value after mechanical recycling, may be most appropriate for use with NFs.

Aramid fibres (AF) also exhibit greater thermal sensitivity than carbon fibres, dependant on the specific polymer structure, these fibres typically undergo some degradation in the region of 400 °C [99], which makes AFRPs similarly unsuitable for thermolytic recycling and thus potentially suitable for low temperature solvolysis.

Fibre architecture and volume fraction. Both architecture and volume fraction of FRPs has a significant influence on their solvolysis rate. Generally, higher volumes of fibre make for slower degradation, as do reinforcements with significant volumes of hard-to-reach intra-tow and intra-weave polymer (i.e. woven fabrics). Fortunately, most authors use composites that are prepared by industrially relevant manufacturing processes (that produce well-consolidated, high V_f laminates) in their solvolytic studies; however, a systematic study in which the effect of resin-to-fibre ratio is examined is not available.

3.2. A typical solvolytic process

In a typical solvolysis process, a composite part (the substrate) is sectioned into small pieces such that they can fit within the reaction vessel. It is typical for there to be some level of diffusion control which influences solvolytic rate [42]; smaller substrates make for shorter diffusion paths, although in some cases entire components can be treated intact. One example of this is the depolymerisation-solvolysis method developed by Hitachi (benzyl alcohol and K_3PO_4), which was used to recycle CFRP tennis racquets [33]. The second phase is generally then the solvolysis itself, whereby the substrate is immersed in hot solution (120–350 °C) with or without the aid of pressure (up to 300 bar), from anywhere between 20 min and 24 h. In some cases, an additional ‘swelling phase’ is added prior to solvolysis. This requires soaking the substrate in a solvent (usually different to the solvolysis medium), generally for a similar duration to the solvolysis itself. After solvolysis, the products (recyclates) are separated by washing under ambient conditions, typically with acetone. The liquid fractions are then separated into solvolysis medium and products, so that the matrix products can be analysed and subject to post-processing (e.g. separation into fractions). Finally, the fibres are dried ready for post-processing (sizing and alignment) and analysis, Fig. 4.

3.3. How is solvolysis success measured?

In the majority of the academic literature, the primary measure of success was (1) the fraction of matrix removed and (2) the quality of the fibrous output, be that rCF or rGF. In some cases, success was also measured in terms of (3) the value of the liquid fraction/matrix degradation products, although this is difficult to quantify, and/or (4) the

environmental impact (usually in the form of a lifecycle assessment).

- (1) is relatively easy to quantify; the percentage of matrix mass content before and after processing can be easily determined by use of thermogravimetric analysis (TGA) and compared. This relies on the fact that organic matrices are much less resistant to thermal degradation (volatilisation) than conventional fibre reinforcement.
- (2) is more difficult to quantify, but in the first instance can be performed with relatively straightforward techniques including SEM and Raman spectroscopy. In the former technique, the surface of fibres can be visually inspected for residual matrix and other defects that could impair mechanical performance. In the latter, a comparison of the D and G bands can give an indication of the degree of graphitisation, which has a significant influence on mechanical performance. More thorough analyses of fibre quality include single fibre (or fibre bundle) [65] mechanical testing experiments that can directly probe the mechanical performance relative to virgin fibres. In addition, the most detailed studies also explore the interfacial strength of recycled fibres in new composites, generally in terms of interfacial shear strength. However, it should be noted that caution should be used when investigating mechanical performance of recycled fibres since the absence of a sizing can greatly influence the results, which is most apparent when testing composites.
- (3) fewer studies examine the non-fibrous recyclates in any detail. In an ideal case the non-fibrous recyclates would be solely the matrix degradation products; however, in some cases large quantities of species originating from the solvent are observed (most often when acetone is used as part of the solvolysis medium). In

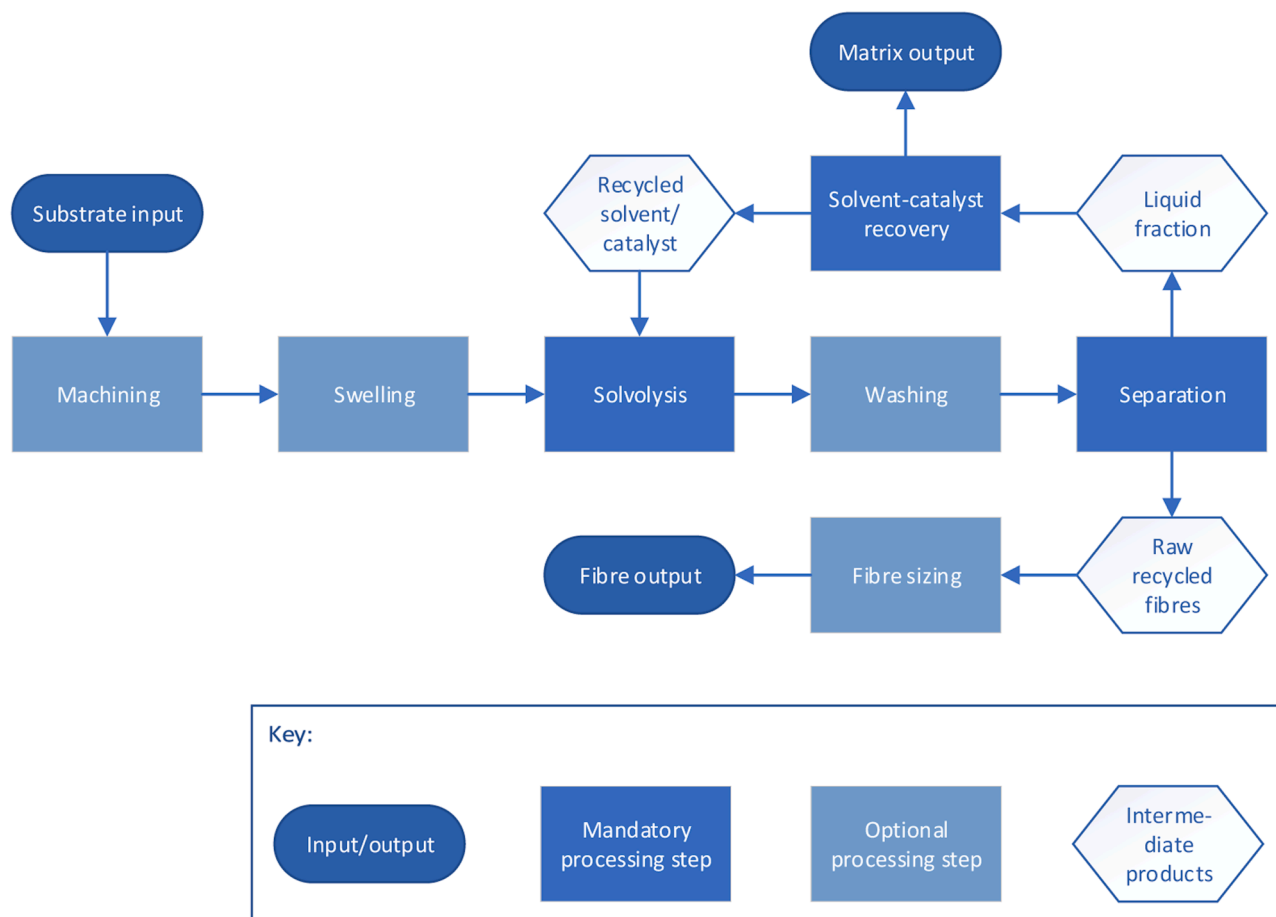


Fig. 4. Flow chart of a generic solvolysis process.

general, one or more spectroscopic techniques such as NMR or FTIR are used to probe the chemical functionality of matrix recyclates and GCMS or LCMS are used to determine individual components and their proportions. Monomers and other small molecules are most frequently produced from higher energy reactions. In contrast, oligomeric species are generally produced from milder solvolysis conditions and are considered to have less value than small molecules, in large part due to their lower (and less reliable) reactivity, which means that they may be most useful for their calorific value (as fuel). However, it is conceivable that chemists may be able to develop these waste oligomers into useful molecules. At present, most authors that address the reuse of these degradation products use them as a replacement additive for new batches of the polymer from which they were degraded (i.e. epoxy). However, even at low replacement levels (<20 wt%), incorporation of recycled oligomers can significantly reduce mechanical performance [26], particularly in terms of lowering T_g [36].

- (4) several studies have included some level of lifecycle assessment to determine the relative pros and cons of their chosen EOL treatment, often comparing one or more solvolysis processes [93, 100], and one or more alternative processes including landfill/incineration [25], steam thermolysis [66], and pyrolysis [6,7, 92].

3.4. Recycled fibres, quality and utility

Despite the consistent production of high performance rCF from solvolysis, as is widely reported in the literature [8,13,22,23,36], the mechanical performance of individual recycled fibres only conveys a partial description of their overall value. In addition to mechanical performance (e.g. single fibre tensile testing, SFTT), the surface properties of the fibres, which dictates the quality of the interface in second-life composites, is also very important [101,102]. The surface characteristics of reclaimed fibres can be studied with relative ease by use of techniques such as XPS, Raman and FTIR spectroscopy, as well as SEM-EDX. In addition, mechanical testing, such as micro-droplet testing, can also be performed to model the performance of second life composites [103]. To give confidence (i.e. demonstrate value) to industry, this suite of testing should be normalised when qualifying reclamation processes—both solvolysis and beyond. The mitigating circumstances for not thoroughly characterising recycled fibre surfaces are that these surfaces may be straightforwardly modified, either by applying a sizing (coating) or other treatment, such as a plasma, that could significantly enhance the surfaces and resultant interfaces [104]. In addition to the characterisation of the individual fibres, numerous studies have incorporated recycled fibres into a new composite and compared the performance of this to a fully virgin material [53,105–107]. Tensile properties, along with flexural strength and interlaminar shear strength (ILSS) are the characteristics most often investigated, with SEM often used to confirm fibre orientation and the failure mechanism. Similar to the results of characterising individual fibres, there is a range in performances reported with some data showing that recycled composites are significantly weaker than their virgin counterparts [53] whilst others report comparable [106,107], if not greater [105], strength. Greater flexural strength in particular may be attributed to a stronger interface between the recycled fibre and the matrix. From contact angle measurements and XPS analysis, this is likely due to an increase in hydrophilicity and the presence of some residual resin on the surface of the polymer [105]. With this in mind, there is a clear need to ensure that recycled fibre surfaces are effectively treated prior to any secondary application.

Although recycled composites can have comparable performance to virgin material, a key consideration is the fibre format, i.e., their length and orientation. These properties are perhaps even more integral to the value of the recycled fibre and this measure of ‘quality’ is not so easily

enhanced after reclamation; discontinuous fibres cannot be restored into continuous fibres. This, therefore, warrants further discussion.

The finite volume of solvolysis reactors and indeed any advanced recycling equipment (e.g. pyrolysis furnace) restricts the size of the substrate than can be treated. Given that most carbon fibre products are currently designed with continuous fibres, any discontinuity produced from machining the end-of-life composite, represents a defect at best or a wholly incompatible product at worst, when considering second life applications. Furthermore, discontinuous but otherwise ‘long’ fibres are not only poor replacements for continuous fibres, but they may also be poor replacements for short fibre applications. To be compatible with typical manufacturing techniques for short fibre applications, e.g. injection moulding or bulk moulding compound (BMC) processes, the fibres need to be a consistent, well-defined length. In order to accommodate current composite manufacturing techniques, recycled fibres should either be reclaimed in such a way that they yield rCF that is pseudo-continuous such as the unwinding-rewinding of a pressure vessel by the NCC in partnership with B&M Longworth Ltd and Cygnet Textimp [67], or pre-shredded to a consistent length that is desirable for short fibre applications. This challenge alone represents a major obstacle for the nascent composite recycling industry. Nevertheless, this also represents an opportunity to reinvent composite manufacturing techniques to accommodate this new (and soon to be abundant) source of material. In summary, researchers in this field are encouraged to be mindful of the current state of manufacturing and thus consider what application their fibres might be used for. However, all interested parties should not lose sight of the opportunity to develop new means of composite manufacture.

Although isolating pseudo-continuous fibres is conceivable with some combinations of reactor and substrates, such as filament wound parts, this is clearly impossible with other parts, such as those prepared from prepreg. For this reason, it would seem prudent to explore ways of creating high performance composites from discontinuous fibres such as the Lineat (HiPerDiF) process [108], the process of de Werken et al. [102], or additive manufacturing techniques including the work of Ismail et al. [109].

This section and indeed most of this article explicitly considers end-of-life composite as the subject of solvolysis. However, manufacturing waste represents a significant volume of alternative substrate for recycling. This material is in large part off-cuts, but intact scrapped parts are also common. The same restrictions apply here. Not only does the material need to be machined to fit in the reactor, it needs to be machined with a view to its second life use.

In the last few paragraphs, the focus of discussion has been rCF. As emphasised in the introduction, carbon fibre represents a large proportion of the *value* in the global composites supply chain, but only a small part of its *volume*. By volume, the composites industry is dominated by GFRP. The surface quality and format of rGF are significant as with rCF. However, because the mechanical performance of rGF cannot be assumed, these other factors, by comparison, are of less immediate concern. The more important debate with GFRP is whether there is a justification for isolating rGF and creating second life composites from it at all. This topic and others are examined in the following section.

3.5. Pros and cons of solvolysis: where should solvolysis be pitched?

One interpretation of the waste hierarchy of composites is given in Fig. 5. In the first instance, composite at EOL should be requalified and/or repaired to extend its original service life. Since this eliminates waste, this is preferred. However, composites that are beyond economical repair or are obsolete due to technological advances must be treated by one of the lower tier processes. The second tier is reuse. The principal advantages of reuse over recycling are the higher level of value retention (there is less material downgrading relative to energy input)—a considerable amount of energy is invested in a composite from manufacture, investing more energy to separate fibres and matrix during

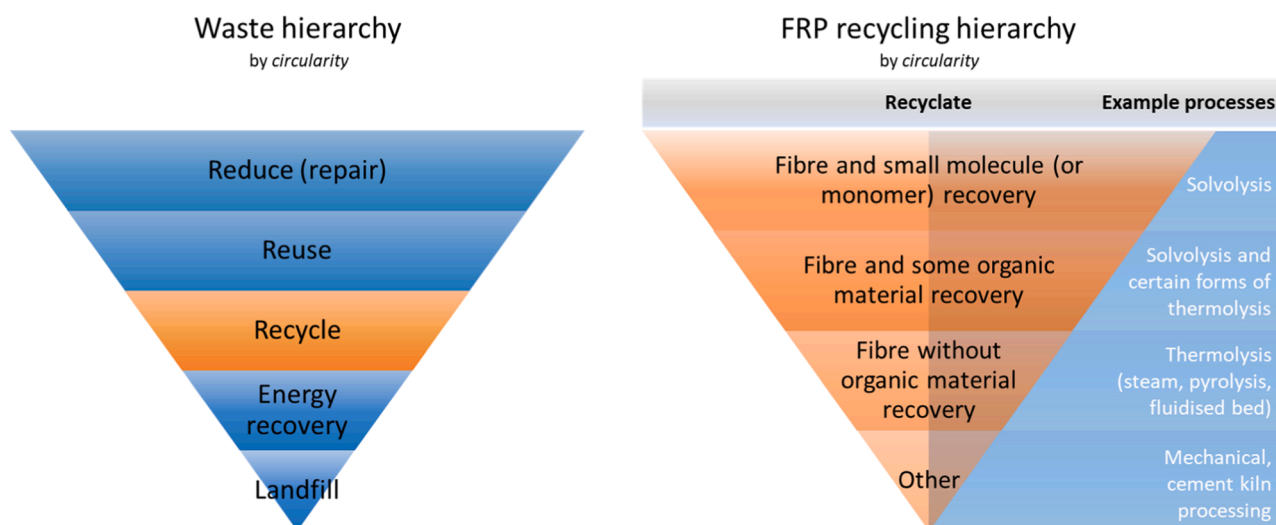


Fig. 5. Left: hierarchy of waste and right: sub-hierarchy of FRP recycling sorted by recyclate circularity.

recycling is inefficient. Accordingly, reusing a part in an analogous application to its original purpose, or repurposing it (structural recycling) with a minimum of machining will almost always be more energy efficient than recycling. Recycling is then the next most preferred treatment for EOL composite whenever repair and reuse are not viable strategies. Reuse strategies are most applicable with larger structures that can be machined into smaller objects, small and irregularly shaped structures are thus obvious candidates for recycling. Reuse is also particularly valuable with FRP structures that would otherwise produce low value recyclates, i.e. where the energy required to separate fibre and matrix is not justified by the value of the recycling products. In contrast, the third tier of the waste hierarchy, recycling, is most useful for small, highly valuable composites and those composites that have an especially low energy cost to recycle, i.e. degradable matrix composites.

A recycling sub-hierarchy is shown to the right of Fig. 5. This hierarchy is sorted in terms of the fraction of recycled material, which broadly corresponds with the recyclate value. All else being equal, solvolysis *would be* the preferred recycling method for all composites given that it can theoretically convert 100% of the original substrate into recyclates and can do so with minimal influence on fibre performance. However, this hierarchy is also roughly proportional to cost and environmental harm (by virtue of energy use, unless zero carbon energy is used), meaning that the different processes may also be ranked as shown in Fig. 6. Accordingly, future composite recycling strategies are likely to

comprise a variety of different techniques based on both suitability and availability.

Several LCA studies have determined that HTP solvolysis is more expensive than pyrolysis and is associated with greater environmental impact, this is in large part due to the energy intensity (production) of solvents and the energy burden of heating them. For comparison, very little information is available concerning LTP solvolyses, which are typically longer and utilise more expensive reagents. As such, it is not immediately apparent if LTP solvolysis compares more favourably with thermolytic processes. The major benefits of solvolysis over pyrolysis, steam thermolysis and other thermolytic processes (e.g. fluidised bed) are twofold:

- (1) With solvolysis, it is possible to recover both rCF *and* thermally sensitive recycled fibres such as E-glass *without* significant damage. In contrast, thermolysis is not appropriate for thermally sensitive fibres as it generally leads to a >20% decrease in mechanical performance.
- (2) With solvolysis, it is possible to recover matrix recyclates, which sometimes include monomers. Although thermolytic processes can yield some matrix recyclates, much of the matrix is typically volatilised.

Accordingly, the added energy and financial burden associated with solvolysis is most likely to be justified when recovering both virgin quality fibres *and* valuable matrix recyclates. Unfortunately, relatively few solvolysis studies have examined the matrix recyclates in any detail and fewer still have explored a viable route to market for them.

One major caveat in the assessment of the value of solvolysis is the future role of unconventional polymers, i.e. Section 1.3.7. Solvolysis becomes much more energy efficient and therefore much more valuable when it is employed to degrade specially designed polymers. Generally, with degradable polymers the matrix recyclates are higher value than those yielded from conventional polymers, particularly in those cases in which the recyclates can be reused for their original purpose. Consequently, it would be prudent to demonstrate pilot-scale solvolysis of one or more of these emerging resin technologies (with degradable linkages), which would be mutually beneficial in terms of technological progress.

Suitable substrates for solvolysis:

- (1) Composites with high performance fibres, where their value retention is important (i.e. where $a > 10\%$ loss of performance

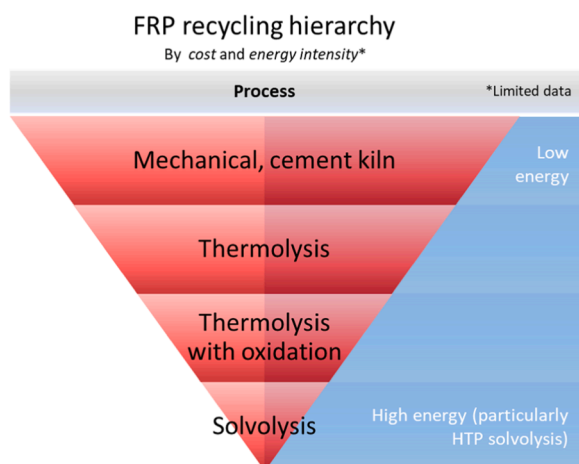


Fig. 6. Sub-hierarchy of FRP recycling processes by cost/energy intensity.

significantly diminishes their value). Particularly where fibre architecture and/or length need to be maintained.

- (2) Composites with valuable and/or non-conventional matrix recyclates, notably degradable polymers.
- (3) Any composite that is *mandated* by circularity legislation to be recycled into both fibres and matrix recyclates or is deemed *inappropriate for other* (more cost-efficient) methods.

Accordingly, carbon fibre composites are the most suitable FRPs for solvolysis due to the high cost of virgin carbon fibre and their highly valuable mechanical performance. This is borne out in the literature with carbon fibre reinforced epoxy being the most common substrate.

Despite one of the major drivers for solvolysis being the isolation of valuable matrix recyclates, this has not been a major focus of research in the academic literature. This may be partially due to the most common substrate, amine-epoxy CFRP, being particularly challenging to degrade, often producing oligomers as the primary matrix products. These products are currently perceived to be low value. Polymers that can more readily be solvolysed into small molecules (ideally monomers), including polyester and polyamides, are less commonly reinforced with continuous carbon fibres.

GFRP is not currently economical to recycle by any *advanced* recycling techniques. The leading EOL strategy is the 'cement kiln' route, which is essentially a form of mechanical recycling in which the polymer is used for its calorific value—this is particularly favourable due to the displacement of fossil fuels that would otherwise be used in cement processing. Nevertheless, it is possible that by using particularly energy efficient techniques (e.g. microwave heating or ultrasonication), or by subsidisation/incentivisation, that GFRP could be treated by solvolysis to recover low-cost rGF of approximately equal performance to vGF. Accordingly, despite the apparent unsuitability of GFRP for solvolysis, it may still be worth pursuing, particularly given the scale of the waste problem with this composite type.

4. TRL assessment

Globally, there has been relatively little movement in terms of solvolysis industrialisation since the Oliveux article in 2015 that highlighted several ventures at and just above pilot scale, including Adherent Technologies Inc. in the US and Panasonic Electric Works Co. Ltd. in Japan [5]. In recent years solvolysis seems to have taken a back foot compared to thermolytic processes, which have been successfully commercialised in several countries including the UK, with Gen 2 Carbon Ltd., formerly ELG Carbon Fibre. A notable exception to this trend is the emergence of Catack-H in South Korea, a start-up that uses an ambient pressure, water-based solvolysis to recycle carbon fibre with reportedly only 10% of the cost of conventional incineration [110]. The initial substrate focus is uncured carbon fibre scrap although the longer-term strategy of the company is to recycle fully-cured composites.

Since 2015, two University spin out companies have been launched in the US, 'Closed Composites LLC' (referenced earlier in Section 1.3.1) and 'Shocker Composites LLC', a spin out from Wichita State University, Kansas. The process employed by Shocker is a low temperature, ultrasound-assisted solvolysis that is used to recover short rCF from aerospace CFRP waste. Shocker use this process to prepare rCF-reinforced thermoplastic pellets (up to 20 wt% rCF) at low cost, making use of the excellent compatibility between unsized rCF and thermoplastics [111]. However, it is unclear if the Shocker process is equally effective at handling fully-cured (EOL) CFRP parts as it is prepreg off-cuts, which seem to be the substrate targeted by their patent [112].

In the UK to date, there appears to be no significant investment in solvolysis outside of universities, with the pilot/lab-scale facility reported at the University of Birmingham the leading technology [91]. Since neither this, nor other processes in the UK have been used to generate saleable products from real EOL waste, this positions UK solvolysis in TRL 3–4. In contrast, solvolysis in the US and East Asia

(Korea/Japan) appears to be in the TRL 6–7 region, as there appears to be functional pilot plants and some commercial utilisation.

To increase the TRL of UK solvolysis, several of the following factors could be addressed and *all* need to be addressed to drive UK solvolysis to the highest readiness levels:

- (1) Perform solvolysis on real composite waste instead of model systems.
 - a Use toughened composites.
 - b Use mixed composite waste.
- (2) Develop a pilot scale facility in a commercial environment.
 - a Use real composite waste (1).
 - b Preferably use a continuous or semi-continuous system.
 - c Fully characterise inputs and outputs for subsequent business assessments.
- (3) Develop a supply chain for:
 - a Waste input.
 - b Fibre output.
 - c Matrix recyclate output (this may require post-processing/separation steps).
- (4) Present business analyses to verify the value of the solvolysis.
 - a Environmental assessment (LCA or related analyses).
 - b Commercial viability of both the processes and recovered products.

Factors (1), (2) and (4) have literature precedent and do not require a substantial technological leap to be achieved in the UK, although significant investment may be required. Factor (3) is the most esoteric and difficult to implement. Given the commercialisation of alternative composite recycling processes in the UK, building a supply chain for high quality rCF should not be difficult, although may be more challenging with other fibre types. Similarly, EOL composite waste (input) must already be sourced by competitor processes, so should not be an insurmountable challenge. In contrast, finding a market and/or processing chain for generating value from matrix recyclates appears to be extremely challenging. This aspect of solvolysis itself remains at TRL1–2 globally and requires significant academic research in addition to industrial scale-up. Government and industry need to incentivise academic research into valorising solvolysis matrix recyclates since it does not seem to be happening organically. One advantage of solvolysis against the wider backdrop of composites in the UK is relatively limited supply chain of domestic fibre and resin producers [1], which means that secondary composite processors (e.g. prepreg manufacturers) need to import their raw materials. As such, there could be a significant market demand for solvolysis recyclates in the UK, assuming that their quality is validated and consistent.

5. Conclusions and outlook

A significant volume of research has been performed on FRP solvolysis in recent years, although relatively few studies have thoroughly examined both fibre and matrix recyclates. In addition, most solvolysis research is performed on small composite samples, even though one of the major advantages of solvolysis is that with a sufficiently large reactor size, full-size parts can be recycled without machining, i.e., they can maintain the added value of woven architectures or long (continuous) fibres. It is crucial that researchers in composite recycling, solvolysis or otherwise, consider the format of the fibres they are recovering and how they could be incorporated into second life composites. Moreover, it is imperative that recent progress in identifying and separating matrix recyclates continues, so that this key benefit of solvolysis (maximum circularity) can be exploited.

Of all the substrates, epoxy composites are by far the most researched, with amine-hardened epoxy used in the substrate in approximately half of the articles reviewed. For HTP amine-epoxy degradation, the leading solvent systems are organic solvent–water

mixtures (typically acetone or alcohols, such as n-butanol), either uncatyalsed or catalysed with a Lewis acid (e.g. AlCl₃ or ZnCl₂), see Table 1. The major issue for acetone-based systems is the production of a side-products from the self-reaction of acetone, although this is generally most significant in the presence of bases. At lower temperatures (and pressures), the leading solvents are generally either acetic acid—as the solvolysis medium or as a swelling agent, hydrogen peroxide (and combinations thereof), ethanolamine with KOH, or benzyl alcohol with K₃PO₄ as a catalyst. Typically, these works manage to remove >95% of the matrix and can produce recycled fibres with as much as 99% of their virgin tensile strength. It is worth noting that several authors used hydrogen peroxide but despite being a very effective solvolytic agent, there are two major drawbacks with its use. (1) H₂O₂ is often such an efficient degradation medium that it appears to destroy the matrix such that there is little if any recoverable matrix recyclate. (2) as a potent oxidiser, H₂O₂ is very hazardous and as such may not be safe to use on large scales.

Anhydride-epoxies have also frequently been the substrate of choice in solvolysis studies. In general, the solvolysis conditions for anhydride-epoxies are milder than amine-epoxies, which is presumably a product of the relatively reactive ester linkages that are formed during their polymerisation; these are not present in amine-epoxies. In the majority of the literature, an organic solvent is used with a basic catalyst that can facilitate transesterification, see Table 2. Of these, two of the leading examples are very similar solvent systems to amine-epoxy solvolysis: K₃PO₄ in benzyl alcohol and KOH in ethanolamine. Another high-performing system is the NMP–ethylene glycol with TBD catalyst system used by Kuang et al. [36]; however, NMP is banned in Europe (above 0.3% in consumer products) under REACH restrictions given its teratogenicity. Accordingly, it is unlikely that this system would be sanctioned for industrialisation. Due to the difficulty in determining the specific matrix type of composite waste streams, solvent systems that are appropriate for as many different matrices as possible (in this case amine-epoxy and anhydride-epoxy) are particularly valuable.

Unsaturated polyesters are the third and final category of composite matrices that have been thoroughly examined in the recent solvolysis literature. Due to the abundance of relatively weak ester linkages, which make anhydride-epoxies susceptible to solvolysis, it is surprising that so much of the literature with UP composites employs HTP solvolysis rather than milder alternatives. Nevertheless, the leading technologies for unsaturated polyesters include acetic acid–based systems, akin to both types of epoxy. HTP acetone-water systems can be effective, particularly in the presence of KOH catalyst. However, as with amine-epoxies, the major issue with using acetone in the presence of base is that it self-condenses producing a complex mixture of products that may hinder the isolation of matrix-derived products.

Few other thermosets have received attention, which is unsurprising given the dominance of epoxy in higher performance carbon fibre applications and polyester in lower performance glass fibre applications. However, the most notable omission from the recent literature is arguably vinyl esters, which are popular as higher performance alternatives to UP. From a molecular structure perspective, vinyl esters share many similarities with both anhydride-epoxy and UP, so it seems reasonable to assume that they would be degradable under similar conditions. The relatively small amount of solvolysis literature concerning TP-matrix composites is somewhat surprising given their often-quoted enhanced recyclability vs. thermoset matrices; although this is in part explained by the importance of mechanical recycling with TPs, the lack of crosslinks should make TPs good candidates for solvolysis. The leading literature examples include acetone dissolution of polyacrylates (Elium) and solvolysis of polyamides with water (either supercritical or HCl-catalysed).

The sensitivity of solvolysis conditions to the specific matrix type is a major challenge; it is far from certain that the exact polymer chemistry will be known for any given sample of composite waste. Even identifying anhydride- vs. amine-hardened epoxy is non-trivial and important for solvolysis given the different conditions they typically require for

effective degradation.

Several authors have performed LCA-type assessments on composite solvolysis and solvolysis-adjacent processes. In general, solvolysis is reported as more energy intensive, expensive, and less environmentally friendly than thermolytic processes such as pyrolysis. However, this is not universally the case, with the 19 MJ/kg rCF reported by Keith et al. a notably competitive energy requirement [113]. Moreover, solvolysis is more complicated to model and most studies use supercritical conditions; accordingly, it is probable that lower temperature solvolysis conditions compare more favourably with thermolysis. Accordingly, there is significant value in performing an LCA on low temperature solvolysis. Nevertheless, assuming that solvolysis is more expensive and complex than other advanced recycling techniques, it is critically important to use solvolysis appropriately to maximise its main advantages: (1) recovery of fibres with near-virgin mechanical performance (this includes recycling non-carbon fibres) and recovery of valuable matrix recyclates—that are not burnt for energy recovery. This means that solvolysis is suitable for composites with particularly high value fibres and valuable matrices, particularly those that are designed for degradability.

UK solvolysis TRL is approximately 3–4, although globally the TRL is as high as 6–7 in leading countries including the USA and Japan. Major limitations of UK technology are the lack of a commercial, pilot-scale facility and the absence of studies using ‘real’ composite waste. The lack of research concerning matrix recyclates and developing a market/process of valorising these is a global issue for solvolysis. The composites and chemical industries as well as legislature should encourage academic research into this specific area of solvolysis such that its full potential can be realised.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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