CATALYTIC DEGRADATION OF A CARBON FIBRE REINFORCED EPOXY RESIN WITH AN ACETONE/WATER SOLVENT

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Abstract

The degradation of a carbon fibre reinforced RTM6 epoxy resin with an acetone/water mixture and range of potential catalysts has been investigated. NaOH, KOH and $ZnCl_2$ were supplied at a concentration of 0.01 to 0.4 M with the data obtained showing that the alkaline salts do not enhance the reaction. $ZnCl_2$, however, is able to effectively strip the resin from the fibre surface with a resin removal yield in excess of 94% observed when processed at 290°C for 1.5 h or at 300°C for 45 min. Fibre tows recovered appeared clean, were perfectly separated and retained their weave architecture. The research presented demonstrates a significant improvement on earlier work by reducing reaction time by 25% and temperature by 30°C. FTIR spectra of the organic liquid fraction suggested that chloride ions cleave the C=N bond and hence accelerate the rate of reaction. Aside from this, spectra obtained from different catalyst systems were similar with all mixtures containing peaks characteristic of O-H, N-H, C=S and $R\text{-}SO_2\text{-}R$ bonds. As these represent a mixture of recoverable, potentially high value compounds, the developed technique could offer an advantage over pyrolysis processes.

1 Introduction

Between 2010 and 2016, the global annual demand for carbon fibre reinforced polymers (CFRPs) has almost doubled from 51,000 to 101,000 t with a further growth rate of between 10 and 13% per year predicted to 2022 [1]. Associated with this growth is the rising need for recycling both end-of-life products and manufacturing waste with the latter estimated to be up to 3,000 t per annum in the UK alone [2]. Currently, pyrolysis is the only commercial recycling technique which is able to recover clean fibres, however this results in the loss of the resinous matrix. As up to 50 wt.% of a CFRP consists of resin [3], it is desirable to develop alternative processes capable of closing the loop of the supply chain thereby improving resource efficiency.

Previous research has demonstrated solvolytic technologies are able to chemically degrade the hardest epoxy resins, facilitating the recovery of fibres and a potentially useful mixture of organic compounds. Under low temperature and pressure (LTP) conditions, where temperature is < 200°C and pressure is approximately 1 bar, it is necessary to use strong acidic or basic solutions or oxidising agents. However, the use of these chemicals pose a hazard to human health, scale-up, safety and the environment and can also lead to significant fibre damage [4-7]. Alternatively, GRAS (generally recognised as safe) solvents such as water, short-chain alcohols and acetone can be used at near- or supercritical conditions in a high temperature and pressure (HTP) recycling process. This avoids the need for more hazardous compounds necessary in LTP conditions [8-13]. Furthermore, it has been demonstrated a mixture of acetone and water is able to accelerate the degradation of an epoxy resin [8, 13]. Under high temperature conditions, both strong alkali and weak Lewis acid solutions have been shown to catalyse the reaction with a variety of solvents [7, 14]. This work aims to identify the effect of these catalysts when supplied in conjunction with an acetone/water mixture and optimum process conditions for the degradation of a carbon fibre reinforced epoxy resin.

2 Materials and Methods

2.1 Materials

A composite material consisting of 20 plies of woven Toray T700 6k carbon fibre fabric and an RTM6 epoxy resin was supplied by a leading aerospace manufacturer. With a high degree of cross-linking, this is one of the most difficult polymers to degrade [15]. Samples were cut into pieces measuring (10 x 10 x 6) ± 1 mm^3. According to the manufacturer's data, the fibre volume content of the investigated material was 53 ± 1%. This corresponded to a resin content of 36 wt. % using densities of carbon fibre and epoxy resin of 1.80 and 1.15 $kg.m^{-3}$ respectively [16, 17]. This was confirmed with thermogravimetric analysis (TGA) using an Exstar 6000 supplied by Seiko Instruments Inc.

Analytical research (AR) grade acetone was supplied by Sigma Aldrich and mixed with water from the mains supply using a ratio of 80:20 acetone:water v/v. Potassium hydroxide (KOH), sodium hydroxide (NaOH) and zinc chloride ($ZnCl_2$) were also supplied by Sigma Aldrich and used to make up solutions in a concentration range from 0.01 to 0.4 M with the acetone/water mixture.

2.2 Fibre Recovery

An electrically heated, 100 mL tubular batch reactor supplied by Parr Instruments Inc. was used for all experiments. Five pieces of the CFRP were stacked in a stainless steel basket before placing into the reactor with 50 mL of the solvent/catalyst mixture to give a reactor loading of 30 ± 1 $mg_{resin}.mL_{solvent}^{-1}$. The heating phase was 30 ± 5 min depending on the desired temperature and the reaction time was varied as shown in Table 1. To stop the reaction as quickly as possible, forced air convection was used to cool the reactor to room temperature in approximately 30 min. Both fibres and the dissolved resin degradation products were recovered for analysis. A light residue of organics was visible on the fibre surface, therefore, it was necessary to wash the recovered material with acetone. Samples were dried overnight at room temperature before being characterised.

In order to identify the optimum catalyst concentration, a series of experiments were carried out at 300°C with a reaction time of 1 h. Subsequent experiments were completed using the conditions specified in Table 1 and a 0.05 M solution of $ZnCl_2$.

Temperature (± 1 °C)	Induced Pressure (± 2 bar)	Reaction Times (min)
270	102	0, 10, 20, 30, 60, 90, 120, 150
280	120	
290	140	
300	160	0, 10, 20, 30, 45, 60

Table 1. Process conditions investigated for the degradation of a carbon fibre reinforced RTM6 epoxy resin using a 0.05 M solution of $ZnCl_2$ catalyst.

2.3 Fibre Characterisation

The resin removal yield (RRY) was determined through the difference in mass of the sample before and after processing using Equation (1) and further verified by calcination. Recovered fibres were divided into 5 aluminium crucibles and heated in air to 500°C. The crucibles were regularly removed from the furnace, cooled to room temperature and weighed. When the reduction in mass was negligible, it was assumed that all organic material had been removed. The resin content after the reaction and RRY were calculated using Equations (2) and (3) and an average from the 5 samples was taken.

$$RRY\ \% = \frac{m_i - m_p}{m_r} \times 100 \tag{1}$$

$$R_f\% = \frac{m_p - m_f}{m_p} \times 100 \tag{2}$$

$$RRY\ \% = \frac{R_i - R_f}{R_i} \times 100 \tag{3}$$

Where: RRY = Resin removal yield (%), m_i = Initial mass of the sample (g), m_p = Mass of the sample after processing (g), m_r = Initial mass of resin present, R_f = Resin content after processing (%), m_f = Mass of sample after calcination and R_i = Initial resin content (%).

2.4 Fourier-Transform Infrared Spectroscopy

Samples of the degradation products were recovered after processing the CFRP for 1 h at 300°C using 0.05 M solutions of KOH, NaOH and $ZnCl_2$ and also at 280°C with the 0.05 M $ZnCl_2$ solution. The mixtures were analysed with a Jasco FTIR-6300 spectrometer using wavenumbers in the range 800 to 4,000 cm^{-1}. The scan rate and resolution was 128 per sample and 4 cm^{-1} respectively. Peaks were identified using Larkin, 2018 [18].

3 Results and Discussion

3.1 Fibre Recovery

The effect of increasing the concentration of KOH, NaOH and $ZnCl_2$ on RRY is shown in Figure 1. The average RRY calculated by both a difference in mass (Equation (1)) and calcination (Equations (2) and (3)) is plotted with the error bars showing the maximum and minimum values. Contrary to earlier work [4, 7, 19], the presence of the OH- ions do not appear to enhance the degradation reaction when used in conjunction with an acetone/water mixture. In the absence of alkaline and weak Lewis acid solutions, (i.e. at a zero catalyst concentration) a RRY of 31.8% is achieved. When NaOH and KOH are used, the maximum RRY obtained was 24.4% and 40.3% respectively, both of which occurred at a concentration of 0.2 M. These results also suggest that OH- ions may inhibit the degradation process; the minimum RRY observed with KOH was 15.5% (at 0.05 M) and with NaOH was 19.5% (at 0.4 M). If these salts were precipitating out of solution and not taking part in the reaction, it would be expected the RRY was constant at around 32%. The difference between this and the minimum RRY observed for KOH and NaOH of 16.5% and 12.5% respectively appear to be outside the margin of experimental error.

The use of $ZnCl_2$, however, has a significant effect on the degradation with near-complete (97.4%) resin removal at a concentration of 0.10 M. For the same conditions, this represents an increase in RRY of

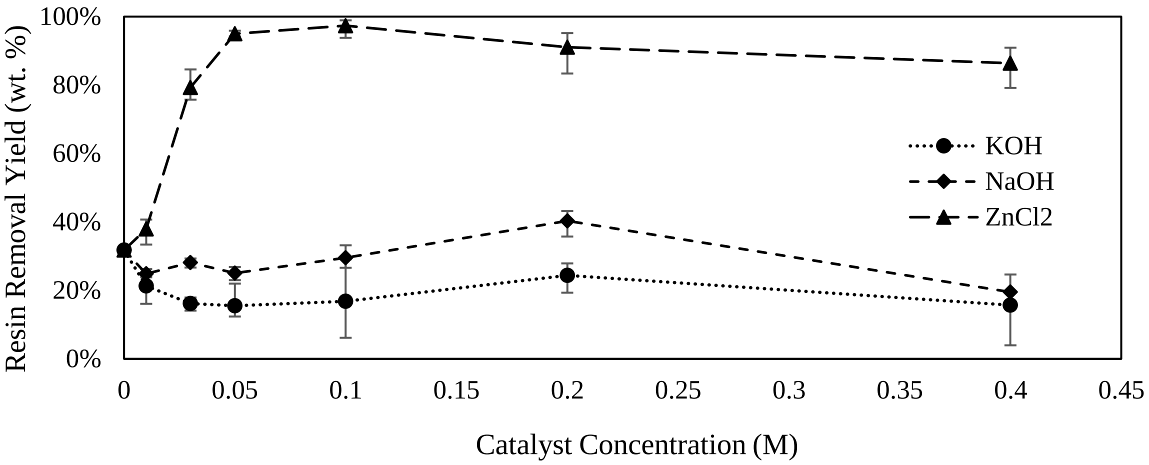

Figure 1. RRY of carbon fibre reinforced RTM6 epoxy resin after processing at 300 °C, 1 h with an acetone/water solvent mixture and various catalyst concentrations.

65.9%. Earlier work has shown process conditions of 320°C, 2 h are necessary to achieve a similar RRY [13] meaning the inclusion of $ZnCl_2$ halves the reaction time and reduces operating temperature by 20°C.

In order to identify the optimum reaction time and temperature, the experiments listed in Table 1 were completed, the results of which are shown in Figure 2. At 270 and 280°C, the RRY reaches a maximum of 75.5% and 86.1% respectively after processing for 2 and 2.5 hours. As these curves appear to plateau, the data suggests a temperature of at least 290°C is necessary in order to achieve sufficient degradation. At this temperature, the RRY is 94.1% in 1.5 h. A similar yield of 95.0% is achieved in just 45 minutes at 300°C, demonstrating the strong dependence of the degradation rate on temperature. This could be due to exceeding the critical point of the solvent mixture which is likely to lie between the critical point of acetone (235°C, 48 bar) [20] and water (374°C, 220 bar) [21]. Supercritical fluids demonstrate excellent solvating power and enhanced diffusivity [22]. For this reason, mass transfer of the solvent molecules and degradation products is likely to be increased which in turn facilitates a significantly faster degradation rate. Although the results suggest that there is some residue on the fibre surface, the

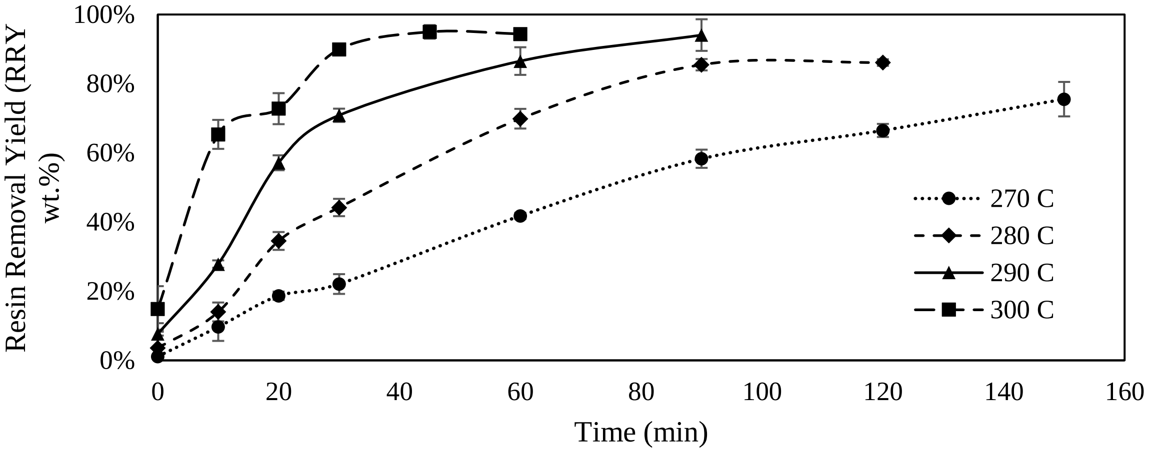

Figure 2. RRY of carbon fibre reinforced RTM6 epoxy resin at various process times and temperatures using a 0.05 M $ZnCl_2$ catalyst.

fibres appeared clean, each ply was perfectly separated and it was possible to separate the material into individual tows as demonstrated in Figure 3b and 3c. Furthermore, it has previously been shown that fibres recovered with a RRY of 90% are suitable for immediate reuse suggesting that a little residue on the fibre surface does not significantly affect adhesion to a new resin [13, 23].

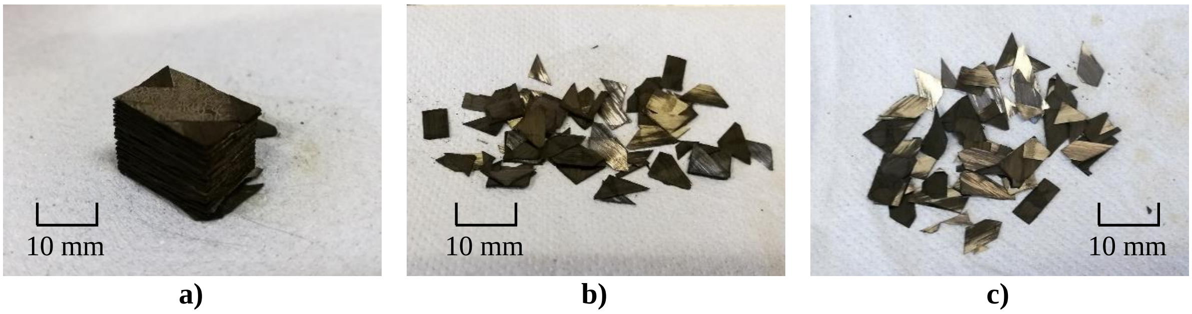

Figure 3. Samples of carbon fibre reinforced epoxy resin after processing with an acetone/water solvent and a 0.05 M $ZnCl_2$ catalyst at a) 280°C, 2.5 h; b) 290°C, 1.5 h; and c) 300°C, 45 min.

3.2 Fourier-Transform Infrared Spectroscopy

Dissolved solutions of the decomposed polymer matrix were analysed after processing for 1 h at 280 and 300°C. Figure 4a demonstrates the effect of using different additives while Figure 4b shows there is little effect on the bonds present when changing the reaction temperature in the presence of $ZnCl_2$. In both spectra, there is a large broad peak between wavenumbers 3,730 – 3,050 cm^{-1} which indicates the presence of O-H and N-H bonds in a range of environments. Due to the mixture of degradation products, these could be a combination of phenolic compounds or amine or amide groups. There is no obvious doublet which would indicate the presence of a secondary amine or primary amide, however, these are both comparatively weak signals and may be lost in the bands given by O-H and N-H bonds [18]. Epoxy rings have a wavenumber in the range 3,100 – 2,900 cm^{-1} [18], however there is no significant peak observed suggesting that these rings are broken to form soluble compounds.

In Figure 4a, there is a doublet given by peaks at 2,960 and 2,870 cm^{-1} suggesting the presence of methyl groups while in Figure 4b, there are also peaks at the lower wavenumbers 2,925 and 2,860 cm^{-1}. This second doublet is also indicative of a methylene group [18] suggesting that the use of $ZnCl_2$ favours the generation of C=C double bonds. As the peak intensity can be used to estimate the relative quantities present, it appears the use of $ZnCl_2$ generates similar amounts of both methyl and methylene groups. After processing with KOH and NaOH, both spectra of the degradation products demonstrates a large peak at 1,660 cm^{-1}, however, this is significantly reduced in the presence of $ZnCl_2$. This peak is characteristic of a C=N double bond [18] which chloride ions are able to cleave. This phenomena has been previously reported [7] and offers an explanation for why $ZnCl_2$ is an effective catalyst.

Below a wavenumber of ~1,500 cm^{-1}, the spectra obtained when using KOH, NaOH and $ZnCl_2$ are similar. Figure 4b highlights 3 further peaks at 1,450, 1,360 and 1,220 cm^{-1}. The former is indicative of either O-CH_3 or C-CH_3 bonds, however, without the use of mass spectrometry, it is not possible to distinguish between the two. A wavenumber of 1,360 cm^{-1} suggests the presence of alkyl sulphones (R-SO_2-R groups) while the peak at 1,220 cm^{-1} indicates thiocarbonyl (C=S) bonds. Although the exact composition of the RTM6 epoxy resin is unknown, common precursors in the manufacture of these materials include diaminodiphenyl sulphone or bisphenol S and it is therefore unsurprising sulphonic compounds are present.

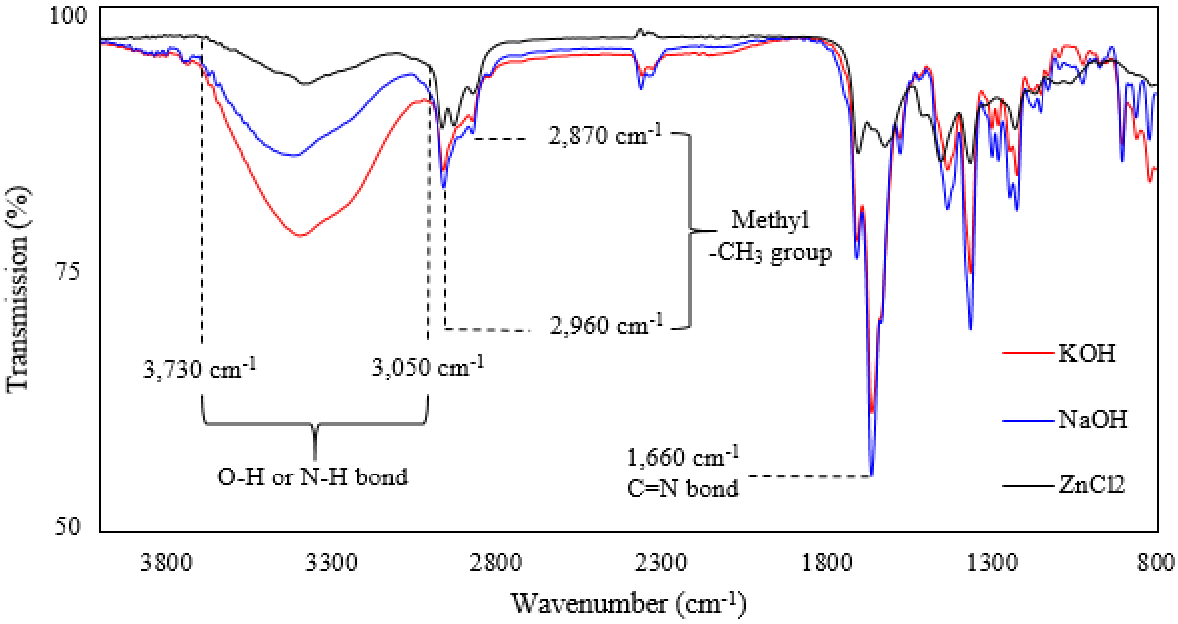

Figure 4a. FTIR spectra of dissolved decomposed resin after processing with an acetone/water solvent mixture and 0.05 M KOH, NaOH and $ZnCl_2$ catalyst at 300°C, 1 h.

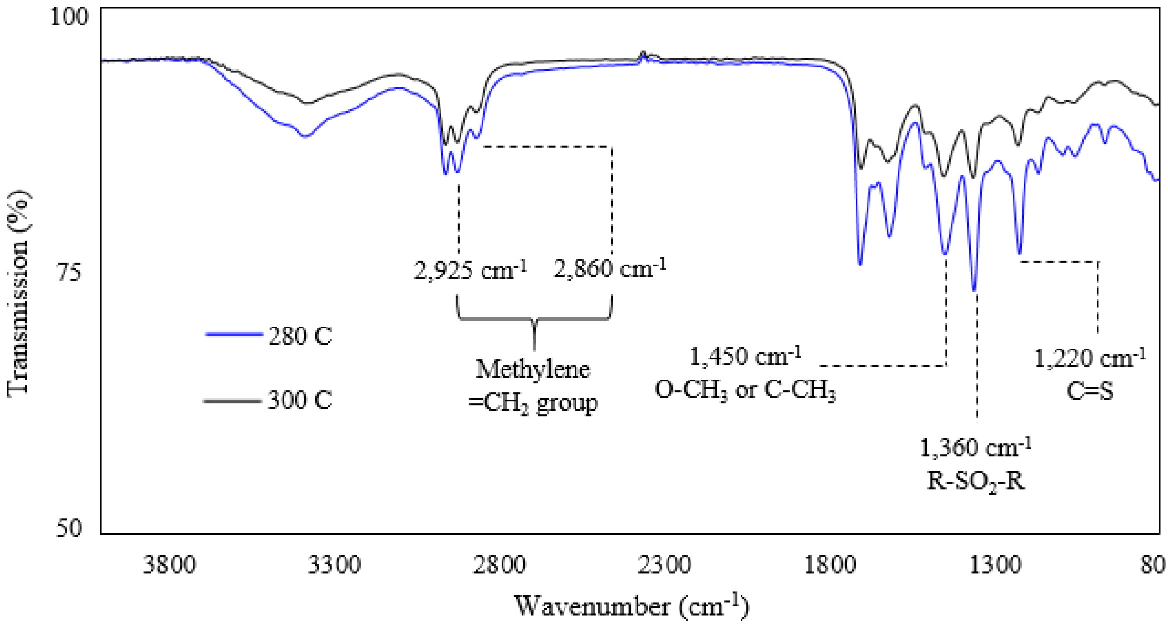

Figure 4b. FTIR spectra of dissolved decomposed resin after processing with an acetone/water solvent mixture and 0.05 M $ZnCl_2$ catalyst for 1 h at 280 and 300°C.

4 Conclusions

The work presented has shown that the use of NaOH and KOH is not able to enhance the degradation of an RTM6 epoxy resin, however, the inclusion of $ZnCl_2$ at a concentration of 0.05 M is an effective catalyst, possibly due to cleavage of the C=N double bond. After processing at 290°C for 1.5 h and 300°C for 45 min, a RRY of more than 94% was achieved. Although a relatively high temperature of at least 290°C is necessary, this reduction in both time and temperature compared to earlier work [13] represents a significant energy saving. Furthermore, it is clear the degradation process has strong dependence on reaction temperature with an increase of 10°C halving the necessary reaction time. For this reason, it appears optimum operating conditions are 300°C, 45 min with a 0.05 M $ZnCl_2$ catalyst, however, further research is necessary to determine whether these reaction conditions have any detrimental effect on the fibre properties.

FTIR spectra of the decomposed polymer matrix identified the presence of O-H and N-H bonds in a range of environments in addition to sulphonic compounds. Therefore, if an effective separation process can be developed, it is possible valuable organic monomers can be obtained which represents a significant advantage over pyrolysis processes.

Acknowledgments

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