

Supercritical Degradation of Unsaturated Polyester Resin Composites Using Alcohols

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Degradation of glass fibre reinforced (GFR) unsaturated polyester (UP) resin composites has been studied in this paper. The degradation was carried out using supercritical ethanol and supercritical 1-propanol and with a reaction time of 30 min. Resin elimination reached between 20–40 % after this treatment, why a second treatment step was necessary to achieve complete degradation. The second treatment step was carried out using heated acetone without any reaction time. This resulted in 100 % resin elimination. The partly solubilized resin after step one was analyzed using GC-MS. From the GC-MS investigations, interesting results were obtained. The majority of the identified compounds were derivatives of UP resin monomers, primarily phthalic acid and maleic acid, clearly indicating a degradation of the UP resin. However, these monomers were not identified as carboxylic acids or anhydrides as expected, but as esters. It was found that depending on the supercritical solvent applied for the degradation, the length of the ester group varied. This esterification of the monomers could, potentially, decrease the value of UP resin degradation using alcohols as solvents, since the original monomers cannot be recovered. However, it was also found that the esterification reactions enhanced the value of a degradation product. 4-phenylbutyric acid propyl ester (4-PBPE) is a product of the esterification of 4-phenylbutyric acid with 1-propanol. Since 4-PBPE is significantly more valuable, in terms of cost, than 4-phenylbutyric acid, production of such compounds is also considered to potentially enhance the overall value of GFR UP composite recycling.

1. Introduction

Fibre reinforced (FR) UP resin composites possesses a high density cross-linked network, which is extensively applied in the industry for applications such as wind turbine blades, naval constructions, offshore applications, water piping, building construction and automotive applications (Dholakiya, 2013). However, despite the wide applicability of FR UP composites, such materials become a crucial issue in terms of disposal routes at the end of their life cycle, exclusively because they are insoluble and infusible materials due to their cross-linked network structure. The majority of such materials are currently disposed on landfills or incinerated without any recycling attempt. This is not sustainable in the long term, why such disposal routes have been regulated by EU directives such as End of Life Vehicles (ELV) and Waste Electrical Equipment (WEEE). ELV and WEEE have put more pressure on solving FR polymer waste problems through recycling and reuse. By 2015, 85 % of ELV's have to be reused or recycled, with only 10 % incineration and 5 % going to landfills (Bontoux et al., 1996). This puts on higher demands for finding efficient recycling routes. Currently three main recycling technologies are available for the recycling of polymer composites: Mechanical recycling, pyrolysis and solvolysis using near-and supercritical fluids. Mechanical recycling and pyrolysis have been implemented in pilot scale, whereas solvolysis using near-and supercritical fluids is still on laboratory scale. Among these technologies, solvolysis using supercritical fluids has shown to be the most promising alternative to degrade the polymer and recover the fibres (Morin et al, 2012). Various alcohols have been applied as near- and supercritical solvents. This includes alcohols such as methanol, ethanol, 1-propanol and 1-butanol (Iwaya et al., 2007), (Kamimura et al., 2008), (Ibarra et al., 2011), (Okajima et al., 2012) and (Okajima et al., 2014). Recovery of clean fibres with satisfactory preserved mechanical properties has been achieved in the majority of the investigations, where the main focus has been on the fibres and not the solubilized resin. The objective

of this paper is to decompose UP composites reinforced with glass fibres using supercritical 1-propanol and ethanol with and without catalyst to observe the effect of catalyst addition. The degradation products obtained after the supercritical treatment will hence be identified by GC-MS, primarily to study the degradation pathways and also to search for value-added degradation products, which potentially could enhance the value of the overall process. The focus in this paper will be on the solubilized resin and not on the recovered fibres.

2. Experimental

2.1 Materials and methods

The waste UP resin composite materials applied for the recycling study was delivered in sheets of 10 cm x 4 cm x 3 cm. For the experiments, these sheets were cut into pieces of 3 cm x 2 cm x 2 cm with a weight of $24 \text{ g} \pm 1 \text{ g}$. The nominal fibre content was approximately 73 wt. %. The starting monomers of the UP applied was maleic anhydride, phthalic anhydride and propylene glycol hardened with styrene. Ethanol and 1-propanol was purchased from VWR Bie & Berntsen with a purity of 99.9 % and 98 %, respectively. The heterogeneous catalyst applied for the study was R-67-7H, which was delivered by Haldor Topsøe A/S. The shape of the catalyst is a 7-hole cylinder and consists of nickel. The base material of the R-67-7H carrier is magnesium aluminum spinel and a ceramic inert oxide of the spinel family. Acetone (ACS reagent grade with a purity of 99.5 %.) was purchased from Aldrich Denmark.

2.2 Supercritical treatment

Degradation of UP resin composites was realized in a non-stirred 280 mL batch reactor constructed in stainless steel. The specimens were put in the reactor together with the solvent and catalyst. The reactor was subsequently sealed with bolts and heated to the desired temperature with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$. The heating was carried out by a heating mantle and a heating plate. Pressure was induced by the increasing temperature, volume of the reactor and the amounts of composite and solvent. To achieve supercritical environments, the recycling process was carried out using the series of experiments listed in Table 1. The reaction time was started after the desired reaction temperature was attained. After the supercritical treatment, the residue was washed in acetone to remove residue particulates from the surface.

Table 1: Shows the design of experiments. The ratio of resin/solvent in g/mL was 0.17 in all the experiments.

Run	Solvent	Reaction time (min)	Temperature ($^\circ\text{C}$)	Pressure (bar)	Catalyst (g) R-67-7H	Initial mass of composite (g)
# 1	Ethanol	30	245	130	-	24.72
# 2	Ethanol	30	245	130	3.38	23.45
# 3	1-Propanol	30	265	120	-	24.71
# 4	1-Propanol	30	265	110	3.37	23.21

2.2.1 Efficiency of resin elimination

In order to determine how efficient the resin has been eliminated from the glass fibre surfaces, the percentage of eliminated resin was calculated according to eq. (1).

$$\text{Eliminated resin (\%)} = \left(\frac{\text{Weight of composite} - \text{weight of solid residue}}{\text{Weight of resin in composite}} \right) \cdot 100\% \quad (1)$$

Accordingly, the percentage of eliminated resin is the ratio of mass resin degraded from the fibres to the total mass of UP resin in the composite. The total mass of UP resin in the composite is determined by multiplying the total weight of the composite by 27 wt. %.

2.3 Analysis of reaction products

Subsequent supercritical degradation of UP composites, the UP resin was partly solubilized in the solvents. Identification of degradation products in the solvent was realized with a gas chromatograph–mass spectrometer (GC-MS). The gas chromatograph was a Perkin Elmer Clarus Model 500 that was coupled with a Perkin Elmer Clarus Model 500 quadrupole mass spectrometer. The analytical column was Elite-5 fused silica capillary column (30 m \times 0.25 mm of inner diameter (ID), 0.10 μm film thickness). The gas chromatograph was operated in temperature-programming mode as following: Initial column temperature was $75 \text{ }^\circ\text{C}$ for 1.5 min, and then the temperature was increased linearly to $275 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C}/\text{min}$. The temperature was held at the upper temperature for 10.5 min. The flow of the carrier gas (helium) was maintained at 1.0 mL/min. All MS analyses were conducted in scan mode (mass range of 75-600 amu) with electron impact ionization (EI) of 70 eV. A Perkin Elmer Clarus 500 auto sampler was used to inject samples into the gas chromatograph (using an injection volume of V_{inj} 1.0 μL). The samples taken from the exit solution were evaporated at room temperature and redissolved in 3 mL acetone, which dissolved all residues. After

filtration with 40 µm filters, the samples were analyzed directly in the GC-MS. The identification of the decomposition products was based on comparison of mass spectra with NIST library data.

3. Results and Discussion

3.1 Resin elimination

Elimination of resin after the supercritical treatments can be observed on Figure 1. 38 % resin elimination was achieved using supercritical 1-propanol and 25 % resin elimination was achieved using supercritical ethanol. The catalyst R-67-7H did not exhibit enhanced resin elimination, why this catalyst is not favored in further studies regarding UP resin degradation. Satisfactory resin elimination was not achieved using supercritical ethanol and supercritical 1-propanol after 30 min reaction time. Therefore, a second treatment step was introduced. The second treatment step implied heating of the partially degraded composite sheet from experiment 3. The heating was also carried out in the batch reactor to a temperature of 235 °C, a pressure below 30 bar and 0 min reaction time. The result from the second treatment step is illustrated on Figure 1, assigned as the light colored column. The appearance of the fibres after the first and second treatment step can be observed on Figure 2.

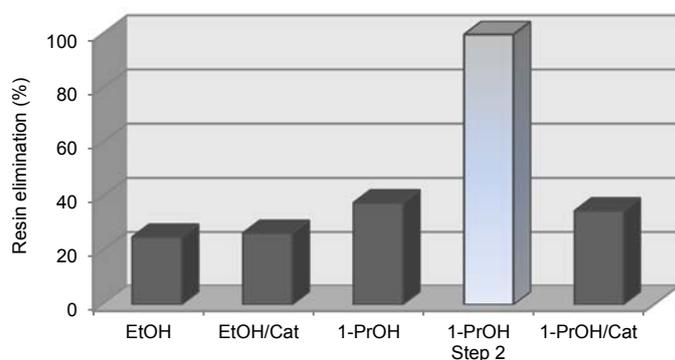


Figure 1: Eliminated resin in %. Ethanol is abbreviated EtOH, 1-propanol is abbreviated 1-PrOH and catalyst addition is abbreviated cat.



Figure 2: UP composite from experiment 3. Appearance after step 1 and appearance after step 2

3.2 GC-MS investigations

Figure 3 shows the total ion chromatograms obtained after supercritical ethanol treatment and supercritical 1-propanol treatment with and without addition of the catalyst R-67-7H. The experiments conducted with ethanol are similar to each other and the experiments conducted with 1-propanol are similar to each other in terms of produced degradation products. This indicates that the catalyst R-67-7H did not have an influence on how the UP resin was degraded and therefore the variety of produced degradation products. However, the catalyst might influence the quantity of the individual degradation products. The exact quantity of the different degradation products was not evaluated in this study. Instead, peak height calculations were performed for the identified peaks, in order to report the height of each peak as a percentage of the total heights of all peaks, see Table 2. This provides an approximation of the relative amount of each degradation product identified. In the experiments conducted with ethanol, the majority of the identified compounds were derivatives of different phthalates. In fact, the two phthalates diethyl phthalate and diethyl terephthalate accounted for approximately 59 % of the total identified peak heights. Diethyl phthalate is considered as being produced from phthalic acid, which has been cleaved off from the polyester resin structure. Phthalic acid reacts further via Fischer esterification with ethanol to produce diethyl phthalate and two water molecules, as observed in Scheme 1. Diethyl terephthalate is considered as being produced through a more complex degradation pattern. This

could involve cleavage of one of the $-\text{COOH}$ groups from the phthalic acid monomer, which subsequently attach to the phthalic acid monomer again in para position to the other $-\text{COOH}$ group. This produces terephthalate. Similarly as diethyl phthalate, Fischer esterification reaction with ethanol produces diethyl terephthalate.

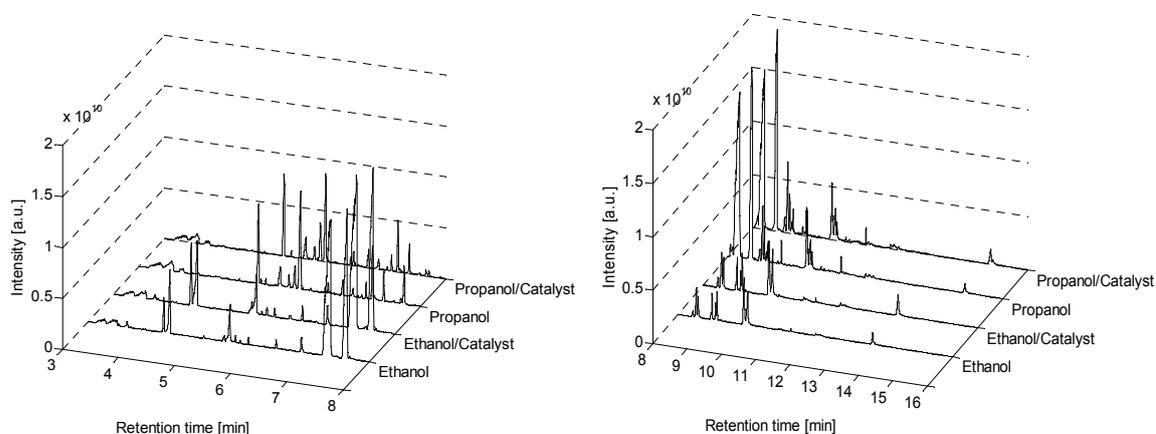
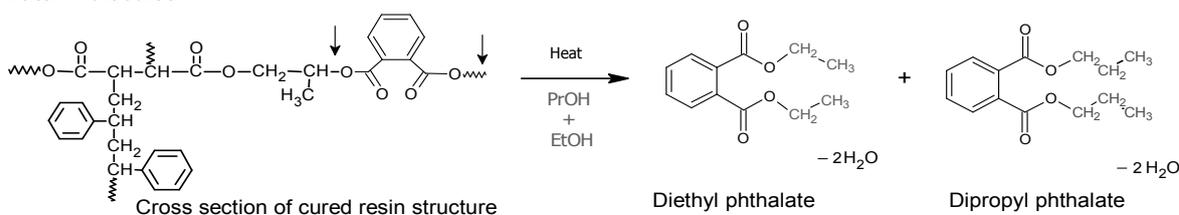
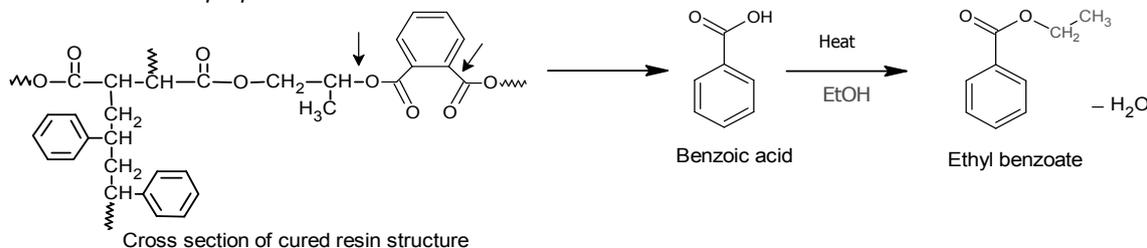


Figure 3: Total ion chromatograms of the degradation products obtained by degradation of UP resin in supercritical ethanol with and without catalyst and supercritical 1-propanol with and without catalyst. The chromatograms to the left show the retention times of 3-7.5 min and the chromatograms to the right show the retention times of 7.5-15 min.

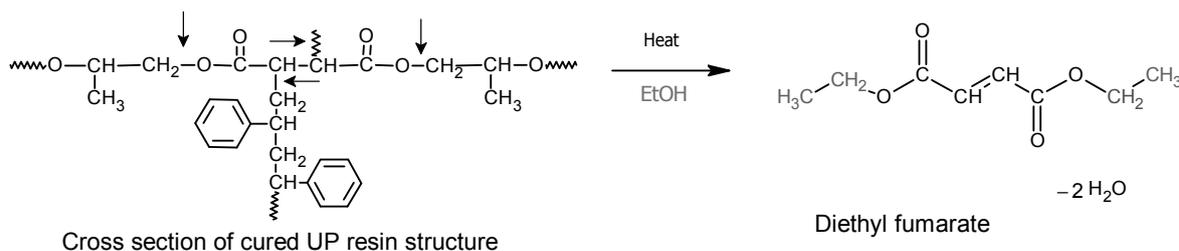
The other derivatives of phthalates are considered being produced similarly as diethyl phthalate, primarily through Fischer esterification reactions with ethanol. The compounds ethyl benzoate and diethyl fumarate were also identified in significant quantities, as they accounted for 7.2 % and 13 % of the total identified peak heights, respectively. Ethyl benzoate is a degradation product of phthalic acid from where one of the COOH -groups has been cleaved off during the supercritical treatment. This produces benzoic acid, which reacts further via Fischer esterification with ethanol to produce ethyl benzoate and water, according to Scheme 2. Diethyl fumarate is considered being produced from the monomer maleic acid, which have been cleaved off from the UP resin structure as shown in Scheme 3. Similarly as the phthalate derivatives and ethyl benzoate, maleic acid reacts with ethanol through Fischer esterification reactions to produce diethyl fumarate and two water molecules.



Scheme 1: Production of diethyl phthalate and dipropyl phthalate through Fischer esterification of phthalic acid with ethanol and 1-propanol.



Scheme 2: Production of ethyl benzoate through Fischer esterification of benzoic acid with ethanol.



Scheme 3: Production of diethyl fumarate through Fischer esterification of maleic acid with ethanol.

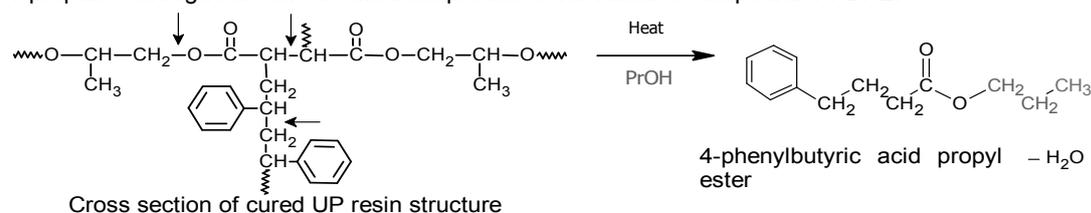
Similar observations have been made in the experiments conducted with 1-propanol. The majority of the identified products were various derivatives of phthalates, originating from the monomer phthalic acid. Dipropyl phthalate and Isophthalic acid dipropyl ester accounted for approximately 54 % of the total identified peak heights. Dipropyl phthalate is produced following a similar pathway as diethyl phthalate, namely through Fischer esterification with 1-propanol, see Scheme 1. Isophthalic acid dipropyl ester is produced through a more complex degradation pattern, similarly as diethyl terephthalate. However, instead of having the $-\text{COOH}$ group attached in para position, the $-\text{COOH}$ group was attached in meta position. The dipropyl groups originated from Fischer esterification reactions with 1-propanol. Based on observations that have been made throughout the interpretations of the results, it is obvious that under supercritical environments, the solvent reacts with the degradation products from the resin to form various esters.

Table 2: Shows the assignment and height percentages of the compounds identified in the chromatograms from Figure 1. The value added compounds are highlighted with grey.

RT (min)	Assignment	Portion of total chromatographic peak height (%)			
		Ethanol		1-Propanol	
		Cat. = 0 wt. %	Cat 14.4 wt. %	Cat: 0 wt. %	Cat 14.5 wt. %
3.74	α -Cumyl alcohol	0.80	0.58	0.33	0.32
4.35	Ethyl benzoate	4.9	6.8	0.09	-
4.46	Diethyl fumarate	8.8	7.2	-	-
5.13	n-Propyl benzoate	-	-	6.8	6.8
5.17	Fumaric acid, ethyl propyl ester	-	-	0.39	-
5.43	Methyl 2-methyl-2-propylhexanoate	0.73	1.23	-	-
5.63	3-MGDE	0.94	0.38	-	-
5.67	Maleic acid, diisopropyl ester	-	-	1.07	1.09
5.78	Dipropyl succinate	-	-	1.93	3.21
5.86	Diethyl adipate	1.04	0.98	-	-
5.88	Fumaric acid, dipropyl ester	-	-	8.38	7.37
6.37	Dimethyl phthalate	1.28	1.70	0.85	1.18
6.80	1-Ethyl 2-methyl phthalate	2.09	2.13	-	-
6.96	4-PBPE	-	-	0.27	0.26
7.04	Dipropyl adipate	-	-	1.38	1.36
7.32	Diethyl Phthalate	19.08	16.98	-	-
7.36	Methyl propyl phthalate	-	-	2.54	2.50
7.54	1,3-Diphenylpropane	-	-	0.17	0.16
7.62	Diethyl terephthalate	20.70	17.86	-	-
8.35	Dipropyl phthalate	-	-	13.38	12.85
8.71	Isophthalic acid, dipropyl ester	-	-	15.66	15.96
9.01	Bis(2-methoxyethyl) phthalate	3.59	3.47	-	-
9.15	Ethyl phthalyl ethyl glycolate	3.50	3.73	-	-
	Total	67.45	63.04	53.24	53.06

3.3 Value added chemicals

Value added chemicals have been identified in the experiments conducted with ethanol and the experiments conducted with 1-propanol. The value added chemical 3-methylglutaconic acid diethyl ester (3-MGDE) was only identified in the experiments conducted using ethanol. The compound accounts for approximately 1.4 % of the total identified peak heights, indicating that only small quantities of the compound were produced in the process. In the experiments conducted with 1-propanol, the value added compound 4-phenylbutyric acid propyl ester (4-PBPE) was identified. 4-PBPE is considered as a degradation product of styrene and maleic acid and produced according to Scheme 4. Cleavage at the highlighted positions in Scheme 4 produces the compound 4-phenylbutyric acid, which is not a valuable chemical. The subsequent reaction with supercritical 1-propanol through Fischer esterification produces the valuable compound 4-PBPE.



Scheme 4: Production of 4-PBPE through Fischer esterification using with 1-propanol.

4. Conclusion

Decomposition of UP resin composites in supercritical ethanol and 1-propanol was investigated in this work. It was found that supercritical alcohol treatment was not enough to decompose the resin completely within a reaction time of 30 min. A second treatment step was necessary to achieve 100 % degradation of resin and hence recovery of clean glass fibres. Degradation products produced during the supercritical treatments was investigated using GC-MS. It was found that monomers of UP resin reacted with the supercritical solvents through a Fischer esterification reaction to produce degradation products such as, diethyl phthalate, dipropyl phthalate, ethyl benzoate, diethyl fumarate etc. However, transformation of the monomers into esters impairs the possibility to recycle them in new composite materials. This makes use of supercritical alcohols for UP resin degradation a poor solvent. Esterification of UP resin degradation products can also result in compounds with a higher value than the original monomer. This was particularly observed by the production of the value added compound 4-PBPE, which was produced through Fischer esterification of 4-phenylbutyric acid with the solvent 1-propanol. Production of such compounds could potentially enhance the overall value of UP composite recycling, especially in terms of the ability to produce different value added compounds by using different solvents as the supercritical solvent.

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