

SWELLING BEHAVIOUR OF EPOXY RESINS IN VARIOUS SOLVENT SYSTEMS

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ABSTRACT

To select an efficient solvent for Supercritical Solvolysis the swelling behaviour of different Specimens was investigated. Three different types of specimen derived from Bisphenol-A epoxy were examined. Epoxy cured with Anhydride hardener and catalyst, Epoxy with Amine based hardener and a unidirectional carbon fibre reinforced specimen out of prepreg plies were immersed in different fluids. Next to Ethanol and Propanol which have already been used for supercritical Solvolysis experiments, Acetone and Dichloromethane were tested. Both fluids exhibit superior performance compared to the alcohols. Both neat epoxy resin materials were heavily degraded by dichloromethane and fairly degraded by acetone. Additionally, Ethanol, Propanol and Acetone were tested with Sodium Hydroxide and Potassium Hydroxide which both were used as catalyst in supercritical Solvolysis experiments. Addition of either Hydroxides did not improve the mass uptake through swelling but induced degradation through reduction of the specimens. The Specimens with carbon fibres showed higher resistance to swelling under all circumstances. Therefore, future work includes swelling experiments at still subcritical conditions but elevated temperature and pressure to especially be able to conduct experiments with gaseous Dichloromethane and attack the composite more effectively.

1. INTRODUCTION

During the past few decades the utilization of carbon fibre reinforced plastic (CFRP) has increased drastically, as Ashby [1] predicted. Not only in the aeronautical field, but also in wind turbines, automobiles, and civil engineering applications CFRPs offer a vastly superior performance compared to previously employed materials. Since the volume of carbon composites was and still is increasing, the question arises how to reutilize the material after the lifecycle ends or irreparable damage in the part terminates the utilization. In order to work environmentally friendly, simple disposal is not sustainable, already caused problems and should therefore be omitted [2]. Since carbon fibres require high-energy-processes in manufacturing and therefore are costly, the reutilization of composite materials comes with an economic motivation for companies that embed CRFPs in their products. To regain the fibres from waste materials, the surrounding matrix material must be removed successfully.

Due to economical as well as practical aspects during the manufacturing of CFRPs, the matrix material predominantly consists of thermoset polymers. Thermoset resins change their aggregate during the irreversible curing process to provide the desired physical properties such as stiffness and strength, along with resistance against environmental impact. After this kind of matrix material is cured it cannot be reshaped or reformed. [3] Thus, if one wants to separate fibres from matrix material, the chemical bond must be broken down. Thermal treatment represents another method to degrade the thermoset matrix by exposing it to hot air at high temperatures from 450 – 700 °C for several hours [4]. Theoretically the fibres could be fully obtained and reused, but the energy extensive fluidized bed method will degrade the carbon fibres through Oxidation. As solution, pyrolysis was introduced: Under absence of oxygen the CFRPs are firstly treated at 500 – 600 °C to degrade the thermoset resin. This method enables the reuse of the fibres without the surface oxidation but induces defects and a significant reduction in Oxygen atoms on the fibre surface. As a result the interfacial shear strength with new thermoset material is reduced considerably, when reutilizing the recycled fibres. [5]

To decrease the energy consumption, i.e. the process temperature, improve the quality of the regained fibres and moreover even utilize some products of the degraded thermoset resin, Solvolysis was developed.

Hereby, a solvent medium is used in supercritical state to break down the thermoset resin into low weight molecules. The supercritical state (depending on the solvent around 300 °C) promotes the diffusion into the solid composite and increases the mass transfer. Even though this method furthermore requires expensive reactors, working in high temperature regimes, Yan [6] states that there is a potential to save energy and thus cost. Also, the obtained fibres offer superior mechanical properties as their strength remains nearly constant and the process is easy to carry out and fast [7].

In order to find a suitable solvent for Solvolysis routes, swelling experiments allow the prediction of the performance in supercritical state experiments as good swelling capability corresponds to efficient catalyst transfer into the Epoxy system and improves degradation rate [8]. Since swelling experiments consume way less energy and do not require expensive reactors, it is an economically feasible and yet good way to predict the performance. Therefore, suitable solvents for energy- and time-efficient Solvolysis routes can be found by testing their swelling performance on Epoxy-resin.

2. MATERIAL AND METHODS

2.1. Materials

As specimen for the experiments, three different materials were investigated. Firstly, two different kinds of neat-epoxy specimen were manufactured. Both have a highly resistant derivate of Bisphenol-A as epoxy base, purchased from Kukdo Chemicals (Korea). One kind of specimen was catalytically cured with an Anhydride hardener from Kukdo Chemical (Korea) in a curing cycle selected to yield maximal mechanical properties and chemical resistance. The used ratio of Epoxy resin, Anhydride curing agent and Dimethylbenzylamine (BDMA) catalyst was (100:80:0.5). The other neat-epoxy specimen takes an aromatic Amine modified hardener purchased from Hitachi Chemicals (Japan) without addition of catalyst. A mass ratio between the epoxy and curing agent of (100:60) was used to produce the specimens. Lastly, a CFRP material is investigated. The Epoxy-Carbon fibre prepreg plies were purchased from Carbon-X (Korea) and cured in an autoclave. Their resin is based on a Bisphenol-A derivate as well and cured with help of a catalytically supported Amine hardener.

As previous research showed, polar solvents exhibit the best degradation behaviour of cured Epoxy resin. Therefore, several polar solvents were selected and the cured specimens are immersed. Several publications introduce supercritical Propanol and Ethanol as solvent in Solvolysis experiments, why both liquids are selected as comparison to other solvents that could also reach supercritical state easily. Ethanol with a purity of at least 94 % was purchased from OCI (Korea). Previously conducted swelling experiments by Wang [8] showed that 1-Propanol exhibits better swelling behaviour compared to iso-Propanol and was thus chosen. It was bought from Samchun Chemicals (Korea) with a purity of at least 99 %. Moreover, Acetone (purity >99.5 %) from OCI (Korea) was used as well as Dichloromethane exceeding 99.5 % purity from Samchun Chemicals (Korea). The solvents were tested with and without Sodium Hydroxide pellets with 95 % minimal purity supplied by Junsei (Japan) and Potassium Hydroxide with more than 85 % purity by Sigma Aldrich (Sweden).

2.2. Experimental methodology

To prevent the formation of voids, the mixed resin and curing agent was subjected to a vacuum environment for prolonged time, promoting the process of outgassing. After this process, the mixture was poured into molds that were treated with release agent before. Due to the different curing agents in the epoxy, the curing cycle had to be adapted to yield maximum material performance, as seen below in Figure 1.

For the CFRP, 30 plies with a stacking sequence of $[0]_{30}$ were cured in an autoclave, packed in a vacuum bag. The number of plies was chosen to meet the 3 mm thickness of the neat-epoxy specimens. A curing pattern corresponding to Figure 2 was used to cure the plate.

Afterwards, the plate was cut into dimensions corresponding to the neat epoxy specimens of 36 mm in length and 20 mm in width with the fibre directions orthogonal to the longer side, as depicted in Figure 3.

Every specimen was weighed and immersed into a glass bottle with 100 ml of liquid phase solvent, sealed and placed in an oven. For the experiments with catalyst a 0.25 M concentration was chosen and the corresponding mass of solid catalyst pellets added. The oven by Daihan Scientific (Korea) was set to maintain a constant temperature for the experiment duration of seven days. Experiments were carried out at 35 °C and 50 °C in an isolated environment to prevent influences from moisture absorption of the solvent or Temperature changes.

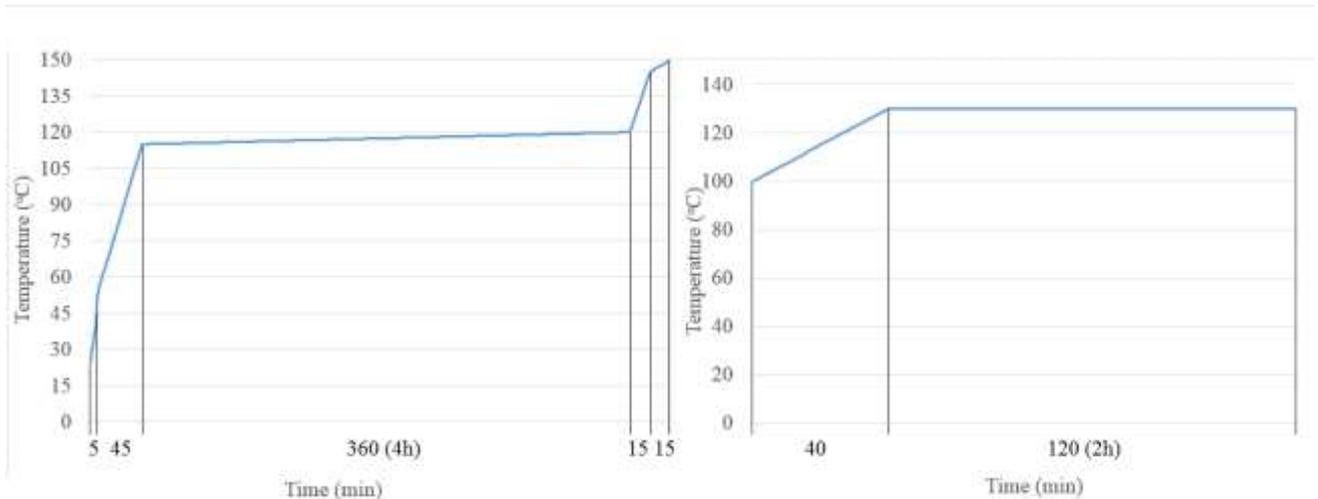


Figure 1: Curing Pattern of Epoxy with Anhydride (left) and Amine (right) hardener

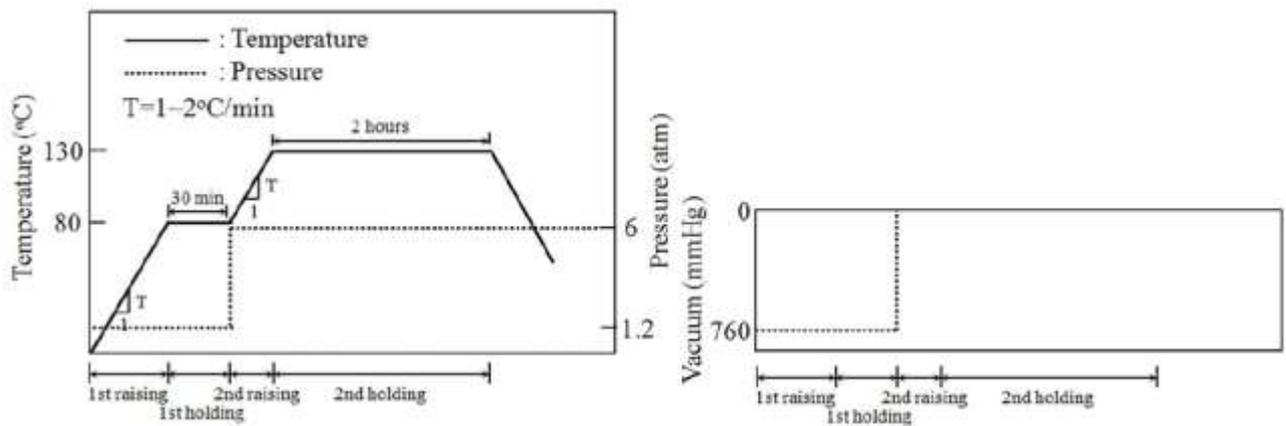


Figure 2: Curing pattern of CFRP

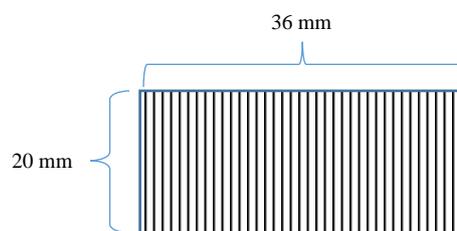


Figure 3: Specimen size and fibre orientation

2.3. Analysis

After the experiment has finished, the tested specimen is taken out of the solvent system, cleaned with distilled water and manually dried, before measuring the weight again. For specimens that did not keep their integrity the parts were collected and dried under warm air. A precision scale HR-250AZ from A&D (Japan) was used for all weight measurements. After the experiments, the weight is taken as soon as no weight loss through evaporation of directly exposed solvent could be observed. The swelling capabilities were calculated by the percentage of mass uptake every specimen exhibits corresponding to Equation (1), where m_f represents the final mass after the experiment and m_0 the initial mass.

$$\text{Mass uptake (\%)} = \frac{m_f - m_0}{m_0} \quad (1)$$

3. RESULTS AND DISCUSSION

For all specimens, several tests were carried out with a duration of one week each. Since Dichloromethane is unstable with both Hydroxides and boils at 40 °C it is not tested at 50 °C or in alkaline solutions.

Regarding the Anhydride-Epoxy specimens, the swelling without catalyst at a moderate temperature of 35 °C exhibited the following behaviour. After one week, the average mass gain of Anhydride-Epoxy specimens in pure Ethanol was 0.34 %, corresponding to small swelling. 1-Propanol lead to actual mass decrease in all tested probes manufactured with Anhydride-hardener. The average – 0.2 % mass change corresponds to the process of dissolving small amounts of resin in the liquid, exceeding the actual uptake inside the material. Compared to both alcohols, acetone lead to a considerably increased mass uptake; on average 12.27 %. Some specimens even broke without mechanical impact. The most astonishing results could be obtained from the immersion in dichloromethane, as specimens did not swell but break down into a big number of small fragments of different size and shape, many of them being in the range of 1 mm or even lower. Because of the sheer number of fragments and dissolved fraction in the Dichloromethane no meaningful mass uptake could be defined. A rise in temperature to 50 °C lead to an increase in mass uptake for all solvents. In the case of Acetone, the mass uptake roughly doubled to 25.11 % and the specimen broke down into several pieces, but especially the specimens in 1-Propanol showed interesting behaviour. The mass loss decreased by percentage which means that at higher temperatures swelling gained more importance compared to dissolving in Propanol.

Under the addition of 1 g of solid Sodium Hydroxide (NaOH) pellets, the same test was repeated, yielding a 0.25 M solution, if fully dissolved. For all solvents, the pellets did not dissolve fully and solid NaOH powder remained on the bottom, corresponding to a saturated solution for all liquids. The ethanol solution stayed clear whereas the Propanol solution turned slightly yellow and the Acetone solution yellow-brownish due to the reducing degradation of the specimen and the Aldol reaction the solvent underwent. Ethanol and Propanol immersed specimens suffered a mass loss of 1.70 % and 0.63 % on average, respectively. Acetone lead to the most drastic colour change of all solvents as well as to an average mass uptake of 7.20 % per Anhydride specimen. As expected, a raise in temperature leads to more significant results in the same manner. For example, the mass uptake in Acetone/NaOH roughly doubles as the temperature rises by 15 degrees. As NaOH was substituted by KOH in a different experiment series, an increased mass loss could be seen. Interestingly, the KOH/Acetone system did lead to a mass loss of 6.17 % and no increase offering a contrary behaviour to the solution with NaOH as catalyst. Since Dichloromethane undergoes a neutralization reaction, it is not mixed with NaOH or KOH but instead a 1:1 mixture between the aprotic solvent and Acetone was exposed to the specimen. The swelling of 47.02 % overlapped with fraction of the specimen that is less severe than for pure Dichloromethane. In Table 1 the percentages of mass uptake for Anhydride-Epoxy are presented and can be compared.

Anhydride-Epoxy	No Catalyst, 35 °C	No Catalyst, 50 °C	NaOH 0.25M, 35 °C	NaOH 0.25M, 50 °C	KOH 0.25M, 50 °C
Ethanol	0.34 %	0.50 %	- 1.10 %	-6.18 %	-9.42 %
1-Propanol	- 0.2 %	- 0.01 %	- 0.63 %	-3.81 %	-4.53 %
Acetone	12.27 %	25.11 %	7.20 %	14.81 %	-6.17 %
Dichloromethane	Not available	-	-	-	-
Dichloromethane/ Acetone 1:1	47.02 %	-	-	-	-

Table 1: Swelling behaviour of Anhydride-Epoxy

The Amine-Epoxy probes displayed a differing swelling behaviour. Without catalyst, the mass uptake in Ethanol was considerably higher with 4.30 % and for 1-Propanol the 2.19 % average mass uptake exceeded the one of Anhydride based neat-epoxy specimens. In the case of the latter, they showed reversed behaviour since none of the probes lost mass, like Anhydride-Epoxy pieces. When immersed in Acetone the Amine-Epoxy material cracked multiple times during the experiment. The mass uptake of 6.00 %, as seen in Table 2, on average disregards the dissolved part of the material since it reacted more actively with Acetone than Anhydride-Epoxy specimens. The edges were brittle while the core exhibited a tough, flexible structure. The anisotropic behaviour was caused by the diffusion of the liquid into the specimen from the edges, exposing more wetting area per volume to the curing mold. Since the metal mold transfers heat into the uncured epoxy resin, the curing process started from the edges, leading to a higher degree of crosslinking compared to the centre for all neat epoxy specimen. In contrast to Anhydride-Epoxy, the Amine cured epoxy resin was more stable against Dichloromethane. A slight pressure increase in the bottle indicated degradation and development of gaseous species during the experiment but the development of a vast number of small fragments make the obtained mass increase of 0.08 % not representative. The actual grade of degradation exceeded the one of Acetone by far and for some specimens like the Anhydride-Epoxy resin it was not possible to get a reliable value. At 50 °C the swelling rate increased for all specimens. Ethanol swelled Amine-Epoxy pieces way better than Anhydride-Epoxy probes and induced a significant reduction in mechanical properties on the averaged 8.50 % swollen specimens with Amine curing agent. They exhibited low torsional stiffness and a failure could be easily induced by bending. 1-Propanol swelled this type less which could be easily observed by the higher rigidity. Acetone immersed pieces cracked multiply internally and the container experienced a slight pressure increase during the test. Nevertheless, Amine-Epoxy showed higher resistance to Acetone compared with Anhydride-Epoxy. After addition of NaOH, the mass uptake in Ethanol and 1-Propanol decreased to 2.99 % and 0.67 %, respectively. The liquid was slightly yellow after the test and an oily film around the specimen could be observed from which degradation of the epoxy can be inferred. The better resistance of Amine-Epoxy compared to Anhydride-Epoxy against a Dichloromethane and Acetone mixture was optically easily recognizable as presented in Figure 4. At 50 degrees NaOH catalysed swelling lead to increased mass uptake for both alcohols. Nevertheless, for Acetone NaOH the mass uptake decreased from 8.08 % to 6.70 %. This can be explained by the higher degree of degradation. All specimens were cracked internally and broke brittlely by low strength physical impact. With KOH as catalyst, the mass uptake of Amine specimens was similar to the absence of catalyst with 8.18 % with Ethanol and 7.22 % in Acetone. For Propanol the mass uptake lay between the one without catalyst and with NaOH as catalytic agent with a value of 3.52 %. This value can be explained by the partly degradation of the specimen as they showed clear signs of etching. When immersed into a 0.25 M KOH Acetone solution, the specimens could be fractured easily and dust covered them.

Amine-Epoxy	No Catalyst, 35 °C	No Catalyst, 50 °C	NaOH 0.25M, 35 °C	NaOH 0.25M, 50 °C	KOH 0.25M, 50 °C
Ethanol	4.30 %	8.50 %	2.99 %	6.48 %	8.81 %
1-Propanol	2.19 %	5.06 %	0.67 %	2.67 %	3.52 %
Acetone	6.00 %	7.17 %	8.08 %	6.70 %	7.22 %
Dichloromethane	0.08 % *	-	-	-	-
Dichloromethane/ Acetone 1:1	18.49 %	-	-	-	-

Table 2: Swelling behaviour of Amine-Epoxy

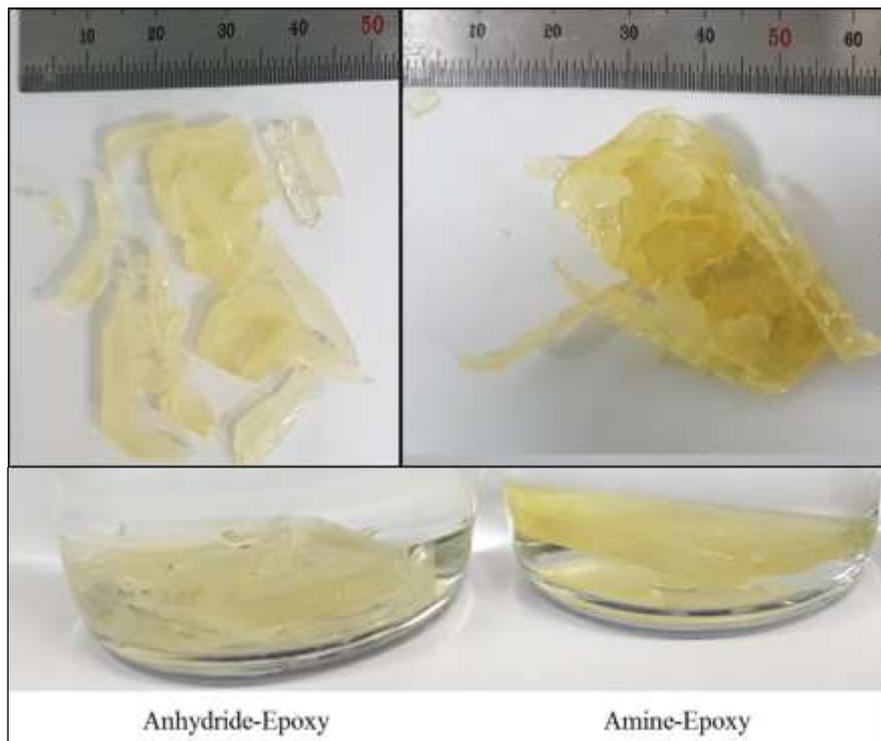


Figure 4: Degradation of Anhydride-Epoxy and Amine-Epoxy in Dichloromethane & Acetone (1:1)

Contrary to both neat-epoxy resins, the specimens consisting of carbon fibre prepreg could not be degraded or broken up into several pieces. Since the resin in the prepreg was also mixed with an Amine curing agent, similarities to the Amine-Epoxy probes should be found. The swelling in Ethanol was higher relative to other solvents and higher than for Anhydride-Epoxy. Acetone swelled the CFRP with 0.04 %, not half as good as the 0.11 % mass uptake of Ethanol. 1-Propanol lead to a slight mass decrease that induces some Epoxy being dissolved in it, since the solution stays clear. Dichloromethane outperformed all other solvents by far in the case of CFRP but with 0.58 % still yielded a low mass uptake, compared to the neat-epoxy specimens and the bottles experience a slight pressure increase. Interestingly, the addition of NaOH decreased the swelling capabilities in Ethanol and did not alter the average of -0.01 % when immersed in 1-Propanol. For Ethanol, the solution had a slightly opaque, yellowish colour caused by degradation of Epoxy. Therefore, the difference in mass uptake might correspond to the dissolving. A similar explanation is valid for increased temperature conditions without catalyst addition, as the mass uptake in Ethanol decreased. For Acetone, the colour of the liquid was dark orange, thus a higher grade of degradation of the cured resin takes place. At 50 °C the mass uptake for 1-Propanol increased slightly, but the small difference was not significant enough to deduce a trend.

When exposed to Acetone CFRP specimens took up 0.13 % of mass in a higher temperature environment, increasing the efficiency to the low temperature tests considerably. Contrary to Anhydride and Amine- neat epoxy specimen the mass uptake of CFRP did not vary significantly when KOH instead of NaOH was used as catalyst. Only for Propanol it increased slightly to 0.04 %. For both catalytic systems that were tested at 50 °C all specimens showed an oily layer on top of the probe with a yellowish colour, corresponding to reacting epoxy and neutralization reactions between propanol and the alkaline substances. This All values are collected in Table 3.

CFRP	No Catalyst, 35 °C	No Catalyst, 50 °C	NaOH 0.25M, 35 °C	NaOH 0.25M, 50 °C	KOH 0.25M, 50 °C
Ethanol	0.11 %	0,07 %	0.06 %	0.15 %	0.16 %
1-Propanol	- 0.01 %	0.01 %	-0.01 %	0.01 %	0.04 %
Acetone	0.04 %	0.13 %	0.05 %	0.22 %	0.22 %
Dichloromethane	0.58 %	-	-	-	-
Dichloromethane/ Acetone 1:1	0.07 %	-	-	-	-

Table 3: Swelling behaviour of CFRP

4. CONCLUSION

The results show that the curing agent had a considerable influence on the swelling capabilities of the epoxy resin system. Depending on the solvent, both hardeners showed different influences on the swelling behaviour. 1-Propanol did not swell Anhydride-Epoxy or CFRP specimens but lead to a slight mass loss. Since CFRP, the material that will be recycled, exhibited drastically increased resistance against all tested solvent systems, one should further test other catalyst systems and solvents. Nevertheless, CFRP and Amine-Epoxy specimen both exhibited comparatively good swelling properties, when exposed to Ethanol contrary to Anhydride-Epoxy resin which is more resistant. Consequently, Ethanol is a promising solvent utilizing Solvolysis for Amine based epoxy resins but not for Anhydride hardened ones. Acetone degraded all specimen in combination with catalyst which will be further investigated at higher temperatures, considering the aldol reaction of the solvent. Generally, KOH lead to a higher degree of degradation or mass uptake for the neat-epoxy specimen and therefore will be used in further experiments. Moreover, higher temperature and increased pressure should be used to find an optimal solvent system to degrade the epoxy matrix and recycle the fibres. Dichloromethane showed superior behaviour to all other solvents under mild conditions as it partially degraded neat epoxy specimens and swelled CFRP more than every other system. Experiments with gaseous, subcritical Dichloromethane in raised temperature and pressure regimes will be conducted. Consequently, more solvent-systems will be surveyed before choosing the most promising one that will then be tested in supercritical conditions.

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