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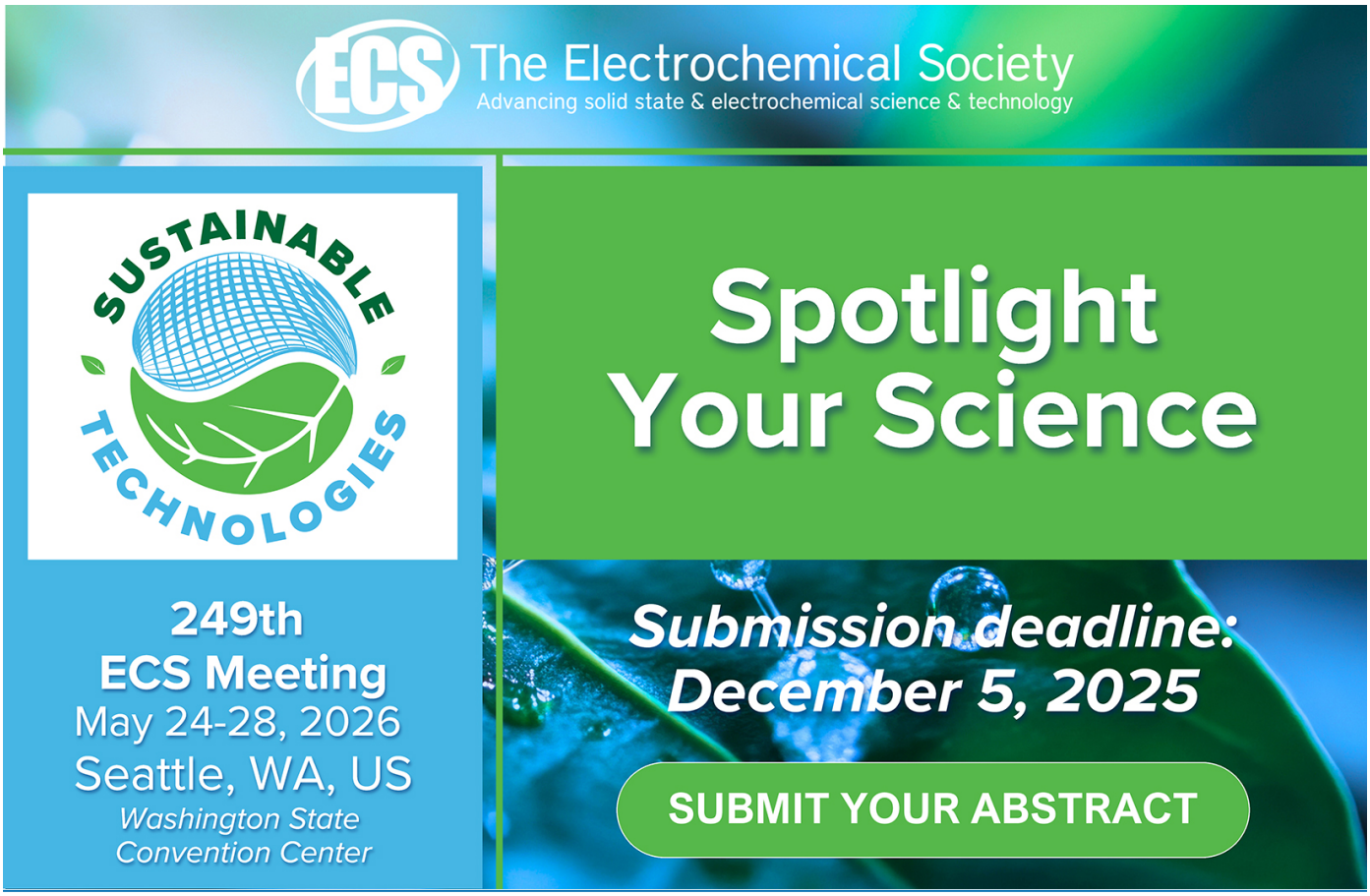

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# Environmental and chemical ageing of epoxy resins cured with bio-based amino acids

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**Abstract.** To achieve efficient and sustainable use of raw materials and energy, structures made of lightweight composites and thermosetting polymers are widely used. For sustainability, it is especially mandatory to extend the operating life of structures and components even under harsh conditions. Recently, the transformation from petrochemical to biobased resources is ongoing, to further improve sustainability. However, because of the more polar state of many bio-based raw materials, it should be ensured, that they are not lacking in long-term use. In this study, specifically, the evolution of absorption and thermo-mechanical properties such as tensile strength or glass transition temperature ($T_g$) are analysed after ageing in demineralised water and chemicals (acetone, isopropanol, hydraulic oil) for L-arginine-cured epoxy compared to fully petro-based epoxies. The changes in properties due to physical ageing (molecular relaxation) and diffusion reveal a complex interplay between plasticization, physical ageing and possible chemical degradation. In particular, water absorption promotes strength-reducing plasticization and strength-increasing molecular relaxation on different time scales. This complex interplay is found for both types of epoxies and is in good agreement with what was previously found for classical epoxy. At the same time, the plasticizing effect of water also significantly reduces the $T_g$, as the water ingress into the molecular structure which increases chain distances and facilitates molecular movements. Furthermore, the resistance of the arginine-cured epoxy against different chemicals is particularly high and the diffusion retarded. Evidence for chemical degradation due to acetone diffusion is detected for both epoxy types via FTIR-analysis.

## 1. Introduction

As industries such as automotive, aerospace, transportation and wind energy rely on the durability of the materials they use and are forced to reduce their environmental impact, a deep understanding of their long-term properties is essential and new sustainable materials are mandatory. One natural approach is to replace petrochemical and non-reusable matrix resins with more environmentally friendly alternatives. Currently, entirely new types of thermosets, such as vitrimers, are developed [1], or existing ingredients are gradually replaced by bio-based alternatives [2]. While the thermo-mechanical properties of such new systems are already very promising, little is known about their ageing behaviour and long-term properties. Therefore, the present study compares the environmental and chemical durability of an industrial (petro-

chemical) amine-cured epoxy resin with an amino acid-cured epoxy resin. As building blocks of proteins, amino acids can be extracted e. g. from plants and are consequently completely bio-based.

The durability of epoxies in the presence of water absorption has already been investigated in numerous studies in the past [3; 4]. Most of them use accelerated ageing processes at elevated temperatures to predict the evolution of properties due to slow diffusion rates at moderate ambient temperatures [5–7]. Therefore, we know that absorbed water can cause significant changes in thermomechanical properties through simultaneous plasticisation and relaxation (physical ageing) [8; 9]. In general, tensile strength and glass transition temperature were shown to be the properties most affected by water absorption. They can be reduced by a factor of 2 or even more [10; 11]. As the plasticising effect of water is understood as a reduction in intramolecular forces by increasing chain spacing, it is often compared to an increase in ambient temperature. In contrast, Gibhardt et al. revealed significant differences between aging conditions, e. g. that physical aging could be easily overseen or misinterpreted by accelerated aging only [12]. While the investigated amine-cured epoxy resin has a dry tensile strength of approx. 70 MPa and a $T_g$ of 89 °C, the values obtained in 22 °C warm water dropped to approx. 50 MPa / 63 °C, while in 50 °C water they only dropped to ≈ 60 MPa / 68 °C, even though slightly more water was absorbed.

The amount of water absorbed at equilibrium in polymers or epoxies in this case depends mainly on the structure of the polymer [13]. In the past, a distinction was often made between ‘volumetrically’ and ‘interactively’ determined explanations. In this case, volumetric approaches mainly consider absorption in the free volume, which can vary depending on the degree of cure and temperature, and in space, which is a consequence of unwanted defects such as micropores or cracks [14]. According to this approach, the interactions between water and the polar sites of the polymer network are largely neglected. However, these interactions between water and the polymer network are often regarded as dominant for water absorption [15].

It has been shown that water molecules are attracted to the polarity of the chemical structure of polymers and that water is also bound to these molecular segments by hydrogen bonds [16; 17]. Furthermore, spectroscopy and absorption-desorption experiments have shown that there are at least three states in which water interacts with the molecular network. These are defined as free or unbound water, weakly bound water (type I) that forms one hydrogen bond with the network, and strongly bound water that forms two hydrogen bonds (type II) [10; 16] found that type II water bonding increases the $T_g$ of wet epoxy.

Components made of continuous fibre-reinforced polymers are occasionally exposed to specific media over long periods of time during use. One example of this is oil-conveying pipes. However, contamination with media can also occur in other applications, for example hydraulic oil in wind power plants. It is also relevant to know which solvents can be used e. g. for surface cleaning without causing lasting damage to the polymer even after brief exposure.

Because particle modifications are often carried out using solvents, many studies deal with the addition of solvents in the uncured state and the influence of their incomplete evaporation on the curing process [18–20]. Regarding the durability of epoxies against chemicals, there is considerably less literature on cured epoxy resins.

Kaplan et al. immersed different epoxy resins in several chemicals at different temperatures to investigate solvent uptake and diffusion. The authors measured the sorption kinetics finding diffusion into the epoxy network, with the rate and extent of diffusion depending on both the epoxy formulation and the solvent properties. The diffusion process generally followed Fickian or

anomalous diffusion behaviour, and the diffusion coefficients for solvents were in the range of $10^{-9}$ to $10^{-11}$ $cm^2/s$ [21].

However, more studies are carried out in industrial research and occasionally published [22]. According to Zheng et al. (Evonik Corporation) and Aziz et al. [23] the curing agent and the formed network have significant influences on the chemical resistance of epoxy resins. The denser the network (high network density), the better the resistance to swelling and diffusion [22]. According to the authors, a chemical attack of a thermoset can be divided into three processes: swelling of the polymer network, chemical diffusion into the network, and chemical reaction and degradation of the network. Standard epoxies show good chemical resistance to alcohols (e.g. isopropanol) and paraffinic or naphthic hydrocarbons (e.g. hydraulic oil). However, resistance to ketones such as acetone is poor and can lead to swelling and irreversible damage due to micro-cracking or network destruction.

To the best of our knowledge, amino-acid cured epoxies have not yet been studied in terms of their behaviour under immersion in water or chemicals. However, because of the more polar state of many bio-based raw materials, it should be ensured, that they are not lacking in long-term use, which would reduce their value regarding sustainability. Furthermore, it is relevant to know if there are any special requirements e. g. for cleaning with solvents when using amino acid-cured epoxy resins in contrast to standard epoxies.

## 2. Materials and Methods

### *2.1 Materials*

In the study, the petrochemical epoxy resin EPIKOTE™ Resin 827 from Westlake (Houston, Texas, USA) based on DGEBA is used and cured with the bio-based amino acid L-Arginine (Buxtrade, Buxtehude, Germany) as well as with the petrochemical amine curing agent EPIKURE™ Curing Agent MGS™ RIMH 137 (Westlake, Houston, Texas, USA). In the following, these systems are labeled as “827/Arg” resp. “827/137H”. The behaviour of the petrochemical epoxy system “135/137H” containing EPIKOTE Resin MGS™ RIMR 135 (Westlake, Houston, Texas, USA) against water has been published in [12] and serves as comparison. Resin 135 is also based on DGEBA but contains 10-20 % 1,6-Hexanediol diglycidyl ether (HDDGE) as reactive diluent.

Immersions at 22°C take place in isopropanol (Ing. G. Linker GmbH, Sprockhövel, Germany) acetone (Lohmann Laborservice GmbH, Marxen, Germany), hydraulic oil (Mobil Nuto H 46, Exxon Mobil Corporation, Irving, Texas, USA) and demineralised water.

### *2.2 Methods*

Within this study, neat epoxy plates without fibres are under investigation. The petrochemical systems 827/137H and 135/137H were cured by vacuum-assisted resin transfer moulding (VARTM) for 8 hours at 50°C in a heat press, followed by a post-curing process for 16 hours at 80°C in a convection oven. As published in detail in [2], Arg was dispersed in 827 using a three-roll mill before plate manufacturing via casting process and curing with a maximum temperature of 180 °C in a convection oven. Specimens were cut with an EUROMOD®-MP (Isel Germany AG, Eichenzell, Germany). The dogbone geometry with 0.5 mm thickness, 6 mm width, a free test length of 10 mm and a radius of 16.25 mm over a length of 4 mm on both sides is published in [12]. In order to compensate slight changes in the thickness of the specimen due to their different manufacturing methods, the immersion time is subsequently standardised to 1 mm. This standardisation was verified using specimens of different thicknesses.

Immersions are taking place in closed vessels ensuring that the test specimens are exposed to the respective medium from all sides. Before immersion, specimens are dried in a vacuum chamber at 40 °C, until consistency of mass. Changes in mass and geometry are tracked with a precision scale (AT261DeltaRange®, Mettler Toledo, Columbus, Ohio, USA), an outside micrometer and a caliper gauge during immersions using at least three specimens.

Dry and immersed specimens are tested on a GABOEPLEXOR®500N (Erich NETZSCH GmbH & Co. Holding KG, Selb, Germany) in static tensile tests 1mm/min (5 % strain/min) until failure. Furthermore, dynamic tests were conducted on the same machine to determine glass transition temperatures ($T_g$) in accordance with DIN EN ISO 6721-1 via onset analysis as well as crosslink densities (1 Hz, 2 K/min, 25 °C to 150 °C resp. -130°C to 230°C for crosslink-densities). Due to small standard deviations, only one or two $T_g$ measurements were taken for individual immersion times to identify trends. The crosslinking density $\nu_C$ was calculated via (1), with R = 8.3145 J/(mol · K) [24]. To receive $\nu_C$ in the unit $mol \cdot cm^{-3}$, the storage modulus $E'$ in the rubbery plateau is inserted in MPa and $T_g$ in K.

$$\nu_C = \frac{E'_{T_g+40K}}{3 \cdot R \cdot (T_g + 40K)} \quad (1)$$

Fracture surfaces are analysed via scanning electron microscopy (SEM). Images were acquired with a SUPRA 55VP (Zeiss, Germany) using secondary electron (SE) detection with an accelerating voltage of 3 kV. All samples were provided with silver conductive paint at the edge of the sample carrier and vaporized with gold for 30 s at 40 mA with a BALTEC SCD 050 SPUTTER (BALTIC Präparation e.K., Germany), creating an electrically conductive layer of a few nanometer thickness on the surface.

A digital microscope VHX-6000 (Keyence Corporation, Osaka, Japan) with transmitted light is used to track diffusion lines.

Fourier transform infrared spectroscopy (FTIR) measurements in the MIR range (4000 $cm^{-1}$ to 500 $cm^{-1}$) are performed for dry as well as immersed and for 48 h at 40 °C under vacuum re-dried specimens on a Tensor II (Bruker Corporation, Billerica, USA) in Attenuated Total Reflectance (ATR) using a MIRacle™ Single Reflection Horizonal ATR Accessory from PIKE Technologies (Fitchburg, Wisconsin, USA). Furthermore, FTIR analysis of the immersion media after immersion of specimens are conducted and compared to references stored in similar vessels without specimens. For background and sample spectra, the mean values of 40 measurements are used and the resolution is set to 2 $cm^{-1}$. The processing of the raw data includes a baseline correction and a normalisation of the spectra on the constant aromatic peak (1605 $cm^{-1}$, C=C stretching) for epoxy specimens resp. on specific suitable peaks for the immersion media.

Immersed specimens were re-dried and weighted in a vacuum oven at 40°C until mass consistency followed by re-drying at 100 °C under vacuum to get additional information on degradation.

## 3. Results

### *3.1 Weight change and swelling*

Figure 1 displays the weight changes in the different immersion media. 827/Arg absorbs higher amounts of water than 135/137H (Figure 1 a), which can be explained by its higher polarity. Maximum values were obtained at ≈ 4.8 wt.-% weight change for 827/Arg vs. ≈ 2.8 wt.-% for 135/137H. Both values are in the range of reported literature values from 1.0 to 5.0 wt.-% [4; 12; 25; 26]. The system 827/137H showed similar absorption behaviour after selective immersion times and is therefore not shown in Figure 1.

As reported in [27], deviations from Fickian absorption can be found in the transition from linear to asymptotic range. A continuous increase of weight changes, typical for two-stage or non-Fickian sorption behaviour, is observed in both cases. Such deviations from Fickian sorption are typically related to water-induced relaxation phenomena in epoxy [28–31].

Immersion in hydraulic oil (b) showed no weight change while specimens immersed in isopropanol (b) lose small quantities of mass first. This phenomena is in line with investigations of Kaplan et al. and is explained with a removal of soluble components and the relatively high viscosity of isopropanol (1.77 cP at 30°C, compared to e.g. methanol 0.51 cP) [21].

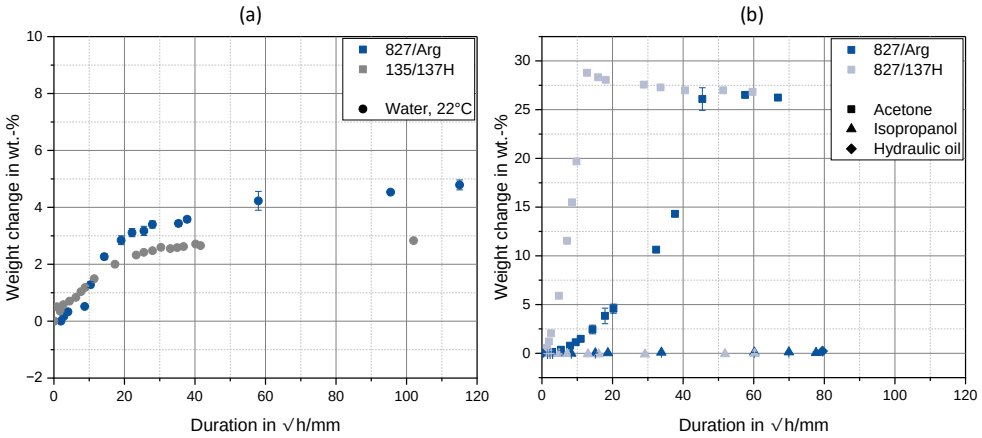


**Figure 1.** Weight change over time for investigated epoxy resins during immersion in water (a) as well as in acetone, isopropanol and hydraulic oil (b).

The highest increase in mass is observed for the immersion in acetone (b) with a mass increase of almost 30 % for the petrochemical reference system 827/137H. For this system, the progression of acetone diffusion could be tracked via digital microscopy with transmitted light, displayed in Figure 2 (a). The time of complete saturation (143 h/mm ≈ 12 √h/mm) corresponds to the maximum mass increase (see Figure 1). This is followed by a decrease in mass (Fig. 1), indicating degradation, which is further analysed in section 3.4. An overshoot was also reported by Kaplan et. al [21].

A diffusion coefficient of $D = 5.29*10^{-8}$ cm/s can be calculated from the microscopy images using the progression of the diffusion lines. This value is slightly lower than the diffusion coefficients reported by Kaplan et al [21]. Due to the two-dimensional evaluation of a three-dimensional process, a more detailed evaluation is omitted in this study.

Stress cracking was observed for 827/137H specimens already after short times (≈ 100h/mm). After the formation of stress cracks, characteristic mechanical properties can no longer be determined. It is remarkable, that 827/Arg specimens show first stress cracks after ≈ 1800 h/mm. The stress cracks occur, when approximately the same weight gain of ≈ 15 wt.-% is observed. Due to the non-transparent appearance, no diffusion lines can be traced.

The change in geometry is shown in Figure 2 (b) for acetone via the change in cross-section of the free test length of the dogbones and is analogous to the change in mass (Figure 1 (b)). Accordingly, swelling of almost 25 % can be observed for the petrochemical reference system.

Swelling of this magnitude explains the formation of the stress cracks and the time delay in their formation in the test specimens cured with arginine.

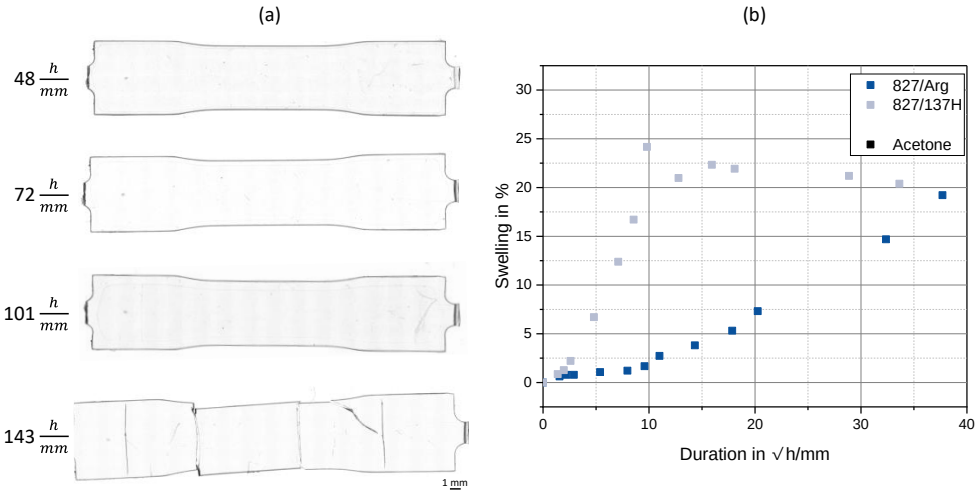


**Figure 2.** (a) Transmitted light microscopy images of an 827/137H specimen after immersion in acetone with formation of a diffusion front and stress cracks. (b) Swelling of 827/Arg and 827/137H with elapsed immersion time in acetone.

A comparison of the crosslinking density of both resin systems at $T_g$ + 40 °C shows that 827/137H ($\nu_C = (2.0303 \pm 0.0167) \cdot 10^{-3}$ mol $\cdot cm^{-3}$) has a higher network density compared to 827/Arg ($\nu_C = (1.0871 \pm 0.0067) \cdot 10^{-3}$ mol $\cdot cm^{-3}$). Contrary to the literature, which states that a higher network density leads to better chemical resistance, the results of this study show that 827/Arg has better resistance to e. g. acetone uptake. This may be due to the higher polarity of arginine as well as ionic components in the arginine molecule. Since ketones, like acetone, can form hydrogen bonds, it is conceivable that diffusion is initially inhibited and thus delayed by the formation of hydrogen bonds. The change in crosslink density with the absorption of different media is not analysed in this study, but is interesting as an explanation for this deviation.

*3.2 Impact on thermomechanical properties*

As observed in the literature, the absorption of water initially shows a reduction in strength due to plastification for both epoxides (Figure 3 (a)). The strength decreases linearly with an increase in the amount of water absorbed (Figure 3 (b)). In relative terms, a decrease of approx. 10 % per wt.-% absorbed water can be observed.

Subsequently, there is an increase in strength due to physical ageing without further water absorption. In 22 °C water, the DGEBA cured with arginine therefore shows no significant changes in long-term behaviour compared to the standard epoxy. Due to the slightly increased water absorption, the strength decreases to approx. 60 % of the initial value, but due to the higher initial strength this corresponds to the absolute value of the minimum observed in the reference system.

Starting from a slightly higher absolute level of tensile strength due to the lacking chain-extending reactive diluent component, the system 827/137H showed similar trends then

135/137H after selective immersion times in water due to the similar reaction mechanisms and is, therefore, not tested for the entire range of immersion times.

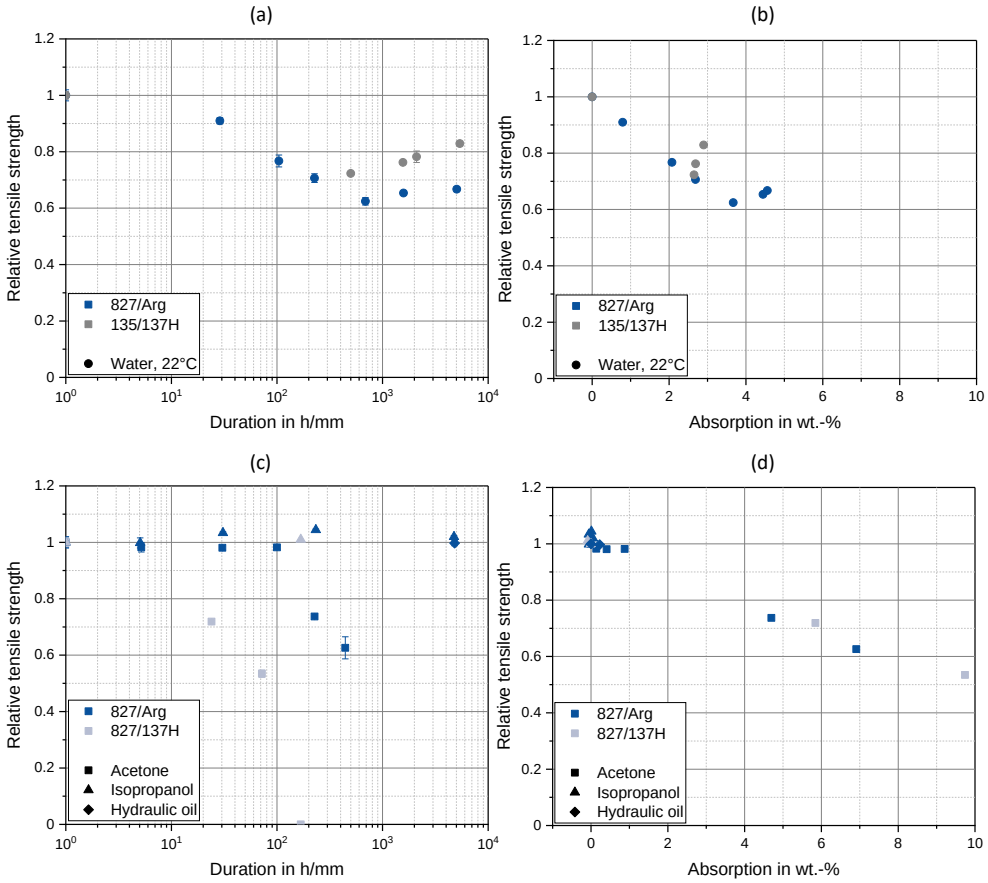


**Figure 3.** Changes in relative tensile strength with (a) immersion time and (b) absorbed mass in water resp. (c)-(d) in acetone, isopropanol and hydraulic oil. Error bars are not displayed in (b) and (d) for readability reasons.

The immersion in the tested chemicals (Figure 3 (c)-(d)) also shows a linear behaviour of the decrease in strength with the amount absorbed and thus the delayed decrease for the amino acid-cured epoxy. Due to the stress cracks that occur in acetone, no subsequent increase in strength can be observed. A small part of the loss in strength can be explained by the swelling and the increase in the effective cross-section of the test specimens, as the strength decreases with the same force. With isopropanol, increased strength can be observed. Hydraulic oil does not have a significant absorption behaviour and does not lead to any changes in strength.

At full saturation, $T_g$ decreases for both systems to approximately 70 % of the respective initial value. The data set indicates that the reduction in $T_g$ correlates linearly with the amount of water absorbed and falls by 8.9 K for 827/Arg and by 9.7 K for 135/137H per percentage of absorbed mass. Absorption of the same amount of acetone has less influence than the absorption of water (Figure 4). It is conceivable that acetone is predominantly present in the free volume

and less between the molecular chains of the polymers due to the larger molecules compared to water. Therefore, inter- and intramolecular forces are less influenced. For hydraulic oil and isopropanol, neglectable decreases of the $T_g$ were measured.

The thermomechanical properties indicate that arginine-cured epoxy resin has no disadvantages compared to standard epoxy regarding long-term exposure in the tested media. The delayed acetone absorption is favourable.

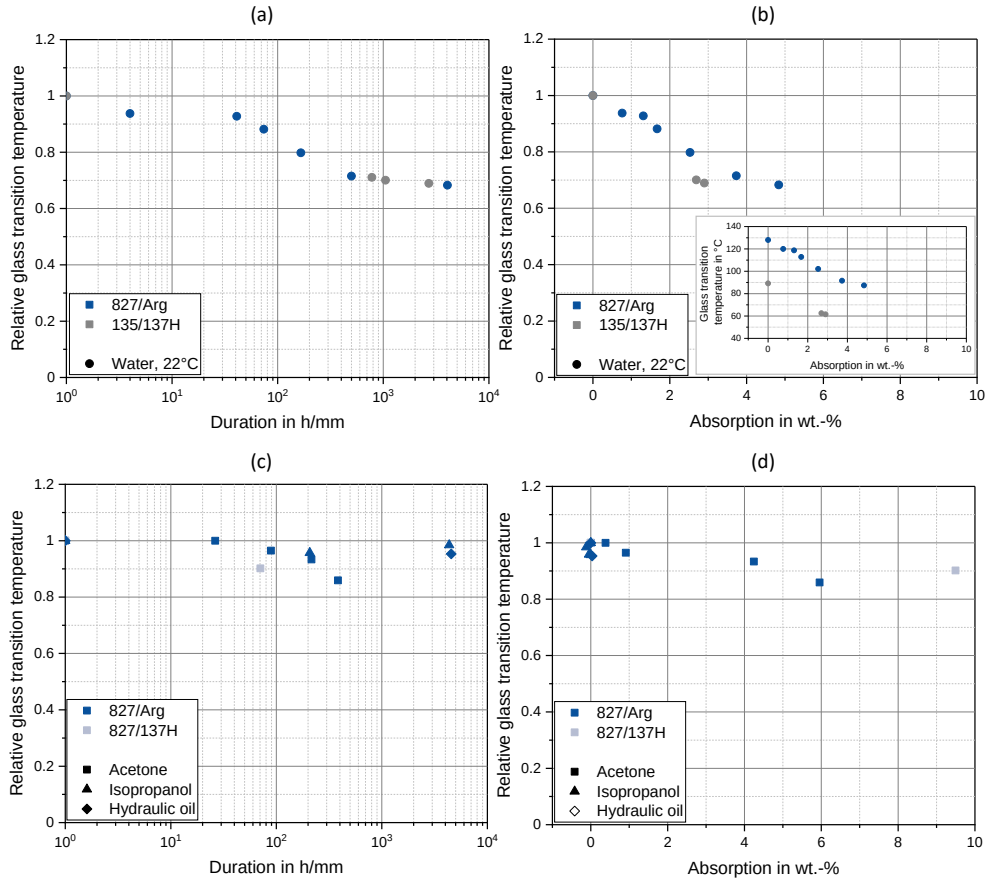


**Figure 4.** Changes in relative glass transition temperature with (a) immersion time and (b) absorbed mass in water resp. (c)-(d) in acetone, isopropanol and hydraulic oil. Absolute values are additionally shown in (b).

*3.3 Microscopic analysis of fracture surfaces*

Figure 5 shows SEM images of fracture surfaces of dry and acetone-immersed 827/Arg specimens after 100 h/mm and 450 h/mm immersion. After 100 h/mm the specimen absorbed less than 1 wt.-% resulting in no significant influences in the tensile strength and fracture surfaces compared to not-immersed specimens. In contrast, the specimen after 450 h/mm immersion with ≈ 7 wt.-% absorbed acetone and ≈ 60 % of the initial tensile strength indicating plastification.

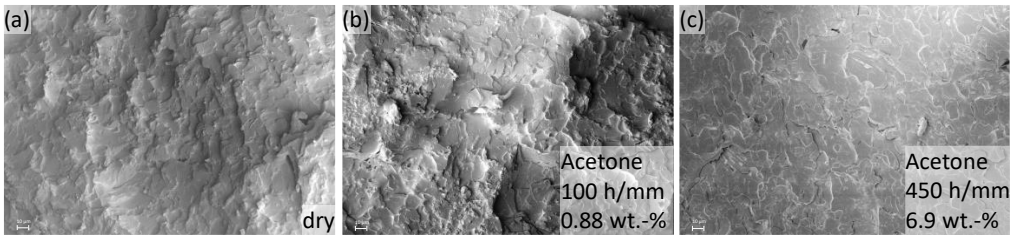


**Figure 5.** SEM pictures of fracture surfaces after tensile test of 827/Arg specimens (a) dry and after immersion in acetone (b) after 100 h/mm immersion (0.88 wt.-% mass increase) and (c) after 450 h/mm immersion (6.9 wt.-% mass increase).

*3.4 Analysis of chemical degradation*

To analyse, if immersion in the investigated media leads to chemical degradation, FTIR-measurements have been conducted. Figure 6 (a)-(b) displays, that there are no detectable (IR-active) changes in the recorded spectra for isopropanol and demineralised water, indicating no chemical degradation within the analysed time. Furthermore, the re-dried specimens show no mass loss compared to the initial dry condition. For re-dried specimens after 3000 h water immersion, 0.8 wt.-% of the nearly 5 wt.-% absorbed water remained, indicating type 2 bound water. Re-drying of 3700 h isopropanol immersed specimen at 40 °C under vacuum shows a reduction of 0.02 ± 0.02 wt.-% for 827/Arg resp. 0.16 ± 0.02 wt.-% for 827/137H of the initial mass, which supports the position that isopropanol removes soluble components.

In contrast, 8.01 ± 0.22 wt.-% of ≈ 26 wt.-% absorbed acetone for 827/Arg and 8.18 ± 0.12 wt.-% of ≈ 29 wt.-% for 827/137H remain after drying at 40 °C (vacuum). This also speaks for the formation of the mentioned hydrogen bonds, which, analogous to type 2 bonded water, require more energy to be broken. The swelling decreased on a similar scale. Subsequent drying at 100 °C under vacuum showed a further reduction in mass. However, a weight gain of 2.67 ± 0.29 wt.-% for 827/Arg resp. 3.04 ± 0.23 wt.-% for 827/137H remains compared to the initial mass. Therefore, no reliable statements can be made about actual degradation processes from re-dried weights.

Figure 6 (c)-(d) displays the FTIR-spectra related to acetone immersion. The additional FTIR-peak at ≈ 1738 $cm^{-1}$ in the acetone spectra after immersion (c) and the resp. specimens after immersion and re-drying (d) may be assigned to phenyl formate, which is likely to form via beta scissioning [32]. Krauklis et al. obtained spectra for hygrothermal aged epoxy indicating that there was no significant difference observed in the chemical structure of the initial and dried samples, except for the peak at 1736 $cm^{-1}$ [33], corresponding to carbonyl groups (νC=O) [34–36] which is part of phenyl formate. It can therefore be expected that chemical degradation occurs for both epoxy resin systems during long-term exposure to acetone. For the standard epoxy 827/137H, a slightly increased peak can already be seen for 820 h of immersion, which is in line with the faster absorption. The test specimens were dried briefly before the FTIR spectra were recorded, but acetone is still present in the test specimens, as indicated by the peak at 1710 $cm^{-1}$, although this has no influence on the peak at 1738 $cm^{-1}$.

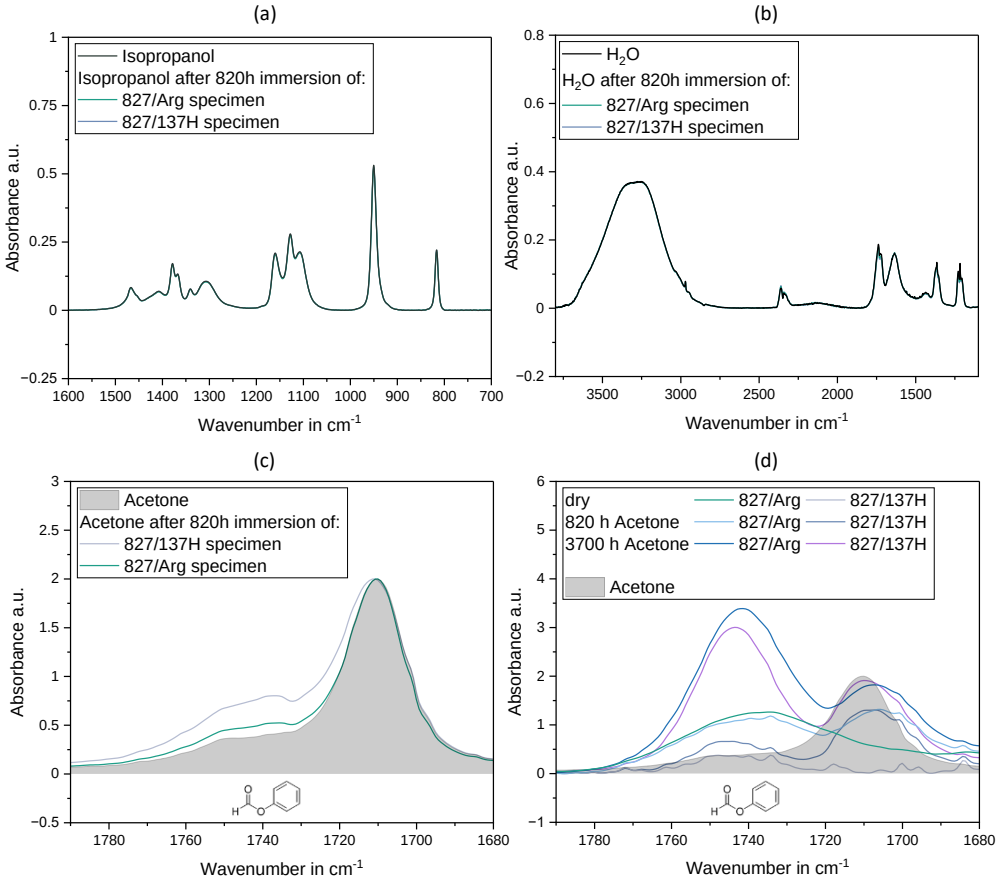


**Figure 6.** FTIR-spectra of (a) isopropanol, (b) water and (c) acetone without and after immersion of 827/Arg resp. 827/137H specimens, as well as (d) dry and immersed specimens after 820 h and 3700 h acetone immersion.

## 4. Conclusions

Under the investigated aspects, arginine-cured epoxy is not lacking in long-term use when exposed at 22 °C to water, isopropanol or hydraulic oil, which would reduce its value regarding sustainability. Additionally, the amino acid-cured epoxy shows advantages in short-term exposure to acetone, e. g. for cleaning purposes, compared to the reference. The most important findings of the study are summarised as follows:

- Water (22 °C) shows a decrease in strength for both systems due to plastification and an increase due to physical aging. Degradation is not detectable for both systems. 827/Arg shows a slightly higher water absorption but high thermomechanical properties.
- Isopropanol and hydraulic oil show no absorption or degradation and no significant deterioration of the thermomechanical properties in the observed time frame.
- The acetone resistance of the partially biobased system is better than that of the petrochemical reference system for short-term exposure despite a lower network density. Degradation is only indicated for both systems in acetone based on an emerging FTIR peak at 1738 $cm^{-1}$.

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**Author Contributions:** Conceptualization and methodology: M.W. and D.G.; investigation: M.W.; data curation: M.W.; visualization: M.W.; writing - original draft preparation: M.W.; writing - review and editing: D.G. and B.F.; supervision: B.F.; project administration: M.W. and B.F.; funding acquisition: B.F. - All authors have read and agreed to the published version of the manuscript.

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