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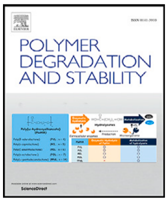

Lifetime prediction of thermo-oxidative degradation of a modified epoxy resin and its glass fiber composite in air atmosphere and correlation with long-term aging behavior

Martin Demleitner [a], Lukas Endner [a], Holger Ruckdäschel [a,b,*]

[a] Department of Polymer Engineering, University of Bayreuth, Universitätsstrasse 30, Bayreuth 95447, Germany
[b] Neue Materialien Bayreuth GmbH, Gottlieb-Keim-Straße 60, Bayreuth 95448 Bayreuth, Germany

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ABSTRACT

Thermal stability and material degradation are critical aspects of polymers and composites, influencing their processing, operating temperatures and overall lifespan. Due to their excellent mechanical and thermal properties, epoxy resins find widespread use in coatings, adhesives, and composites across various industries. This study examines the thermo-oxidative stability of high-Tg epoxy resin and glass fiber composite systems (GFRP), focusing on long-term degradation mechanisms in air atmosphere and kinetic modeling for accurate lifetime predictions. Here, the influence of commonly used additives such as polyethersulfone as toughener, and aluminum diethyl phosphinate (AlPi), as flame retardant on the thermo-oxidative degradation and resulting weight loss was investigated.

Model-free kinetic approaches were employed to characterize the thermo-oxidative degradation. In this study, model-free methods such as Flynn–Wall–Ozawa and Friedman are used because they offer flexibility and do not require detailed knowledge of the chemical reactions involved. Thermogravimetric analysis (TGA) was used for dynamic degradation measurements and weight loss predictions, while oven aging experiments in air atmosphere at three temperatures for up to 1000 h were conducted to verify the predictions.

The study highlights the challenges in extrapolating short-term degradation data to long-term behavior, especially under oxidative conditions. It also explores the influence of various additives and fiber reinforcement on thermo-oxidative stability, with the goal of enhancing future material formulations for high-performance applications. Additionally, it provides improved insight into the predictability of a material's lifespan.

1. Introduction

Thermal stability and thermal degradation of polymers and composites are crucial properties, as they determine the temperature range for processing, application, and overall service life. Due to the remarkable properties of thermosets and here especially epoxy resins, they are widely used as coatings, adhesives, insulation materials, and as composites in various industries. In several applications, it is necessary to extend the limits towards a longer service life and higher temperature resistance, such as molding compounds for power electronics or semiconductors [1,2], heatshields in aerospace or close-to-engine parts in the aviation industry [3,4]. However, the wide variety of available resins, hardeners, and additives makes rapid material development and reliable characterization for long-term operating conditions challenging. For example, to determine the Relative Temperature Index (RTI), aging periods of 5000 h, equivalent to nearly 7 months, are common in the automotive and electronics industries [5,6].

In this context, kinetics modeling and lifetime predictions based on a relatively small number of fast experiments are of great interest as they help reduce the number of potential formulations in the early stages of development [7].

The commonly used Arrhenius approach models degradation effects by describing the temperature dependence of reaction rates:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} f(\alpha) \tag{1}$$

where $(d\alpha/dt)$ is the reaction rate, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and $f(\alpha)$ is the reaction model which can be chosen to fit the data or a priori if reasonable information about the mechanism is known.

However, it assumes a one-step reaction, which is rarely the case for material degradation, where complex, multi-step processes occur in reality. This makes the extrapolation of short-term characterization

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* Corresponding author at: Department of Polymer Engineering, University of Bayreuth, Universitätsstrasse 30, Bayreuth 95447, Germany.
E-mail address: ruckdaeschel@uni-bayreuth.de (H. Ruckdäschel).

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to long-term behavior challenging due to different mechanisms over extended time spans. Non-linear behavior during thermal or thermo-oxidative aging arises from the complex interplay of various kinetic parameters and degradation mechanisms. For example, the rate of degradation may not remain constant over time due to chain scission, which reduces molecular weight, and diffusion-limited oxidation. These effects can either slow down or accelerate degradation during different aging phases. Both mechanisms often lead to embrittlement of the polymer matrix, which promotes microcrack initiation and propagation. This, in turn, can further accelerate chain degradation and create new pathways for oxygen, resulting in non-linear and non-uniform degradation characteristics. Therefore, accurate lifetime predictions require careful consideration of these time- and temperature-dependent phenomena and their limitations.

Extensions of the classic Arrhenius model, such as model-free and model-based kinetic approaches, have been developed to address these limitations. They rely on fitting experimental data from isothermal and dynamic degradation studies to enable more accurate lifetime predictions. Model-based kinetic modeling assumes specific reactions based on material composition and aging conditions, offering a deeper understanding at the molecular level. However, it proves challenging for complex systems such as cross-linked thermoset resins undergoing various degradation conditions [8]. Here, the chemically diverse structure based on resin and hardener with varying amount of heteroatom bonds and cross-linked structures makes it difficult to model the various possible pathways.

In contrast, model-free kinetic modeling, also known as isoconversional methods, does not make assumptions about the underlying reaction pathways. It assumes that the activation energy for degradation is solely a function of conversion α. In this context, conversion represents the extent to which the material has undergone chemical changes, such as oxidation (e.g., oxidation induction time measured by differential scanning calorimetry) or decomposition (e.g., weight loss measured by thermogravimetric analysis), at a given time or temperature. Model-free kinetic modeling includes integral methods like Ozawa–Flynn–Wall (OFW), Kissinger–Akahira–Sunose (KAS), and differential methods such as the Friedman method. For methods involving relative changes, such as dynamic TGA measurements, differential approaches offer increased sensitivity to data variations and enable more accurate results by measuring the difference between two signals or values. In the Friedman plot, the conversion rate for various heating rates is logarithmically plotted against the reciprocal value of absolute temperature. Straight lines are used to connect points of equal degree of conversion where the slope is equal to the activation energy.

To employ model-free kinetic methods, several preconditions must be met. These include: dependence of $E(\alpha)$ and A only on α, the reaction rate at the same conversion α being solely a function of temperature, change of mechanism occurring at the same conversion, and the total effect (equal mass loss or total peak) being the same for all curves.

The choice between model-free and model-based kinetic modeling depends on the study's specific goals, the nature of experimental data, and the level of understanding of underlying chemical processes. Model-free methods offer more flexibility and do not require detailed knowledge of the material system and its degradation behavior. For a more comprehensive overview of model-free and model-based kinetics, we refer to the available literature [9–11].

The literature offers various methods for estimating the lifetime of thermoset resins based on short-term measurements. However, these methods often involve measurements in inert atmospheres, such as nitrogen or argon, which fail to reflect the realistic degradation behavior occurring under standard environmental conditions involving oxygen [12].

Generally, the activation energies for degradation in air atmosphere are lower, up to 50%, at the onset of degradation, compared to nitrogen atmosphere, as shown in the literature for several epoxy resin systems [13–18]. This can be linked to the oxidative degradation via free radical chain reaction initiated by free radicals formed from peroxides which leads to faster degradation. Only few publications address measurements conducted under air atmosphere [19] or comparing inert and oxidative environments [20–22]. Most of these studies lack validation of their TGA-based lifetime predictions — derived from weight loss data — against long-term oven aging results. Only Blanco et al. made a comparison between short-term TGA based prediction and long-term oven experiments for some common thermoplastic polymer grades [19].

A lot of publications deal with the influence of different fillers on the thermal stability of resin systems, including organic fillers e.g. carbon black [23], fly ash [24] thermoplastics [25], elastomers [26] or inorganic filler (layered silica [27], silica [28], eggshell [29], metal oxides [30,31], zinc-based compounds [15]) and many more. However, again most studies are conducted under inert conditions, relying primarily on TGA measurements and neglecting long-term oven aging experiments, which are essential for gaining a more comprehensive understanding of the material's behavior.

One common additive type for epoxy resins are tougheners (e.g. core shell rubber, graphite [32], CNTs [33], elastomers, polyester [34] polyether sulfone powder, block copolymers [35,36]) to increase the fracture toughness of otherwise brittle thermosets. Here, similar to other filler influence investigations, thermal stability is mostly only measured via dynamic TGA measurements [37–46]. In general, depending on the nature, size, and concentration of the filler, the results can vary significantly, ranging from an increase to a decrease in the thermal stability of the filled material systems compared to the neat resin as summarized by Bikiaris [47].

The thermal stability of fiber-reinforced thermoset composites has been extensively investigated, particularly in relation to natural fibers [48–53], carbon fibers [54–58] or glass fibers [59–64]. However, the precise influence of fiber reinforcement, and the comparison between neat resin and fiber-reinforced composites on thermal stability and degradation mechanism, have been less explored, as many researchers often rely on off-the-shelf semi-finished products [53,57,61].

Thus, the aim of this study is to establish a lifetime prediction for rather complex polymer systems based on model-free reaction kinetics and to explore the influence of fillers and fiber reinforcement on the degradation mechanism. Finally, the accuracy of the generated lifetime predictions is validated through long-term oven aging data, providing a practical assessment of the model's predictions under realistic conditions in air atmosphere.

2. Material & methods

The multifunctional semi-solid novolac epoxy resin *Epiclon HP-7250* (DIC Corporation, Tokyo, Japan) with an epoxy equivalent weight (EEW) of 162 was used. The resin was already under investigation as a matrix for composite parts and extrusion-based additive manufacturing, with a focus on high-temperature applications [65,66]. As curing agent, micronized 4,4-diaminodiphenyl sulfone *Technicure K-10* provided by Acci Speciality Materials (Linden, NJ, USA) with a particle size of $D_{50} = 10$ µm was used. The amine hydrogen equivalent weight (AHEW) of the curing agent was 62.

As toughener, polyethersulfone (PES) powder *Sumikaexcel 5003P* (Sumitomo Chemical Europe NV, Machelen, Belgium) with a molecular weight (M_w) of 42,000 g/mol and with an average particle size of $D_{50} = 45$ µm was used. This material is a well-established toughener in high-performance prepregs for aviation applications [67]. As flame retardant, aluminum diethyl phosphinate (AlPi) *Exolit OP935* (Clariant AG, Muttenz, Switzerland) with an average particle size of $D_{50} = 10$ µm was used. With a high phosphorus content of 23%, good flame-retardant properties can be achieved even at low filler loading. In combination with its small particle size, the flame retardant is well-suited for composite applications and has been, among

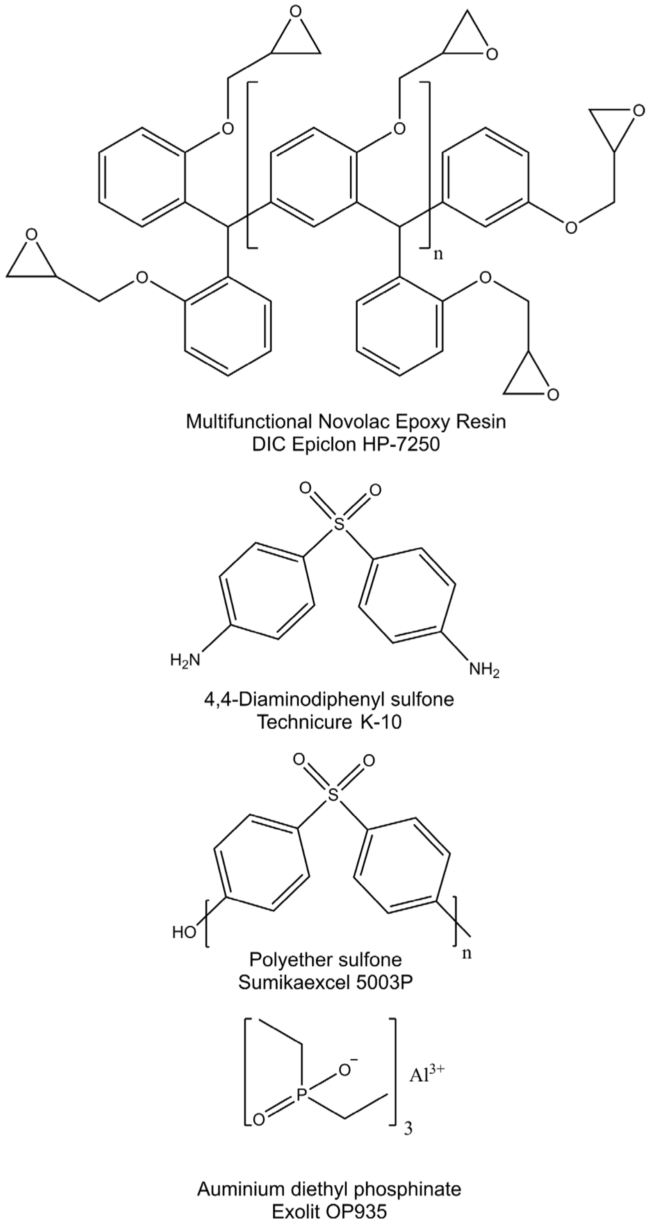


Fig. 1. Chemical structure of the components used in this study to formulate the resin systems.

other applications, successfully used in printed circuit board substrate manufacturing [68,69].

Fig. 1 shows the chemical structure of the resin system and additives.

The resin, curing agent and additives were homogenized at 120 °C for 20 min using a vacuum dissolver VMA Getzmann Dispermat (Reichshof, Germany). The mixture was poured into preheated vertical moulds at 120 °C. The curing cycle was performed in a convection oven *Memmert ULE 400*. It consisted of the following steps: 1 h at 120 °C, 3 h at 180 °C and an additional post-curing step for 2 h at 250 °C all with heating rates of 3 K/min. The cooling to room temperature took additional 8 h at a cooling rate of 1 K/min. The curing cycle was designed and monitored using DSC measurements of the cured samples. Since no residual enthalpy was detected up to 350 °C, the samples with 4 mm thickness were considered fully cured. Due to the high aromaticity and functionality of epoxy resin and curing agent a glass transition temperature (T_g) up to 325 °C can be achieved. T_g of the resin systems measured via dynamical mechanical analysis are shown in the supporting information (S1).

For the manufacturing of the glass fiber-reinforced composites (GFRP), the prepreg route was used. Herefore the resin was mixed with the curing agent and the additives and homogenized accordingly. With the hotmelt prepreg impregnation unit *EHA Composite Machinery* the aero-grade fiberglass weave 8HS fabric *7781* (Porcher Industries Germany GmbH, Erbach, Germany) with an aeral weight of 296 g/m^2 was impregnated. The prepregs were subsequently cut, and eight plies were stacked in a [0/45/-45/90]s layup, resulting in a laminate thickness of 2 mm. Curing was performed under autoclave conditions at 6 bar, following the same curing cycle used for the neat resin samples. A fiber volume content of 50 vol.-% was determined using density measurements and thermogravimetric analysis (TGA), heating the samples in air up to 800 °C to fully pyrolyze the resin, leaving only the glass fibers.

Thermogravimetric analysis

The input data for the lifetime predictions were obtained through dynamic TGA measurements. The measurements were carried out with the *TG209 F1 Libra* by *NETZSCH-Gerätebau GmbH*. All samples were tested in synthetic air atmosphere at three different heating rates β of 1, 5 and 10 K/min up to 900 °C in accordance with ICTAC recommendations [70]. Comparatively slow heating rates were used to allow the samples to reach a homogeneous state more easily. Each measurement was carried out three times to check for reproducibility.

Samples were prepared using CNC milling or a table saw, with a focus on achieving the same or very similar surface-to-volume ratios for the neat resin (SVR: 1.74) and composite (SVR: 1.87). The slight difference can be explained by variations in thickness and maximum sample size due to TGA crucible geometry. SVR was preferred over weight, as it was considered more suitable for the aging experiments in an air atmosphere, where oxygen diffusion and subsequent oxidation are surface-dominated processes. The impact on the thermal or thermo-oxidative degradation of different SVR was shown in various publications [71,72]. Fig. 2 shows the geometry of the specimen used for the TGA measurements and oven aging experiments.

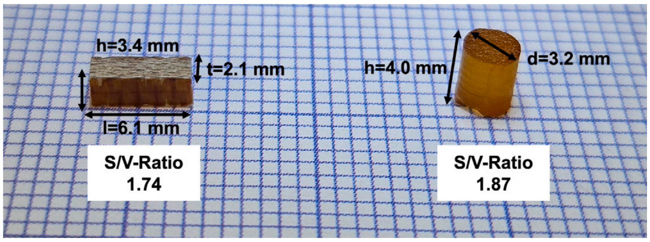


Fig. 2. Specimen geometry for TGA measurements and oven aging experiments.

Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) measurements were carried out at a heating rate of 3 K/min in torsional mode at an elastic deformation of 0.1% and an applied frequency of 1 Hz using a Rheometrics Scientific ARES RDA III rheometer (Germany). The specimens had a rectangular shape with 50 × 10 × 2 mm3 according to standard ISO 6721-7. The glass transition temperature was evaluated at the maximum of loss factor tan (δ)curve.

Oven aging experiments

The same samples used in the TGA measurements were also employed for the long-term oven aging experiments. Oven aging was carried out in standard convection ovens (Memmert UF500) at three different temperatures (175 °C, 200 °C, 225 °C). Samples were taken after 125 h, 250 h, 500 h, 1000 h and the weight loss was recorded. For each data point, three samples were used, resulting in a total of 216 samples for oven aging.

Kinetic modeling

The software *Kinetics Neo* provided by NETZSCH Gerätebau GmbH (Selb, Germany) was used for kinetic modeling. Kinetic analysis in Kinetics Neo software is based on ICTAC Recommendations for multi-step kinetics [73]. In this study, the methods ASTM E1641 based on the Ozawa–Flynn–Wall-method for 5% weight loss, and the numerical method based on Friedmann were employed.

3. Results and discussion

Thermal analysis-short-term degradation behavior

Fig. 3 presents the thermograms of the single components used in the resin formulations. Although direct comparison is not feasible due to the thermal cure process enhancing the thermal stability of the resin and hardener, the figure illustrates the complex degradation behavior of each individual component. Significant differences are observed in the onset of thermal degradation, the degradation steps, and the residual mass.

For instance, 4,4’-DDS begins to decompose in air at 326 °C (Td5), likely due to the scission of the C-S bond. This bond has a relatively low bond strength of 272 kJ/mol, in contrast to C–C bonds, which have a strength of 346 kJ/mol, and C-O bonds, with a strength of 358 kJ/mol [74,75]. At 348 °C, 50% of the weight is retained, likely due to the presence of aromatic components, which continue to decompose gradually until 700 °C. A competing reaction involving the volatilization of certain parts of 4,4’-DDS must be considered, alongside a complex degradation pattern in air atmosphere involving oxidation.

In contrast, polyether sulfone (Toughener 5003P), which is chemically similar to 4,4’-DDS and contains a sulfone group bridging two phenyl rings, exhibits significantly higher thermal stability. It shows a Td5 of 500 °C, which is approximately 255 K higher, and a Td50 of 580 °C, which is about 230 K higher than DDS. This increased stability can be attributed firstly to the more stable ether groups replacing the amine groups, and secondly to its higher molecular weight of roughly 42,000 g/mol. The higher molecular weight enhances the resonance stabilization of the connected aromatic groups. This allows the material to withstand higher temperatures before fragments form and evolve into the gas phase [76–78].

Degradation of the flame retardant AlPi takes place in two steps, which proceed rapidly between 370 and 430 °C, in line of the findings of Duquesne [79]. AlPi decomposes by forming diethylphosphinic acid, which is released into the gas phase, and aluminum phosphate, which remains in the condensed phase. The decomposition product $AlPO_4$ remains with a significant residue of 40 wt%.

The uncured multifunctional Epoxy Novolac resin exhibits an initial weight loss at 290 °C (Td5). This phenomenon can be attributed to thermally induced ether cleavage and oxygen-induced β-scission at the CH_2 group adjacent to the phenyl ether group, which is particularly susceptible to oxygen attack in the uncured resin. Stabilization during heating might arise due to homopolymerization which could explain the broad decomposition range observed between 220 °C and 600 °C, as reported in the literature [80].

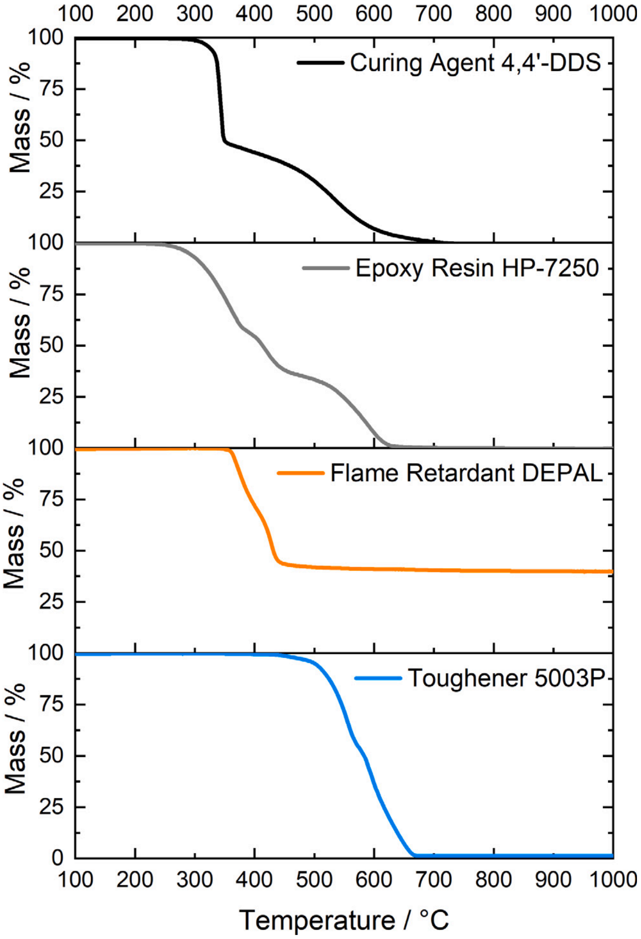


Fig. 3. Thermograms based on TGA measurements with 10 K/min of the used educts at air.

Fig. 4 shows the weight loss and conversion based on TGA curves obtained for the investigated fully cured formulations. For the resin systems in air atmosphere (left), a two-step degradation process takes place. This can be linked to first initial charring between 400 to 550 °C with subsequent total degradation. It can be seen, that the initial decomposition for all systems is very similar however at higher temperatures starting from 400 °C a stronger deviation occurs. Here, the toughened and especially the flame-retardant systems shows higher residue. This can be explained with the degradation of the flame retardant diethyl aluminum phosphinate AlPi to $AlPO_4$ as explained earlier. For the 10% AlPi-formulated resin systems therefore an residue of 4% is expected. However, a char yield of 6.3% is measured indicating synergistic effects between the AlPi and the resin system, which increase the char yield.

For the GFRP composite systems (right), similar trends are visible leading to a residue between 70% for the neat and 73% for the flame-retardant system. In literature, many publications compare the degradation stability of resin and composite systems using absolute weight loss, whereas relative weight loss values, based on the volatile organic content, are more appropriate. Therefore the conversion based on relative weight loss (Tc5, Tc50) is shown taking into account the glass fiber content focusing only on the degradation of the organic content.

The temperatures for absolute weight loss of 5% (Td5) and 50% (Td50), and relative 5% and 50% weight loss based on the volatile content (Tc5 and Tc50) and remaining char at 900 °C are shown in Table 1. Based on the volatile content, it can be shown, that the glass-fiber reinforced composites show significantly lower Tc5 values compared to the resin systems. The sizing of the glass fibers was not

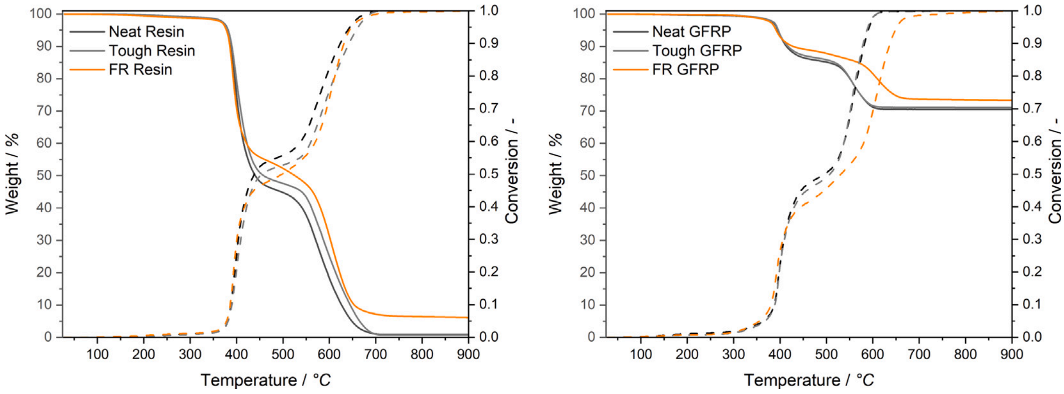


Fig. 4. TGA curves of resin systems (left) and glass fiber-reinforced composite systems (right) in air for 10 K/min heating rate. Weight loss is depicted as solid line and corresponding conversion as dashed line.

Table 1
Overview of thermal stability values at 10 K/min heating rate.

System	Td5 °C	Td50 °C	Tc5 °C	Tc50 °C	Char Yield % (900 °C)
Neat Resin	382	440	382	440	0.9
Tough Resin	382	456	382	456	0.7
FR Resin	379	532	378	515	6.2
Neat GFRP	395	/	364	495	70.5
Tough GFRP	396	/	368	507	71.1
FR GFRP	392	/	356	533	73.3

considered to be influential on the weight loss as the weight is normally around 0.5% or less on glass fibers, and therefore for the composite below 0.3% [81]. However, the degradation of the sizing — and the resulting deterioration of the fiber–matrix interface — may enhance both oxygen ingress and the outflow of volatile degradation products through capillary effects. As a result, the presence of glass fibers can accelerate the thermal degradation of the resin.

Tc50 values for the composites are roughly 50 K higher compared to the neat and toughened resin systems. This can be explained with better charring and reduced volatilization of the remaining resin after faster initial degradation leading to higher char yield and Tc50 values. For the FR GFRP system, the increase is only 17 K compared to the FR Resin system. The lower increase, in comparison to the neat resin, can be linked to the lower absolute amount of the flame-retardant in the composite system, which has hence a less pronounced impact on thermal stability.

Kinetic analysis

As seen in the supplementary information (S2), the systems show in nitrogen atmosphere in dependence of the heating rate different char residue due to better stabilization with slower heating rates. In contrast, the systems exhibit the same degradation behavior and char residue in air atmosphere, regardless of the heating rate, making them suitable for model-free kinetic analysis.

For a first estimate of the activation energy, the standard ASTM E1641-13 based on the Ozawa–Flynn–Wall (OFW) was used. Using the Doyle approximation, which simplifies the calculation of the temperature integral, Eq. (2) gives for each (α) the activation energy plotting $\ln(\beta)$ against 1/T:

$$\ln \beta = 5.3305 + \ln\left(\frac{A(\alpha)}{F(\alpha)}\right) - 1.052 \cdot \frac{E(\alpha)}{R} \cdot \frac{1}{T} \tag{2}$$

where β is the heating rate (K/min), $F(\alpha)$ represents the accumulated reaction progress up to conversion α, R is the universal gas constant and T is the temperature at which the conversion (α) is reached for that heating rate.

The conversion or rather weight loss of 5% is often used as a common failure criterion in industry. Although this method assumes first-order kinetics, which can lead to substantial errors in lifetime estimations, it can still provide a rough estimation of the material’s thermal stability.

One of the most used methods for thermal degradation kinetics is the Friedmann method, a differential model-free method. An optimized method based on the Friedman method is called “Numerical optimization” implemented in the NETZSCH Kinetics Neo software. It searches optimal functions E(α) and log(A(α)) in order to get the best fit for the conversion as a function of temperature and time. The results of Friedman method are then optimized numerically in order to achieve the better fit between experimental and simulated curves (see Eq. (3)):

$$\Psi = \sum_{\text{curves}} \sum_{\text{points}} \left(\alpha_i^{\text{calc}} - \alpha_i^{\text{exp}}\right)^2 \tag{3}$$

This method shows in general better results compared to the standard Friedman method for various kinetic research questions [82–84].

Table 2 shows the activation energies for the different systems based on ASTM E1641 and the Numerical Optimization Friedman are shown. For the neat resin system 169 kJ/mol based on ASTM E1641 and 221 kJ/mol for the Numerical Optimization of Friedman are obtained. Compared to literature values for the activation energy of various polymer systems (measured using ASTM E1641 at 5% weight loss), the value of 169 kJ/mol indicates good thermo-oxidative stability. For standard DGEBA epoxy resin-based systems, values between 105 and 120 kJ/mol are reported in air atmosphere [17,85]. For naphthalene-based epoxy systems, values between 178 and 196 kJ/mol are found [16], while for polyimide systems, around 155 kJ/mol are measured [86,87]. Higher values in air are reported for high-performance resins, such as poly(m-phenylene isophthalamide) or BMI resins, with approximately 200 kJ/mol [88,89].

In the ASTM E1641 method (OFW-based), the filler increases the activation energy for both resin and composite systems. In contrast, numerical optimization using the Friedman method shows a decrease in activation energy with filler addition. This difference arises from the nature of the methods: OFW is an integral approach using heating rate, while Friedman is a differential method based on the reaction rate. The Friedman method better captures the influence of glass fibers as inert fillers, which nonetheless promote degradation by lowering the Tc5 value.

Table 2 further shows that, in both kinetic models, the activation energy for 5% weight loss decreases with fiber reinforcement. This reduction indicates lower thermal stability, as discussed in detail in the previous chapter. There are few publications that directly examine how fiber reinforcement influences the activation energy for decomposition in air, based on comparisons between neat and reinforced systems. Chen et al. investigated neat epoxy resin and its carbon fiber-reinforced composite, showing that, especially in the later stages of

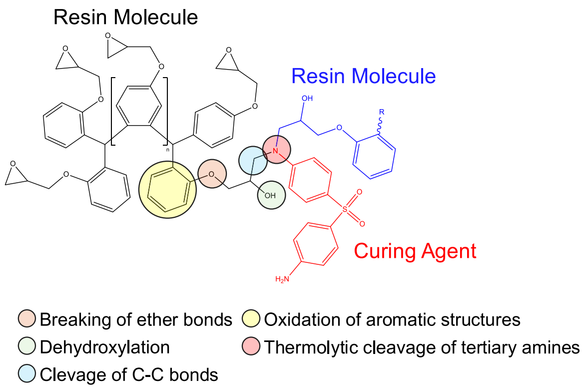


Fig. 5. Schematic overview of possible degradation mechanism of the cured epoxy resin used in this study.

Table 2
Activation Energies of the systems with different kinetic models.

System	ASTM E1641		Numerical optimization Friedman	
	E_a kJ/mol	R^2	E_a kJ/mol[a]	R^2
Neat Resin	169	0.93	221	0.99
Tough Resin	183	0.89	213	0.99
FR Resin	179	0.89	201	0.97
Neat GFRP	155	0.92	175	0.98
Tough GFRP	159	0.92	177	0.99
FR GFRP	160	0.90	135	0.97

[a] E_a for 5% weight loss.

degradation, the composite system exhibited lower activation energies and, consequently, lower thermo-oxidative stability [17].

Overall, the NETZSCH numerical optimization method provided a better fit to the TGA data (R^2) and captured variations in activation energy throughout the entire degradation process. In contrast, ASTM E1641 yields only a single activation energy value, limiting its ability to reflect such changes. Furthermore, the systems under investigation, based on epoxy resin, curing agents, additives such as tougheners and flame retardants, and combined with glass fibers as reinforcement, makes model-based fitting and prediction challenging.

For the cured epoxy resin and the resulting network alone, a high variety of degradation mechanisms can occur leading to the weight loss observed in the TGA signal respectively during oven aging. Fig. 5 schematically illustrates a single hardener molecule cured with two epoxy groups originating from two different resin molecules. Taking the resin backbone into account, more than five distinct reaction mechanisms are possible—this number increases to over ten when the presence of oxygen is considered. The formation of radicals during degradation further adds to the complexity, as it leads to time-dependent radical oxidation processes that accelerate over time and are limited by diffusion.

Furthermore, as shown in the literature, model-based predictions are prone to overfitting and can lead to misleading results, especially in the case of complex material systems and when there is no knowledge of competing, temperature-dependent reaction pathways [90,91]. Janković et al. investigated the thermo-oxidative degradation of wolfberry pulp using model-free methods (Friedman, OFW, KAS, and numerical optimization) as well as a complex six-step model-based approach. Ultimately, the highest accuracy in determining the kinetic parameters and the reaction mechanism was achieved using numerical optimization. Therefore, the numerical optimization method was selected for further lifetime predictions.

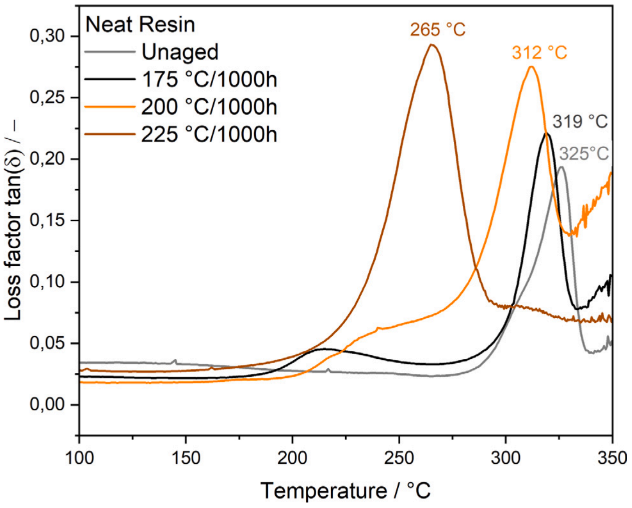


Fig. 6. Influence of different aging conditions varying aging temperature after 1000 h on T_g.

Oven aging

The long-term degradation of resin and composite systems was studied for up to 1000 h in air atmosphere at temperatures ranging from 175 to 225 °C. The results are shown in Fig. 6. For the resin systems at 175 °C and 200 °C, an initial rapid degradation phase was observed during the first 250 h. This then stabilized, reaching approximately 2% weight loss at 175 °C and 3% at 200 °C by 1000 h. This suggests that the intrinsic thermo-oxidative stability of the system is sufficient to prevent significant further degradation well below the commonly considered threshold of 5% weight loss. Additionally, the formation of an oxidative layer appears to protect the interior material from ongoing degradation.

At 225 °C, however the weight loss continued steadily up to 1000 h, reaching values of 6 to 7%. The 25 K increase in temperature resulted in significantly higher thermo-oxidative degradation of the resin system. This network degradation of the resin is visible in Fig. 6, which shows the loss factor obtained by DMA measurements after 1000 h at three different temperatures, exemplarily for the neat resin. After 1000 h at 175 °C and 200 °C, only a slight decrease in T_g of 6 K (a reduction of 1.8%) and 13 K (a reduction of 4%), respectively, can be observed. Furthermore, a shoulder develops around 220 °C for the aging temperature of 175 °C, and in the range of 225–275 °C for the aging temperature of 200 °C, indicating initial deterioration of the resin network. At 225 °C, however, a drastic drop of 90 °C in T_g (a reduction of 18.5%) is observed. This aligns with the high weight loss at 225 °C, as such significant network degradation leads to a higher amount of volatile compounds being released.

Within the systems, the flame-retardant (FR) resin exhibited continously approximately 10% less weight loss compared to the neat resin, which aligns closely with the 10% FR content. Here, the flame retardant can be considered unaffected by degradation processes at temperatures well below 350 °C, where the first initial weight loss was detected in dynamic TGA measurements. Besides the higher thermal stability of the filler in comparison with the matrix, the lower weight loss can be furthermore attributed to the decrease of the oxygen diffusion by adding particles as described for several filled polymer systems [92–95]. The filler extend the pathways for oxygen and volatiles created by the thermo-oxidative degradation of the resin. Although this behavior is more pronounced the higher the aspect ratio e.g. with platelet-shaped filler, it can be considered contributing to the higher thermal stability and lower weight loss of the filled systems.

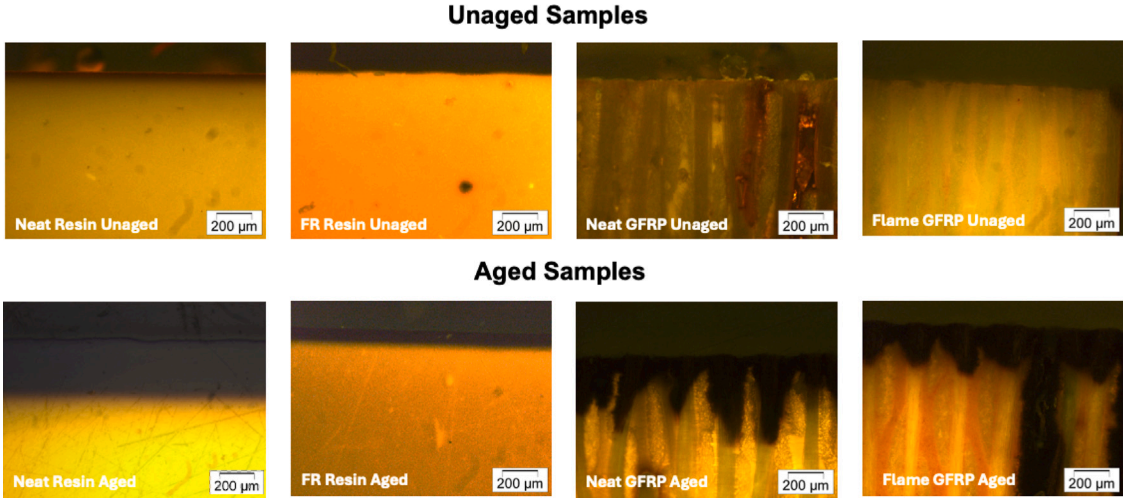


Fig. 7. Fluorescence microscopy images of the TGA samples of the neat and FR resin systems and its composites before and after aging for 1000 h at 225 °C.

The GFRP composite systems exhibited similar behavior in comparison to the resin systems, with approximately 1% weight loss at 175 °C and 2% at 200 °C oven temperature. At 225 °C, a weight loss between 4% and 5.5% was observed. The overall weight loss was lower compared to the resin systems. However, considering the 70 wt% glass fibers, the resin experienced relatively higher degradation in the composite systems. This can be attributed to the fiber reinforcement, where the fiber–matrix interfaces act as pathways for oxygen, allowing it to penetrate deeper into the composites and resulting in a higher proportion of oxidized material.

The strong influence of the fiber on the degradation process is visible in Fig. 7. Here, fluorescence microscopy images of unaged and aged samples of the neat and FR resin and its GFRP systems are shown as examples. It seems that the flame retardant particles slow the oxygen diffusion leading to a lower oxidation thickness (ca. 100 μ m vs. 200μ m) as described above. For the fiber-reinforced composites, an oxidation layer thickness up to 400μ m is visible perpendicular to the fiber reinforcement. Here again the flame-retardant system shows in general a thinner oxidation layer.

Again the neat GFRP (glass fiber-reinforced polymer) without filler showed the highest weight loss compared to the Tough GFRP and FR GFRP systems. At higher temperatures, the positive effect of the filler became more pronounced, particularly in the composite systems. In the resin systems, the filler reduced weight loss by approximately 10% to 12%, corresponding to the filler content of 10 wt%. In contrast, the filled composite systems exhibited a significantly reduced weight loss of 25% to 30%. This suggests that the filler might extend the oxygen diffusion pathways, thereby reducing the amount of oxidized material and thus having a greater impact on the thermal stability of the composite systems compared to the resin systems.

In Fig. 8, the macroscopic-level findings are depicted, illustrating the differences between the various systems and showing the influence of filler and glass fiber reinforcement at 175, 200, and 225 °C on oxygen diffusion, volatile outflow, capillary effects at the fiber–matrix interface, and oxidized layer thickness.

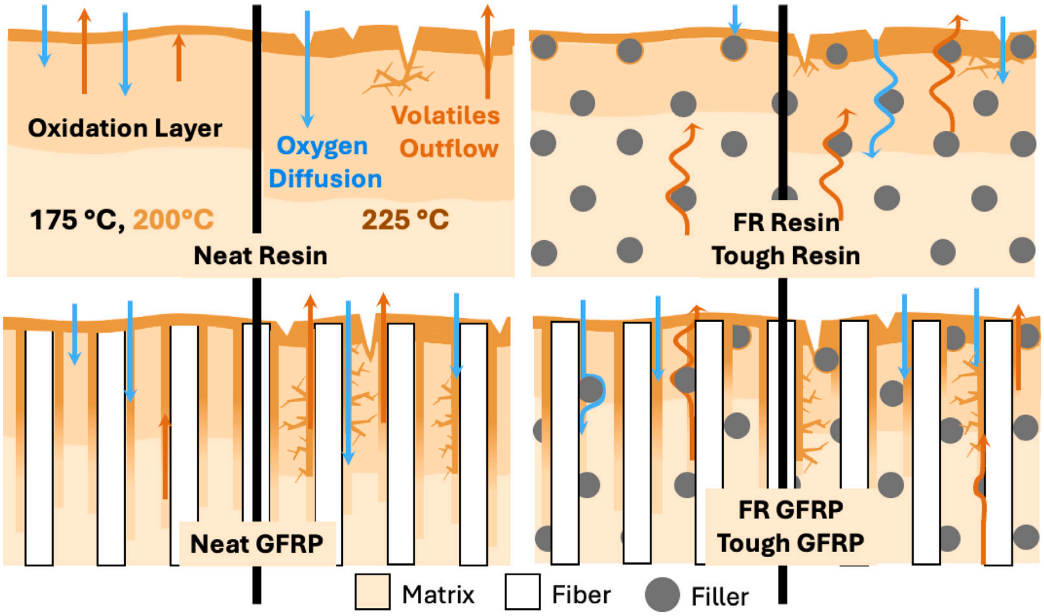


Fig. 8. Schematic representation of possible macroscopic behavior during aging of the investigated systems.

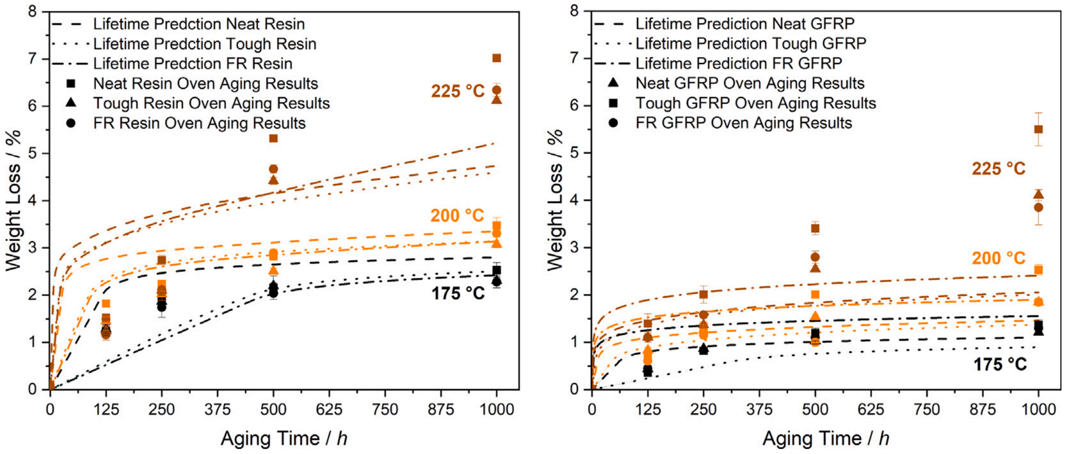


Fig. 9. Weight loss prediction (Numerical Optimization) based on resin system (left) and glass fiber-reinforced composite (right) in air with measured oven aging results.

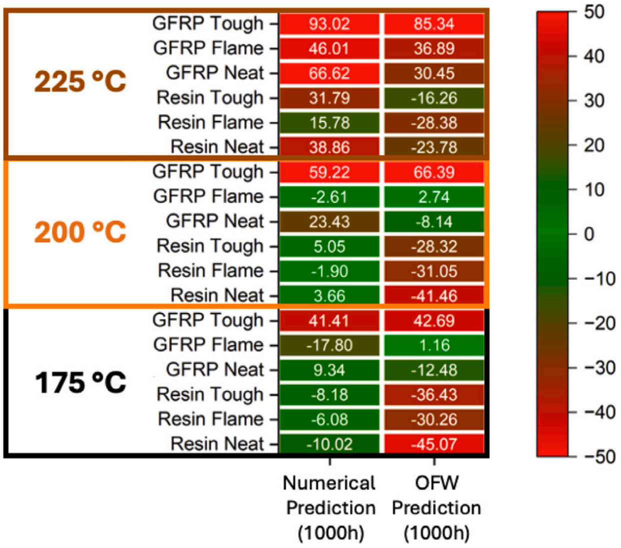
Lifetime prediction

The kinetic model “NETZSCH Numerical optimization based on Friedman”, deemed most suitable in chapter “Kinetic Analysis” with the best fit to the TGA data, was compared and verified with real oven aging data. Fig. 9 (left) shows the predicted weight loss based on this model for the resin and glass-fiber reinforced systems together with the experimentally observed long-term weight loss determined by oven aging results. For the resin systems (left), some deviation in the beginning is visible for the temperatures of 175 and 200 °C, whereas the predicted weight loss after 1000 h is in good alignment with the experimentally verified values.

These early deviations likely arise from initial differences between the dynamic conditions in TGA and the isothermal conditions in oven aging. TGA-based models are typically derived from high heating rates and short exposure times, which may not fully capture early-stage diffusion effects or protective oxidized layer formation present in long-term isothermal oven aging. Over time, as the system approaches a more stable degradation regime, these differences diminish, leading to better agreement between model predictions and experimental data at 1000 h. For 225 °C, the prediction underestimates the weight loss after 1000 h with roughly 2%. It seems, that for the 225 °C different degradation mechanisms are already at play which cannot be fully covered by the prediction based on dynamic TGA measurements. At 225 °C, at least 25 K higher than the other aging temperatures, the reaction rates are roughly two to three times higher, leading to increased oxidation and embrittlement over time, which can result in strong increase in microcracks. These microcracks further facilitate oxygen penetration, creating a self-accelerating decomposition process. These predominantly long-term effects cannot be fully linked to TGA-based weight loss predictions.

Similar results are observed for the composite systems (Fig. 9, right), with a good match between the predicted and experimental values for 175 °C and 200 °C and rather high deviation at 225 °C. In addition to the different aging mechanisms occurring at 225 °C, this might also be linked to the time-dependent oxygen diffusion and subsequent oxidation of the material due to fiber reinforcement. This cannot be fully captured by dynamic TGA experiments, which have a measurement time ranging from one to fifteen hours, leading possibly to a higher deviation for 225 °C isothermal long-term oven aging for the composite systems compared to the resin systems.

Furthermore, as shown earlier, the variety of degradation mechanisms and reaction pathways is another factor to be considered when explaining the discrepancies between predicted and experimental data. Nevertheless, the results demonstrate that the simplified approach of determining kinetic triplet values using the isoconversional differential method yields robust predictions. This method provides average values for the kinetic triplet, and the precision of these long-term predictions suggests that simulations based on these mean values — despite inherent limitations — can reliably represent the combined chemical degradation processes.



		Numerical Prediction (1000h)	OFW Prediction (1000h)
225 °C	GFRP Tough	93.02	85.34
	GFRP Flame	46.01	36.89
	GFRP Neat	66.62	30.45
	Resin Tough	31.79	-16.26
	Resin Flame	15.78	-28.38
	Resin Neat	38.86	-23.78
200 °C	GFRP Tough	59.22	66.39
	GFRP Flame	-2.61	2.74
	GFRP Neat	23.43	-8.14
	Resin Tough	5.05	-28.32
	Resin Flame	-1.90	-31.05
	Resin Neat	3.66	-41.46
175 °C	GFRP Tough	41.41	42.69
	GFRP Flame	-17.80	1.16
	GFRP Neat	9.34	-12.48
	Resin Tough	-8.18	-36.43
	Resin Flame	-6.08	-30.26
	Resin Neat	-10.02	-45.07

Fig. 10. Heatmap of the relative deviation of Numerical Prediction and the OFW method compared to oven-aging weight loss.

For comparison, the lifetime prediction based on the OFW method (ASTM E1641) was also compared with the oven-aging results and is shown in the Supporting Information (S3). An overprediction of the weight loss is evident, which can be explained, as detailed in the section “Kinetic Analysis”, by the method itself and by the lower activation energies determined for thermo-oxidative degradation.

Fig. 10 summarizes the results of both methods in a heatmap plot of the weight-loss predictions. The relative deviations from the oven-aging results after 1000 h are shown for all systems. Numerical Prediction generally provided better agreement at 175 °C and 200 °C. In particular, for the resin system a maximum deviation of only 10% was observed, whereas the GFRP systems exhibited higher deviations. The OFW prediction captured the GFRP system weight loss within a similar error range but performed poorly for the resin systems.

4. Conclusion & outlook

Thermal stability and degradation are crucial for the safe performance and durability of polymeric materials, particularly in industries like semiconductor packaging and aerospace. This study highlights the importance of accurate lifetime predictions for thermoset resins, such as epoxy systems, which are widely used in these demanding applications. The specific influence of commonly used tougheners, flame retardants, and glass fibers on thermo-oxidative stability was determined in detail for the first time, providing new insights into tailoring novel resin and composite systems.

The organo-aluminum-based flame retardant DEPAL was found to enhance the thermal stability of resin and composite systems, whereas fiber reinforcement significantly reduced the thermal stability of composite systems by creating pathways for oxygen diffusion.

As a fast and straightforward approach, model-free methods were explored to predict the weight loss of the investigated systems in a thermo-oxidative atmosphere. These methods allow reliable long-term property predictions without requiring in-depth knowledge of the system. Among them, the numerical optimization method based on the Friedman model showed the best fit quality and was selected for lifetime prediction. Validation with long-term oven experiments revealed a good match for temperatures up to 200 °C, despite the complexity of the material system and aging environment. However, at 225 °C, changes in degradation mechanisms led to aging behavior not fully captured by the chosen kinetic model.

Future work could explore model-based methods to gain deeper insights into specific degradation pathways, including activation energies of individual components. Additionally, fibers with different sizing should be investigated to evaluate the influence of fiber–matrix bonding on both mechanical and thermal properties in short- and long-term scenarios.

CRediT authorship contribution statement

Martin Demleitner: Writing – original draft, Investigation, Formal analysis, Conceptualization. **Lukas Endner:** Writing – review & editing, Investigation, Formal analysis. **Holger Ruckdäschel:** Writing – review & editing, Validation, Project administration, Funding acquisition.

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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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.polymdegradstab.2025.111686.

Data availability

Data will be made available on request.

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