EFFECTS OF THE HYGROTHERMAL AGING HISTORY ON EPOXY RESINS AND GFRP COMPOSITES

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Abstract: *As the success of fiber reinforced polymers (FRP) has reached a wide range of industries, sustainability, reliability, and durability are increasingly important requirements. Complex processes occur in the polymeric matrices and the multiscale composites, especially under challenging conditions (humidity, water, temperature). Due to the variety of available constituents (fibers, sizings, resins) and the high time pressure for new products and innovations, long-term property predictions rely mostly on accelerated aging procedures. However, since the available materials can differ considerably in their characteristics, aging effects need to be understood better. Therefore, long-term studies on four epoxies demonstrate the importance of the hygrothermal aging temperature affecting their thermo-mechanical properties by plasticization and physical aging processes. Additional investigations on several glass fiber composites under the same aging conditions reveal that the matrix and interphase dominated properties are likely to develop differently from neat epoxy. The sizing durability is essential here.*

Keywords: Glass fiber; Durability; Interphase; Sizing; Long-term properties

1. Introduction

In order to make a decisive contribution to the efficient and sustainable use of raw materials and energy, the potential of lightweight composites must be exploited even better in the future. To achieve this, it is necessary to extend the operating life of structures and components even under harsh environmental conditions while at the same time ensuring safe operation. Therefore, it is essential for composites and their polymer matrices to know how their mechanical properties develop over time under the influence of water, moisture, and different temperatures. In the past, academia and industry regularly concentrated on accelerated aging procedures at elevated temperatures aiming to make reasonable estimations for the long-term properties of polymers and composites [1]. However this approach produces quick results, but there is a danger of overestimating or generating effects that do not occur in the field. It is known and expected that thermo-mechanical properties of epoxies and composites might suffer from water absorption and aging. Loss of strength [2], decrease of the glass transition temperature (T_g) [3] or swelling induced cracks and defects [4] are typical phenomena. Accordingly, in the present study, the changes of the mechanical properties of epoxy resins due to water absorption (water bath/climate chamber) over a wide temperature range and long aging periods are investigated in detail. Tensile tests, DMTA, and FTIR investigations allow, for example, to reveal the current material condition and predict the development of strength as a function of environmental conditions and aging time [5]. Time-dependent investigations impressively show under which conditions the plasticizing effect of water is determinant and under which the polymer relaxation and water-network interaction [5, 6]. A comparison of four commercially widely used epoxies within this study points out commonalities and differences.

doi:10.5075/epfl-298799_978-2-9701614-0-0

Alongside the changes in matrix properties, the fiber-matrix interphase plays a decisive role in composites' durability [7]. Therefore, the interphase properties' changes were investigated similarly in the second part of the study. Transverse tensile tests on numerous fiber-matrix combinations examine the unique role of fiber sizing for the performance and durability of glass fiber reinforced polymer (GFRP) composites. In principle, the transverse tensile strength develops first similarly but over time more and more contrary to the matrix strength. With increasing water absorption, a plasticizing and at elevated temperatures detrimental damage appears, which does not recover over time. Furthermore, the composite properties are not reversible by re-drying and rejuvenation to the same extent as those of the epoxy matrices [5, 6, 8]. In summary, the study will help enhance predictions regarding the effects of various environmental conditions on epoxy and epoxy composites in the future. For both neat polymers and GFRP composites, the importance of the time-temperature-humidity history concerning their operational durability is highlighted.

2. Materials and Methods

2.1 Epoxy resins and glass fibers

In total, four low viscosity epoxy resin systems based on compositions of bisphenol A diglycidyl ether (DGEBA) or bisphenol F diglycidyl ether (DGEBF) and amine-based hardeners were selected to investigate the hygrothermal aging behavior of epoxies and GFRP composites. All systems are applicable for infusion and resin transfer molding (RTM) processes and are widely used in the wind and maritime industry. Due to their chemical formulations, the chosen systems differ in the extent of their water absorption under constant environmental conditions. The epoxy resin system primarily investigated for long-term aging is EPIKOTE™ Resin MGS™ RIMR 135 and the amine hardener EPIKURE™ Curing Agent MGS™ RIMH 137 (Hexion Inc., USA). Additionally, EPIKOTE™ Resin MGS™ RIMR 035c and the hardener EPIKURE™ Curing Agent MGS™ RIMH 037 (Hexion Inc., USA), Araldite® LY 1568 and the hardener Aradur® 3489 (Huntsman, USA), and CeTePox® AM 3329 A/B (CTP Advanced Materials GmbH, Germany) were studied.

Glass fiber fabrics made of different fiber inputs (E-glass, ECR-glass, and R-glass) and finished with different commercial fiber sizings were used to manufacture unidirectional GFRP composite laminates. Different fibers and matrix systems were combined to study the impact of material selection on the hygrothermal durability of the composites. A detailed overview of all used fiber types and fabrics is given in Table 1.

Table 1 : Overview of the glass fiber fabrics structures and properties. All fabrics are sized with epoxy compatible sizes according to the manufacturers' data sheets.

Supplier	Fabric	Fiber	Manufacturer	Type	Areal weight in g/m²	0°-share
Saertex	UE1182	SE 2020	3B, Belgium	ECR-Glass	1182	97 %
Saertex	UE1192	W 2020	3B, Belgium	R-Glass	1192	97 %
Saertex	UVE1166	Hybon 2002	NEG, Japan	E-Glass	1166	99 %
Gurit	UE-500	ER469L	CPIC, China	ER-Glass	500	99 %

2.2 Manufacturing processes and specimen preparation

All neat epoxy plates and GFRP laminates were manufactured using vacuum-assisted RTM processes (VARTM). A two-part, polished aluminum mold was used in combination with frames of either 0.5 mm (neat epoxy) or 2.0 mm (GFRPs) thickness. The fiber fabrics were cut to size and placed unidirectional and parallel to the long side into the mold. The resins were mixed and degassed for 30 minutes according to the mixing ratios provided by the manufacturers' data sheets using a vacuum stirrer. The infusion process was done at 50 °C (RIMR135 and RIMR035c) or 40 °C (LY1568 and CeTePox 3329A/B) mold temperature and held for 15 hours. The ambient pressure of the trap side was only a few mbar during infusion and curing. The plates and laminates were demolded and subsequently post-cured at 80 °C for 15 hours (RIMR135 and RIMR035c) or 10 hours (CeTePox 3329A/B), or at 100 °C for 5 hours (LY1568). Rectangular GFRP transverse tensile specimens of 250x25x2 mm³ were cut using aluminum-oxide blades on a Brillant 265 (QATM, Germany) semi-automatic saw. Dogbone-shaped neat epoxy specimens for tensile tests and DMA investigations were elaborated using a Euromod 35 (Isel Germany AG, Germany) CNC-mill with a 1.8 mm diamond bit. The cutting edges of neat epoxy were polished with SiC sandpaper up to a grit-size of P2500, to minimize the effects of edge roughness. The specimen geometries and dimensions are given in Figure 1.

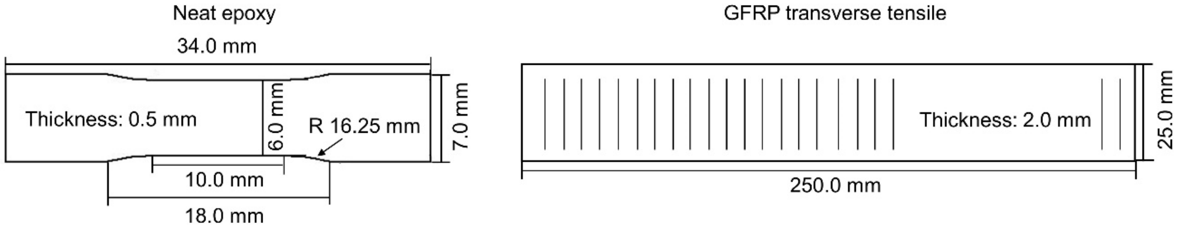

Figure 1. Specimen dimensions and geometries.

3. Results and Discussion

3.1 Water absorption and impact of aging temperature on epoxy strength

The water absorption process in highly cross-linked thermosets like epoxy resins is nowadays known to be mainly a result of the polymers' structure and chemical composition [9, 10]. For non-hydrolyzable epoxies, the process is regularly modelled with the Fickian absorption model [11]. Differences during isothermal water absorption result from molecular interactions between absorbed water molecules and polar groups within the polymers [10]. Therefore, the molar attraction and volume define hydrophilicity. Furthermore, the diffusion rate and, to some extent, the maximum content of absorbed water are temperature dependent [5, 12]. The isothermal water absorption process in a water bath at 8 °C is representatively shown with experimental data, and Fickian absorption models in Figure 2A for all studied neat epoxies. It is revealed that even though the epoxies are quite similar in terms of their main molecular components, the maximum water content at saturation shows differences of up to 1.0 m% due to the different chemical compositions. The effects of the water absorption on the tensile yield strength were analyzed for water bath and humid air aging temperatures between 8 °C and 70 °C. In Figure 2B, the residual strength is displayed exemplarily for aging at 8 °C and 40 °C related to the amount of absorbed water at saturation. The results demonstrate that the tensile strength of all epoxies decreases due to the plasticizing effect of water.

Furthermore, it becomes clear that the extent of the strength depression is, on the one hand, directly related to the amount of absorbed water and, on the other hand, also associated with the aging conditions (temperature and time). Based on the same gradients of the isothermal linear regressions, it can be concluded that the effects of water absorption on the strength are identical for all epoxies tested. The higher the water absorption of a system, the higher the strength loss. However, for specimens tested directly after reaching saturation, the impact of the aging temperature is significant. While aging at cold temperatures can lead to a strength loss of up to 9.57 (±0.39) MPa/m%, the impact is only about half as big for aging at 40 °C. This is because relaxation (physical aging) and polymer-water interaction (e.g. hydrogen bonding) co-occur with water absorption and, in contrast to plasticizing, increase the strength. Aging at elevated but sub-Tg temperature significantly accelerates the physical aging processes [5, 6]. As a result, aging in cold water leads almost entirely to a decrease in strength due to plasticization, while aging at elevated temperatures counteracts the strength reduction.

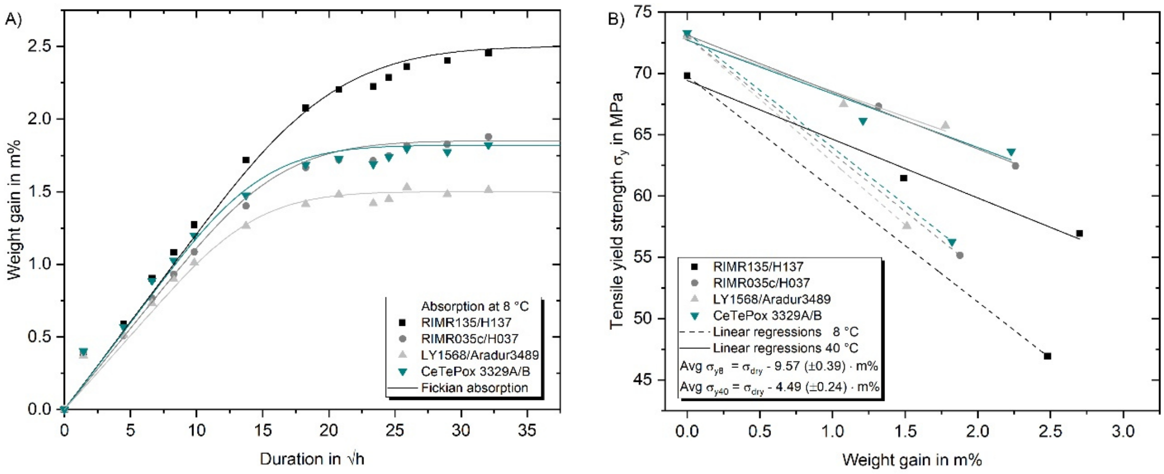

Figure 2. A) Weight gain curves of all neat epoxies for aging in 8 °C water. B) Correlation between tensile yield strength and amount of absorbed water at 8 °C and 40 °C. Tensile tests were performed as soon as saturation was reached.

As a consequence of these results, it can be deduced that the epoxy strength depends on the amount of absorbed water and on the time-temperature history of the environmental conditions. Assuming that the physical aging process and the formation of strong water-polymer bonds follow an Arrhenius like temperature relation, the Kohlrausch-Williams-Watts (KWW) correlation can be used to describe the strength evolution $\sigma_y(t,T)$ as follows [6]:

$$\sigma_y(t,T) = \sigma_0 + \Delta\sigma\,\left(1 - e^{-\left(\frac{t}{\tau(T)}\right)^{\beta}}\right), \tag{1}$$

where σ_0 is the plasticized strength without additional aging, $\Delta\sigma$ is the maximum strength change due to physical aging, t is the aging duration, β is a stretching parameter and $\tau(T)$ is the temperature-dependent relaxation time. Taking into account that the epoxies are in an unknown physical aging state after manufacturing, but that the increase of physical aging at cold temperatures is negligible for short durations, σ_0 can be designated based on the strength evolution shown in Figure 2B as:

$$\sigma_0 = \sigma_{dry} - 9.57\ (\pm 0.39) \cdot \mathrm{M}_{\infty}, \tag{2}$$

with the initial dry strength σ_{dry} and the amount of absorbed water at saturation M_{∞}. $\Delta\sigma$ can be determined experimentally with aging at elevated but sub-T_g temperatures within a short time. In Figure 3A, the strength evolution is shown exemplarily for the epoxy with the highest water absorption and most significant strength variations (RIMR135/RIMH137) for aging at four different temperatures of up to 6200 hours. The lines represent the KWW model predictions according to the given values of $\tau(T)$ and with constant values of $\beta = 0.5$ and $\Delta\sigma = 18.6$ MPa. The Arrhenius plot of the relaxation time is shown in Figure 3B, revealing an activation energy of 137.8 kJ/mol. This implies that an increase of the aging temperature by 10 K accelerates the aging process by a factor of more than five. Thus, if the strength is predicted for a service temperature of 10 °C using accelerated aging at 50 °C, this corresponds to an acceleration factor of 915. In other words, it also means that the strength achieved after less than eight days in a hot water bath, will take more than 20 years of service use. These enormous accelerations should be critically checked and reconsidered if accelerated aging is used to estimate long-term properties.

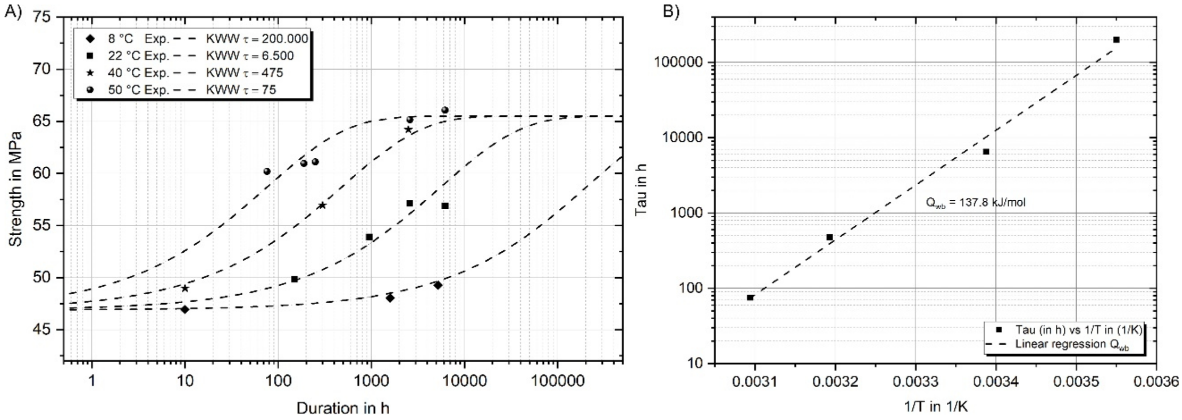

Figure 3. Tensile yield strength development over aging time for aging in water at four different temperatures of the RIMR135/RIMH137 neat epoxy. Kohlrausch-Williams-Watts (KWW) models with respective relaxation times τ are shown with lines.

3.2 Relation between epoxy strength and glass transition temperature

The linear relation between the T_g and the amount of absorbed water is shown in Figure 4A for all investigated epoxies. The plasticizing effect of the water molecules absorbed into the polymer structure decreases the T_g by about 8.4 °C/m% to 9.9 °C/m% and corresponds well with reported values [13]. Accompanying with the change of the T_g, a change of the polymer strength is expected and typically described by the Kambour or Eyring relationship [14]. Therefore, in Figure 4B, the RIMR135/RIMH137 epoxy strength is presented concerning the distance between the testing temperature and the T_g. The expected linear relationship can be verified for dry epoxies tested at various environmental temperatures. But for the wet-aged epoxy, clear deviations can be found. The two main characteristics affecting the strength and the T_g are the aging time and temperature. While the strength increases significantly with long-term aging (indicated by arrows) and elevated aging temperatures as shown in Figure 3 and Figure 4B, the T_g does not to the same extent. For this reason the Eyring prediction can only provide an approximate dimension by estimating wet properties based on tests with dry material. Wet-aging at cold temperatures (without additional physical aging) depresses the strength more than expected and wet-aging at elevated temperatures depresses the strength less than expected.

As described in more detail in Gibhardt et al. [5], the results show that the epoxy strength is particularly affected by plasticization and physical aging, while the T_g is mainly affected by the plasticization.

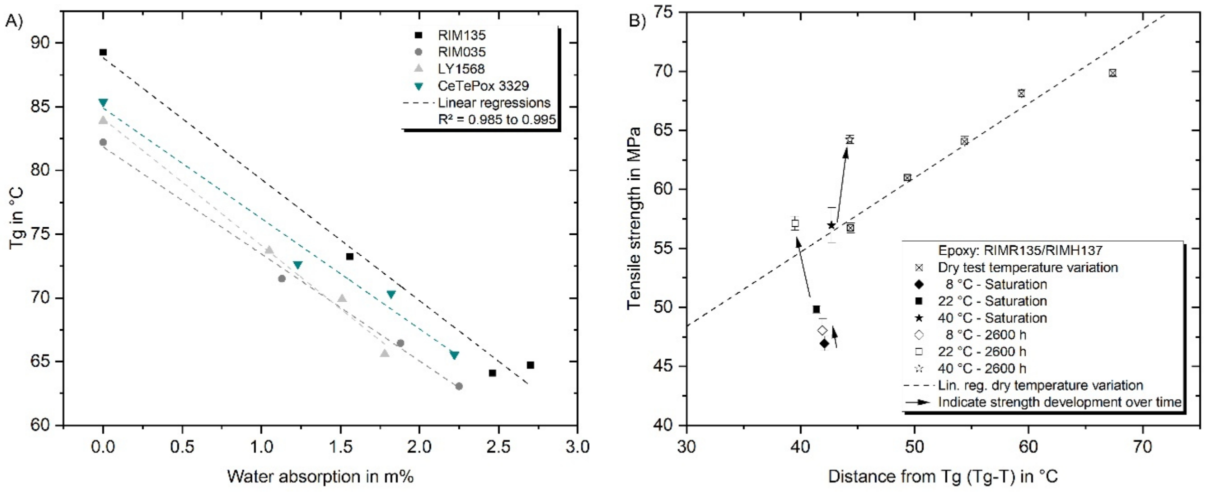

Figure 4. A) Relation between T_g and water absorption for all epoxies after aging in water between 8 °C and 40 °C. B) Tensile strength in relation to the distance between testing temperature and T_g of RIMR135/RIMH137. Line represents Eyring relationship of dry tests.

3.3 Aging history effects on transverse tensile strength of GFRP

Following the studies on epoxies, the question arises of how the aging behavior of the polymers affects the matrix and interphase dominated strength of GFRP composites. Therefore, transverse tensile specimens of four different fiber inputs were likewise aged in water baths at temperatures of 8 °C to 50 °C. The initial absolute transverse tensile strengths and the developments during aging are presented in Figure 5. First, the initial dry strength comparison shows significant differences between the four composites and highlights the importance of good interaction between fiber sizing and epoxy resin. As the dry epoxy strength is considerably higher than the transverse strength, it is reasonable to assume that the interphase strength limits the measured strength. While the SE 2020 and W 2020 composites perform well with an initial strength of about 55.0 MPa, the 25.0 MPa found for the NEG 2002 composites is relatively low.

The long-term wet-aging at different temperatures reveals different resistances to a water-induced reduction of the interphase strengths. When aged in 8 °C cold water (to about half-saturation within 3000 h), all systems' strength reductions are lowest. In fact, the strength of the SE 2020 composite was decreased by only 1.5 MPa (3.0 %), which is even less than 3.0 MPa (5.5 %) of the W 2020 or 4.9 MPa (20.0%) of the NEG 2002 composites. Taking the long-term epoxy strength at saturation at low temperatures into account (< 50 MPa), it is expected that the transverse strength will remain in this range during long-term aging (or service conditions) for the fiber-matrix combinations with the highest interphase strengths (SE 2020 and W 2020). Aging up to saturation at 30 °C, which is still about 30 °C lower than the wet-Tg of the epoxy, leads to a more pronounced strength reduction. While the NEG 2002 composite already loses about 13.0 MPa (53.0 %) and thus only has a minimal residual strength, the loss of all other systems is still moderate with about 6.0 MPa. Even though accelerated aging at 50 °C results in the most severe interphase strength reductions, huge differences arise. In contrast to the NEG

2002 and ER469L composites, which almost completely lose their integrity, the SE 2020 composite continues strong and has a residual interphase strength of about 48.0 MPa.

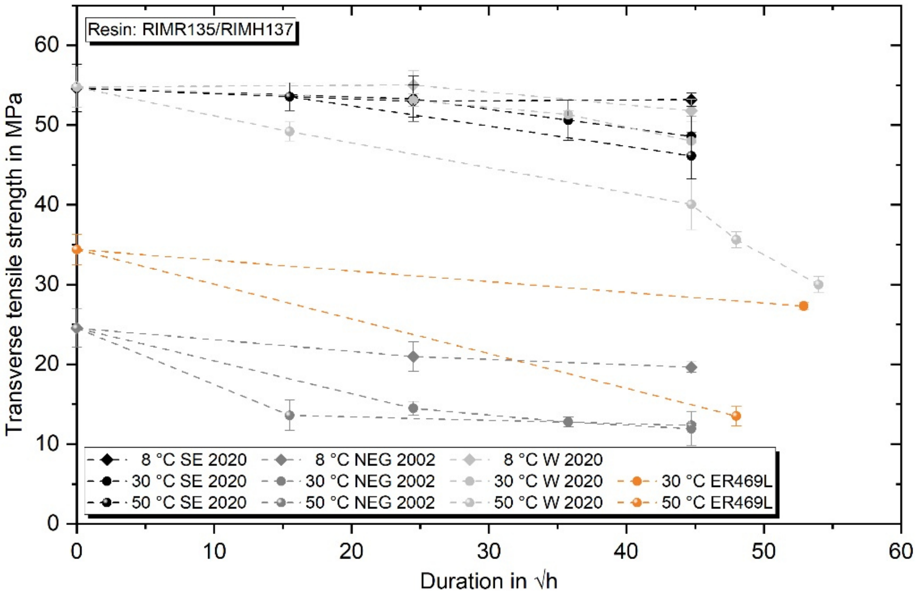

Figure 5. Transverse strength development of four different GFRPs for aging in water bath conditions from 8 °C to 50 °C over a period of up to 3000 h.

4. Conclusions

Long-term aging demonstrated a very similar behavior for all studied epoxies. It could be shown that the plasticizing effect on strength and T_g is primarily dependent on the amount of absorbed water. Based on the results, the KWW relationship for strength development was extended by the water absorption dependent initial strength prediction and verified for a wide temperature range. Overall, the identified changes of the epoxy strength during aging have been shown to have rather negligible effects on the transverse strength of the composites. Here, instead, the sizing-dominated interphase strength is of importance. Sizing and, therefore, interphase related durability differences could be uncovered considering the investigated temperature range. While water-induced plasticization at cold or moderate aging temperatures results in minor impacts in the majority of cases, elevated temperatures often severely affect the interphase integrity. In contrast to the water-polymer interactions increasing the strength by physical aging processes inside the neat epoxies, the interphase region seems not to be subjected to these processes. The complex combination of matrix polymer and various sizing components appears to be significantly more susceptible to water-induced weakening than the neat epoxy. The main reason for this could be an increased water affinity of polar components in the interphase and possible hydrolysis reactions of the silanes at high temperatures as highlighted by Thomason et al. [7]. For GFRP composites with wet-aging resistant interphase, matrix aging plays a more important role. The changes in strength and stiffness, the decrease in T_g and strong changes in elongation at break could affect the lifetime performance significant, especially under fatigue loads. However, this needs to be investigated further in the future.

5. References

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