STRESS CRACKING AND FAILURE BEHAVIOUR OF GLASS FIBRE REINFORCED COMPOSITES UNDER THE INFLUENCE OF DIFFUSING (CORROSIVE) MEDIA

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ABSTRACT

Aqueous media are absorbed by resins and composites. It is possible to describe the sorption behaviour of glass fibre reinforced composites knowing the sorption behaviour of the resin fraction and the absorption in the volume of interfaces and flaws.
Concentration changes lead to dimensional changes; these swelling strains of anisotropically reinforced layers can be determined from the swelling behaviour of the matrix resin. In general concentration distributions during diffusion processes cause residual stresses (swelling stresses).
Swelling strains and swelling stresses have be superimposed to a mechanical load.
The phenomenon of the "stress-crack-corrosion" also occuring in polymers can be explained by residual stresses due to diffusion processes.

KEYWORDS

Composites; resins; sorption and diffusion behaviour; swelling behaviour; residual stresses (swelling stresses); individual layer; multi-layer composite; micro-cracking; stress cracking

INTRODUCTION

The mechanical properties of glass-fibre reinforced composites in an air environment can be determined fairly accurately from the properties of the invidivual components, glass and resin, even for the long term (Brintrup, 1975; Puck, 1969; Tsai, 1978 and others). "Chemical-corrosive" influences on the other hand, are virtually impossible to calculate and particularly so for the long term. Nevertheless, it is, in fact, possible to estimate a number of the more "physical" effects of a diffusing medium on the basis of sorption and swelling behaviour (Gitschner, 1980 a, 1980 b; Menges, 1980) and these can then be applied to clarify aspects of material behaviour, such as the "stress-crack-corrosion" (Fischer, 1970) also found in plastics.

FUNDUMENTAL OBSERVATIONS TAKING THE EXAMPLE OF
WATER ABSORPTION

Sorption and Diffusion Behaviour of Resins and Composites

In the case of water absorption, the equilibrium states are dependent upon temperature and relative humidity.
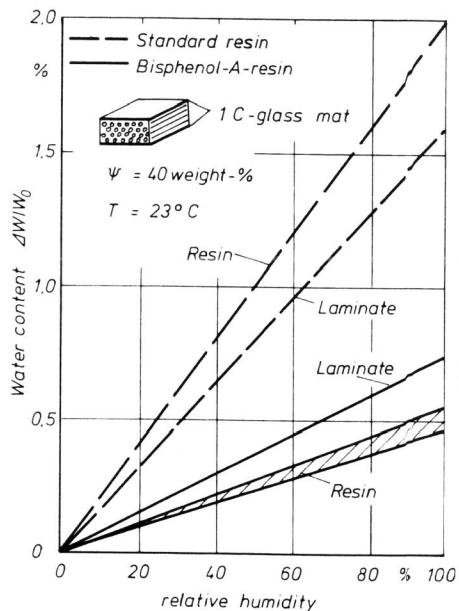

Fig. 1 Sorption isotherms of UP-resins and GR-UP-laminates

Fig. 2 Sorption isotherms of the volume of interfaces and flaws in GR-UP

Figure 1 shows typical sorption isotherms for polymers with the example of two different UP-resins.

Even glass-fibre reinforced composites which have a polymer resin matrix absorb aqueous media too. The saturation or equilibrium values for water absorption, for example, in the laminates are dependent on environmental conditions in the same way as is the pure matrix. Hence composites also possess a sorption isotherm (Fig. 1) with an equilibrium concentration which is markedly dependent upon air humidity (Gazit, 1976; Gitschner, 1980 b; Loos, 1979)
For ideal conditions it can be reliably assumed that only the resin volume fraction will be able to absorb the water. Since ideal manufacturing conditions are never achieved in practice additional absorption takes place in the volume of interfaces and flaws. Fig. 2 shows this additional absorption in the GR-UP-laminates. When expressed in terms of the resin or laminate weight, sorption behaviour in the interface volume again corresponds to the theoretical behaviour of a sorption isotherm (Fig. 2).

The medium absorption of laminates, expressed in the standard form as a function of weight, can then be calculated for each glass con-
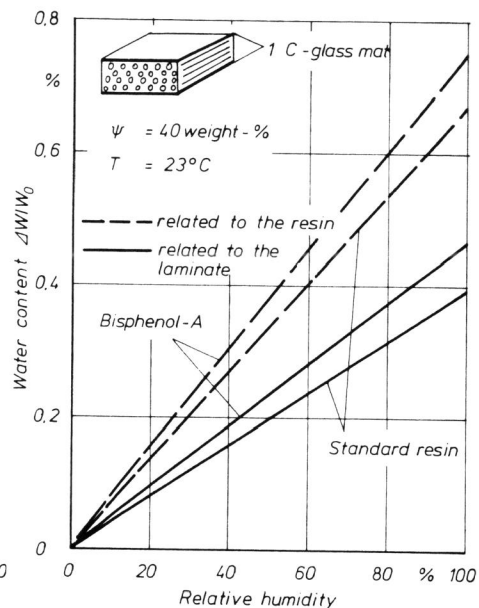
tent using the complete relationship in Eq. (1) (Gitschner, 1980 b; Menges and Gitschner, 1980)

$$C_{lam(\varphi)} = (1-\psi) \cdot C_s(r.h.)_{resin} + \frac{C_s(r.h.)}{C_s 100} \cdot B_{100} \cdot \varphi \cdot \frac{\rho_{H2O}}{\rho_{lam(\varphi)}} \quad (1)$$

where
c_s = (equilibrium) Water absorption
ρ^s = specific weight
ψ = glass weight fraction; φ = glass volume fraction
B_{100} = ("Interface")-proportionality factor at maximum saturation

If the environmental conditions are changed then resins and composited also undergo compensation processes, in accordance with the corresponding sorption isotherms, until such point as the new equilibrium state is reached. In a large number of cases the diffusion behaviour tally with the theoretical behaviour. This means that composites of this type can be formally ascribed a mean diffusion coefficient D as a measure of the speed at which the compensation process takes place (Loos and Springer, 1979; Menges and Gitschner, 1980).

Dimensional Changes (Swelling Behaviour) in Resins and Composites

Assuming that the solution diffuion theory applies, water absorption in a polymer will take place in that portion of free volume which is available to take up the medium. In practical polymers, though, additional volume is created over and above this free volume, to absorb the medium, and as a result the polymer swells (Gazit, 1976; Gitschner, 1980 b; Puetz, 1977).
If we take the longitudinal change in dimension as the swelling strain ε_{sw} then the course or extent of this strain will be more or less directly proportional to the change in weight or concentration (Fig. 3). In analogy to the coefficient of thermal expansion, the literature requently defines a "swelling coefficient α_{sw}" (Gazit, 1976; Tsai and Hahn, 1978) which gives the proportional relationship between strain and change in concentration through the following expression:

$$\varepsilon_{sw} = \alpha_{sw} \Delta C \quad (2)$$

The creation of swelling volume and the "filling" of available free volume must therfore be simultaneous and proprotionate processes. If cosideration is then given to geometrical relationships between changes in volume and changes in length in isotropic materials, this will give the following equation for swelling coefficient α_{sw}.

$$\alpha_{sw} = \frac{\varepsilon_{sw}}{\Delta C} = \frac{1}{3} \left(\frac{\rho_{polymer}}{\rho_{liquid}} - \bar{c}_{fv} \right) \quad (3)$$

where ΔC = change in concentration
$\bar{c}_{fV}$ = (proportionate) reference index for the free volume (0.4 - 0.5 for the case of water absorption)

In composites this isotropic swelling of the homogeneous matrix resin is influenced by the reinforcing fibres, in so far as adhesion between fibres and matrix can be assumed (Fig. 3). In the case of

anisotropically reinforced composites, consideration has therefore to be given to the drectionality of the reinforcement (Fig. 3).
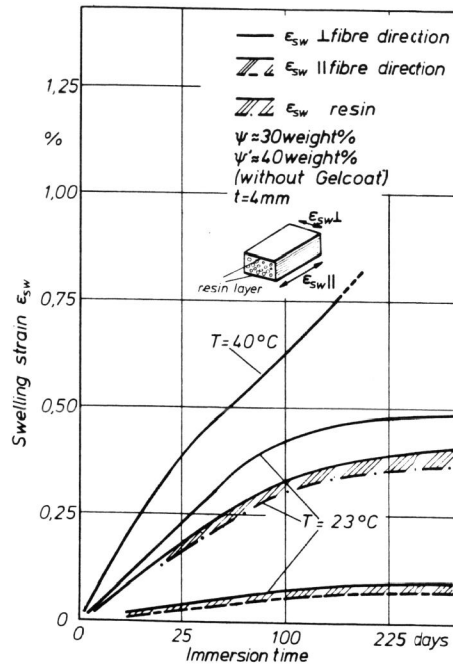

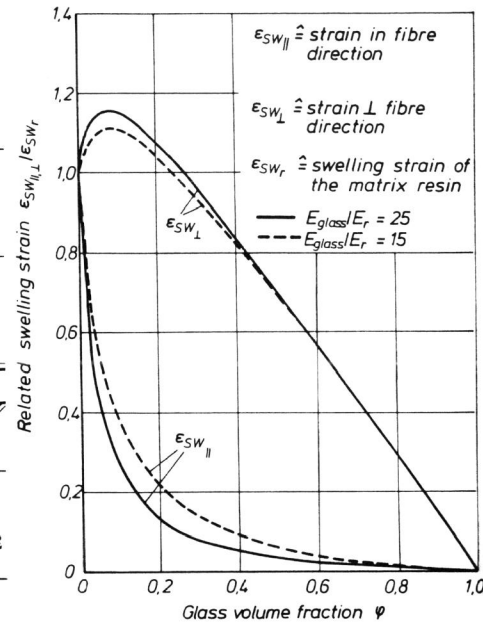Fig. 3   Swelling behaviour of unidirectionally rein-fored GR-UP(standard) in distilled water

Fig. 4   Swelling behaviour of ani-sotropically reinforced in-diviudal layers due to ma-trix swelling

Using force and strain balances per volume element it is possible to derive relationships for the dimensional change in an anisotropically reinforced individual layer, both in the fibre direction ($\varepsilon_{sw\parallel}$) and perpendicular to fibre direction ($\varepsilon_{sw\perp}$) (Gitschner, 1980 b). Fig. 4 shows the relationships plotted in related form against the glass volume fraction.

According to Fig. 4 the dimensional change in glass-fibre reinforced individual layers can be established quite simply if the sorption and swelling behaviour (Eq. (3)) of the matrix resin used is known. By taking mechanical reference indexes for the individual layers or the rigidity matrix (e. g. Brintrup, 1975; Tsai and Hahn 1978) it is thus also possible to calculate dimensional change in a practical multi-layer laminate (made up of individual layers) for a given change in concentration or change in environmental conditions (e. g. on a sorp-tion isotherm), solely from reference values for the matrix resin (Gitschner and Mayer, 1979; Gitschner and Grüters, 1980).

ESTIMATION OF RESIDUAL STRESSES IN GRP DUE TO DIFFUSING MEDIA

Local Residual Stresses Due to Matrix Swelling Between Equilibrium States

Once swelling strain has occured in the fibre direction the indi-vidual components of glass and resin are obviously no longer in a stress-free state. In the "transverse direction" ($\perp$ fibre direction) macroscopic observation suggests that the resin matrix swelling be-haviour is scarcely hindered at all to begin with. Nevertheless, lo-cal residual stresses do build up in the "transverse direction" as well and these are caused through the influence of the fibres (Git-schner, 1980 a).
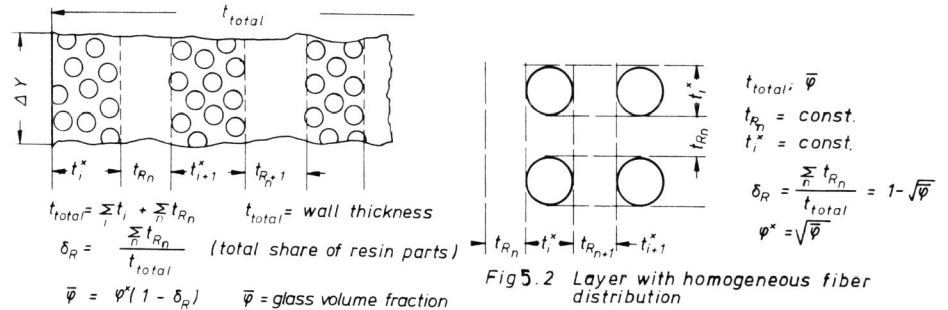

Fig. 5.1   Inhomogeneous fiber distribution in a (statistically) representative volume element

Fig. 5.2   Layer with homogeneous fiber distribution

Fig. 5   Schematical representation of resin and fibre distribution

The following observations will serve to explain this: if we picture a volume element of a transverse layer of height Δy, with a fibre distribution representative (in statistical terms) of the whole cross-section or the whole layer, then this volume element can be di-vided up into "pure resin pockets" which are virtually non-reinforced and zones with a high degree of glass-fibre reinforcement (Fig. 5.1). The ratio δ_R of pure resin components to layer thickness is a meas-ure of the non-uniformity of fibre distribution. The actual glass content in the reinforced zones can be obtained from the relationship given in Fig. 5.1.

Zones with a glass content of φ^x, however, show similar behaviour to a "transverse layer" again. Between sorption equilibrium states (changes in concentration) these layers are ascribed a dimensional change dependent upon glass content φ^x as indicated in Fig. 4. In ca-ses with a high proportion of pure resin pockets (high δ_R), in par-ticular, local glass content can be relatively high, even if the layer as a whole has a low to medium glass content. Since the equilibrium swelling $\varepsilon_{sw\perp}(\varphi^x)$ of the non-hindered case is then considerably lower than that of the "pure resin pockets" (Fig. 4) excess strain occurs in

the reinforced zones and this gives rise to residual stresses. This strain, which discribes the extent of the residual stress, is repre-sendted by $\Delta\varepsilon_{\perp\sigma}$ and is given in Fig. 6, standardised in terms of matrix swelling, as a function of $\bar\varphi$ and the distribution ration δ_R. Depending on the sorption and swelling behaviour of the matrix used, considerable (excess) strain $\Delta\varepsilon_{\perp\sigma}$ can develop in the "transverse layer" in this way (Gitschner and Mayer, 1979).
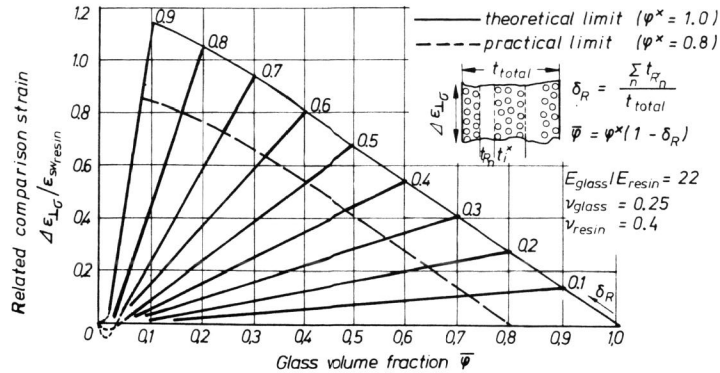

Fig. 6   Representation of the residual stress state due to swelling (inhomogeneous fibre distribution)

The oberservations relative to non-uniform fibre distribution can also be applied to fibre distribution which is, in fact, uniform. By taking the following configuration of pure resin zones extending un-broken in one direction and reinforced zones together with the inter-relationships presented (Fig. 5.2), it is possible to give the excess strain in the glass/resin zones in related form using force or strain balances (Fig. 7). Even with this method of observation, considerable local residual stresses can occur precisely in zones with a real glass content of 0.2-C.6.
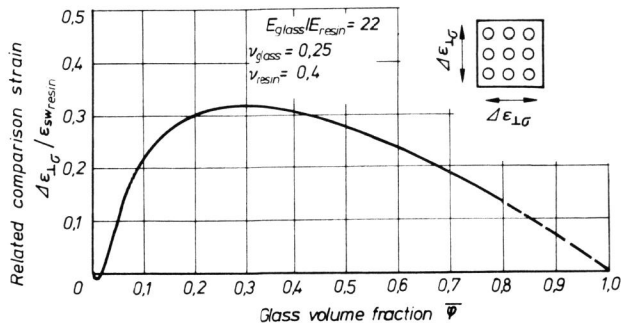

Fig. 7   Representation of the residual stress state due to swel-ling (homogeneous fibre distribution)
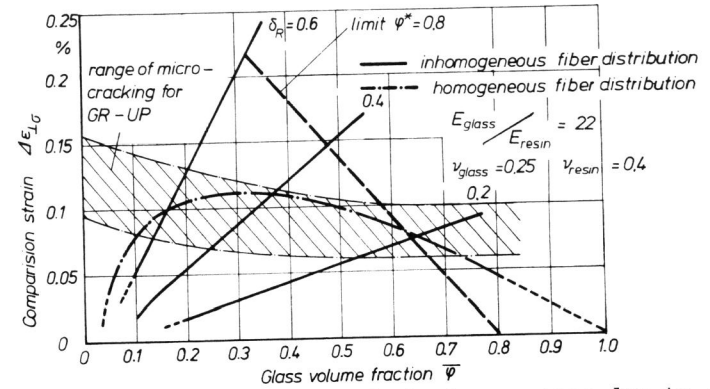
Fig. 8   Representation of the residual stress state due to swel-ling ($\varepsilon_{SW_{resin}} = 0.35$ %; $\Delta C_{H_2O} = 1.5$ weight-%)

If we take the concrete case of sorption and swelling behaviour of the standard resin in Fig. 3, then, using the swelling strain for the pure resin $\varepsilon_{SW} = 0.35$ % (Fig. 3) it is possible to calculate the re-sidual stresses, as per Fig. 6 and 7, for "transverse layers", with this matrix resin, as a function of glass content. Figure 8 gives the resultant (theorectically calculated) residual stress states, presented in the form of refernce strains, for both cases of uniform distribution and assumed non-uniform distribution. These residual strain states can be compared with the known micro-cracking range for relatively brittle UP-resins in "transversely loaded" layers (e. g. Brintrup, 1975; Puck, 1969). In the case in question, both methods of observation lead to residual stresses or strains of an order of mag-nitude that could cause micro-cracking.

Swelling Stresses Due to Concentration Profiles

Individual layers. In addition to the influence of fibres and fibre distribution, consideration must also be given to the fact that in composites, as in homogeneous polymers, a marked distribution of con-centration takes place during non-stationary-state phases of diffus-ion processes (Sandorff, 1979). The location and concentration depen-dent swelling behaviour which would take place in a non-hindered case means that swelling stresses are created in the compact material on account of the mutual hindrance (Gitschner, 1980 a; Menges and Gitschner, 1980; Puetz, 1977). Either tensile or compressive stresses may bild up, depending on whether strain components are superimposed or suppressed in relation to the swelling strain that would normally take place for the location-dependent change in concentration. Allo-wing for the laws of diffusion and with knowledge of the maximum swelling strain between equilibrium sorption states, it is possible to describe these stresses as a function of location and time (Puetz, 1977). The maximum resultant swelling stresses can be calculated with Equations (4) to (6). (Gitschner, 1980 a; Menges and Gitschner, 1980; Puetz, 1977).

Sorption

$$\sigma_{sw_{max}}(0, t^*) = 0,331 \; \varepsilon_{sw} \frac{E(0,\perp,\|)}{1 - \nu_{(0,\|\perp,\perp\|)}} \qquad (4)$$

Desorption

$$\sigma_{sw_{max}}(\frac{d}{2}, 0) = \varepsilon_{sw_{max}} \frac{E(0,\perp,\|)}{1 - \nu_{(0,\|\perp,\perp\|)}} \qquad (5)$$

Stationary Permeation

$$\pm \sigma_{sw_{max}}(\frac{d}{2}) = 0,5 \; \varepsilon_{sw_{max}} \frac{E(0,\perp,\|)}{1 - \nu_{(0,\|\perp,\perp\|)}} \qquad (6)$$

By taking the swelling strain of glass-firbre reinforced individual layers, Equations (4) - (6) can also be used to calculate residual stresses due to concentration profiles, if the (anisotropic) mechanical properties of the individual layer are introduced as well.

Multi-layer materials. Practical laminates consist of several individual layers. Each of them can have different (anisotropic) mechanical properties, different sorption and diffusion behaviour and anisotropic swelling behaviour. In addition in practice a diffusing medium is acting one-sided. Even in the state of stationary permeation, which-dependent on diffusion behaviour-will perhaps be reached only after years, a pronounced concentration distribution will occur.
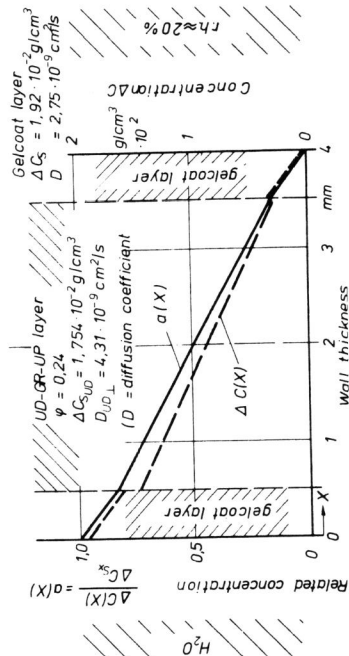

Fig. 9   Concentration distribution in the state of stationary water permeation (T = 23°C)
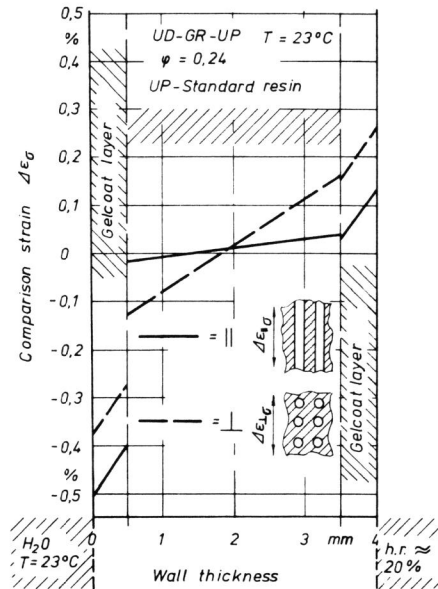
Fig. 10   Residual stress state in GR-UP laminate because of swelling

Knowing the absorption behaviour and the diffusion coefficients of each layer and the thichness distribution it is possible to determine the diffusion resistance and to calculate the related concentration distribution through a laminate wall (Gitschner and Mayer, 1979). Fig. 9 shows the course of the a (x)-distribution (related concentration) in a "multi-layer material" (unidirectionally reinforced UP-standard resin with two gelcoat layers, according to Fig. 1) in the state of stationary waterpermeation. Applying this a (x)-distribution in connection with the known swelling behaviour of the individual layers (e.g. Fig. 4) the swelling strain distribution of the non-hindered case can be determined. In the compact material this "theoretical" strain distribution again must cause complex residual stress profiles, dimensional changes and/or distortion states (Gitschner und Grüters, 1980; Gitschner and Mayer, 1979). In the case that the bending of the wall is impeded additional bending moment occur. The residual stress states (direction dependent) for this condition (bending-free) and the water-concentration distribution (Fig. 9) is shown in Fig. 10. The stress profiles represented as reference strains can be compared with the known range of micro cracking for GR-UP (Brintrup, 1975; Puck, 1969). The much more dangerous case seems to be in transverse direction. Strains of more than 0.1 % in the outer that means dryer parts of the laminates may lead to micro-cracking even without an acting mechanical load.

CONCLUSIONS

Sorption, diffusion and swelling processes also occur with simultaneously acting mechanical stresses (Puetz, 1977). The corresponding swelling deformation has therefore to be superimposed upon the polymers and composites. Consideration must, however, be given to the fact that this overall deformation does not describe the actual stress state. Local and concentration dependent swelling stresses have to be superimposed on the mechanical stresses. Micro-cracking in the most critically loaded parts of a laminate should be avoided. In the case of diffusing media like water the critical regions will be in the outer that means dryer parts of the wall. The well known "weeping "of pipes or containers may be a result of micro-cracking in dryer parts which then will loose the diffusion resistance. But the known stress cracking of protection layers inside under the influence of aggressive chemicals may be an effect of superimposed swelling stresses too. Chemicals which da not diffuse themselves or only very little can cause drying effects because of their hygroscopic nature. The occuring swelling stresses may lead to microcracking. Secondly penetrating medium to the load bearing layers then will cause the failure of the laminate.

In general, the fact that it is possible to estimate the sorption, diffusion and swelling behaviour of composites from the values for the components, opens up the path for including at least a "physical corrosion influence" of diffusing media in calculations for the desingn of composites.

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