

# Applicability of FT-IR Techniques and Goniometry on Characterization of Carbon Fiber Surfaces

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**ABSTRACT:** Carbon fibers have been widely used as structural reinforcement in aeronautical composites, because of their exceptional mechanical properties. However, carbon fibers present few polar groups on their surfaces inducing a weak interaction with some thermosetting and thermoplastic matrices. Surface treatments, such as thermal and electrochemical oxidation, are generally followed by sizing in order to improve interfacial adhesion between carbon fibers and some matrices. The precise surface characterization, by means of its chemical groups and radical identification, has been pointed out as an effective tool of carbon fibers finishing assessment process. Goniometry and Fourier transform-infrared spectroscopy are widely used to characterize some materials applied in industry, but not for carbon fibers, mainly because of their filamentary shape and the high concentration of carbon even in their near surface. In this paper, unsized and sized Torayca T300 carbon fibers were characterized by goniometry tests to evaluate hydrophilic or hydrophobic character. Qualitatively, it was noticed the effect of sizing on carbon fibers by their hydrophilic behavior, which has not been observed in unsized samples. Chemical analysis was performed by Fourier transform-infrared spectroscopy using different setups: photoacoustic, attenuated total reflectance and universal attenuated total reflectance. The Fourier transform-infrared spectroscopy/attenuated total reflectance/Germanium was shown to be the most promising technique to analyze carbon fibers surface, despite the low level of relative intensities of some bands. By this technique, it was possible to observe differences between unsized and sized carbon fibers spectra.

**KEYWORDS:** Carbon fiber, Infrared spectroscopy, Wettability, Characterization, Surface properties.

## INTRODUCTION

In the last decades, carbon fibers (CF) have become a requisite and worthy material used in strategic applications. They have been widely used in structural reinforcement in composites, mainly in aeronautics, aerospace and automotive industries because of their excellent mechanical, thermal and electrical properties. Furthermore, their low volumetric expansion coefficient and low density turned them more attractive for these industries. CF used in structural applications are normally obtained at temperatures above 1500 °C. They present special characteristics, such as ordered graphitic structure disposed preferentially in parallel to the fiber axis and their high concentration of carbon is at least 92% (Chung 1994). The crystallinity of CF is strongly influenced by the carbonization process parameters (Chung 1994; Morgan 2005). However, the concentration of elements like nitrogen and oxygen is poor in CF, even on their surface. Thus, the low content of polar groups in the CF surface can compromise their adhesion to some polymeric matrices (Chan *et al.* 1996; Montes-Morán *et al.* 2001; Xu *et al.* 2008).

A surface treatment is necessarily employed at the end of the process to obtain CF, in order to reduce the electrostatic charge on their surface and to handle them. It is important to improve the interfacial adhesion between CF and the composite matrix. Basically, these treatments can be divided into two groups: wet and dry processes. In dry processes, plasmas have been widely used for this purpose (Donnet *et al.* 1986, 1987; Chan *et al.* 1996; Montes-Morán *et al.* 2001; Park *et al.* 2010; Oliveira Jr

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*et al.* 2011). On the other hand, the wet processes based on electrochemical reactions, such as oxidation, fluorination, and oxyfluorination, have been employed to modify the CF surface (Basova *et al.* 1999; Ho *et al.* 2008; Seo and Park 2009). Generally, following these processes, a coating of polymeric sizing, also denoted as finishing, can be applied to protect the CF surface.

These treatments generally increase the surface energy and wettability of some materials. Goniometry has been a simple technique that can be applied to analyze these thermodynamic properties. The hydrophobic or hydrophilic features of any material can be quickly assessed just by measuring the contact angle of a liquid dropped over its flat surface, in order to determine its adhesive potential. Fowkes (1964) showed the contribution of some molecular interactions to the total surface energy. For polymers, dispersive and polar forces are usually the main components that make up the total surface energy. These parameters are generally calculated by measuring contact angles of two different liquids. Owens and Wendt (1969) and Kaelble and Uy (1970) developed a method called geometric mean that is applied to calculate the surface energy of polymers using polar and apolar liquids in the goniometry setup. Wu (1971) described a method called harmonic mean that can be suitable when goniometry measurements are made with high surface tension liquids. However, the contact angle of samples with high surface energy can not be measured reliably, mainly for polymers, because the liquid usually spread irregularly over the surface, but the wettability can be analyzed in a qualitative way.

In order to infer from mechanical and chemical changes occurred on CF by a specific treatment, the characterization of their surface is important to evaluate how efficient this treatment is. For chemical analysis, the spectroscopy techniques are widely used to characterize polymers. The use of light-based spectroscopy, like Fourier transform-infrared spectroscopy (FT-IR), is a challenge in the analysis of CF, because they intensively absorb electromagnetic radiation and the scattering can make it difficult to obtain good spectra from them. Thus, few authors have worked intensively with various FT-IR techniques to characterize CF (Morita *et al.* 1986; Graf *et al.* 1987; Ishida 1987; Ohwaki 1993; Boehm 1994; Ohwaki and Ishida 1995; Yang and Simms 1995).

Ohwaki (1993) characterized CF by some FT-IR techniques and X-ray photoelectron spectroscopy (XPS). It was possible to identify some chemical bonds on the CF surface with good sensibility by FT-IR analysis, and the results are in agreement with those obtained by XPS analysis. By varying some parameters

from FT-IR/attenuated total reflectance (ATR), such as the light polarization states, the crystal type and the beam incident angle, Ohwaki also verified an improvement of the signal/noise (S/N) ratio spectra. The improvement in the S/N ratio was better for small incident angles in non-polarized light, but it aims a deeper layer from the bulk sample (Ohwaki and Ishida 1995).

Jiang *et al.* (2015) have recently studied CF surface modified by electrophoretic deposition using FT-IR and other techniques. Despite of FT-IR spectra have indicated formation of C=O and C-O groups on CF surface, they used the transmission mode that is inappropriate to analyze surfaces. Samples prepared with KBr pellet are inadequate, because of its hygroscopic character that can introduce bands related to OH groups from humidity around 3300 and 1650  $\text{cm}^{-1}$ , interfering in spectrum interpretation. Therefore, it can be supposed that the analysis of CF surface through specific techniques could be promising.

Thus, this study was focused on the investigation of chemical contents on unsized and sized CF surfaces by FT-IR and goniometry. These techniques are useful and applied to some materials, being cheaper than XPS. By comparing already-known photoacoustic (PAS), ATR and the new technique universal attenuated total reflectance (UATR), it was possible to verify that each technique has an appropriate sensibility to identify some differences between these two types of fibers. Goniometry analysis was also employed to evaluate qualitatively the hydrophilic or hydrophobic characteristics of these CF.

## EXPERIMENTAL

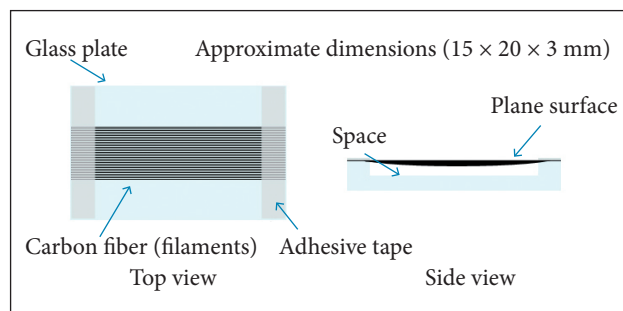
### RAW MATERIAL

Tows with 3,000 filaments of unsized and sized Torayca T300 CF have been used in this paper. The polymeric sizing coating of these CF is based on epoxy resin and it represents 1 wt%.

### GONIOMETRY

Unsize and sized CF were analyzed by goniometry using a 500-00 Goniometer Drop Image Advanced-2004 from Hamé-Hart. The contact angle measurements of the samples were performed just after placing a drop of deionized water with  $13 \pm 1 \mu\text{L}$  on the surface at room temperature and controlled relative humidity (40%). Samples were prepared in accordance with the illustrated scheme as shown in Fig. 1. This procedure was employed in order to make the surface as flat as possible to obtain enough reproducibility and achieve good qualitative results. Goniometry is widely used to analyze flat and continuous

surfaces. However, CF tows (3,000 filaments) have a non-planar and discontinuous surface, and it is difficult to make a quantitative analysis by this technique.



**Figure 1.** Sample of CF prepared for goniometry analysis.

### FT-IR ANALYSIS

The chemical analysis of the CF surface was made using the PAS accessory coupled to a FT-IR Spectrometer Spectrum 2000 – PerkinElmer as well as ATR and UATR accessories coupled in a Spectrum One FT-IR Spectrometer – PerkinElmer. For FT-IR/PAS analysis two distinct speed conditions were set up under nitrogen. The fast scan was made with a speed of 0.2 cm/s, 32 scans, 8 cm<sup>-1</sup> of resolution and spectral range from 4000 to 400 cm<sup>-1</sup>. The slow analysis has the same parameters, but a speed of 0.05 cm/s. FT-IR/UATR analysis was made using a ZnSe crystal in the region between 4000 and 550 cm<sup>-1</sup> and 40 scans. A pressure of 100 N over the sample was set up to improve the surface contact with the crystal. The FT-IR/ATR analysis was made using Ge crystals. Each of these two techniques operates with the following parameters: 40 scans, light beam incident angle of 45° and, in this case, the samples were spread over both faces of the crystal. For FT-IR/ATR/Germanium (Ge), the range of operation was from 4000 to 700 cm<sup>-1</sup>. The environmental condition of all spectroscopy analysis was 25 ± 2 °C and 45 ± 3% of humidity.

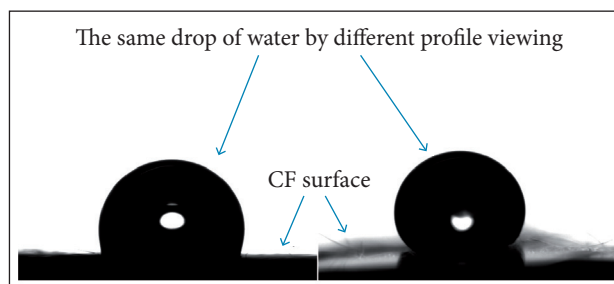
## RESULTS AND DISCUSSION

### GONIOMETRY CHARACTERIZATION

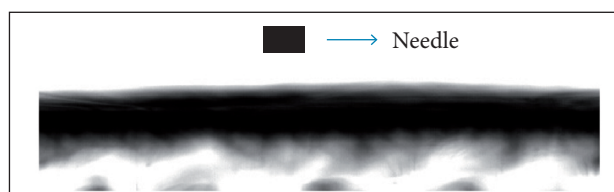
Drops of deionized water were deposited on the CF surface. The drop profile was taken for analysis in the parallel and transverse CF axis direction, in order to infer from the influence of the roughness of the whole sample (multiple filaments), as shown in Fig. 2. In the parallel direction, roughness tends to be smoother than in a transverse direction, because transversal filaments hold the drop by mechanical anchorage.

The geometric form of the drop, oval, is similar to the form visualized at the middle of the drop shown in Fig. 2a. These results are qualitative, because the measurement of the contact angle is compromised by the difficulty to obtain the baseline that is necessary to define the interface between the drop and the surface which allows measuring correctly the angle. The contact angle seems to be near to 90° in the parallel profile. On the other hand, the angle seems to be higher in the transversal profile, as shown in Fig. 2b. When unsized CF were compared with sized ones, the latter proved to be more hydrophilic, because the drop of water spread out the whole sample, as shown in Fig. 3.

These results obtained by goniometry technique are important in order to show that the sized CF have a surface energy higher than that of the unsized ones, despite having a low percentage in weight of polymeric sizing over the CF surface. With these results, the FT-IR techniques were applied in order to compare both fibers and identify some chemical bonds.



**Figure 2.** Profile of deionized water on the CF surface. (a) Parallel to the CF axis; (b) Transverse to the CF axis.



**Figure 3.** Drop of water deposited on sized CF surface.

### FT-IR ANALYSIS

The spectroscopic analysis of CF was carried out by three different FT-IR techniques starting by those considered near-surface, such as FT-IR/PAS. Other techniques, FT-IR/UATR and FT-IR/ATR/Ge, were also used in order to obtain good spectra from unsized and sized CF Toray T-300.

### PHOTOACOUSTIC DETECTION

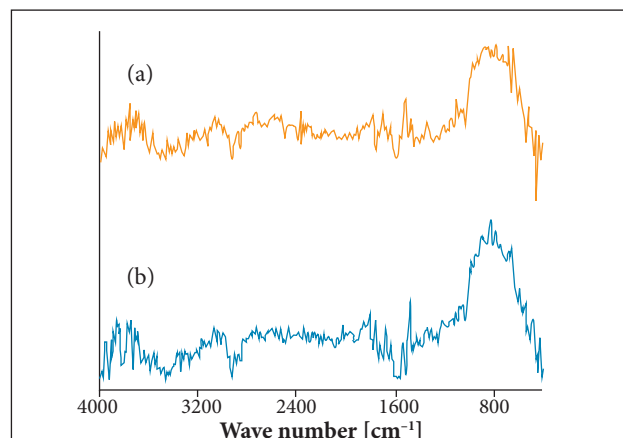
It is possible to obtain spectra in different degrees of depth with FT-IR/PAS. The control of the depth degree of IR beam

is reached basically by choosing the adequate scan speed. This technique proved to be effective in the analysis of opaque materials, such as the CF and most of its composites (Graf 1987). The first analyses of unsized (A) and sized (B) CF were performed at speed scan of 0.2 cm/s. This condition is considered the fastest and prior to detect chemical groups near to the surface. In this case, as can be seen in Fig. 4, the relatively low S/N ratio spectrum was obtained due to the absence of strong absorption bands, leading to a difficult assessment among spectra band with specific chemical species.

The results obtained by the speed scan of 0.2 cm/s led to the decision of carrying out the analysis with the slow speed scan of 0.05 cm/s. This choice was based on previous study performed in other researches, in which a better S/N ratio was obtained in the spectra produced by using a slower scan speed (Nogueira *et al.* 2007). Slow scan keeps the incident beam at the same region for a considerable time, contributing to the spectra accumulation, which becomes favorable to enrich the main spectrum (Stegge and Urban 2001).

The FT-IR/PAS (0.05 cm/s) spectra of unsized (A) and sized (B) CF are presented in Fig. 5. It was noted an attenuation of the noise, but the profile of the spectra presented the same appearance of those in the fast speed scan. It was not possible to clearly identify any chemical bonds on CF bulk or on their surfaces.

In our case, the procedure of obtaining FT-IR/PAS of CF was limited. The results were not satisfactory, mainly because the spectra had a low S/N ratio and did not show any difference between them. This result could be related to the fact that the PAS technique investigates more properly near-surface specimens, and the chemical content of CF can be placed in a depth between 1 – 4  $\mu\text{m}$ . Therefore, FT-IR/UATR was chosen

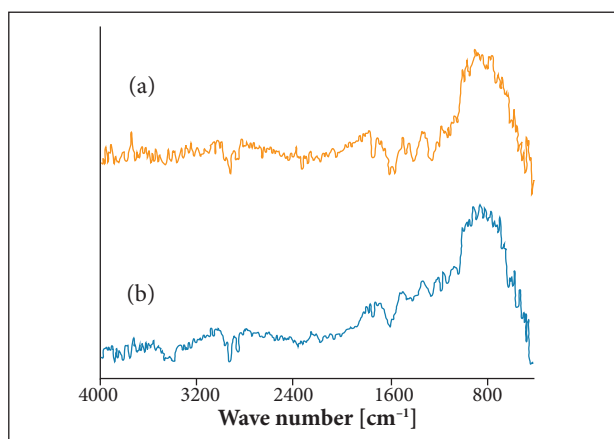


**Figure 4.** FT-IR/PAS spectra (0.2 cm/s). (a) Unsized CF; (b) Sized CF.

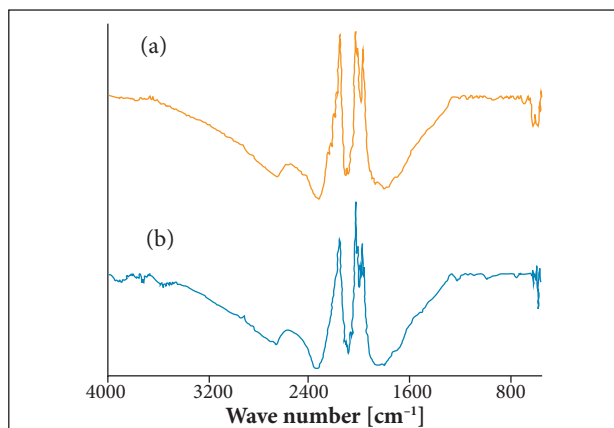
to be the next step to analyze the surface of both CF (Abidi and Hequet 2005; Sanches *et al.* 2008).

## UNIVERSAL ATTENUATED TOTAL REFLECTANCE

The FT-IR/UATR method does not need a considerable amount of samples, because the exposed surface area of the crystal is positioned to make the contact with the sample which has a diameter of 2 mm (Sanches *et al.* 2008). The FT-IR/UATR spectra of unsized (A) and sized (B) CF showed an anomalous spectrum in the region between 1220 and 3600  $\text{cm}^{-1}$ . Inverted bands with high intensities in the region between 1900 and 2200  $\text{cm}^{-1}$  were given, producing spectra in which the main baseline was easily lost, making it difficult a good analysis of the spectra, as shown in Fig. 6. These results lead to the conclusion that it was not possible to explore this technique, at least by the method of the direct analysis of CF. Thus, the FT-IR/ATR/Ge technique was employed to analyze CF in order to verify the chemical



**Figure 5.** FT-IR/PAS spectra (0.05 cm/s). (a) Unsized CF; (b) Sized CF.



**Figure 6.** FT-IR/UATR spectra. (a) Unsized CF; (b) Sized CF.

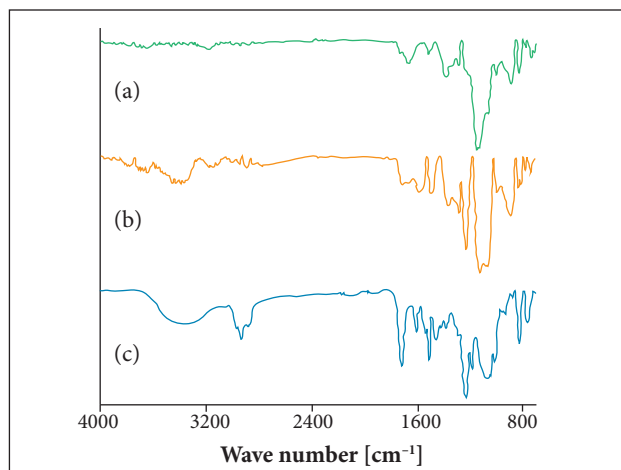
changes in the surface not observed by other techniques (Ohwaki 1993; Ohwaki and Ishida 1995).

The use of Germanium crystal as fiber samples holder was introduced in this part of the study aiming at the analysis of carbon layers close to the sample surface, due to its better efficiency presented against the use of the Thallium Bromo-Iodine crystal (KRS-5) (Urbaniak-Domagala 2012; Barbeş *et al.* 2014; Technical Note, 2004).

### ATTENUATED TOTAL REFLECTANCE

FT-IR/ATR/Ge was also employed to make a comparative analysis between unsized and sized CF. The advantage of this technique over FT-IR/UATR consists of a larger contact area of the crystal used in the present method (20 × 50 mm) in relation to the crystal size used in the UATR method, which uses a small crystal of 2 mm in the diameter. The refractive index of Ge crystal is 4.0, consequently, it allows to access near-depth surface up to 0.67  $\mu\text{m}$ , which can be useful for thin-films, composites and fibers (Urbaniak-Domagala 2012). This means that the FT-IR/ATR/Ge method permits a near-surface analysis in a large amount of points of the sample, enriching the spectrum. The FT-IR/ATR/Ge spectra of unsized (A) and sized (B) Torayca T-300 CF showed well-defined absorption band profiles and baselines, as shown in Fig. 7.

However, it is known the Torayca T-300 is not graphitized CF and some elements of the precursor can be presented in its structure. These CF could also have been undergone a surface treatment, even being sold as an unsized CF. This was evidenced by the observation of some bands, mainly in

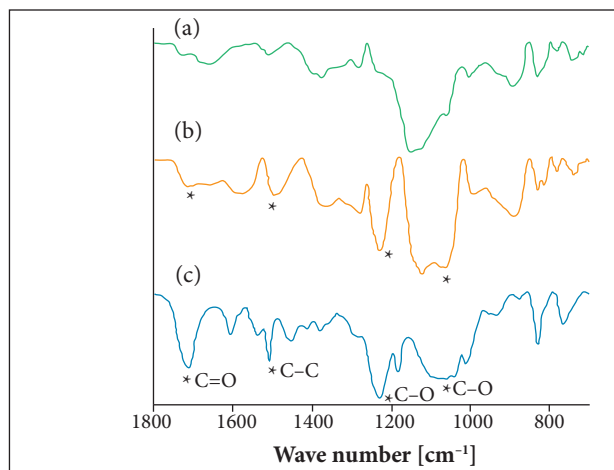


**Figure 7.** FT-IR/ATR/Ge spectra. (a) Unsized CF; (b) Sized CF; (c) FT-IR/UATR spectrum of residual substance removed from sized CF.

the region near 1200  $\text{cm}^{-1}$  of FT-IR/ATR/Ge spectrum (A), as shown in Fig. 7. Sized CF were characterized with the same technique and their FT-IR/ATR/Ge spectrum (B) was a little richer than that of the unsized CF. A pasty residual substance was extracted from sized CF (B) by immersion in acetone at room temperature. In this case, a little amount of sample was obtained because the quantity of sizing in the CF surface is near 1 wt%. However, this residue was enough to be characterized by UATR, as can be observed by the FT-IR/UATR spectrum (C) in Fig. 7. The region between 700 and 1800  $\text{cm}^{-1}$  is rich in absorption bands and some of them have their correspondent on sized CF.

The partial spectra from this region are presented in Fig. 8, in which there is a variation of approximately 5% in intensities of some bands from unsized (A) and sized (B) CF, mainly in the region between 700 and 1300  $\text{cm}^{-1}$ . The intensity of FT-IR/ATR/Ge bands is somewhat 10 times higher than FT-IR/UATR spectrum bands, at the same region.

It can be observed some intense bands in the UATR spectrum of the residue (C) and some of them can also be observed in sized CF (B), as shown in Fig. 8. The appearance of bands in the regions 1070 – 1150  $\text{cm}^{-1}$  and 1230  $\text{cm}^{-1}$  are probably related to the stretching of C–O bond, corroborating the presence of epoxy resin in CF, because this bond is presented in the basic structure of this resin. The band at 1500  $\text{cm}^{-1}$  can be attributed to the stretching of C–C bond, which is a characteristic of aromatic molecules and it can compose complementary structures of some resins, such as C=O bond, observed at 1710  $\text{cm}^{-1}$ , commonly present in modified epoxy resins and/or esters (Smith 1979;



**Figure 8.** FT-IR/ATR/Ge partial spectra. (a) Unsized CF; (b) Sized CF; (c) FT-IR/UATR partial spectrum of residual substance removed from sized CF.



Ohwaki 1993; Boehm 1994; Dutra *et al.* 1995; Ohwaki and Ishida 1995; Pamula and Rouxhet 2003).

## CONCLUSIONS

In this study, it was clearly observed in a qualitative way that unsized and sized CF showed hydrophobic and hydrophilic behavior, respectively, indicating goniometry as a quick and cheap technique for CF surface assessment. It was possible to verify the limitations and advantages of PAS, ATR and UATR techniques to analyze near-surface chemical groups of CF. The FT-IR/PAS is one of the most efficient techniques to do near-surface analysis. However, its response was not satisfactory to characterize CF, mainly due to difficulties in preparing samples and the depth of chemical content. As CF are filamentary, it is difficult to keep them in rest and

consequently the signal detection of PAS is compromised. A low S/N ratio was obtained, independently of the speed scan used. The characterization of CF by FT-IR/UATR was also compromised, in function of the appearance of a negative absorption in a large area in the middle of the spectra for both fibers. The reason why this phenomenon occurred must be deeply studied and other ways must be explored. The FT-IR/ATR/Ge was shown to be the most promising technique to analyze CF, despite the low level of relative intensities of some bands presented by CF. However, it was possible to verify that unsized CF (as received) had already been submitted to a surface treatment through comparative analysis. It was also possible to identify some chemical bonds present in both sized CF as in the residue removed from them. These results showed that FT-IR/ATR/Ge can be useful to the characterization of carbon fiber surface, mainly after the surface treatment made at the end of carbonization processes.

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