ASSESSMENT OF A HIGH TEMPERATURE RESISTANCE POLYIMIDE AS A SELF-SIZING POLYMER MATRIX FOR CARBON FIBER-BASED COMPOSITES

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ABSTRACT

In addition to the requirement of maximum fiber and matrix performance, fiber wetting by matrix and interfacial adhesion between the fibers and the matrix play a major role in attainment of high specific properties in structural composites. High performance thermoplastics such as polyetherimide (PEI) require high processing temperatures above 300°C and prolonged mold time to obtain adequate penetration of the matrix within fiber tows. In this research, a recently developed N-methyl-2-pyrrolidone (NMP) solvated polyimide (Tetrimide™, Tetramer Technologies LLC) was investigated as a self-sizing agent as well as the polymer matrix for carbon fiber-based thermoplastic composites. Mini-composite coupons were prepared by using T300 carbon fiber tow (Cytec Inc.) in NMP diluted polyimide solution. The superior heat resistance and mechanical properties of the resulting composite materials are reported.

1. INTRODUCTION

Since the early 1960s, there has been an increasing demand for materials that are stiffer and stronger yet lighter in fields as diverse as aerospace, energy, sports, and civil construction [1]. As far back as the ancient times, it was realized that it is difficult to attain the optimal properties and performance in one single material and thus the concept of combining different materials in an integral-composite material to satisfy the user requirements.

Carbon fibers have risen to the top of advanced engineering structural materials because of their excellent stiffness and strength and low weight (density). However, despite those excellent properties, the fibers need to get glued together with a matrix to form a composite. Thermoset matrices include epoxy, phenolic, and furfuryl resins, whereas thermoplastic matrices include polyetheretherketone (PEEK), polyethersulfone (PES), polyphenyl sulfide (PPS), polyetherimide (PEI), and polyimide (PI). Thermosetting matrices are more widely used in composites because of their ease of fabrication into composite parts because they have low viscosity prior to curing and uniformly wet the fibers. In contrast, thermoplastic matrices have high viscosities and require high processing temperatures, usually above 300 °C. However, there is increasing use of thermoplastic

SAMPE Conference Proceedings. Charlotte, NC, May 20-23, 2019. Society for the Advancement of Material and Process Engineering – North America.

matrices because they have superior toughness and suitable stiffness in additional to reduced cycle times and ability to melt and reform [2].

Apart from the properties of constituent materials (fiber and matrix), structural performance of composites is also strongly dependent on the interfacial bonding between the matrix and the fiber [3,4]. Unfortunately, the adhesion of carbon fibers with the many engineering thermoplastics is poor [5]. To enhance the interfacial strength between carbon fibers and the matrix, surface of the carbon fiber is oxidized and sizing is applied. These sizing compounds have the chemistry to interact with both the fiber and the matrix, thus improving the matrix-fiber adhesion and increasing the mechanical properties of the composite part.

Because thermoplastic structural composites are processed at high temperatures, the thermal stability of the matrix and any sizing compounds set the upper limit of the processing window. Therefore, the sizing compound used must have adequate thermal stability to enable sufficiently high molding temperatures for a lower viscosity melt that can penetrate the fibers tows during part fabrication[6]. Many of the available sizing compounds are suitable for low temperature molding, which is typically experienced during use of thermoset matrices and commodity thermoplastics.

Tetramer Technologies LLC (Pendelton, SC) has developed a new polyimide coating compound that has excellent thermal stability. Tetrimide™ high temperature polyimide coatings possess superior thermal stability, hydrolytic stability, and ease of application compared to current commercial polyimide fiber coatings. Two grades of such polyimides have been optimized for potential commercial applications in harsh environment fiber optic coatings using structure/property relationships and the design of unique molecular architectures. These new polyimides were evaluated as fiber sizing compounds and self-sizing thermoplastic matrix for carbon fiber-based thermoplastic composites.

2. EXPERIMENTATION

2.1 Materials and Processing

Two grades of polyimide solutions in NMP solvent were used throughout this study: Tetrimide-ICP solution and Tetrimide-SCP (produced in-house by Tetramer Technologies LLC, Pendleton, SC). For reinforcing material, PAN-based Thornel T300 (Unsized, untreated) carbon fibers were used.

2.1.1 Film formation

The supplied polymer solutions were evaluated for their thermal stability and tensile properties by casting them into films. As received solutions were poured in a glass petri dish, and the solvent was evaporated. After 24 hr at room temperature, the films were further dried in the oven at 90 ºC to remove residual solvent. Some were further heat-treated at 250 °C.

2.1.2 Mini-composite preparation

As illustrated in Fig. 1, a single tow of unsized carbon fibers (T300) was passed through a multi-bath coating device to self-size and coat the fiber tow with polyimide polymer solution. The polyimide solutions were diluted to 13 V/V% with NMP solvent to reduce the viscosity and improve the impregnation of resin into a tow. To avoid any dry spot formation due to fiber

agglomeration, air knife was used to separate the fibers prior to entering the first solution bath and the tow was pulled through two more solution baths of 40 V/V% polyimide in NMP at the rate of about 5 mm/s. After wetting of the carbon fiber tow, it was kept under vacuum for 12 hr and later in the oven at 70 °C.

Figure 1 Set up for the wetting and infusion of the fiber tow with polyimide matrix

2.2 Thermal and Microstructure Properties Analysis

Thermogravimetric analysis (TGA) analysis of the films was performed using a Perkin-Elmer Pyris TGA from 30 to 600 °C at 10 °C/min in nitrogen atmosphere.

Scanning electron microscopy was conducted using a SEM-Hitachi S4800 to analyze the microstructure of cryogenically cut cross-section surfaces of the fiber-polyimide composites. An Olympus BX60 optical microscope was used to assess fiber volume fraction and distribution in the composites using polished samples of the composites.

Fourier transform infrared spectroscopy (FTIR) analysis was conducted using a Nicolet ATR-FTIR on polymer film treated at 120 ºC.

2.3 Tensile Properties Analysis

Tensile testing of cast polymer films was conducted following the ASTM D638-10 procedure using dog-bone specimen (type V) cutting die. For the micro-composites, 4-inch-long specimens were cut. Epoxy end-tabs (approximately 1 inch long) were further applied on the samples for adequate gripping during tensile tests that were conducted at a cross-head speed of 0.25 cm/min (Applied Test Systems Inc., Series 900).

2.4 Surface characterization of the reinforcing fibers

PHI Versa Probe III scanning XPS microprobe with beam size of 10 micron was used to determine the O:C ratio on the surface of carbon fiber used in this study. As received fibers were used for the scanning. Element percentage was calculated using Multipak (Physical Electronics) software.

Carbon 1S peak appears around 284 eV and Oxygen 1S peak appears around 531 eV. Area under peak is calculated to find the % concentration of carbon and oxygen.

3. RESULTS AND DISCUSSION

3.1 Thermal stability of base PI matrix

Figure 2 displays TGA thermograph of Tetrimide SCP resin cured at 120 and 250 ºC. When resin is cured at 120 ºC, there is a solvent loss and degradation around 300 ºC. However, if the same resin is cured at 250 ºC, SCP had minimum mass loss upto 550 ºC, which indicate that Tetrimide SCP polyimide has good thermal stability. This is important property for sizing of carbon fibers that are processed with thermoplastic matrix that require high temperature for resin impregnation.

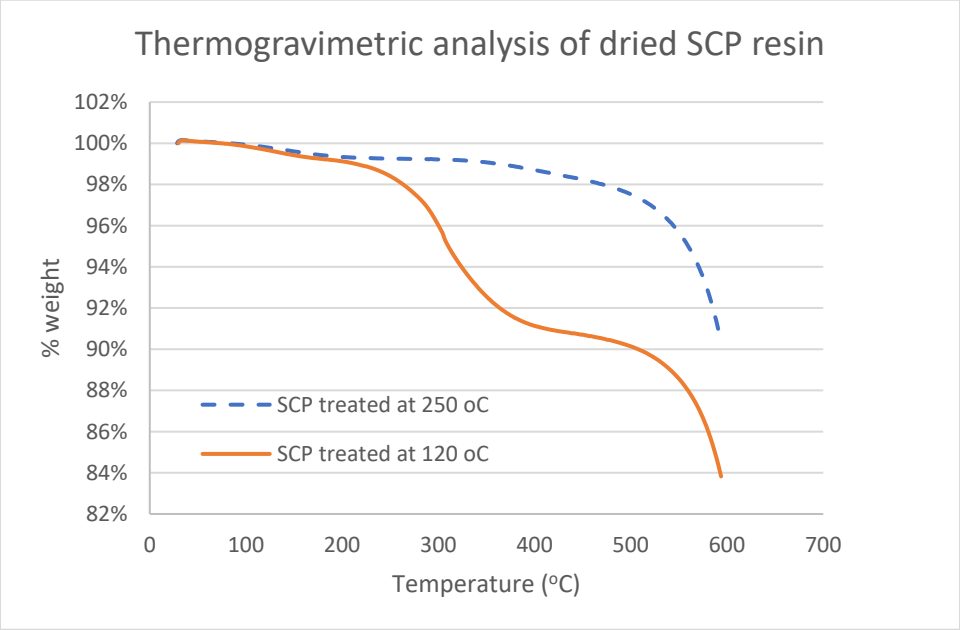


Figure 2. TGA thermograph of Tetrimide SCP resin cured at 120 and 250 ºC

3.2 O:C ratio on surface of the carbon fiber

Fig 3 shows the XPS spectra for Thornel T300 carbon fiber. There is main graphitic C(1s) peak at 284.5 eV. The peak at 533 eV is for oxygen. The calculated O:C ratio for T300 was 0.1. This is consistent with the values reported in literature for surface-untreated carbon fibers[7]. The observed oxygen content is attributed to adsorbed moisture on the carbon fiber surface since typical shoulder peak of C-O bond is absent[7].

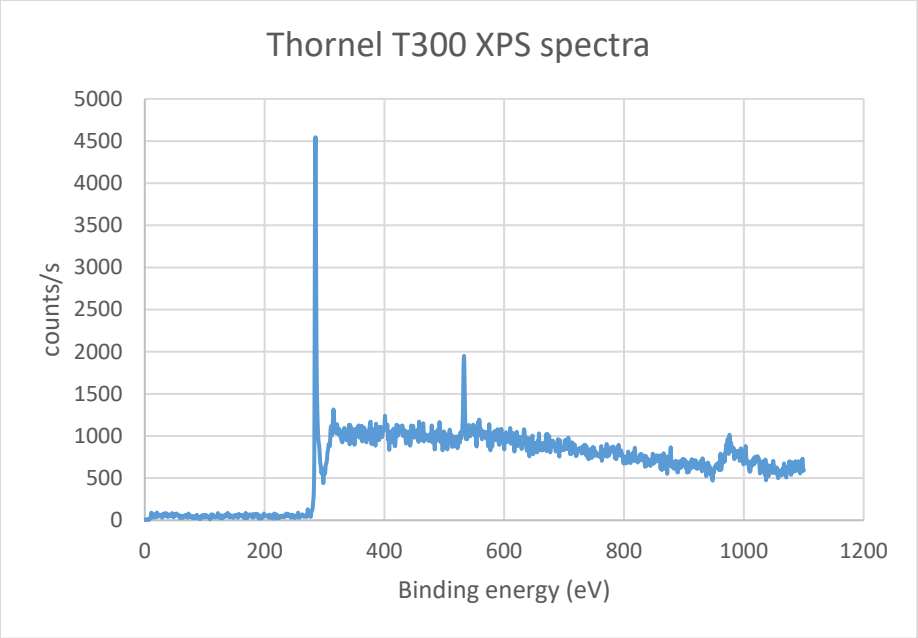
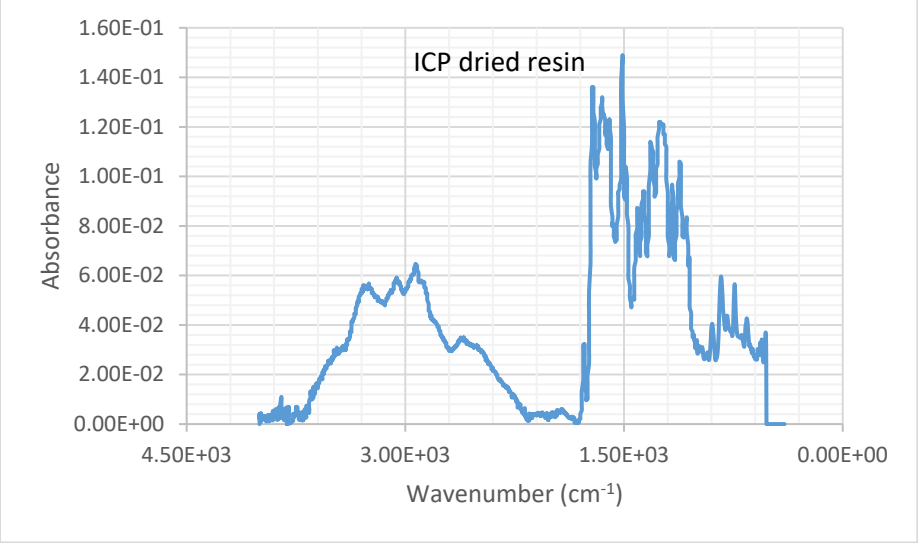


Figure 3: XPS spectra for Thornel T300 carbon fiber

3.3 Microstructure

Figure 4 displays FTIR spectra of Tetrimide-ICP and Tetrimide-SCP solutions. Broad peak between 3000 and 3600 cm^{-1} was observed, with a peak height of 3:1 (relative to carbonyl peak) showing the presence of –COOH group in ICP when compared with the relative peak height of 8:1 for SCP. This free carboxylic group may be responsible for tolerance to moisture of ICP. During solvent evaporation in film casting process, SCP turned into turbid film while left at ambient atmosphere for solvent evaporation, which became clear after solvent evaporation.



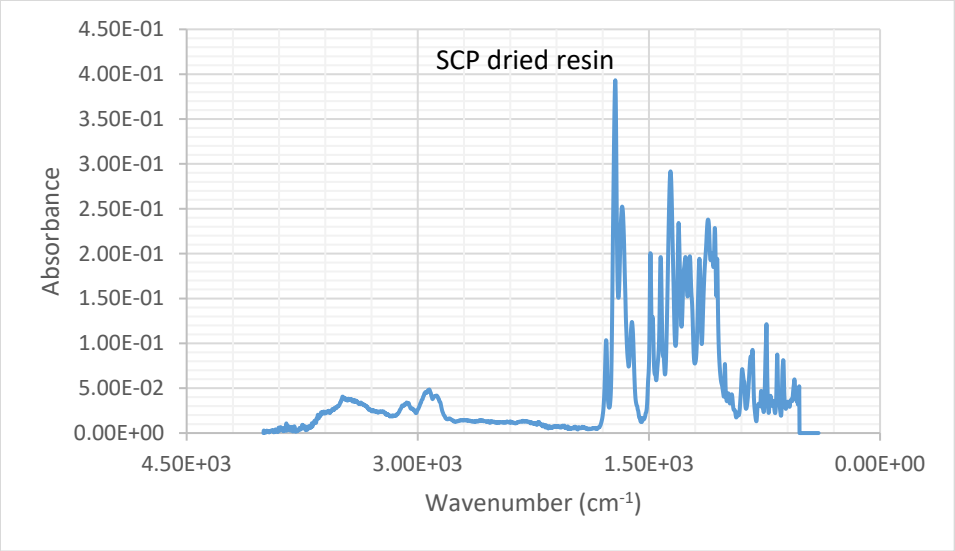


Figure 4 FTIR spectra of Tetrimide-ICP and Tetrimide-SCP.

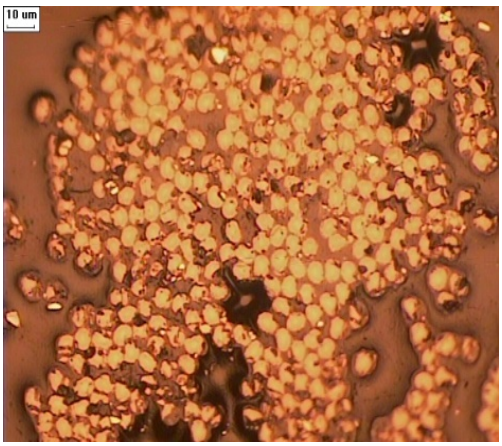


Figure 5 Optical image of cross section of polished mini composite sample

A polished optical cross-section of the CF/PI composite is displayed in Figure. 5, which confirms an adequate level of PI coating on the fibers. Overall, regions of resin-rich and resin-poor areas are visible due to the lab-based protocol using a semi-continuous unit. Volume fraction of fibers in mini-composites with vacuum bagging ranged from 55% to 64 vol% whereas composites produced without vacuum bagging contained 47 to 58 vol% fiber content in the fiber-rich regions. These percentage were similar in both cases ICP and SCP. However, several regions were devoid of any fibers (i.e., 0% fiber content), largely due to the lab-scaling techniques. Since mini-composites with vacuum bagging has less resin material in final composites, it shows higher tensile strengths. Overall, the fiber content was estimated at about 30-35 vol% only. Figure 6 shows SEM micrographs of mini-composites formed (a) without and (b) with vacuum bagging respectively.

These micrographs confirm the fact that vacuum bagging enhanced the impregnation of the resin in the tow.

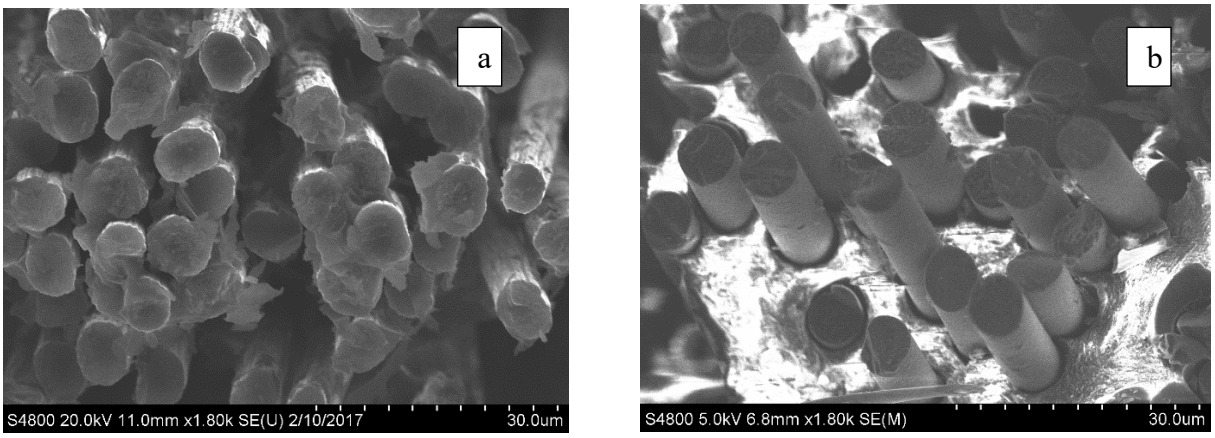


Figure 6:SEM Micrographs of carbon fiber/polyimide mini-composites processed; (a) without vacuum bagging and (b) with vacuum bagging

3.4 Tensile properties of PI matrix

Table 1 displays tensile properties of ICP and SCP resin films. It was observed that curing at 250 ^{0}C imparts high tensile strength to the polymer. Data shows that ICP has higher tensile strength than SCP. It was also observed that drying SCP resin in vacuum oven does not form any bubbles on surface when cured at 250 ^{0}C, whereas those dried at atmospheric pressure forms bubbles hinting the presence of residual solvent in it, which was then confirmed with TGA analysis. Thus, lower values of tensile strength properties in case of resin dried at 90 ^{0}C can be attributed to presence of residual solvent.

3.5 Resin impregnation and fiber adhesion to the matrix

Figure 7 shows the resin impregnation for ICP resin(a) and SCP resin(b) inside the tow. This also confirms the fact that there is uneven distribution of resin inside the carbon fiber tow. SEM images in fig.7 also show the fiber pullout has occurred during cryogenic breaking in both cases and that indicates the poor bonding between the matrix and the reinforcement, which may be due to untreated surface of the fiber as observed with the low O:C ratio from the XPS data in Figure 3.

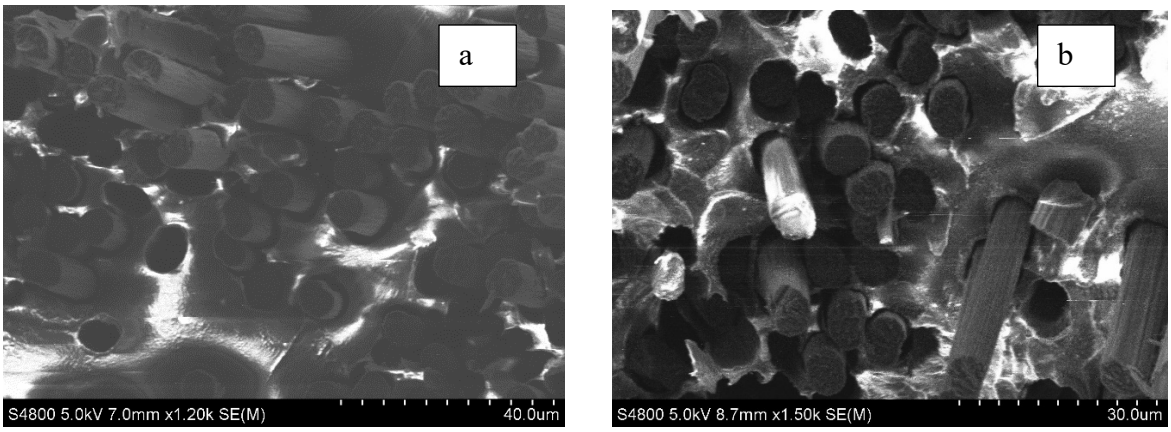


Figure 7: SEM micrographs of the minicomposites cured at 120 C and impregnated with a) ICP resin b) SCP resin

3.6 Tensile properties of mini-composites

Table 2 displays the tensile properties of minicomposites formed by resin-infused Thornel T300 (12K) carbon fiber tow. Mini-composites were processed at different temperatures and vacuum bagging. Vacuum bagging minimized bubbles formed during the wetting process and final composites were found to have less defects. The final curing temperature also enhanced the tensile properties of mini-composites by removing residual solvent from the cured resin. The highest TS of mini composites with vacuum bagging of 742 MPa is still small when compared to commercial composites that have a tensile strength between 1600 and 1800 MPa [8]. The smaller TS is attributed to lower volume fraction attained in our batch process in contrast to commercial composites that typical have over 60 % carbon fiber volume fraction.

Table 1 Tensile properties of the polyimide films after drying at 90C and subsequent 250 °C cure. Tensile properties of commercial grade ULTEM 1000 PEI is also displayed for comparison.

1	**Drying and Curing**	**Tensile Strength (MPa)**	**Tensile Modulus (GPa)**
ICP	90ºC (24 hr)	64±10	2.8
ICP	90ºC (48hr) - 250ºC (2hr)	166±18	2.5
SCP	90ºC-24hr	58±5	2.9
SCP	90ºC (48hr) - 250ºC (2hr)	118±12	2.1

PEI	Commercial sheet [9]	113-117	3.3-5.9

Table 2:Tensile properties of composites derived from self-sized polyimide resin.

Matrix	**Vacuum bagging**	**Processing method**	**Tensile Strength (MPa)**	**Tensile Modulus (GPa)**
ICP	No	120ºC -24hr 250ºC -2hr	569±91	25.3
ICP	Yes	120ºC -24hr 250ºC -2hr	742±354	31.1
SCP	No	50ºC -12hr 90ºC -12hr 250ºC -5hr	413 ±82	18.9
SCP	Yes	50ºC -12hr 90ºC -12hr 120ºC -5hr	466±84	20.1

4. CONCLUSIONS

In this study, two new polyimide Tetrimide^{TM} (Tetramer Technologies LLC) ICP and SCP were investigated as a potential self-sizing compound and polymer matrix for carbon fiber-based composites. Although composite strengths comparable to commercially produced composites were not obtained, this was largely due to dry spots, uneven resin distribution and lower adhesion between the resin and the untreated fiber. The present results establish the potential use of these resins as self-sizing matrix for carbon-fiber composites. Due to high thermal resistance shown by these resins, they also can be used for sizing for carbon fibers to be impregnated in thermoplastic resins where resin impregnation takes place at higher temperatures.

5. ACKNOWLEDGEMENT

This material is based upon work supported by the National Science Foundation under Grant No. IIP-1330498 and made use of ERC shared facilities supported by the National Science Foundation under Award Number EEC-9731680. We would also like acknowledge Mrs. Kim Ivey for help with FTIR and Mr. George Wetzel for helping with XPS.

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