Development of Carbon Nanotube Epoxy Matrix Composite Coatings for Aerospace Structural Applications

[1]Maria Sibtain, [2]Usama Zaheer, [3]Atiq ur Rehman, [4]Tayyab Subhani
Institute of Space Technology
Islamabad, Pakistan
[1]mariyasibtain@ymail.com
[4]drtayyabsubhani@gmail.com

***Abstract—* The composite coatings of carbon nanotubes (CNTs) reinforced in epoxy matrix were developed on aluminum alloy plates by hand lay-up technique. The underlying aim was to protect the aerospace structures of aluminum alloy against space environment. CNTs were functionalized through acid-treatment for better dispersion in epoxy matrix after mechanical mixing. The functionalized and un-functionalized CNTs were characterized using SEM. The mechanical performance was evaluated by hardness test. For better adhesion of the composite coating, the substrate Aluminum plates were both sand blasted and shot-peened at three different angles of 30^o, 60^o and 90^o. It was found that the increased surface roughness through sand blasting and shot peening increased the adhesion of composite coating with aluminum plates.**

***Keywords—* : composite coating, carbon nanotubes, epoxy, hand lay-up**

1. INTRODUCTION

Since the introduction of nano reinforcements, much importance has been gathered by polymer matrix composite coatings reinforced with nano particles [1]. According to the demands of particular application, many fillers are being used to make nanocomposite coatings e.g. NDs, grapheme, CFs etc. [1],[2]. Out of numerous fillers, CNTs have managed to gather significant amount of attention as structural reinforcements because of their unique mechanical, electrical and thermal properties. Different types of CNTs are available e.g. Single-walled carbon nanotubes (SWCNTs), Double-walled carbon nanotubes (DWCNTs), Multi-walled carbon nanotubes (MWCNTs) etc. MWCNTs consist of numerous concentric graphite tubes. They exhibit extraordinary mechanical as well as electrical properties that caused the scientists to be more interested in their potential uses. A single MWCNT carries the tensile strength value of around 63 GPa.[3],[4] This remarkable mechanical strength, unique atomic structure, very high aspect ratio, good electrical conductivity and flexibility of MWCNTs allow them to be used as promising reinforcing materials to integrate in epoxy matrix. The basic reason behind the outstanding mechanical performance of MWCNTs is the high bond strength of carbon-carbon double bond(C=C) [5]. However, this high aspect ratio and huge surface area of CNTs make them susceptible to agglomeration, leading to inhomogeneous dispersion of MWCNTs into the polymer. Different techniques have been studied and compared for better dispersion of CNTs into the matrix.[6]

The major problems that we face regarding nanocomposite coatings include the requirement of good interfacial adhesion between tubes and polymer matrix, uniform dispersion of nanotubes into the matrix and adhesion of the coating with the substrate material. In such conditions, the functionalization of CNTs help in improving interfacial adhesion and also it aids the dispersion into the matrix due to strong interaction with the dispersion medium. Increased surface roughness of substrate material can help to improve the adhesion of coating with the substrate [3].

Currently, Indium tin oxide (ITO) coating is being used mainly as a transparent, conductive material for mobile information devices, touch panel PCs and on the outer structures of satellites as a part of multi-layer insulation (MLI) system[6]. It uses indium, a metal which is facing the problem of unstable supply due to international affairs and also the concern of depletion. Another issue with ITO film is that it cannot stand bending because of its brittle nature. This makes it difficult to use for the development of high strength, flexible coatings that will be able to survive bending, folding and severe space environment. Therefore, an alternative transparent conductive material is needed to replace ITO coating. The CNTs transparent conductive coatings come in handy to resolve these issues that we face while dealing with ITO coatings[7][8].

Improved hardness, wear resistance, high thermal stability, good electrical properties and flexibility makes this CNTs reinforced coating reliable to be used in satellite structures[9]. The dispersion and interfacial adhesion of coating is achieved through functionalization[3] but for the purpose of adhesion between coating and the substrate, different surface roughening methods can be used e.g. surface roughening using steel brush, sand blasting, shot peening etc.[10] Peel off adhesion testing is used to measure the adhesion of coating with the substrate material[11]. Highest adhesion is recorded for sand blasting while minimum adhesion is achieved in unprocessed sample of substrate[9]–[11].

Different coating techniques are available to successfully synthesize CNTs reinforced nanocomposite coatings e.g. thermal spray coatings, Air spray gun coating, Simple Hand lay-up technique etc.[9], [12], [13]. Better coating quality is recorded for thermal spray coating methods than simple hand lay-up technique[12]–[14].

In this research, MWCNTs are incorporated into the epoxy by simple mixing, followed by sonication with the aim of achieving good mechanical properties in the resulting nanocomposite coating[2], [3], [13]. This combination of conductive CNTs filler and polymer matrix helps in defeating the limitations of brittleness and poor mechanical properties that we face with ITO coatings[4], [15], [16]. The coating is characterized using Scanning electron microscope (SEM) and different mechanical testing methods i.e. Hardness testing, Peel off adhesion test etc. to measure and analyse the properties of coating which permits the beginning of a wide range of applications depending upon the mechanical response of the composite coatings [3], [17]–[20]

2. MATERIALS AND EXPERIMENTATION:

2.1. Materials:

The Epoxy resin, Hardener and Aluminum alloy 6061 used in this work were provided by Space and Upper atmosphere Research Commission of Pakistan (SUPARCO). 2mm thick sheets of Al alloy was cut into samples of size 15 x 4 cm with the help of Meta cut.

MWCNTs used in the research were obtained from NCP, Islamabad. They were having purity of 95%, length 20-50 µm and diameter in the range of 80 to 100 nm.

For functionalization of MWCNTs, Sulphuric and Nitric acids (H_2SO_4 and HNO_3) were taken from Institute of Space Technology, Islamabad.

2.2. Experimentation:

2.2.1. Substrate preparation:

The Al sheets were cut to make different samples for adhesion and hardness test. One sample was kept un-processed as reference sample. For the purpose of better adhesion between coating and substrate, rest of the Al samples were subjected to different surface treatments to increase their surface roughness. Samples were shot peened and sand blasted at three different angles i.e. 30^o, 60^o, and 90^o. Surface of one sample was roughened using the emery paper of 120D.

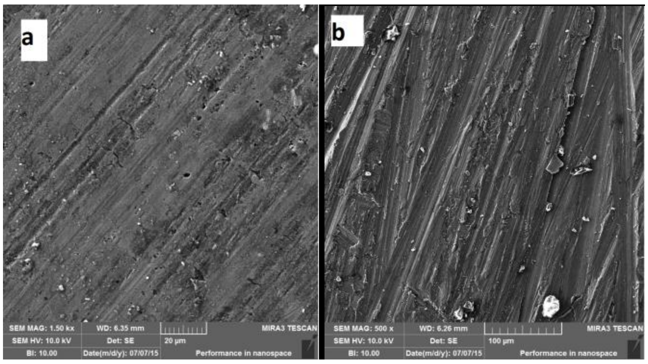


Figure 01: SEM images of surface of (a) unprocessed Al sample and (b) Al sample roughened using emery paper

The basic purpose of taking these images is to see the difference in the surfaces of different samples.

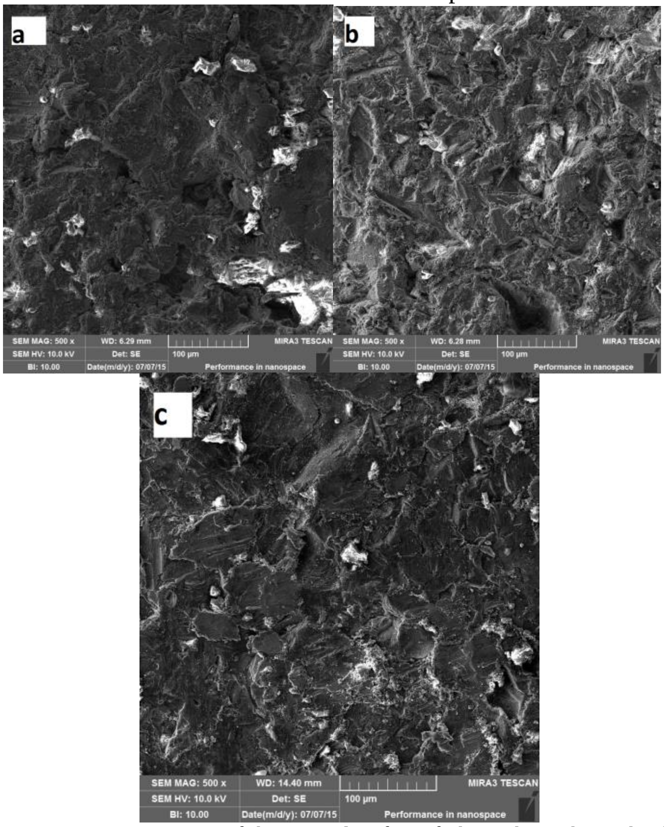
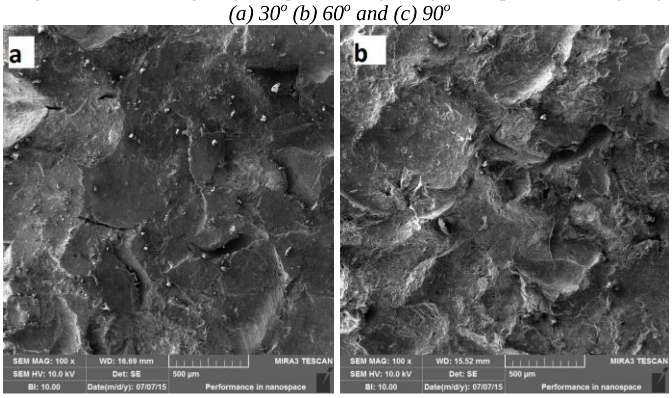


Figure 02: SEM images of shot peened surface of Al samples at the angle of (a) 30^o (b) 60^o and (c) 90^o



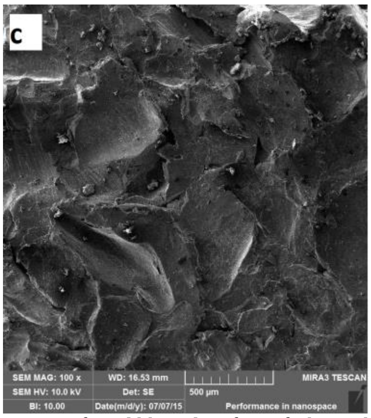


Figure 03: SEM images of sand blasted surface of Al samples at the angle of (a) 60^o (b) 30^o and (c) 90^o

2.2.2. Functionalization of CNTs:

As received 1 gram of MWCNTs were suspended into 30ml mixture of conc. H_2SO_4 and HNO_3 (3:1). The suspension was stirred and heated at 120^{o}C. 500ml distilled water was added to above prepared suspension. The resultant black solid solution was cooled at room temperature. At this stage pH was 2, which shows it was highly acidic. After cooling the black solid solution to room temperature, it was filtered and then washed vigorously with distilled water to neutralize it until pH around 7. The collected solid was then dried.

2.2.3. Synthesis of Nanocomposite coating:

The nanocomposite coating was prepared using the method of sonication. For the purpose of better dispersion of MWCNTs into the epoxy matrix, the CNTs were first treated with a mixture of Sulphuric and Nitric acid (3:1) for the deagglomeration of nanotubes in the matrix. The acid treated CNTs (1 wt.%) were then mixed with epoxy by manual stirring and sonicated for about 2.5 hours at room temperature. After sonication, hardener was added to Epoxy-CNTs mixture by 30 wt.% and was stirred constantly.

Keeping in view the cost effectiveness, the author used the hand lay-up technique to coat the Al sheets followed by vacuum assisted resin pressing technique. (The coating is applied to the substrate after a few minutes of adding hardener into Epoxy-CNTs mixture[21], [22].)

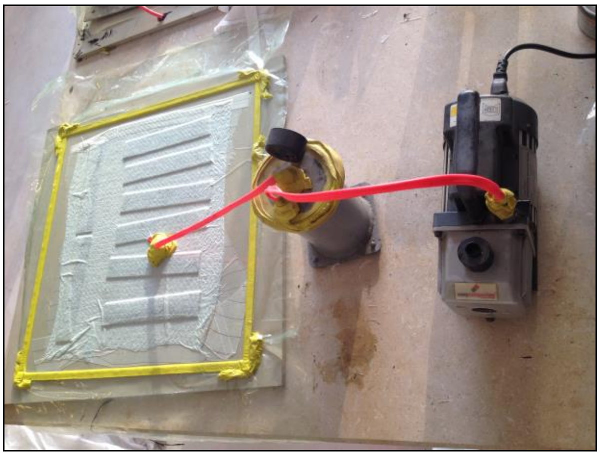


Figure 04: Experimental set up for coating using hand layup method followed by vacuum assisted resin pressing technique

2.2.4. Hardness Testing:

Hardness testing of composite coating was carried out using Vickers Hardness tester. Load was kept constant at 10g and the dwell time of 15s. Each sample was tested at three different locations and the mean value was taken as hardness of the particular sample.

2.2.5. Adhesion Testing:

The adhesion of the specimens was investigated qualitatively by Scratch test. Each sample was scratched using a sharp pointed object, using normal loading. Multiple scratches were made over the first scratch until the coating peeled off completely of that particular area. The number of scratches were noted till failure. The same process was carried out at three different points over each composite coated sample surface for the purpose of precision of results.

2.3. Nomenclature:

TABLE 01: THE NOMENCLATURE OF SAMPLES

Sample symbol	Nature of the Sample
UP	Unprocessed substrate surface sample coated with composite coating
SR	Surface roughened substrate coated with composite coating
S30	Substrate sand blasted at 30^o coated with composite coating
S60	Substrate sand blasted at 60^o coated with composite coating
S90	Substrate sand blasted at 90^o coated with composite coating
P30	Substrate shot peened at 30^o coated with composite coating
P60	Substrate shot peened at 60^o coated with composite coating
P90	Substrate shot peened at 90^o coated with composite coating

3. RESULTS AND DISCUSSION

3.1. SEM:

3.1.1.Un-functionalized CNTs:

These images were taken at different SEM magnifications.

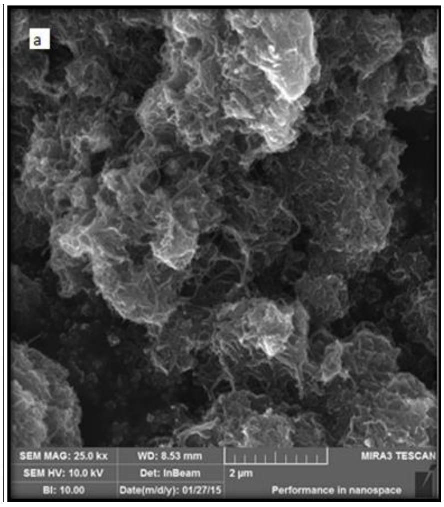


Figure 05: SEM image for un-functionalized CNTs

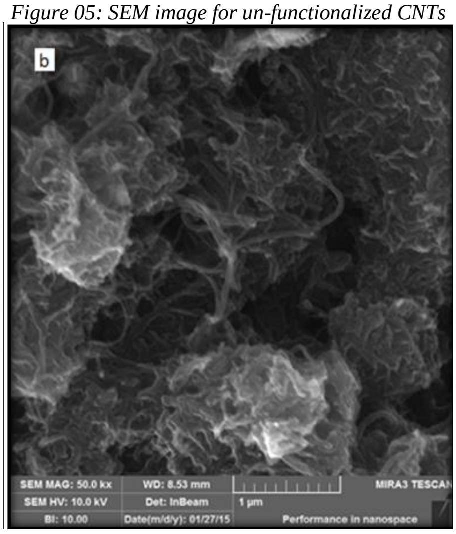


Figure 06: SEM image for un-functionalized CNTs

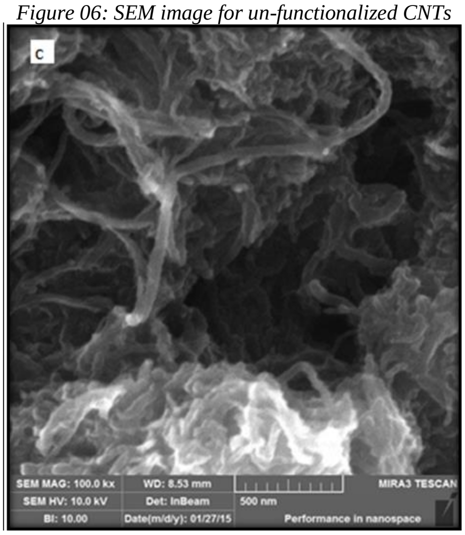


Figure 07: SEM image for un-functionalized CNTs

For the un-functionalized CNTs, the SEM images showed unclear clouds of CNTs. These SEM images were taken at three different magnifications i.e. (a) at 25kx (b) 50kx and (c) 100kx.

3.1.2. Functionalized CNTs:

To see the difference between functionalized and un-functionalized MWCNTs, these results are also taken at three different magnifications i.e. (a) at 25kx (b) 50kx and (c) 100kx.

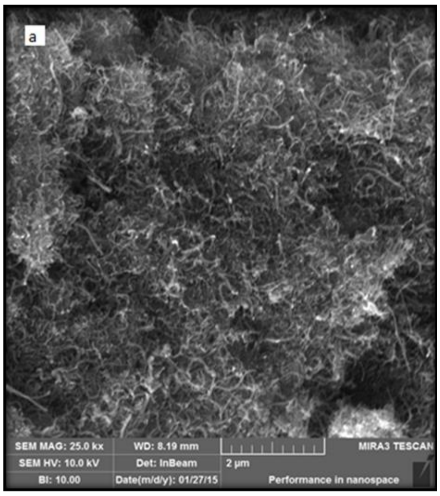


Figure 08: SEM image for functionalized CNTs

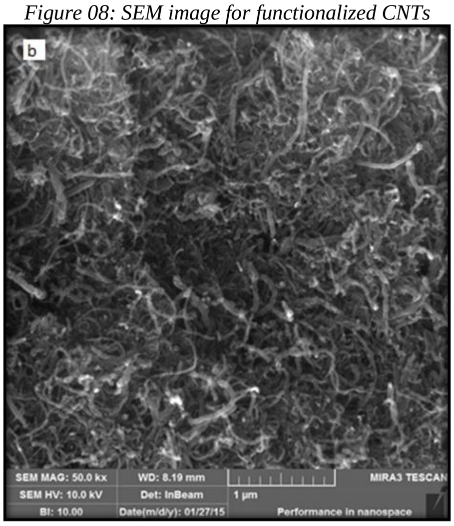


Figure 09: SEM image for functionalized CNTs

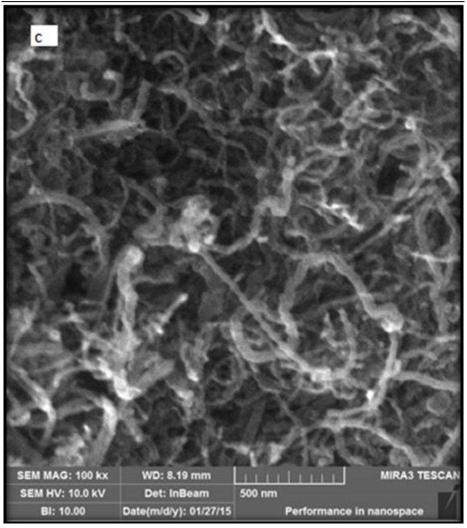


Figure 10: SEM image for functionalized CNTs

The results for functionalized CNTs showed the clear difference. After Functionalization, the CNTs got aligned, their length got shorter and they became more clear and visible unlike the unclear and cloudy SEM images of un-functionalized CNTs.

3.2. Dispersion of CNTs into the matrix:

Following images show the homogeneous dispersion of CNTs into epoxy which was the most important requirement because the final network of CNTs into the matrix decides the properties of the composite coating.

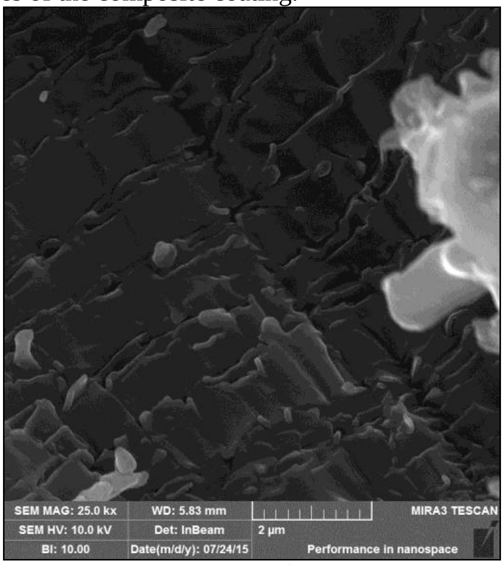


Figure 11: Dispersion of Cnts into epoxy

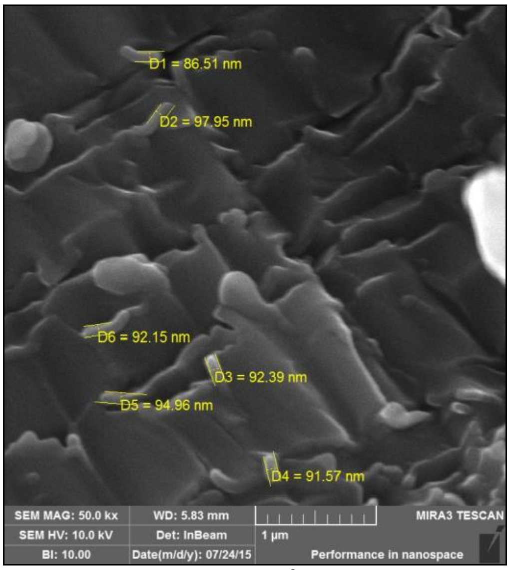


Figure 12: Dispersion of Cnts into epoxy

3.3. Hardness:

Increase in the hardness value was noted after the introduction of CNTs into the polymer matrix. Increased coherence of the CNTs/Epoxy mixture, due to strong linkages between CNTs and epoxy matrix at the interface, is the reason for the increased hardness of the mixture. These linkages at interface hinder the movement of polymer molecules and increases the resistance to scratch or indentation, hence results in increased hardness as shown in table.

TABLE 02: HARDNESS RESULTS

Sample type	Vickers Hardness (HV)
Neat Epoxy	19
CNT reinforced Epoxy over UP sample	22
CNT reinforced Epoxy over SR sample	23.05
CNT reinforced Epoxy over S30 sample	24
CNT reinforced Epoxy over S60 sample	22.75
CNT reinforced Epoxy over S90 sample	23
CNT reinforced Epoxy over P30 sample	23
CNT reinforced Epoxy over P60 sample	25
CNT reinforced Epoxy over SP90 sample	25.25

3.4. Adhesion:

The adhesion of the coating was increased with the application of different surface treatments on the Al samples. Least adhesion was recorded for the UP sample while the maximum adhesion was shown by sample P90^{o}. The reason behind this is the increased mechanical interlocking between the substrate and the coating. This mechanical interlocking is due to the presence of peaks and velleys formed on substrate surface deformation on the substrate surface, caused by steel shots, due to shot peening process. This mechanical interlocking holds the coating over the substrate and increases its adhesion, as shown in following figure.

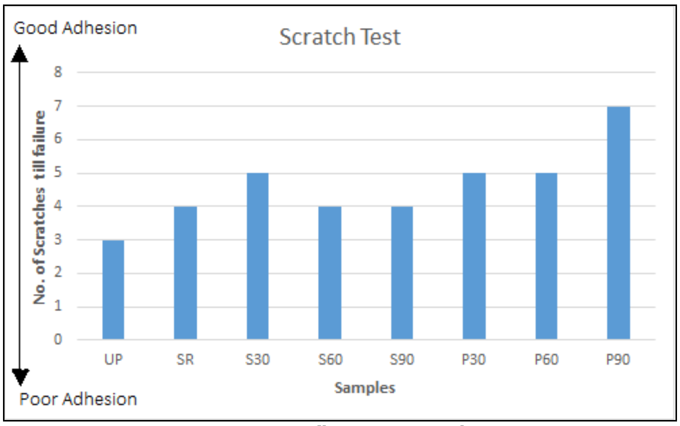


Figure 13: Adhesion test Results

4. CONCLUSION

Functionalized CNTs show better dispersion because of their short length than un-functionalized CNTs. They show less agglomeration during mixing and hence show better dispersion in epoxy matrix. And good dispersion of CNTs in the epoxy increases its mechanical properties e.g. hardness, due to the presence of high strength carbon nanotubes in the polymer matrix.

Good scratch resistant composite coating is obtained having the improved hardness and good retention of CNTs into the matrix.

Before the application of coating, surface treatments like shot-peening at optimum angles enhance the adhesion of the coating with the substrate and hence improves the life of the product.

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