Composite Materials Reinforced with Carbon Nanotubes

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Abstract

The main goal of this work is to overview the potentiality of the carbon nanotubes (CNT) in the reinforcement of composite material, with polymer and cementitious materials. The objectives of this work are: (i) to show new techniques and procedures to manufacture CNT nanocomposite materials, (ii) to present the main advantages and major drawbacks in the usage of these nanocomposites and (ii) to present in this way the highest degree of information on CNT-based materials, filling the gap in knowledge on these new materials.

Throughout this study, the evaluations has bigger emphasis on the modifications triggered by the presence of CNT in the polymers and cement matrices. In order to improve the interaction between the CNT and the cement paste as well as the CNT dispersion in the matrix, different processes were taken into account and described herein. In order to compare the main properties exhibited by the CNT based composites, reference was made to several works connected out by other researchers. Laboratorial tryouts were carried out in order to measure fresh and hardened properties of concrete under the influence of the addition of CNT in the mixture, the data of these results are experimental results reported in literature.

Contradictory results are observed in literature. It’s noted that greater or lesser influence of CNT on physical, mechanical and durability properties of these composite matrices content, depends on the CNT characteristic the dispersion in the matrix, interaction and adherence with the composite. It is shown that the functionalization processes leads to modifications on the CNT characteristics. However, these processes seems to be less effective in improving the dispersion and interaction between the CNT and cement matrix.

1. Introduction

Concrete is the most common material used in construction, and is known for its versatility. However, its durability and some other properties, such as tensile strength and ductility are also the target of several studies aimed at optimization and future improvement.

Several investigations into these areas and the use of cement matrices reinforced with nanomaterials have been carried out, demonstrating that their component bodied in a suitable dosage may allow only changes in microstructure of hydrated cement paste. Leading this to production of mortars and concretes tougher, less porous and more durable. In present paper it will be analyzed the incorporation of CNT for its enormous potential and now have been the subject of several investigations.

Some researchers achieve significant improvements using CNT in composite matrices. However, there are still some difficulties that prevent the implementation of these materials in construction market, such as, their high production costs and difficulty in the dispersion of CNT in mixture and its effect and interaction with the matrix.

The research conducted in this field aim to prove the benefits and the efficiency of CNT use to stimulate investment in the area. Currently under study are a number of procedures to improve effective dispersion of CNT cement related matrices and thus examine the outcome of these reinforcing materials in cement composites.

As it develops a large-scale production of the CNT, the costs associated will tend to decrease and its application in the construction will start occurring more naturally.

2. Carbon nanotubes

High importance has been given in recent years to the impact that nanomaterials can cause in several different areas, therefore nanotechnology have been aim of several different research fields.

Carbon nanotubes are one of the latest discoveries in the field of nanomaterials, being composed of tubes with dimensions up to 100 thousand times smaller than the diameter of a human hair (Toma 2004). His extraordinary strength and resistance, could not be comparable to any other material currently known, it gives this material a high potential in various areas of engineering. Paragraphs then far will reference the constitution, production and main properties of these materials.

CNT have a short history so far, since they are considered virtually materials of the XXI century. Much of the literature attributes the discovery of these materials to Sumio Iijima (NEC's fundamental research laboratory).

In 1992, Ebbesen and Ajayan (1992) conducted the first production of macroscopic CNT, having created SWNT (single-walled nanotubes) and MWNT (multi-walled nanotubes) using the arc discharge (electrical related method).

Theoretically, CNT are considered known materials with higher hardness and mechanical strength, these properties are a consequence of their structural arrangement of perfect oriented and high bond energy between the atoms resulting of the orientation being so perfect. The CNT are very flexible materials that do not suffer damages in their structure when bent or subjected to high pressures.

When multiple wall nanotubes are subjected to high voltages, only the last layer has a tendency to break. The presence of imperfections in its structure leads to lower the resistance value. Still, its resistance is considerably higher than other materials (Yakobson et al. 2001).

The CNT are characterized for having high strength and stiffness in the axial direction and extraordinary flexibility in the transverse direction. The elasticity modulus in better quality CNT reaches values in the order of 1 TPa which is about 5 times higher than steel (Konsta-Gdoutos et al. 2010, Salvetat et al. 1999).

Tensile strength of 63 GPa in MWNT were observed by Yu et al. (2000) and about 100 GPa were reported in SWNT by Peng et al. (2008). Molecular mechanics simulations suggest that CNT extensions break with 10-15 % for tensile stresses 65-93 GPa (Belytschko 2002).

In compression, the resistance of CNT tends to be lower due to buckling phenomena. Indicatively that the SWNT can have tensile strength from 20 to 100 GPa and elastic modulus 500 to 1500 GPa, while MWNT have from 10 to 60 GPa for strength and 200 to 1000 GPa on elastic modulus.

The thermal properties of the CNT are very important because they play a key role in controlling the stability and performance of the bonding mechanisms of this material. One of the most important properties in the CNT is its stability under thermal reaction conditions, encompassing also its specific heat.

The researches carried out show that the CNT have a high thermal stability up to 2800 °C in vacuum and a high thermal conductivity reaching values 2800-6000 $W.K^{-1}.m^{-1}$ at room temperature, which is higher conductivity compared with known conductor materials, such as graphite and diamond (Han and Fina 2010).

In addition to these properties CNT show other relevant properties. The fact that they are materials with low density gravity tubes, flexible and resilient with a high Young's modulus, contributed to their use in technological applications which required high strength, stability and reduced weight.

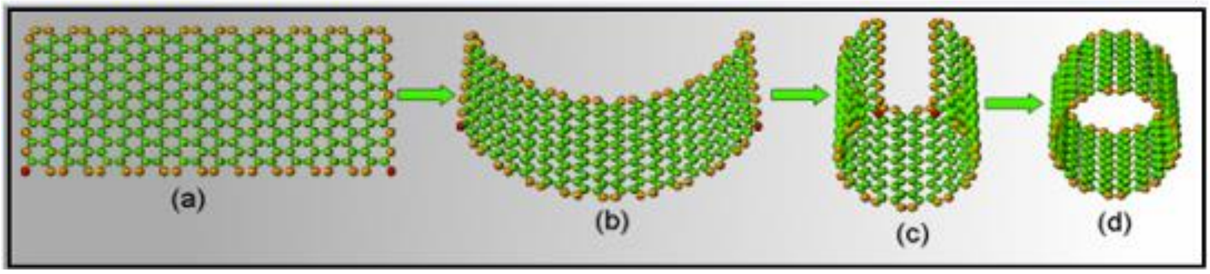

Figure 1 - Formation of CNT (a) graphene sheet, (b) and (c) graphene sheet to form a cylinder, (d) nanotube formed (Couto 2006).

Due to its properties, CNT are an interest in various fields such as electronics, optics, aerospace, shipbuilding, composite materials and other fields of science materials (Nochaiya and Chipanich 2011, Kumar et al. 2012, Paiva et al. 2004).

The mechanical characteristics of CNT makes them suitable for matrix reinforcement (Lau and Hui 2002 Wei et al. 2008, Zhu et al. 2008, Lee et al. 2007, Esawia et al. 2009 Chen et al. 2003).

CNT mechanical properties are unique, with a high elasticity modulus and mechanical strength that exceeding by in three and ten times high-strength steels. CNT can be conditioned by the presence of defects and type accordingly, they can resist up to 63 GPa and the tensile strength can reach up to 1,500 GPa in the elasticity modulus (Gao et al. 1998, Walter September al. 1999, Yu et al. 200 and Thostenson et al. 2001).

3. Composite materials reinforced with carbon nanotubes

Performance of materials it’s currently demanded to be more and better of what is available nowadays on the market. Many of them are combined in order to extract the unique properties which cannot be individually identified in metals, ceramics or polymers. Knowing that it is a composite, consisting in the addiction of two or more materials which influence each of the properties of the final material, it may be classified accordingly to the type of matrix array.

To seize the composites, the addition in materials already known, can give a unique advantage of the carbon nanotubes characteristics when used as reinforcement. Therefore, this nano-composite it becomes both the matrix and the reinforcement and improves the properties of the used materials on a microscopic scale influencing positively by the carbon nanotubes.

The latest research seeking to establish the very best way to incorporate the various CNT matrix arrays already known to improve processing methods, mechanical performance and possible future applications.

Due to its unique physical and chemical properties the CNT allows to be used in several areas, since the formation of nano-circuits to the reinforcement of metallic, ceramic or polymeric matrices.

Current studies are constantly looking for a solution to obtain a uniform dispersion of CNT matrix arrays in order to extract of the mix the most of all its qualities (Cornelia 2006).

The CNT reinforcement has been the subject of intensive investigations to achieve and thus provide great advances in methods of synthesis and processing of these materials, but although they have already showed many advantages, there are still many aspects to be investigated further and study related due to the size, shape, volume fraction, degree of dispersion and agglomeration of the dispersed phase (Krishnamoorti and Vaia 2007).

The reinforced metal matrix composite materials with carbon nanotubes are of great interest since the CNT enables reduction of thermal expansion coefficient, increases strength and reduce density. These composites combine low coefficient of thermal expansion and high thermal conductivity, and by taking advantage of its low density it allows its use in electronic equipment-oriented aerospace and space structures.

The ceramic matrix composite may also be an option depending on the purpose for which they are intended to be used, although they are associated with very fragile and brittle objects. Most metals will fracture toughness his a 40 times superior to the conventional ceramic (Curtin et al. 2004). While applying stress or tension, chemical impurities or cavities of the ceramic material results in a brittle fracture of the object. Considering this aspect, the ceramic matrix composites related on ductility and resistance to crack propagation are the properties of most interest to improve. Thus, the addition of CNT in ceramic matrices aims to improve its toughness (Curtin et al. 2004). With the addition of a small fraction of CNT is possible to improve the thermal shock resulting from the high thermal conductivity of carbon nanotubes. It should also have an effect at the level of the bound of the cracks which normally tends to propagate on weak points.

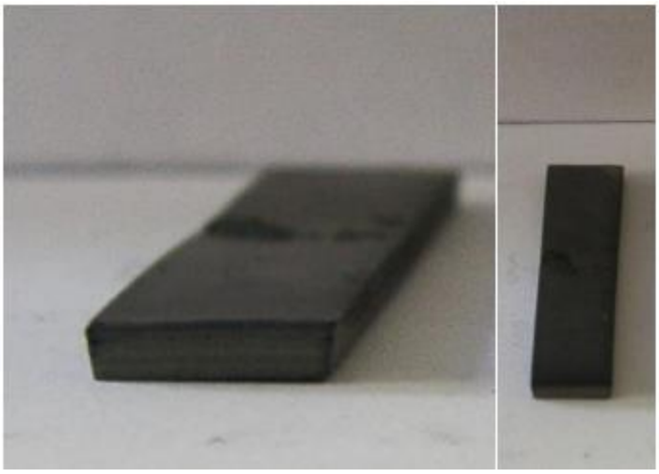

Figure 2 - Aspect bar of a multilayer CNT-SiC (Carlson et al. 2013).

The CNT-SiC elasticity modulus composite was measured with an average value of 325 GPa However, compared to pure SiC multilayer sample was obtained a significant reduction in maximum flexural strength of 321 MPa to 270 MPa. This effect is probably related to the low density samples of multilayer composites which regards to theoretical density. The polished sections of specimens and their fracture surfaces were also investigated using scanning electron microscopy images.

The polymer matrix composites allows the material to become stronger and more tenacious thermal shock resistance than conventional graphite. The carbon becomes a material suitable to their low density, its high strength, high elastic modulus, high thermal conductivity and low thermal expansion coefficient, with unique characteristics (Faming 2005).

Depending strongly on the temperature at which carbonization or graphitization occurs, the resulting matrix can have properties of graphitic or amorphous carbon. At this time, manufacturing costs, poor corrosion resistance, the difficulty of adherence of these materials to the matrices and also poor interlayer properties are considered the main disadvantages.

The reinforcement of polymeric materials with CNT leads to the shear stress in the nanotubes bonding matrix increases with the increment of carbon nanotubes (Lau 2003).

Table 1 shows the average values of laboratorial tests performed with reference to properties of tensile strength, deformation by elongation at rupture point and elasticity modulus of the nanocomposites against pure PVC and PVC with MWNT with CNT concentration that vary between 0.2 and 0.8 %.

Table 1 - Results of tensile testing of composites (Bertoncini 2011).

CNT content		Tensile strength (MPa)		Strain at rupture (%)		Elasticity modulus(MPa)	
MWNT-COOH (%)	MWNT-non treated	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
0,0	0,0	52,3	3,3	45,4	26,0	2324,8	170,2
0,2	-	54,9	1,4	10,6	1,6	2281,0	202,7
0,4	-	51,7	1,8	7,5	2,5	2363,8	205,0
0,6	-	50,7	3,3	13,3	4,7	2546,5	242,5
0,8	-	52,3	5,2	5,6	1,2	2528,6	190,9
-	0,2	57,2	3,0	27,4	24,2	2559,6	114,4
-	0,4	54,3	1,5	16,0	9,6	2204,1	131,1
-	0,6	54,5	7,9	17,6	14,9	2480,7	299,0
-	0,8	57,7	1,8	26,2	19,1	2593,0	224,2

4. Cementitious materials reinforced with carbon nanotubes

The production of cement matrix composites reinforced with CNT is firstly mentioned by Makar and Beaudoin (2003) where the introduction of CNT was analyzed by an electronic microscope. Despite no mechanical test results were achieved, these authors highlighted the main advantages of using CNT, compared to traditional fibers, their high strength the increased form factor and its reduced diameter, which would be responsible for a better mechanical stresses distribution, despite increasing the contact area between the fiber and the matrix, improving the anchorage of the nanotubes in the array.

Given the youth of this subject and the difficulties inherent in the research (cost and dispersion of material and quality) are still a few studies in this area and are still huge uncertainties in the behavior of these materials. In the literature regarding the performance of the NTC in cementitious matrices there was observed several contradictions, in regards to functioning properties, dispersal type results, content of NTC in the mix, inclusion and testing techniques.

Cwirzen et al. (2008) used two solutions of polyacrylic acid with arabic gum to disperse functionalized and non-functionalized MWNT in cement. The use of 0.8% arabic gum, delayed hydration process of the cement for 3 days, but did not cause any other problems in strength properties of the material. In order to evaluate the mechanical properties of the composite, flexure and compression tests were conducted. The mixture had in its composition 0.045% of MWNT achieving an improvement in the compressive strength of the order of 50%.

Shah et al. (2009) improved the mechanical properties of the cement matrix composites reinforcing with CNT by ultrasonic processes with 0.1% MWNT dispersed in water with surfactants. The results showed an increase in flexural strength from 8 to 40% and an increase in elasticity modulus of 15 to 55 %.

Abu Al-Rub et al. (2012) and Tyson et al. (2011) investigated carbon fibers and MWNT at different concentrations in the cement mix, with a water/cement ratio of 0.4. The authors also investigated the effect of functionalization of the CNT. The results were obtained at 7, 14 and 28 days whenever making proper comparisons with pure cement samples. The results show that the cement composites with carbon fibers had, in general, performed better than the MWNT composite cement. The non-functionalized MWNT showed a delay in strength up to 28 days, but compared to the pure cement samples showed large improvements in ductility. Furthermore, the MWNT functionalized showed degradation of mechanical properties over time. The authors attributed the cause of the formation of degradation products of hydration to weak or harmful components such as excessive formation of ettringite.

The compressive strength is one of the main mechanical properties that must be taken into account in reinforced concrete evaluation with CNT. If experimental values are much lower than expected, this indicates that the concrete structure has problems that can be caused by miss-dosages, use of unsuitable materials or even a defect structure inside the thickening due to lack or absence of proper curing.

Some researchers have studied the addition of 0.5% and 1.0% CNT in Portland cement mortars. The CNT were subjected to sonication for 10 minutes in order to give a dispersion in water. In this study the authors used fly ash, cement and binder in order to study the compressive strength of the composite. The results show that the use of CNT allowed to raise the strength of the cement matrix, having the highest strength being obtained with the addition of 1.0% CNT in cement, with 20% fly ash, where the compression resistance after 28 days reached a value of 51.8 MPa, representing an increase of 10% compared to the mixture without CNT, whose strength was 47.2 MPa (Chaipanich et al. 2010).

Kowald (2004) with the use of CNT in mortars with water / cement ratio of 0.3 was obtained increases of around 7% in the compressive strength in a 7 days period and 12% at 14 days. For water / cement ratios greater than 0.39 were not significant differences.

Li, Wang and Zhao (2005) when working with cement mortar, had an increase in compressive strength and flexural strength in the order of 19% and 25%, respectively. The mortars had a content of 0.5% CNT and water / cement ratio was 0.45.

At Marcondes (2012) work, was observed that adding CNT to concrete, results also led to improvements in tensile strength results, and the best result was for the CD composition consisted of concrete with the addition of CNT and dispersion in water prior by sonication, together with a super plasticizer, which achieved a gain in resistance of 19%, followed by SD concrete , which is a mixture containing only added CNT without pre dispersion also without the additive and the process of sonication with 17%, the AQUA mix, which was based on a prepared composition with the product AQ0301 AQUACYL marketed by Nanocyl SA, with 6% tensile strength gain. Although the SD composition having the best values with respect to tensile strength, is one that has the greatest standard deviation between the samples tested.

According Gleize (2005), the addition of 0.02% of CNT in cement pastes has a tendency to reduce the autogenous shrinkage. This reduction is linked to the hardening of the structure since their experiments that the effect became more pronounced in time.

Makar et al. (2005) presented the chance of influencing the CNT crack control, due to their size, they are better distributed and prevent the cracks propagation, causing generated cracks show smaller openings. In his work with content CNT used were 2% with a water/cement ratio of 0.4 and a content of 1% of plasticizer additive. In Figure 3 you can see the microcrack in cement paste with 3 days of hydration, and the distribution of CNT bridging adhesion.

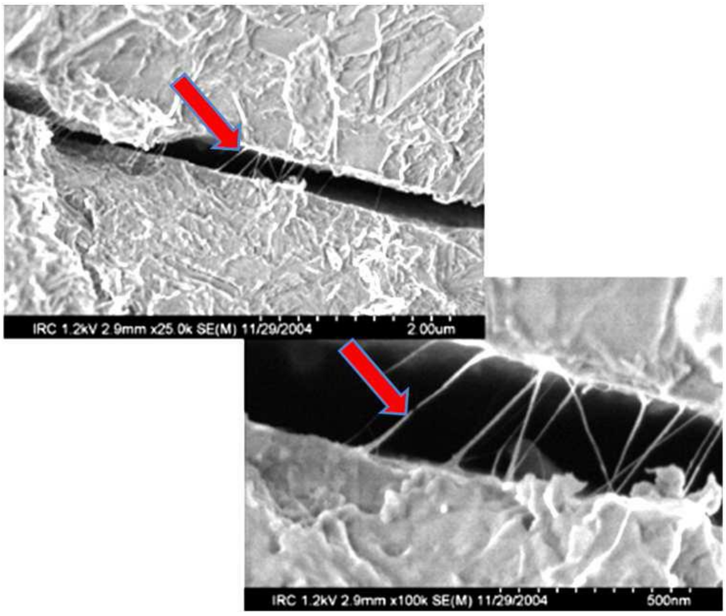

Figure 3 - Microcrack in the cement paste in the presence of CNT acting as bridges grip (Makar et al. 2005).

The formation of these adherence bonds is one of the reasons recommended for adding CNT to the cement paste in order to provide the production of mortars and concretes with higher resistance, lower porosity and thus more durable solutions (Makar et al. 2005).

Many researches related to the dispersion of CNT into cementitious matrices, have been based on the functionalization in acid environment, but to Koshio et al. (2001), discloses the ultrasound is provided with an effective technology to disperse CNT in water, oil or polymers. According to some researchers, the tangential forces generated by the ultrasound are higher than the bonding forces between the CNT, being able to separate them. Konsta et al. (2010) was able to prove this latter aspect by achieving an efficient dispersion through the application of ultrasonic energy, showing results obtained by the MWNT can reinforce the cement matrix, decreasing the porosity and increasing the amount of CSH.

Makar and Beaudoin (2004) showed two procedures in its work to improve the dispersion of CNT in the cementitious matrix. One was the excitement of CNT in water with the addition of superplasticizer, but the trials were not sufficiently enlightening as to argue through this procedure, would be possible dispersion of the quantities necessary for the proper performance of the material, which is set accordingly to the authors from about 2% to 10% relative to the weight of cement. The other procedure was to use CNT dispersed solution in ethanol, which was added in an amount of cement followed by stirring of the mixture. After evaporating the ethanol to give followed by testing the material. This procedure was used for Makar et al. (2005), to produce samples with CNT.

Table 2 based on results of different compositions performed by Marcondes (2012) gives a sense of potential concrete costs produced with CNT. Note that for the 26.5% increase in the compressive strength of concrete the cost of the final product increases by approximately 74%. However, when compared to reference composition with the composition AQUA in addition there is a rise in the compressive strength of 22.5% was increased unreasonably high costs to reach a value of the order of 96%.

Table 2 - Cost of concrete by m^3 (Marcondes 2012).

Materials and components	Concrete	CNT	Sand	Gravel	Water	Additive	€/m^3	Compressive strength (Mpa)
Consumption/m^3	352 (Kg)	1,056 (Kg)	792 (Kg)	968 (Kg)	193,6 (l)	3,52 (Kg)		
Cost of Material	115€/t	Em pó - 198€/Kg Aquacyl - 1652€/Kg	18€/m^3	16€/m^3	0,8€/m^3	3,1€/Kg		
Reference Composition	40,5	0	8,8	12	0,15	10,9	72,4	25,77
AQUA composition	40,5	1744	8,8	12	0,15	0	1805,5	33,25
CD composition	40,5	209,1	8,8	12	0,15	10,9	281,5	35,08
SD composition	40,5	209,1	8,8	12	0,15	10,9	281,5	30,55

5. Conclusions

The reinforcement NTC has advantages in relation to traditional fibers allowing detachment of certain properties such as, their high strength, increasing the form factor and its reduced diameter, allowing a better distribution of mechanical loads, while increases the area of contact with the matrix, improving the anchoring of the NTC.

The addition of the NTC cementitious matrix has an effect on the rheology of the concrete. The presence of NTC and the dispersion form, have an influence on its consistency. An efficient dispersion can be obtained by allowing sonication to disperse the additives in aqueous environment incorporating the polymer additives present in the surface of the NTC, thus achieving an improvement in the consistency of the concrete. However, there is a great degree of difficulty in retaining the workability of the concrete with the NTC, indicating that this is only possible through the addition of chemical additives to increase their plasticity, due to the high water demand of the NTC material.

The mechanical properties in cementitious matrices may suffer increases or loses with the addition of NTC, depending on the content, amount and concentration of NTC, the water/cement ratio, the functionalization process and the effective dispersion of the NTC in the matrix. However, the majority of studies analyzed throughout this thesis, show an increase in the mechanical properties of the cementitious materials reinforced with NTC. It is to highlight that an increase of 37% and 19% resistance to compression and tension, respectively, obtained by the study done by Marcondes (2012) resulting from concrete with the addition and prior dispersion of NTC by sonication along with a superplasticizer. We can then conclude that as compressive strength increases, the tensile strength also increases. It was also found that the ductility of the concrete increases with the increase content of the NTC composites in the mix.

The mechanical properties of the composites are improved only if there is an adequate dispersion of the NTC. This dispersion is often successfully achieved via sonication. The ultrasound feature can be used for dispersion of the NTC but if they are used without any type of chemical surfactant is proved not effective. In several investigations analyzed throughout this work only a few results showed improvements in the mechanical properties of cementitious materials reinforced with NTC, proving that its performance is strongly correlated with the level of dispersion achieved.

The NTC also influence the crack control, since, due to its size is better distributed and prevent the propagation of cracks, causing cracks generated show smaller openings. It is recommended to add the NTC to the cement slurry due to the formation of bridges grip which can lead to the production of mortars and concretes sturdier and more durable.

The interaction of the compounds with NTC hydrated cement should be adequate and may require functionalized them. This demonstrate the need to create a good adherence between the NTC and the cement matrix. However, the functionalization of NTC can have a negative effect on its mechanical properties.

The price of concrete with NTC reaches very high values suggesting its economic non-practicality. However, with the large-scale production the cost will surely reach sensibly lower values , such as fiber optics, which initially had a high cost and is currently accessible.

Although research in this field is increasingly high, currently are still many uncertainties in the long term behavior and characterization of composites reinforced with NTC. Thus, given the huge potential of the NTC is necessary to invest in additional research in order to contribute to increased knowledge in this area and contribute to a better use of the NTC, or alternately notice any adverse effects on its utilization.

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