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Glass-like Carbon Made from Epoxy Resin Cured with 2,4,6-Trinitrophenol

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It has been found that a glass-like carbon can be produced by the slow and carefully controlled pyrolysis of the epoxy resin (Epikote 828) cured with 2,4,6-trinitrophenol (TNP) with a weight of 10—15%. The most characteristic property of the glass-like carbon was seen in its change in density with the heat-treatment temperature. Under heat treatment at temperatures up to 1000 °C, a dense glass-like carbon of which density was 1.65—1.70 g/cm^3 was formed. The density of the glass-like carbon decreased, however, at heat-treatment temperatures above 1000 °C. Upon heat treatment at the temperature of 3000 °C, the density dropped to a low value of 1.04—1.11 g/cm^3. The former increase in density is connected with the large-scale dehydration reaction which may proceed between nitro groups and hydrocarbon chains in the cure resin. The latter decrease in density is caused by the progress of the graphitic orientation of carbon-layer planes in the cross-linked structure of the highest degree. If carbon fibers were present in this glass-like carbon, the graphitization of the glass-like carbon in the composite proceeded more easily than that of the glass-like carbon alone.

In general, there is a 40—50% loss in weight when carbon-rich materials are carbonized under atmospheric pressure, for pores or cracks then develop in the carbonized product as a result of the release of volatile matter and the shrinkage in volume. It is well known that some thermosetting polymer resins are converted into carbonized products resembling glass in appearance and in fractural property. The glass-like carbon is characterized by a low density, a very low gas permeability, and an isotropic disordered structure.[1—6] Phenol-formaldehyde resin and furfuryl alcohol resin are suitable as starting materials to obtain glass-like carbon in a good yield.

We have previously reported that 2,4,6-trinitrophenol (TNP) can be used as the curing agent of the liquid expoxy resin, Epikote 828. Moreover, the explanation of the curing mechanism and some applications of this cure system have been attempted.[7,8] It is a good example of the applications that the pre-heated cure resin at 150 °C turned to the glass-like carbon upon slow and carefully controlled pyrolysis. If the common curing agents such as aliphatic polyamines were used instead of TNP for the epoxy resin, the cure resin could not maintain its original shape during carbonization. In this glass-like carbon there can be seen some characteristic behavior in the process of carbonization and graphitization. In the present paper this behavior is examined by means of thermogravimetric analysis, the measurement of the density, a microindentation hardness test, an X-ray diffraction study, and optical observation, and the behavior is compared with that of the usual glass-like carbons made from phenol-formaldehyde resin and furfuryl alcohol resin. Moreover, the graphitization of the glass-like carbon containing carbon fibers is examined.

Experimental

The epoxy resin was Epikote 828 (Shell Chemical Co., diglycidyl ether of bisphenol A). The TNP used here was of a commercially guaranteed reagent grade and was dried after grinding. As furfuryl alcohol resins, Hitafuran 302 (Hitachi Kasei Co.) and its curing agent, A_3 (the same company) were used. The phenol–formaldehyde resin was of a resol type, which scarcely needed the curing agent. The carbon fibers of PAN-based Torayca T300 were chosen.

A sample containing carbon fibers was prepared in the following manner: the carbon fibers aligned in the same direction were stacked in the vessel, and then the resin was poured upon them and cured at 130 °C in air. After curing, the composite was cut in small pieces (about 10×10×20 mm) by means of a diamond cutter. On the basis of a photographical survey, the carbon-fiber content in the composite was found to be in the range of 30—42% in volume.

The heat treatment was accomplished at a rate of 30 °C/h up to 500 °C, and thereafter at a rate of 120 °C/h to 1000 °C in a stream of argon. The heat treatment at temperatures from 1500 to 3000 °C was carried out in a graphite-resistance furnace in a stream of argon. Each heat treatment was achieved at a rate of 256 °C/h, after which the maximum temperature was held for 30 min.

The thermogravimetric analysis of the samples (a 100-mg portion of each sample was placed in a platinum cup) was run by heating at a rate of 2 °C/min in an argon atmosphere by using the electronbalance (Cahn 1000).

To obtain a clear indent with the Vickers hardness tester (Shimadzu Seisakusho Ltd.), the surfaces of the carbonized samples were polished as plane mirrors. The indents were marked by means of a Vickers diamond for 30 s under a load of 1000 g.

The X-ray diffraction profile of (002) line on the powdered sample was obtained with Ni-filtered Cu *Kα* radiation. The interlayer spacing, d_{002}, and the crystallite thickness, L_c, were estimated from profiles in which the corrections of the Lorentz-polarization, atomic-scattering, and absorption factors were made in a usual way.[9] The profile of the composite made from cure resin containing carbon fibers was separated into the component profiles of the matrix carbon and the fiber carbon. The separation was made as follows: the profile of fiber carbon was obtained at an individual temperature. We assumed that the profile of fiber carbon agreed with the fiber-carbon component in the composite profile at the individual temperature. The composite profile could be separated into its component profiles based on the fiber-carbon component.

Results

Carbonization. It is most proper to use 10—15%

TABLE 1. COMPARISON OF PROPERTIES OF GLASS-LIKE CARBONS MADE FROM EPOXY RESIN CURED WITH TNP, PHENOL–FORMALDEHYDE RESIN, AND FURFURYL ALCOHOL RESIN

	Epoxy resin/TNP		Phenol resin	Furfuryl resin Fur./A_3=99.7/0.3
	90/10	85/15		
Curing conditions	130 °C, 48 h ↓ 140 °C, 48 h ↓ 150 °C, 48 h	130 °C, 48 h ↓ 140 °C, 48 h ↓ 150 °C, 48 h	40 °C, 10 d ↓ 60 °C, 10 d ↓ 80 °C, 10 d	40 °C, 10 d ↓ 60 °C, 10 d ↓ 80 °C, 10 d
Bulk density of cure resin/g cm^{-3}	1.23	1.24—1.25	1.24	1.29—1.3
Shrinkage[a)] $(V_1-V_2)/V_1\times 100$ (%)	75—77	74—75	50—51	50—51
Yield/wt%	29—30	32—34	56—58	56—57
Density/g cm^{-3} [b)]	1.65	1.70	1.52	1.50
Vickers hardness	400—420	430—440	360—390	360—370

a) Carbonized to 1000 °C. b) Densities of finely ground samples were measured by the immersion method in 1-butanol using a pycnometer at 20 °C.

of TNP as a curing agent for the epoxy resin. The polymerization reaction of the system was dependent on the curing temperature, as has been reported previously.[7)] Under the curing condition at 130 °C in air, at first a linear structure was formed, and then it was converted into a cross-linked one. The system containing 10% TNP was converted from the linear structure into the cross-linked one at 130 °C after 24 h. The converting time for the system containing 15% TNP became short (about 3 h). When carbonized at a heating rate of 30 °C/h in a stream of argon, the resin cured at 130 °C was burned with smoke by means of the rapid exothermic pyrolysis of nitro groups in the cure resin, and a porous carbonized product was formed. When the resin cured at 130 °C for 48 h in air was carefully heated at 150 °C in steps and then maintained at this temperature for about 48 h, its colour changed from yellow-orange to brown-black. When the cure resin preheated at 150 °C was heated at a rate of 30 °C/h in a stream of argon, it was gradually pyrolyzed, while keeping its shape, and was converted into a nonporous carbonized product considered to a glass-like carbon. This appearance is shown in Fig. 1. There are some cracks in the glass-like carbon, as denoted by the arrow.

The curing condition of the resins used and some properties of the glass-like carbons obtained from the cure resins heat-treated at 1000 °C are given in Table 1.

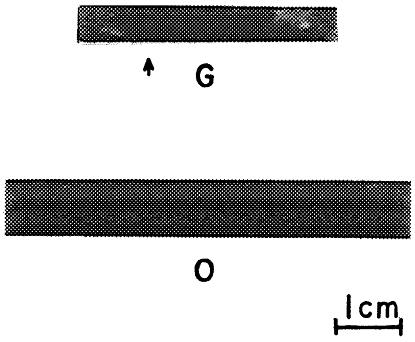


Fig. 1. Appearance of glass-like carbon made from epoxy resin cured with 10% of TNP.
O: Original resin heat-treated at 150 °C. G: Glass-like carbon obtained by heat treatment at 1000 °C.

It is worth noting that the density and the hardness of the glass-like carbon made from the epoxy resin cured with TNP are high, though its yield is low and the shrinkage in volume is larger than those of phenol–formaldehyde resin and furfuryl alcohol resin.

The pyrolysis of the epoxy resin cured with TNP was compared with that of samples heat-treated at 130 and 150 °C. The weight loss with the temperature is shown in Fig. 2. On the sample treated at 130 °C (Fig. 2, Curve 3) a rapid loss appeared at 215 °C, while on the other one, no corresponding loss could be seen (Fig. 2, Curve 4). This fact showed the difference in the appearance of the carbonized products; the former product was porous, and the latter, glass-like.

Change in Density with Heat-treatment Temperature. The changes in density on the glass-like carbons heat-treated at various temperatures up to 3000 °C are shown in Fig. 3. The density of the glass-like carbon made from the epoxy resin cured with TNP decreases as the heat-treatment temperature rises (Fig. 3, Curves 1 and 2). Although the decrease in density introduced by heat-treating glass-like carbons has previously been reported by Honda *et al.*[10)] and Bose *et al.*,[11)] no such large

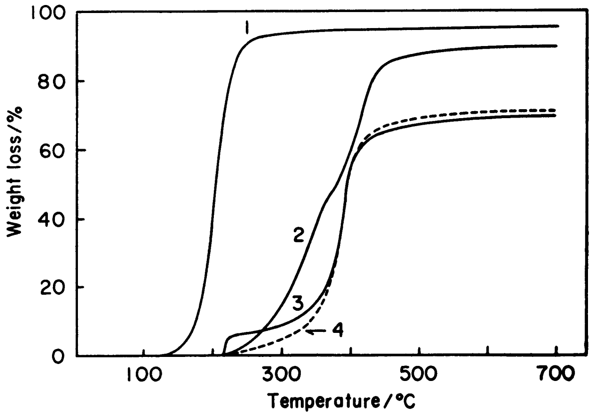


Fig. 2. Thermogravimetric analyses of TNP, epoxy resin and epoxy resin cured with 10% of TNP.
1. TNP. 2. Epoxy resin. 3. Epoxy resin cured with 10% of TNP at 130 °C for 48 h. 4. Epoxy resin cured with 10% of TNP at 130 °C for 48 h and then heat-treated at 150 °C for 48 h.

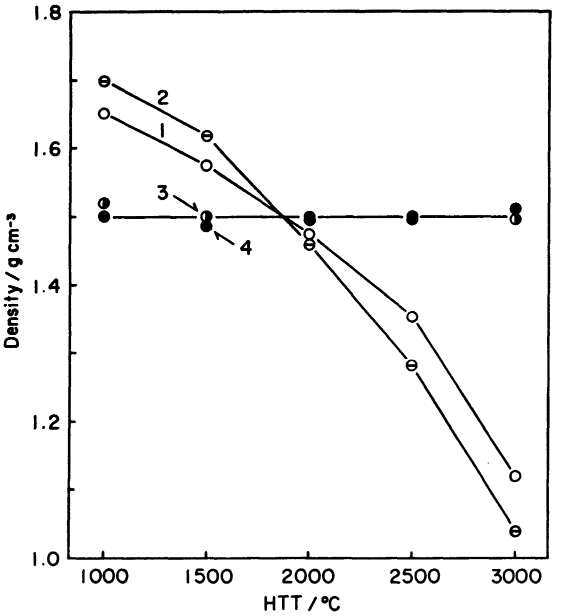
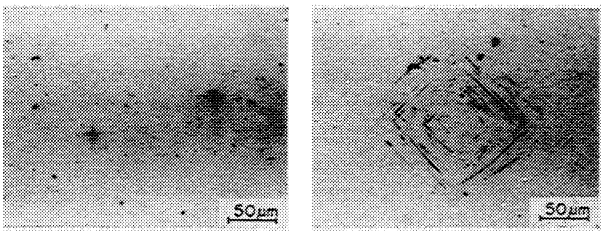


Fig. 3. Change in density of glass-like carbons with heat-treatment temperature (HTT).
1. Glass-like carbon made from epoxy resin cured with 10% of TNP. 2. Glass-like carbon made from epoxy resin cured with 15% of TNP. 3. Glass-like carbon made from phenol–formaldehyde resin. 4. Glass-like carbon made from furfuryl alcohol resin.



(a) (b)

Fig. 4. Typical indent impressions obtained on polished surfaces of glass-like carbon made from epoxy resin cured with 10% of TNP.
(a) Heat-treatment temperature 1000 °C. (b) Heat-treatment temperature 3000 °C.

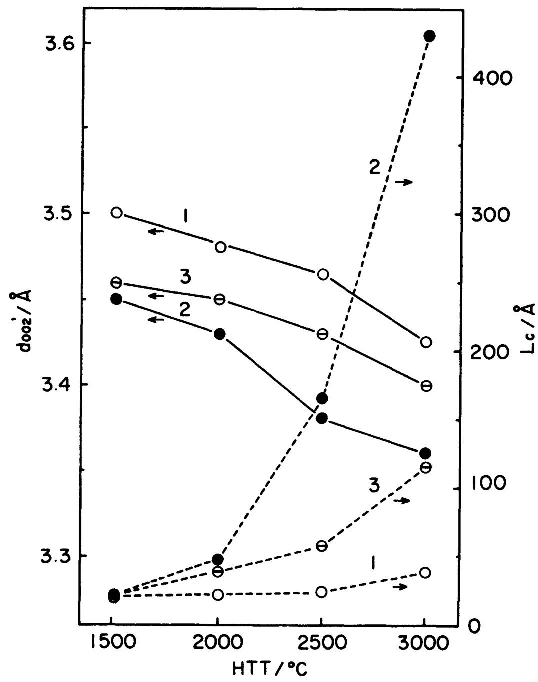


Fig. 5. Changes of interlayer spacing d_{002} and crystallite size L_c with heat-treatment temperature (HTT).
1. Glass-like carbon made from epoxy resin cured with 10% of TNP. 2. Glass-like carbon component in composite made from carbon fibers and epoxy resin–TNP (90 : 10) mixture. 3. Fiber carbon.

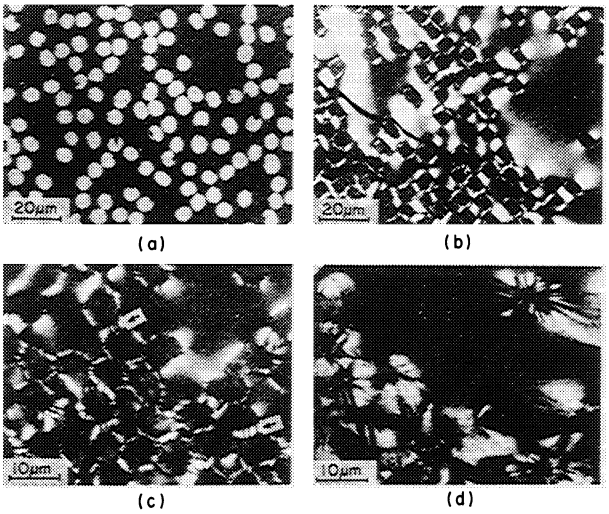
decrease in density as that here obtained has been known. When the glass-like carbon was made from the epoxy resin cured with 10% TNP in the heat-treatment temperature range from 1000 to 3000 °C, its density dropped from 1.65 g/cm^3 to 1.11 g/cm^3. On the other hand, when the glass-like carbon made from the epoxy resin was cured with 15% TNP, the density fell from 1.70 to 1.04 g/cm^3. The differences in the densities of these samples are equivalent to 34 and 70% increases in the volume respectively. The change in volume is calculated by this equation; $(V_1-V_2)/V_1\times 100$, where V_1 and V_2 show the volume of the glass-like carbons heat-treated at 1000 and 3000 °C. No remarkable decrease in the density with an increase in the heat-treatment temperature can be seen on the glass-like carbons from phenol-formaldehyde resin and furfuryl alcohol resin (Fig. 3, Curves 3 and 4). They are almost constant with the heat-treatment temperature. The change in the density of Curve 2 is larger than that of Curve 1. This shows that the large decreases in density is caused by the TNP which is used as the curing agent of the original resin.

Microindentation Hardness. Figures 4(a) and (b) show the imprints of the glass-like carbon heat-treated at 1000 and 3000 °C respectively. These photographs indicate that the imprint changes from a diagonal to a concave pattern as the heat-treatment temperature increases. This change can also be seen in the glass-like carbons made from phenol-formaldehyde resin and furfuryl alcohol resin in spite of the small change in the density, as is shown in Fig. 3, Curves 3 and 4. The concave imprint may show that the hardness of the glass-like carbon is remarkably lowered.

X-Ray Diffraction. The volume of the epoxy resin cured with TNP decreased extremely in the process of carbonization and increased largely on heat-treating above 1000 °C. If carbon fibers are contained in this cure resin, the graphitization of the matrix carbon of the composite may be influenced. This phenomenon is of interest in connection with the stress graphitization of glass-like carbon,[12–17)] because the effect of a large change in the volume of the matrix carbon on the process of carbonization and graphitization has not yet been examined.

Figure 5 shows the changes in the values of d_{002} and L_c on the glass-like carbon made from the epoxy resin cured with TNP (Fig. 5, Curve 1), on the matrix carbon in the composite (Fig. 5, Curve 2), and on the fiber carbon (Fig. 5, Curve 3) heat-treated at 1500—3000 °C. Above 2000 °C, the glass-like carbon is more difficult to graphitize than the carbon fibers. The graphitization of the matrix carbon in the composite proceeded greatly in comparison with that of the glass-like carbon only, regardless of the large increase in volume above 1000 °C.

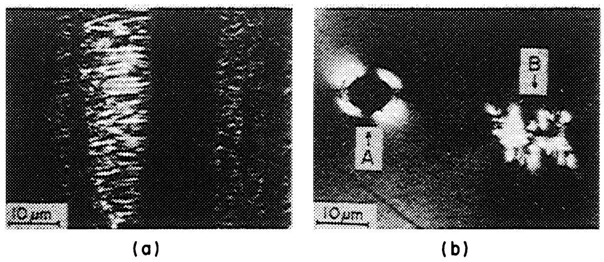
Microscopic Observations. Micrographs of the composite made from the carbon fibers and the epoxy resin–TNP mixture are shown in Fig. 6. The matrix precursor before being carbonized had an isotropic structure (Fig. 6(a)). After heat-treatment at 1000 °C, anisotropic areas appeared in the matrix carbon around the carbon fibers and then spread out in the matrix (Fig. 6(b)). The area decreased somewhat after heat treatment at 2500 °C (Fig. 6(c)). This phenomenon is caused by the increase in the volume of the matrix carbon, which takes place upon heat treatment above 1000 °C. However, the development of a graphite-like structure was clearly recognized in the anisotropic region in the matrix, as is denoted by arrows. The carbon fibers were extremely deformed after heat treatment at 3000 °C (Figs. 6(d) and 7(b)-B). When the carbon fiber separates from the matrix carbon on heating, the shape of the carbon fiber is deformed a little (Fig. 7(b)-A). The micrograph of the cross-section parallel to the fiber axis in the composite heat-treated at 3000 °C (Fig. 7(a)) shows that the graphite-like layers are not simply aligned parallel to the fiber axis, but are zigzagged.



(a) (b)

(c) (d)

Fig. 6. Optical micrographs of composite made from carbon fibers and epoxy resin–TNP (90 : 10) mixture. (a) Original. (b) Heat-treatment temperature 1000 °C (polarized light). (c) Heat-treatment temperature 2500 °C (polarized light). (d) Heat-treatment temperature 3000 °C (polarized light).



(a) (b)

Fig. 7. Polarized light micrographs of cross section parallel (a) and perpendicular (b) to carbon fiber axis of carbon fiber–carbon composite made from carbon fibers and epoxy resin–TNP (90 : 10) mixture heat-treated at 3000 °C.

Discussion

Generally polynitro compounds are easily decomposed by heating, so it is difficult to keep the pyrolysis under control. This property does not change if they are present in cure resins.[18,19] The epoxy resin cured with 10—15% of TNP also has the property of rapidly decomposing upon heating. When the cure resin was preheated at 150 °C in air, however, the pyrolysis went on gently. It is considered that this gentle pyrolysis is brought about by the building of a highly cross-linked structure in company with the structural change in the nitro groups in the cure resin. The improvement of cross-linking formed by preheat treatment at 150 °C is proved by the insolubility in acetone. The resin cured with 10% of TNP and heat-treated at 130 °C for 48 h contained an insoluble part amounting to 70—80%. After heat treatment at 150 °C, the insoluble part increased to above 99% by weight.

Yamada, from the analytical results on gases evolved by the pyrolysis of a mixture of pitch and a nitro compound, found that the gases volatilized up to 500 °C were almost entirely occupied by water.[20] The formation of water in the present sample was suggested by the fact that the quartz window of the furnace used for carbonization was clouded by water drops at an early stage of the pyrolysis. A large-scale dehydration reaction during carbonization may lead to the formation of the highest degree of cross-linking in the structure.

The decrease in density above the heat-treatment temperature of 1000 °C can be interpreted in terms of the development of micropores and/or spaces caused by thermal swelling and structural change in the glass-like carbon. The thermal swelling may be brought by a relaxation of the rigid structure formed through the carbonization. It may be instructive to consider that nitro groups in the cured resin play an important role in pulling the carbon networks through the dehydration reaction. As a result, a rigid structure is established after carbonization. When the glass-like carbon in this state is heated at a temperature above 1000 °C, a partial bond-breaking may take place at the unstable positions of carbon networks in the glass-like carbon. The bond-breaking results in an expansion in volume. On the other hand, the structural change arises from the graphitic orientation of the carbon-layer planes in the glass-like carbon, as is shown in Fig. 5. When the values of density are plotted against those of the interlayer spacing, d_{002} (Figs. 3 and 5), along with the heat-treatment temperatures, a linear relationship is seen, as is indicated in Fig. 8. This relationship suggests that the spread of micropores and/or spaces originate in a narrowing of the interlayer spacing. This suggestion would mean that small-waved and entangled carbon-layer planes in the glass-like carbon are oriented straightly, accompanied by a combination of the carbon-

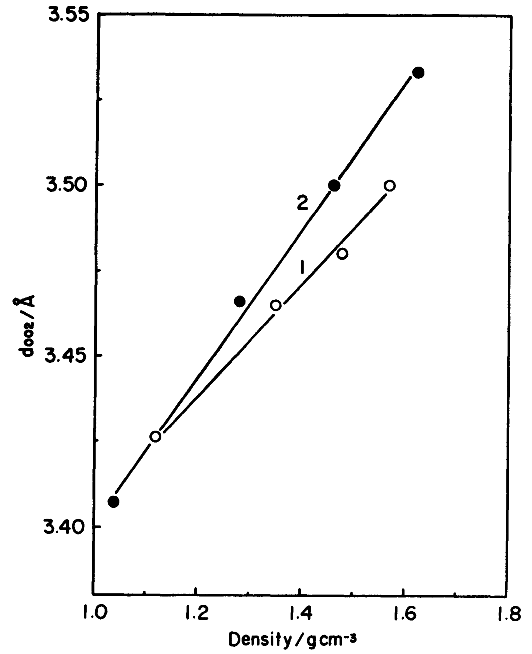


Fig. 8. Relation between interlayer spacing d_{002} and density.
1. Glass-like carbon made from epoxy resin cured with 10% of TNP. 2. Glass-like carbon made from epoxy resin cured with 15% of TNP.

layer planes, and that they jostle each other as the graphitization proceeds. The combination of carbon-layer planes and the complicated jostling may bring about the expansion in the volume of the glass-like carbon following the spread of micropores and/or spaces.

If the carbon fibers are contained in the glass-like carbon, its volumetric change will be suppressed to some degree by the stiffness of the carbon fibers. The carbon fibers in the matrix did not appear to be deformed during the carbonization (Fig. 6(b)). The expansion in volume of the matrix carbon which was caused by the high heat-treatment brought about the deformation of the carbon fibers (Figs. 6(d) and 7(b)-B). From the point of view of the stress graphitization of the matrix carbon in the carbon fiber–glassy carbon composite, the orientation of molecules (carbon-layer planes) of the matrix carbon formed in the process of carbonization is little influenced, even if a large volumetric expansion takes place in the matrix carbon of the composite after carbonization. Inagaki *et al.* have proved that the stress accumulation caused by shrinkage in the process of carbonization plays a significant role in the graphitization of matrix carbon in the carbon fiber-glassy carbon composite.[17] Our results also support their finding.

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