

Extrinsic Conducting and Superconducting Polymer Systems. IV. Superconducting Properties of YBaCuO Composites Based on PVDF/PS/Carbon Black and PVDF/PS/Copper Polymer Systems

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SYNOPSIS

In this work, the critical temperature (T_c) of a series of polymeric superconducting systems is determined which, sintered or not, are obtained through the incorporation of the superconducting ceramic YBaCuO into two extrinsic conducting polymer systems: PVDF/PS/carbon black and PVDF/PS/copper. In addition, the diamagnetic characteristics of these systems are studied on the basis of susceptibility measurements as a function of temperature. As regards the unsintered systems and according to the experimental results, copper-based composites can be termed as insulating materials and the samples with the highest carbon black content as reaching metalliclike conductivities. In no case, however, is an abrupt leap in conductivity observed as a function of temperature, indicating the superconducting nature of these systems from an electrical point of view. On the contrary, magnetic susceptibility measurements as a function of temperature detect in all cases a superconducting transition, i.e., a shift in the critical temperature range, bringing it close to that of pure YBaCuO (≈ 100 K). After sintering, the samples retained their original shape as well as reasonable mechanical properties. The electrical conductivity study confirmed the absence of superconductivity as a consequence of polymer combustion during sintering and thereby implying the disappearance of the orthorhombic phase of YBaCuO, which X-ray evidence proved to be accountable for superconductivity in this ceramic material. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Since 1987,¹ the superconducting material YBa₂Cu₃O_{7-x} has been commercially available. This material has excellent superconducting properties and an enormous application potential in fields such as the production, storage, and transfer of electrical energy, high-speed trains based on magnetic levitation, high-field magnets, high-precision instruments, computer links, and magnetic screens. In the majority of these applications, however, it has not yet been possible to use YBaCuO at 100% efficiency due to a series of technological drawbacks: first and foremost, the poor mechanical properties of this

material; because these oxides are brittle, their mechanical properties cannot compete with those of conventional metallic superconductors (Nb₃Sn, NbTi). Second, YBaCuO cannot be pressed into the shape of simple or complex profiles by any of the conventional procedures applicable to ceramics, and, third, due to its low stability in polluted environments (especially in moist air or CO₂), the material degrades relatively easily.

For YBaCuO to become a competitive material, these inconveniences have to be overcome. One of the methods of achieving this might be to incorporate YBaCuO into a polymer. In this context, several developments have been described, where these problems are tackled by incorporating or embedding superconducting ceramics into polymeric matrices.²⁻⁸ Yet, none of these approaches has succeeded in optimizing the mechanical properties and

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Table I Composition and Critical Temperatures of Different Systems

PVDF/PS	Composition (% ϕ_v)			T_c (K)
	YBaCuO	N	Cu	
100/0	40	10		94.5
100/0	30	20		95.3
100/0	40		10	98.3
100/0	30		20	101.2
70/30	40	10		95.5
70/30	30	20		91.3
70/30	40		10	95.8
70/30	30		20	98.6
50/50	40	10		97.1
50/50	30	20		
50/50	40		10	95.7
50/50	30		20	93.7
30/70	40	10		92.7
30/70	30	20		95.4
30/70	40		10	95.7
30/70	30		20	93.0

material stability and, at the same time, maintaining the superconducting properties of the ceramic.

Another route which has been used to solve these problems is sample sintering, which has given fairly good results, both regarding particle crosslinking through solid densification and interesting mechanical properties in most cases. The term sintering⁹ is used to describe a process by which a compact inorganic powder is converted into a solid product. This is an important phase in ceramics and metal manufacture which basically consists of heating the compact powder to a certain temperature at which the mass transportation mechanisms become operative. As a result of the initial particle movement,

the pores of the compact powder diminish as the free volume gradually disappears.

In this work, the superconducting properties are studied, before and after sintering, in a series of polymeric composites obtained by incorporating YBaCuO into certain conducting systems based on a PVDF/PS polymeric matrix, which were described in previous work.¹⁰⁻¹² The study of superconducting behavior is based, on the one hand, on the analysis of conductivity as a function of temperature to the purpose of determining the critical temperature of the samples and, on the other hand, on the determination of magnetic susceptibility, again as a function of temperature.

EXPERIMENTAL

The materials used were conventional polymers: poly(vinylidene fluoride) (PVDF) supplied by Solvay under the trade name Solef 6010 ($M_w/M_n = 4.5$) and polystyrene (PS) polystyrol from BASF ($M_w = 200,000$). The conducting fillers were carbon black (CB) Isaf N200 supplied by Cabot Laboratories in powder form (20 nm) and a density of 1.8 g/cm³ and metallic copper (Cu) from Merck, also in powder form, with grain size 63 μm and density 8.9 g/cm³. The superconducting ceramic used was YBa₂Cu₃O_{7-x} Superamic Y200 from Rhône Poulenc, with particle size below 35 μm , and density 6.3 g/cm³.

Component blending was carried out in a Brabender torque rheometer which gave a homogeneous material dispersion for all blends. To optimize the dispersion, several factors were taken into account: a sufficient total blend volume to fill the mixing chamber, which was heated to the appropriate temperature to soften and melt the blend but avoiding component degradation, and a rotor rate which en-

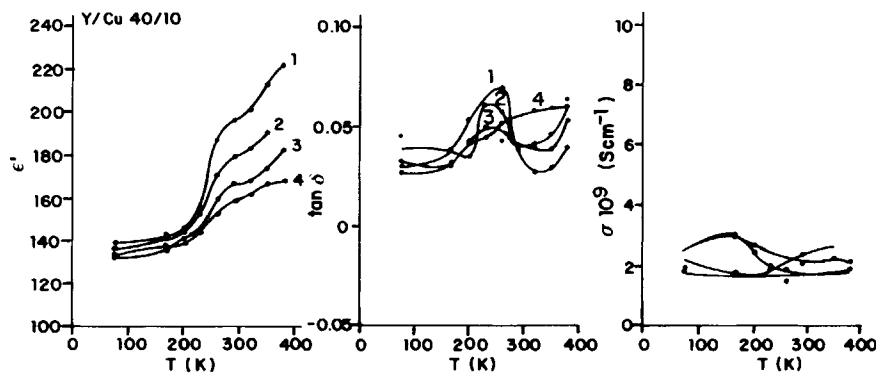


Figure 1 ϵ' , $\tan \delta$, and σ as a function of temperature for Y/Cu 40/10 systems: (1) PVDF/PS 100/0; (2) PVDF/PS 70/30; (3) PVDF/PS 50/50; (4) PVDF/PS 30/70.

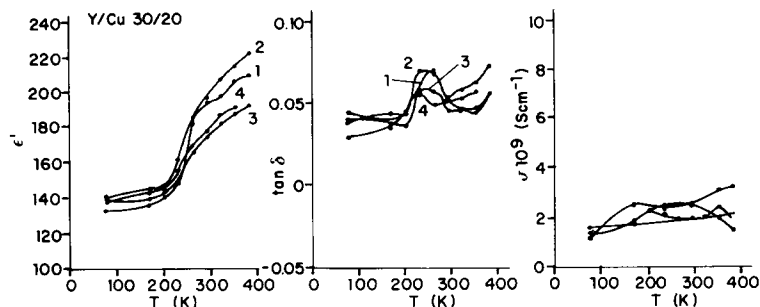


Figure 2 ϵ' , $\tan \delta$, and σ as a function of temperature for Y/Cu 30/20 systems: (1) PVDF/PS 100/0; (2) PVDF/PS 70/30; (3) PVDF/PS 50/50; (4) PVDF/PS 30/70.

sured optimum shear. The mixing chamber used was of the W-60 type, the temperature was set at 468 K and the rotor rate at 55 rpm, and the blend was allowed to set in the chamber for 10 min after torque stabilization.

Conductivity measurements as a function of temperature were conducted using complex impedance spectroscopy in the temperature range 76.5–383 K and applying a heating program geared through an Oxford Instruments ITC 4 temperature controller. The sample was placed in an Oxford Instruments DN 1710 cryostat provided with a liquid nitrogen chamber especially designed for measurements at variable temperature. The surfaces of the pellets (diameter 1 cm, thickness 0.1 cm) were coated with a thin Ag film (Lustre Cerámico 200, supplied by Emetron) to ensure good contact between the sample surface and the measuring electrode, which in this research were two Ag wires welded to the top and bottom surfaces of the sample, respectively, and connected to two electrical terminals of the cryostat which led to the impedance analyzer.

Magnetic susceptibility measurements were conducted with a DSM 4 Manics magnetosusceptometer, designed for the measurement of permanent or induced magnetic moments on small samples

(powders, crystals, or films) and a wide range of temperatures and applied magnetic fields. The apparatus allows changes in susceptibility in the order of 2×10^{-10} emu/g to be detected. Regarding the magnetic moment, sensitivity is 10^{-6} emu for an applied field of 1.5 T.

The samples were sintered in a CHESA oven following a time-temperature profile, which basically consisted of slowly heating the material ($1^\circ\text{C}/\text{min}$) up to 500°C to avoid organic component combustion which could give rise to considerable gas development from oxidation and to ensure that the gases are gradually eliminated. The temperature was then increased at a slow rate ($3^\circ\text{C}/\text{min}$) to 940°C and the sample was held at this temperature for 4 h to achieve densification. Subsequently, the sample was cooled slowly to 500°C where it was held for another 8 h to achieve oxygenation. Finally, the sample was cooled to room temperature at a rate of $1^\circ\text{C}/\text{min}$. Prior to sintering, the samples were machined in the shape of a parallelepiped (2 cm in length, 0.7 cm wide, and 0.1 cm thickness) and were then placed into the oven on aluminum plates coated with a sintered YBaCuO layer.

The direct current measurements were performed using the four-point probe technique. The wires were

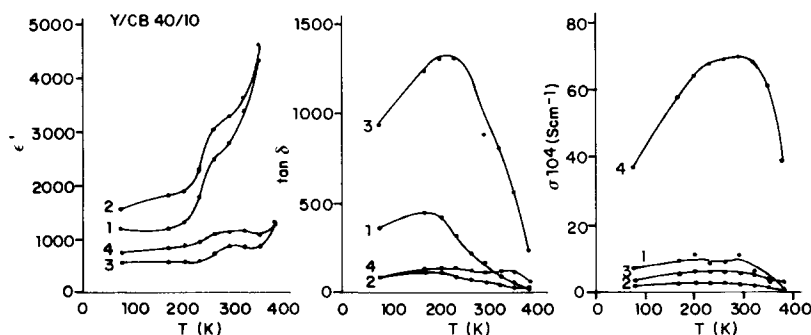


Figure 3 ϵ' , $\tan \delta$, and σ as a function of temperature for Y/CB 40/10 systems: (1) PVDF/PS 100/0; (2) PVDF/PS 70/30; (3) PVDF/PS 50/50; (4) PVDF/PS 30/70.

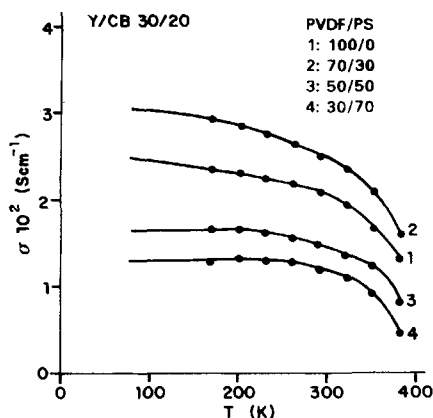


Figure 4 σ as a function of temperature for Y/CB 30/20 systems: (1) PVDF/PS 100/0; (2) PVDF/PS 70/30; (3) PVDF/PS 50/50; (4) PVDF/PS 30/70.

attached to the sample at four points using Ag paint (Lustre Cerámico 200 supplied by Emetron). The direct current source was a Tektronix PS 280 and two HP 34401 A multimeters provided with a high internal resistance, one of these operating as an ammeter and the other as a voltmeter. The temperature was monitored using a similar procedure to that described for the alternating current measurements. X-ray diffraction of the samples was carried out on a Sieman's diffractometer D-500 using a Ni-filtered $\text{CuK}\alpha$ X-ray beam excited at 40 kV.

RESULTS AND DISCUSSION

Initially, a number of samples were selected on the basis of their previously obtained conductivity data.¹² Two experimental conditions had to be met: On the one hand, the total filler concentration should not surpass the 50 vol % threshold, above which the components could no longer be blended into a composite, while on the other hand, systems possessing the highest conductivity should be used to incorporate the greatest possible YBaCuO portion. These conditions were fulfilled only by a few carbon black systems. To make a wider and more comparative study possible, however, it was also decided to incorporate YBaCuO into a set of copper systems. The experimental samples used and their compositions are shown in Table I.

Unsintered Systems

Critical Temperature

The main objective of this study was to examine the existence of critical temperatures in the different

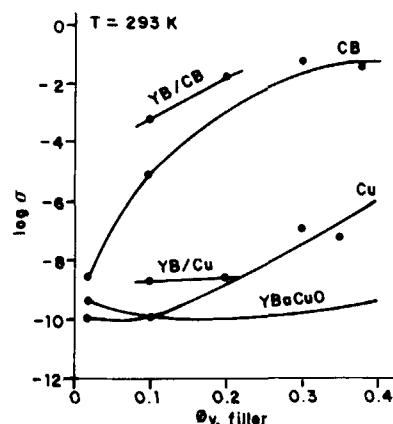


Figure 5 σ as a function of filler content for different systems.

synthesized samples, as a reliable proof of YBaCuO particle crosslinking within the polymeric matrix and, hence, of superconductivity. Thus, the samples were examined for any abrupt change in their conductivity which is present in superconducting materials when conductivity is studied as a function of temperature. Nevertheless, to widen the range of available data, other electrical characteristics were also examined. For the YBaCuO/Cu composites, Figures 1 and 2 show the conductivity data (σ), the dielectric constant (ϵ'), and the loss tangent ($\tan \delta$) as a function of temperature, leaving no doubt about the fact that, independent of the YBaCuO/Cu ratio, there is no sudden change in conductivity. Similarly, the conductivity values obtained and their behavior vis-à-vis temperature confirm these composites as insulating materials, in which YBaCuO particle percolation has not been achieved. The remaining electrical characteristics show similar traits for all the samples in this series. On the one hand, the dielectric constant increases with temperature and the

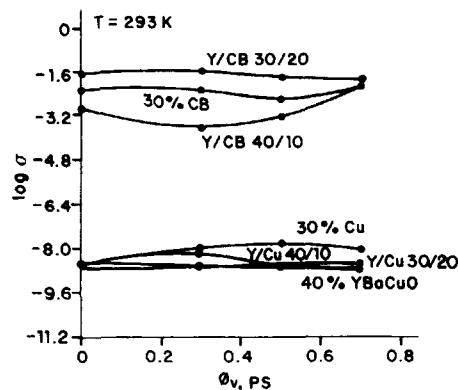


Figure 6 σ as a function of PS content for different systems.

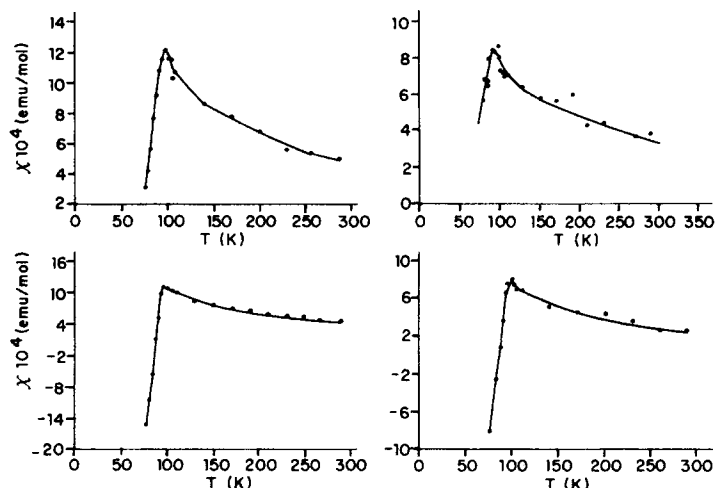


Figure 7 χ as a function of temperature.

loss tangent reaches a peak at temperatures below 273 K which is attributable to a dielectric relaxation associated with the polymer (PVDF). The effect of the composition of the polymer system is minimal, with regard to the conductivity and the other electrical properties investigated, although in general terms a slight decrease in all of the properties was observed with increasing PS portion.

Figures 3 and 4 show the σ , ϵ' , and $\tan \delta$ values as a function of temperature for the YBaCuO/CB composites. In this series, the electrical behavior was found to vary as a function of CB content. At low CB concentration (YBaCuO/CB 40/10) (Fig. 3), the samples show conductivity values typical of semiconductors approaching conducting materials, whose variation with temperature depends on the

polymer blend used. At the highest PS content, e.g., the conductivity values become considerably higher with a maximum at about ambient temperature, which is typical of materials in which conductivity is generated through a hybrid between the percolation and the tunnel mechanism. Hence, these materials are highly temperature-sensitive as a consequence of the different thermal expansions occurring among the components. These expansions cause the particles to move together to a greater or lesser extent, depending on the temperature, thus either favoring or hindering the percolation or tunnel conduction mechanisms. The effect of temperature on the remaining electrical properties is similar to that observed for the copper composites: The dielectric constant increases with increasing temper-

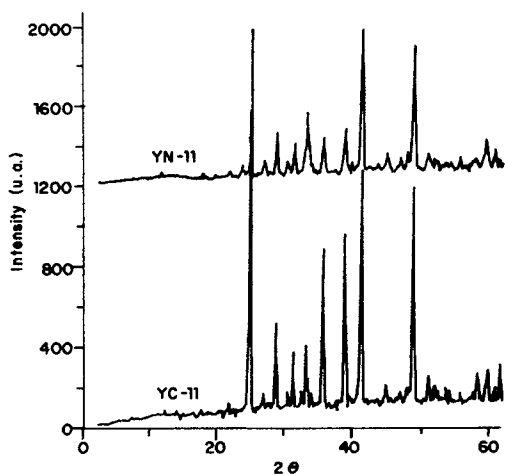


Figure 8 RX diagrams of samples: YN-11: PVDF/PS 70/30 and Y/CB 40/10; YC-11: PVDF/PS 70/30 and Y/Cu 40/10.

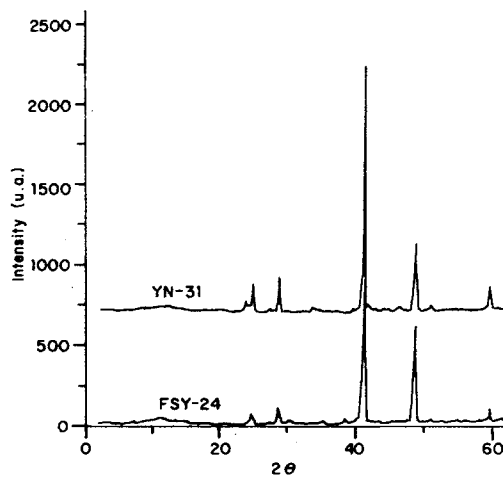


Figure 9 RX diagrams of samples: YN-31: PVDF/PS 30/70 and Y/CB 40/10; FSY-34: PVDF/PS 30/70 and Y/Cu 40/10.

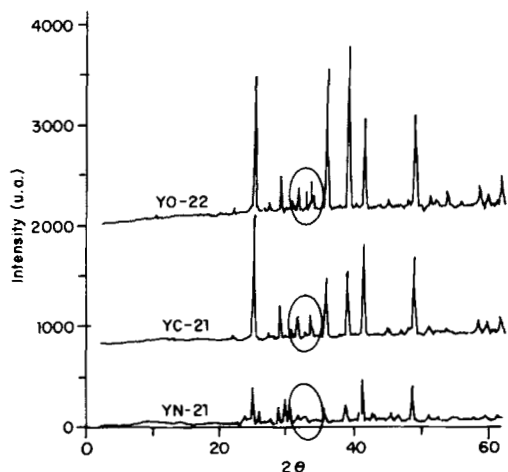


Figure 10 RX diagrams of samples: YC-22: PVDF/PS 50/50 and Y/Cu 30/20; YC-21: PVDF/PS 50/50 and Y/Cu 40/10; YN-21: PVDF/PS 50/50 and Y/CB 40/10.

ature and the loss tangent is at its highest below room temperature, which is a consequence of the dielectric relaxation associated with the polymer system (PVDF). At higher CB content (YBaCuO/CB 30/20) (Fig. 4), the material becomes more highly conducting and exhibits induction, and as regards the electrical effects, it may be considered to be a metal. With increasing temperature, the conductivity decreases, which is a characteristic of metallic conductors. However, no prominent jump in conductivity was observed in the experimental temperature range which legitimates the statement that YBaCuO is not percolated and, hence, does not transmit electricity with zero resistance below its critical temperature, for the simple reason that it does not possess any such temperature.

For comparison, Figure 5 presents a synopsis of the effect exerted by the fillers (CB or Cu) individually or in association with YBaCuO on the conductivity of the composite at 293 K. The YBaCuO composites prove to be insulating materials over the whole range of concentrations studied; the Cu composites, however, cease to be insulating at high concentrations and become semiconducting, whereas the CB composites with 10% or higher filler concentrations have metalliclike conductivities. When the superconducting ceramic is added to the Cu composites, for one and the same filler portion, the conductivity increases by one order of magnitude within the range of the experimental concentrations, yet it does not cross the semiconductor borderline. In the case of the CB composites, the presence of YBaCuO increases the conductivity by between 10 and 100 times as compared to the YBaCuO-free materials, yet it fails to percolate the ceramic particles.

By the same token, Figure 6 shows conductivity as a function of PS content at 293 K, with a view to gaining insight into the effects of composition of the original polymer blend. As can be observed, variation in blend composition does not significantly affect the conductivity of the material.

Magnetic Susceptibility

One of the most conclusive tests of the superconducting nature of a material is to determine whether it excludes a magnetic field (Meissner effect) and, if so, at which temperature the effect occurs (critical temperature). All YBaCuO composites were examined in this way by means of magnetic susceptibility measurements as a function of temperature using the Faraday method.

From the susceptograms obtained, one of which has been reproduced in Figure 7 by way of example, all the samples exhibited an abrupt change in susceptibility at their critical temperatures which were close to that of pure YBaCuO (100 K) (Table I) and which can be interpreted in terms of all these samples being superconductors, independent of CB, Cu content, or polymer composition. Differences were found, however, in the critical superconduction transition temperatures which are due not only to the effect exerted by the presence of CB or copper, but also by the composition of the polymer systems which acts as a supportive matrix for the YBaCuO particles. In general terms, the values obtained for the copper composites were slightly higher than those of the CB samples. On the other hand, the most negative effect arising from the presence of PS was found in the copper composites: The higher the PS content, the lower the critical temperature, an effect which was not prominent in the CB composites in which the differences were much smaller.

In the light of these results, the systems under study are not superconducting from an electrical point of view, i.e., they do not have a superconducting transition at a temperature close to the critical temperature of YBaCuO, although they do behave like superconductors from a magnetic point of view since they exclude the magnetic field below their critical temperature.

Sintered Systems

Such behavior, however, seems to be quite usual as regards the few superconducting composites described in the literature.¹³⁻¹⁵ In an attempt to tackle this problem, the experimental materials were sintered following the time-temperature profile opti-

mized for pure YBaCuO.¹⁶ On the whole, the sintered samples preserved their original shape and had satisfactory mechanical properties regardless of the composition of the initial polymer system and the CB or Cu concentration.

The sintered samples were analyzed by direct current using the four-point probe technique which allows the superconducting transition temperature to be determined by plotting resistivity against temperature. The results showed that, although the composites had fairly high conductivities, no superconducting transition was observed. X-ray diffraction studies revealed that sintering gave rise to three different structures (Figs. 8–10). The basic structure corresponds to the diffractograms shown in Figure 8 which, in spite of their complexity, shows the presence of a complex blend of the oxides of the initial elements. In only two samples were the diffractograms shown in Figure 9 found, which are difficult to interpret in structural terms, although it seems that some of the original elements were reduced to the respective metals. Finally, and only in the three samples shown in Figure 10, a minor superconducting YBaCuO phase was generated during the sintering process which is detectable in the framed angles illustrated in the figure.

The destruction of the superconducting character of YBaCuO during composite sintering is attributable to the fact that the combustion of the polymers present in the material entails a drastic drop in the oxygen content of the superconducting ceramics and, hence, the destruction of the orthorhombic phase, which is the superconducting phase in this material. Therefore, the results presented to date indicate that sintering composites based on the polymer system PVDF/PS does not generate any superconducting material.

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