Crystallization in J-1 polymer/carbon-fibre composites: bulk and interface processes

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The process of crystallization, during isothermal treatments from the melt, of a composite of a J-1 polymer (a polyamide homopolymer produced by Du Pont) containing a single carbon fibre was studied. Two main crystalline morphologies develop in the polymer, depending on the temperature. This was directly observed during the treatment of the sample in a hot-stage chamber placed under a light microscope, and confirmed by both X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses. Moreover, a transcrystalline layer grows at the interface with the carbon fibre. The kinetics of bulk and interface crystallization were evaluated and compared by measuring, at different temperatures, the radii of crystals and the thickness of the transcrystalline layer with time. Moreover, bulk crystallization kinetics, measured by the depolarization of the light passing through the polymer sample during the isothermal treatment, indicated the apparent presence of two regimes of bulk crystallization.

1. Introduction

Composite-materials research in the past few years is characterized by an increasing interest in semicrystalline thermoplastic polymers as an alternative to epoxy matrices [1-3], due to the fact that the former possess higher toughness, longer shelf life, good solvent resistance and satisfactory mechanical properties, coupled with an easier fabrication process. The mechanical properties of a semicrystalline polymer or composite have been shown [4-7] to be dependent on three levels of microstructure, namely, the intracrystalline, the crystallite and the spherulite levels, which can all be strongly affected by processing conditions. This fact requires an accurate definition of the processing conditions and specific knowledge of how the process affects structure and morphology.

J-1 polymer is semicrystalline polyamide homopolymer which has been studied by a number of researchers [4-6, 8-10]. Its low density (1040 kg m^{-3}) and relatively high glass-transition temperature, T_g (149 °C), combined with inertness to most organic solvents, make it suitable as matrix for high-performance composites. Moreover due to its low melt viscosity, it can be processed at a lower temperature than many other high-performance thermoplastic resins. In this study it is shown that the microstructural features of the material strongly depend on its thermal history. It is known [9] that J-1 polymer cast from m-cresol solution at different temperatures present polymorphic transitions, some of which may be significant to composite materials. This investigation is concerned with the process of crystal-lization from the melt of the neat polymer and of polymer microcomposite samples, containing a single carbon fibre, during isothermal treatments at different temperatures between 275 and 235 °C. During the treatment, crystallinity develops in the bulk as well as at the interface with the carbon fibre, and both their kinetics are evaluated. This paper is part of a larger study dedicated to the thermal, morphological and mechanical characterization of the matrix and its carbon-fibre composite (11-13).

2. Experimental procedure

The following materials were used: a polyamide homopolymer based on bis(para-amino cyclohexyl) methane (PACM) produced by Du Pont under the name J-1 polymer and supplied as a 0.2 mm thick film, and a high-modulus pitch-based carbon fibre PRD-172 produced by Du Pont.

The as-received J-1 polymer contains some water, which is eliminated after a treatment under vacuum in an oven at 60 °C; this was revealed by the DSC scans shown in Fig. 1. These were performed with a DSC30 Mettler Calorimeter, using a heating rate of 10 °C min^{-1}. From the as-received J-polymer film, samples in the shape of thin sheets about 100 μm thick were prepared by compression moulding as follows: four layers of the film, wrapped in aluminium paper (in order to avoid contact with air), were hot pressed at 320 °C for 20 min in a Carver press and then quenched in ice water. To obtain composites, single carbon-fibre filaments were sandwiched between the polymer inner
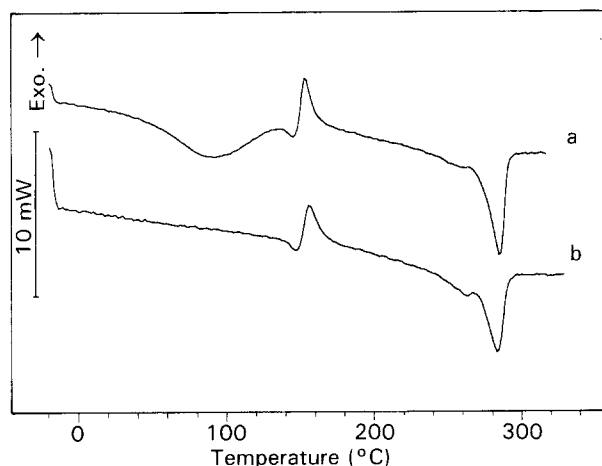
Figure 1 DSC thermograms of a J-1 polymer from 0 to 330 °C: (a) as-received, and (b) as-received and dried.

Figure 2 Cross-polarized micrographs of polymer crystallized at: (a) 275 °C, and (b) 255 °C.

layers, prior to pressing. A hot-stage Mettler FP82 and a Nikon microscope equipped with a micrometer ocular were used for the determination of the growth of the spherulites. For the determination of the bulk-crystallization kinetics, a hot-stage Mettler FP52, a heat-controller Mettler FP80 and a light-analyser Mettler GA17 were used. These measurements were performed by recording the depolarization of light passing through the samples during isothermal treatments at temperatures in the range 275–235 °C. In all of the reported tests, samples, cut in the shape of small disks from either the polymer or the composite sheets, were used. They were heated to 300 °C in the hot stage, kept at this temperature for 3–4 min, in order to assure their complete melting, as determined by DSC analysis, and then cooled to the test temperature.

There was a noticeable difference between the two crystallization measurements described above, depending on the method of cooling after melting. Whereas the first method employed free-air convection, without any auxiliary system, the second involved flushing with nitrogen gas passing through a serpentine immersed in liquid nitrogen. In both experiments, the highest cooling rates allowed by the system were used, namely, 10 and 35 °C min^{-1}, respectively. XRD was performed with a Rigaku D/max diffractometer, with a scintillation counter, and with a graphite curved-crystal monochromator in the diffracted beam.

3. Results and discussion

Cross-polarized micrographs of the polymer crystallized in the hot stage reveal two different crystalline patterns depending on the temperature of the thermal treatment, as shown in Fig. 2a and b for single-fibre microcomposites treated at 270 and 255 °C, respectively. When crystallized at a temperature in the range 275–260 °C, the polymer develops well-defined spherulites (with a Maltese-cross extinction pattern) in its bulk, while after isothermal treatments at lower temperatures a less distinct morphology is evident.

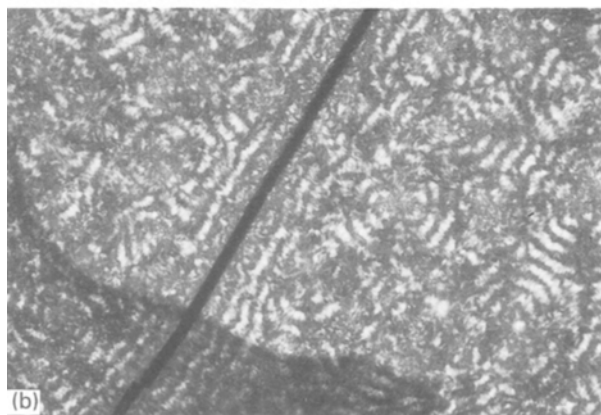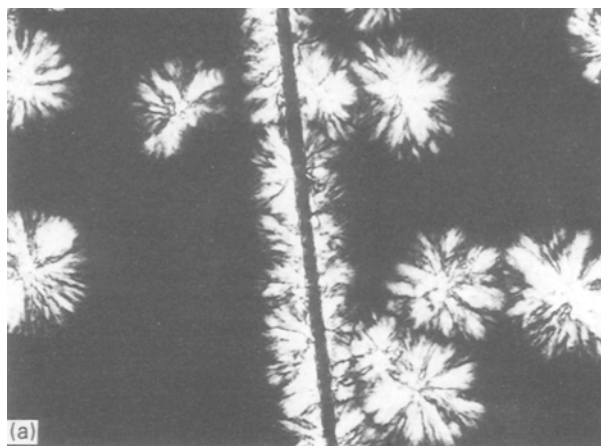The presence of a high-modulus pitch-based carbon fibre induces nucleation and growth of crystals on its surface (transcrystallization). This mechanism may compete with the bulk-crystallization process, depending on their respective kinetics as a function of the thermal-treatment temperature. At relatively higher temperatures, bulk crystallization develops first and progresses faster, thus entrapping and limiting the growth of the transcrystalline layer. At lower temperatures, however, the bulk crystallization kinetics are slower than the transcrystallization kinetics, and the transcrystalline layer appears to be already well developed when spherulites in the bulk just start to form.

The nucleating effect of the carbon fibre is shown clearly by the results of the XRD analysis, performed on melted and quenched samples annealed for different periods at 270 °C. After 15 min at 270 °C, two different crystal structures develop in the polymer and the composite, as shown in Fig. 3a and b. The diffractogram of the neat polymer exhibits only two broadened peaks at $2\theta = 17.5°$ and $19.6°$, superimposed on an amorphous halo (Fig. 3a). This results from the small dimension and imperfect structure of the crystals developed in the polymer after 15 min at 270 °C. Whereas the hump of the amorphous phase is still present, the diffraction pattern of the crystalline structure developed in the microcomposite reveals more detail and peak sharpening (Fig. 3b), expressing better crystallization of the polymer. The difference between the two XRD patterns is considered highly significant, being produced by a single carbon filament, whose
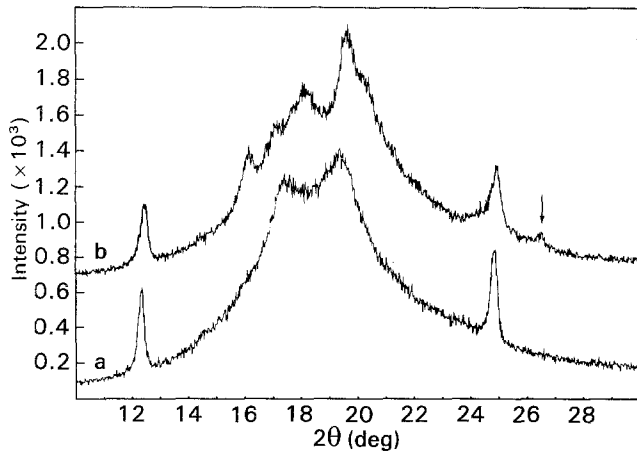
Figure 3 XRD diffractograms, after annealing for 15 min at 270 °C, of: (a) the melted and quenched polymer, and (b) a carbon-fibre-reinforced microcomposite.

XRD peak is marked by the arrow. After longer treatment times at 270 °C, the XRD patterns of the polymer and the composite become quite similar, as the crystallization of the bulk prevails. The diffractograms of all the samples exhibit a couple of additional peaks at $2\theta = 12.6°$ and $24.7°$, which may be attributed to some additives.

The experimental data in Fig. 4a, b and c show the effect of time and temperature on the size of the spherulites and on the transcrystalline-layer thickness around the fibre. As expected, both the spherulites and the transcrystalline layer grow linearly with time, while the gradients (the growth rates) are inversely proportional to the temperature (see below).

Crystallization growth rates are reported in Fig. 5 for the spherulite radius and the transcrystalline-layer thickness. The curve of the transcrystalline growth rate has a maximum at 240 °C. The curve of the spherulitic growth rate seems to follow the same trend, even though data for temperatures lower than 240 °C are missing, due to difficulty in following the crystallization process, which is very fast at this temperature.

In addition, Fig. 6 reports the spherulitic- and transcrystalline-growth-rate ratio versus temperature. It is seen that despite a moderate increasing trend, the ratio is equal to one over a wide temperature range. Below and above the 245–270 °C temperature range either transcrystallization or bulk crystallization are favoured, respectively.

To obtain additional evidence of the bulk-crystallization kinetics, the intensity of the depolarization of light passing through J-polymer samples during the isothermal treatment was measured. The intensity of depolarized light has an S-shaped dependence on the logarithm of time; this is exemplified by the treatment at 265 °C reported in Fig. 7. For every treatment temperature, $t_{(1/2)}$, the time at which the depolarized light reaches one-half of its final value, was recorded; it is correlated with the bulk crystallization kinetics factor, K by the following equation [14]

$$K = 1/t_{(1/2)}$$
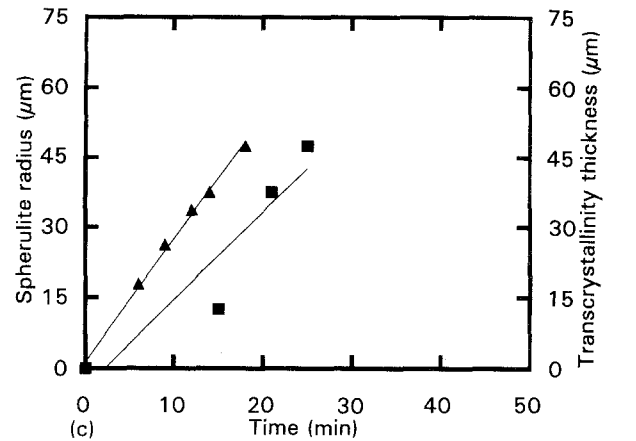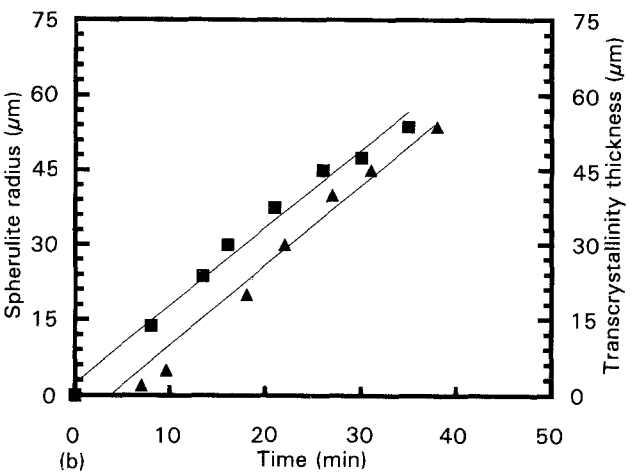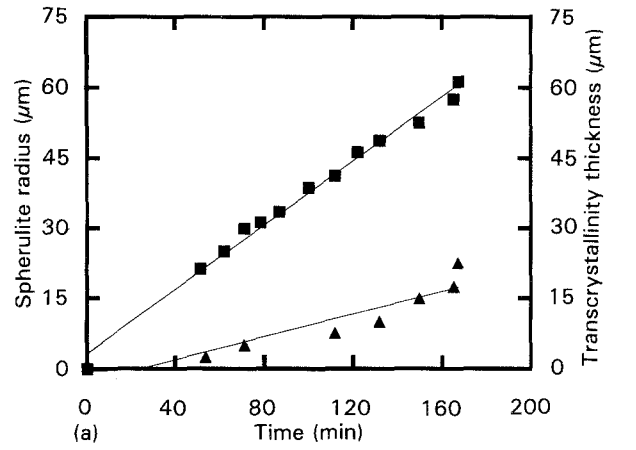
Measurement of the crystallization kinetics by the

Figure 4 Spherulite size during isothermal bulk crystallization and layer thickness of isothermal transcrystallization versus time at different temperatures: (a) 275 °C, (b) 265 °C, and (c) 260 °C.
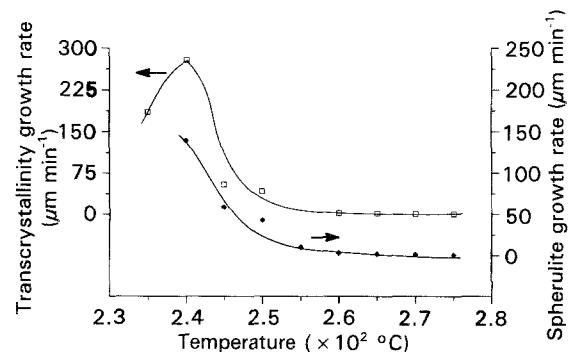

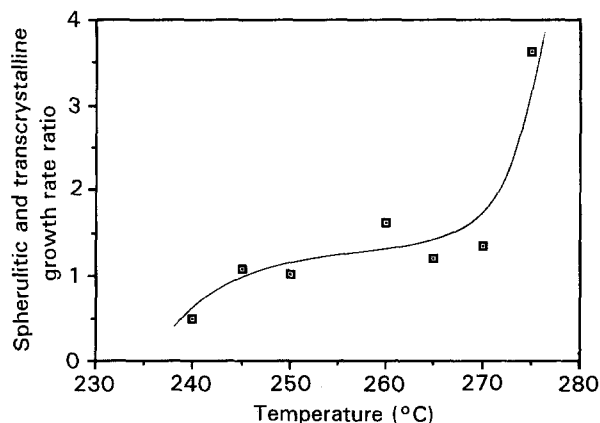Figure 5 (□) Transcrystallinity growth rate and (◆) spherulitic growth rate versus temperature.

Figure 6 Bulk-crystallization and transcrystallization-rate ratio versus temperature.
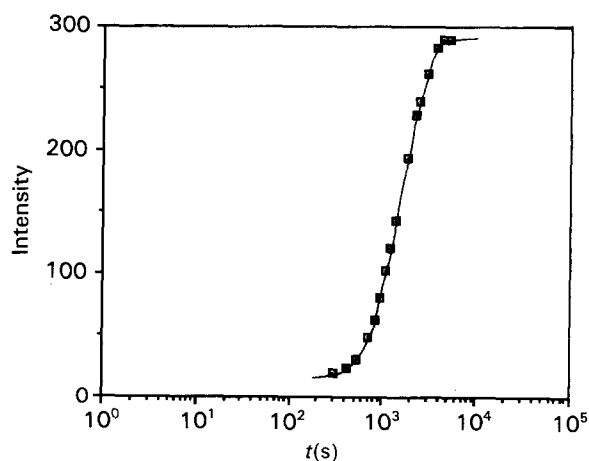

Figure 8 Measured values of the bulk crystallization constant, $K(T)$, at different crystallization temperatures.

Figure 7 Intensity of depolarized light during isothermal crystallization at 265 °C versus time.

Figure 9 Intensity of depolarized light during isothermal crystallization at 238 °C versus time.

light-depolarization method and the parameter K is easier and more accurate than measurements based on a single spherulite size. Obviously, the first technique follows the growth of a large number of crystals; hence, its results have a representative significance as well as a higher intrinsic accuracy. The calculated values of K are plotted in Fig. 8 as a function of different crystallization temperatures. The points can be approximately fitted by two straight lines which intersect at 257.6 °C. This suggests the existence of at least two crystallization regimes in the range 240–275 °C. Moreover, K assumes very high values as the temperature is lowered to 240 °C. At still lower temperatures, however, the crystallization process becomes very fast and starts, in the hot stage, before the material reaches the imposed isothermal condition. This is demonstrated in Fig. 9 by the results of the depolarized-light measurement for isothermal crystallization at 238 °C.

Following Clark and Hoffman [15] and other recent papers [16–18], crystallization of polymers proceeds through three different thermodynamic regimes (according to the rates of surface nucleation and growth of crystals) which are designated regime I, regime II and regime III.

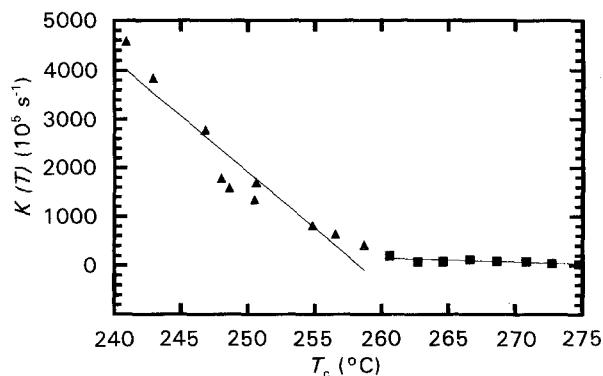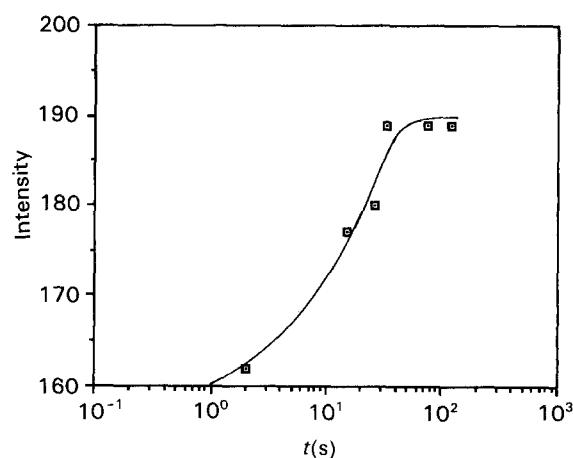In Hoffmann's modified equation [14], the crystallization-kinetics factor, K, can be correlated to the

nucleation constant, K_g, by the relation

$$\log K + \frac{U^*}{2.303R(T_c - T_0)} =$$

$$\log K_o - \frac{K_g}{2.303T_c(T_{mo} - T_c)} \quad (1)$$

where, U^* is the constant activation energy of transport of molecules to the crystal interface (6280 J mol^{-1}); R is the universal gas constant (8.31 J mol^{-1}K^{-1}); T_c is the isothermal crystallization temperature; T_0 is the temperature at which any viscous flow is assumed to be negligible, $(T_0 \approx T_g - 30)$; K_0 is a pre-exponential factor (a $priori$ unknown); and T_{mo} is the thermodynamic melting temperature. In order to define the two different regime ranges, $K(T)$ values were used to calculate the nucleation constants, K_g and K_0, in Equation 1.

Fig. 10 presents a plot of the left-hand side of Equation 1 as a function of $1/[2.303T_c(T_{mo} - T_c]$. Values of T_g and T_{mo} for the J-polymer equal to 149 °C and 288.4 °C, respectively, (see Fig. 1) were assumed in the calculation [13,19]. The data in Fig. 10 can be fitted with two straight lines, whose change in gradient signifies the presence of a regime transition, probably from III to II. Regime III exists at the lower-temperature range and represents very high nucleation rates, while regime II represents slower rates. The regime-transition point occurs at 260.5 °C. The gradient and
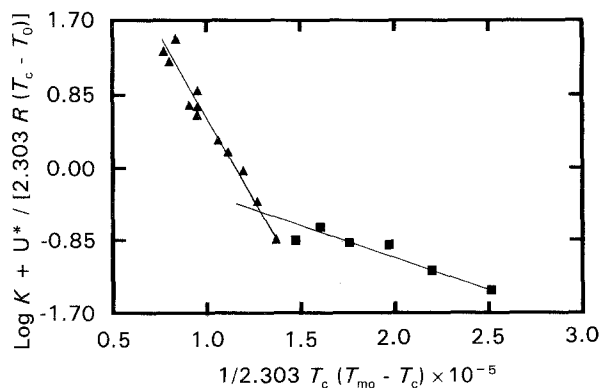
Figure 10 Calculated values of the first member of Hoffmann's modified equation, $\log K + U^*/[2.303R(T_c - T_0)]$, versus $1/2.303T_c(T_{mo} - T_c) \times 10^5$

the intercepts of the two straight lines in Fig. 10 produce the values $K_{gII} = 0.606$ and $K_{0II} = 455.8$, and $K_{gIII} = 3.07$ and $K_{0III} = 23.7$ for the respective regimes.

Although Point and Dosiere (20) questioned the existence of a transition from regime II to regime III, a transition has been observed in several polymers, such as polyethylene [21], polyoxymethylene [22], polypropylene [15], poly(3-hydroxybutyrate) [23], poly-(phenylenesulphide) [24], cis-poly(isoprene) [25], poly-L-lactic acid [14] and poly(ethylene oxide) [26]. However, the ratio of K_{gIII}/K_{gII} in this study is 5.1, far above the value of 2 predicted by the Hoffmann theory [27], and also higher than the value (about 3) found elsewhere [14] for another polymer. This difference cannot be fully explained on the basis of the experimental data, and a further investigation is required. It may, however, be attributed to the observed existence of different crystalline morphologies.

4. Conclusion

The objective of this study was to determine the effects of thermal history on the microstructural features of both the neat J-1 polymer and its carbon-fibre microcomposite, as a starting point for a wider investigation of the relationship between thermal history, structure and properties.

Crystallization from the melt produced different crystalline morphologies for different isothermal treatment temperatures. The kinetics of the isothermal crystallization process were evaluated both by measurements of the radial crystal size and of the kinetics constant of bulk crystallization. These parameters revealed the presence of a transition from regime III of crystallization to regime II at about 260 °C. For the carbon-fibre-reinforced material, the high-modulus pitch-based carbon fibre turned out to be an effective nucleating agent. The transcrystalline layer grew linearly with time and its growth rate reached a maximum at 240 °C. Both the spherulitic and transcrystalline growth rates increased sharply in the range 245–240 °C, while keeping almost constant at very low values for higher temperatures (up to 275 °C).

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