A study of plastic plateau disappearance in stress-strain curve of annealed polypropylene films during stretching

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ABSTRACT

The change of plastic plateau in the stress-strain curve of annealed polypropylene (PP) films was followed and the corresponding melting properties and microstructure were characterized by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). It was found that during stretching under room temperature, the plastic plateau disappeared progressively with the increase of drawing ratio. The presence of the plastic plateau was attributed to the stretching of unstable crystalline part which was formed by tie chains around initial row-nucleated lamellar during annealing. During stretching, the unstable part was stretched and converted to bridges connecting separated lamellae. There was direct relationship between the disappearance of plastic plateau and pore formation.

1. INTRODUCTION

Polypropylene (PP) is a well-known semi-crystalline polymer and it has been used for the fabrication of microporous membranes based on melt stretching mechanism. During the fabrication process, there are three main consecutive stages: (1) production of the precursor film with row-nucleated lamellar structure through crystallization under shear or elongation field, (2) annealing of the film to remove imperfections in crystalline phase and to thicken the lamellae, and (3) stretching at low and high temperatures to create and enlarge pores, respectively.

Obtaining a precursor film with uniform row-nucleated lamellar structure is the most important step in the fabrication of microporous membrane. Both raw material physical properties and processing conditions have an important influence on the row-nucleated lamellar structure. (Sadeghi 2007.5) found that the resin with a higher molecular weight had a tendency to form a planar crystalline morphology as the draw ratio increased. Air cooling, the temperatures of chill rolls and thermal-setting rolls and draw ratio are believed to be the main factors to control the crystal structure in the processing of precursor film, which can be found in the work given by (Tabatabaei 2009).

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Annealing is able to eliminate some drawbacks in lamellae. After annealing, lamellae are rearranged and the row-nucleated lamellar structure with thicker lamellae and narrower lamellae thickness distribution is obtained.

In the third stage, the lamellae and amorphous parts between the lamellae are separated by cold stretching and then pores are created. The hot-stretching enlarges the pores. (Sadeghi 2007.1) found that during the hot stretching, some lamellae melt and formed a 'bridge' structure through re-crystallization in the micropores. The lamellae thickness was reduced when a large number of 'bridge' structures were created.

It has been well known that annealing stage is of great importance for the fabrication of microporous membrane. (Lei 2012) found that compared with that of precursor film, the significant change after annealing was that a low temperature melting plateau endotherm appeared in the differential scanning calorimetry curves. During stretching under room temperature, the plateau disappeared progressively and there was a direct relationship between the plateau disappearance and void formation during stretching.

Sadeghi (2007.1) compared the stress-strain curves of precursor and annealed film and the difference after annealing was that a plastic shoulder and later strain-hardening appeared after the initial elastic region. Many investigations have shown that the shoulder was related to the lamellae separation and pore formation. However, up to now, no work has reported its change during stretching and its direct relationship with pore structure.

In this article, the stress-strain curve of PP film which has been stretched to different ratio under room temperature was followed. Before stretching, the PP precursor film was annealed under 145℃ for 30min.The corresponding melting curves and microstructure were tested using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1 Materials
A 2.0 g/10min PP (230℃,2.16 Kg) from Yangzi petrochemical company, China, was used. Its peak melting point (T_m) and crystallization temperature (T_c), obtained from differential scanning calorimetry (DSC, PerkinElmer DSC 7, Massachusetts, United States) at a rate of 10℃/min, were 167.7℃ and 115.1℃, respectively.

2.2 Preparation of stretched PP film
Firstly, the precursor film was prepared. It was made by cast extrusion through a T-slit die followed by stretching and thermal-setting. During extrusion, the uniaxial (machine direction, MD) stretching was applied to PP melt, which resulted in the oriented crystalline structure. The die temperature was set at 210℃ and a draw ratio of 125 was applied. The films were produced under chill roll temperature of 80℃ and then annealed at 145℃ for 30 min.

The annealed film was stretched under room temperature. The drawing ratios for sample A, B, C, D, E and F were 2.5%, 6%, 15%, 25%, 60% and 100%, respectively. Samples were chosen according to the stress-strain curve of annealed PP film shown in

Fig. 1 Sample A represented the film before yielding point. Sample B was around the yielding point. Sample C and D were in the plastic region, especially sample D was near the strain-hardening zone. Sample E was within the strain-hardening region. Sample F represented the film after its second yielding point.
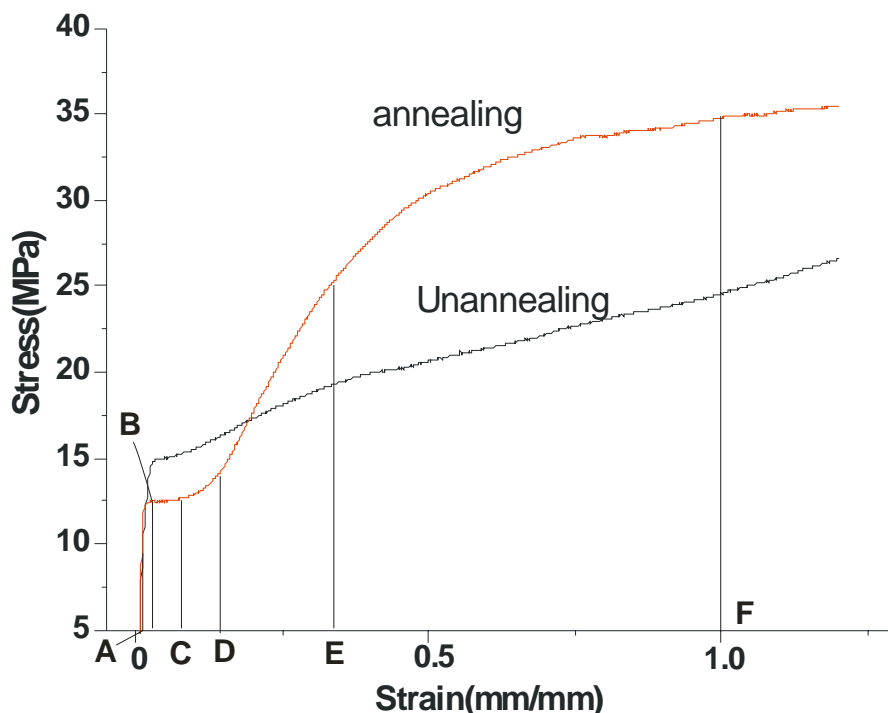

Fig. 1 Sample designation in the stress-strain curve of annealed PP film

2.3 Characterization

The stress-strain curve of stretched PP film was tested using Hualong WDW-10C machine equipped with a environmental chamber for tests at high temperature. The initial length of test samples was 50mm and the strain rate was 50mm/min.

A PerkinElmer DSC 7 was used to measure the melting curves of stretched samples at a heating rate of 10℃/min. Surface morphology was characterized by scanning electron microscopy (SEM; LEO SUPRA 55, Carl Zeiss, Germany).

3 RESULTS AND DISCUSSION

In Fig. 1, it could be seen that compared with that of precursor film, the significant difference in the stress-strain curve of annealed film was the appearance of plastic plateau after the initial elastic region. To investigate the plateau change during stretching under room temperature and its direct relationship with pore structure, samples with different drawing ratio were chosen and their stress-strain curves were tested.

Fig. 2 gives the stress-strain curves of stretched PP films. Similar to that in annealed film, an apparent plastic plateau was still observed in sample A and B, but it became weak for sample C. For sample D, which was in the transition zone from plastic to strain-hardening region, the plateau almost disappeared. In sample E and F, the

plateau vanished completely. During stretching under room temperature, the plastic plateau disappeared progressively，which was similar to the variation of low temperature melting plateau endotherm in DSC curves of PP films during stretching, given in our previous article (Lei 2012). We believe there must be some relationship among the disappearance of plastic region, melting plateau endotherm and micropore formation.
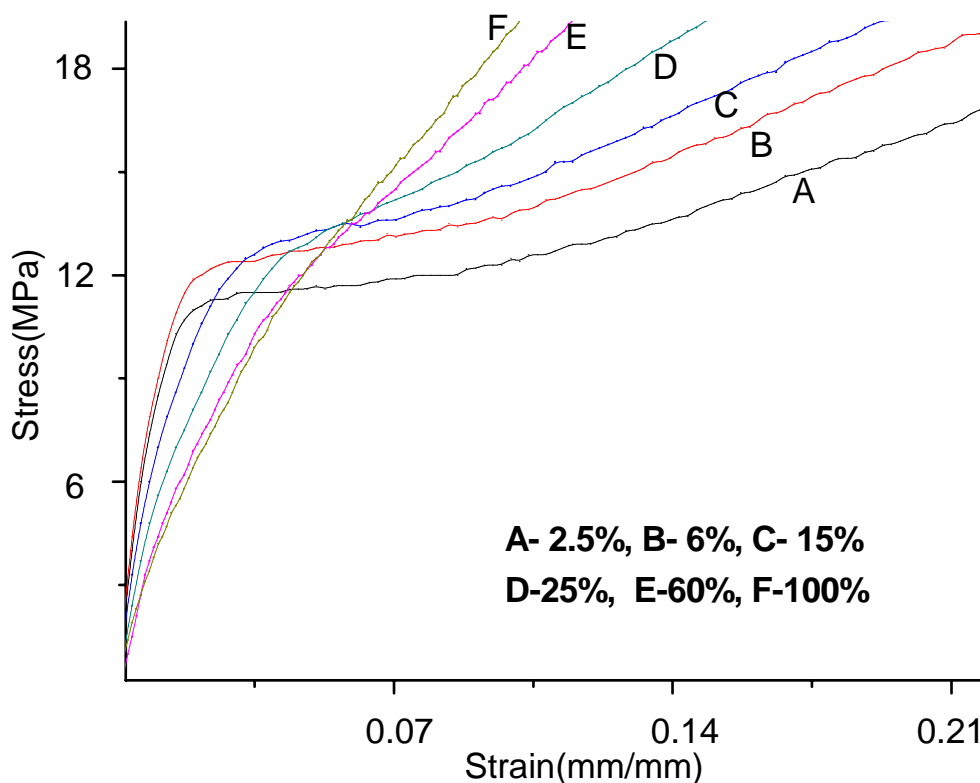

Fig. 2 Stress-strain curves for PP films with different drawing ratio

The DSC curves of PP samples are given in Fig.3. With the increase of drawing ratio from sample A to F, the low-temperature endotherm plateau formed during annealing disappeared progressively and it could not be seen in sample D, E and F. In our previous work (Lei 2012), the low-temperature endotherm plateau in the DSC curve was believed to come from the crystallization of some tie chains directly contacting with initial lamellae. The DSC curves in Fig.3 indicated that the grown crystals around initial lamellae during annealing were unstable and could disappear during stretching.

Fig. 4 gives SEM results for stretched PP films. On the surface of sample A and B, no voids could be observed. For sample C, some chains were pulled out and standing near the lamellae. For sample D, the pulled out chains connected and formed bridges between the lamellae. In sample E, the connecting-bridge structure became more apparent and some scission of bridges and deformation of lamellar crystal were also observed. With further drawing to sample F, serious lamellae deformation, bridges scission and pores disappearance were observed. It was well known that the deformation of lamellar crystal was due to the interaction between lamellae by connecting-bridges. Some weak bridges broke during stretching and the direct results

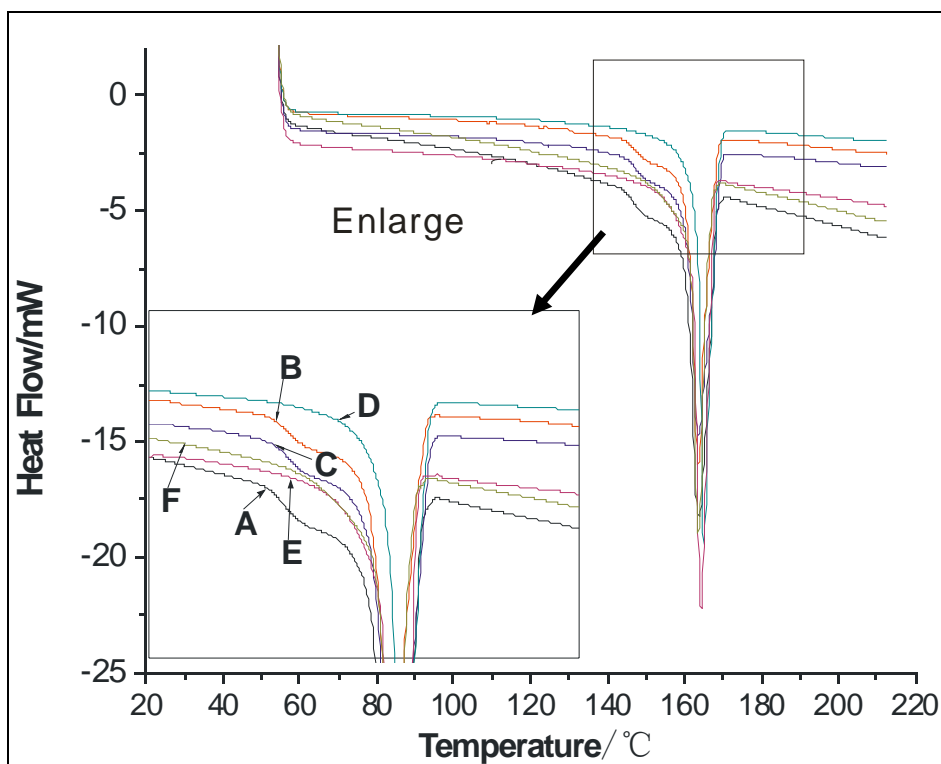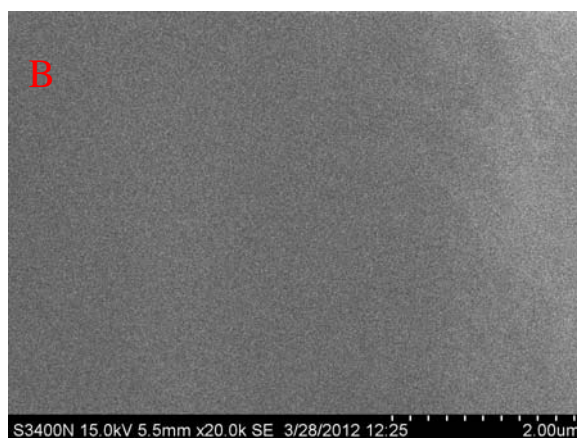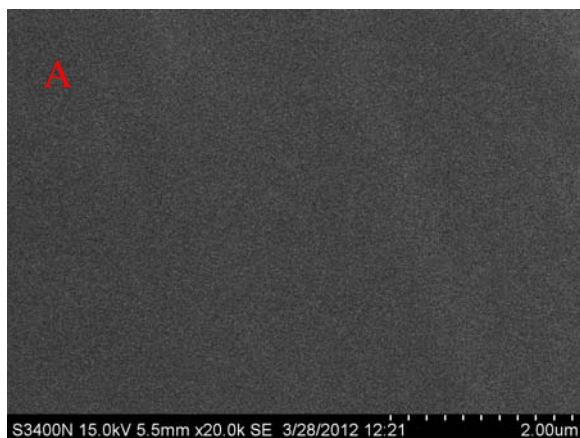were that the number of bridges decreased and the size of pores reduced.

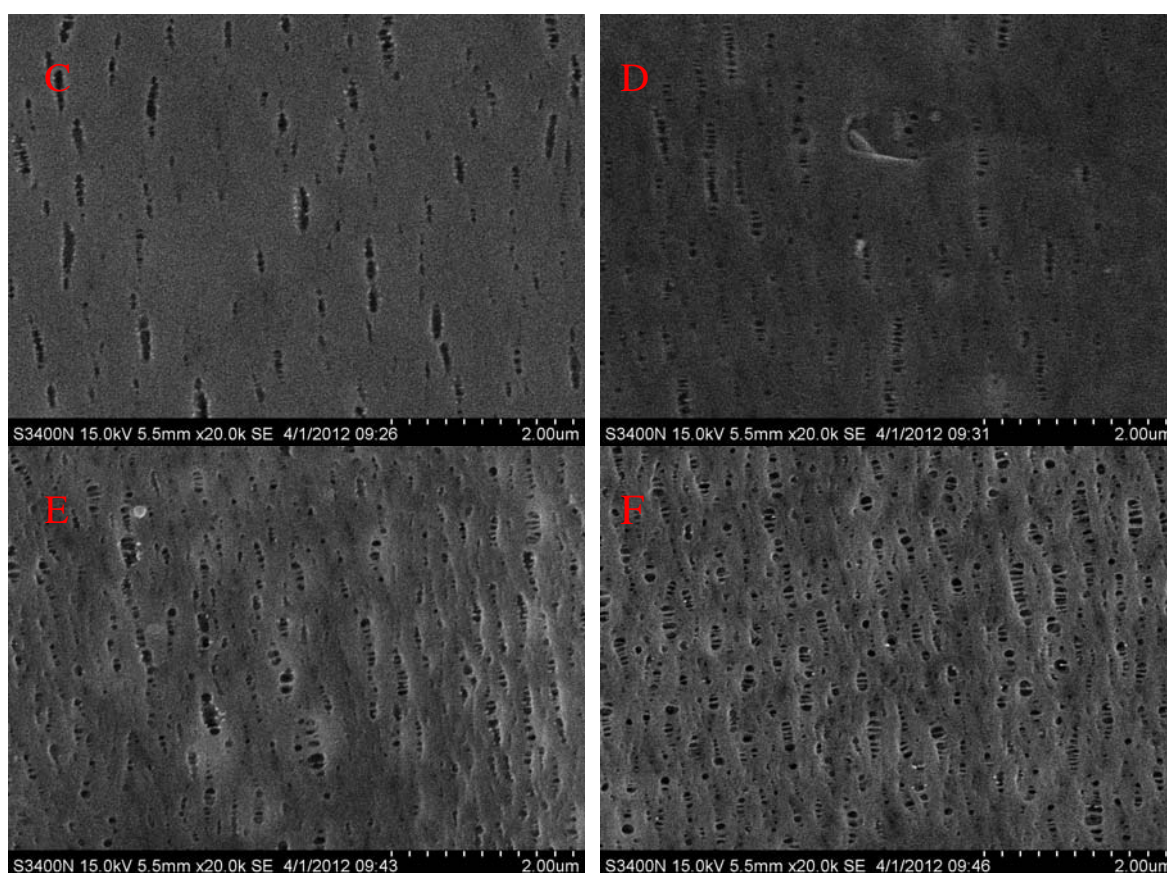Fig. 3 DSC curves for PP films with different drawing ratio

Fig. 4 SEM for PP films with different drawing ratio

It could be seen that the disappearance of plastic plateau was directly related to the disappearance of low temperature endotherm plateau and appearance of pore structure. Within the plastic region, the unstable crystalline part formed during annealing was slowly pulled away from the fold-chain lamellae and converted to connecting-bridges. In the strain-hardening region, the unstable part completely disappeared, and the lamellae interacted with each other through the bridges. Therefore, the presence of the plastic region could be attributed to the conversion of unstable crystalline part.

Based on the above results, the pore and bridge-formation process during stretching under room temperature was illustrated in Fig. 5. For the precursor film, besides row-nucleated lamellae structure, tie chains, amorphous chains and chain entanglements existed among the interlamellar region. After annealing, some tie chains and amorphous chains would attach to the initial lamellae and formed the unstable crystalline part. (Rastogi 2005) had discussed that the entanglements in the amorphous regions limited the drawability in the solid state. (Feng 2007) also proved that during stretching under room temperature, the local entanglement stress concentration would be stronger than that for lamellae fragmentation. For the annealed film, the weakest part during stretching was the formed crystals around initial lamellae. During stretching within the plastic region, these unstable parts were gradually pulled out and converted into connecting bridges. At the same time, pores were formed. During stretching, the unstable crystalline part was like a buffer zone which prevented the increase of stress,

explaining the existence of plastic plateau in the stress-strain curve of annealed PP films. During the strain-hardening stage, some scission of formed bridges within the plastic region occurred and the load was transferred to the residual tie chains which were not included in the crystallization process during annealing. The stretched residual tie chains crystallized locally. Local crystallization created more apparent bridges between the crystal blocks. (Noether 1978) proved that the bridge between lamellae was crystalline and the stabilization of micropores structure was due to the crystallization of interlamellar bridges. The interaction between the lamellae became stronger through bridges. Further stretching induced bridges fracture and severe lamellae deformation. At the same time, pores were closed.
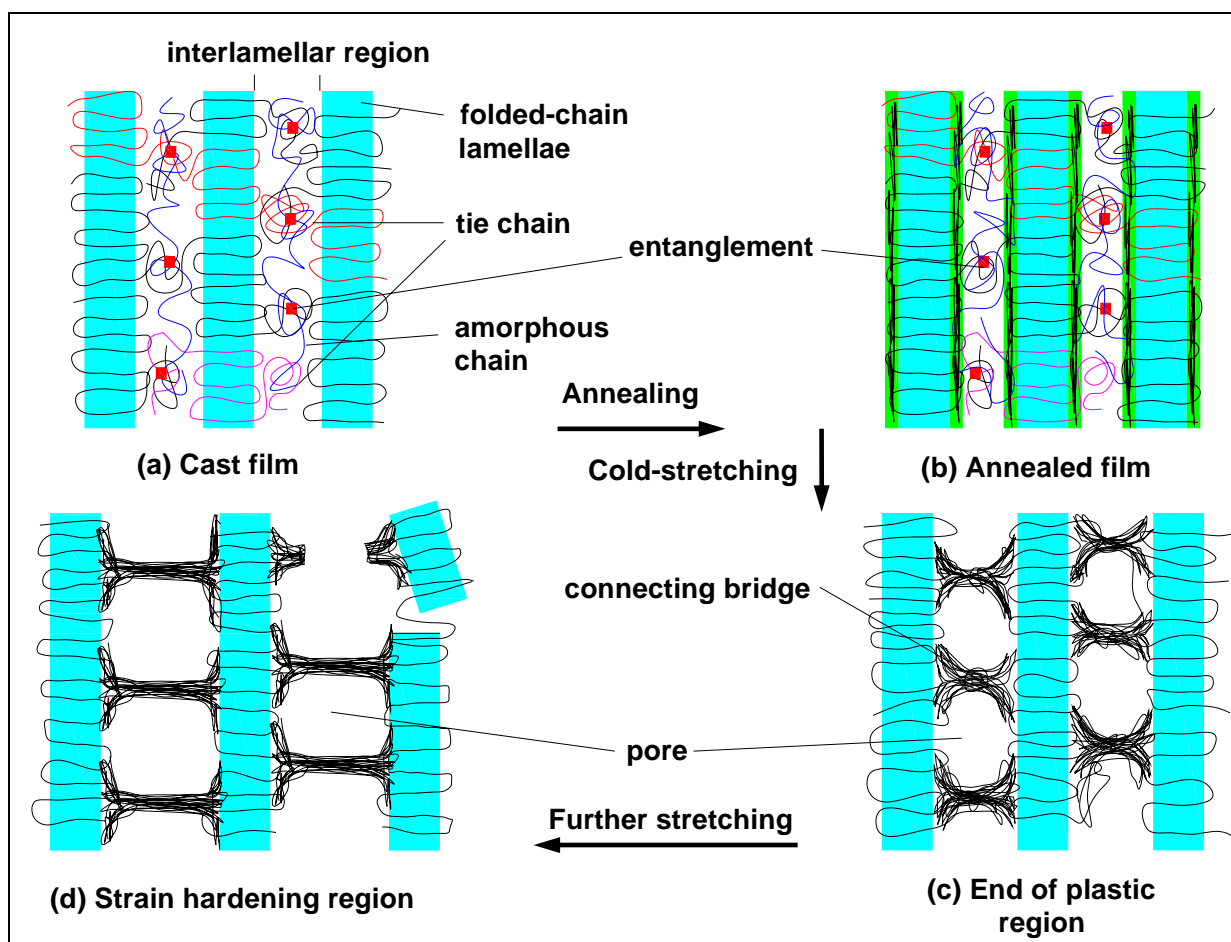

Fig. 5 Proposed pore-creation process during stretching of annealed PP film

CONCLUSIONS

The direct correlation between the plastic plateau in stress-strain curve, endotherm plateau in DSC melting curve and bridge formation was built up. The existence of the plastic plateau was attributed to the formation of unstable crystalline part during annealing. The disappearance of the plastic plateau coincided with the disappearance of unstable crystalline part and formation of pore and

connecting-bridges.

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