

# Preparation, Morphology, and Thermoelectric Property Studies of BaTiO<sub>3</sub> Superfine Fiber/Castor Oil Polyurethane-Based IPN Nanocomposites

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**ABSTRACT:** A series of castor oil polyurethane/poly(methyl methacrylate) interpenetrating polymer networks (IPNs) and gradient IPNs, cured at room temperature, were prepared by a simultaneous IPN method. The polymerization processes were traced through IR techniques; results for the morphology and miscibility among multiple phases of materials, obtained by transmission electron microscopy, indicated that the systems belonged to graft-mode IPNs, and the domains between two phases were controlled on a nanometer scale. Thermomechanical analysis detection results showed that through interpenetration between networks, the glass-transition temperatures of the systems could be linked up effectively. Furthermore, the systems were combined with selected barium titanate superfine fibers. The composite techniques were determined, and the thermoelectric and mechanical properties were examined in detail. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 709–715, 2002; DOI 10.1002/app.10024

**Key words:** castor oil polyurethane; BaTiO<sub>3</sub> superfine fibers; IPNs; thermoelectric property; nanocomposites

## INTRODUCTION

Polymer blends, effective ways and techniques for developing polymer-based functional materials with excellent properties, have gained more and more attention in recent years. Among them, interpenetrating polymer networks (IPNs), special kinds of polymer blends, refer to polymer systems formed by interpenetration and entanglement between two or more sorts of crosslinked polymers through physical or chemical methods.<sup>1</sup> The large amount of interpenetrating and entanglement structures formed among the components can po-

tentially improve the miscibility of multicomponent polymers a lot. Also, these structures make the materials exhibit macroscopic homogeneity and microscopic phase separation, so the glass-transition temperatures ( $T_g$ 's) of multicomponent systems can be linked up effectively. Because polymers usually change their properties with  $T_g$ , IPN techniques have shown great significance for obtaining functional materials with special or outstanding properties.<sup>2</sup> Nanocomposites are new kinds of composites, formed by the dispersal of one or more types of dispersant on an almost molecular level in the polymer matrix. The size of the dispersed phase of nanocomposites is situated between macroscopic and microscopic ranges, leaving the transitional region and also bringing special physical and chemical changes to materials; there is much focus on such fields.<sup>3–5</sup> Among these are organic–inorganic hybrids, which com-

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bine the advantageous of both and can endow composites with many outstanding properties, such as mechanical, thermal, optical, electromagnetic, and biological properties; such fields have been popular in the research into these materials.<sup>6,7</sup> Until now, most reports on IPNs have been based on polyurethane (PU) systems and have mostly concentrated on the preparation methods and the relationship between the structure and property of the systems formed; there are also reports in many fields of application.<sup>8,9</sup> Reports concerning the preparation and properties of nanocomposites with inorganic superfine powders or superfine fibers are relatively uncommon.

In this study, a series of simultaneous and gradients IPNs, cured at room temperature, were prepared with a castor oil PU matrix. Barium titanate ( $\text{BaTiO}_3$ ), as superfine fiber, a substance with good piezoelectric characteristics, was selected to form the composites. Thus, inorganic-organic hybrids were obtained, and their morphology, electric conductivity, and mechanical properties were determined.

## EXPERIMENTAL

### Raw Materials and Treatment

All reagents except the 2,4-tolylene diisocyanate (TDI) precursor were purchased from commercial resources in China as analytically pure materials. Inhibitor was removed from the methyl methacrylate (MMA) monomer; it was then dried over a molecular sieve. Dimethyl aniline (DMA) and benzoyl peroxide (BPO) were used to form a co-initiator system. Castor oil (hydroxyl value = 120) was dehydrated at 80°C under reduced pressure for 1 h. The TDI precursor (TDI content = 9%) was prepared at the Chemical Factory of the Harbin Institute of Technology. Dibutyltin dilaurate (DBTL) and ethyl acetate were used as the catalyst and solvent, respectively.

### Preparation of the IPNs and Gradient Coatings

A weighed amount of the TDI precursor and MMA monomer (inhibitor-free) was dropped into a three-necked, round-bottom flask and thoroughly mixed with the dehydrated castor oil, BPO, and ethyl acetate homogeneous systems; DBTL and DMA were then added under continuous stirring for about 30 min. When the solution became an increasingly viscous fluid, it was

poured into a polycarbonate ester film mold, and curing took place at room temperature. Thus, the IPNs were produced. We synthesized several different types of IPNs in this way by varying the —NCO and —OH molar ratios in the PU network and the PU (soft segment)/poly(methyl methacrylate) (PMMA; hard segment) weight ratios in the system. We obtained the gradient IPNs by casting the films in molds at various times during the curing process of the IPNs.

### Preparation of the $\text{BaTiO}_3$ Superfine Fiber

Purified water (23 wt %) was added to the  $\text{K}_2\text{CO}_3$  and  $\text{TiO}_2$  system, which had a molar ratio of 1:3 and had been mixed for about 1 h. The mixture obtained was placed on a platinum plate, dried at 80°C for 72 h, calcined at 1000°C for 100 h, cooled down quickly to room temperature, and immersed in distilled water for about 1 week. After being stirred thoroughly and filtered *in vacuo*, the system was immersed in a 1 mol  $\text{L}^{-1}$  HCl solution for 1 week, filtered, and dried. Afterward,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was added to the aforementioned system in the same amount, and all these materials were poured into a hot reaction vessel with an appropriate amount of water. Heated at 140°C for 72 h, the products were rinsed with hot water to neutralization and dried.

### Composite Techniques

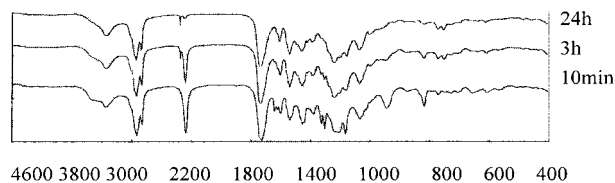
The coupling agents and superfine fibers prepared were added into IPN systems. The mixtures were then grained for 25 min, dispersed for 20 min with a supersonic device, and then cast in molds. A series of composite films were obtained with variations in the amount of fiber added.

### Property Measurements

IR spectral techniques were used to examine the changes in the particular absorption peaks in IPNs with a Nicolet-5DX IR spectrometer through the casting of homogeneous systems of the TDI precursor, castor oil, MMA, BPO, and DMA on KBr discs for various reaction times. The —NCO/—OH ratios and soft/hard component ratios were found to be 1.2:1 and 60/40, respectively.

The sample  $T_g$ 's were determined by thermomechanical analysis (TMA). The testing temperature range was -15 to 150°C, and the heating rate is 10.0°C/min.

Morphology studies were performed with a Nippon Electron 1200-EX transmission electron



**Figure 1** IR spectra of IPNs at various reaction times.

microscope. The samples were stained with  $\text{OsO}_4$  vapor and cut into sections about 100 nm thick at room temperature.

Electric resistivity and current–voltage (I–V) characteristics of samples were determined, after specimens were pressed into button shapes, with a ZC36-mode high-resistance tester (Shanghai, China) to study the thermoelectric properties of composites with various types of  $\text{BaTiO}_3$  super-fine fibers.

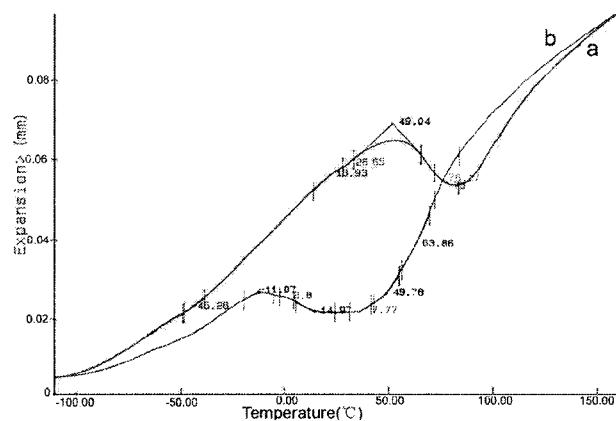
The tensile strength, elongation at break, permanent set of IPNs, gradient samples, and composites were measured with a Nippon Shimadzu DSS-10T-S tester at room temperature at a crosshead speed of 5 mm/min with dumb-bell-shaped specimens, according to Chinese Standard Method GB4456-84.

## RESULTS AND DISCUSSION

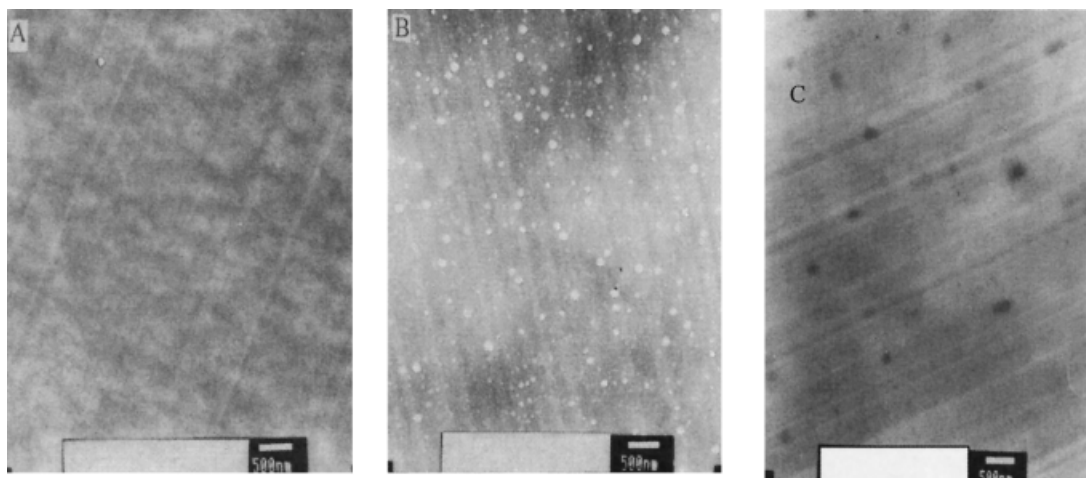
### IR Results and Polymerization Mechanism Analysis

The Fourier transform infrared spectra of castor oil mixed with the TDI precursor, MMA monomer, BPO, DMA, and DBTL for various reaction times are given in Figure 1. During the polymerization, all the absorption peaks of the reactive functional groups changed, such as the  $\text{—NCO}$  absorption peak at  $2278\text{ cm}^{-1}$ , the  $\text{—OH}$  absorption peak at  $3400\text{ cm}^{-1}$ , the  $\text{—NH}$  absorption peak at  $3350\text{ cm}^{-1}$ , and the  $\text{—NHCO}$  absorption peak at  $1528\text{ cm}^{-1}$ . In this study, we considered the intensity changes of the absorption peak at  $2278\text{ cm}^{-1}$  (representing the changing of the  $\text{—NCO}$  group) as the forming standard of the PU network and  $965\text{ cm}^{-1}$  (representing the changing of the  $\text{—OH}$  group) as the polymerization standard of MMA. The disappearance rate of the  $\text{—NCO}$  absorption peak was a little faster than that of the  $\text{C=C}$  absorption peak initially. However, in a later part of the reaction, the absorption peak of  $\text{C=C}$  disappeared nearly completely, whereas the  $\text{—NCO}$  peak had not disappeared

completely. This indicates that during the formation of the IPNs, although an attempt was made to equalize the reaction rates of PU network formation and MMA network polymerization through the simultaneous method, overall the rate of PMMA formation was relatively fast. This was mainly because the MMA polymerization happened via a free-radical mechanism, and the existence of the initiating step in the first part of the reaction tended to make it proceed slowly before moving to the self-promoting step. The hydrogen-transfer polymerization of PU could happen rapidly in the first period, but the time needed for the free-radical reaction (from initiation to complete polymerization) was much shorter. Additionally, when considering the material types of each network forming IPNs, we should note that castor oil also has an unsaturated double bond in its molecular linkage (besides the three  $\text{—OH}$  groups to react with TDI). Therefore, it was expected that the unsaturated double bond of the castor oil could participate in the polymerization of MMA simultaneously with the PU network formation in the IPNs. Also seen from the IR spectra, the reaction rate during the later stages of the reaction was faster than that of the polyaddition of PU, so the systems thus obtained probably belonged to graft-mode IPNs; that is, the acrylate group was grafted to the PU network. As such, various types of chemical crosslinking occurred, in addition to physical entanglement, leading to a further shrinkage of the molecular linkage and increasing the degree of interpenetration. This ultimately decreased the domain scale of the two phases, even in the nanometer range. This could also moderate the com-



**Figure 2** TMA results of (a) simultaneous IPNs and (b) gradient IPNs.



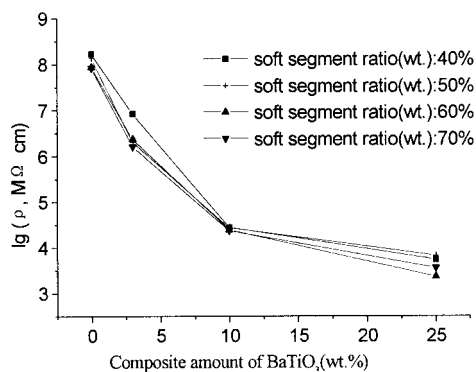
**Figure 3** TEM images of IPNs with various amounts of soft and hard segments ( $-\text{NCO}/-\text{OH} = 1.2/1$ ): (A) 60/40 soft/hard ratio, (B) gradient IPNs, and (C) 40/60 soft/hard ratio.

ponent ratio over a relatively wide range, without phase separation, thus leading to more miscible materials with better integrated properties. Transmission electron microscopy (TEM) and mechanical property characterization results illustrated the results even further.

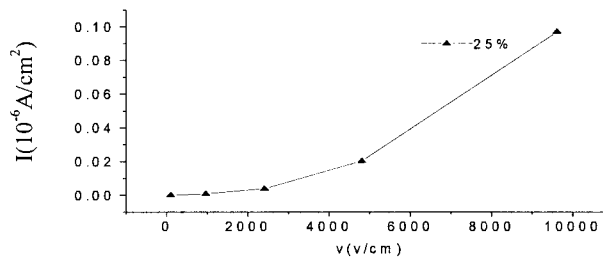
#### TMA Testing Results

TMA thermograms of temperature–expansion results are shown in Figure 2. The  $T_g$  values on the high and low scales are near those of pure PU (its  $T_g$  is near  $-50^\circ\text{C}$ ) and pure PMMA (its  $T_g$  is near  $100^\circ\text{C}$ ), respectively. However, both have an inward shifting tendency of  $T_g$  compared with that of the pure polymers. In addition, all these formulations, especially the gradient IPNs, create many sublevel transitional temperature ranges. The reason may be that after the formation of the

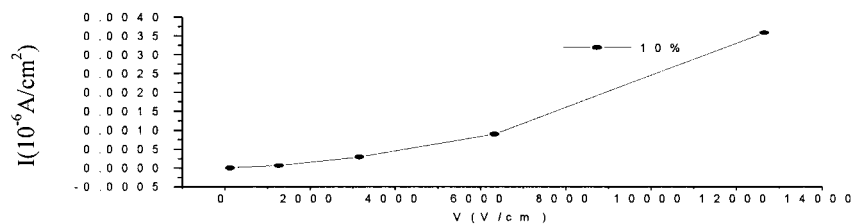
IPNs, the interpenetrating PMMA increases the positional resistance for the movement of the main PU backbone, thereby making the  $T_g$ 's of the IPNs slightly higher than that of pure PU, whereas the distance increase in the PMMA molecular linkage by the interpenetration of PMMA to the PU network decreases the positional resistance for the movement of PMMA. The decrease value is larger than that of the increase induced by the interaction between linkages. Therefore, the  $T_g$ 's of the IPNs decrease a little in comparison with that of pure PMMA. Furthermore, the crosslinking of the PMMA chain into the PU network also restricts the movement of the side groups of PMMA. The sublevel transitions are the result of creations of multiphase systems, so the miscibility among components of gradient IPNs is reinforced even further because of the graft structures. This inevitably leads to the existence of a large volume of transitional regions. TMA thermograms can also show the effective merging of the  $T_g$  value through an IPN technique.



**Figure 4** Resistivity curves of IPNs.



**Figure 5** I–V curve of gradient IPN composites with 25% BaTiO<sub>3</sub>.



**Figure 6** I–V curve of gradient IPN composites with 10% BaTiO<sub>3</sub>.

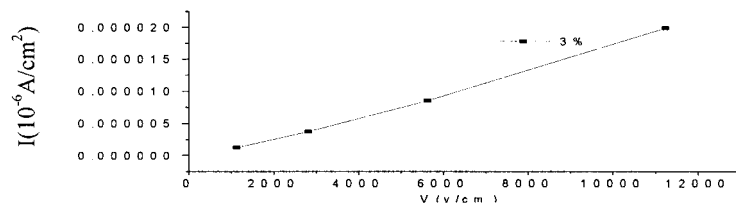
### Morphology Measurements

TEM images of the castor oil PU/PMMA IPNs, with various component ratios, are shown in Figure 3. The OsO<sub>4</sub>-stained regions refer to PU segments. It can be seen from the figure that the network systems formed have cell-like structures. PU mainly forms the cell wall, whereas PMMA forms the globules dispersed in PU in Figure 3(A,B), and has phase inversion in Figure 3(C). This is because the changing of the soft/hard segment ratio can completely affect the type of continuous phase. The generation of globules is the result of first-grade phase separation, that is, the result of phase separation led by miscibility decreasing because of polymerization, whereas the fine structures are the result of subgrade phase separation after the polymerization. This is mainly because the increasing viscosity in the system and the crosslinks make the subgrade phase separation proceed on a narrow scale during the process, generally forming granules of several nanometers. The PU component solidifies in the IPN systems first, but during the formation of these networks, the PMMA component is cured. According to the immiscibility polymer theory, after the formation of the first component, the entropy ( $\Delta S$ ) in the system decreases, and the Gibbs free energy ( $\Delta G$ ) increases. Although the existence of interpenetration and entanglement between two phases increase the compatibility in networks, the phase separation increases, and thus the networks formed later become just the filler for the first. However, by controlling the rate

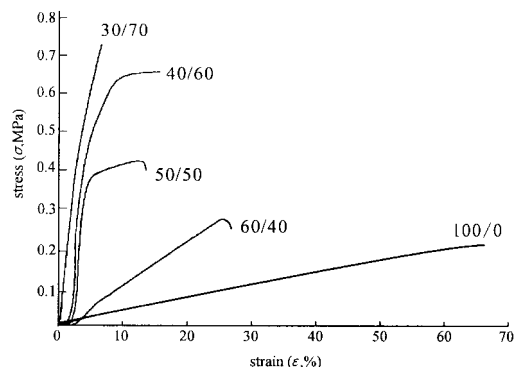
of the formation of the two networks and making the two types of polymerizations finish almost simultaneously, that is, as a simultaneous IPN process, we can effectively control the extent of first-grade phase separation and the formation of the nanocomposite system. In these studies, the samples prepared were on the nanometer scale, and the domains of the gradient IPNs were even smaller because of a large number of transitional regions among the phases.

### Electric Resistivity Detection Results and I–V Character

Resistivity varied with the composite amount of BaTiO<sub>3</sub> in the complex systems, as shown in Figure 4. Overall, the resistance value decreased rapidly with the nanofiller. With filler loadings of less than 10 wt %, the resistivity of the materials was higher than 10<sup>7</sup> MΩ cm, making them basically insulating materials. Above a 10% filler loading in a composite, the value of resistivity decreased rapidly; in this case, the materials can be regarded as electrically conductive systems. The I–V characteristics of the composite system are shown in Figures 5–7. The character of the samples showed linearity in lower electric fields. Resistivity decreased, which led to a conductivity increase with heat generation and a temperature increase in higher voltages. This indicates that the systems had a negative-temperature coefficient effect. The I–V curves were nearly linear at the small filler loading (<10%). This illustrates that the change in resistance was not very evi-



**Figure 7** I–V curve of gradient IPN composites with 3% BaTiO<sub>3</sub>.

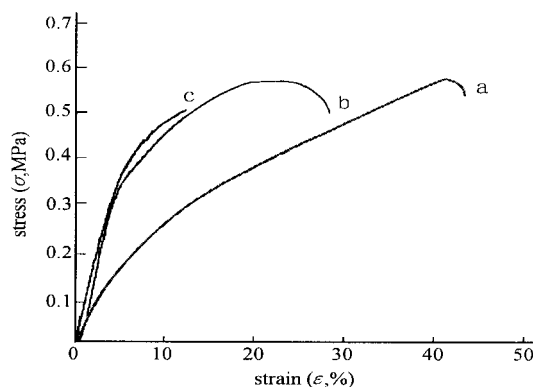


**Figure 8** Mechanical property of composite IPNs with various soft/hard segment ratios.

dent, whereas above a 10% loading, the temperature increased rapidly on the I–V curves, and the resistivity changed, apparently with voltage. According to the conductivity network theory, after the formation of the conduction networks, the main mechanism of heat-excitation electron transition in the lower field was current conductivity, and the number of heat-excited electrons increased with increasing voltage, so resistivity decreased. In higher fields, the main mechanism of current conduction was the channeling effect of electrons, and the effect became evident with increasing voltage and decreasing resistivity.

### Mechanical Property Results

Previous research by others<sup>10</sup> has shown that compatible IPNs can change many properties of blending systems greatly. This is mainly due to a large number of interpenetration and entanglement structures that form. The stress–strain curves of the IPNs prepared are shown in Figures 8 and 9. As shown in Figure 8, the materials range from elastomeric to plastic materials with changes in the soft/hard segment ratios in the systems.



**Figure 9** Mechanical property of gradient systems with the composite amount of BaTiO<sub>3</sub>: (a) 0, (b) 3, and (c) 10%.

Table I gives the results for the mechanical properties of the IPNs with various soft/hard segment ratios. Although the component ratios of the IPN soft/hard segments have a relatively wide range, from 30/70 to 60/40, the materials show elastomeric strengthening and plastic toughness effects as well. This occurs mainly because of the existence of interpenetration and entanglement molecular structures between components, giving reinforcement when the materials are elongated, thereby greatly improving the mechanical properties compared with those of the usual materials. These effects provide a valid means of improving the materials from the viewpoint of component and blending technique devices and so have great significance in obtaining functional materials with outstanding properties. We also can conclude that there is an apparent tensile strength increase with an increasing content of MMA in the IPNs, whereas their elongation decreases. This is because the first developed network mostly determines the mechanical properties of the system. When one of the components has a stronger molecular interaction (like the PU net-

**Table I** Mechanical Properties of IPNs and Gradient IPNs

Property	Pure PU	Soft/Hard Segment Ratio (w/w)				Gradient IPNs BaTiO <sub>3</sub> Composite Amount (wt %)		
		60/40	50/50	40/60	30/70	0	3	10
Stress ( $\sigma$ , MPa)	0.21	0.28	0.50	0.66	0.75	0.56	0.52	0.49
Strain ( $\epsilon$ , %)	67.2	26.8	12.7	15.8	5.9	24.6	28.6	15.8
Permanent set ( $H$ , %)	55.2	—	—	4.04	4.80	7.10	9.79	5.48

work), the relationship of the property and component is nonlinear. At a particular range of component ratios (from 60/40 to 40/60), the mechanical properties usually exceed those of the separate polymer systems. The existence of the highest tensile value is the result of the crosslink density increasing because of the interpenetration and entanglement between the components (there is physical crosslinking). As seen in Figure 9 and Table I, when the component ratio is 50/50 (and also in gradient systems), a coordinate action apparently appears; in this case, the tensile strength and elongation both increase, whereas the mechanical properties of the composite decrease slightly.

## CONCLUSIONS

Component analysis and IR spectroanalysis of the reactions showed that the systems obtained were graft-mode IPNs. TEM and TMA methods indicated that the domains of the simultaneous systems were on a nanometer scale.  $T_g$ 's of these IPN systems could be related effectively by types of interpenetration, especially with respect to gradient systems. The mechanical property tests showed that the castor oil PU/PMMA IPNs had superior mechanical properties in relatively high soft/hard segment ratios and exhibited types of characteristics that varied from elastomers to

brittle plastics. The conductivity of these systems could be changed considerably by combination with BaTiO<sub>3</sub> superfine fibers. As seen from the I-V studies, with a loading of less than 10 wt % filler, the IPNs were insulators. Above 10 wt %, the I-V studies showed linear, lower fields, but decreases in resistance as the voltage increased also showed negative temperature effects.

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