

Preparation of Novel Polyindene/Polyoxymethylene Blends and Investigation of Their Properties

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ABSTRACT: In this study, the conducting homopolymer of indene was synthesized by a chemical polymerization method in a nonaqueous medium, and polyindene (PIn)/polyoxymethylene (POM) blends were prepared. The physical, chemical, thermal, and spectral properties of the synthesized homopolymer and their blends were investigated. The conductivities of PIn and the PIn/POM blends were measured with a four-probe technique. The conductivity of PIn was determined as 1.16×10^{-5} S/cm, whereas the conductivities of the PIn/POM blends were determined to be in the range 3.16×10^{-6} to 9.8×10^{-6} S/cm. From Gouy scale magnetic susceptibility measurements, we found that PIn and the PIn/POM blends had polaron natures. The amount of Fe (milligrams per gram) in the PIn and PIn/POM structures were determined by inductively coupled

plasma–optic emission spectrometry. Fourier transform infrared spectra were taken to analyze the structural properties of PIn and the PIn/POM blends. The thermal properties of PIn and PIn/POM blends were investigated with thermogravimetric analysis and differential scanning calorimetry analyses, and we found that they showed adequate thermal stability. According to the initial decomposition temperature among the blends, the blend including 16% PIn had the highest decomposition temperature with 244°C. The morphological structures of the PIn, POM, and blends were clarified with scanning electron microscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3659–3664, 2010

Key words: blends; conducting polymers; thermal properties

INTRODUCTION

In recent years, conducting polymers have been studied extensively because of their use in applications such as batteries, sensors, electrorheology, and solar cells.^{1–5} However, they have poor mechanical and physical properties. To improve these properties, several approaches have been developed, one of which is to prepare blends with insulating polymers.⁶

Indene is a byproduct of the petrochemical industry and a cheap raw material source for the preparation of polymeric materials with many valuable properties.^{7,8} Polyindene (PIn) has also elicited much interest in recent years because of its high glass-transition temperature (T_g) and special optical properties.⁹ Among insulating polymers, polyoxymethylene (POM) is a polymer that shows good flexibility and thermomechanical properties. In the literature, it was determined that the chain flexibility of POM was greater than that of polystyrene and comparable to that of polyethylene.^{10,11}

The aim of this study was to improve PIn/POM blends with controlled conductivities and enhanced

physical, thermal, mechanical, and solubility properties. In this study, the preparation and characterization of conducting blends of PIn and POM were investigated. There are limited articles in the literature about PIn-based composite and blends. To the best of our knowledge, there have been no reports in the literature about the synthesis and characterization of PIn/POM blends.

EXPERIMENTAL

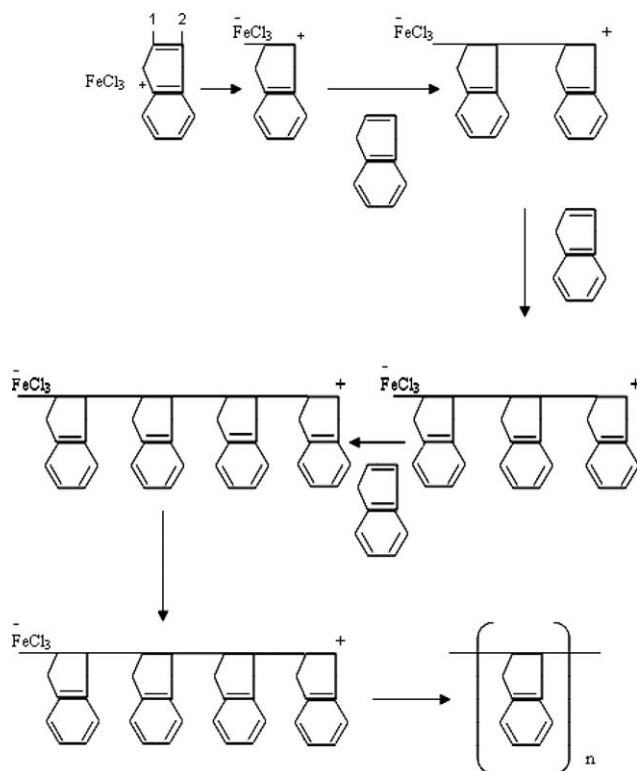
Materials

POM ($T_g = -13^\circ\text{C}$, T_m (Melting temperature) = 175°C , with acetate side groups, d (density) = 1.42 g/cm^3) was purchased from Aldrich, Germany. Indene (Acros Organics, Germany) was freshly distilled under reduced pressure. Anhydrous FeCl_3 (Aldrich), CHCl_3 , and *N,N*-dimethylformamide (DMF; Labscan Ltd, Dublin, Ireland) were used as received.

Synthesis of PIn

Indene was polymerized with FeCl_3 as an oxidant in anhydrous media. The ratio of oxidant to monomer was 4 : 1. FeCl_3 (68.2 mmol, 11.08 g) was dissolved in 60 mL of CHCl_3 and stirred for 20 min at 15°C under an $\text{N}_2(\text{g})$ atmosphere. Then, 17.05 mmol (2 mL) of distilled indene was added dropwise into the

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Scheme 1 Polymerization mechanism of indene.

previous solution and stirred slowly. The polymerization was first carried out under an $N_{2(g)}$ atmosphere for 1 h and then continued without an $N_{2(g)}$ atmosphere for 1 h. After we carried out the polymerization reaction, the crude PIn was recovered and washed several times with distilled hot water and diethyl ether until the filtrate became colorless to remove any impurities. Finally, the PIn was dried in a vacuum oven at 70°C for 24 h. The yield percentage of PIn was 94 wt %. The synthesis mechanism of polyindene is given in Scheme 1.

Preparation of the PIn/POM blends

A certain amount of POM was dissolved in DMF. Then, PIn and DMF were added to the POM suspension, and the mixture was stirred for 17 h at room temperature. After the preparation process, the resulting blend was filtered, washed with distilled water, and dried in a vacuum at 50°C for 24 h. All of the blends were prepared homogeneously. According to same procedure, PIn/POM blends at different percentages were prepared.

Characterization

Four-point probe technique

The conductivity of compressed pellets ($5 \text{ ton}/\text{cm}^2$) of the polymers was determined with the standard four-point probe technique at room temperature.

Dielectric measurements

Dielectric measurements were taken with an HP 4192 A LF model impedance analyzer (UK).

Gouy balance

Magnetic susceptibility measurements were carried out with a Sherwood Scientific model MKI Gouy scale (UK). Finely powdered polymer samples were placed in a glass tube at a height of not less than 1.5 cm. This glass tube was placed into the hole of the magnetic balance, which was on a wooden bench, to obtain a constant value.

Infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the polymers were taken in KBr pellets with an Mattson 1000 model FTIR spectrometer (Ati Unicam Ltd, Cambridge, UK).

Inductively coupled plasma–optical emission spectrometry (ICP–OES)

The amount of Fe (milligrams per gram) in the polymer structures was determined by a PerkinElmer model ICP–OES 5300 DV instrument (USA).

Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymer samples were recorded with a SETARAM ET 8 Y8 Evolution 1760 model (Caluire, France) thermal analyzer under a nitrogen atmosphere up to 800°C at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Scanning electron microscopy (SEM)

The morphologies of the polymers were examined by a JEOL JSM 6360LV model SEM instrument (Japan).

RESULTS AND DISCUSSION

Yield, electrical conductivity, dielectric constant, magnetic susceptibility, and density results

The yields, electrical conductivities, dielectric constants, magnetic susceptibilities, and densities of the PIn homopolymer and PIn/POM blends are summarized in Table I. The different yields of the polymers were obtained from the preparation of the PIn/POM blends, including different percentages of PIn.

As shown in Scheme 1, there were no conjugated bonds along the backbone of the PIn. It is known that conjugation is not enough to make a polymer

TABLE I
Yield, Conductivity, Dielectric Constant, Density, and Gouy Balance Measurements of the Polymers

Polymer	Yield (wt, %)	Conductivity (S/cm)	Magnetic susceptibility (Xg, cm ³ /g)	Density (g/cm ³)	Dielectric constant
PIn	94	1.16×10^{-5}	4.8×10^{-5}	0.63	3.8
PIn (92%)/POM	97.5	9.8×10^{-6}	6.1×10^{-6}	0.65	9.0
PIn (80%)/POM	93.7	8.69×10^{-6}	9.6×10^{-6}	0.68	8.1
PIn (60%)/POM	100	7.17×10^{-6}	1.6×10^{-5}	0.71	6.6
PIn (48%)/POM	92.5	6.08×10^{-6}	9.8×10^{-6}	0.75	7.1
PIn (33%)/POM	90	5.52×10^{-6}	4.1×10^{-6}	0.78	2.8
PIn (16%)/POM	90	3.16×10^{-6}	2.9×10^{-6}	0.99	2.3

material conductive. In addition, charge carriers in the form of extra electrons have to be injected or adsorbed into the material. Therefore, the conductivity value of PIn was determined to be lower than that of the other conjugated polymers. As shown in Table I, the conductivity of PIn was found to be higher than those of the PIn/POM blends. Among the blends, PIn (92%)/POM had the highest conductivity with a value of 9.8×10^{-6} S/cm. The conductivity values of the PIn/POM blends slightly increased with increasing amount of PIn into the blends. Sarikaya et al.¹² determined that the conductivity values of PIn and the PIn/CaCO₃ conducting composites varied from 0.64×10^{-6} to 2.11×10^{-6} S/cm. We also obtained similar conducting values in this study. So, PIn and the PIn/POM blends could be used as novel materials in electrorheological studies. A similar study has also been reported in elsewhere in the literature.¹³ Among the blends, PIn (60%)/POM had the highest yield, with a value of 100%.

The magnetic susceptibility data of the polymers are also given in Table I. The values obtained from the Gouy measurements showed that the PIn homopolymer and all blends had paramagnetic properties, and their conducting mechanisms had a polaron nature.¹⁴ When the density values of the blends were investigated, the densities of blends were found to decrease with increasing PIn in the blends. Table I shows that the dielectric constants and conductivities of the PIn/POM blends increased with increasing PIn content. The conductivities of the PIn/POM blends increased with added PIn.

TABLE II
ICP-OES Results of the PIn Homopolymer and PIn/POM Blends

Polymer	Fe (mg/g)
PIn	11.10
PIn (92%)/POM	11.05
PIn (80%)/POM	10.39
PIn (60%)/POM	8.81
PIn (48%)/POM	6.15
PIn (33%)/POM	4.47
PIn (16%)/POM	2.10

ICP-OES results

Table II shows the amount of Fe (milligrams per gram) in PIn and the PIn/POM blends, including different percentages of PIn. As shown in Table II, the amount of Fe in the polymer structures increased with increasing PIn in the structure of blends. According to the obtained results, we concluded that Fe was adsorbed in the PIn or formed a complex with PIn. This result indicates that Fe in the polymer structure affected the conductivity.

FTIR results

Figure 1 shows the FTIR spectra of the PIn homopolymer [Fig. 1(a)], POM homopolymer [Fig. 1(b)], and PIn (48%)/POM (52%) blend [Fig. 1(c)]. As shown in the FTIR spectrum of PIn [Fig. 1(a)], the aromatic C–H stretching band shifted to 3020 cm^{-1} , the aromatic C=C stretching bands shifted to $1650\text{--}1485 \text{ cm}^{-1}$, the C–C stretching band belonging to C₁–C₂ atoms shifted to 1480 cm^{-1} , and the C–H out-of-plane bands belonging to benzene shifted to $750\text{--}735 \text{ cm}^{-1}$. The FTIR spectrum of PIn exhibited the characteristic absorptions reported for PIn in the literature.^{15–17}

When the spectra of the PIn/POM blend [Fig. 1(c)] was investigated, we found that the

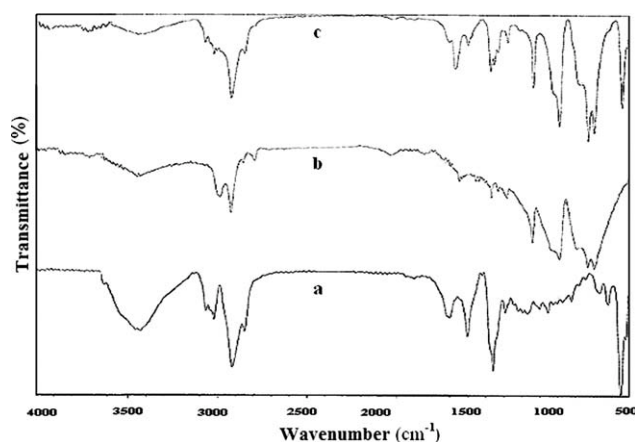


Figure 1 FTIR spectra of (a) PIn, (b) POM, and (c) the PIn (48%)/POM (52%) blend.

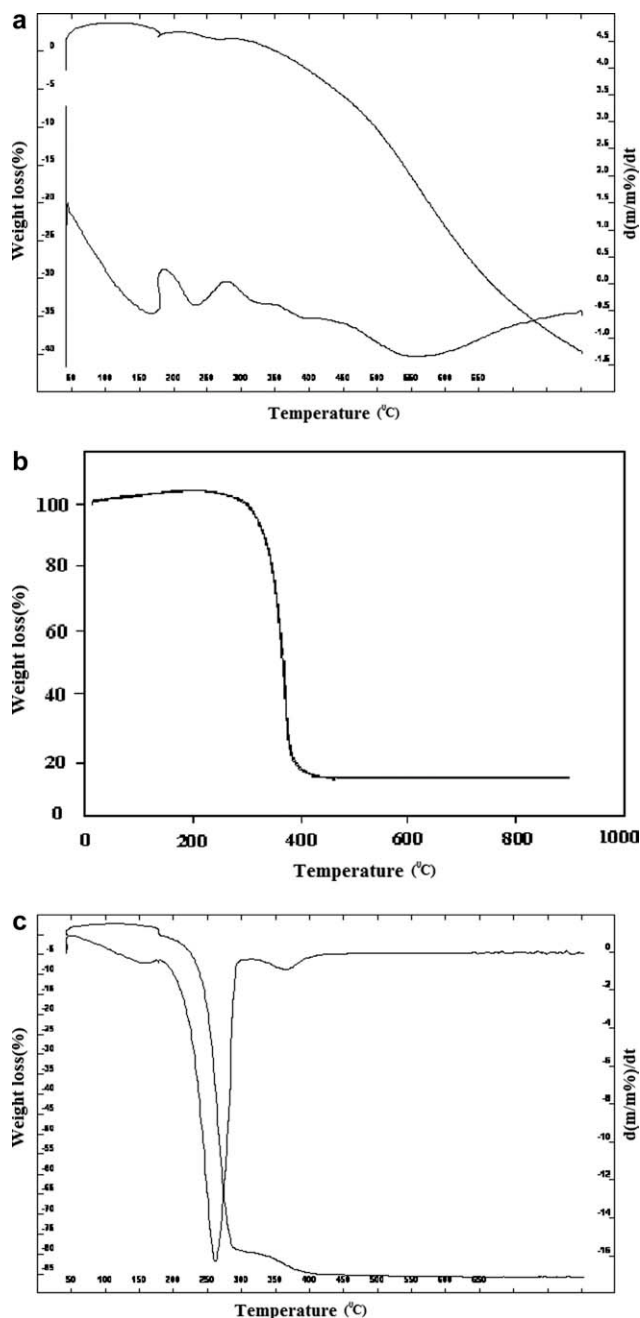


Figure 2 TGA curves of (a) PIn, (b) POM, and (c) the PIn (16%)/POM (84%) blend.

characteristic peaks corresponding to both homopolymers (PIn, POM) were observed, and the shifts in wave numbers of these peaks were determined. The band at 3010 cm^{-1} corresponded to aromatic C—H stretching, and the bands at $1620\text{--}1450\text{ cm}^{-1}$ corresponded to aromatic C=C stretching. The C—C stretching band of the $\text{C}_1\text{—C}_2$ atoms, C—O—C stretching band, and C—H out-of-plane bands were seen at 1460 , 1099 , and 750 cm^{-1} , respectively. Thus, this was thought to proof of the blend. Similar peaks were determined in the FTIR spectra of the other blends.

TABLE III
Thermal Decomposition Temperatures of the Homopolymers

Polymer	T_i (°C)	T_m (°C)	T_f (°C)
PIn	199	232	250
POM	450	563	674
POM	323	334	368

T_m = maximum degradation temperature; T_f = final degradation temperature.

TGA results

The decomposition temperatures of polymers were determined by TGA. The TGA curves of PIn, POM, and PIn/POM blends are shown in Figure 2(a–c). The obtained results are also tabulated in Tables III and IV. As shown in the tables, POM showed a one-step weight loss, whereas PIn and the PIn/POM blends decomposed in two steps. The first weight loss indicated the removal of dopant anions (Cl^- or FeCl_4^-), and the second weight loss step showed the decomposition of the polymer structure.¹⁸ However, the decomposition occurring at step one was due to the degradation of the POM chain structure.¹⁹

According to the initial decomposition temperature (T_i) among the blends, the blend including 16% PIn had the highest decomposition temperature at 244°C , although blends including 80 and 92% PIn had the lowest thermal stability at 171°C . In the PIn/POM blends, the thermal degradation temperatures (T_i) increased with increasing POM. The thermal stability of PIn increased with the prepared PIn/POM blends. So, the thermal properties of PIn improved.

TABLE IV
TGA Results of the PIn/POM Blends

Percentage of PIn in the PIn/POM blend	Degradation temperatures (°C)		
	T_i	T_{max}	T_f
92	171	179	192
	338	371	392
80	171	179	192
	344	375	396
60	183	199	221
	350	388	408
48	191	238	258
	354	383	400
33	213	250	263
	342	367	383
16	244	262	282
	336	362	386

T_{max} = maximum degradation temperature; T_f = final degradation temperature.

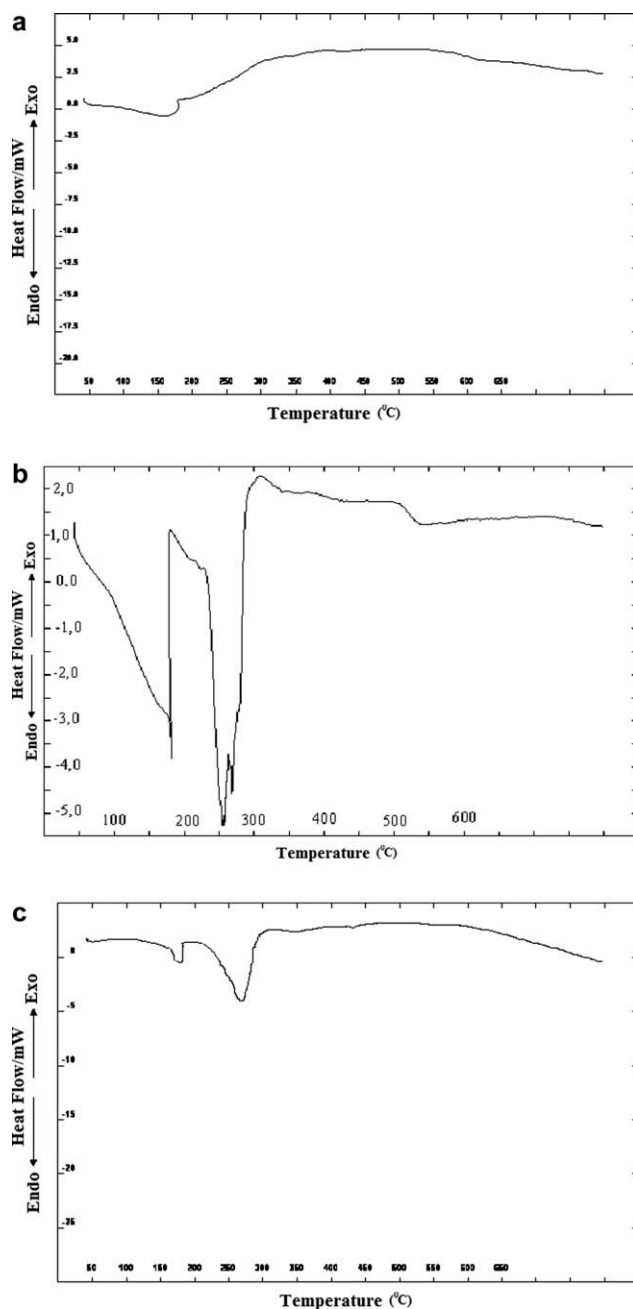


Figure 3 DSC curves of (a) PIn, (b) POM, and (c) the PIn (16%)/POM (84%) blend.

DSC results

The DSC curves of the homopolymers and blend [PIn/POM (84%)] are shown in Figure 3(a–c). The thermal transition temperatures obtained from DSC curves are given in Table V. Endothermic transitions were seen in all of the polymers.

When the DSC curve of POM was investigated [Fig. 3(b)], three endothermic transitions (175, 255, and 270°C) were observed. The peak at 175°C corresponded to the melting temperature of POM. The transitions observed at 255 and 270°C indicated the degradation of the polymer.²⁰ The endothermic peak obtained from the DSC curve of PIn at 177°C could be described as the T_g of PIn [Fig. 3(a)].¹⁵ In parallel, the endothermic peaks obtained from the DSC curves of the blends were also found between 177 and 181°C this can be attributed to the T_g of PIn. The endothermic peaks present between 238 and 270°C arose from the degradation of the polymer (Table V).

SEM results

The SEM micrographs of the homopolymers and blends are shown in Figure 4(a–d). The SEM micrograph of PIn [Fig. 4(a)] shows a granular and spongelike structure. The micrograph of POM [Fig. 4(b)] showed a spongelike and porous structure.

When the morphologies of the homopolymers and PIn/POM blends were compared, we observed that the blends had similar morphologies with PIn with increasing PIn. PIn (60%)/POM (40%) showed a porous layered and granular structure [Fig. 4(c)], whereas PIn 80%/POM/(20%) showed a closely granular and porous structure [Fig. 4(d)].

CONCLUSIONS

In this study, we modified the thermal and conductivity properties of PIn and POM by preparing

TABLE V
DSC Results of the Homopolymers and Blends

Polymer	Endothermic T_g (°C)	Endothermic T_m (°C)	Endothermic T_d (°C)
PIn	177	—	—
POM	—	175	255
			270
PIn (92%)/POM	181	—	—
PIn (80%)/POM	181	—	270
PIn (60%)/POM	178	—	266
PIn (48%)/POM	179	—	238
PIn (33%)/POM	179	—	253
PIn (16%)/POM	177	—	264

T_m = melting temperature; T_d = degradation temperature.

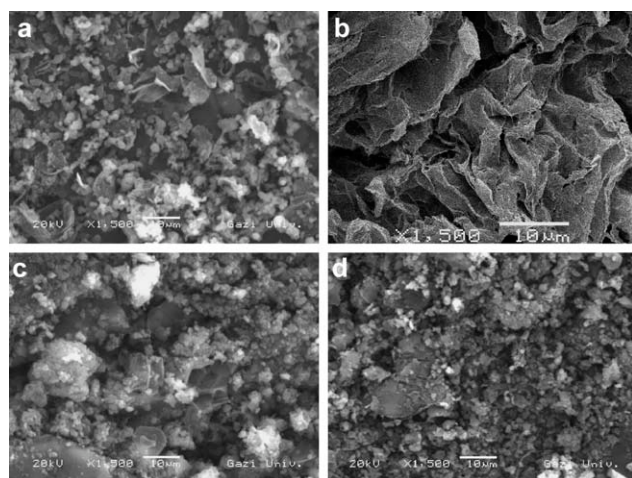


Figure 4 SEM micrographs of (a) PIn, (b) POM, (c) PIn (60%)/POM (40%), and (d) the PIn (80%)/POM (20%) blend.

PIn/POM blends. All of the blends were prepared homogeneously. The thermal properties of PIn improved. So, thermally stable and conductive blends were prepared. The conductivity values of the PIn/POM blends slightly increased with increasing PIn amount. However, the blends showed similar properties in the results of the DSC and FTIR analysis. The blends also showed different morphologies according to the amount of PIn. We propose that the PIn and PIn/POM blends could be used as novel materials in the electrorheological studies. These samples could also be used as novel materials in most areas of applications of conductive polymers, such as corrosion inhibitors, gas separation membranes, and electroluminescent diodes. We believe that our results could also help

in future studies connected with PIn blends and composites.

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