

Preparation and Mechanical Properties of Polypropylene–Clay Hybrids Using a Maleic Anhydride-Modified Polypropylene Oligomer

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ABSTRACT: Polypropylene–clay hybrids (PPCH) were prepared using a maleic anhydride-modified PP oligomer (PP–MA) as a compatibilizer. PP was melt-blended with organophilic clay which was intercalated with PP–MA. In these PPCHs, the particles of silicate layers were dispersed at the nanometer level. The particles became smaller and were dispersed more uniformly, as the ratio of PP–MA to the clay was increased. The dynamic storage moduli of the PPCHs were higher than that of PP up to 130°C. For example, the modulus of the PPCH with 5 wt % clay and 22 wt % PP–MA was 1.8 times higher compared to that of PP at 80°C. As the dispersibility of the clays was improved, the reinforcement effect of the clays increased. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 87–92, 1998

INTRODUCTION

In recent years, organic–inorganic nanometer composites have attracted the great interest of researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components.^{1–11} One of the most promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of silicate layers.^{4–11} In our previous works, we synthesized nylon 6–clay hybrid (NCH) in which 10 Å-thick silicate layers of clay minerals are dispersed homogeneously in the nylon 6 matrix.⁵ The NCH exhibits various superior properties such as high strength, high modulus, and high heat resistance compared to nylon 6.^{6,7} Since then, other polymer–clay hybrids such as polyimide,⁷ epoxy resin,⁸ polystyrene,⁹ polycaprolactone,¹⁰ and acrylic polymer¹¹ were reported.

Polypropylene (PP) is one of the most widely used polyolefin polymers. However, there was no

report of polyolefin–clay hybrids. The silicate layers of the clay have polar hydroxy groups and are incompatible with polyolefin. Recently, we reported a novel approach to prepare a PP–clay hybrid (PPCH) by using a functional oligomer as a compatibilizer.¹² In the PPCH, the silicate layers were dispersed uniformly at the nanometer level. In this article, we prepared PPCHs by using a maleic anhydride-modified PP oligomer as a compatibilizer and studied the dispersibility of clays and the mechanical properties of PPCHs.

EXPERIMENTAL

Materials

The materials used for the preparation of the PPCHs are purified montmorillonite (Kunipia-F) from Kunimine Co., stearyl amine from Wako Pure Chemical Co., maleic anhydride-modified PP oligomer (termed PP–MA) from Sanyo Chemical Industries, and homopolypropylene (MA2, melt flow rate: 16 g/10 min, JISK6758) from Mitsubishi Chemical. The acid value of PP–MA is 52 mg KOH/g. Its softening temperature is 145°C and its M_w measured by GPC is 30,000.

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Table I The Compositions of the C18-Mt/PP-MAs

Sample	C18-Mt/PP-MA (Wt/Wt)	Kneader	Interlayer Distance (Å)
C18-Mt/PP-MA-1/3	1/3	Twin-screw extruder	63
C18-Mt/PP-MA-1/2	1/2	Twin-screw extruder	57
C18-Mt/PP-MA-1/1	1/1	Labo-plastmill	34

The Preparation of Organophilic Clay

Sodium montmorillonite (80 g, cation-exchange capacity: 119 meq/100 g) was dispersed into 5000 mL of hot water (about 80°C) using a homogenizer. Stearyl amine (31.1 g, 115 mmol) and concentrated HCl (11.5 mL) were dissolved into hot water. It was poured into the montmorillonite-water solution under vigorous stirring using the homogenizer for 5 min to yield white precipitates. The precipitates were collected and washed with hot water three times and freeze-dried to yield an organophilic montmorillonite intercalated with stearyl ammonium. It is termed C18-Mt. The interlayer distance of C18-Mt was about 22 Å measured by X-ray diffraction (XRD). The XRD measurements were taken using a Rigaku RAD-B diffractometer with CuK α radiation at 30 kV and 30 mA. The inorganic content was 69.2–72.4 wt % by measuring the weights before and after burning its organic parts.

The Preparation of Clays Intercalated PP-MA

PP-MA was melt-mixed with C18-Mt at 200°C using a twin-screw extruder SIKRC (Nissei Plastic Industrial Co.) or a labo-plastomill (Toyo Seiki). Table I shows the mixing weight ratio of PP-MA to C18-Mt and the interlayer distances of the obtained organophilic clays intercalated with PP-MA. It is termed C18-Mt/PP-MA. The interlayer distances of C18-Mt/PP-MAs were larger than that of C18-Mt. The distances increased as

the ratio of PP-MA increased. These results indicated that the PP-MA was intercalated between the layers of C18-Mt. The details of the intercalation behavior of PP-MA will be published elsewhere.¹³

The Preparation of PP-Clay Hybrids

The compositions of prepared hybrids are shown in Table II. The pellets of PP and C18-Mt/PP-MAs were melt-blended at 200–230°C using the twin-screw extruder to yield the hybrids. The obtained strands were pelletized and dried under a vacuum at 80°C. To consider the effect of PP-MA as a compatibilizer, the composites of PP and C18-Mt without PP-MA were prepared. The sample is abbreviated PPCC (PP-clay composite).

The contents of the inorganic clay of the PPCHs and PPCC were measured by burning the samples. The results are listed in Table III.

The dried pellets of the hybrids were injection-molded into test pieces for tensile tests and measurements of the dynamic moduli by using an injection molder PS40E2ASE (Nissei Plastic Industrial Co.). The temperatures of the cylinders were 170–190°C and that of the mold was 30°C.

Evaluation of Dispersibility of the Clay in the PP Matrix

The dispersibility of the silicates layers in the PPCHs were evaluated using the X-ray diffracto-

Table II Compositions of PPCHs, PPCC, and PP/PP-MAs

Sample	C18-Mt/PP-MA [C18-Mt + PP-MA] (Wt %)	PP-MA (Wt %)	PP (Wt %)
PPCH-1/3	C18-Mt/PP-MA-1/3	[7.2 + 21.6]	71.2
PPCH-1/2	C18-Mt/PP-MA-1/2	[7.2 + 14.4]	78.4
PPCH-1/1	C18-Mt/PP-MA-1/1	[7.2 + 7.2]	85.6
PPCC	C18-Mt	6.9	93.1
PP/PP-MA-22	—	21.6	78.4
PP/PP-MA-7	—	7.2	92.8

Table III The Clay Contents of PPCH and PPCC

Sample	Clay Contents (Wt %)
PPCH-1/3	4.83
PPCH-1/2	4.66
PPCH-1/1	5.00
PPCC	4.37

meter and transmission electron microscopy (TEM). The XRD patterns of the thin films of the PPCHs were obtained. TEM observations were performed for the thin sections of the injection-molded samples by a JEOL-2000EX TEM using an acceleration voltage of 200 kV.

Tensile Test

The tensile tests were carried out with an Instron Model 4302 at 25°C. The head speed was 5 mm/min. All measurements were done in five replicates and the value averaged.

Measurement of Dynamic Moduli

The dynamic moduli of the PPCHs were measured by using an Iwamoto viscoelastic meter VES-F. The storage moduli of the PPCHs vs. temperature were obtained by sinusoidally vibrating the samples in the tensile mode at 10 Hz within the elastic region of the samples. The temperature range was between -50 and 160°C. The heat speed was 2°C/min.

RESULTS AND DISCUSSION

The Dispersibility of the Clay in PPCHs

Figure 1 shows TEM photographs of the PPCHs containing the PP-MA, where the dark lines are the cross sections of silicate layers of 10 Å thickness. Some of the particles of silicate layers were dispersed at the nanometer level. These particles became smaller and were dispersed more uniformly, as the ratio of the PP-MA to the clay was increased. On the other hand, in the PPCC without PP-MA, there were the aggregates of the clay at the micrometer level. It is apparent that PP-MA improved the dispersibility of the clays in the PPCHs.

Figure 2 shows the XRD patterns of the PPCHs and the C18-Mt/PP-MAs, where peaks correspond to the (001) plane reflections of the clays. The XRD patterns of the PPCHs did not change from those

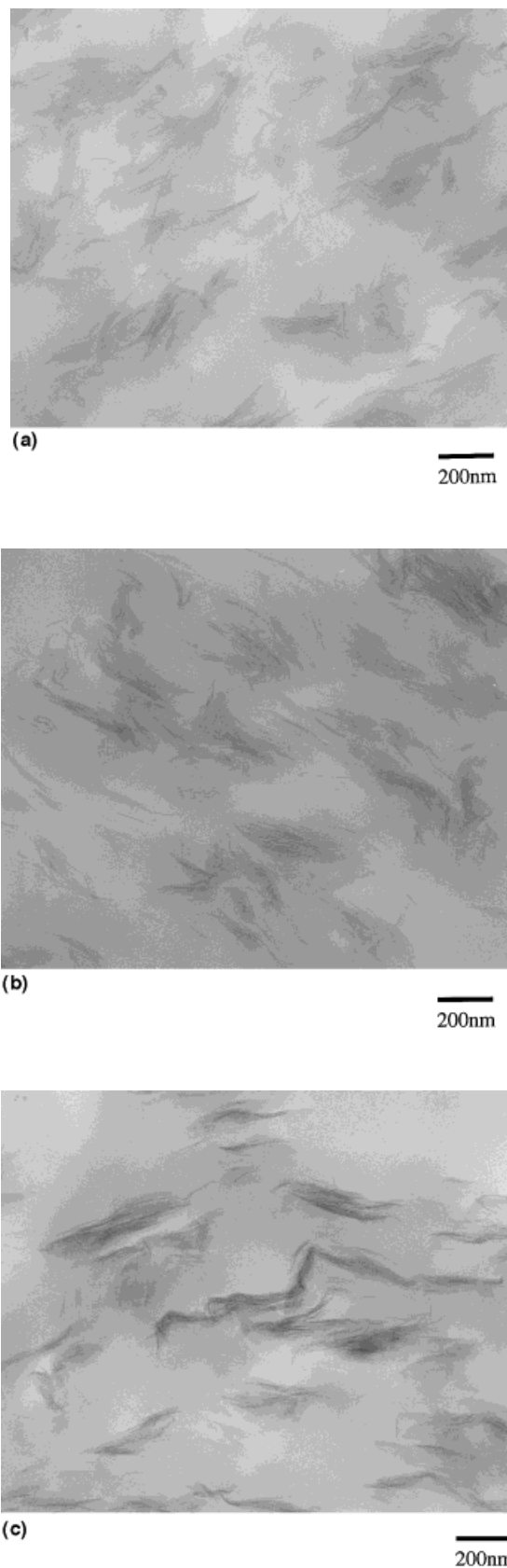


Figure 1 TEM photographs of the PPCHs: (a) PPCH-1/3; (b) PPCH-1/2; (c) PPCH-1/1.

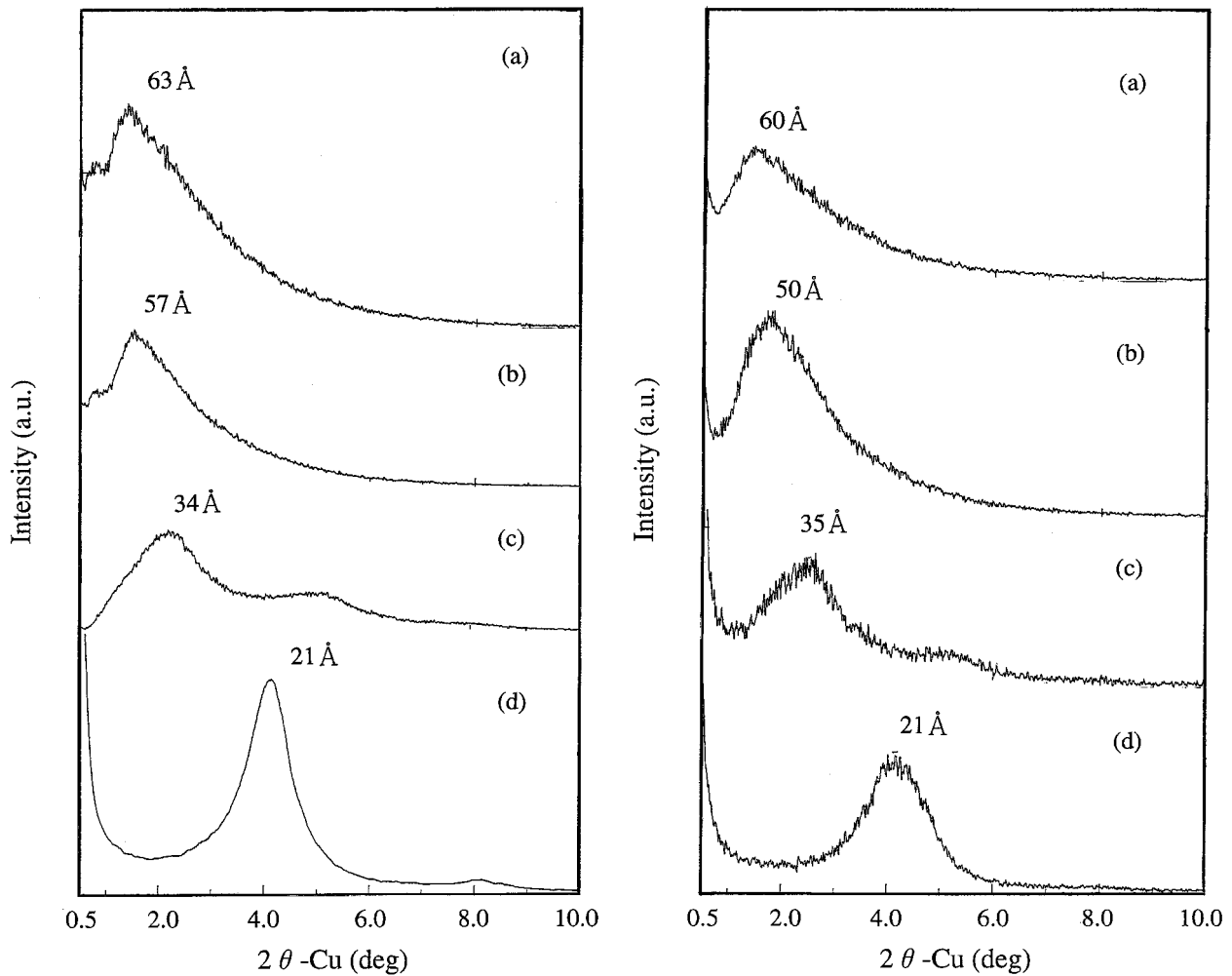


Figure 2 (1) X-ray diffraction patterns of the C18-Mt/PP-MA_s and the C18-Mt: (a) C18-Mt/PP-MA-1/3; (b) C18-Mt/PP-MA-1/2; (c) C18-Mt/PP-MA-1/1; (d) C18-Mt. (2) X-ray diffraction patterns of the PPCHs and PPCC: (a) PPCH-1/3; (b) PPCH-1/2; (c) PPCH-1/1; (d) PPCC.

Table IV Results of the Tensile Test^a

Sample	Modulus (MPa)	Strength (MPa)	Elongation (%)
PPCH-1/3	1010 ⁺²⁵ ₋₄₂ (1.29)	31.7 ^{+0.2} _{-0.2} (0.98)	5.6 ^{+0.3} _{-0.3}
PPCH-1/2	964 ⁺¹³ ₋₁₂ (1.23)	34.6 ^{+0.2} _{-0.2} (1.06)	8.6 ^{+0.5} _{-0.6}
PPCH-1/1	838 ⁺²² ₋₄₀ (1.07)	29.5 ^{+0.5} _{-0.2} (0.91)	7.5 ^{+0.4} _{-0.5}
PPCC	830 ⁺²² ₋₄₀ (1.06)	31.9 ^{+0.1} _{-0.2} (0.98)	105 ⁺³⁵ ₋₃₀
PP/PP-MA-22	760 ⁺²⁴ ₋₅₇ (0.97)	32.6 ^{+0.2} _{-0.3} (1.00)	40.3 ⁺¹⁶ ₋₁₁
PP/PP-MA-7	714 ⁺³⁰ ₋₃₂ (0.92)	31.4 ^{+0.2} _{-0.1} (0.97)	> 150
PP	780 ⁺¹⁶ ₋₁₀	32.5 ^{+0.1} _{-0.2}	> 150

^a The values in parentheses are the relative values of the hybrids to those of PP.

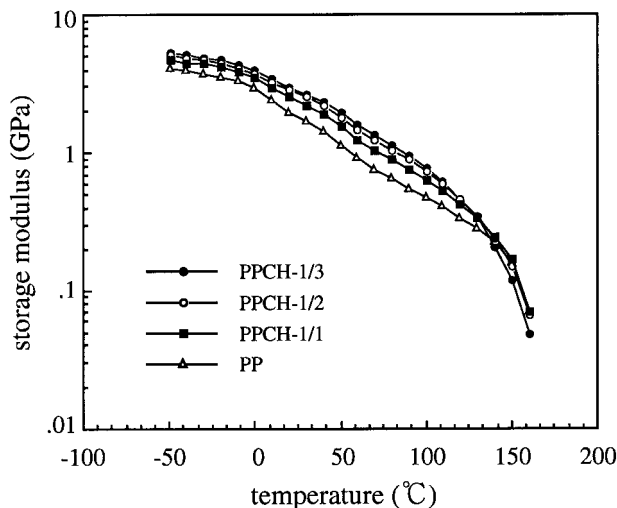


Figure 3 The dynamic storage moduli of the PPCHs and PP.

of the C18-Mt/PP-MAs. It was thought that PP did not intercalate between the layers of C18-Mt/PP-MAs during melt-blending. To improve the dispersibility of the clays in hybrids, modified PP oligomers with the larger miscibility to PP should be used so that PP can be inserted between the inter-layer of the clays.

The Study of Mechanical Properties of PPCHs

Table IV shows the results of the tensile test of the PPCHs. The tensile moduli of the PPCHs became

higher, as the ratio of PP-MA in the PPCHs increased. The modulus of PPCH-1/3 was 1.3 times higher than that of PP. The tensile strengths of the PPCHs were almost equivalent to that of PP. The elongations of the PPCHs were smaller than that of PP. The PPCHs exhibited brittle fracture. The elongations of PPCC and PP/PP-MA-22 also decreased compared to PP. It was thought that not only the clays but also the PP oligomer were the factors of the decline in the elongations of the PPCHs.

The dynamic storage moduli of the PPCHs are plotted vs. temperature in Figure 3. The representative values of the storage moduli at -40 , 20 , 80 , and 140°C and glass transition temperatures (T_g) are listed in Table V. The dynamic storage moduli of the PPCHs were higher than those of PP below about 150°C . To clarify the effect of the hybridization with the clays, the relative storage moduli of the PPCHs to those of PP are plotted in Figure 4(a). The relative storage moduli of the PPCHs below T_g (around 10°C obtained from $\tan \delta$) were relatively small and were 1.1–1.3 to those of PP. However, above T_g , they drastically increased up to the peak tops at about 80°C and then decreased to melt. The tendency was emphasized more strongly as the clays were dispersed more uniformly in the PPCHs. On the other hand, the relative storage moduli of the PPCC were relatively small and almost constant vs. temperature.

On the other hand, the relative moduli of the

Table V Dynamic Storage Moduli of the Hybrids and the Related Samples at Various Temperatures and Their Glass Transition Temperatures Obtained from $\tan \delta$

Sample	Storage Modulus ^a (GPa)				Glass Transition Temperature ^b (°C)
	-40	20	80	140	
PPCH-1/3	5.06 (1.29)	2.98 (1.51)	1.14 (1.76)	0.202 (0.91)	13
PPCH-1/2	4.90 (1.25)	2.85 (1.44)	1.05 (1.62)	0.237 (1.07)	12
PPCH-1/1	4.50 (1.15)	2.57 (1.30)	0.887 (1.37)	0.246 (1.11)	11
PPCC	4.50 (1.15)	2.36 (1.19)	0.818 (1.26)	0.278 (1.25)	9
PP/PP-MA-22	3.92 (1.00)	1.99 (1.01)	0.597 (0.92)	0.153 (0.69)	13
PP/PP-MA-7	3.80 (0.97)	1.97 (0.99)	0.612 (0.94)	0.19 (0.86)	11
PP	3.92	1.98	0.648	0.222	13

^a The values in parentheses are the relative values of the hybrids to those of PP.

^b The glass transition temperatures were measured at the peak tops of $\tan \delta$.

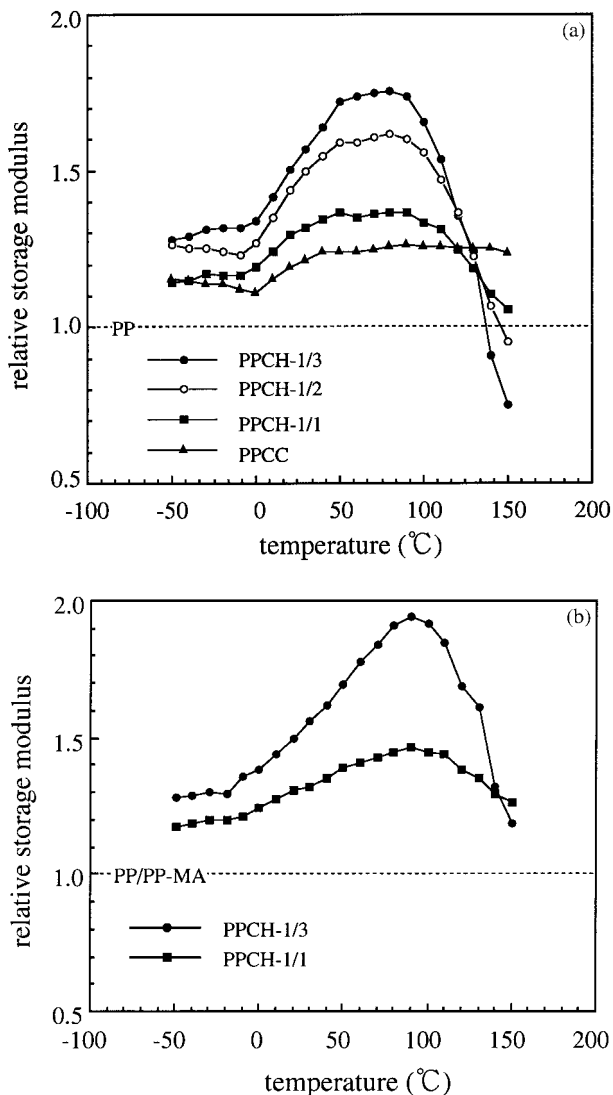


Figure 4 (a) The relative dynamic storage moduli of the PPCHs and the PPCC to PP. (b) The relative dynamic storage moduli of the PPCHs to PP/PP-MA.

PPCHs were lower than those of PP above about 140°C. The temperatures at which the moduli of the PPCHs were lower than those of PP decreased, as the ratio of PP-MA in the PPCHs increased. The decline of the storage moduli of the PPCHs above about 140°C should be attributed to the lower softening temperature of PP-MA. Figure 4(b) shows the relative storage moduli of PPCH-1/3 and -1/1 to those of the matrices PP/PP-MA-22 and PP/PP-MA-7, respectively. The relative moduli of the PPCHs were higher than those of the respective matrices at the whole temperature.

CONCLUSION

We prepared polypropylene-clay hybrids (PPCHs) by using the maleic anhydride-modified PP oligomer. In these PPCHs, some of the particles of silicate layers were dispersed at the nanometer level. The particles became smaller and were dispersed more uniformly, as the ratio of PP-MA was increased. It became apparent that PP-MA improved the dispersibility of the clays in the PPCHs. The dynamic storage moduli of the PPCHs were higher than that of PP up to 130°C. As the dispersibility of the clays was improved, the reinforcement effect of the clays increased. In the case of PPCH-1/3, the storage modulus was 1.8 times higher than that of PP at 80°C.

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