

Mechanical Properties and Fracture Morphology of Al(OH)₃/Polypropylene Composites Modified by PP Grafting with Acrylic Acid

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Received 2 March 2000; accepted 29 August 2000

ABSTRACT: Al(OH)₃/polypropylene (PP) composites modified by polypropylene grafted with acrylic acid (FPP) were prepared by melt extrusion. Effect of PP grafting with acrylic acid on mechanical properties and fracture morphology of Al(OH)₃/polypropylene composites were investigated. Although incorporation of Al(OH)₃ reduced the mechanical properties of PP, addition of FPP increased the mechanical properties of Al(OH)₃/PP composites. It is suggested that addition of FPP improve the dispersion of Al(OH)₃ and the interfacial interaction between filler and matrix. Mechanical properties of Al(OH)₃/FPP/PP composites depend on the grafting rate and the content of FPP. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2617–2623, 2001

Key words: polypropylene; functionalized polypropylene; Al(OH)₃; mechanical properties; fracture morphology

INTRODUCTION

The usefulness of polypropylene (PP) can be limited by its high flammability. Al(OH)₃ is an effective environmentally friendly flame retardant, which is acid and halogen free, and in addition to inhibiting polymer ignition, the function as effective smoke suppressant. However, studies have been shown that the effective flame retardation of PP requires Al(OH)₃ levels in excess of 60% by weight. The improvement in flame retardance usually resulted in a reduction in the strength properties of composites, in particular impact

strength. To achieve an optimum balance of flame retardance and mechanical properties of composites, the interfacial interaction and adhesion between PP and Al(OH)₃ have been improved. Generally, the application of modifiers onto the filler surface to enhance interfacial adhesion at this interface, or through chemical functionalization of the polymers to generate sites for reaction with the filler surface. Studies have been shown that functionalized polymers can act as effective coupling agent for the modification of the compatibility of the immiscible polymer blends and the interfacial adhesion in polymeric composites.^{1–24} However, effect of functionalized polymers on physical and mechanical properties of Al(OH)₃/PP composite has not been reported.

In our laboratory,^{25,26} polypropylene grafting with acrylic acid, PP-*g*-AA (FPP), was prepared by a melt-extrusion process. Experimental results showed that an increase in the grafting rate of FPP resulted in an increase in the crystallization

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Contract grant sponsors: National Natural Science Foundation, The Foundation for Trans-Century Training Program, and for the University Key Teacher by the State Ministry of China, The Talent Training Program Foundation for the Education Department, and Natural Science Team Foundation of Guangdong Province.

Journal of Applied Polymer Science, Vol. 80, 2617–2623 (2001)
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peak temperature (T_c), melt peak temperature (T_m), and degree of crystallization of PP due to enhanced nucleation and crystallization ability of PP by adding of FPP. The grafting of AA onto PP chain improved the thermal stability and mechanical properties of PP materials. Addition of FPP significantly increased the melt flow index of Al(OH)₃/PP composites, but decreased with increasing the grafting rate of FPP due to enhanced interfacial interaction between FPP and Al(OH)₃. With adding Al(OH)₃ and increasing the content of Al(OH)₃, limiting oxygen index(LOI) values of composites increased and further improved by adding FPP. Crystallization temperature of PP shifted to high temperature with increasing the content of Al(OH)₃ due to the interfacial heterogeneous nucleation of Al(OH)₃, and further increased by addition of FPP and with increasing the FPP content due to the improvement of the dispersion of Al(OH)₃ in the PP matrix.

The work in this article aims to understand the effect of polypropylene grafting with acrylic acid on mechanical properties and fracture morphology of Al(OH)₃/PP composites. Further insight into the mechanism of interfacial interaction between FPP and the surface of Al(OH)₃ is also sought.

EXPERIMENTAL

Materials

Polypropylene (PP), powdered F401, was a commercial product of Guangzhou Petrochemical Co. China. Pelletized PP, 1600, was obtained from Beijing Yanshan Petrochemical Co. China. Chemical-grade acrylic acid (AA) was purchased from Fushan Chemical Factory, Guangdong, China, and used without further purification. Chemical-grade dicumyl peroxide (DCP) used as an initiator for the AA grafting reaction was a commercial product of Shanghai Chemical reagent Factory, China. Al(OH)₃ was obtained from Shandong Aluminum Co., China. The solvent, acetone, was obtained from Guangzhou Chemical reagent Factory, China.

Preparation of Samples

Preparation of FPP

DCP and AA were dissolved in acetone, totally blended with powdered PP in a GH-10 high-speed mixing machine. After the solvent, acetone, had

completely evaporated, the mixture of AA and DCP was coated on the surface of the powdered PP, and the pretreated PP was prepared. The pretreated PP was then extruded by a SHJ-53 twin-screw extruder at temperature of 185–190°C, with the screw speed set at 60 rpm. The extruded products, the AA grafting-modified PP (FPP), were frozen in-line in a water bath, dried, and granulated to less than 3 mm.

Preparation of Test Specimens

The mixtures of pelletized PP, Al(OH)₃, and the FPP with different grafting rate were dried at a temperature of 90°C for 4 h before injection molding. The mixtures were injection molded into test specimens using a CJ150 ME-NC injection-molding machine, set with barrel temperature profile ranging from 190 to 210°C. The shape and size of the test specimens was described elsewhere.²⁷

Characterization of Structure and Properties

Mechanical properties were determined in both tension and flexure, and under impact loading. Tensile properties were measured on a WD-5A electronic universal testing machine (Guangzhou test machine factory, China) at a crosshead speed 10 mm/min, in accordance with GB/T1040-92. Flexural properties were measured on a LWK-5 electronic tension testing machine (Guangzhou test machine factory, China) following GB1040-92, using a crosshead speed of 10 mm/min and specimen span length of 50 mm. Notched impact strength was performed on a XJJ-5 impact testing machine (Chengde test machine factory, Hebei Province, China) on notched specimens, using procedures given in GB/T1043-93. Reported values were the average of five measurements for each sample at room temperature.

Fracture morphology of specimens for Al(OH)₃/PP and Al(OH)₃/FPP/PP composites were obtained by scanning electron microscopy (SEM) using a Hitachi S-520 electron microscopy operated at 25KV. Fracture surface of specimens broken during impact tests and a thin layer of gold was deposited prior to observation.

RESULTS AND DISCUSSION

Mechanical Properties of Al(OH)₃/PP Composites Modified by FPP

Tensile, flexural, and impact results of Al(OH)₃/PP composites modified by FPP are pre-

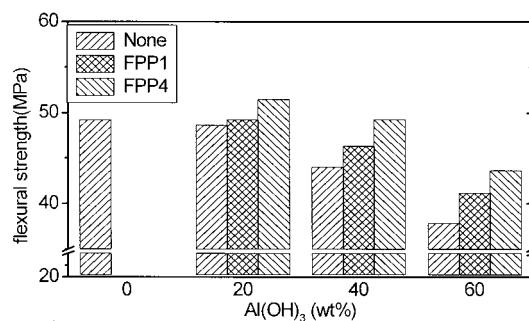
Table I Mechanical Properties of Al(OH)₃/PP Composites Modified by FPP

Code	FPP Grafting Rate (mol %)	Al(OH) ₃ /FPP/PP (wt)	IS (KJ/m ²)	FS (MPa)	FM (MPa)	TS (MPa)	TM (GPa)	EB (%)
0	None	0/0/100	3.76	49.2	1.65	30.9	1.5	>250
1	None	20/0/80	6.41	48.6	1.8	28.0	2.0	40
2	None	40/0/60	3.97	44.0	2.6	23.9	2.6	40
3	None	60/0/40	1.95	37.8	4.1	20.3	3.5	1.08
4	FPP1(0.15)	0/5/95	3.57	52.4	1.4	31.2	1.6	>250
5	FPP1(0.15)	20/5/75	4.25	49.2	1.8	27.0	1.9	6.17
6	FPP1(0.15)	40/5/55	2.62	46.3	2.9	24.0	2.4	3.79
7	FPP1(0.15)	60/5/35	1.47	41.1	4.6	21.3	3.5	1.10
8	FPP1(0.15)	60/2.5/37.5	2.05	39.4	4.4	22.1	3.6	0.79
9	FPP2(0.23)	60/5/35	1.70	40.0	4.3	20.6	3.5	1.25
10	FPP3(0.23)	60/5/35	1.82	36.7	4.2	20.4	3.5	1.17
11	FPP4(0.30)	0/5/95	4.03	51.4	1.4	31.9	1.6	>250
12	FPP4(0.56)	20/5/75	4.16	51.4	2.1	31.3	1.6	11.3
13	FPP4(0.56)	40/5/55	2.70	49.2	3.1	25.6	2.6	13.6
14	FPP4(0.56)	60/5/35	1.83	43.6	3.8	21.9	3.4	1.31
15	FPP4(0.56)	60/2.5/37.5	1.78	39.7	4.6	21.0	3.7	1.14

sented in Table I. Comparing mechanical properties of neat PP with composites containing the Al(OH)₃ content of 60% by weight, confirms the fall in tensile strength (TS), flexural strength (FS), impact strength (IS), and, in particular, elongation at break (EB) due to the presence of the filler.^{5,28} The reduction in strength properties with increasing the filler content was caused both by the effective matrix cross-section reduction and stress concentration increase. On the other hand, a lack of interfacial adhesion between PP and Al(OH)₃ due to large surface differences led to decreased mechanical strength of composites. However, addition of Al(OH)₃ and increasing the filler content resulted in an increased tensile modulus (TM) and flexural modulus (FM) due to the stiffening effect of the filler. For the Al(OH)₃/PP composites containing 20% Al(OH)₃, it can be seen that addition of Al(OH)₃ resulted in a significant increase in notched impact strength of PP. This observation is not consistent with results reported from many other PP composites, where the presence of inorganic filler (such as talc and mica) are frequently detrimental to toughness properties.^{5,29} Generally, mechanical properties of polymer containing rigid inorganic particles are determined by the size, shape, concentration, and properties of the filler,^{29,30} in particular by its interfacial interaction with the surrounding matrix.^{31,32} Impact properties of filled polymer depend strongly on effective filler dispersion, with

larger agglomerates acting as stress-raising flaws. However, under optimum conditions, incorporation of fillers such as calcium carbonate can enhance the ductility of PP by enabling the composite to undergo stable crack propagation through a crack pinning mechanism, rather than by brittle failure.²⁸ It is suggested that increase in impact strength of PP composite filled with the 20% Al(OH)₃ above matrix can be due to toughening mechanism associated with filler–matrix debonding and crack pinning. However, the impact strength of Al(OH)₃/PP decreased with increasing the Al(OH)₃ content. The impact strength Al(OH)₃/PP containing 60% Al(OH)₃ came to be lower than that of neat PP.

For the Al(OH)₃/PP composite modified by FPP, the impact strength, tensile strength, flex-

**Figure 1** Effect of 5 wt % FPP on flexural strength of Al(OH)₃/PP composites.

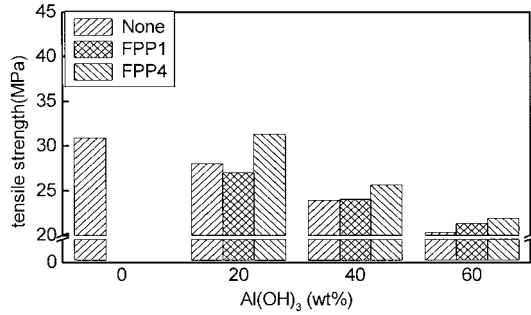


Figure 2 Effect of 5 wt % FPP on tensile strength of Al(OH)₃/PP composites.

ural strength, and elongation at break all also decreased, and tensile modulus and flexural modulus both increased with increasing the filler content, similarly to that of unmodified composite. The higher impact strength was also observed for the composite containing 20% Al(OH)₃. It was apparent that the presence of FPP led to a slight increase in flexural strength (Fig. 1), tensile strength (Fig. 2), and flexural modulus (Fig. 3) of the composites containing the same filler content, relative to the unmodified composites. These properties increased with increasing the grafting rate of FPP. For an adhesion strength by interfacial interaction sufficient to compensate the reduction of effective matrix cross-section, incorporation of FPP gives rise to enhance the tensile and flexural strength of composites. In the composite containing 20% Al(OH)₃, the increase in the grafting rate of FPP resulted in a reduced tensile modulus (TM), but the grafting rate of FPP had little influenced on the tensile modulus of composite containing high filler content (Fig. 4). Although the impact strength of Al(OH)₃/PP modified by FPP was lower than that of the unmodified composite, an increase in the grafting rate of FPP

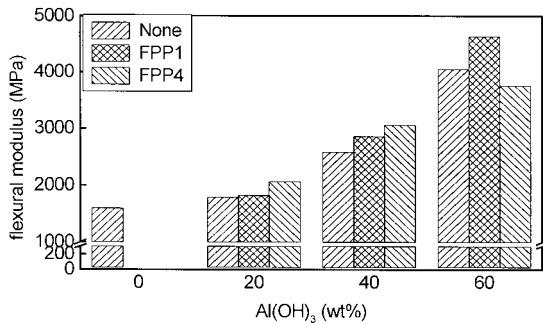


Figure 3 Effect of 5 wt % FPP on flexural modulus of Al(OH)₃/PP composites.

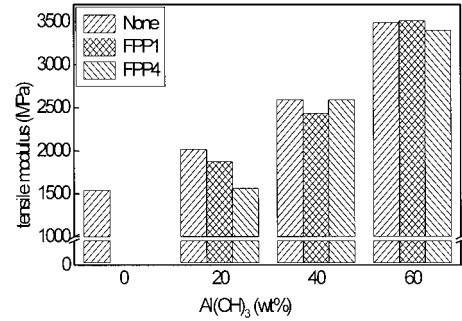


Figure 4 Effect of 5 wt % FPP on tensile modulus of Al(OH)₃/PP composites.

caused a slight increase in the impact strength of the composite containing higher filler content (Fig. 5). In the Mg(OH)₂/PP composites modified by acrylic acid functionalized PP, significantly increased flexural properties were observed by Hornsby and Watson.⁵ It was suggested that the presence of acid-modified polymer improved filler wet-out and markedly enhanced bonding of the filler surface, although this offered no greater resistance to crack propagation.

The grafting rate of FPP has more significant effect on the mechanical properties of Al(OH)₃/PP composites. For the composite containing 60% filler, the impact strength of the composite increased with increasing the grafting rate of FPP. The impact strength of the composite modified by FPP with a grafting rate of 0.56% reached the same as the value of unmodified composite (Fig. 6). However, increasing the grafting rate of FPP resulted in a decrease in the flexural modulus (Fig. 7). The grafting rate of FPP had little influenced on the tensile strength (Fig. 8) and tensile modulus (Fig. 9). A maximum value of flexural strength was observed for the composite modified by FPP with the grafting rate of 0.56%.

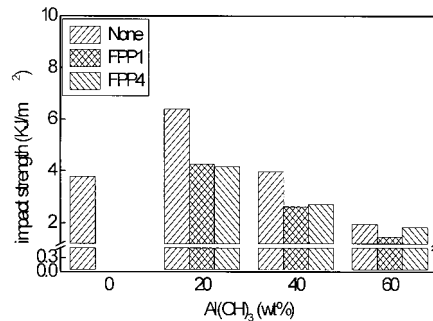


Figure 5 Effect of 5 wt % FPP on impact strength of Al(OH)₃/PP composites.

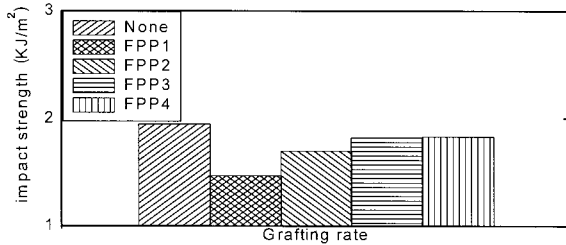


Figure 6 Effect of FPP with different grafting rate on impact strength of Al(OH)₃/FPP/PP (60/5/35) composites.

It can be seen from the Table I that addition of Al(OH)₃ caused a markedly fall out in the elongation at break (EB) of unmodified and modified composites, and the elongation at break continued to decrease with increasing the filler content. It was found that elongation at break of the composite modified by FPP with a higher grafting rate was higher than that of the lower grafting rate of FPP. The elongation at break of composites modified by FPP with a high and low grafting rate all increased with increasing the FPP content.

Fracture Morphology of Al(OH)₃/PP Composites Modified by FPP

The SEM photographs of impact fracture surface of unmodified and modified Al(OH)₃/PP composites containing 60% Al(OH)₃ are shown in Figure 11. For the unmodified composites, examination of fracture surfaces obtained from impact test specimen observed lack of bonding at the filler-matrix interface because PP has little affinity for Al(OH)₃ filler due to large surface energy differences. Interfacial interaction between the components is very limited, resulting in extensive par-

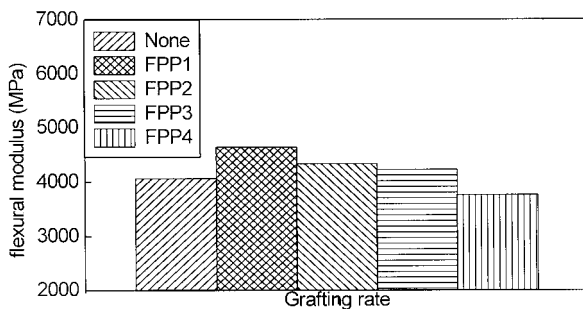


Figure 7 Effect of FPP with different grafting rate on flexural strength of Al(OH)₃/FPP/PP (60/5/35) composites.

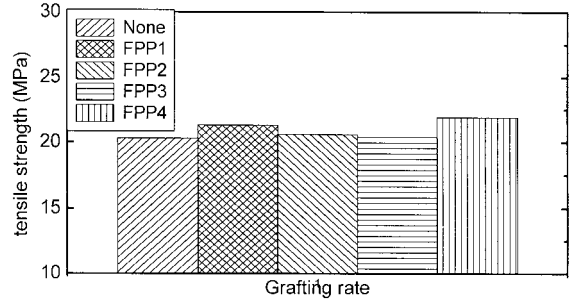


Figure 8 Effect of FPP with different grafting rate on tensile strength of Al(OH)₃/FPP/PP (60/5/35) composites.

ticle pullout from the fracture surface. Hence, the fracture proceeded along the Al(OH)₃-PP interface so that abundant unattached Al(OH)₃ particles can be observed on the impact fracture surface. This filler-matrix debonding and drawing of matrix ligaments between filler particles cause the high impact strength. Therefore, the impact strength of unmodified composites was higher than that of composites modified by FPP. For the modified composites, different failure characteristics are observed. The surface texture was much smoother than that of unmodified composites, and the filler particles remain well wetted by the matrix, indicating a high degree of compatibility between matrix and filler. These observations demonstrated that by adding of FPP, the surface properties of the filler and the interfacial interaction between the phase can be influenced. With increasing adhesion strength, the fracture propagates mainly through the matrix, and to a much lower extent along the interface. When the strength of adhesion is greater than the matrix cohesion strength, no filler particles can be observed on the fracture surface. Increasing interfacial adhesion between filler and matrix caused

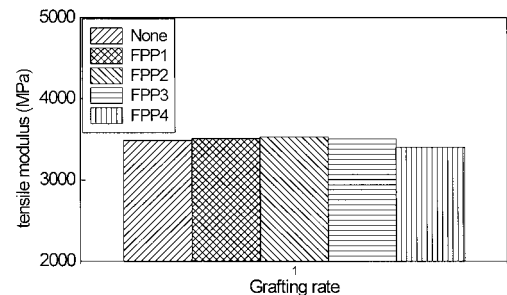


Figure 9 Effect of FPP with different grafting rate on tensile modulus of Al(OH)₃/FPP/PP (60/5/35) composites.

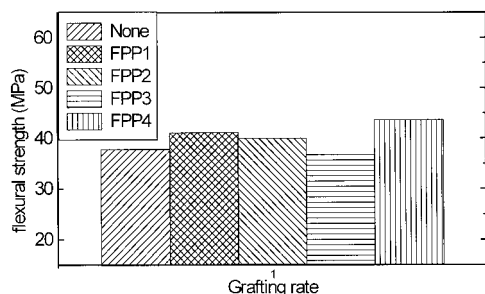


Figure 10 Effect of FPP with different grafting rate on flexural strength of $\text{Al}(\text{OH})_3/\text{FPP}/\text{PP}$ (60/5/35) composites.

the matrix to fracture over the top of the filler particles, and resulted in the particles being buried beneath a “blanket” of matrix. The increase in interfacial adhesion between the filler and matrix is attributed to the presence of the interfacial interaction. Jancar and Kucera²³ suggested that upon increasing the strength of adhesion, molecular mobility in the interlayer became more brittle and sensitive to the stress concentration. This caused the reduction in the composite yield stress with increasing adhesion strength.

The above observations demonstrated that addition of FPP resulted in improved mechanical properties of $\text{Al}(\text{OH})_3/\text{PP}$ composites. Filler dispersion was good in all composites, with filler agglomeration not being observed. Therefore, mechanical properties were governed by the interfacial interaction. It was suggested

that there existed a chemical and physical interaction between the filler and FPP, influencing the mechanical properties. During the preparation of $\text{Al}(\text{OH})_3/\text{PP}$ composites modified by FPP, FPP molecules are chemically bonded on the filler surface by acid-base interaction between carboxy groups grafted on FPP and hydroxy groups from the filler surface. Compared to aliphatic chains of low molecular weight organic modifiers, FPP molecules are sufficiently long to create physical entanglements with PP molecules from the matrix bulk and FPP activates nucleation centers on the filler surface. On the other hand, PP chains in the FPP can cocrystallize with the PP matrix. The change in matrix crystallinity also affects interfacial properties. Hence, the interfacial adhesion between two components (filler and FPP, FPP, and PP matrix) can be improved by addition of FPP. Studies have been shown that surface modification of fillers with fatty acids generally reduces the nucleation ability of the filler.³³ Our work indicated that addition of FPP increased the nucleation ability of the $\text{Al}(\text{OH})_3$.²⁶ McGenity³³ and Hutley^{34,35} found the enhance nucleation of PP by filler reduces composite toughness. In $\text{Al}(\text{OH})_3/\text{PP}$ composites, the effects of enhanced filler–matrix interactions generated by nucleating filler and FPP modifier, and the influences of filler content as well as the number and quality of interlamellar and interspherulitic ties need to be taken into account.

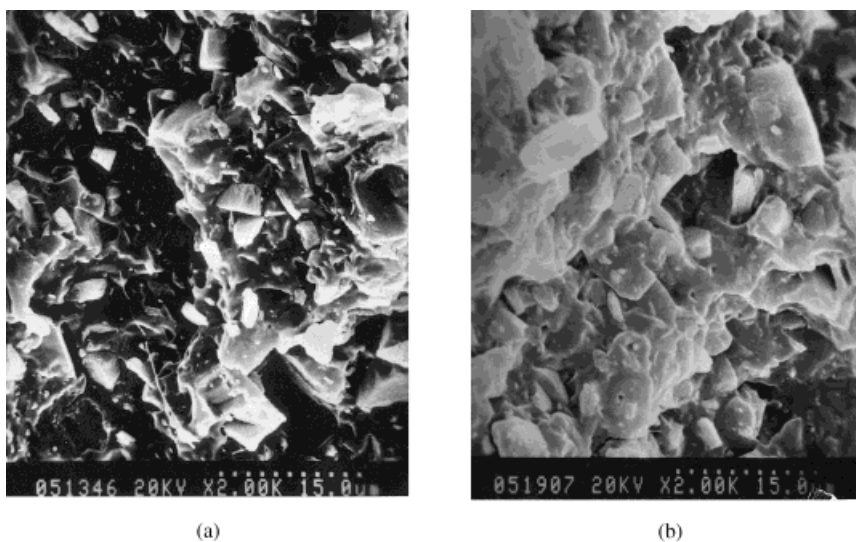


Figure 11 Fracture morphology of impact sample of unmodified $\text{Al}(\text{OH})_3/\text{PP}$ composite (a) and $\text{Al}(\text{OH})_3/\text{PP}$ composites modified by 5 wt % FPP4 (b); $\text{Al}(\text{OH})_3$: 60 wt %.

The authors thank the National Natural Science Foundation; Foundation for Trans-Century Training Program and for the University Key Teacher by the State Education Ministry of China; and the Talent Training Program Foundation of the Education Department and Natural Science Team Foundation of Guangdong Province.

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