

# Synthesis and characterization of hybrid organic-inorganic materials based on EA-MAn-APTES and silica

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**Abstract:** Poly (EA-MAn-APTES)/silica hybrid materials were successfully prepared from Ethyl acrylate (EA), maleic anhydride (MAn) and tetraethoxysilane (TEOS) in the presence of a coupling agent 3-aminopropyltriethoxysilane (APTES), by free-radical solution polymerization and in situ sol-gel process. The mass fraction of TEOS varied from 0 to 25%. The hybrid materials were characterized by the methods of FT-IR spectra, solvent extraction, scanning electron microscope (SEM), transmission electron microscope (TEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measuring apparatus to get their structures, gel contents, morphologies, particle sizes and thermal performances. The results show that the covalent bonds are between organic and inorganic phases, gel contents in the hybrid materials are much higher, the SiO<sub>2</sub> phase is well dispersed in the polymer matrix, silicon dioxide exist at nanoscale in the composites and have excellent thermal stability.

**Key words:** organic-inorganic hybrid material; sol-gel process; Ethyl acrylate; maleic anhydride; 3-aminopropyltriethoxysilane (APTES)

The sol-gel process is of interest in preparing organic-inorganic hybrid materials due to its mild conditions, such as low temperature and pressure<sup>[1–3]</sup>.

The process provides a convenient route to prepare homogeneous hybrid materials. These hybrid materials possess organic and inorganic properties<sup>[4]</sup> and their properties can also be tuned through changing the functionality or segment size of each component, including thermal, mechanical, electronic, optical and optoelectronic properties. Common applications of the hybrid materials as passive or active layer in optoelectronic devices have been reported, including protective coating<sup>[5]</sup>, contact lenses<sup>[6]</sup>, high refractive index films<sup>[7]</sup>, thin film transistors<sup>[8]</sup>, solar cells<sup>[9]</sup>, light-emitting diodes<sup>[10]</sup>, optical waveguides materials<sup>[11]</sup> and photo chromic materials<sup>[12]</sup>. These properties are associated with  $\sigma$  conjugation<sup>[13]</sup>. Many researchers have demonstrated that monolithic, transparent hybrid materials without macroscopic phase separation can be prepared by properly controlling the conditions of hydrolysis and condensation of sol-gel materials such as

tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS)<sup>[14–16]</sup>. Organic and inorganic constituents can be chemically bonded or just physically mixed in these hybrid materials. But a significant feature to enhance the compatibility in the hybrid material is the formation of the covalent bonds between organic polymers and inorganic components.

In this study, copolymer was prepared by free radical copolymerization of Ethyl acrylate (EA) with maleic anhydride (MAn). Copolymer precursor holding trimethoxysilyl-functionality was prepared by 3-aminopropyltriethoxysilane (APTES), coupling of the copolymer with miscible TEOS as an inorganic silica matrix for a sol-gel process. Then the copolymer precursor was hydrolyzed and condensed in the presence of an aqueous HCl catalyst to generate poly (EA-MAn-APTES)-SiO<sub>2</sub> hybrid material as shown in Fig. 1.

## 1 Experiment

### 1.1 Materials

EA, MAn, 2, 2'-azobisisobutyronitrile (AIBN) and TEOS were purchased from Shanghai Chemical Reagent Company. Initiating agent AIBN was purified by recrystallization from alcohol and then dried in a vacuum oven. APTES was purchased from Nanjing Shuguang Chemical Plant. Tetrahydrofuran (THF) was purified by distillation, and other reagents and

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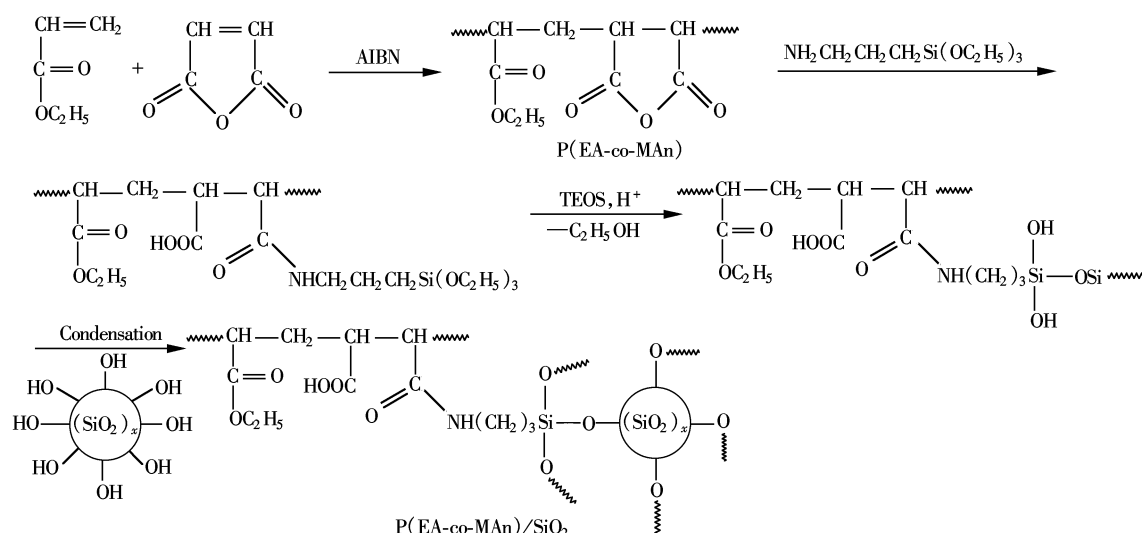


Fig. 1 Preparation of organic-inorganic hybrid films by sol-gel process

solvents were obtained commercially and were used as received.

## 1.2 Preparation of hybrid P(EA-MAN-APTES)/SiO<sub>2</sub>

Hybrid films were prepared according to the scheme, as shown in Tab. 1. EA and MAn were taken in a 500 mL three-neck round-bottomed flask. The THF and initiator AIBN were added under nitrogen purging. The reaction temperature was maintained at 70 °C for 3 h and the copolymerization was carried out. Then APTES was added under nitrogen and stirred for 2 h. The copolymer precursor for preparing the hybrid films was obtained. Then the TEOS homogeneous hydrolysate, prepared using deionized water, hydrochloric acid and THF, were added into the copolymer precursor solution. Meanwhile the sol-gel process was carried out. The synthetic route is shown in Fig. 1. The homogeneous transparent sol can be obtained and then transferred to a conical flask. The resulting gel was evaporated solely for 5 d and then was dried at 110 °C under vacuum for 5 h to remove residual solvent and by-products (water and alcohol, etc.). The thermally stable sol-gel hybrid material was obtained. The results of determination of molecular weight and element analysis are shown in Tab. 2.

Tab. 1 Monomer compositions for preparing hybrid thin films

Sample	<i>m</i> (EA)/g	<i>m</i> (MAn)/g	<i>m</i> (APTES)/g	<i>w</i> (TEOS)/%
S <sub>1</sub>	27.51	26.96	40.53	5
S <sub>2</sub>	26.06	25.54	38.40	10
S <sub>3</sub>	24.61	24.31	36.26	15
S <sub>4</sub>	23.17	22.70	34.13	20
S <sub>5</sub>	21.72	21.28	32.00	25

Tab. 2 Determination of molecular weight and element analysis

Sample	<i>M<sub>n</sub></i> /10 <sup>3</sup>	<i>M<sub>w</sub></i> /10 <sup>3</sup>	Polydispersity	<i>w</i> (C)/%	<i>w</i> (H)/%	<i>w</i> (N)/%
S <sub>1</sub>	10.4	20.6	1.98	45.86	5.25	3.13
				44.97	4.86	2.87
S <sub>3</sub>	11.8	23.2	1.97	40.53	4.82	2.88
				39.21	4.10	2.11
S <sub>5</sub>	12.0	26.4	2.20	36.68	4.36	2.61
				35.12	4.27	2.08

All of polymerization mixtures have the following fixed compositions:  $x(\text{APTES/EA}) + x(\text{MAn}) + x(\text{APTES}) = 25\%$ ;  $x(\text{AIBN/EA}) + x(\text{MAn}) + x(\text{APTES}) = 3.25\%$ .

## 1.3 Measurement

IR spectra of the prepared thin films were obtained on KBr pellets using Nocolet AVATAR 360 spectrometer. The fracture surfaces of hybrid thin films were examined on the HITACHI X-650 scanning electron microscope (SEM). HITACHI H-600 transmission electron microscope (TEM) measured the particle sizes. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA449C. The programmed heating range was from room temperature to 800 °C, at a heating rate of 10 °C/min under nitrogen atmosphere. The measurement was taken using 6 to 10 mg samples. TGA and DSC curves were recorded. The element analysis was determined on the Foss Heraeus CHN-O-Rapid. Because of the good solubility of the hybrid in DMF, the molecular weight can be measured by using gel permeation chromatography (GPC). The determination of sol fraction was to put the obtained hybrid materials in the sorbite extraction set and use acetone circulation reflux for 36 h. Then it was dried to constant weight in the vacuum drying oven. The calculating equation is as follows:

$$A = \frac{m_1 - m_2}{m_1} \times 100\%$$

where  $A$  is the sol fraction;  $m_1$  and  $m_2$  are the mass before extraction and the mass after extraction, respectively.

## 2 Results and Discussion

### 2.1 Fourier transform infrared spectra

The results of FT-IR spectra ( $4\,000$  to  $400\text{ cm}^{-1}$ ) of TEOS, APTES and hybrid materials  $S_1$  to  $S_5$  are shown in Fig. 2 and Tab. 3. It can easily be found that  $1\,790$  and  $1\,852\text{ cm}^{-1}$  were attributed to stretching peaks of carbonyl in carboxylic group ( $-\text{COOH}$ ).  $1\,730$  and  $1\,702\text{ cm}^{-1}$  belonged to stretching peaks of carbonyl in amidogen ( $-\text{CONH}$ ). Therefore it can be confirmed that amino-group of coupling agent APTES broke maleic anhydride of copolymer to form carboxylic acid and amide. However the TEOS and triethoxy-silicon group of APTES form inorganic network by hydrolysis and condensation, which could be demonstrated by the absorption, peaks of  $\text{Si}-\text{O}-\text{Si}$  asymmetric stretching ( $1\,100$  to  $1\,050\text{ cm}^{-1}$ ) and symmetric stretching ( $728\text{ cm}^{-1}$ ).

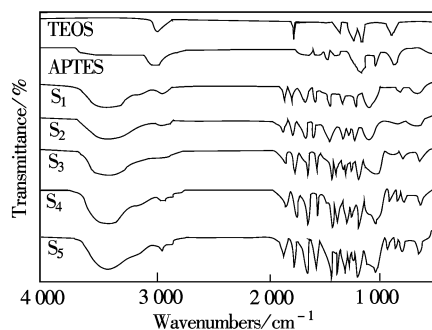


Fig. 2 FT-IR spectra of TEOS, APTES and hybrid materials

Tab. 3 Assignment of the FT-IR peaks shown in Fig. 2

No.	Peak positions/ $\text{cm}^{-1}$	Assignments
1	698	Siloxane rings
2	728	$\text{Si}-\text{O}-\text{Si}$ symmetric stretching
3	860	$\text{Si}-\text{C}$ stretching
4	962	$\text{Si}-\text{OH}$ stretching
5	1 100 to 1 050	$\text{Si}-\text{O}-\text{Si}$ asymmetric stretching
6	1 206	$-\text{Si}-\text{CH}_2-$
7	1 320 to 1 248	Skeletal $-\text{CO}-\text{O}-$
8	1 408 to 1 450	$\text{CH}_2$ wagging
9	1 730, 1 702	$-\text{C}=\text{O}$ ( $-\text{CONH}-$ stretching)
10	1 790, 1 852	$-\text{C}=\text{O}$ ( $-\text{COOH}$ stretching and anhydride)
11	3 300 to 3 500	$-\text{O}-\text{H}$ ( $-\text{COOH}$ ; $\text{H}-$ bonded; incompletely-condensation $-\text{OH}$ )

### 2.2 Determination of sol fraction

Good solvent will extract the parts, which do not cross link with chemical bond. After the synthetic hybrid materials were extracted with acetone, the extraction sol is the copolymer, which does not combine to

the inorganic network with the covalent bond. The results of extraction experiments are 5.9% ( $S_1$ ), 5.8% ( $S_2$ ), 5.2% ( $S_3$ ) and 5.0% ( $S_4$ ) and 4.8% ( $S_5$ ), respectively. This shows a combination with the chemical bonds between organic and inorganic parts. Coupling agent APTES can integrate the organic unit of the copolymer and the inorganic network with the covalent bond and restrain the extracted hybrid materials.

### 2.3 Microstructure analysis

Fig. 3 shows the TEM diagrams of  $S_2$  and  $S_5$ . The morphology of the hybrids based on the TEOS alkoxide is quite homogeneous, appearing as a very fine dispersion of silica particles at the lowest TEOS concentration and as a fine interpenetrating phase at a mass fraction of 25% ( $S_5$ ). Because TEOS has high reactivity, it quickly undergoes hydrolysis and cross-links in solution before phase separation occurs, which results in a highly interpenetrating network of polymer and silica structures. The  $\text{SiO}_2$  phase size is about 50 to 70 nm.

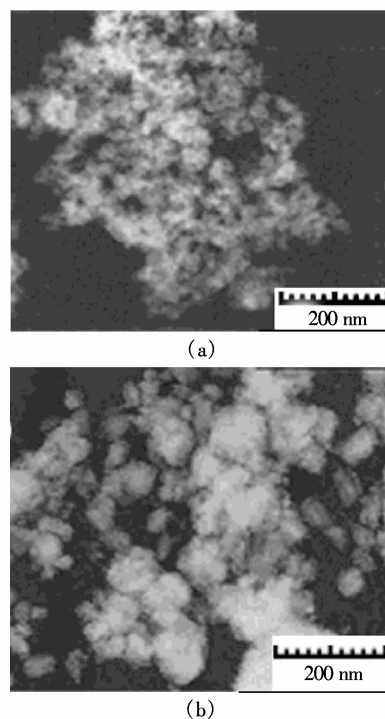


Fig. 3 TEM diagrams of poly (EA-Man-APTES)/ $\text{SiO}_2$ . (a)  $S_2$ ; (b)  $S_5$

The compatibility between the organic copolymer and silica has a great effect on the thermal, mechanical and optical properties. To investigate the distribution of silica and microphase separation in the hybrid matrix, the morphology of the fractured surfaces was observed by SEM (see Fig. 4). Based on the photograph, it can be seen that the interaction between poly-

mer and  $\text{SiO}_2$  in hybrid composite membranes is very strong. The strong interaction between polymer and  $\text{SiO}_2$  in hybrid composite membranes results in the restriction of molecular chain motion. These results show that silica networks are restrained at the molecular level in the hybrid materials.

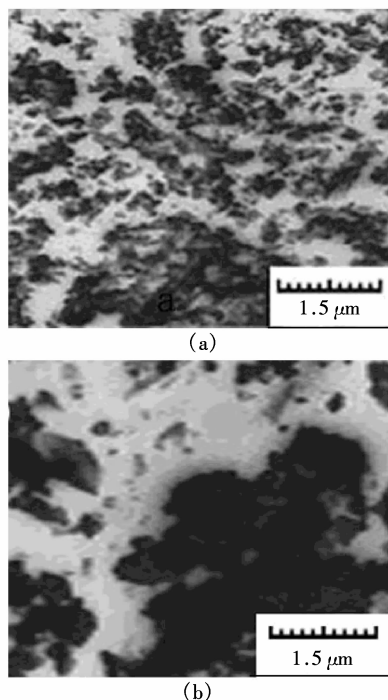


Fig. 4 SEM photographs. (a)  $S_2$ ; (b)  $S_5$

## 2.4 Thermal analysis

The thermal properties of hybrid films were characterized by DSC and TGA (see Tab. 4). The glass transition temperature  $T_g$  was obtained from DSC curves, which were produced at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. The thermal degradation temperature  $T_d$  is the weight loss of TGA thermogram at a mass fraction of 5%.  $T_g$  of the hybrid films increases with the increase of APTES content. This is due to the fact that the plasticizing trimethoxysilyl groups have transformed to a silica network during the sol-gel process.

Tab. 4 Thermal properties of hybrid materials  $^\circ\text{C}$

Hybrid materials	$T_g$	$T_d$
$S_1$	117	289
$S_2$	123	293
$S_3$	132	299
$S_4$	147	306
$S_5$	158	310

## 3 Conclusion

This paper concerns the study of P(EA-MAn-APTES)/ $\text{SiO}_2$  nanocomposite membranes and some

different  $\text{SiO}_2$  contents with physical properties and thermal properties. The hybrids were very homogeneous. The  $\text{SiO}_2$  structures in TEOS based hybrid systems were completely condensed, resulting in cross-linking with the polyimide matrix. So these hybrid materials have network structures and small inorganic phases. The hybrids were nanocomposites. Covalent bonds between the organic and inorganic components enhanced miscibility between the silica and the copolymer, which was further confirmed by FT-IR, SEM, TEM and the determination of sol content. These hybrid materials have excellent thermal stability.

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## P(EA-MAn-APTES)/二氧化硅 有机-无机杂化材料的合成和表征

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**摘要:** 采用  $\gamma$ -氨丙基三乙氧基硅烷 (APTES) 作为偶联剂, 以丙烯酸乙酯 (EA)、顺丁烯二酸酐 (MAn) 和正硅酸乙酯 (TEOS) 为原料, 通过自由基溶液聚合和溶胶-凝胶过程制得了 P(EA-MAn-APTES)/二氧化硅有机-无机杂化材料, 其中 TEOS 的质量分数从 0 变化至 25%。利用傅立叶红外 (FT-IR) 光谱、溶胶抽取、扫描电子显微镜 (SEM)、透射电子显微镜 (TEM)、示差扫描量热法 (DSC) 和热重分析 (TGA) 性能测试装置对材料的结构、凝胶含量、表面形貌、粒子大小和热性能进行了表征。结果表明: 有机相与无机相之间是以共价键结合的, 杂化材料中凝胶的含量较高, 聚合物基体中 SiO<sub>2</sub> 是纳米复合的, 具有较好的分散性和热稳定性。

**关键词:** 有机-无机杂化材料; 溶胶-凝胶过程; 丙烯酸乙酯; 顺丁烯二酸酐;  $\gamma$ -氨丙基三乙氧基硅烷  
**中图分类号:** O631