

Synthesis and Characterization of Novel Ultraviolet-Curing Polyurethane Acrylate/Epoxy Acrylate/SiO₂ Hybrid Materials via Sol-Gel Reaction

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ABSTRACT: A series of ultraviolet-curable hybrid materials was first synthesized here by sol-gel process based on tetraethoxysilane (TEOS) and polyurethane acrylate/epoxy acrylate resin. The functional groups in the hybrid materials were investigated by infrared spectroscopy (IR) analysis. The crystallinity of the hybrid materials and polymer resin was examined by X-ray diffraction. Then, nearly uniform dispersion of SiO₂ particles with the diameters 100 nm were revealed by field emission scanning electron micrographs. The surface morphology was scanned by atomic force microscope. And, thermal stability was measured by thermogravimetric analysis for hybrid materials produced from different mass ratio of TEOS to polymer. The results show that the hybrid material from the mass ratio of TEOS to polymer of 0.4 : 1 performed desirable optimal thermal stability and uniform microstructure which is suitable for optical fiber coating in high temperature application. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: sol-gel reaction; UV-curing PUA/EA/SiO₂ hybrid materials; surface morphology; thermal stability

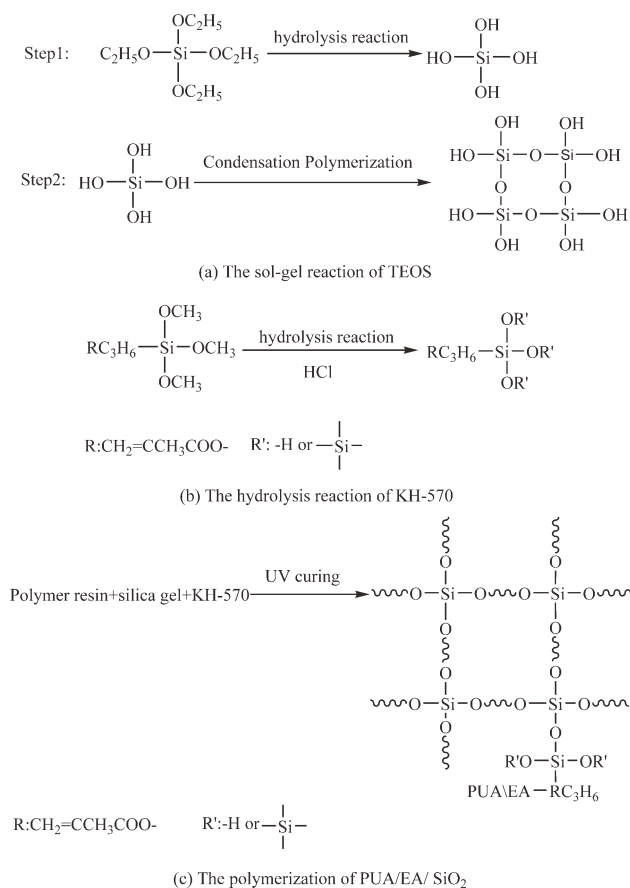
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INTRODUCTION

Ultraviolet (UV)-curing has many advantages for polymer processing, including low volatile organic compounds emission, energy saving, rapid curing, and high efficiency in production. Polyurethane acrylate (PUA) and epoxy acrylate (EA) were generally UV-cured. Acrylate oligomer belongs to free radical polymerization initiated by photoinitiator. PUA exhibits high plasticity, excellent abrasion resistance, and high breaking elongation, but unsatisfactory thermal stability. On the other hand, EA exhibited outstanding inflexibility and thermal stability. The two types of resin complemented each other when they were combined. For instance, epoxy resin was modified by poly(ether urethane) and the impact strength of the system was doubled according to the research by Li and Li.¹ Acrylic-polyurethane hybrid aqueous emulsions prepared by Hirose showed an increase of 3.9°C in the glass transition temperature (T_g).² Inorganic fillings were always added into polymer to enhance thermal properties including thermal stability. Organic-inorganic hybrid materials synthesized with sol-gel process exhibit

the properties both of the organic and the inorganic materials simultaneously. Furthermore, the hybrid materials may have interesting properties that are found neither in the organic polymer nor in the inorganic materials independently.^{3–6} PUA/SiO₂ hybrid materials were prepared with sol-gel process by Han and 50°C increase in the thermogravimetric temperature was achieved.⁷ EA/SiO₂ hybrid nanocomposites were prepared by Amerio, and the T_g detected by DMA increased with the content of tetraethoxysilane (TEOS).⁸ In this article, the hybrid materials using PUA and EA as matrix and TEOS as the resource of inorganic system are synthesized via sol-gel process for the optical fiber coating application. High temperature application of silica optical fibers is often limited by the thermal stability of their coatings, because the thermal degradation in the coatings can lead to degradation in the fiber performance. Therefore, the influence of the mass ratio of TEOS to resin on the properties of the final product is investigated here so that a recipe can be determined to obtain coating materials with high thermal stability and uniform microstructure at the same time.



Scheme 1.

Meanwhile, the mechanism of the sol-gel reaction is discussed as follows. At the first step, TEOS is hydrolyzed and Si-OH groups are generated, as shown in Scheme 1. At the second step, dehydration reaction starts between Si-OH and other Si-OH from TEOS or KH-570 and 3D network is formed.^{9,10} The silane coupling agent KH-570 also can be hydrolyzed. The production Si-OH can react with the terminal Si-OH from 3D network to avoid network growing. Si-OH from KH-570 also can form hydrogen bond with hydroxyl group from the matrix resin.¹¹ Under UV lamp, C=C from KH-570 and acrylate are polymerized and even cross linked. Consequently, KH-570 coupled the organic and inorganic segments.

Table I. The Concentration of Components for the Hybrid Materials

Sample	PUA (g)	EA (g)	Reactive diluent (g)	Photoinitiator 1173 (g)	TEOS (g)	Deionized water (g)	Alcohol (g)	HCl (g)	KH-570 (g)	TEOS : (PUA and EA) (mass ratio)
1	20	10	20	1.2	0	0	0	0	0	0
2	69.33	34.67	69.33	4.16	10.4	3.6	9.2	0.1165	3.1	0.1
3	34.66	17.33	34.66	2.08	10.4	3.6	9.2	0.1165	3.1	0.2
4	23	11.55	23	1.39	10.4	3.6	9.2	0.1165	3.1	0.3
5	17.33	8.67	17.33	1.04	10.4	3.6	9.2	0.1165	3.1	0.4
6	13.87	6.93	13.87	0.83	10.4	3.6	9.2	0.1165	3.1	0.5
7	11.55	5.77	11.55	0.70	10.4	3.6	9.2	0.1165	3.1	0.6

EXPERIMENTAL

Materials

The tetraethoxysilane (TEOS), HCl, and absolute ethyl alcohol (wt 99.7%) used were supplied by Kaifeng Dongda Chemicals Ltd, China, which were all analytical reagents. The PUA (DY5600), EA (DY3100), trimethylolpropane triacrylate (TMPTA), tripropylene glycol diacrylate (TPGDA), and Darocure 1173 photoinitiator were supplied by Dongyang Chemical Coating Ltd., China. 3-(Trimethoxysilyl) propyl methacrylate (KH-570) was used as a secondary inorganic source and simultaneously a silane coupling agent to improve the compatibility between the organic polymer and inorganic materials and was supplied by Wuhan University Silicon Co., China. In addition, deionized water was used to hydrolyze the inorganic monomer precursors. All the materials were utilized without further purification.

Preparation

First, TEOS was added into some alcohol. Second, the catalyst HCl (12 mol/L) was dropped into deionized water and alcohol, and then the mixture was added into TEOS in drops under violent stirring at room temperature for 12 h. HCl was used as a catalyst to initiate the hydrolysis of the inorganic monomer precursors. The mole ratio of TEOS, water and alcohol was 1 : 4 : 4. The pH of the mixture was controlled to be 2 by the content of HCl.¹² Third, KH-570 was dropped into the solution. Finally, the whole mixture was aged at room temperature for 24 h and modified silica was obtained.

DY5600, DY3100, reactive diluents TMPTA, TPGDA, and Darocure 1173 photoinitiator were charged into a three-neck flask, and the mixture was vigorously stirred for 1 h. The mass ratio of PUA to EA was fixed to be 2 : 1 and the mass ratio of (PUA and EA) to (TMPTA and TPGDA) to be 1.5 : 1¹³ to achieve optimal thermal stability. Then, silica sol was added into the different mixtures. The exact dosage for mixture is listed as follows in Table I. The stirring would not stop until the mixtures get transparent. Then, the mixtures were left in an oven at 80°C till the solvent was removed completely. At the end, each mixture sample was applied onto a polished substrate and cured by UV lamp for 3 min with the intensity of the UV lamp of 80 mW/cm².

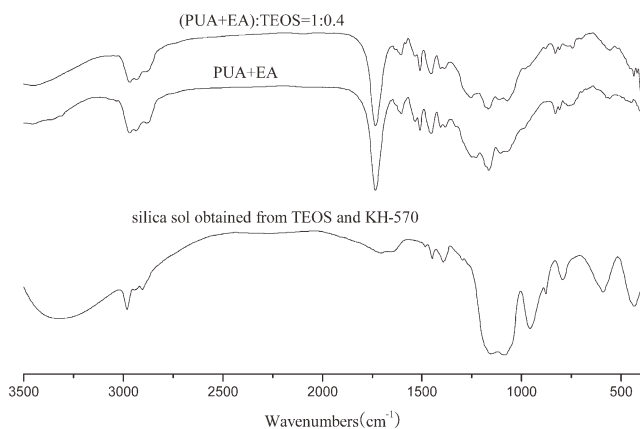


Figure 1. The FTIR spectra of silica sol modified by KH-570, PUA/EA, and the hybrid material.

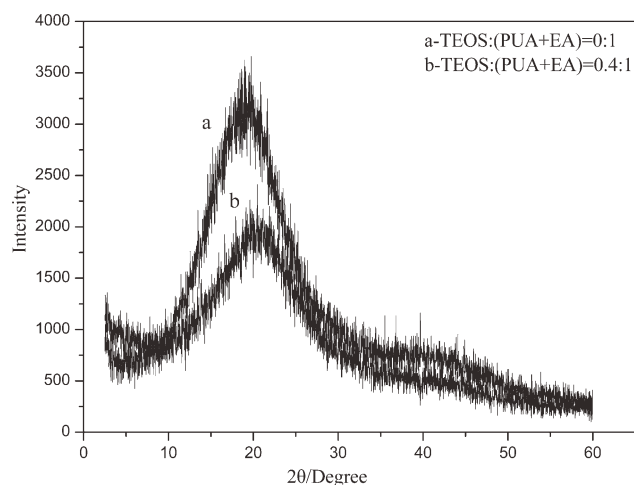


Figure 2. The XRD of PUA/EA and the hybrid material with TEOS : (PUA + EA) = 0.4 : 1.

Characterization

Chemical reactions were monitored by Fourier transform infrared (FTIR) spectroscopy which is a Thermo-Nicolet Nexus instrument. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-RB X-ray diffractometer with a Cu tube ($\lambda = 0.154 \text{ nm}$). The angle region tested was from 2.5° to 10° . The microstructures of the hybrid materials were investigated by

the field emission scanning electron micrographs (FESEM) S4800 produced by Hitachi Ltd., Japan. The surface morphology of these materials was examined by the atomic force microscope (AFM) from Veeco instruments Ltd, USA. And, the thermal stability of the hybrid materials was examined by the STA449c/3/G thermogravimetry (TGA) from Netzsch Inc., Germany, with a

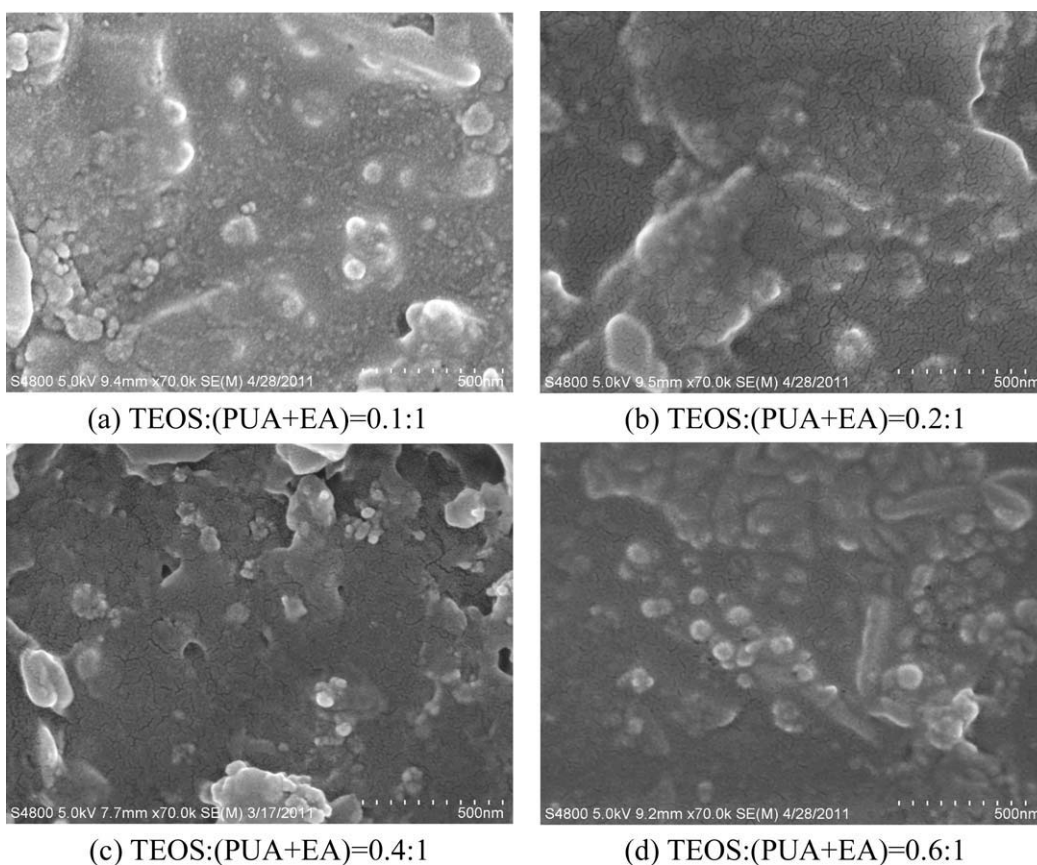


Figure 3. The FESEM photographs of the hybrid materials.

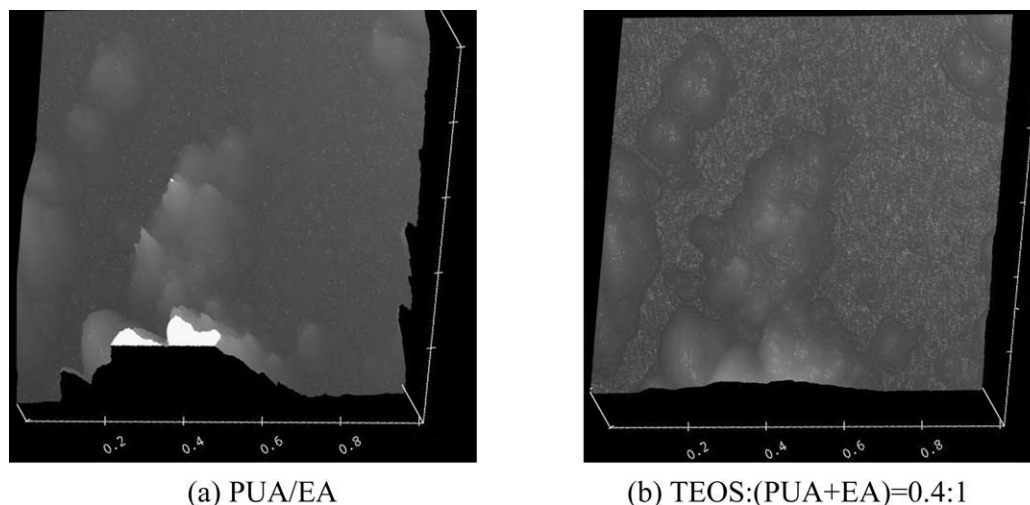


Figure 4. The 3D AFM images of PUA/EA and the hybrid material from TEOS : (PUA + EA) of 0.4 : 1.

heating rate of 10°C/min from room temperature to 500°C under stable nitrogen gas flow.

RESULTS AND DISCUSSION

The FTIR spectra of silica sol modified by KH-570, PUA/EA, and the hybrid materials are shown in Figure 1. The curves are very close to each other. As shown in Figure 1, the absorption peak at 3400 cm^{-1} , which indicated the peak of N—H in PUA/EA for hybrid materials can be assigned to the bond Si—OH and N—H. The peak at 1536 cm^{-1} can also be considered as weak N—H peak. Meanwhile, the C=O peak from KH-570 and PUA/EA appears at 1725 cm^{-1} . However, in the curve of the hybrid materials, the peak at 783 cm^{-1} represents the $\text{SiOCH}_2\text{CH}_3$, which can only come from TEOS and KH-570, and this indicates incomplete hydrolyzation of TEOS and KH-570. Clearly, there is a strong peak at 1120 cm^{-1} , which shows the existence of the stretching vibration of siloxane bond (Si—O—Si). The band at 454 cm^{-1} is the delegate of the bending vibration of Si—O—Si.^{14,15}

XRD is so far the most powerful technique to monitor the formation and structure of nanocomposites. From Figure 2, the diffused diffraction peaks emerged at $2\theta=20^\circ$ for both materials. For PUA/EA, it indicates the crystallinity of rigid segments.¹⁶ The hydrogen bond is formed in rigid segments rather than in soft ones because of the strong electronegative element of hydrogen bond. Hydrogen bond makes the structure of rigid segments arranged; whereas for the hybrid material, the peak is attributed to the short-range-order arrangement of chain segments of PUA/EA and the formation of network structure of SiO_2 , which is penetrated by PUA/EA. With the addition of SiO_2 , it is difficult to distinguish the soft and the rigid segments, so the crystallinity of hybrid material is declined.

The microstructure of the hybrid materials was investigated by FESEM as shown in Figure 3. The silica particles are nearly uniformly dispersed in PUA/EA polymer for the ratio of TEOS to (PUA + EA) less than 0.4 and the statistical diameter of the silica for TEOS : (PUA + EA) = 0.4 : 1 is 100 nm as indicated by the ruler, which was smaller than Hong's¹⁷ research using the same method. High ratio of TEOS : (PUA + EA) may result in SiO_2

agglomeration in the hybrid material, as shown in Figure 3(d). This is attributed to the large content of TEOS and limited polymer resin, which was partly hydrolyzed to modify the silica particles.

The surface morphology of PUA/EA and the hybrid material synthesized with the TEOS : (PUA + EA) of 0.4 : 1 were probed by AFM. As shown in Figure 4, the surface of PUA/EA is smoother than the hybrid material. This is because the lower surface energy of TEOS creates surface roughness, and the SiO_2 particles lead to an increase in surface area. The properties including water and friction resistances are also enhanced. Some protuberances are seen in Figure 4(b). The microspheres are silica clad by polymer resin. Again, the diameter of silica is approximately 100 nm, which is consistency with the measurement of FESEM.

The TGA curves were shown in Figure 5 to describe the thermal stability of these hybrids obtained. The T_d (temperature at 5% weight loss) and IDT (initial decomposition temperature) were shown in Table II. From Table II, weight loss took place in the temperature region from 100°C to 150°C for all the hybrid materials. The ratio of TEOS : (PUA + EA) of 0.4 : 1 showed the best thermal

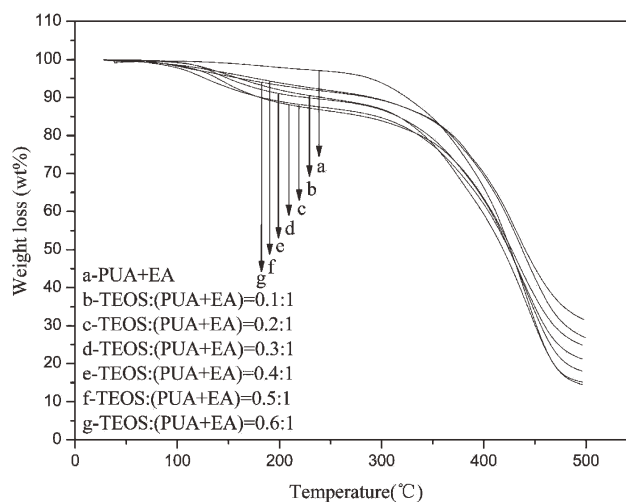


Figure 5. The TGA curves of PUA/EA and hybrid materials with different concentration.

Table II. The Data of T_d and IDT for Hybrid Materials with Different Concentration

	0 : 1	0.1 : 1	0.2 : 1	0.3 : 1	0.4 : 1	0.5 : 1	0.6 : 1
T_d (°C)	179	153	149.4	128.5	155.3	145	143
IDT (°C)	155	108	108	78.5	110	89	85.7

stability. The T_d and IDT were 155.3°C and 110°C. This may be the result of the evaporation of the remaining reactive diluent, water, alcohol and unreacted TEOS, and the dehydration of siloxane bond at the same time.¹⁸ The turning point for PUA/EA is at 300°C. Significant weight loss begins when temperature becomes higher than 300°C compared with the previous stage for all the hybrid materials. Particularly the hybrid material made from the ratio of TEOS : (PUA + EA) of 0.4 : 1 started to lose weight at 350°C. Furthermore, the weight loss for PUA/EA was more obvious than all hybrid materials. This phenomenon is probably attributed to the bond energies for Si—O and C—O that are 367.8 kJ/mol and 357.4 kJ/mol, respectively. It might also be because KH-570 and SiO₂ are successfully bonded by polymer resin and the particles restrict the movement of the polymer chain.¹⁹ The force of hydrogen bond can also enhance the thermal stability, which is formed by the hydroxyl group from KH-570 and matrix.

CONCLUSIONS

The UV-curing PUA/EA/SiO₂ hybrid material was successfully synthesized by sol-gel process. Nearly uniformly dispersed nano particles in resin were obtained with the ratio of TEOS : (PUA+EA) of 0.4 : 1, while higher ratios of TEOS:(PUA+EA) may lead to SiO₂ agglomeration in the hybrid material and coarse surface. Furthermore, the diameter of the nanoparticles, which was 100 nm, was smaller than those obtained from other ratios. Polymer resins were combined with SiO₂ by chemical bond produced by KH-570. From the study on different ratios of TEOS : (PUA + EA) used in the synthesis, the hybrid materials produced from TEOS : (PUA + EA) of 0.4 : 1 shows the best thermal stability. The T_d and IDT were 155.3°C and 110°C, respectively. The thermogravimetric temperature of this hybrid material was 50°C higher than that of the polymer material.

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