

Preparation of Poly(methyl Methacrylate-*co*-Maleic Anhydride)/SiO₂-TiO₂ Hybrid Materials and Their Thermo- and Photodegradation Behaviors

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ABSTRACT: The optically transparent poly(methyl methacrylate-*co*-maleic anhydride) P(MMA-*co*-MA)/SiO₂-TiO₂ hybrid materials were prepared using 3-aminopropyl triethoxysilane as a coupling agent for organic and inorganic components. Real-time FTIR was used to monitor the curing process of hybrid sol, indicating that imide group formation decreased with increasing titania content. scanning electron microscopy, atomic force microscopy, and differential scanning calorimetry results confirmed their homogeneous inorganic/organic network structures. TGA analysis showed that incorporated titania greatly prohibits the thermodegra-

ation of hybrid films, especially at the content of 5.3 wt %, showing an increase of about 32.6°C at 5% loss temperature in air. The UV degradation behavior of P(MMA-*co*-MA) studied by quasi-real-time FTIR showed that TiO₂ incorporated in the hybrid network provides a photocatalytic effect rather than a UV-shielding effect. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1714–1724, 2005

Key words: inorganic/organic hybrid; titania; FT-IR; thermogravimetric analysis (TGA); degradation

INTRODUCTION

Research on organic–inorganic hybrid materials continues to attract interest in material science. The incorporation of flexible organic polymer segments in an inorganic network can greatly alleviate the problems of shrinkage and cracking, while maintaining the advantages of inorganic components, such as good chemical resistance, high thermal stability, and excellent scratch resistance. The sol-gel chemical technique, which is usually performed at low temperature, offers the advantage of producing homogenous films with high purity. A lot of organic–inorganic hybrid materials were prepared using the sol-gel technique and used for contact lenses, UV-protective coatings on polycarbonate,¹ nonlinear optical materials,^{2,3} optical waveguides^{4,5} and chemical sensors,⁶ perm-selective barriers,⁷ etc.

Poly(methyl methacrylate)(PMMA) is the most popular resin owing to its excellent properties, such as high transparency, light weight, great resistance to

chemicals, and easy processing. Much work on the synthesis of PMMA/SiO₂ and PMMA/TiO₂ or PMMA/SiO₂-TiO₂ has been reported. Zhang et al.⁸ synthesized a PMMA/TiO₂ hybrid material using a chelating ligand as a coupling agent. However, a large amount of solvent and chelating agent remained in the resulting materials. Lee and Chen⁹ prepared PMMA/TiO₂ hybrid optical thin film with high loading of titania using catalyst-free polymerization and studied its optical properties. Lu et al.⁷ prepared poly(2-hydroxyethyl acrylate-*co*-methyl acrylate)/SiO₂-TiO₂ hybrid membranes using free radical polymerization and studied their water vapor permeability.

The microstructure, morphology, mechanical properties, optical properties, and thermal properties of PMMA/SiO₂ hybrid materials have been investigated extensively. The interfacial structure and resulted inorganic network in the hybrid materials have great influence on the thermal and mechanical properties of the incorporated polymers.^{10,11} However, little work has been performed with the degradation of PMMA at the existence of TiO₂, especially the photodegradation of the organic component. In this work, a detailed study of the gelling process in hybrid sol using real-time FTIR and the thermal degradation and photodegradation of the organic component in P(MMA-*co*-

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TABLE I
Feed Ratios for Preparing Hybrid Films TH1–TH4^a

Sample	PMMK (g)	Ti(OBu) ₄ (g)	PMMK ^b content (wt%)	Film (calculated)		
				Organic	Inorganic	
					SiO ₂	TiO ₂
P(MMA- <i>co</i> -MA)	5.0	0	21.4	94.5	5.5	0
TH1	5.0	1.04	15.4	89.5	5.2	5.3
TH2	5.0	1.80	8.93	86.1	5.1	8.8
TH3	5.0	2.33	6.91	84.0	4.9	11.1
TH4	5.0	2.97	5.41	81.5	4.7	13.8

^a All samples have the following fixed compositions: (1) [MA]/([MMA]+[MA]) = 10 mol %; (2) [AIBN]/([MMA]+[MA]) = 1.25% (mol/mol); (3) [H₂O]/[Ti(OBu)₄] = 1; (4) The amount of dioxane was adjusted so that the concentration of Ti(OBu)₄ was 0.032 wt %; (5) No acid catalyst in the system.

^b PMMK content in the dioxane solution.

MA)/SiO₂-TiO₂ hybrid materials using TGA and quasi-real-time FTIR measurement are presented.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), maleic anhydride (MA), titanium tetra *n*-butoxide (Ti(OBu)₄, >95%), dioxane, and 2,2'-azobis-isobutyronitrile (AIBN) were all purchased from Shanghai First Reagent Co., China. MA is analytically pure and was used as received. MMA was distilled under vacuum in the presence of methoxyphenol (0.1% by weight). Dioxane was refluxed with KOH pellets for 20 h before distillation. AIBN was recrystallized from methanol twice and chloromethane once before use. The coupling agent, 3-aminopropyltriethoxysilane (KH550), was supplied by Nanjing Yudeheng Co., China, and was distilled under vacuum.

Preparation of P(MMA-*co*-MA)/SiO₂-TiO₂ hybrid materials

Synthesis of P(MMA-*co*-MA)

P(MMA-*co*-MA) was synthesized by radical copolymerization of MMA and MA in a solution of dioxane. A total of 9.02 g (90 mmol) MMA, 0.98 g (10 mmol) MA, and 1.25 mmol AIBN was mixed with 70 mL of dioxane in a 250-mL three-neck round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a N₂ inlet. After being degassed with nitrogen for 10 min, the reagents were heated to 75°C and continuously stirred under nitrogen atmosphere for 4.5 h. The resulting solution was transparent and viscous.

Synthesis of KH550-modified P(MMA-*co*-MA) (PMMK)

After the solution was cooled to room temperature, KH550 (10 mmol) was added with a dropping funnel

during 10 min. Then the temperature was raised to 60°C and the reagents were stirred for 2 h before proceeding for 0.5 h at room temperature.

Synthesis of TH1–TH4

Different amounts of Ti(OBu)₄ according to Table I were added to the above solution. Dioxane was used to adjust the content of Ti(OBu)₄ to 0.032 wt %. The solution was stirred vigorously for 0.5 h before the addition of the desired amount of water and then heated to 60°C for 2 h. The obtained products were named TH1, TH2, TH3, and TH4 (see Table I), respectively.

Preparation of hybrid films

The mixture of PMMK and TH1 to TH4 was spin-coated at 3000 rpm for 20 s on different substrates. The coated films were then cured at 60°C for 30 min and 120°C for another 2 h.

Measurements

The real-time FTIR spectra were recorded using a Nicolet Magna-IR 750 spectrometer (Nicolet Instrument Co.) equipped with a heating device with a temperature controller as reported in the literature.¹² The sample was coated on KBr pellets and placed in a ventilated oven. The FTIR software was used to collect the spectra of samples and to compare the peak intensity before and after curing. Differential scanning calorimetry (DSC) was conducted in a Mettler-Toledo DSC 822^e (Mettler Toledo Co.) with about 7 mg of sample at a scanning rate of 10°C/min under a nitrogen flow of 60 mL/min. Thermodegradation behaviors were measured using a Shimadzu TG-50 instrument (Shimadzu Co., Japan) with about 10 mg of sample at a heating rate of 10°C/min and a gas flow rate of 20 mL/min in air or nitrogen. The microstructures of the prepared hybrid films were examined by

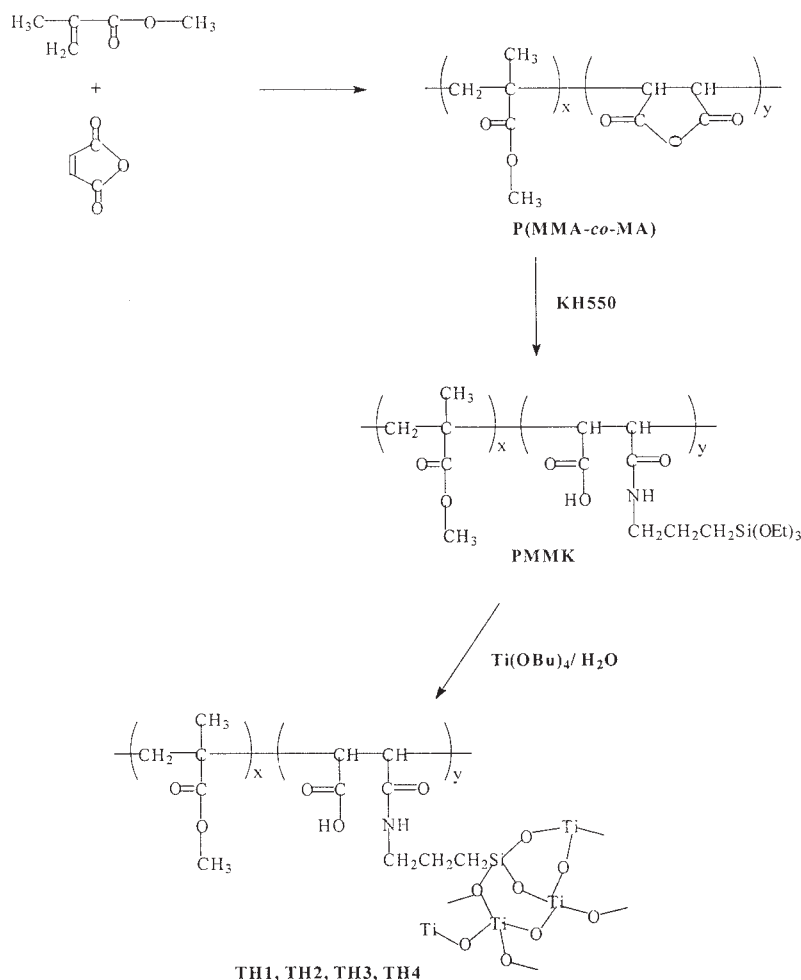


Figure 1 Schematic outline of the synthesis for P(MMA-co-MA)/SiO₂-TiO₂.

scanning electron microscopy (SEM, Philips-XL30, Philips, Holland). The topography images of the films were measured in air using an atomic force microscopy instrument (AFM, Nanoscope IIIa, D.I.) in a tapping mode with silicon TESP cantilevers. The root mean square of roughness (RMS) of the sample was obtained using the off-line software.

Ultraviolet irradiation was conducted under a UV lamp (80 W/cm, made by Lantian Co, Beijing, China) in air. The chemical changes in the samples were monitored by FTIR.

RESULTS AND DISCUSSION

Synthesis of hybrid sol

The schematic description for the synthesis of TH1 to TH4 is shown in Figure 1. First, P(MMA-co-MA) was prepared by copolymerization of MMA and MA in dioxane for 4 h until the peak at 1636 cm⁻¹ for C = C in the IR spectrum disappeared, as shown in Figure 2.

The synthesis of PMMK involved the open ring reaction of the anhydride group with the -NH₂ group

in KH550, which is an exothermic reaction. The reaction, therefore, proceeded at room temperature for 1 h before being heated to 60°C and then continued until the peaks at 1784 and 1853 cm⁻¹ for the anhydride group in the IR spectrum disappeared completely, while the peaks at 1575, 1632, and 3307 cm⁻¹ for the amide group as well as the peaks at 478, 792, and 1077 cm⁻¹ for Si-OCH₂CH₃ appeared, as shown in Figure 3. This demonstrates that KH550 has attached to the chains of P(MMA-co-MA).

In general, for a sol-gel reaction, HCl solution was added as an acid catalyst. Due to the high reactivity of Ti(OBu)₄ toward H₂O, the incorporation of titania in this work was performed through hydrolysis reaction under catalyst-free conditions to prevent the production of unexpected inhomogeneous materials. A ratio of 1 for H₂O/Ti(OBu)₄ and 0.032 wt % Ti(OBu)₄ were used. The resulting solutions were transparent and homogenous. Figure 3 shows the FTIR spectra of the series of materials before curing. Compared with PMMK, the band around 478 and that at 988 cm⁻¹, corresponding to Ti-O-Ti and Ti-O-Si, respectively,

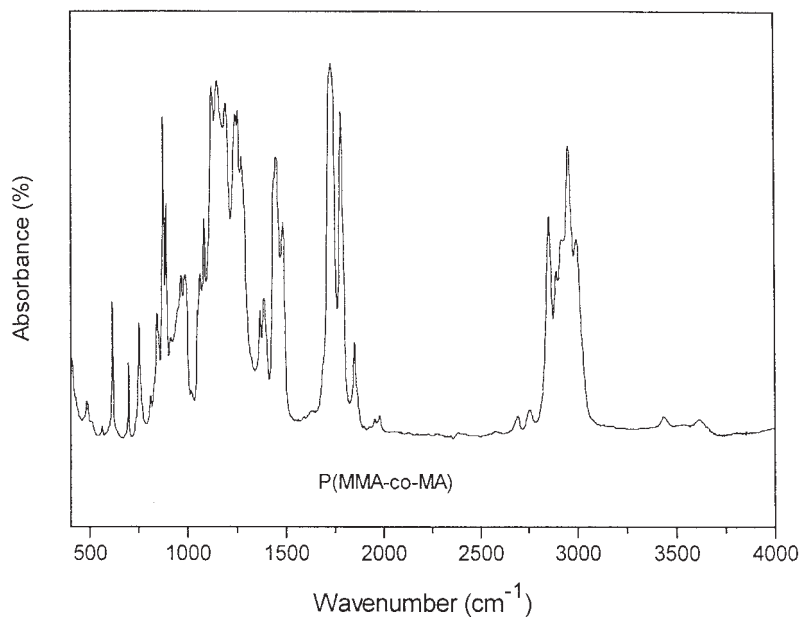


Figure 2 FTIR spectrum of P(MMA-co-MA).

appear and increase with increasing the Ti(OBu)₄ content in the hybrid films, while the peak at 1077 cm⁻¹ for Si-O-C decreases.

Gel process of the hybrid sol samples

TH1, TH2, and TH3 gelled in 3, 7, and 10 days, respectively, while TH4 gelled in more than 15 days and PMMK had not gelled in 1 month. The gelling time is

related to the PMMK content in the hybrid sol, as shown in Figure 4. Gelling time increases with decreasing PMMK content in hybrid sol while the titania content is kept constant. For comparison, the same amount of H₂O was added to PMMK, which gelled during 20 days. This observation indicates that the gels result from the crosslinking between -Si-OCH₂CH₃ and -Ti-OCH₃ more than with -Si-OCH₂CH₃. The resulting gels are transparent and in-

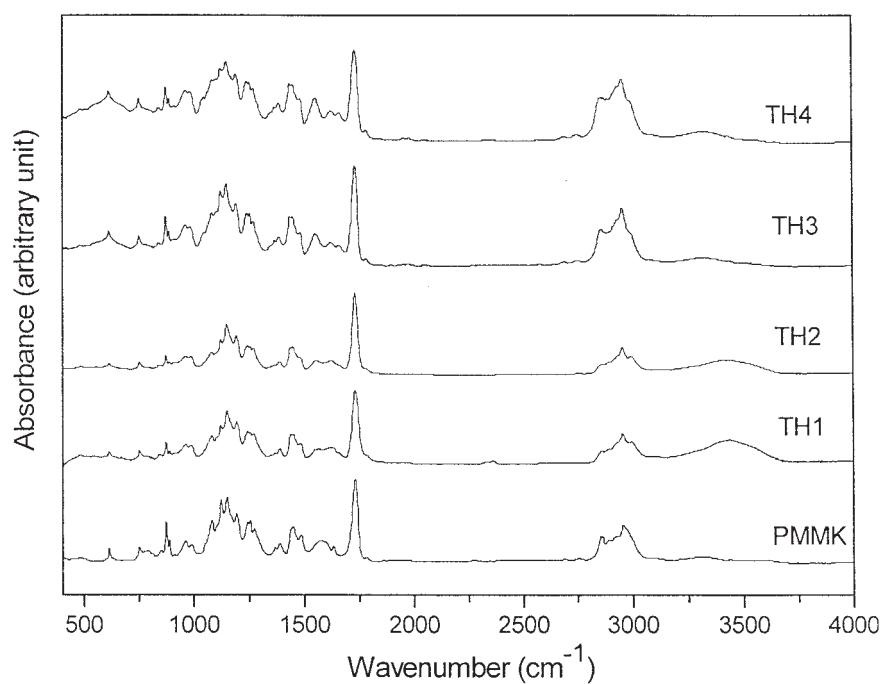


Figure 3 FTIR spectra of the hybrid sols.

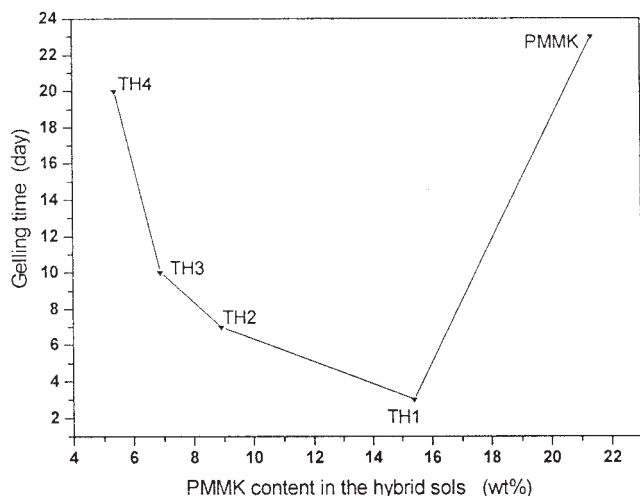


Figure 4 Relationship between gelling time and PMMK content in the hybrid sols.

soluble in dioxane, tetrahydrofuran, and toluene. This also confirms that the organic component has attached to the inorganic networks.

Curing of the hybrid gel

After being spin-coated on substrates, the hybrid gel was cured at different temperature stages. The enhancement of the peak at 1786 cm^{-1} , together with the decrease in the band around 3345 cm^{-1} , 1633 , and 1577 cm^{-1} , corresponds to the dehydration of the amide

group, which is a ring-closure reaction leading to the imide group. The relative strength change of the peak at 1786 cm^{-1} compared to that at 1731 cm^{-1} is taken as a measurement of the degree of ring closure. Figures 5 and 6 present the representative real-time FTIR spectra of PMMK and TH3 sol, respectively. The ring-closure becomes less with more incorporated titanium, which indicates that inorganic titania dispersed between the polymeric chains of PMMK at a molecular scale.

The peaks at 1077 and 959 cm^{-1} for Si-O-C in these spectra decrease, while the peak at 988 cm^{-1} in the FTIR spectrum of PMMK and the peak at 910 cm^{-1} in the FTIR spectra of TH3 increase, corresponding to the vibration of Si-O-Si and Ti-O-Si, respectively. All cured films are transparent in visible light region as measured by UV-vis spectroscopy, without absorbance above 400 nm .

Morphology of hybrid films

Since transmission electron microscopy (TEM) often fails to provide useful morphological data because of weak contrast, more researchers fall back on other imaging techniques, such as SEM and AFM.¹⁵ But unfortunately, the SEM images in this work reveal no distinguishing feature in these hybrid films, as shown in Figure 7. In all hybrid films, there are no obvious inorganic aggregates, indicating that inorganic particles present in nanoscale in these hybrid films, which was confirmed through the observation of hybrid film

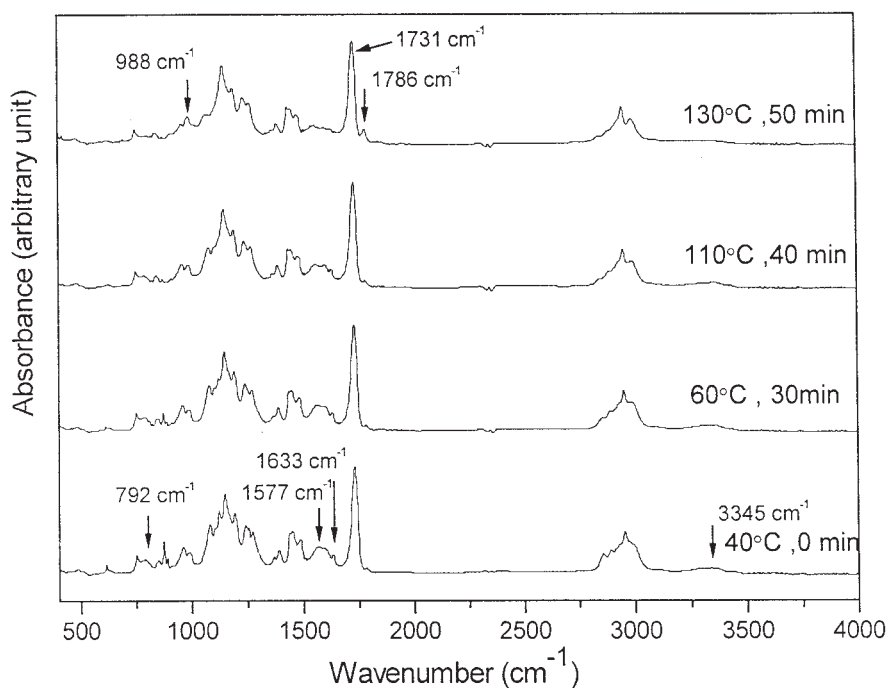


Figure 5 FTIR spectra of PMMK sol at different curing times.

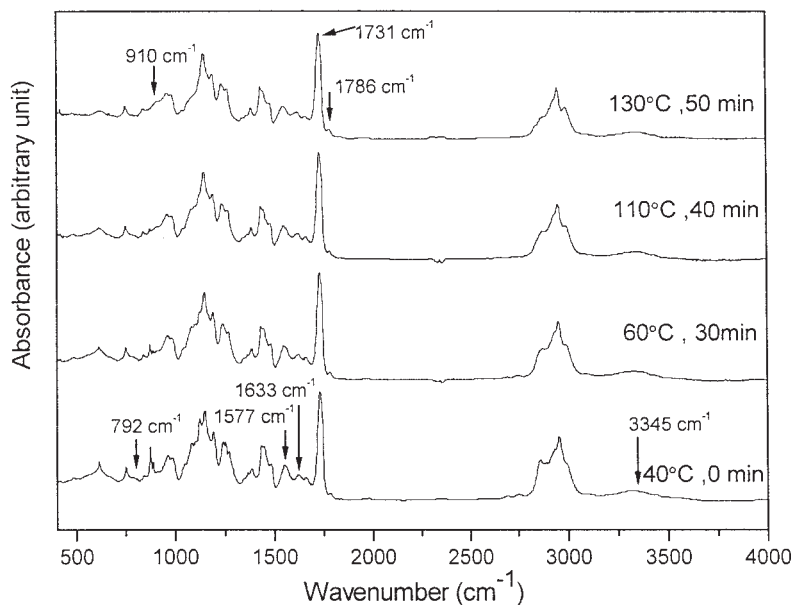


Figure 6 FTIR spectra of TH3 sol at different curing times.

by AFM. Because the tapping force on the inorganic component is higher than that on the polymeric component, the contrast should be observed in two component areas. As shown in Figure 8, the phase images of the hybrid films (face image) show two obvious regions: a dark region (inorganic component) and a bright region (polymeric component); both disperse evenly into each other. No macro-phase separation can be observed in the hybrid films. The average roughness (R_a) and mean square roughness (R_q) of the PMMK film are 0.236 and 0.301 nm, while that of TH4 is 0.356 and 0.470 nm, respectively, indicating that all hybrid films exhibit a high degree of smoothness.

Thermal properties of cured films

In inorganic/organic hybrid systems, the inorganic particles, which result from hydrolysis of metal alkoxide, disperse within the polymeric chains, reducing the free volume of organic components and making T_g increase, while at the same time, the interaction between these polymeric chains decreases due to hindrance from the inorganic components, which resulted in decreased T_g . In the prepared hybrid films, T_g increases with increasing the content of titania as shown in Figure 9. The lowered T_g (78°C) of PMMK compared with pure PMMA (about 113°C) is due to

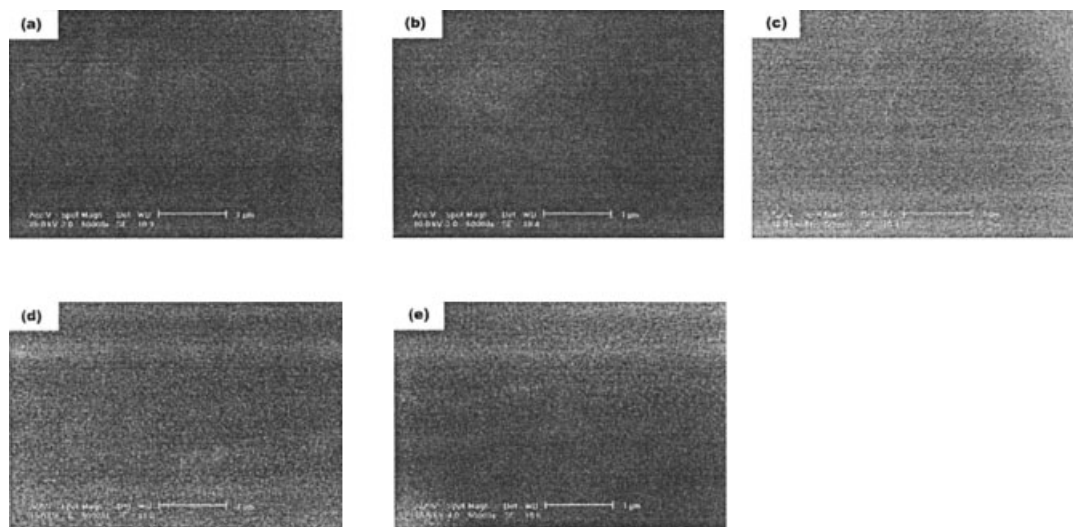


Figure 7 SEM images of hybrid films of (a) PMMK; (b) TH1; (c) TH2; (d) TH3; (e) TH4.

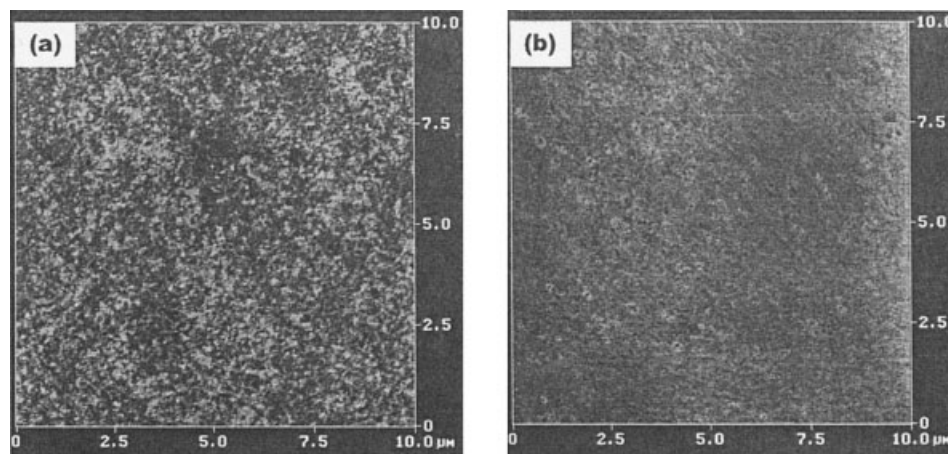


Figure 8 AFM topography images of the hybrid films: (a) PMMK; (b) TH4.

the presence of maleic anhydride in the copolymer and its lower molecular weight. However, T_g increases from 78°C for PMMK to 110°C for TH3 with titania content of 11.1%. This implies that the effect from the constraint of inorganic network exceeds the effect from the weakening of hydrogen-bond interaction between polymeric chains. Moreover, there is no increase with T_g when the titania content increases from 11.1% in TH3 to 13.8% in TH4, which indicates that there is a counterbalance between the effect of free volume and that of the H-bond interaction.

TGA was used to investigate the nonoxidative (in N_2) and oxidative (in air) thermal degradation of the obtained hybrid films to assess the influence of inorganic titania incorporated into the polymeric phase as well as to determine the inorganic content from the

other way. The degradation curves under nitrogen and air atmospheres are shown in Figures 10 and 11, respectively, and the results are summarized in Table II.

All hybrid films have similar nonoxidative degradation behavior in the range of 150–310°C, which is attributed to the condensation of the remaining $Ti(Si)-OH$ or $Ti(Si)-OR$ (methyl or butyl), the dehydration of $-COOH$ with the $-CONH-$ group, and the scission of side chains on the copolymer. It is noteworthy that TH1 containing 5.3 wt % titania (theoretically) shows the most obvious effect of thermostabilization in the nonoxidative degradation. The same trend is also observed in oxidative degradation, in which the 5% loss temperature rises from 190.9°C for PMMK to 223.5°C for TH1 and then decreases to 204.8°C for

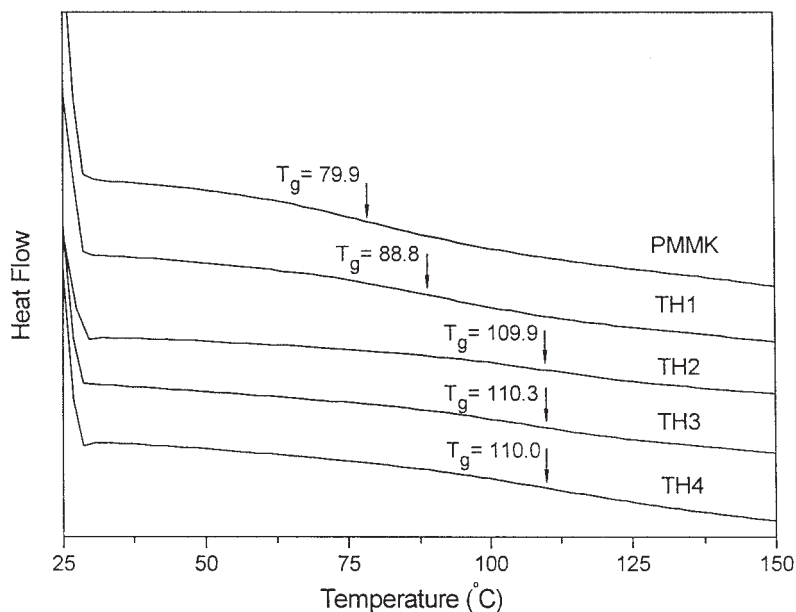


Figure 9 DSC curves of the hybrid films with different titania contents.

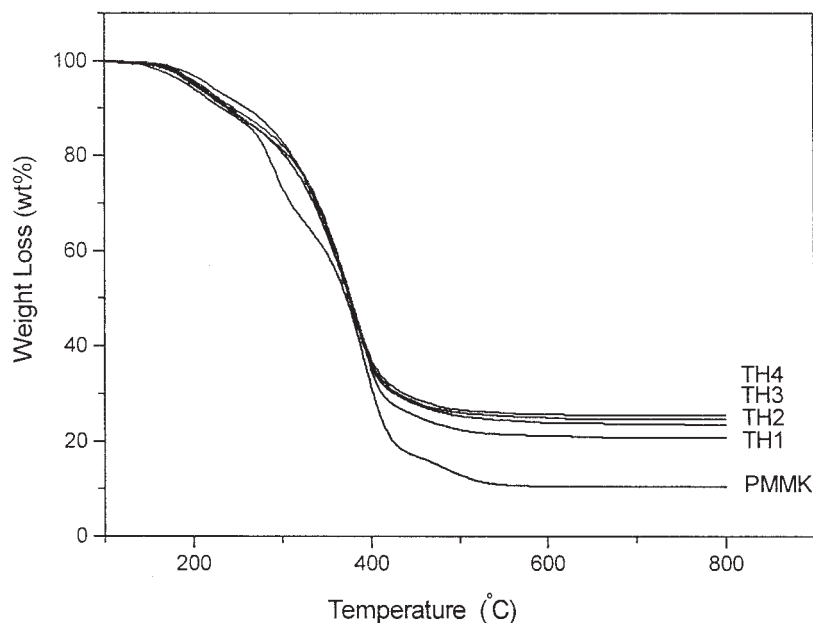


Figure 10 TGA curves of the hybrid films at a heating rate of 10°C/min in N₂.

TH4. The phenomenon may be ascribed to the lower degree of dehydration of the polymeric chain with more titania incorporated, which is in accord with the results from FTIR measurements as mentioned above. It is concluded that the stiffening of polymeric chains resulting from the formation of imide groups is more crucial than the constraint from the inorganic network during the decomposing stage of hybrid films.

From Figure 10, it can be also seen that the hybrid films show a slower degradation rate than PMMK film at above 310°C. The breaking up of polymer main

chains is dominant at elevated temperatures, while the incorporated titania network limits the motion of polymeric chains, which requires more energy to bring the polymeric chains to break up. There is one sharp degradation stage from 310 to 420°C in N₂ atmosphere, whereas in air, there are two, one of which is from 310 to 420°C, which is a similar degradation behavior to that in N₂. The other temperature range of 470–620°C shows a big difference between PMMK and the TH series. PMMK shows a small sharp degradation from 540 to 620°C, while the TH series from

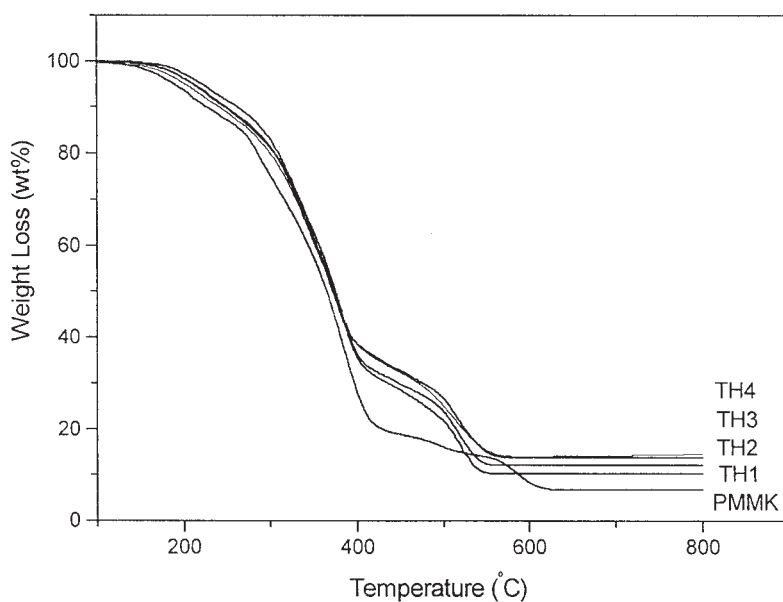


Figure 11 TGA curves of the hybrid films at a heating rate of 10°C/min in air.

TABLE II
Thermal Properties of the Hybrid Films

Sample	T_g (°C)	T_5 (°C) ^a		T_{max} (°C) ^b		Residue at 800°C (%)		
		N ₂	Air	N ₂	Air	N ₂	Air	Theoretically ^c
PMMK	77.9	191.0	190.9	392.5	383.1	10.5	6.8	5.5
TH1	88.8	215.7	223.5	387.0	382.4	20.6	10.4	10.5
TH2	109.9	196.2	213.1	378.5	378.5	23.4	12.1	13.9
TH3	110.3	205.3	213.1	381.7	378.2	24.6	13.7	16.0
TH4	110.0	200.1	204.8	383.3	370.2	25.5	14.2	18.5

^a Temperature of 5% weight loss.

^b Temperature of the maximum weight loss rate.

^c Theoretical calculation on the presumption that all added metal alkoxides were transformed into their oxides.

shows a degradation from 470 to 560°C. There also is a remarkable difference in the remained weight percentages after nonoxidative and oxidative degradation. The remained weight percentages after nonoxidative degradation are larger than the theoretical values (see Table II), while that after oxidative degradation is almost the same as the theoretical values. This observation can be explained by the insulation effect of the inorganic network, which traps the organic fragments and prevent them from further degradation, while in the presence of oxygen, the majority of the organic components were burned into gases. The relative derivation of the remainder at 800°C between the nonoxidative condition and the theoretical value decreases with decreasing organic component content in the hybrid films, which seems to indicate that TH1 has the densest network. But in air, why the second decomposition stage decreased to a lower temperature range after titania is incorporated remains a question for further study.

Photodegradation

TiO₂/poly(dimethylsiloxane) hybrid films were prepared by Iketani et al. and used for coatings on polymeric substrates.¹³ The films showed good photocatalytic activity for decomposing the methylene blue coated on their surface, but suppressed the photodegradation of PMMA substrate. This study aimed to examine the photodegradation of PMMA incorporated in TiO₂ network for determining whether such hybrid materials are suitable for photostabilizing protective coatings.

The chemical changes in the structures of hybrid materials during photooxidation can be measured using FTIR spectroscopy.¹⁴ All prepared hybrid films were found to exhibit similar characteristic spectral changes but to differing extents. All spectra were recorded by a quasi real-time FTIR approach with the films formed on KBr pellets, which fixed on the bracket of the FTIR instrument and were exposed to

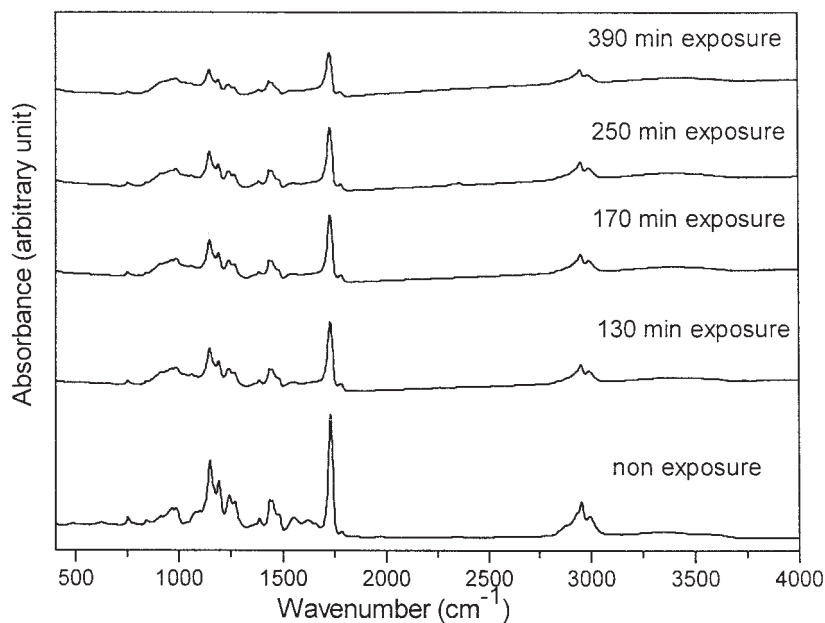


Figure 12 FTIR spectra of TH3 after different exposure times under a lamp (40 mw/cm²) in air.

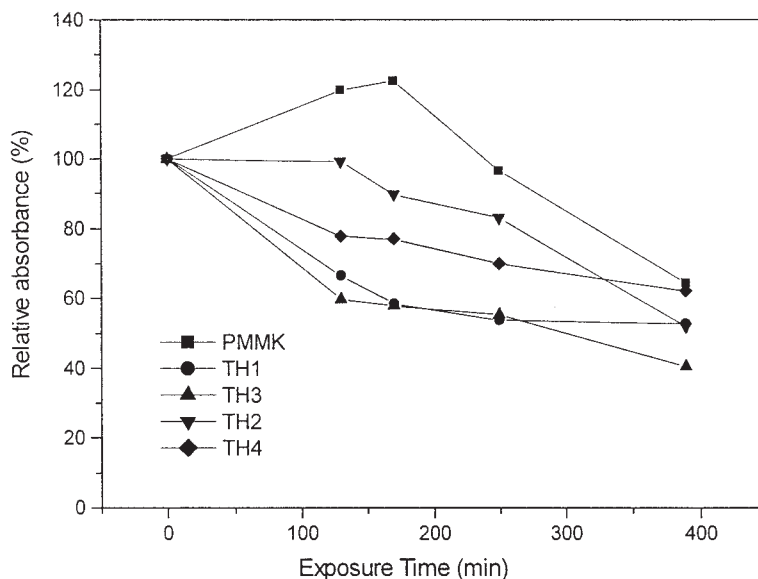


Figure 13 Changes in FTIR spectra of the hybrid films under different irradiation times between 1766 and 1676 cm⁻¹.

UV irradiation with the bracket. The differences between the obtained spectra were absolute deviation from their original spectra and no calibration was needed for a sample. The FTIR spectra of TH3 at different UV irradiation time are compared in Figure 12. The strength of most peaks decreases with increasing exposure time, indicating that photodegradation occurred during irradiation. To investigate the effect of titania on the photodegradation of polymeric chains, two absorbance changes of the bands in the range of 1766 to 1676cm⁻¹ and the range between 3141 and 2761cm⁻¹ were taken to assess the degree of photodegradation, corresponding to C = O and C-H

groups, respectively. The absorbance was normalized to the unirradiated one. The changes in the relative absorbance are demonstrated in Figures 13 and 14, respectively. The absorbance of the PMMK sample without titania shows an increase in the range of 1766 to 1676 cm⁻¹ after 170 min of irradiation, corresponding to C = O resulting from the photooxidation of C-H, accompanying with the decrease for C-H from 3141 to 2761 cm⁻¹. All hybrid samples containing titania show a decrease in the absorbance of C = O, indicating a greater degradation of C = O, which may contribute to the photocatalytic oxidation effect of titania. The UV shielding effect due to the absorbance of

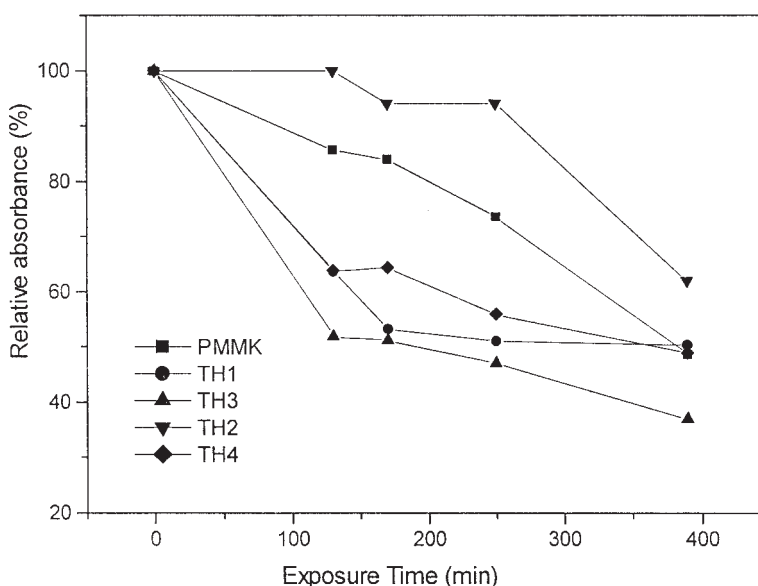


Figure 14 Changes in FTIR spectra of the hybrid films under different irradiation times between 3141 and 2761 cm⁻¹.

titania at the UV region plays a little role in the protection from photodegradation of these samples.

CONCLUSIONS

The P(MMA-*co*-MA)/SiO₂-TiO₂ was prepared from P(MMA-*co*-MA), modified by KH550 and Ti(OBu)₄. The gel process monitoring with real-time FTIR showed that the imide group formation decreased with increased titania in the system. All hybrid films exhibit high transparency and have homogeneous structures at nanoscale. The TH1 sample incorporating 5.3 wt % titania showed the highest 5% loss weight temperature and all samples containing titania showed a lower thermodegradation rate compared with the original sample in nitrogen, but a lower temperature in the second decomposition.

The photooxidation degradation of the prepared films monitored by quasi-real time FTIR showed that the sample containing titania accelerated the photodecomposition of polymeric chains.

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