Synthesis, Characterization, and Thermal Stability of PMMA/SiO$_2$/TiO$_2$ Tertiary Nanocomposites via Non-Hydrolytic Sol–Gel Method

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ABSTRACT: In this study, we use PMMA, tetraethoxysilane and titanium ethoxide to prepare tertiary nanocomposites via non-hydrolytic sol–gel method. Boron trifluoride monoethylamine was used as catalyst. Silica and titanium dioxide are incorporated into nanocomposites to improve the thermal stability. Thermogravimetric analysis was used for rapid evaluation of the thermal stability of different materials. The integral procedural decomposition temperature has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of PMMA copolymer. Two methods have been used to study the degradation of hybrid during thermal analysis. These investigated methods are Kissenger', Ozawa's methods to classify the thermal stability of nanocomposites. The activation energies of hybrids were higher than that of the copolymer. From the results, silica and titania will enhance the thermal stability of PMMA. We use the solubility test to check the network structure of nanocomposites. The results show the residues of composites after extraction increase with the increasing of inorganic contents. We can conclude that the composites possess network structure. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1959–1965, 2009

Key words: nanocomposite; thermal property; thermogravimetric analysis(TGA); sol–gel methods; thermoplastics

INTRODUCTION

Recently, organic–inorganic hybrid materials have been extensively studied[1–3] as they could exhibit better mechanical, thermal, optical, and electronic properties, compared with the corresponding pure organic or inorganic materials. The properties of hybrid materials could be tuned through the functionality or segment size of each component.

Poly(methyl methacrylate) (PMMA) is an important thermoplastic material with excellent transparency. However, its poor thermal stability restrains it from applications in higher temperature region. One possible solution to address the above problem is to hybridize with inorganic oxides such as silica or titania. The sol–gel technique is often used to produce hybrid materials. Generally, homogenously dispersed inorganic–organic hybrid materials are synthesized by a hydrolytic sol–gel process involving the hydrolysis and condensation reactions of alkoxides precursors in a solvent system. There lie some problems for the preparation of PMMA/titania nanocomposites. It is difficult to control the hydrolytic reaction of TiO$_2$ precursors due to their high reactivity, which often results in the accumulation of inorganic particles.[4–6] It is necessary to use some chelating agents such as allyl acetylacetone to stabilize the fast condensation of titanium alkoxides and the addition of overmuch chelating agent may do harm to the resulting hybrids because the chelating agents are found difficult to be completely removed from the titanium center.[7,8] Figure 1(a) shows the catalytic mechanism using BF$_3$MEA as catalyst and Figure1(b) shows traditional sol–gel reaction.

In this article, we present a new non-hydrolytic sol–gel method to prepare the PMMA/silica/titania nanocomposites in which the reactivity of titania precursors can be well controlled without using any chelating agents. Optical property will be investigated by UV–visible (UV/vis) spectra and photographs. Thermal properties will be discussed by TGA, integral procedural decomposition temperature (IPDT), respectively. Another objective of this work is to study the kinetics of thermal degradation of PMMA containing silica and titania hybrid and of copolymer by means of thermogravimetric analysis (TGA). Two
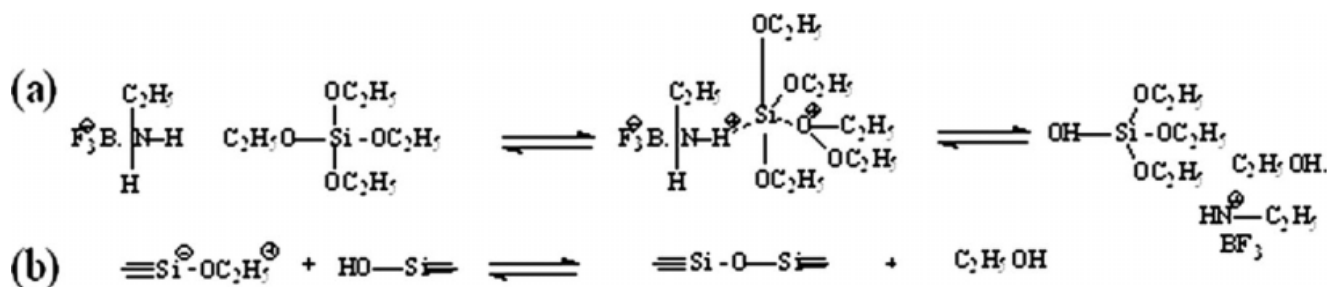
Figure 1 (a) Catalytic mechanism between BF3MEA and TEOS (b) traditional sol–gel reaction.

analytical methods, Ozawa,[9] Kissinger's[10] methods were used to obtain the kinetic parameters of thermal degradation for comparison.

EXPERIMENTAL

Materials

The monomer used was methyl methacrylate (MMA) which was purchased from the Showa, Japan. 3-(Trimethoxysilyl)propyl methacrylate(MSMA) was obtained from the Acros Organics, Janssens Pharmaceuticalaan, Geel, Belgium. Azobisisobutyronitrile (AIBN) as the initiator for free radical reaction was obtained from the Showa Chemical, Japan. Tetraethoxysilane (TEOS) was supplied by Showa Chemical, Japan. Titanium ethoxide (TiEO) was from the Acros Organics, Janssens Pharmaceuticalaan, Geel, Belgium. Tetrahydrofuran (THF) was reagent grade and supplied by the Echo Chemical, Taiwan. Boron trifluoride monoethylamine (BF$_3$MEA) as catalyst for the sol–gel reaction was obtained from the TCI Chemical Industry, Tokyo, Japan.

Preparation of MMA–MSMA copolymer

The monomers, MMA and MSMA, and the initiator, AIBN (0.02 wt % in the monomers), were added directly together to a sample bottle and mixed mechanically at 70°C under nitrogen atmosphere for 6 h. The molar ratio of MSMA to (MMA+MSMA) was 0.02. The transparent fluid was obtained. BF$_3$MEA

(0.1 wt % in the monomers) was poured into copolymer and stirred at 70°C for 6 h. The final solution was white and cloudy liquid.

Preparation of silica/titania precursor

TEOS and TiEO were mixed and stirred at room temperature for 3 h. The molar ratio of TEOS to TiEO was 1.

Preparation of PMMA/silica/titania nanocomposites

Figure 2 shows the flowchart of the experiment. The recipe for the preparation of PMMA/silica/titania tertiary nanocomposites was listed in Table I. The molar ratio of TEOS to TiEO was 1. Adequate amounts of silica/titania precursor were fed into a THF solution of MMA–MSMA copolymer and the final solution was stirred mechanically at room temperature for 20 min to obtain a transparent and light orange liquid. For example, when we prepare 10 g PMMA/TEOS/TiEO 5 nanocomposites whose inorganic content is 5 wt %, we should add 9.042 g MMA, 0.458 g MSMA, 0.239 g TEOS, and 0.261 g TiEO into the sample bottle. The products were cast into aluminum dishes to gel at room temperature. The wet gels were aged at room temperature for 24 h, and were then dried at 100°C for 5 h in a vacuum oven.
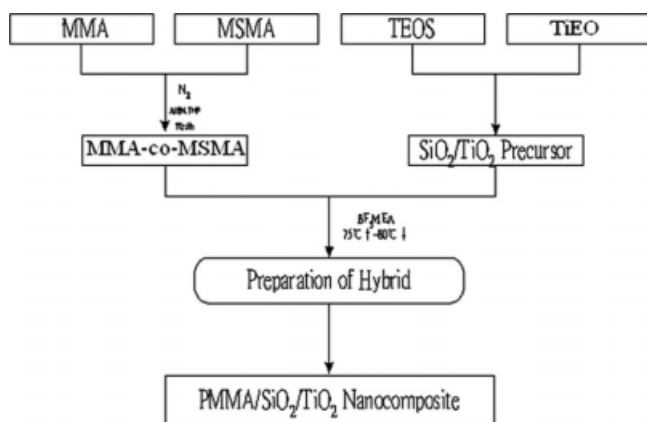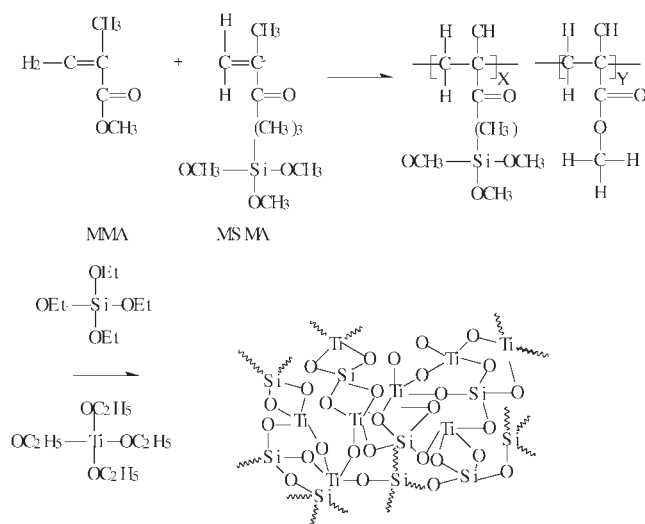
Reaction schemes

Figure 2 Flowchart of the experiment.

TABLE I
Compositions of PMMA Hybrid Systems with Different Inorganic Contents

Sample no.	MMA	MSMA (%)	TEOS (%)	TiEO (%)
PMMA 0	95.42	4.58	0	0
PMMA/TEOS/TiEO 5	90.42	4.58	2.39	2.61
PMMA/TEOS/TiEO 10	85.65	4.35	4.80	5.20
PMMA/TEOS/TiEO 20	76.13	3.87	9.56	10.44

Solid state ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR)

^{29}Si nuclear magnetic resonance spectroscopy(^{29}Si NMR) was performed using a Bruker DSX-400WB (Bruker BioSpin, Germany). The samples were treated at 180°C for 2 h and then grounded into fine powder and their particle size is almost less than 1 mm in diameter. They should better be uniform.

TGA

Thermal degradation of hybrid was investigated by a thermogravimetric analyzer (Perkin Elmer TGA 7) at room temperature to 800°C with various heating rates (i.e. 5, 10, 20, 40°C/min) under nitrogen atmosphere. The measurements were conducted using 6–10 mg samples. Weight-loss/temperature curves were recorded.

UV/vis spectra

UV/vis spectra were tested on a Hitachi (Japan) U-3300 spectrophotometer and the sample was prepared as a thin film on a glass substrate by spin coating method using the spin coater (TA-01, Yeong-Shin, Taiwan) at 2000 rpm for 30 s. The thickness of
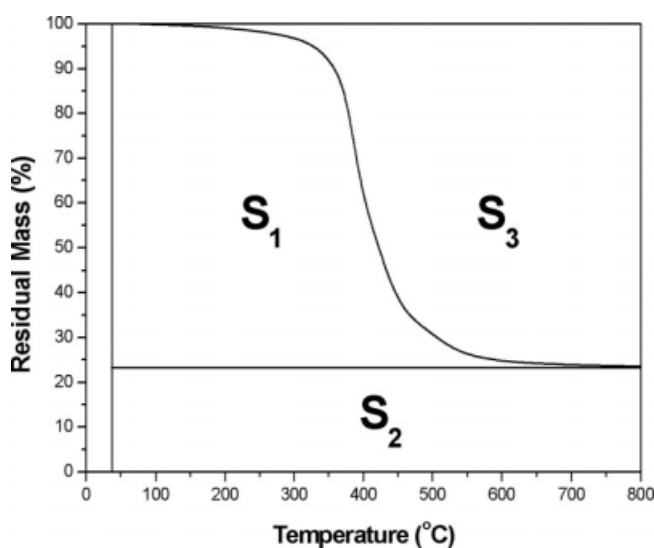

Figure 3 Schematic representation of S_1, S_2, and S_3 for A^* and K^*.

film is about 100 μm. The thickness of film was measured by the Microfigure Measuring Instrument (Surfcorder, ET4000, Kosaka Laboratory, Japan).

IPDT[11]

IPDT was calculated from

$$IPDT\,(°C) = A^*K^*(T_f - T_i) + T_i \qquad (1)$$

$$A^* = (S_1 + S_2)/(S_1 + S_2 + S_3) \qquad (2)$$

$$K^* = (S_1 + S_2)/S_1 \qquad (3)$$

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i the initial experimental temperature, T_f the final experimental temperature. Figure 3 shows a representation of S_1, S_2 and S_3 for calculating A^* and K^*. S_1, S_2, and S_3 are the surface area under the curve shown in Figure 3.

RESULTS AND DISCUSSIONS

FTIR

FTIR is a powerful tool to monitor the reaction course. Figure 4 shows the FTIR of reaction process. Curve (a) presents that TEOS and TiOS were just added into MMA and MSMA monomers, but the initiator for the free radical reaction and the catalyst for the sol–gel reaction were not put into the reactants. It could be found that the characteristic peaks at 1640 cm^{-1} for C=C group and at 1108–1085 cm^{-1} for —OMe function group which was sharp shape still exist. Curve (b) shows that AIBN and BF$_3$MEA were poured into the sample bottle. The wide absorbance at 3600–3200 cm^{-1} for OH group appears and the peak at 1640 cm^{-1} for C=C group decreased. It was
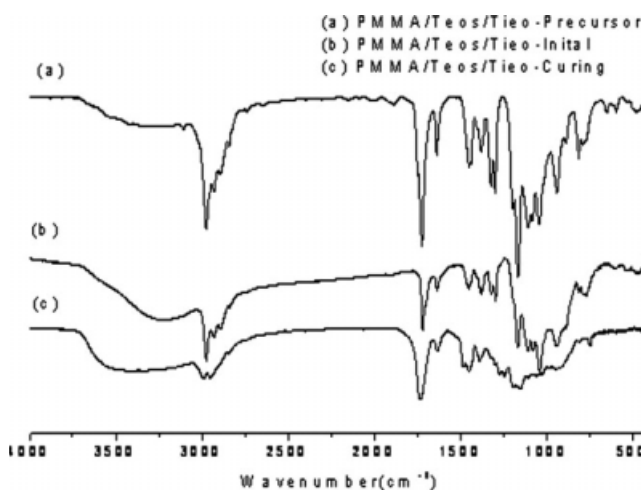

Figure 4 FTIR of reaction process (a) precursors (b) before the curing reaction (c) after the curing reaction.
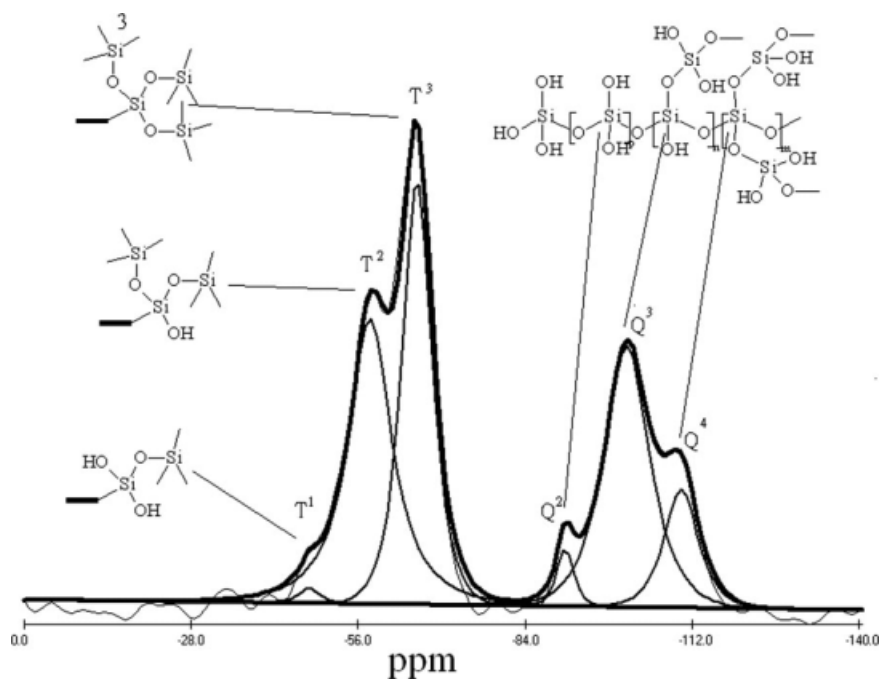
Figure 5 Typical curves of solid-state 29Si-NMR spectra of nanocomposite.

suggested that the free radical reaction and the sol–gel reaction take place. Curve(c) shows that the free radical reaction and the sol–gel reaction are complete. The decreasing intensity of 1085 cm^{-1} clearly indicates the further condensation of OCH$_3$ groups with OH groups of precursors. The spectral region at 1100–1000 cm^{-1} was broadened which also indicates the enhanced silica condensation. It means that the condensation reaction has occurred.

NMR

Figure 5 displays the curve of solid-state ^{29}Si-NMR spectra of the epoxy nanocomposite. In condensed siloxane species for TEOS, silicon atoms through mono-, di, tri, and tetra-substituted siloxane bonds are designated as Q^1, Q^2, Q^3, Q^4, respectively. The chemical shifts of Q^2, Q^3, and Q^4 are –90, –101, and –109 ppm respectively, and are in good agreement with the literature.[12] For MSMA, mono-, di, tri, tetra-substituted siloxane bonds are designated as T^1, T^2, and T^3. The chemical shifts of T^2 and T^3 are –58 and –65 ppm, respectively, and conform to the literature values.[13] Results revealed that Q^4, Q^3, and T^3 are the major microstructures, forming the network structure. The network structures will promote the thermal stability of hybrids.

UV/vis

Figure 6 shows the UV/vis spectrum of PMMA with different inorganic contents. According to this picture, there is high transmittance over a range of 400–800

nm which is for visible light. This phenomenon revealed the hybrids possess excellent optical transparency. This transmittance may be used as a criterion for the formation of a homogenous phase. These results demonstrate the excellent optical transparency of hybrids, which is the most important characteristic for their application in protective coating.

Solvent extraction results

We use MMA and MSMA to react together to form MMA-co-MSMA copolymer in the reaction scheme. The copolymer is one kind of thermoplastic resin, which possesses line structure. It is easily dissolved in
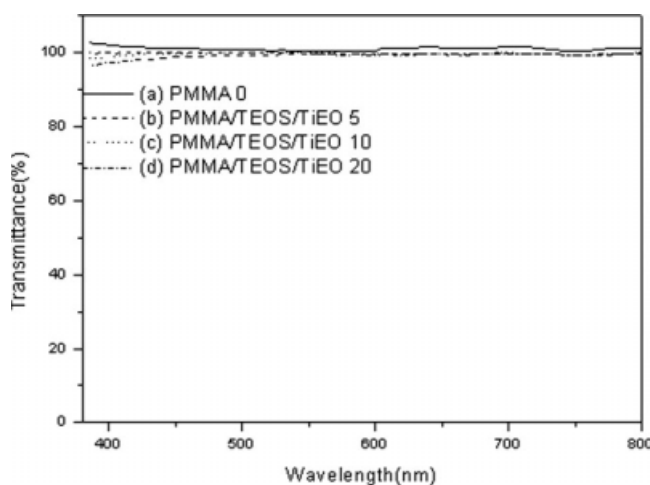

Figure 6 UV/vis spectra of PMMA with different inorganic contents.

TABLE II
THF Extraction Results of the Hybrids

Sample no.	Appearance	Residue (%)
Pure PMMA	Transparent	0
PMMA 0	Transparent	35.2
PMMA/TEOS/TiEO 5	Cloudy	67.5
PMMA/TEOS/TiEO 10	Cloudy	70.1
PMMA/TEOS/TiEO 20	Cloudy	87.2

TABLE III
Weight Loss Characteristics of the PMMA with Various Contents of Inorganic Contents

Sample no.	T_{d10} (°C)	IPDT (°C)	Char yield (wt %)
PMMA 0	225	326	1.53
PMMA 5	260	525	12.15
PMMA 10	279	664	19.09
PMMA 20	289	799	24.54

organic solvent. When we add TEOS and TiOS into the copolymer, TEOS and TiOS will react with copolymer to form the network through the sol–gel reaction. If the polymer is network structure, it is hardly dissolved in organic solvent. So we use solvent extraction experiment to identify the structure of final composite. THF extractions of the hybrid powders were performed for 7 days to comprehend the interaction between organic and inorganic phases. Table II shows THF extraction results of the hybrids. From the table, PMMA 0 in THF solvent appears transparent; it means the copolymer is completely dissolved. Meanwhile, composites containing TEOS and TiOS appear cloudy; it means they are not easily dissolved in THF solvent. Residues were calculated the amount of non-soluble material using 80 mesh filters after extraction and drying. Table II shows the residues of composites after extraction increase with the increasing of inorganic contents. Owing to the phenomenon, we can conclude that the composites possess network structure. The strong interaction between organic and inorganic components and silica/titania are covalent bonds and they can avoid the PMMA components extracting from hybrid networks. When we add more TEOS and TiOS components into hybrids, they will favor to build up the organic–inorganic networks. So we can further propose that for hybrids of higher inorganic content more condensed inorganic networks were formed.
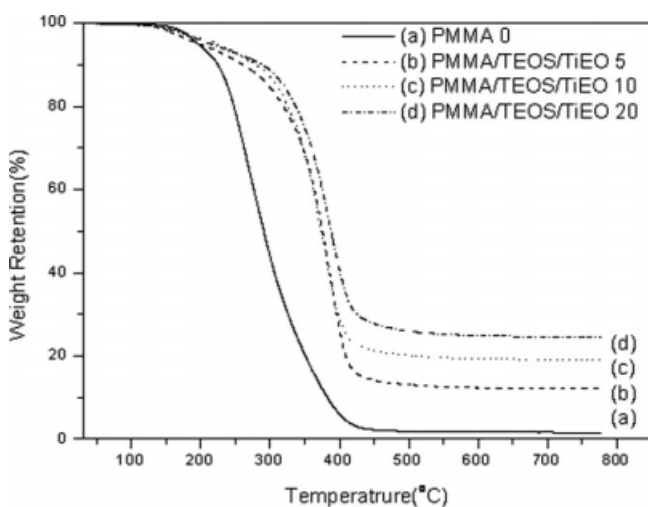
Thermal properties

TGA is a technique used to accurately track the *in situ* weight changes of a sample during a heating process, thereby providing information on thermal degradation. Figure 7 presents TGA thermograms of PMMA with various inorganic contents, from room temperature to 800°C, in nitrogen atmosphere. Table III shows weight loss characteristics of PMMA with various contents of inorganic contents. The thermal degradation procedure consists of three stages for pure PMMA. The first and second stages are caused by cleavage of head-to-head linkages and end-initiated vinyl-terminated PMMA.[14,15] The third thermal decomposition stage is induced by random scission of PMMA main chains.[16] The thermal stability of hybrids was higher than copolymer when the thermal degradation just occurred from T_{d10} data. The values of T_{d10} for hybrids increase with inorganic contents. The char yields of hybrids are higher than copolymer during high temperature. The TGA results show chars contents that are higher than the amounts of inorganic filler in the different samples. It was obvious that the actual residual mass was higher than the theoretical value due to the trapping of the polymer moieties in titania and silicon networks.[2,13,17] It means the inorganic contents can prevent the thermal degradation of polymer matrix and leave more char to stop fire spreading. From DTG curves, the temperatures of
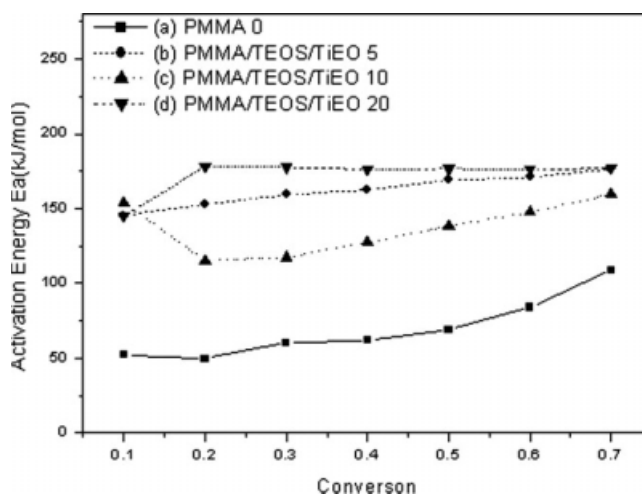

Figure 7 TGA thermograms of PMMA with various inorganic contents.

Figure 8 The plot of the thermal degradation activation energy with various conversions by Ozawa method.

TABLE IV
The Calculated Activation Energy of Thermal Degradation by Ozawa Method

α	PMMA 0	PMMA/TEOS/ TiEO 5	PMMA/TEOS/ TiEO 10	PMMA/TEOS/ TiEO 20
Activation energy of thermal degradation, ΔE (kJ/mol)				
0.1	53	146	154	145
0.2	50	153	115	178
0.3	60	159	117	178
0.4	62	163	127	176
0.5	69	169	138	177
0.6	84	171	148	176
0.7	109	177	160	177
Average	69	162	137	173

maximum decomposition rate for hybrids are higher than that of copolymer distinctly. It means the inorganic components can retard the thermal degradation of polymer happening.

The IPDT proposed by Doyle[11] has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials. From Table III, the IPDT of copolymer was 326°C and the IPDTs of hybrids were higher than that of copolymer. High temperature thermal stability can be increased with the addition of silicon and titanium-containing compounds because their products are silicon dioxide and titanium dioxide, which cannot be degraded further. The phenomena revealed the thermal stability of hybrids increased with the contents of inorganic components.[12-19] The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of PMMA copolymer.

Kinetics of thermal degradation in nitrogen atmosphere

The degree of conversion, α, is defined as the ratio of the actual weight loss to the total weight loss, $\alpha = \frac{m_0 - m}{m_0 - m_\infty}$, where m is the actual weight at time t (or at temperature T); m_0 is the initial weight, and m_∞ is the weight at the end of isothermal or non-isothermal experiments. Consequently, the rate of degradation $d\alpha/dt$, depends on the temperature and the weight of sample, as given by eq. (4)

$$d\alpha/dt = k(T) \times f(\alpha) \quad (4)$$

where $k(T)$ is the rate constant and $f(\alpha)$ is a function of conversion.

If $k(T) = A\exp(-Ea/RT)$ and $f(\alpha) = (1-\alpha)^n$, then eq. (1) can be expressed as follows

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n \quad (5)$$

where A represents the pre-exponential factor; E_a, activation energy; R, gas constant; T, absolute temperature, and n, reaction order.

$$\frac{d\alpha}{(1-\alpha)^n} = \left[\frac{A\exp(-Ea/RT)}{\beta}\right]dT \quad (6)$$

where β = heating rate

Ozawa's method[9] considers several TGA curves obtained at various heating rates (β). From the isoconversion curve, apparent activation energies are calculated from the slopes of the lines using the expression,

$$E_a = -\text{slope} \times R/0.457 \quad (7)$$

Figure 8 illustrates the relationship between the activation energies of the hybrid and the degree of conversion, due to continuous change of degradation mechanisms. The activation energy of thermal degradation generally increases with the extent conversion for different contents of inorganic components. The thermal stability of hybrid increases with the degree of conversion. The formed char protects the polymer from further degradation. Table IV shows the data of the calculated activation energies of copolymer and hybrids. The average activation energy of copolymer
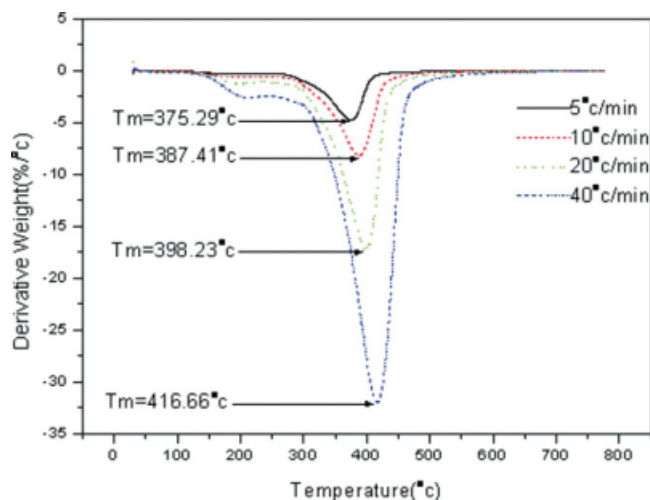

Figure 9 Typical DTG curves of PMMA/TEOS/TiEO 20. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
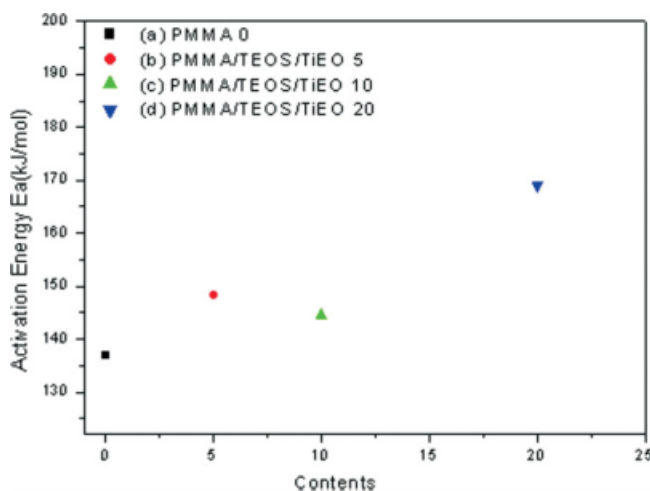
Figure 10 The plot of thermal degradation activation energy with various contents by Kissinger's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was 69 kJ/mol. The activation energies of hybrids containing different contents of inorganic fillers were 162, 137, 173 kJ/mol, respectively. The average activation energies of hybrids were higher than that of the copolymer. The phenomena revealed the incorporation of silica and titania into the networks of hybrids would promote the thermal stability of hybrids.

Kissinger's method[10] considers the maximum temperatures (T_m) of the first derivative weight loss curves. Therefore, eq. (5) is differentiated with respect to T and the resulting expression set to zero. With some rearrangement and using β = heating rate, the following expression,

$$\frac{d\left[\ln(\beta/T_m^2)\right]}{d(1/T_m)} = \frac{-E}{R} \quad (8)$$

was derived. Therefore, the activation energy can be determined from a plot of $\ln(\beta/T_m^2)$ against $1/T_m$. Figure 9 displays the typical DTG curves for PMMA/TEOS/TiOS 20 composite, from which T_m can be obtained. Figure 10 presents that the plot of thermal degradation activation energy with various contents by Kissinger's method. The activation energy of copolymer was 136 kJ/mol. The activation energies of hybrids containing different contents of inorganic fillers were 148, 144, 168 kJ/mol, respec-

tively. The activation energies of hybrids were higher than that of copolymer. The incorporation of silica and titania into PMMA would promote the thermal stability of PMMA. Kissinger's method and Ozawa's method yield similar calculation results, which are therefore reasonable.

CONCLUSIONS

Novel PMMA nanocomposites containing silica and titania were prepared successfully via the non-hydrolytic sol–gel method. The hybrids possess excellent optical transparency from UV–vis experiment. The non-hydrolytic sol–gel technique was used to incorporate silica and titania into the network of hybrids, increasing the thermal stability. The thermal stability of PMMA nanocomposites at high temperature is higher than that of the PMMA copolymer. From Kissinger's and Ozawa's method, the activation energies of hybrids were higher than that of PMMA copolymer during the thermal degradation. The incorporation of silica and titania into PMMA would promote the thermal stability of pure resin.

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