

Poly(methyl methacrylate)–titania hybrid materials by sol–gel processing

JUN ZHANG, SHENGCHENG LUO, LINLIN GUI*
*Institute of Physical Chemistry, Peking University, Beijing 100871,
People's Republic of China*

Sol–gel derived poly(methyl methacrylate)–titania hybrid materials were synthesized by using acrylic acid or allyl acetylacetone (3-allyl-2,4-pentanedione) as coupling agent. Titanium butoxide modified with acrylic acid (or titanium isopropoxide modified with allyl acetylacetone) was hydrolysed to produce a titania network, and then poly(methyl methacrylate) (PMMA) chains, formed *in situ* through a radical polymerization, were chemically bonded to the forming titania network to synthesize a hybrid material. Transparent hybrid materials with different contents of titania were achieved. With increase of the titania content, the colours of the products changed from yellow to dark red. The synthesis process was investigated step by step by using Fourier transform–infrared spectroscopy, and the experimental results demonstrated that acrylate or acetylacetonato groups bound to titanium remain in the final hybrid materials. The thermal stability of the hybrid materials was considerably improved relative to pure PMMA. Field emission scanning electron microscopy analyses showed the hybrid materials are porous and pore diameters vary from 10–100 nm. The hybrid materials using allyl acetylacetone as coupling agent exhibited a thermochromic effect that neither pure PMMA nor titania exhibit.

1. Introduction

Recently, there has been increasing interest in the development of organic/inorganic hybrid materials, which exhibit some characteristics and properties of both organic polymers and ceramics [1–9]. They are mostly produced by a sol–gel process, which can synthesize an inorganic network by wet chemical routes. The low processing temperature also allows the preparation of organic/inorganic hybrid materials. Using organic starting materials, such as metal alkoxides, permits incorporation of a variety of polymers into inorganic metal oxides such as silica [2–5], titania [6, 7] and zirconia [8, 9]. In these hybrid materials, organic and inorganic constituents can be chemically bonded to each other or just physically mixed. The properties of these hybrid materials can be controlled by choice of organic and inorganic components, the phase morphology, the degree of interpenetration, and the presence of chemical bonds between the organic and inorganic components [10].

Carbon family elements, such as silicon, tin and lead, can be usually chemically linked to the organic component through M–C covalent bonds (M = Si, Sn or Pb), which are chemically stable and do not undergo hydrolysis during the sol–gel process. Transition metals, such as titanium and zirconium, whose M–C covalent bonds (M = Ti, Zr etc.) are not stable in the

chemical condition of the sol–gel process, can be bonded to the organic component through coordinative or ionic bonds [1], and most of them can maintain their structure during the hydrolysis and condensation. In the present work, we prepared organic/inorganic hybrid materials by copolymerizing methyl methacrylate with titanium alkoxides modified with acrylic acid or allyl acetylacetone. The synthesis process was investigated by Fourier transform–infrared spectroscopy [FT–IR], and the final hybrid materials were characterized by thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE–SEM) and UV–VIS spectroscopy.

2. Experimental procedure

2.1. Preparation of hybrid materials

Acrylic acid and allyl acetylacetone were chosen as coupling agents to connect PMMA chains and the titania network. Allyl acetylacetone was synthesized according to the method given by Davis and Hurd [11]. Using acrylic acid as coupling agent, the starting metal alkoxide was titanium butoxide. When allyl acetylacetone was used as coupling agent, the starting metal alkoxide was titanium isopropoxide, because it is difficult to obtain transparent hybrid materials using titanium butoxide as starting metal alkoxide

*Author to whom all correspondence should be addressed.

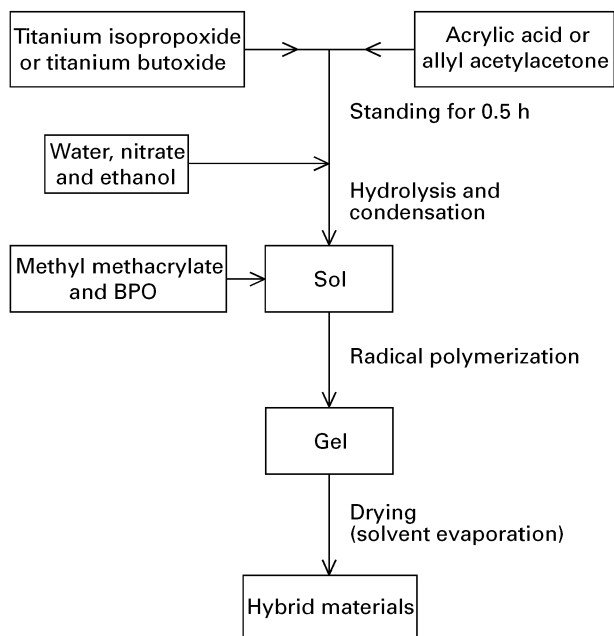


Figure 1 The sol-gel process for the production of the PMMA-titania hybrid materials.

agent. In a typical formulation, titanium butoxide was mixed with acrylic acid (or titanium isopropoxide was mixed with allyl acetylacetonone) in a molar ratio of 1:2. After standing at room temperature for half an hour, the mixture was hydrolysed using a solution of water, ethanol and nitrate. Their molar ratios to titanium were 2, 7 and 0.08. After 24 h, the organic monomer, methyl methacrylate, was added along with a small amount of benzoyl peroxide (BPO). After half an hour, glass tubes were filled with the solution and sealed. The tubes were heated to 60 °C. Usually, after a few days, the content of the tubes gelled and heating was continued for about 1 week. Then the caps on the tubes were slightly loosened to allow the solvent to evaporate slowly. The samples were dried at 60 °C for a further week. The synthesis procedure is illustrated in Fig. 1.

2.2. Characterization

FT-IR spectra were obtained using a Nicolet Magna-IR™750 spectrometer. Thermogravimetric analysis on the samples were performed under an argon atmosphere with a DuPont 1090 System at a heating rate of 15 °C min⁻¹. Optical transmission was measured on a General TU-1221 UV-VIS spectrometer. Field emission scanning electron microscopy (FE-SEM) was carried out using an AMRY 1910FE microscope.

3. Results and discussion

3.1. Infrared spectroscopy

Fig. 2a shows the FT-IR spectrum of the products of the Ti(OBu)ⁿ reaction with acrylic acid. The broad band at 3334 cm⁻¹ is assigned to stretching vibrations of OH groups. It exhibits sharp bands around 2873–2959 cm⁻¹ corresponding to the stretching vibrations of aliphatic CH₂ and CH₃ groups, and the

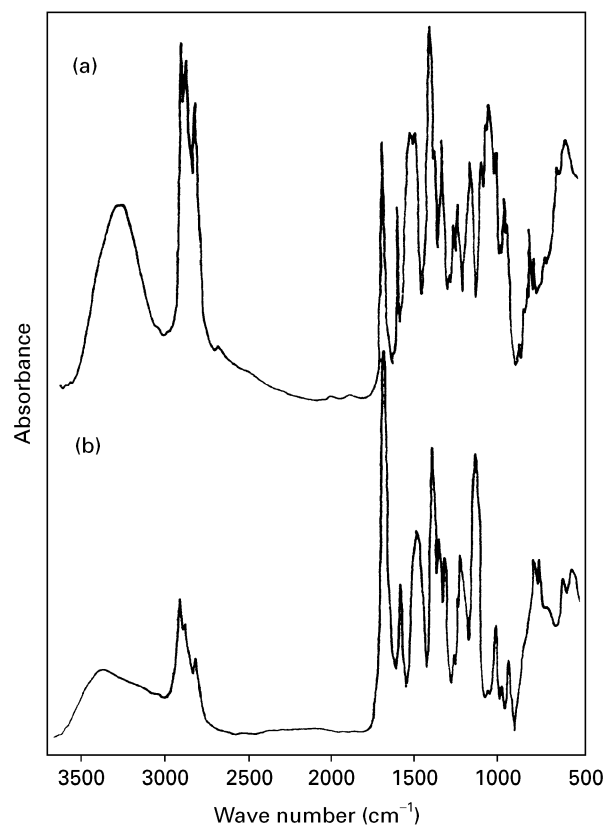


Figure 2 FT-IR spectra of the samples using acrylic acid as coupling agent. (a) Titanium butoxide-acrylic acid, (b) the final hybrid materials.

sharp bands at 1730 and 1637 cm⁻¹ are assigned to C=O and C=C stretching vibrations, respectively. The bands at 1529–1562 cm⁻¹ correspond to the acrylate groups bonded to titanium [12]. They could be assigned to the asymmetric stretching vibration of the carboxyl group. The symmetric stretching vibration of the carboxyl group is around 1441 cm⁻¹ and might be a superposition with bonding vibrations of aliphatic CH₂ groups. Fig. 2b shows the FT-IR spectrum of the final hybrid materials using acrylic acid as coupling agent. The bands in the 1400–1600 cm⁻¹ range, characteristic of acrylate groups bonded to titanium, still remain intense. This indicates that acrylate groups remain bonded to titanium during the synthesis process and in the final hybrid materials.

Fig. 3a shows the FT-IR spectrum of the productions of Ti(OPrⁱ)₄ reacting with allyl acetylacetonone. The broad band at 3423 cm⁻¹ is assigned to *i*-PrOH formed by the substitution of an O-Prⁱ group in Ti(OPrⁱ)₄ by allyl acetylacetonone [13], whereas the sharp bands around 2863–2968 cm⁻¹ and 1357–1464 cm⁻¹ correspond to the stretching and bending vibrations of aliphatic CH₂ and CH₃ groups, respectively. The bands around 1718 cm⁻¹ could be attributed to ν (C=O) vibration of free allyl acetylacetonone (keto-form). The intense bands around 1580–1602 cm⁻¹ could be assigned to ν (C-O) and ν (C-C) vibrations of acetylacetonato groups bonded to titanium (enol form) [13]. The FT-IR spectrum (Fig. 3) of the final hybrid materials using allyl acetylacetonone as coupling agent shows characteristic

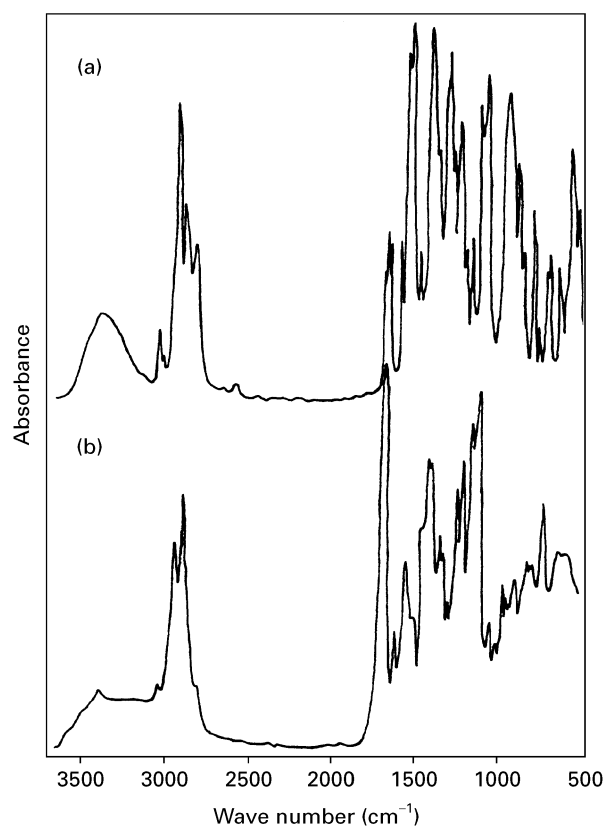


Figure 3 FT-IR spectra of the samples using allyl acetylacetonate as coupling agent. (a) Titanium isopropoxide-allyl acetylacetonate, (b) the final hybrid materials.

bands of acetylacetonato groups bonded to titanium in the $1500\text{--}1600\text{ cm}^{-1}$ range. This indicates that acetylacetonato groups remain bonded to titanium during the synthesis process.

3.2. Thermogravimetric analysis

Transparent PMMA-titania hybrid materials with titania contents ranging from 6.4%–53.6% by weight have been prepared when acrylic acid was used as coupling agent. Transparent PMMA-titania hybrid materials with titania contents ranging from 15.7%–38.1% have been prepared when allyl acetylacetonate was used as coupling agent. The TGA curves of the two systems of PMMA-titania hybrid materials and pure PMMA are shown in Fig. 4. The hybrid materials and pure PMMA begin to lose weight around $200\text{ }^{\circ}\text{C}$, but the pyrolysis temperatures of the organic components in hybrid materials, which are around $400\text{ }^{\circ}\text{C}$, are higher than that of PMMA.

3.3. Field emission scanning electron microscopy

The microstructure of the PMMA-titania hybrid materials was characterized by FE-SEM. All the hybrid materials are porous. The microstructure of hybrid materials differs when different compounds are used as coupling agent, as shown in Fig. 5. With similar titania contents, the hybrid material using acrylic acid as coupling agent has a more homogenous

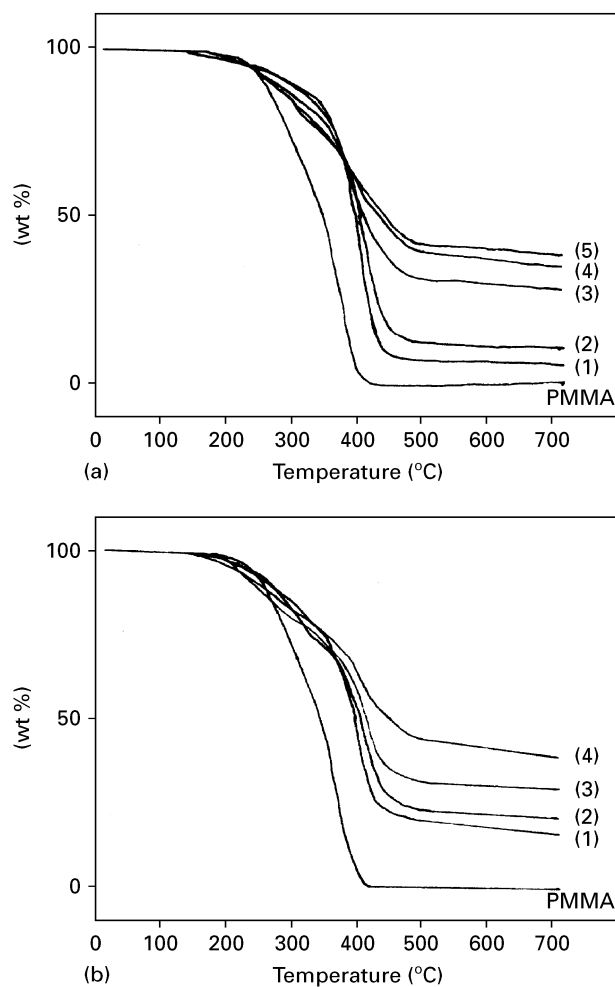


Figure 4 TGA curves of the PMMA-titania hybrid materials and PMMA, (a) using acrylic acid as coupling agent, with titania contents of (1) 6.4%, (2) 11.3%, (3) 28.4%, (4) 36.8% and (5) 39.3%, and (b) using allyl acetylacetonate as coupling agent, with titania contents of (1) 15.7%, (2) 21.6%, (3) 29.9% and (4) 38.1%

distribution of pores and smaller pore sizes. The results indicate that in the hybrid materials using acrylic acid as coupling agent, organic and inorganic components have a higher degree of interpenetration.

3.4. UV-VIS spectroscopy

The hybrid materials are transparent and are coloured. With the increase of titania content, the colours of the hybrid materials vary from yellow to dark red. The hybrid materials using allyl acetylacetonate as coupling agent show a thermochromic effect that neither PMMA nor titania exhibit. The hybrid materials are red and transparent at room temperature and change to yellow and opaque when they are cooled. The reverse transformation is observed as the temperature is raised. Fig. 6 shows the UV-VIS absorption spectra of one sample in $\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH}$ 10:1 solution at different temperatures. The mechanism responsible for thermochromism is currently being studied. It may be due to an equilibrium between the ketonol form of acetylacetonato groups and phase transition.

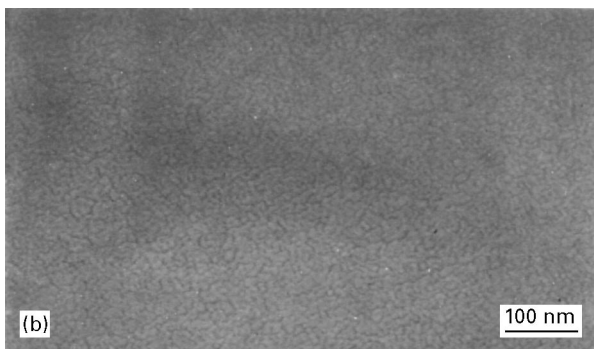
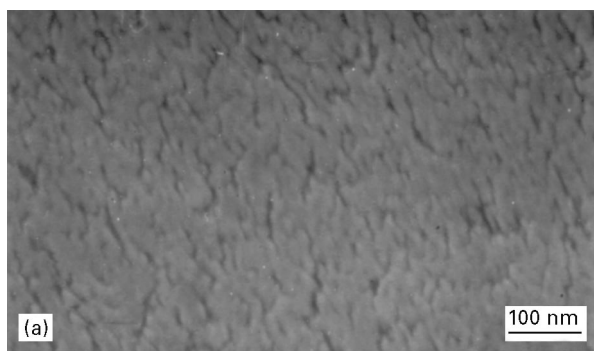


Figure 5 Field emission scanning electron micrographs of the PMMA-titania hybrid materials, (a) using allyl acetylacetonate as coupling agent, titania content 38.1%, (b) using acrylic acid as coupling agent, titania content 36.3%.

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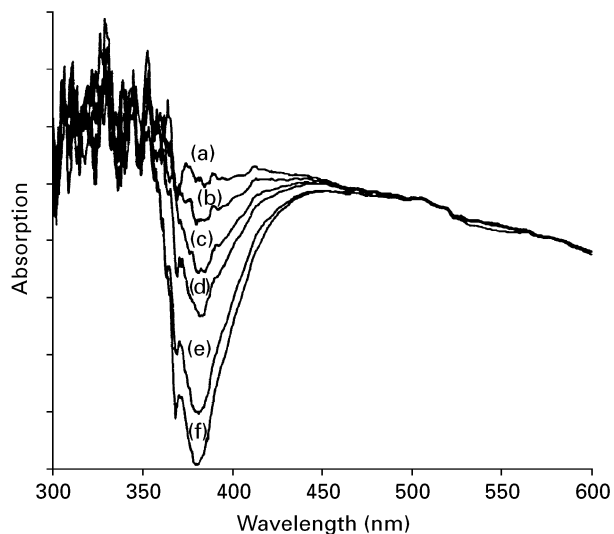


Figure 6 UV-VIS absorption spectra of one sample in $\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH}$ 10:1 solution at different temperatures: (a) 15 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C, (e) 40 °C, (f) 50 °C.

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