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Preparation and thermal property of poly(methyl methacrylate)/silicate hybrid materials by the in-situ sol-gel process

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Summary: A type of hybrid material incorporating poly(methyl methacrylate) with tetraethoxysilane (TEOS) has been successsfully prepared by using the in-situ sol-gel process. The bonding between the organic phase and inorganic phase involved (3-trimethoxysilyl) propyl methacrylate. The thermal properties of the hybrid materials varied with the acid content, the TEOS content and the molecular weight of polymer were investigated by thermal gravimetric analysis.

Introduction

The sol-gel process is the method for preparation of the inorganic glasses and ceramic precusors under mild conditions such as low temperature and pressure[1,2]. This method involves the hydrolysis of metal alkoxides to produce metal hydroxides, followed by polycondensation of hydroxyl groups to form metal oxide network, and the process has many advantages and unique aspects. One is the possibility of preparing ceramic alloys or composites with dispersions at the molecular level. The metal alkoxides can be, for example, mixed with polymer solution or with monomers to be polymerized, which has the groups that can react with the hydroxyl groups generated by the hydrolysis of metal alkoxide, thus, the organic/inorganic hybrid materials can be obtained.

Some workers have already investigated the synthesis of new polymer/inorganic hybrid gels. Schmidt[3] has reported several types of organic modifications to the sol-gel process. One example is the coupling of oligomeric species terminated with functional groups which can react with the metal hydroxide. The sol-gel condensation of tetraethoxylsilane(TEOS) in the presence of poly(dimethylsiloxane) (PDMS) with silanol terminal groups can give a PDMS/silicate hybrid materials[4,5], this material showed good optical transparency and very different mechanical properties compared to the pure

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PDMS system. Other types of the hybrid materials also have been synthesized, for example, polymers, such as poly(tetramethylene oxide)[6], polyamides[7], poly(oxyethylene)[8], poly(ether ketone)[9], and polyoxazoline[10], etc., have been successfully incorporated into SiO_2 or TiO_2 inorganic networks by sol-gel process.

Poly(methyl methacrylate)(PMMA) is an important commercial glass polymer, if it could be covalently combined with an inorganic glass such as SiO_2 at the molecular level by the sol-gel process, the new hybrid glass that would have tailored combinatons of the hardness of the inorganic glass and the toughness of the polymer would be obtained. Wei and coworkers[11] synthesized the coplymer of PMMA-co-poly(3-trimethoxysilyl propyl methacrylate) with the functional groups which could react with the silanol groups generated by hydrolysis of alkoxysilane. The PMMA/SiO_2 hybrid material can be obtained by the sol-gel process when the copolymer is combined with tetraethoxysilane(TEOS). This hybrid could show superior optical transparency and thermal property. However, it is very difficult to obtain the soluble coplymer because the ethoxysilyl groups are easy to condensate with moisture while exposuring to air[12], thus, the insolubility of copolymer in THF and other organic solvents would make it difficult to combine with TEOS.

In this paper, we described the method of synthesizing the PMMA/SiO_2 hybrid material by the in-situ process, which the polymerization of monomers, hydrolysis and condensation of TEOS would happen simultaneously. The goal of this work was to synthesize such hybrid materials without incorporating polymer precursors, and the ceramic networks would result in homopolymerization and condensation which would happen simultaneously. The effects of acid content, TEOS content and the content of initiator on the hybrid materials were investigated. The resulting materials were also characterized by FTIR spectroscopy and thermogravimetric analysis(TGA).

Experimental

Materials and instruments

High-purity tetraethoxysilane was used as received, and methyl methacrylate and 3-(trimethoxysilyl) propyl methacrylate(MSMA) were purified by distillation under vaccum. AIBN was purified by recrystallization. The infrared spectra were collected on a Nicolet Magna-IR 750 instrument, and the thermogravimetry was performed on a Shimadzu DT-30 thermal analyzer under nitrogen flow in a range of room temperature to 700 ^{o}C at a heating rate of 20 ^{o}C/min. The samples for TG analysis were dried at 60 ^{o}C for 24 hours under vaccum.

Synthesis

Table I lists the contents of the reactants. An appropriate amount of MMA, MSMA and AIBN was dissolved in THF, and the homogeneous mixture of deionized water, hydrochloric acid and TEOS with THF was added, followed by vigorous stirring for 10 min. resulted in a homogeneous solution. Then, this solution polymerized and gelled at 60 ^{o}C. After 6 hours, the mixture was allowed to stand at ambient temperature. Upon slowly drying over 20 days, a monolithic, transparent sample of PMMA/SiO_2 was obtained with slight cracks.

Table I. Preparation of monolithic PMMA/SiO_2 hybrid materials by in-situ sol-gel process

Sample	f[a]	TEOS(wt.%)	$[H_2O]/[TEOS]$[b]	[HCl]/[TEOS][b]	AIBN(wt.%)[c]	P.D.[d]
1	0	33	2	0.06	0.2	M/O
2	0.25	33	2	0.02	0.2	M/T
3	0.25	33	2	0.10	0.2	M/T
4	0.25	0	2	0.06[e]	0.2	M/T
5	0.25	33	2	0.06	0.2	M/T
6	0.25	43	2	0.06	0.2	M/T
7	0.25	33	2	0.06	0.5	M/T
8	0.25	33	2	0.06	1.0	M/T
9	0.25	33	2	0.06	2.0	M/T

a. f = [MSMA]/ { [MMA]+[MSMA] } (mol. ratio)
b. mol. ratio
c. wt.% AIBN of vinyl monomers
d. P.D.: product description, M: monolithic, O: opaque, T: transparency
e. the amount of HCl is calculated as [HCl]/[MSMA] (mol. ratio)

Results and discussion

All the samples obtained in the presence of MSMA are transparent monolithic glasses, while the samples obtained without MSMA were opaque. This reveals that

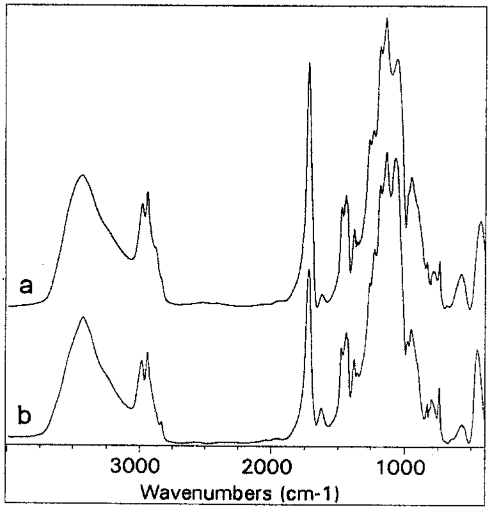

Fig.1. FTIR spectra of the hybrid materials.
a) the material with the presence of MSMA(sample 5)
b) the material without the presence of MSMA(sample 1)

the $Si(OCH_3)_3$ group of MSMA combined covalently the PMMA with SiO_2 network, and the phase separation would not happen, and it is also confirmed by the extractions of the samples. Solvent extractions of sample 1 and 5 were performed in THF for 2 days. The gel content of sample 1 is 26.2% (wt.%), which is approximately comparable to the calculated value of the SiO_2 content, and that of sample 5 is 90.9% (wt.%). The obvious difference of two systems is due to the effect of chemical bonding between silica and organic polymer. In the sample with MSMA, the CH_2-Si bond linking the silica and organic polymer makes the hybrid homogeneous, however, in the sample without MSMA, silica and polymer separate in that no linkage exists, so the gel content is almost the pure SiO_2 content.

The chemical structure of the hybrid materials were confirmed by means of FTIR spectroscopy. Figure 1 illustrates the FTIR spectra of the glasses. The one is the material with the presence of MSMA, and the other has no MSMA. The characteristic absorption bands for C=O of the units from PMMA and PMSMA, for Si-OH and Si-O-Si of the units from SiO_2 network, appear at 1731, 3443, 843 and 1000-1100 cm^{-1}, respectively. In the spectrum (a), a band of medium intensity at 1244, 1273cm^{-1}, arising from symmetrical CH_2 deformation of the CH_2-Si group, can be seen[13], but the band at 1250-1175 cm^{-1} which is consistent with a Si-C linkage is not observed obviously because of being covered by the broad band around 1170 cm^{-1}[14]. In the spectrum (b), no band which is

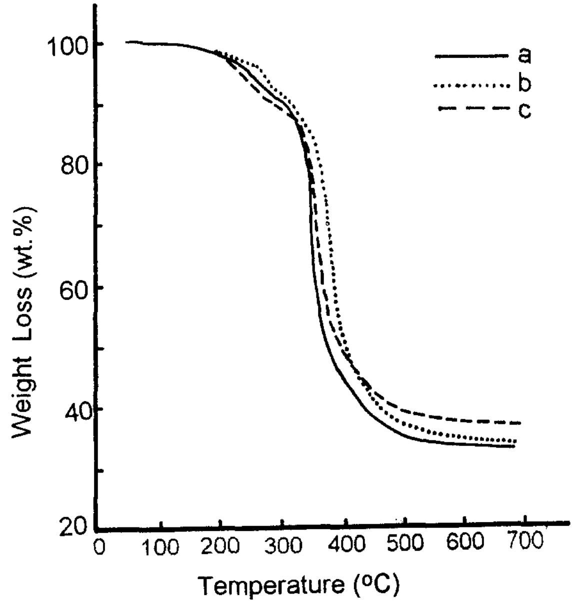

Fig.2. The TGA curves of the hybrid materials.
a) [HCl]/[TEOS]=0.02 (mol. ratio)(sample 2)
b) [HCl]/[TEOS]=0.06 (mol. ratio)(sample 5)
c) [HCl]/[TEOS]=0.10 (mol. ratio)(sample 3)

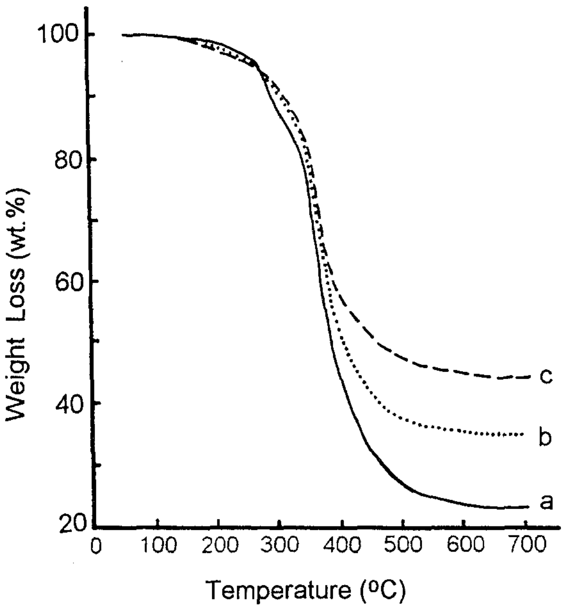

Fig.3. The TGA curves of the hybrid materials. a) 0 wt.% TEOS(sample 4) b) 33 wt.% TEOS(sample 5) c) 43 wt.% TEOS(sample 6)

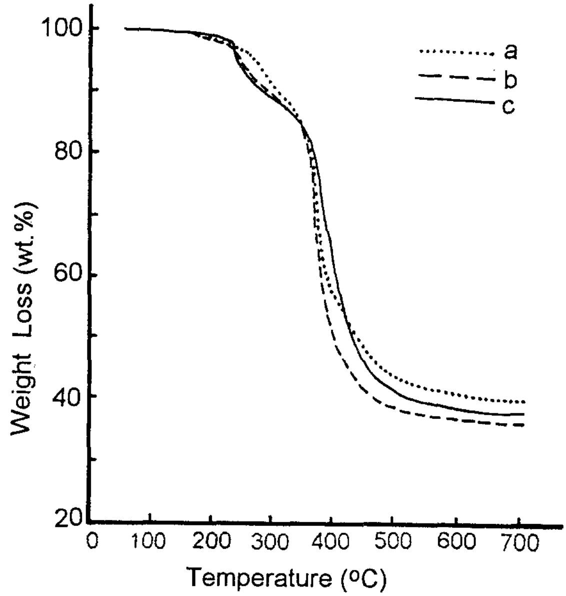

Fig.4. The TGA curves of the hybrid materials. a) 0.5 wt.% AIBN(sample 7) b) 1 wt.% AIBN(sample 8) c) 2 wt.% AIBN(sample 9)

consistent with the symmetrical CH_2 deformation of CH_2-Si group appears.

In the sol-gel process of making hybrid materials, the conditions of the reactions, for examples, the acidity of the system, the TEOS content, and the molecular weight of the polymer, etc., has been proved to display a critical effect on the structure and properties of the final products[4,15]. The thermal stability of these hybrid materials was measured by means of TGA, and three kind conditions, the acidity of the medium, the content of TEOS and the content of the initiator(AIBN), were considered. Figure 2 shows TGA curves of the hybrids with the same conditions but different amounts of acid (HCl). These results showed that the thermal decomposition occurs at approximately 230 °C, but the content of HCl affected obviously the initial decomposition temperature of the materials, this is because the content of acid affects directly the process of hydrolysis and condensation of TEOS[15], and the micro-structures of the final products are different with varying the content of acid.

The system would become higher cross-linking with increasing the content of TEOS, and the thermal weight loss of the hybrid materials would decrease with increasing the silica content. Figure 3 shows this tendency. At the temperature of about 600 °C, the weight residue was the content of the SiO_2 (the inorganic component), which is approximately comparable to the calculated value. The decomposition behavior of the materials is similar with that of the materials which synthesized by the two-step processs, the synthesis of copolymer followed by combining it with TEOS[11].

Since the thermal decomposition of the hybrid materials begins with the component of the polymer, the molecular weight of the polymer in the system would affect the initial decomposition temperature at low temperature. In order to obtain the polymeric contents with different molecular weight, the polymerizations with the different contents of initiator (AIBN) were applied, and the thermal properties of the final products (the hybrid materials) were also investigated by TGA. Figure 4 shows the results of the thermal decomposition of the hybrid materials. It is obviously that the initial thermal decomposition temperature increases with decreasing the content of AIBN. When the content of AIBN is in highest range (almost 2 wt.% of vinyl monomer), the decomposition pioint at low temperature (about 210 °C) is observed clearly. However, at higher temperature(>370°C), all the samples have the similar rate of thermal decomposition.

Conclusions

A type of hybrid material incorporating PMMA-co-PMSMA copolymer with inorganic glasses (SiO_2) by in-situ sol-gel process had been successfully produced. This material shows high optical transparency and great hardness. The acid content of the reacting system is crucial in determining the structure of the product, and affects its thermal decomposition. Increasing the content of the inorganic component would increase the thermal decomposition temperature of the material, but higher content of SiO_2 would make the product stiffer and cracking. With the use of different contents of the initiator, the product would show different thermal decomposition properties due to the varying molecular weight of the polymeric component in the hybrid system.

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