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有机聚合物／SiO_2有机无机杂化材料的研究

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致　谢

我的博士学位论文的研究工作是在导师史铁钧教授的悉心指导和热情关怀下完成的，尤其在论文的成文阶段，导师对论文进行了逐字修改，倾注了大量的心血。导师严谨求实的治学态度、一丝不苟的敬业精神和丰富的经验、渊博的知识、无私的品格、高尚的修养，豁达开朗的大家风范，使我受益匪浅，并将影响到我以后的学习和工作。多年来，本人在学习、生活、工作等方面都得到了导师无微不至的关怀和帮助，让我能得以在繁忙工作的同时，挤出时间学习和研究，撰写完成论文，感激之情难于言表，在此，谨致以最诚挚的敬意和谢意。

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王华林

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摘　要

有机无机杂化材料是一种分散均匀的多相材料，兼备有机聚合物或无机聚合物的性能优势。它可以是无机改性有机聚合物，也可以是有机改性无机玻璃。可以通过调节有机相与无机相的组分及比例，实现对材料功能的“剪裁”和“组装”。论文以正硅酸乙酯（TEOS）为硅源，制备出系列有机聚合物/SiO_2有机无机杂化材料，并研究其制备原理、杂化与聚合机理、结构与性能。

1. 基于溶胶凝胶法，以 TEOS 为硅源，利用甲基丙烯酸-β-羟丙酯（HPMA）与 TEOS 直接杂化，再引发 HPMA 聚合，制备出以共价键结合的块状聚甲基丙烯酸-β-羟丙酯（PHPMA）/SiO_2均质有机无机杂化材料。这种方法是制备以共价键结合的有机无机杂化材料的一种最简洁的方法，对制备类似的有机无机杂化材料，具有重要参考价值。

HPMA 分子中的—OH 可以与 TEOS 分子中的—OCH_2CH_3发生缩合反应，且 HPMA 与 TEOS 的缩合反应是分步进行的。PHPMA/SiO_2杂化材料中有机组分与无机组分间形成以 Si—O—C 链结合的杂化网络，热稳定性能优良，耐热性能达到 350℃左右，具有广阔的应用前景。

2. 基于两步法，以 TEOS 为硅源，制备硅溶胶，然后与 HPMA 及 MMA 进行杂化反应，制备出活性 PHPMA-MMA/SiO_2杂化溶胶，再将 PHPMA-MMA/SiO_2杂化溶胶与尼龙 6（PA6）混合、加工，制备出 PA6/SiO_2有机无机杂化材料。这种两步法制备 PA6/SiO_2有机无机杂化材料工艺，未见其他相关报道。研究结果将会为有机无机杂化材料的制备提供一种崭新的方法，为聚合物增强增韧开辟一条新途径。

用于改性 PA6 的是含有 PMMA 的 PHPMA-MMA/SiO_2杂化溶胶，并不是传统意义上的无机纳米粒子。在杂化溶胶内部，PMMA 是通过共价键

与无机组分 SiO_2 发生作用，形成有机无机杂化网络。PMMA 与无机组分 SiO_2 间的共价键作用将 SiO_2 纳米粒子固定在杂化网络中，限制了 SiO_2 纳米粒子的团聚，使其在与 PA6 基体复合时保持粒子尺寸稳定；在 PA6/SiO_2 有机无机杂化材料内部，PA6 与无机 SiO_2 组分以氢键或间接通过共价键结合。

发现 PHPMA－MMA/SiO_2 有机无机杂化材料能诱导 PA6 由 α 晶型转化为 γ 晶型，当 SiO_2 含量达到或超过 3wt％时，PA6 基本上转化为 γ 晶型 PA6，这对研究 PA6 的晶型转化具有重要价值。当相对结晶度 $X(t)$ 接近或超过 60％左右时，Jeziorny 法不能有效地描述 PA6 和 PA6/SiO_2 有机无机杂化材料的非等温结晶过程，但在 $X(t)$ 小于 60％左右时，仍然有效，而 Liu 法却能成功地描述 PA6 和 PA6/SiO_2 有机无机杂化材料的非等温结晶全过程。

PHPMA－MMA/SiO_2 有机无机杂化材料对 PA6 具有增强增韧效果，SiO_2 的含量为 1wt％时，PA6/SiO_2 有机无机杂化材料的拉伸强度较 PA6 提高 12.6％，冲击强度较 PA6 提高 2.9 倍，断裂伸长率较 PA6 降低 13.9％。

PHPMA－MMA/SiO_2 杂化材料与 PA66 基体具有很好的相容性，在 PA66/SiO_2 有机无机杂化材料内部，PA66 与无机 SiO_2 组分以氢键或间接通过共价键结合。

Jeziorny 法能有效地描述 PA66 非等温结晶过程，不能有效地描述 PA66/SiO_2 有机无机杂化材料非等温结晶过程，但 $X(t)<1-1/e$ 时仍然有效。Ozawa 法能够成功地描述 PA66 的非等温结晶过程，对 PA66/SiO_2 有机无机杂化材料无效。Liu 法却能成功地描述 PA66 和 PA66/SiO_2 有机无机杂化材料的非等温结晶全过程。PHPMA－MMA/SiO_2 有机无机杂化材料对 PA66 具有异相成核作用，使 PA66 结晶能力增强，加速 PA66 的结晶过程。

PHPMA－MMA/SiO_2 有机无机杂化材料对 PA66 也具有一定增强增韧效果，SiO_2 的含量为 1wt％时，PA66/SiO_2 有机无机杂化材料的拉伸强度较 PA66 提高 15.6％，冲击强度较 PA66 提高 2.5 倍，断裂伸长率变化相对较小。

3. 以 TEOS 为硅源，乙烯基三乙氧基硅烷（VTEOS）为偶联剂，乙醇和乙酸乙酯为分散介质，采用分散聚合，制备核壳型聚丙烯酸（PAA）/聚苯乙烯（PS）/SiO_2 有机无机杂化微球。核壳型 PAA/PS/SiO_2 有机无机杂化微球

以 SiO_2 粒子为核，壳层分别由 PAA 和 PS 组成。在对极性聚合物共混改性时，外壳层极性 PAA 对聚合物基体具有良好的相容性，保证了 SiO_2 纳米粒子在聚合物基体中分散的均匀性。PS 具有优良的加工流变性能，在 SiO_2 核与外壳层 PAA 间起润滑作用，从而使 PAA/PS/SiO_2 有机无机杂化微球在改性聚合物时具有良好的加工性能。这种多层核壳型 PAA/PS/SiO_2 有机无机杂化微球的制备，未见其他相关报道，研究结果将为多层核壳型有机无机杂化微球的制备，提供理论依据。

当分散介质 v(乙酸乙酯)/v(乙醇)＝1∶1，搅拌速率为 300rpm，大多数 PAA/PS/SiO_2 有机无机杂化微球的 SiO_2 核的直径为 15nm，PS 层厚 7.5nm，PAA 层厚 5nm，且 SiO_2 核与 PS、PS 和 PAA 间均以共价键键合。这种核壳型 PAA/PS/SiO_2 有机无机杂化微球耐热性能优良，当温度超过 420℃时，才发生热氧化分解。

核壳型 PAA/PS/SiO_2 有机无机杂化微球的制备分为 core stage、shell stage Ⅰ、shell stage Ⅱ三个阶段，相应形成表面带有的乙烯基活性 SiO_2 粒子、带有活性自由基的核壳型 PS/SiO_2 有机无机杂化微球和核壳型 PAA/PS/SiO_2 有机无机杂化微球。当 PAA/PS/SiO_2 有机无机杂化微球增大到一定的程度，从乙醇和乙酸乙酯中析出，发生相分离。在散聚合过程中，由于均聚 PAA 对 PAA/PS/SiO_2 有机无机杂化微球具有稳定作用，不需要另外再加分散剂。这种无分散剂的分散聚合是对传统分散聚合方法的一种有益的补充，为制备类似的有机无机杂化微球提供一种新方法。

搅拌速率和分散介质的组成对核壳型 PAA/PS/SiO_2 有机无机杂化微球粒径具有一定的影响，搅拌速率过低，会致使微球粒径偏大，搅拌速率过高时，会导致 SiO_2 粒子偏离 PAA/PS/SiO_2 有机无机杂化微球的中心。随着 v(乙酸乙酯)/v(乙醇)比值的增大，PAA/PS/SiO_2 有机无机杂化微球的粒径有减小的趋势，且 v(乙酸乙酯)/v(乙醇)比值介于 1～1.5 时，可以得到单分散的核壳型 PAA/PS/SiO_2 有机无机杂化微球。

关键词：溶胶凝胶技术　PHPMA/SiO_2 有机无机杂化材料　两步法 PA6/SiO_2 有机无机杂化材料　PA66/SiO_2 有机无机杂化材料　分散聚合　核壳型 PAA/PS/SiO_2 有机无机杂化微球

ABSTRACT

Organic-inorganic hybrid material is an even multiphase material with the advantageous properties over organic and inorganic polymers. This hybrid material can be ranged from organic polymer modified by inorganic substance to inorganic glass modified by organic substance, and the properties of material are able to be tailored and constructed by adjusting the component and ratio of organic and inorganic phase. In this book, a series of organic polymer/SiO_2 organic-inorganic hybrid materials were prepared with tetraethoxysilane (TEOS) as silica source, moreover, the preparation principle, hybrid and polymerization mechanisms, structures and properties of the organic polymer/ SiO_2 organic-inorganic hybrid materials were investigated.

1. Based on sol-gel method, using TEOS as silica source to hybridize with poly (2-hydroxy propylmethacrylate) (HPMA) before the polymerization of HPMA, the bulk poly (2-hydroxy propylmethacrylate) (PHPMA)/SiO_2 organic-inorganic hybrid material bonded by covalents was prepared in fully transparent homogeneous form. This method is the simplest method to prepare organic-inorganic hybrid material bonded by covalents and will have important references on the preparation of the similar organic-inorganic hybrid materials.

HPMA and TEOS could be hybridized and reacted completely by step polycondensation between the hydroxyl group of HPMA and ethoxyl group of TEOS. The organic-inorganic network in the hybrid material was formed by Si—O—C chains. This PHPMA/SiO_2 organic-inorganic hybrid material

possesses advantage thermal properties and can be used even at about 350℃, implying good application future.

2. Based on two-step method and using TEOS as silica source, the poly 2-hydroxy propylmethacrylate-methyl methacrylate (PHPMA-MMA)/SiO_2 hybrid sol was prepared by the hybrid reaction among the silica sol, HPMA and MMA at first, then the hybrid sol was used to synthesize polyamide 6(PA6)/SiO_2 organic-inorganic hybrid materials via blending method. No other reports were found about this two-step method to prepare PA6/SiO_2 organic-inorganic hybrid material. This research result will provide a new method for preparing organic-inorganic hybrid material and a new way for reinforcing and toughening polymer.

The material used to modify PA6 is PHPMA－MMA/SiO_2 hybrid sol and not traditional nano-inorganic particles. The stable organic-inorganic hybrid network dispersed by nano-SiO_2 particles have been formed in the hybrid sol, and the SiO_2 inorganic dispersion phase and the organic component were bonded by covalents. The covalents among PMMA and SiO_2 inorganic dispersion phase fix the nano-SiO_2 particles in the organic-inorganic hybrid network, so the assembling phenomena of nano-SiO_2 particles can be avoided and this characteristic structure can limit the nano-SiO_2 particle size when blended with PA6 matrix. Moreover, nano-SiO_2 particles and PA6 matrix are bonded by hydrogen bonds directly or covalents indirectly in PA6/SiO_2 organic-inorganic hybrid material.

It was found that PHPMA-MMA/SiO_2 organic-inorganic hybrid material could induce PA6 to transit from α to γ crystal form, and when the content of SiO_2 was approximately 3 wt% or more, PA6 was changed into γ crystal form almost completely. This finding will be very important in studying the crystal transition of PA6. Based on our experimental data, if the relative degree of crystallinity was approximately 60% or more, the Jeziorny method was not valid to describe the nonisothermal crystallization process, while Liu's method was successful to describe the whole noniso-

thermal crystallization process.

PHPMA－MMA/SiO_2 organic-inorganic hybrid material has both reinforcing and toughening effects on PA6. Compared with PA6, when the content of SiO_2 is 1wt%, the tensile strength and impact strength of PA6/SiO_2 organic-inorganic hybrid material are improved by 12.6% and 290% respectively, while the tensile elongation PA6/SiO_2 organic-inorganic hybrid material is decreased by 13.9%.

3. Based on two-step method and using TEOS as silica source, the PHPMA－MMA/SiO_2 hybrid sol was prepared by the hybrid reaction among the silica sol, HPMA and MMA at first, then the hybrid sol was used to synthesize polyamide 66(PA66)/SiO_2 organic-inorganic hybrid materials via blending method. No reports were found about this two-step method to prepare PA66/SiO_2 organic-inorganic hybrid material also.

There exists good compatibility between PHPMA－MMA/SiO_2 organic-inorganic hybrid material and PA66 matrix. Moreover, nano-SiO_2 particles and PA66 matrix were bonded by hydrogen bonds directly or covalents indirectly in PA66/SiO_2 organic-inorganic hybrid material.

Jeziorny method was suitable to describe the nonisothermal crystallization process of PA66 and not suitable for PA66/SiO_2 organic-inorganic hybrid material, but when $X(t)$ was less than $1-1/e$, Jeziorny method was still valid. Ozawa method was suitable to describe the nonisothermal crystallization process of PA6, and not suitable for PA66/SiO_2 organic-inorganic hybrid material. Liu's method was successful to describe the nonisothermal crystallization processes for both PA66 and PA66/SiO_2 hybrid material. It was conformed that the presence of PHPMA－MMA/SiO_2 composite could increase crystallization rate and had hetero phase nucleation effect on PA66 matrix.

PHPMA－MMA/SiO_2 organic-inorganic hybrid material has both reinforcing and toughening effects on PA66 also. Compared with PA66, when the content of SiO_2 is 1wt%, the tensile strength and impact strength of

PA66/SiO_2 organic-inorganic hybrid material are improved by 15.6% and 250% respectively, but the change of the tensile elongation is not obvisiously.

4. Using TEOS as silica source and vinyltriethoxysilane (VTEOS) as silane agent, core-shell poly(acrylic acid)/polystyrene/SiO_2 (PAA/PS/SiO_2) organic-inorganic hybrid microspheres were prepared by dispersion polymerization in ethanol and ethyl acetate mixture medium. In the core-shell PAA/PS/SiO_2 hybrid microsphere, the core is silica particles and the shell is composed of PAA and PS. When polarity polymer is modified by these hybrid microspheres, there exists good compatibility between the polarity PAA outermost shell and polymer matrix, which makes it possible for silica particles to disperse evenly in polymer matrix. Moreover, PS layer may work as lubricant owing to its superior processing rheological property between silica core and PAA outermost shell and contributes superior processability in polymer modifying.

These core-shell PAA/PS/SiO_2 hybrid microspheres have potential as new materials for polar polymer modification. No other reports were found about the preparation of these multilayer core-shell PAA/PS/SiO_2 organic-inorganic hybrid microspheres. This research result will provide fundamental theory for preparing multilayer core-shell organic-inorganic hybrid microsphere.

When v(ethyl acetate)/v(ethanol) =1∶1 and stirring rate is 300rpm, most PAA/PS/SiO_2 hybrid microspheres are composed of silica cores about 15nm in diameter, a layer of PS shell about 7.5 nm thick and a layer of PAA outermost shell about 5 nm thick. Moreover, the silica core, PS shell and PAA outermost shell are bonded by covalents. This PAA/PS/SiO_2 hybrid microsphere possesses advantage thermal properties and it begins to decompose when the temperature exceeds 420℃.

The preparation of PAA/PS/SiO_2 organic-inorganic hybrid microsphere includes three stages, that is core stage, shell stage and shell stage, the

functional organic-inorganic silica particles structured vinyl groups on surfaces, PS/SiO_2 organic-inorganic hybrid microspheres with active free radicals and PAA/PS/SiO_2 organic-inorganic hybrid microsphere were formed correspondingly in these three stages. When the PAA/PS/SiO_2 hybrid microsphere increased at a certain size, they were separated out in ethanol and ethyl acetate mixture medium, then the phase separation phenomena was obtained. Because the homogeneous polymer PAA has stable effect on PAA/PS/SiO_2 organic-inorganic hybrid microsphere, no dispersion agent is needed in dispersion polymerization. This dispersion polymerization without dispersion agent is a useful supplement to traditional dispersion polymerization, which will provide a new method for preparing similar organic-inorganic hybrid microsphere.

The stirring rate and the component of dispersion medium have certain effects on the size of PAA/PS/SiO_2 organic-inorganic hybrid microsphere. When the stirring rate is too slow, the hybrid microsphere size is bigger, while the stirring rate is too fast, the SiO_2 core will shift from the centre of the hybrid microsphere. The size of PAA/PS/SiO_2 organic-inorganic hybrid microsphere is decreasing with the increase of volume ratio value of ethyl acetate and ethanol, and when the volume ratio of ethyl acetate and ethanol is between 1 and 1.5, monodisperse PAA/PS/SiO_2 organic-inorganic hybrid microsphere can be obtained.

KEYWORDS: Sol-gel method; PHPMA/SiO_2 organic-inorganic hybrid material; Two-step method; PA6/SiO_2 organic-inorganic hybrid material; PA66/SiO_2 organic-inorganic hybrid material; Dispersion polymerization; PAA/PS/SiO_2 organic-inorganic hybrid microsphere

目　录

第1章 绪 论

有机无机杂化材料在新型功能材料如选择性催化、分子识别、可逆性主客体分子(离子)交换、超高纯度分离、生物传导材料、光电材料、磁性材料和芯片等新材料开发中显示了诱人的应用前景,而成为20世纪90年代末化学和材料学科中最为活跃的研究领域之一。有机无机杂化材料能够实现有机相与无机相间以分子键合[1],已广泛应用于涂料、薄膜、纳米复合材料、玻璃及有机陶瓷等领域[2~6]。有机无机杂化材料的力学性能、热学性能及加工性能介于有机聚合物和无机聚合物之间[7~9]。

1.1 有机无机杂化材料的分类

有机无机杂化材料是一种分散均匀的多相材料,有机相与无机相间的界面面积非常大、界面相互作用强,使常见的清晰的界面变得模糊,其中至少有一相的尺寸至少有一个维度在纳米数量级,在有些情况下甚至达到“分子复合”的水平。因此,其结构和性能与传统的复合材料相比有本质的区别。与单一的有机聚合物或无机聚合物相比,有机无机杂化材料在光学透明性、可调折射率、力学性能、耐温性能、耐磨性、柔韧性、功能性等方面具有明显的性能优势[10~13]。有机无机杂化材料可以是无机改性有机聚合物,也可以是有机改性无机玻璃。可以通过调节有机相与无机相的组分及比例,实现对材料功能的“剪裁”和“组装”。

有机无机杂化材料的制备一般基于溶胶凝胶法。溶胶-凝胶法是将烷氧

基金属氧化物或金属盐，经水解缩合反应低温形成溶胶，溶胶经凝胶化和热处理，制备氧化物或其他固体化合物的方法[14]。溶胶凝胶技术的优点在于其低温反应性，易于控制材料的最终组成，并能形成纤维状、块状、薄膜及纳米分散粒子等各种形态，但是在干燥的过程中易产生应力，导致材料开裂，制备大体积的块状材料比较困难。为克服这一缺陷，在无机溶胶中加入有机聚合物单体或低聚体，进行杂化反应，形成杂化网络结构，制备出有机无机杂化材料。由于杂化材料中有机相和无机相间的作用力可以是共价键强作用力，也可以是范德华力、氢键、配位键、亲水-憎水平衡等弱作用力[15~19]，在凝胶化和热处理过程中，不发生相分离。

有机无机杂化材料可以根据有机相和无机相间的界面特性、基体材料的种类和制备方法、杂化组分的种类和数量等进行分类。根据两相间的界面特性和材料的组成，Mackenzie[20]将有机无机杂化材料分为三类：

Ⅰ. 无机包埋有机相(Entrapped organics)；

Ⅱ. 有机填充无机相(Impregnated inorganics)；

Ⅲ. 化学键合的有机相与无机相(Chemically bonded organics - inorganics)；

与 Mackenzie 相似，也有文献[21]将有机无机杂化材料分为下述三类：

Ⅰ. 有机分子或聚合物简单包埋于无机基质中，有机相与无机相间通过弱键，如范德华力、氢键或离子间作用力而互相连接。

Ⅱ. 有机相与无机相间通过强的化学键如共价键或离子-共价键结合，有机相通过化学键嫁接于无机网络中，而不是简单包裹于无机基质中。

Ⅲ. 在上述Ⅰ类和Ⅱ类杂化材料中加入掺杂物(有机物或无机物)，掺杂组分嵌入有机无机杂化基质中。

Sanchez[14]等人进一步将杂化材料简化分为两大类：

Ⅰ. 有机相仅简单地嵌埋在无机基体中，根据其结晶形态可分为非结晶和有序排列两种；

Ⅱ. 有机相和无机相以共价键(或部分共价键)紧密联合。因为这种分类方法基本上体现了材料的微观特征，因而在最新文献中已经开始陆续被采用。