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厦 门 大 学

硕士学位论文

**SiO<sub>2</sub>@含磷聚合物核壳结构纳米粒子  
阻燃改性环氧树脂**

**SiO<sub>2</sub>@Phosphorous-containing Polymer Core-shell  
Structure Nanoparticles Flame Retardant Modified Epoxy**

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## 摘要

环氧树脂是一种非常重要的热固性材料，由于具有良好的化学稳定性、黏结性、低收缩、优异的热性能及机械性能等，它广泛应用于黏结剂、涂料、电子封装及复合材料等领域。然而，环氧树脂阻燃性能的不足是其应用受到限制的主要因素之一，因此，建立新型无卤、无毒的环氧树脂阻燃体系越来越成为广大研究者关注的焦点。本文首先合成了一种 DOPO 衍生物—甲基丙烯酸 DOPO 乙酯(简称 HEPO)，然后采用 RAFT 聚合法调控制备了尺寸可控的含磷嵌段共聚物  $\text{PHEPO}_m\text{-}b\text{-PGMA}_n$  (简称 PHDG) 和均聚物 PMOEP。将它们接枝在  $\text{SiO}_2$  纳米粒子表面，得到了新型含磷、硅阻燃核壳结构杂化纳米粒子  $\text{SiO}_2\text{-PHDG}$  和  $\text{SiO}_2\text{-PMOEP}$ ，并将  $\text{SiO}_2\text{-PHDG}$  引入环氧树脂体系中，形成纳米  $\text{SiO}_2$  为核、含磷嵌段共聚物为壳的纳米核壳结构，阻燃元素 Si、P 和微量 N 以“捆绑式”均匀分散在环氧树脂基体中，达到低 Si、P 含量下优良的协同阻燃效果，改善环氧树脂的热稳定性能。工作具体如下：

1. 通过分子设计，首先合成了 DOPO 的衍生物甲基丙烯酸 DOPO 乙酯，然后采用 RAFT 聚合法合成了  $\text{PHEPO}_m\text{-}b\text{-PGMA}_n$  嵌段共聚物和 PMOEP 均聚物，通过核磁共振波谱 (NMR)、红外光谱 (FT-IR) 和热失重分析 (TGA) 等表征手段对合成产物的结构及热性能进行表征。分析结果表明，成功合成了 HEPO 单体、 $\text{PHEPO}_{100}\text{-}b\text{-PGMA}_{15}$  两嵌段共聚物和  $\text{PMOEP}_{100}$  均聚物。

2. 分别采用  $\gamma$ -氨丙基三乙氧基硅烷 (KH-550) 和 3-缩水甘油基氧基丙基三甲氧基硅烷 (KH-560) 处理  $\text{SiO}_2$  纳米粒子，使  $\text{SiO}_2$  表面修饰上氨基和环氧基；通过嵌段共聚物 PHDG 中的环氧基与  $\text{SiO}_2$  表面的氨基反应，得到  $\text{SiO}_2\text{-PHDG}$  杂化纳米粒子；通过均聚物  $\text{PMOEP}_{100}$  上的磷羟基与  $\text{SiO}_2$  表面的环氧基反应，得到  $\text{SiO}_2\text{-PMOEP}$  杂化纳米粒子。采用 FT-IR、元素分析仪和 TGA 等表征手段对杂化纳米粒子的结构及热性能进行表征；通过扫描电镜 (SEM) 和透射电镜 (TEM) 对核壳结构杂化纳米粒子进行形貌观察。研究表明，嵌段共聚物 PHDG 和均聚物  $\text{PMOEP}_{100}$  成功化学接枝在  $\text{SiO}_2$  纳米粒子，得到  $\text{SiO}_2$  为核、聚合物为壳的核壳结构杂化纳米粒子  $\text{SiO}_2\text{-PHDG}$  和  $\text{SiO}_2\text{-PMOEP}$ 。核结构尺寸约为 60-80 nm，壳层厚度约为 5-10 nm。通过元素分析仪测得  $\text{SiO}_2\text{-PHDG}$  (12 h)、 $\text{SiO}_2\text{-PHDG}$

(24 h)中 C 元素含量的增加算出聚合物 PHDG 的接枝率分别为 18.9 %、22.6 %，通过  $\text{SiO}_2\text{-NH}_2$  及  $\text{SiO}_2\text{-PHDG}$  的 TGA 曲线计算出  $\text{SiO}_2\text{-PHDG}$ (12 h)、 $\text{SiO}_2\text{-PHDG}$  (24 h) 的接枝率分别为 19.8 %、27.7 %。采用 TEM 和 SEM 观察得出：随着接枝反应时间的延长，接枝到  $\text{SiO}_2\text{-NH}_2$  表面的 PHDG 逐渐增多，使得聚合物层的厚度由 5 nm 增加到 10 nm 左右。

3. 含 P、Si 阻燃杂化纳米粒子  $\text{SiO}_2\text{-PHDG}$  改性环氧树脂的研究。通过将合成的含 P、Si 阻燃杂化纳米粒子  $\text{SiO}_2\text{-PHDG}$  引入到环氧树脂 (E51) 中，以 4,4'-二氨基二苯甲烷 (DDM) 为固化剂，制备了一系列不同 P、Si 含量的阻燃改性环氧树脂。采用差示扫描量热法 (DSC)、TGA 和动态机械热分析 (DMA) 等表征手段对阻燃改性环氧树脂热性能进行研究；通过 SEM 对阻燃改性环氧树脂的断面形貌进行观察；通过氧指数 (LOI) 对阻燃改性环氧树脂的阻燃性能进行评估。研究表明， $\text{SiO}_2\text{-PHDG}$  在环氧树脂中能够自组装成以纳米  $\text{SiO}_2$  为核、含磷嵌段 PHDG 为壳的纳米核壳结构，阻燃元素 P、Si 以“捆绑式”均匀分散在基体树脂中，在较低 P、Si 含量 (0.27 %、2.51 %) 下表现出优良的协同阻燃效果 (氧指数 32.8)。DSC 和 DMA 分析表明， $\text{SiO}_2\text{-PHDG}$  的加入使得固化体系交联密度升高，且各组分添加量改性环氧树脂都显示出单一的  $T_g$ ，当  $\text{SiO}_2\text{-PHDG}$  添加量为 3 % 时，DMA 所测  $T_g$  为 170.5 °C、DSC 所测  $T_g$  为 162.1 °C，均高于纯环氧树脂 DMA 和 DSC 所测  $T_g$ ，说明  $\text{SiO}_2\text{-PHDG}$  杂化纳米粒子与环氧树脂相容性良好，并一定程度上提高了环氧树脂的热机械性能；TGA 测试表明，由于 P、Si 优良的协同阻燃效果，阻燃改性环氧树脂的  $T_{d-5\%}$  较纯环氧树脂最高提高 7.6 °C，成炭率最高提高了近 5 倍。

关键词：纳米粒子；嵌段共聚物；无卤阻燃；环氧树脂



## Abstract

Epoxy resin (EP) is a kind of very important thermosetting material, which is widely used in the fields of adhesive, coating, electronic/electrical insulation, and composite applications, due to its low shrinkage, excellent adhesion, superior thermal and mechanical stabilities and excellent chemical resistance. However, the more extended applications of EP is limited by its poor flame resistance properties to some extent. Therefore, more and more attentions have recently been paid to improving the fire resistance of EP. In this paper, a kind of DOPO derivatives named DOPOethyl methacrylate (HEPO) is synthesized. It can be easily performed RAFT polymerisation with glycidyl methacrylate (GMA), getting size controllable phosphorous block copolymer PHEPO<sub>m</sub>-*b*-PGMA<sub>n</sub> (PHDG) and homopolymer PMOEP. After PHDG and PMOEP being grafted onto the surface of SiO<sub>2</sub> nanoparticles, the new type of flame retardant SiO<sub>2</sub>-PHDG and SiO<sub>2</sub>-PMOEP are obtained. Adding SiO<sub>2</sub>-PHDG into the epoxy resin system can form nano core-shell structure with nano SiO<sub>2</sub> acting as the core and phosphorous block copolymer as the shell. Retardant elements P, Si and little N are homogeneously dispersed in epoxy matrix with a “bundled” form, which leads to an excellent synergistic flame retardant effect with a relatively low P and Si content, thus improving the thermal stability of epoxy resin. The main achievements of our work are shown as below:

1. Through molecular designing, we synthesized a kind of DOPO derivatives named DOPOethyl methacrylate (HEPO). Then we synthesized diblock copolymer PHEPO<sub>m</sub>-*b*-PGMA<sub>n</sub> and homopolymer PMOEP via RAFT polymerisation. Furthermore, the structure and thermal properties of these products were characterized by FT-IR, NMR and TGA, which showed that monomer HEPO, the diblock copolymers PHEPO<sub>100</sub>-*b*-PGMA<sub>15</sub> and homopolymer PMOEP<sub>100</sub> had been synthesized successfully.

2. SiO<sub>2</sub> nanoparticles was modified by 3-triethoxysilyl-1-Propanamine (KH-550)

and 3-Glycidyloxypropyl-trimethoxysilane (KH-560) respectively, thus coating the epoxy groups and amino on it. SiO<sub>2</sub>-PHDG hybrid nanoparticles can be prepared by the reaction between the epoxy groups of PHDG and amino groups of SiO<sub>2</sub> surface. SiO<sub>2</sub>-PMOEP hybrid nanoparticles can be obtained through a similar way, replacing epoxy groups of PHDG with P-OH of PMOEP<sub>100</sub>. Furthermore, the structure and thermal properties of these hybrid nanoparticles were characterized by FT-IR, Elemental Analyzer and TGA. Meanwhile, the morphology of core-shell structure hybrid nanoparticles were studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). The study showed that the diblock copolymers PHDG and homopolymer PMOEP<sub>100</sub> had been grafted onto SiO<sub>2</sub> nanoparticles successfully, obtaining a new type of flame retardant core-shell hybrid nanoparticles SiO<sub>2</sub>-PHDG and SiO<sub>2</sub>-PMOEP. The size of SiO<sub>2</sub> core is about 60-80 nm and the thickness of polymer shell is about 5-10 nm. The increase of C element content of SiO<sub>2</sub>-PHDG nanoparticles under 12 hours and 24 hours measured by Elemental Analyzer showed that the weight grafting ratio of the hybrid nanoparticles was 18.9 percent and 30.9 percent respectively. Besides, the weight grafting ratio of SiO<sub>2</sub>-PHDG (12 h), SiO<sub>2</sub>-PHDG (24 h) were respectively 19.8 percent and 31.3 percent which calculated by TGA curve of SiO<sub>2</sub>-NH<sub>2</sub> and SiO<sub>2</sub>-PHDG. The observation and measurement by SEM and TEM indicated that with the extension of grafting reaction time, more and more PHDG were grafted onto SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles, which increased the thickness of polymer layer from 5 nm to 10 nm.

3. The research of flame retardant hybrid nanoparticles SiO<sub>2</sub>-PHDG containing phosphorus and silicon modified epoxy resin. A series of flame retardant epoxy resins composed of different content of phosphorus and silicon were prepared by mixing hybrid nanoparticles SiO<sub>2</sub>-PHDG with diglycidyl ether of bisphenol-A (E51), using 4,4'-diaminodiphenylmethane (DDM) as curing agent. The thermal properties of flame retardant modified epoxy resin were evaluated by dynamic mechanical thermal analysis (DMA), differential scanning calorimetry (DSC) and TGA; The fracture surfaces morphology of flame retardant modified epoxy resin was studied by SEM,

and the flame retardant properties were evaluated by limiting oxygen index (LOI). The research showed that SiO<sub>2</sub>-PHDG could form core-shell structure in E51 with SiO<sub>2</sub> nanoparticles as the core, and phosphorus-containing block PHDG as the shell. Retardant elements P, Si were homogeneously dispersed in epoxy matrix with “bundled” form, which led to an excellent synergistic flame retardant effect (LOI=32.8) under low P and Si content (0.27 %, 2.51 %). DSC and DMA tests showed that the addition of SiO<sub>2</sub>-PHDG made the crosslinking density of the cured systems increased and the epoxy resins modified by different content of SiO<sub>2</sub>-PHDG all exhibited a single T<sub>g</sub>. When the content of SiO<sub>2</sub>-PHDG was 3 %, the T<sub>g</sub> measured by DSC and DMA were 162.1 °C and 170.5 °C that were higher than the ones of the neat epoxy resin, which indicated that the compatibility between SiO<sub>2</sub>-PHDG hybrid nanoparticles and epoxy resins was good and the thermomechanical properties of flame retardant epoxy resins had been improved to some extent. TGA tests showed that because of the excellent synergistic flame retardant effect of phosphorus and silicon, T<sub>d-5%</sub> of the flame retardant modified epoxy resins had mostly been increased 7.6 °C and char yield had mostly been increased fivefold compared to pure epoxy resins.

**Keywords:** nanoparticles; block copolymer; halogen-free flame retardant; epoxy resin

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