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硕　士　学　位　论　文

含硅无卤阻燃环氧树脂的制备及性能研究

The preparation of the silicon-containing halogen-free flame-retardent epoxy resins and their properties

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摘 要

环氧树脂作为一种热固性的高分子，具有许多突出的特性，如较好的耐湿、耐溶剂、耐化学腐蚀性，突出的粘附性，优良的电学和力学性能，广泛应用于铸件、涂料、粘合剂、复合材料等领域，迄今已有 60 多年的历史。但是，它也有两大缺点：（1）阻燃性能差；（2）韧性不佳，冲击性能差；特别是阻燃性能的欠缺成为限制环氧树脂应用的瓶颈因素，如在印制线路板（PWBs）、半导体封装等电子领域，汽车、飞行器等交通领域，由于使用条件苛刻，对环氧树脂的耐热阻燃性能提出了更为严格的要求。

本文在分析了国内外无卤阻燃技术和增韧研究的基础上，设计用含硅化合物对环氧树脂进行改性，使其满足无卤阻燃和增韧要求的技术路线。主要研究内容包括：

（1）含硅环氧单体的合成与表征

以二甲基二乙氧基硅烷、烯丙醇和间氯过氧苯甲酸为原料，采用新方法制备了一种反应型的含硅环氧单体-二缩水甘油氧基二甲基硅烷（DGDMS），用核磁（^{1}H NMR和^{13}C NMR）和红外（FTIR）对其结构进行了表征证明。同时，研究了反应条件对反应产物和反应产率影响，结果表明，酯交换反应时选用苯作为反应溶剂，过酸氧化反应时控制温度在 0℃即可成功合成目标产物DGDMS，产率为 59.2%。

（2）无卤增韧含硅阻燃环氧树脂的制备

将不同含量的反应型含硅环氧单体（DGDMS）加入到普通环氧树脂（DER332）中混合均匀，再与 4, 4′-二氨基二苯砜（DDS）固化剂反应，生成无卤阻燃增韧的多功能环氧树脂。探讨了不同的硅含量对环氧混合体系固化温度的影响，结果表明随着 DGDMS 含量的增加，固化温度逐渐下降（240℃下降到163℃）。

（3）无卤增韧含硅阻燃环氧树脂的性能综合研究

①研究了不同硅含量对改性环氧树脂阻燃性能、力学性能的影响。结果发现，当 DGDMS:DER332 质量比大于 25:75 时，就能实现环氧树脂的阻燃目的

（LOI>27），且对固化体系的力学性能没有明显不利的影响。

②利用 TGA 对不同硅含量改性环氧树脂的热分解行为进行了比较研究。结果表明，在空气和氮气中，随着硅含量增加，环氧体系的残炭率逐渐增大，初始分解逐渐降低。

③研究了不同硅含量对改性环氧树脂热力学性能的影响。结果发现，随着 DGDMS 含量的增加，环氧体系的玻璃化温度逐渐下降（229℃下降到 101℃），同时间接证明了 DGDMS 对环氧树脂具有增韧作用。

④利用 SEM 研究了不同硅含量对改性环氧树脂体系韧性的影响。结果表明，不同硅含量的环氧体系呈单一均相，没有出现相分离现象，同时随着硅含量增加，环氧体系韧性断裂的趋势逐渐增大，说明在普通商用环氧树脂中引入 DGDMS 后，体系韧性可明显得到改善。

综上所述，通过将反应型含硅环氧单体 DGDMS 引入环氧树脂 DER332 中，体系的阻燃性能优异、热稳定性高、力学和韧性较好，具有良好的应用前景。

关键词：二缩水甘油氧基二甲基硅烷 含硅环氧树脂 增韧 阻燃剂

Abstract

Epoxy resins, as a type of thermoset polymers, are commercially available for about 60 years and are widely used in many fields, such as castings, coatings, adhensives, composite applications and so on, owing to their excellent characteristics such as great versatility, good moisture, solvent and chemical resistance, outstanding adhesion, superior electrical and mechanical properties. However, poor flammability and poor toughness are the two main intrinsic disadvantages that epoxy resins have. Particularly, the poor flammability of the epoxy resins is a major limitation for their applications in many fields such as electronics (printed wiring boards and semiconductor encapsulation) and transportation (automobiles and aircraft).

On the basis of analyzing the previous works, the design of silicon-containing compound modifying epoxy resins was adopted to halogen-free flame retardant and toughening requirements. The main research contents include:

(1)Synthesis and characterization of silicon-containing epoxy monomers

The reactive silicon-containing monomer called diglycidyloxydimethyl silane (DGDMS) was synthesized from diethoxydimethyl silane, allyl alcohol and m-chloroperbenzoic acid by a new method. The NMR (^{1}H NMR and ^{13}C NMR) spectra and FTIR spectra show that DGDMS was synthesized successfully as it designed. In addition, the effect on reaction condition and yield of the product was discussed and the results indicated that DGDMS was successfully obtained in a 59.2% yield when we used benzene as a solvent to the transesterification and controlled the temperature at 0 ^{o}C to the further epoxidation.

(2)Preparation of halogen-free, toughening and silicon-containing flame retardant epoxy resins

To obtain halogen-free, toughening and silicon-containing flame retardant multifunctional epoxy resins, the reactive silicon-containing monomers were blended in various portions with DER 332 and cured by stoichiometric amounts of diamine type 4, 4´-diaminodiphenyl sulfone (DDS) curing agent. The effect of silicon content on the mixed epoxy system of DGDMS/DER 332/DDS was discussed. The results show that the curing temperatures of mixed epoxy system decreases from 240 ^{o}C to 163 ^{o}C when the DGDMS content increases.

(3)Comprehensive study of the properties about halogen-free, toughening and silicon-containing flame retardant epoxy resins

①The relation of silicon content versus the flame retardant and mechanical properties of modifying epoxy resins was evaluated and the results indicated that the flame retardancy in epoxy resins was evidently improved (LOI>27) when the DGDMS/DER 332 mass ratio is grater than 25:75. Moreover, the original physical and mechanical properties are maintained.

②The thermal stability and decomposition behavior of the mixed epoxy system of DGDMS/DER 332/DDS were investigated by TGA from all proportions. When the silicon content increases, the onset decomposition temperature ($T_{5\%}$) of the mixed epoxy system obviously decreases in air and nitrogen, while the char yield at 700 ^{o}C increases significantly with the silicon content increased.

③The influence of silicon content on thermodynamic properties of the modified epoxy resins was studied. The Tg values decrease continuously from 229 ^{o}C to 101^{o}C as the DGDMS content increases, which indirectly proves that DGDMS can toughen epoxy resins effectively.

④To investigate the toughness of the mixed epoxy system of DGDMS/DER 332/DDS directly, the section morphology of the mixed systems were studied by SEM. All mixed epoxy systems with different silicon-containing show that there are no phase separations. Additionally, with the DGDMS content increases, the sections of the mixed epoxy resins become more and more folded and the fracture direction gets more dispersive, which presents the features of the ductile rupture.

In conclusion, the reactive silicon-containing epoxy monomers (DGDMS), which covalently incorporates halogen-free fire retardant element-silicon into polymer chains, is recognized to be the efficient means of permanently improving flame retardancy in epoxy resins and is considered to be the novel ways to reducing internal compressive stress availably to toughen the epoxy resins.

Key Words: Diglycidyloxydimethyl silane; Silicon-containing epoxy resins; Toughen; Flame retardant

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