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酚醛树脂改性脲醛树脂胶黏剂的研究进展

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摘　要:脲醛树脂是一种氨基树脂类热固性合成树脂,是尿素和甲醛在碱性或酸性催化剂作用下,经加成反应、缩聚反应生成的缩聚物. 脲醛树脂具有原料廉价易得、制造工艺简单,无色透明,对木质纤维素有优良的粘附力,是木材胶黏剂中用量最大的品种,约占木材液胶黏剂的 80%以上,主要用于胶合板、刨花板、密度纤维板等的粘接. 脲醛树脂胶黏剂有两个主要的缺点:游离甲醛释放和耐水性差,是脲醛树脂在实际生产应用中亟待解决的问题. 酚醛树脂被广泛地用于提高脲醛树脂胶黏剂的耐水性及降低脲醛树脂胶黏剂的游离甲醛的含量. 介绍了酚醛树脂对脲醛树脂胶黏剂的改性技术,综述了国内外酚醛树脂改性脲醛树脂胶黏剂的研究现状,并对其发展前景提出了展望.

关键词:脲醛树脂;苯酚;低甲醛;改性技术;
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0　引　言

脲醛树脂具有原料廉价易得、制造工艺简单,无色透明,对木质纤维素有优良的粘附力,不污染木材等优点, 是木材胶黏剂中用量最大的品种,约占木材液胶黏剂的 80%以上,主要用于胶合板、刨花板、中密度纤维板等的粘接. 但是,脲醛树脂胶黏剂存在游离甲醛含量高、固化物脆性大、耐水性差、耐老化性较差等缺点[1-5]. 通过降低甲醛尿素摩尔比、改进制备工艺、改善固化条件等方法可以降低脲醛树脂的游离甲醛释放量以及耐水性和耐老化性能[6-8]. 此外,还可通过加入不同改性剂如三聚氰胺[9]、苯酚[10]、单宁[11]、缩水甘油醚[12]、白乳胶[13]等来提高脲醛树脂的综合性能. 其中有关三聚氰胺和苯酚改性脲醛树脂的研究报道较多. 通过三聚氰胺或苯酚与尿素、甲醛共缩聚,可以综合利用三醛树脂的优点,使三醛树脂的性能得到互补,达到降低生产成本,提高木材胶黏剂综合性能,满足不同胶接制品使用要求的目的. 近些年,有关三聚氰胺改性脲醛树脂的综述报道较多[14-15],较系统的报道酚醛树脂改性脲醛树脂的综述较少[16-17]. 基于此,本研究综述了酚醛树脂改性脲醛树脂胶黏剂的改性技术并对酚醛树脂树脂改性脲醛树脂胶黏剂的发展前景提出了展望.

1　酚醛树脂改性脲醛树脂的化学基础

酚醛树脂具有优良的胶接性、耐热性、耐水性以及化学稳定性好等优点,广泛应用于木材工业中. 但是酚醛树脂也存在着固化速率慢、固化后的胶层较脆、易龟裂、成本较脲醛树脂的成本贵、苯酚毒性较大等缺点[18-19]. 从物料性能看,用酚醛树脂改性脲醛树脂是可行的,利用酚醛树脂改性脲醛树脂可以克服各自的缺点. 利用苯环的疏水性提高脲醛树脂的耐水性;利用苯酚与甲醛反应平衡常数比较大的特点,降低改性脲醛树脂的游离甲醛含量. 用酚醛树脂改性脲醛树脂的优点在于使用少量的酚醛树脂达到改性要求,在增加较少成本的基础上,改善脲醛树脂胶黏剂的胶接性能,降低脲醛树脂游离甲醛的含量. 酚醛树脂中含有较多的反应性官能团羟甲基(—CH_2OH),在一定条件下对许多化合物都有较高的反应活性,比较容易进行脱水缩合反应. 酚醛树脂改性脲醛树脂胶黏剂是通过酚醛树脂的羟甲基与脲醛树脂的羟甲基、氨基或亚氨基等含有活泼氢的基团发生化学反应形成共价键. 据文献报道,酚醛树脂中的羟甲基可以和脲醛树脂的羟甲基或氨基分别生成醚键或亚甲基键[20-22],减少脲醛树脂分子结构中的羟基数目,达到改善脲醛树脂耐水性的目的. 在脲醛树脂分

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子结构中引入刚性的苯环使得固化后的产品机械强度提高.

2 酚醛树脂改性脲醛树脂的改性技术

分析总结有关酚醛树脂改性脲醛树脂胶黏剂的报道研究,酚醛树脂改性脲醛树脂的改性方法主要分为三种:一是直接利用苯酚、尿素与甲醛在碱性条件下进行羟甲基化反应,即反应早期加入苯酚进行反应改性;二是利用分子量较高的酚醛树脂改性脲醛树脂;三是利用小分子的酚醛衍生物改性脲醛树脂. 下面分别进行介绍.

2.1 直接利用苯酚、尿素和甲醛制备改性脲醛树脂胶黏剂

采用苯酚、尿素、甲醛在分子水平上进行共缩聚的方式是一种比较常用的制备苯酚改性脲醛树脂的方法. 该方法主要是通过在脲醛树脂制备过程中添加一定量的苯酚作为改性剂来制备改性脲醛树脂[23-30],如徐亮等[25]以苯酚、尿素和甲醛为原料,在 90 ℃条件下缩聚反应制备苯酚-尿素-甲醛共缩聚树脂,制备的改性树脂游离甲醛质量分数小于0.3%,游离苯酚质量分数小于 0.5 %,采用该改性树脂压制的胶合板力学性能较好, 板材甲醛释放量符合 GB18580-2001E2 级水平; 刘璇等[28]研究了以苯酚和聚乙烯醇作为改性剂脲醛树脂性能的影响,研究结果表明:将苯环引入到脲醛树脂结构中提高了改性脲醛树脂的胶接强度,脲醛树脂的耐水性也得到改善,同时由于引入了柔性的聚乙烯醇分子链, 固化后的改性脲醛树脂的韧性和抗老化性能也得到了改善. 值得一提的是,Fan 等[30]研究表明,利用苯酚与羟甲基脲反应可以制备无醛胶黏剂,为制备环保型甲醛脲醛树脂提供了一个新的途径.

通过直接在脲醛树脂制备过程添加苯酚作为改性剂来制备苯酚改性脲醛树脂具有操作简便的优点,但是该方法存在一个缺点,制备的改性胶中苯酚残留量较大,这是由于相同 pH 条件下,尿素与甲醛反应速率大于苯酚与甲醛的反应速率,因而在脲醛树脂制备的 pH 反应时间条件下,部分苯酚未能与甲醛反应生成相应的羟甲基酚,造成苯酚残留.

2.2 利用分子量较高的酚醛树脂改性脲醛树脂

利用分子量较高的酚醛树脂改性脲醛树脂包括共混法和化学改性法. 共混法是指先分别制备酚醛树脂和脲醛树脂,然后按比例混合. 共混法制备工艺比较繁琐,制备得到的分子量较高的酚醛树脂与脲醛树脂的相容性较差,混合后贮存稳定性差,此外,从已有的试验结果看,无论是将酚醛树脂胶的 pH 调低后再混合,还是混合后再调低 pH 值,都常常因为结块而无法使用[1],因而共混法用的比较少;化学改性法是指先在碱性、较高的反应温度条件下使苯酚和甲醛反应,生成分子量较高的水溶性酚醛树脂,然后添加尿素和甲醛,在较低温度下反应制得改性脲醛树脂[30-36]. 如申迎华等[31]利用化学改性法在碱性条件下制备得到低游离酚、低游离甲醛含量,水溶性、贮存性好,原料成本低的酚醛树脂改性脲醛树脂胶黏剂;范东斌课题组[33-34]利用化学改性法首先在碱性环境下制备分子量合适的酚醛树脂, 然后在碱性条件下添加不同量的尿素继续反应一段时间制得改性树脂,研究结果表明,随着尿素用量的增加,改性树脂的胶接性能下降,此外,范东斌课题组[35]还研究了碱性环境下水溶性酚醛树脂与羟甲脲化合物反应一段时间制得改性树脂的固化性能,研究结果表明,氧化锌、氧化镁等化合物可以加速改性树脂的固化,提高改性树脂的固化效率.

从所检索到的文献分析,化学改性法制备较高分子量的酚醛树脂改性脲醛树脂具有一个大致相同的共性,就是碱性条件下制备分子量较高的酚醛树脂,然后添加适量的尿素或脲醛中间体如羟甲基脲等制备得到改性树脂. 该方法具有操作简便以及制备的改性树脂能够满足多数木材的胶接要求,同时,该方法也存在一定的不足,比如,尿素的添加量有限造成成本的降低受到限制;碱性条件下羟甲基间容易形成不稳定的醚键以及尿素和酚醛树脂在碱性条件下的反应机理有待进一步完善.

2.3 利用小分子量的酚醛衍生物改性脲醛树脂

在碱性条件及较低的温度条件下, 甲醛和苯酚进行加成反应, 生成各种小分子的羟甲基苯酚化合物,其反应机理如图 1 所示[37]. 有文献报道,苯酚和甲醛在强碱性条件下可以高效地转化为多羟甲基苯酚[38-40],其中三羟甲基苯酚是最主要的酚醛中间体之一,采用小分子量的酚醛衍生物改性脲醛树脂可以克服相同 pH 条件下,苯酚、尿素与甲醛反应速率相差太大的缺点,也可以避免苯酚在脲醛树脂中的残留,此外小分子量的酚醛衍生物的水溶性较好.

Tomita B 等[20]提出了一种利用三羟甲基苯酚与尿素的反应来制备苯酚改性脲醛树脂. 该方法是通过三羟甲基苯酚与尿素在酸性条件下共缩聚

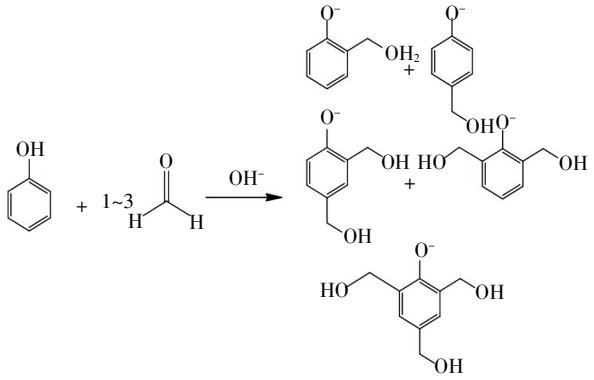

图 1　碱性条件下苯酚与甲醛反应示意图

Fig.1　Reaction schematic of phenol and formaldehyde under alkali condition

反应制备得到,制备示意图如图 2 所示. Tomita B 指出,酸性条件下,三羟甲基苯酚与尿素以共缩聚为主,羟甲基苯酚间羟甲基间的缩合很少,可以忽略. 利用三羟甲基苯酚与尿素反应制备的树脂可以降低树脂中甲醛的含量,也可以提高树脂的耐水性. 该报道的贡献在于证明了可以从小分子中间体的角度出发制备低毒的木材用胶黏剂,为环保型胶黏剂的开发提供了新的思路.

荣磊等[41]研究了多羟甲基苯酚以不同的投料方式对脲醛树脂性能的影响. 研究表明,多羟甲基苯酚在脲醛树脂制备后期加入,可以有效利用低甲醛尿素摩尔比的脲醛树脂中后加入的尿素来提高

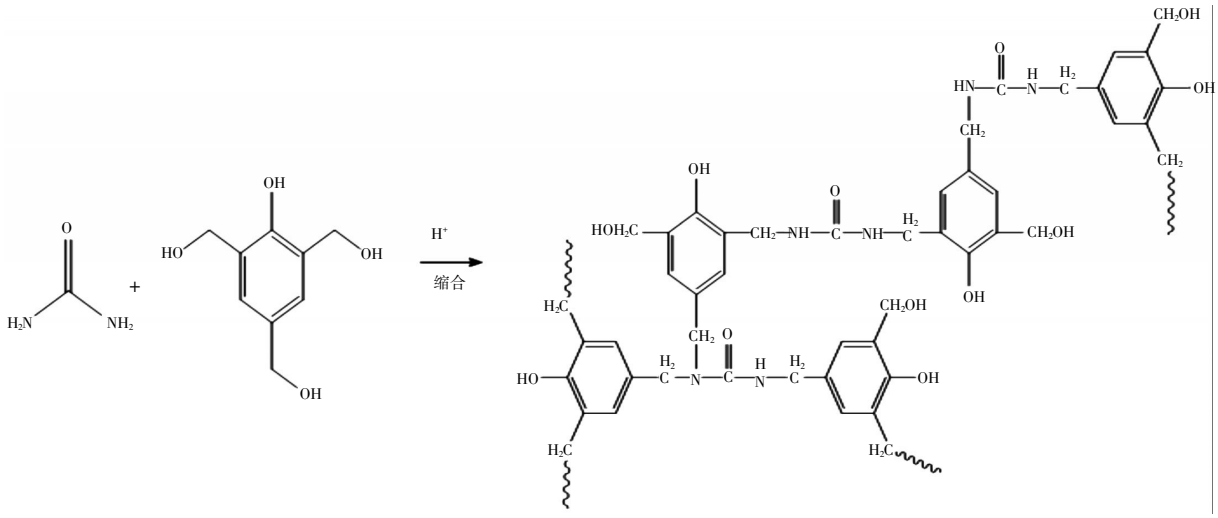

图 2　酸性条件下三羟甲基苯酚与尿素反应示意图

Fig.2　Reaction schematic of trimethylol phenol and urea under acid condition

粘接强度的目的,通过引入苯环提高改性脲醛树脂的耐水性能.

Zhang Y F 等[42]研究了弱碱–弱酸–弱碱工艺条件下三羟甲基苯酚盐对脲醛树脂性能的影响. 研究表明,少量的三羟甲基苯酚盐就可以对脲醛树脂中游离甲醛起到明显的降低作用,而且通过改性树脂浸渍滤纸的拉伸实验表明,三羟甲基苯酚可以提高浸渍滤纸的拉伸强度. 不足之处在于添加了三羟甲基苯酚盐后,固化的浸渍滤纸脆性比较大,此外,关于三羟甲基苯酚参与脲醛树脂的反应机理分析的不够透彻.

由于酚醛树脂在改性脲醛树脂反应机理有待进一步探究,加上本身制备工艺的多样化,导致各研究之间对酚醛树脂改性脲醛树脂的分子结构的探究有所出入,值得肯定的是,从大部分制成的酚醛树脂改性脲醛树脂胶的综合性能来看,可以认为酚醛树脂和脲醛树脂之间存在某种反应. 具体的反应机理有待进一步研究.

3　结　语

开发高性能的脲醛树脂胶黏剂是脲醛树脂胶黏剂的发展趋势. 酚醛树脂改性脲醛树脂可以发挥酚醛树脂和脲醛树脂的优点, 可用于绿色人造板的生产,具有广阔的应用前景. 今后的研究方向可以从理论角度分析酚醛树脂对脲醛树脂中甲醛影响规律及对脲醛树脂稳定性和相容性的影响因素,指导稳定的高固含量的低毒酚醛树脂改性脲醛树脂胶黏剂的合成并使其制备工艺趋于多样化和成熟稳定方向发展.

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Research progress on phenol formaldehyde resin modified urea formaldehyde resin adhesives

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Abstract: Urea formaldehyde resin, a kind of thermosetting amino resin, was prepared by the reaction between urea and formaldehyde under alkaline or acidic catalyst. Urea-formaldehyde resin has been widely used as adhesives for wood-based panel such as plywood, particleboards and density fiberboards because of their excellent properties including low cost, fast curing, colorless and excellent adhesion to wood. Nevertheless, their main drawbacks are low water resistance and emission of formaldehyde from the wood panels, which are critical problems to be solved in actual application. Phenol formaldehyde resin (PF) has been widely used to improve the water resistance of urea formaldehyde resin (UF) and to reduce the formaldehyde content of UF adhesives. The modification technology of UF adhesives with PF was presented. Current research progress of PF modified UF adhesive was reviewed and the trends in the future were prospected.

Keywords: urea formaldehyde resin; phenol; low formaldehyde content; modification technology;

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Synthesis and application of zinc sulfide quantum dots/graphite-like carbon nitride heterojunction

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Abstract: Zinc sulfide quantum dots/graphite-like carbon nitride heterojunction photoelectrocatalyst was synthesized by solvothermal method and mixing composite. The structure, composition, morphology, and optoelectrical properties of the as-prepared Zinc sulfide quantum dots/graphite-like carbon nitride composites were characterized by X-rays diffractometer, energy dispersive spectrometer, X-ray photoelectron spectrometer, transmission electron microscopy and UV-visible spectroscopy, respectively. The results show that Zinc sulfide quantum dots/graphite-like carbon nitride with ratio of 1:9 exhibits the highest photocatalytic activity for the degradation of RhB, and the degradation rate is 0.802 4 h^{-1}. At 2.5 h, the degradation rate is 86.7%, which is 41.7% higher than that of pure graphite-like carbon nitride. By comparing the samples with different compound methods, the result reveals that photoelectrocatalysis activity of mixing composite samples is significantly higher than that of grinding calcined samples.

Keywords: zinc sulfide quantum dots/graphite-like carbon nitride; heterojunction; solvothermal method; photoelectrocatalysis activity

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