

摘 要

聚酯酰胺(PEAs)由于结合了聚酯良好的生物降解性能和聚酰胺优异的力学性能、加工性能而受到越来越多研究者的重视。

本文在聚酯酰胺的合成中引入多官能团支化剂,如季戊四醇(PAT)、丙三醇(GL)、酒石酸(TA)和柠檬酸等,以己二酸(AA)、1,4-丁二醇(1,4-BD)、己二胺(HMDA)和己内酰胺(CLM)为单体,通过熔融缩聚法合成了脂肪族的聚酯酰胺。利用FT-IR、 ^1H NMR、DSC、TG等技术对产物的结构和性能进行了表征,并讨论了聚合物的溶解性能以及支化对亲水性的影响。实验发现,季戊四醇和丙三醇是理想的支化剂,能有效提高产物熔体粘度、缩短反应时间,提高产物分子量。以酒石酸为支化剂时效果不明显,以柠檬酸为支化剂时得不到高分子量物质。适宜的季戊四醇和丙三醇加入量分别为单体总量的1%和0.9%以下。随着支化剂含量的升高,聚合物中酯/酰胺链段的含量比升高;PEAs的熔点和结晶温度下降;聚合物的热稳定性下降。聚酯酰胺溶解性能与聚酰胺相似,易溶于间甲酚中。支化链的引入对聚酯酰胺的亲水性影响甚微。

本论文首次研究了支化结构的脂肪族聚酯酰胺的水解降解行为,并用FT-IR、 ^1H NMR、DSC和SEM技术对聚合物在降解过程中的结构和性能变化进行了表征。实验结果表明聚酯酰胺在水溶液中的降解是以酯键水解断裂为主导的过程。

随着支化剂含量的升高,聚酯酰胺在水溶液中降解加快。原因可以归结为:PEAs中酯/酰胺链段比随着支化剂含量的升高而升高,而聚酯酰胺的水解降解又以酯键水解断裂为主;其次,短支化链的引入,一方面使聚合物的结晶度下降,水更易进攻聚合物分子而加快降解,另一方面使链末端基数量增多,从而促进PEAs的降解;由降解残留物形成的酸性微环境客观上也加快了降解。在三个系列的支化聚合物中,酒石酸支化PEAs具有最快的水解降解速度。

本文初步研究了聚酯酰胺薄膜在自然环境中的降解行为,并用FT-IR、 ^1H NMR和SEM技术对降解过程中的聚合物进行了研究。在室内高浓度氧、潮湿环境中,降解主要以杆状细菌的腐蚀开始,初期以酰胺键断裂为主要机制。土壤掩埋降解初期以酯键断裂为主导过程,后期开始受到细菌侵袭而降解。这两项实验表明所合成的脂肪族聚酯酰胺是可生物降解的。在三个系列的支化聚合物中,酒石酸支化PEAs

在自然环境中具有最快的降解速度。

本文首次制备了天然苧麻纤维/PEAs 的复合材料。利用 FT-IR、TG、DSC 和 SEM 技术分析了复合材料的性能，并研究了材料的水解降解行为及其影响因素。苧麻原麻纤维经脱胶、丝光、表面浸渍 PEAs 处理后，与聚酯酰胺间的界面粘合能力提高；复合材料的热稳定性介于纤维和基体树脂 PEAs 之间，脱胶处理有助于提高复合材料的热稳定性；与苧麻纤维复合后，聚酯酰胺的结晶能力有所提高；材料的亲水性提高。

苧麻纤维/PEAs 复合材料在水溶液中的降解过程，首先是基体树脂 PEAs 的水解降解过程。一般地，纤维含量越高，纤维与聚酯酰胺界面结合越紧密，材料的水解降解越慢；复合材料内纤维较长时，降解速度较快。复合材料在碱性溶液中降解最快，而在酸性和中性环境中降解较慢；由于水分子极易侵入材料内部而迅速达到吸水平衡，因而环境温度和材料的尺寸大小对复合材料的降解速率影响不大。

关键词：聚酯酰胺；支化；苧麻纤维/聚酯酰胺复合物；降解

Preparation and degradation study of aliphatic branched poly(ester amide)s and their natural fiber Composites

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Abstract

Poly(ester amide)s have been interested more recently since they encompassed the degradability of polyesters with the good mechanical and processing properties of polyamides.

In this paper, branching agents, such as pentaerythritol (PAT), glycerol (GL), tartaric acid (TA) or citric acid were introduced in the synthesis of aliphatic poly(ester amide)s. The polymers were prepared from adipic acid (AA), 1,4-butanediol(1,4-BD), hexamethylene diamine(HMDA) and caprolactam(CLM) by melt polycondensation method. The obtained polymers were characterized by FT-IR, ^1H NMR, DSC and TG analysis et al. It has been turned out that introduction of PAT or GL could increase the melt viscosity and molecular weight of products, and shorten the reaction time. The effect of TA was not very good. For citric acid, it even could not obtain high-molecular-weight polymer. The feasible content of PAT is under 1.0% of monomers, and for GL it is under 0.9%. With the increase of branching agent content, the ester/amide ratio increased; the melting and crystallization temperatures decreased, and thermal stability of polymers decreased slightly. The solubility of PEAs is similar to aliphatic polyamides. They are easily soluble in m-cresol. Branching scarcely affects the hydrophilicity of PEAs.

The hydrolytic degradation of linear or branched PEAs was performed and characterized by FT-IR, ^1H NMR, DSC and SEM techniques. It showed that PEAs are degradable in aqueous solutions, mainly involving the cleavage of ester linkages.

With the increase of braching agent contents, the hydrolytic degradation rate increased, which was attributed to as: the increasing ratio of ester/amide linkages; the decreasing crystallinity by branching and increasing amount of end groups; and the micro-acidic environments around the acidic degradation products. PEAs branched by TA

showed the highest hydrolytic degradation rate.

A preliminary study of PEAs in different natural environments was performed. When PEAs were exposed in environments with high concentration of O₂ and moisture, they could be eroded by bacillus, and the early stage of biodegradation was involved with the breakage of amide bonds. In soil burial test, it showed that cleavage of ester linkages was the primary process; bacillus was also found on the surface of PEAs. It indicated that aliphatic PEAs were biodegradable. PEAs branched by TA showed the highest degradation rate in both environments.

Finally, we prepared full-biodegradable ramie fiber/PEA composites, and studied the influence of chemical surface modification on the properties of composites by FT-IR, TGA, DSC and SEM techniques. After dewaxing, mercerization or being wetted by PEA solution, the adhesion between matrix polymer and fiber was strengthened.

The thermal stability of composites was between the ramie fiber and PEA, and dewaxing is helpful to improve the stability of composite. PEA can be induced to crystallize by ramie fiber. The hydrophilicity of composites was enhanced by the hydrophilic ramie fiber. And the surface modification of fibers had great effect on the water absorption of composites.

The hydrolytic degradation of ramie fiber/PEA composites was also investigated. The main process was the hydrolytic degradation of PEA. Generally, with the increase of fiber content, the degradation rate decreased. The closer between the matrix and fiber interface, the slower the degradation. The composites degraded more quickly in alkaline than in acidic or neutral solutions. Because water adsorption equilibrium can be reached quickly, the temperature and size of samples showed little influence on the degradation of composites.

Keywords : Poly(ester amide)s (PEAs); Branching; Ramie fiber/PEA composite; Degradation

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简 写 列 表

在本文中使用到的英文简写如下表所示:

1,4-BD: 1,4-butanediol, 1,4-丁二醇;

AA: adipic acid, 己二酸;

CLM: caprolactam, 己内酰胺;

GL: glycerol, 丙三醇;

HMDA: hexamethylenediamine, 己二胺;

Merramie: mercerized ramie, 丝光苧麻纤维;

Merramie (x%)/PEA: 丝光苧麻纤维/PEA 复合物, x%为丝光苧麻纤维重量百分比;

PAT: pentaerythritol, 季戊四醇;

PEAgx: 丙三醇支化聚酯酰胺, x 为丙三醇相对含量;

PEApx: 季戊四醇支化聚酯酰胺, x 为季戊四醇相对含量;

PEAs: poly(ester amide)s, 聚酯酰胺;

PEATx: 酒石酸支化聚酯酰胺, x 为酒石酸相对含量;

Ramie(x%)/PEA: 苧麻原麻纤维 PEA 复合物, x%为苧麻原麻纤维重量百分比;

Reframie: refined ramie, 精干苧麻纤维;

Reframie (x%)/PEA: 精干苧麻纤维/PEA 复合物, x%为精干苧麻纤维重量百分比;

TA: tartaric acid, 酒石酸。

