

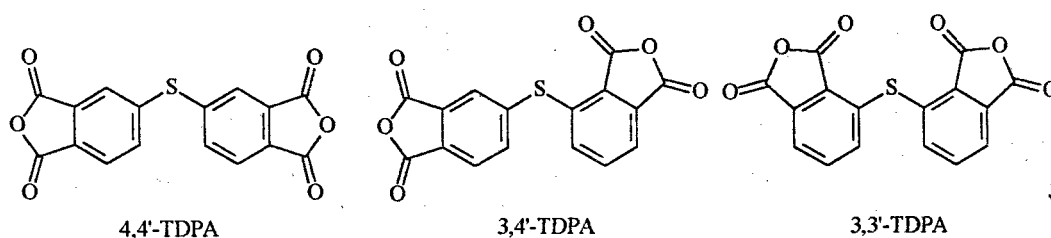
# Polyimides for resin transfer molding

Zhen Wang<sup>1</sup>, Min Zhang<sup>1</sup>, Lianxun Gao<sup>1</sup>, Mengxian Ding<sup>1</sup>,  
Xiaosu Yi<sup>2</sup>, Hongyun Li<sup>2</sup>

1. The State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China
2. The National Key Laboratory of Advanced Composites, Beijing Institute of Aeronautical Materials, Beijing, 100095, P. R. China

Most research of PIs was focused on 4,4-bridged dianhydride in the past decades. Recently, isomeric of PIs based on 3,3- and 3,4- bridged dianhydride are attracted much attention for their unique properties, different from conventional PIs based on 4,4-bridged dianhydride. Most of the dianhydrides, such as biphenyltetracarboxylic dianhydride (BPDA), oxydiphthalic dianhydride (ODPA), thiodiphthalic dianhydride (TDPA), etc. can be synthesized by 3- or 4-chlorophthalic anhydride. We found that isomeric polyimides based on asymmetric dianhydride showed better solubility and processing ability than that based on symmetric dianhydride, while they hold the thermo-stability and mechanical property in about the same level.

PMR (in situ Polymerization of Monomer Reactants) type polyimides (PIs) are well known for their outstanding high temperature resistance, mechanical properties, and good processability. It can lead to substantial component and vehicle weight reduction. Processing of PMR resin is limited in prepreg-based method, which are extremely low efficiency. And the fabrication of high quality complex shaped composite structures is difficult using autoclave technique. Resin transfer molding (RTM) offers an alternative method, which can reduce component fabrication costs by as much as 50% over compression or autoclave processing of prepreg materials. Most PMR PIs endcapped with norbonene are crosslinked above 250°C, which viscosity is usually above 100Pa·s at that time. While, phenylethynyl terminated imide (PETI) oligomers are cured at above 350°C, which can up-broaden the processing window and stable viscosity below 300°C for more than 2h. Thus, PETI oligomer become one of the candidate materials for RTM.



2HEC  
+ODA

浸透性佳  
好打!

Three isomers of thiodiphthalic anhydride (TDPA) were prepared starting from 3- and 4-chlorophthalic anhydride. The polyimides based on TDPA and ODA end-capped with phenylethynyl phthalic anhydride were synthesized by the conventional procedure. Three PIs resin's rheological behavior is shown in Figure 1. We can see the three oligomers based on TDPA exhibit very low viscosity from 250 to 350°C, which are much lower than the viscosity of PMR-15. The lowest viscosity of the oligomers is 1.5Pa·s at 310°C. The resin's viscosity increase only after the temperature reaches 325°C, showing more broadened window than PMR-15 resin to process. The processing window is lifted about 100°C compared with nadic endcapping. A series of copolyimides with different percent weight of TDPA show the viscosity below 1 Pa·s

(shown in Figure 2) at high temperature. The viscosity of polyimide resin increase no more than 1Pa.s within 120min(260°C and 280°C), which show polyimide resin at high temperature is quite stable (shown in figure 3). The temperature of 5% weight loss of cured resins in air are above 500 °C. Study on the PIs resins based on TDPA demonstrates a promising potential application for advanced materials via resin transfer molding processing. Further studying on polyimide for RTM processing is still undergoing in our lab.

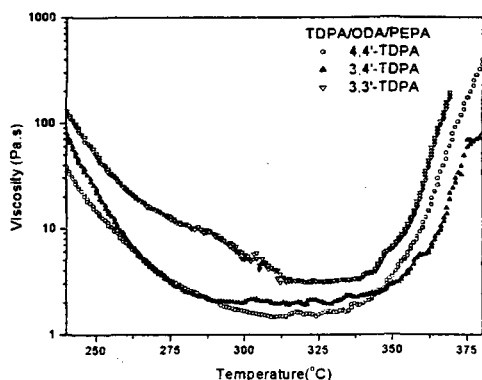


Fig.1 The rheological behavior of polyimides

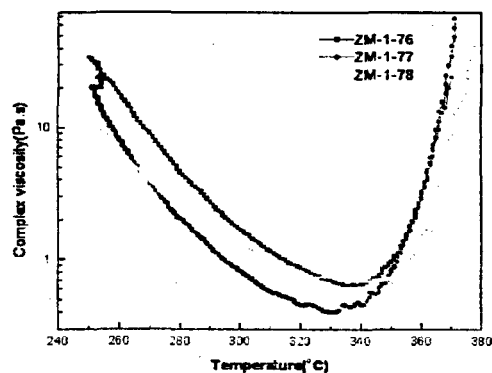


Fig.2 The rheological behavior of polyimides

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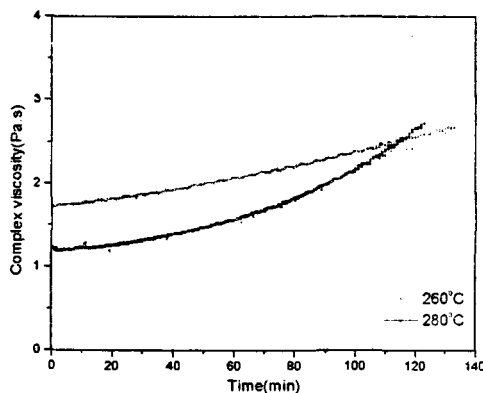


Fig.3 The stability of polyimides resin at high temperature

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#### ACKNOWLEDGEMENT:

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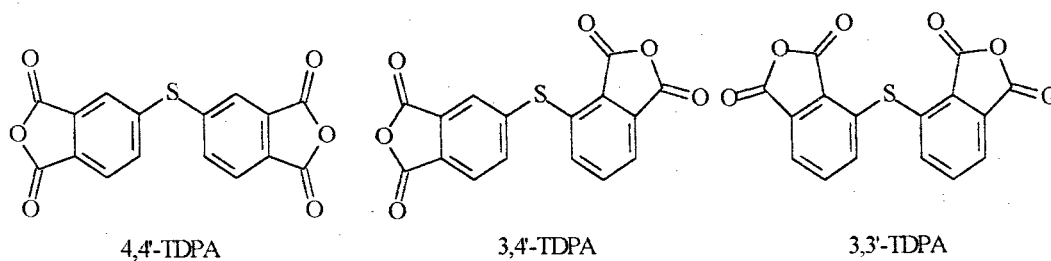
# RTM 成型工艺用聚酰亚胺树脂

王震\* 张敏 高连勋 丁孟贤 苏效益 李宏远

摘要: 本文报道了具有低熔体粘度和高熔融稳定性的聚酰亚胺, 还讨论了它在高温下的流变行为以及粘度稳定性。

在过去关于聚酰亚胺的研究都集中在 4, 4-位桥连二酐上。近年来, 基于 3, 3-位和 4, 4-位二酐的异构聚酰亚胺的研究引起了人们的关注。异构聚酰亚胺拥有独特的性质, 如较高的  $T_g$ , 较低的熔体粘度, 相当的机械性能。大部分二酐比如联苯二酐 (BPDA)、二苯醚二酐 (ODPA)、二苯硫醚二酐 (TDPA) 等都可以由 3-位或 4-位氯代苯酐直接合成。

我们发现基于不对称二酐的异构聚酰亚胺在保持热稳定性和机械性能的基础上拥有高的溶解性和可加工性。众所周知 PMR 型聚酰亚胺具有高的耐温稳定性, 良好的机械性能和可加工性, 已经成为制备热固性聚酰亚胺复合材料的最主要原料。但它也仍存在许多缺点, 只能采用低效率的预浸料模压方法制备简单制品, 无法加工为复杂制品。树脂转移模塑 (RTM) 成型工艺提供了可选择的方法来加工复杂制品以及大幅度降低加工成本 50% 和提高工作效率。大部分 PMR 型聚酰亚胺以 NA 封端, 在 250°C 以上就开始发生交联, 粘度在 100Pa.s 左右。而以苯乙炔封端的 PETI 低聚物则在 350°C 以上才开始交联, 300°C 以下的粘度可以稳定在 2 小时以上, 加工窗口向高温端变宽。因此, PETI 低聚物是适于 RTM 树脂的最佳选择。



这三种 TDPA 异构体由 3-位或 4-位氯代苯酐直接合成。以 PEPA 封端的基于 TDPA 和 ODA 的聚酰亚胺由传统方法合成。这三种 PIs 的流变行为见图 1。我们可以看出三种 TDPA 低聚物在 250°C 到 350°C 的粘度远远低于 PMR-15。低聚物在 310°C 达到最低粘度为 1.5Pa.s, 325°C 之后粘度才开始上升, 加工窗口远远宽于 PMR-15 树脂。比 NA 封端的加工窗口提高 100°C。一系列的不同配比的异构 TDPA 共聚的高温熔体粘度低于 1Pa.s (见

图 2), 该树脂粘度在 1Pa.s 以下保持 2 小时 (260°C 到 2805%), 显示了树脂的高温稳定性 (见图 3), 5% 的热失重均在在 500°C 以上。对基于异构 TDPA 的 PIs 树脂的研究表明 RTM 成型加工的复合材料聚酰亚胺树脂有着更为广阔的应用前景。我们实验室正在进一步深入的研究聚酰亚胺 RTM 树脂。

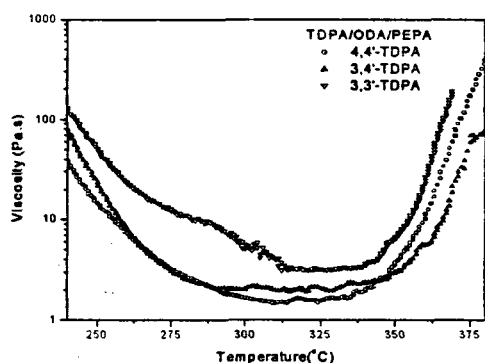


图 1. 聚酰亚胺树脂的流变行为

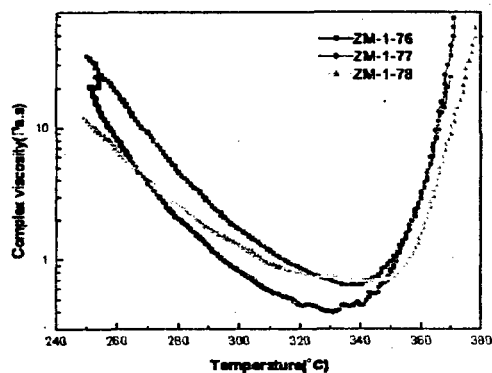


图 2. 共聚聚酰亚胺的流变行为

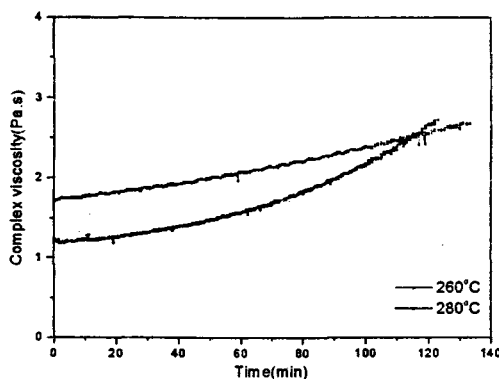


图 3. PI 树脂的高温稳定性

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通信联系人: 王震, wangzhen@ciac.jl.cn

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