

Wood fiber-polycaprolactone-polylactic acid "core-shell-shell" toughened polylactic acid composites and toughening mechanism study

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Abstract: This study aims to improve the compatibility and toughness of wood fiber/poly(lactic acid) (WF/PLA) composites by employing a surface-initiated ring-opening polymerization (SI-ROP) approach. The method involves fabricating a "core-shell-shell" structure with wood fibers at the core, a poly(caprolactone) (PCL) rubber shell layer, and an outer poly(lactic acid) (PLA) shell layer. The WF-rD-PLA/PLA composites were fabricated via melt blending and extrusion. The chemical structure, crystalline properties, morphology, thermal and thermal degradation properties, tensile properties and impact strength were comprehensively analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), universal mechanical tester and pendulum impact tester. The results showed that: (1) The absorption peaks corresponding to -C-H and C=O were stronger after modification, confirming the successful grafting of PCL flexible chains and PLA onto the WF surfaces via the SI-ROP reaction. (2) XRD results showed a significant decrease in the crystallinity of the modified wood fibers, suggesting that the polymer chain introduction disrupted the regularity of the wood fiber structure. Conversely, the crystallinity of the composite increased significantly, indicating improved interfacial adhesion and mobility. (3) The SEM of the modified composite showed a stretching and ductility morphology, suggesting the enhanced toughness of the composite. (4) Mechanical testing revealed that the tensile toughness of the alkali-treated WF-rD-PLA/PLA composites increased by 335.9%, albeit with a slight reduction in its strength. (5) The modified composite did not exhibit distinct relaxation peaks within the glass transition temperature (T_g) range, and the T_g increased, suggesting a reduction in the mobility of the PLA chains and an enhancement of the interfacial compatibility of the composites. The TGA data showed that the thermal stability of the modified composites was decreased, which was attributed to the formation of low molecular weight PLA chains on the WF surfaces. The SI-ROP technique effectively enhances the compatibility and mechanical properties of WF/PLA composites, offering a promising approach for the development of high-performance bio-based materials.

Keywords: Wood fiber; Polylactic acid; Toughening mechanism; Composites

木质纤维-聚己内酯-聚乳酸“核-壳-壳”增聚乳酸复合材料及增韧机制研究

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摘要: 为改善木质纤维/聚乳酸(WF/PLA)的界面相容性及韧性, 通过表面引发开环聚合(SI-ROP)反应, 以木质纤维为核在其表面引发开环聚合形成聚己内酯(PCL)橡胶壳层及聚乳酸(PLA)外壳层, 构筑WF-rD-PLA“核-壳-壳”结构, 进一步通过熔融共混挤出的方式制备得到WF-rD-PLA/PLA复合材料。通过傅里叶变换红外光谱仪、X射线衍射仪、扫描电子显微镜、差示扫描量热仪、热重分析仪、万能力学试验机和摆锤冲击试验机对复合材料的化学结构、结晶性能、微观形貌、热性能、拉伸性能及冲击强度进行综合表征。结果表明: (1) WF-rD-PLA和AL-WF-rD-PLA的红外光谱中表现出更强的-C-H键振动吸收峰和羰基(C=O)伸缩振动吸收峰, 表明SI-ROP反应成功地将PCL柔性链和PLA分子链引入到木质纤维表面。(2) SI-ROP反应后, 改性木质纤维结晶度显著下降, 表明表面重构修饰引入的聚合物分子链破坏了木质纤维整体结构的规整度。改性之后复合材料的结晶度显著升高, 这是因为表面修饰改善了复合材料的界面相容性。(3) 改性之后的复合材料断面形貌较为粗糙, 呈现出一定的拉伸延展现象, 表明复合材料的韧性得到了显著改善。(4) 在不大幅牺牲复合材料强度的情况下, 木质纤维经碱处理之后制备的WF-rD-PLA/PLA复合材料的拉伸韧性提升了335.9%。(5) “核-壳”和“核-壳-壳”结构组成的复合材料在玻璃化转变温度(T_g)范围内没有明显的松弛峰且 T_g 有所升高, 表明改性之后复合材料中聚乳酸的链段运动能力有所下降, 木质纤维的表面改性结构改善了复合材料的界面相容性。改性之后复合材料的热失重曲线向低温方向偏移, 说明改性之后的复合材料的热稳定下降, 说明SI-ROP反应成功将乳酸在木质纤维表面接枝形成低分子量聚乳酸分子链, 从而导致复合材料的热分解温度显著下降。

关键词: 木质纤维; 聚乳酸; 增韧机制; 复合材料