过氧化物交联聚 -己内酯热性能的研究

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关键词:生物降解高分子,交联,热性能,聚-己内酯

交联是改善聚合物耐热和化学性能的有效方法。交联赋予聚合物一个很重要的特色,就是在受热后不会熔融和流动。另一方面交联后半结晶型聚合物在结晶 温度下展示热塑性材料的力学行为,而在熔点以上展示橡胶的力学行为¹。本文 通过 DSC 研究了交联对 PCL 热性能的影响。

图 1 为典型的交联后 PCL 和纯 PCL 的 DSC 曲线,从图中可以看出交联后的 PCI 的熔点和结晶度均有所下降,而结晶温度比纯 PCL 的结晶温度有所提高,从 DSC 测试中得到的详细数据列于表 1 中。过氧化物交联在聚合物的熔融态下进 行,在结晶过程中,由于交联点的存在限制了高分子链的折叠和有序化排列,因 而阻碍了高分子链的结晶,导致熔点和结晶度的下降。通常过氧化物交联后,聚 合物的结晶温度会有所下降,但是在我们的研究中发现交联后 PCL 的结晶温度 有所提高,可能的原因是过氧化物分解后的物质或交联点起到成核剂的作用,使 得其结晶温度有所提高。



Figure 1. Typical DSC curves of PCL and PCL crosslinked with 3%

| Peroxide content (%) | $\Delta H_m \left(J/g \right)$ | X_{c} (%) | T _m (|) T _c () | |
|----------------------|---------------------------------|-------------|------------------|----------------------|--|
| 0.0 | 68.2 | 50.1 | 59.4 | 24.4 | |
| 0.5 | 67.0 | 49.3 | 57.2 | 28.1 | |
| 1.0 | 66.4 | 48.8 | 55.5 | 30.5 | |
| 1.5 | 63.4 | 46.6 | 55.5 | 37.5 | |
| 2.0 | 60.3 | 44.3 | 54.5 | 39.7 | |
| 2.5 | 59.5 | 43.8 | 53.3 | 38.2 | |
| 3.0 | 58.9 | 43.3 | 53.2 | 37.4 | |
| E3.0 ^a | 58.5 | 43.0 | 53.1 | 35.3 | |

Table1. Thermal properties and crystallinity of PCL and crosslinked PCL.

^a Extraction residual of crosslinked PCL with 3.0% peroxide

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Study on the thermal properties of crosslinked PCL

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In this paper, the thermal properties of the crosslinked PCL by peroxide were studied. The melting point, crystallinity of the crosslinked PCL decreases with increase of peroxide content. Formation of crosslink junctions disturbs the reorganization and chain folding during crystallization process, and results in formation of imperfect crystallite with smaller size and also less in content. Hence the melting point, total crystallinity decreases with increase in crosslink density. However, the crystallization temperature increases with increase in crosslink density maybe due to the by-product of curing reaction or the crosslink that served as a nucleation agent.

Key words: biodegradable polymer, crosslinking, thermal properties, PCL