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Thermal degradation of PVC synthesized with a titanocene catalyst II. Complementary isothermal results

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Abstract

The use of an isothermal degradation method on metallocene produced PVC and commercial PVC, under nitrogen and air atmospheres, reveals more details about degradation routes. Without regard to the polymer origin, the hydrochloric acid release occurs in two steps, which are reflected in molecular weight only under a nitrogen atmosphere; otherwise, the oxygen appears to be included in the scission/crosslinking process. On the one hand, Met PVC has unsaturations from its synthesis, producing a faster HCl release compared to Com PVC; consequently, its degradation resistance is lower. On the other hand, Com PVC has more oxidized species and has a natural tendency to include more of them. Surface area seems to have an important effect and is directly related to the rate of hydrochloric acid release. The latter is not supported by the chain oxidation mechanism, making the effect of the applied atmosphere more critical to the results obtained from the degradation experiments.

Keywords: Synthesis; Poly(vinyl chloride); Degradation; Metallocene catalyst

1. Introduction

The low-heat resistance of PVC is known to be caused by the structural defects inherent in this material because the traditional polymerization method permits the eventual monomer head-to-head linking, instead of the correct head-to-tail bond. These abnormal sequences are the sites of such defects, namely double bonds, tertiary chlorine (branching) and allylic chlorine, where each one of these is able to begin the hydrochloric acid release by the well-known zipper mechanism. The latter produces colouration, chain scission and loss of many desirable properties [1,2]. Nowadays it is believed that these structural defects can be eliminated in PVC by limiting the bonding to only head-to-tail vinyl chloride units during the polymerization reaction. This would be possible mainly by substituting the radical reaction mechanism with a different mechanism. Using this approach attempts have been made using anionic polymerization [3,4], coordination chemistry polymerization [5−7], photopolymerization [8] and living radical polymerization [9]; but, as can be seen from the papers, the degradation feasibility still remains without showing related results. This paper describes the thermal degradation of PVC produced by coordination polymerization of vinyl chloride using a half sandwich titanocene catalyst activated with low catalyst/MAO ratios [10] and is a continuation of previously reported thermal degradation behaviour [11], where the resistance of the metallocene produced polymer was higher during dynamic evaluations (TGA) but lower for static degradation methods. The difference in chemical origin and inherent morphology between produced and commercial PVC is believed to be the reason.

2. Experimental

The Met PVC was produced in the laboratory as described in detail elsewhere [10,11], and compared with a commercial

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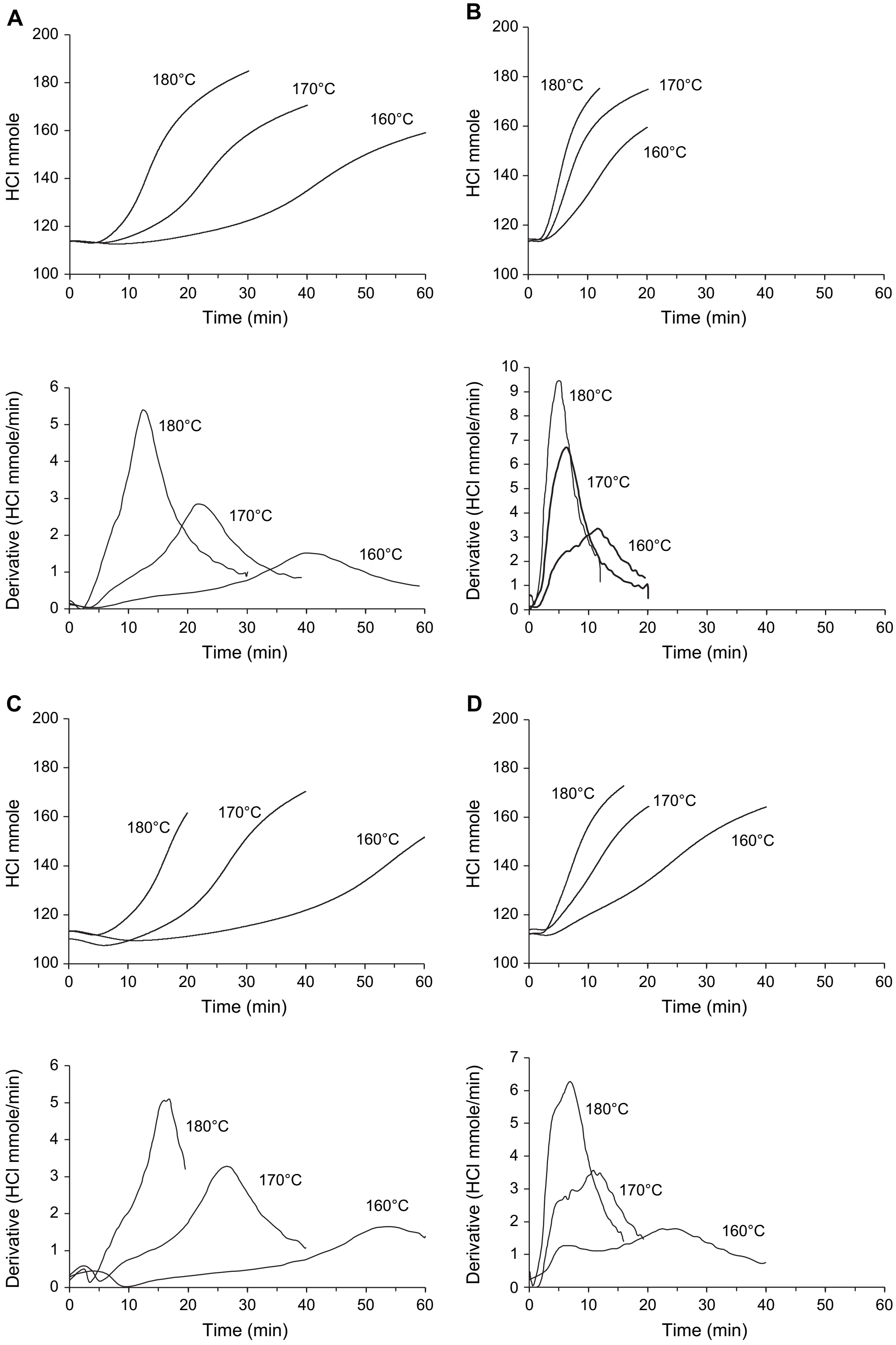

Fig. 1. HCl evolution of PVC samples: (A) Com PVC under air, (B) Met PVC under air, (C) Com PVC under N_2, and (D) Met PVC under N_2.