

# Modified preparation of HDPE/clay nanocomposite by in situ polymerization using a metallocene catalyst

Ali Alikhani<sup>1</sup> · Shokoufeh Hakim<sup>1</sup> · Mehdi Nekoomanesh<sup>1</sup>

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**Abstract** In this study, preparation of high-density polyethylene (HDPE)/clay nanocomposite by in situ polymerization of ethylene using a zirconocene catalyst (*bis*-(cyclopentadienyl) zirconium dichloride ( $Cp_2ZrCl_2$ )) was investigated. To obtain higher efficiency, nanoclay particles (Na-montmorillonite) were modified by ammonia ( $NH_3$ ),  $NH_3$ /methylaluminoxane (MAO),  $NH_3$ /dodecylamine (DDA), and  $NH_3$ /MAO/DDA systems. The results showed that the activity of the catalyst supported on the nanoclay particles modified by  $NH_3$ /MAO ( $762 \text{ g}_p/\text{mmol}(\text{Zr}) \text{ t} [\text{atm}]$ ) was higher than that of the one supported on the unmodified nanoclay as well as the other prepared modified nanoclay-supported catalyst systems. The catalyst activities versus MAO concentration in  $NH_3$ /MAO treatment system and versus DDA concentration in  $NH_3$ /DDA system showed a maximum. Unexpectedly, a very low catalyst activity ( $180 \text{ g}_p/\text{mmol}(\text{Zr}) \text{ t} [\text{atm}]$ ) was obtained using  $NH_3$ /MAO/DDA system. X-ray diffraction patterns showed that the HDPE/clay nanocomposites prepared by  $NH_3$ /MAO/DDA treatment system had less intercalated structure. Fourier transform infrared (FTIR) spectroscopy confirmed that water molecules of the nanoclay particles were reduced by  $NH_3$  modification. DSC results revealed that crystallinity of the HDPE/clay nanocomposites increased with the modification of the nanoclay particles. The maximum degree of crystallinity of 80.8% was obtained for HDPE/clay nanocomposites prepared by the nanoclay modified by  $NH_3$ . In addition, nanoclay modification with  $NH_3$ ,  $NH_3$ /MAO, and  $NH_3$ /DDA systems resulted in higher thermal decomposition temperature

(~30 °C higher than 480 °C of the unmodified one). Such increase was not observed for the  $NH_3$ /MAO/DDA treatment system. Dynamic mechanical analysis showed an increase in the elastic modulus of the nanocomposite samples prepared by modified nanoclay particles, as well. Meanwhile, modification of the nanoclay particles by  $NH_3$  led to the highest elastic behavior compared to the other modification systems. It was about 4.6 GPa which was 28% higher than the elastic modulus of the nanocomposite prepared by unmodified nanoclay particles.

**Keywords** Polyethylene · Clay · MAO · Metallocene · In situ polymerization · Ammonia

## Introduction

Polyethylene (PE) is one of the most widely used polymers with numerous applications due to its specific properties such as high chemical resistance, low dielectric constant, etc. [1, 2]. Since most types of PE have some disadvantages such as inadequate stiffness and gas permeability, improvement of its properties is a crucial subject. One of the most convenient ways to improve such drawbacks is reinforcing of PE with nanofillers. This is a promising area for elimination of such disadvantages [2–4].

Polymer nanocomposites are a fascinating class of materials that possess multi-functional properties far better than conventional micro-composites. Different nanofillers such as nanoclay [2, 5, 6] and grapheme [3, 7, 8] have been used in preparation of the polymer nanocomposites. Among all nanocomposites, those filled with nanoclay particles have been most widely studied. Polymer/layered silicate nanocomposites have attracted much interest in academic and industrial sectors due to extraordinary physical and

✉ Shokoufeh Hakim  
s.hakim@ippi.ac.ir

<sup>1</sup> Iran Polymer and Petrochemical Institute,  
P.O. Box: 14975-112 Tehran, Iran