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Synthesis of PE/graphene nanocomposite via *in-situ* polymerization using a multinuclear catalyst of late transition metals based on cobalt

Enayat Rahimipoor, Gholam Hossein Zohuri*

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Po. Box 91775-1436 Mashhad, Iran

**Email: zohuri@um.ac.ir*

Abstract: A bispyridilimine catalyst based on cobalt was synthesized and used for polymerization of ethylene. Effect of in-situ addition of a graphene nanocomposite on the catalyst activity was studied. As a general result, the activity of the catalysts was increased in presence of the graphene in the range studied (from 210 to 350 g PE. mmol $(Co)^{-1}$. h^{-1}). However, vinyl content of the obtained polyethylene was increased with increasing concentration of the graphene.

Keywords: late transition metals catalyst, ethylene polymerization, nano-composites.

Introduction

Polyethylene composites are properly used instead of PE in numerous applications. Various types of additives in different size of particles can be used to prepare these composites for different purpose [1]. Graphene, as one of the additive used, is a two-dimensional, single-layer hybrid of Sp^2 carbon atom with a macroscopic dimension but with atomic thickness. The properties of graphene-based polymer composites depend heavily on the dispersion of the graphene plates in a polymer matrix. In-situ polymerization is one of the most effective method to synthesis nanocomposites in presence of nano-materialis to a homogenous dispersion [2] expected to represent better results.

Experimental

Ligand of (1E,1'E)-N,N'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(1-(6-((E)-1-((2,6-diisopropylphenyl)imino)pyridine-2-yl)ethan-1-imine) was synthesized using condensation reaction of 2,6-diisopropyl aniline, 2,6-diacetylpyridine and 2,3,5,6-tetramethyl-p-phenylenediamine. The catalyst was prepared by reaction of the ligand with corresponding metal halide [3,4]. The optimization of polymerization condition for the catalyst based on obtaining yield was carried out at different cocatalyst-catalyst molar ratio, temperature and monomer pressure, while methylaluminoxane (MMAO) was used as cocatalyst [5]. Graphene was used through in-situ polymerization (graphene, 1.7-2 nm with 10-12 layers).

Results

The optimum polymerization condition was attained at 50 °C, for 30 minutes, with [Al]:[Co] molar ratio of 1000:1. The PE/graphene nanocomposites (0.22 w%) were synthesized through *in-situ* polymerization using the catalyst. The results showed that activity of the catalyst enhanced (from 210 to 350 g PE. mmol $(Co)^{-1}$. h^{-1}). The behavior could be due to supporting of the catalyst via surface of the graphene [2].

The polyethylene samples obtain from the optimum polymerization condition were analyzed using FTIR technique (Fig. 1), and as expected, the resultant products distinguished as high density polyethylene (HDPE), and as indicated, the sample which was prepared in presence of graphene showed higher vinyl content and lower branching density than the neat prepared PE (Fig. 1).

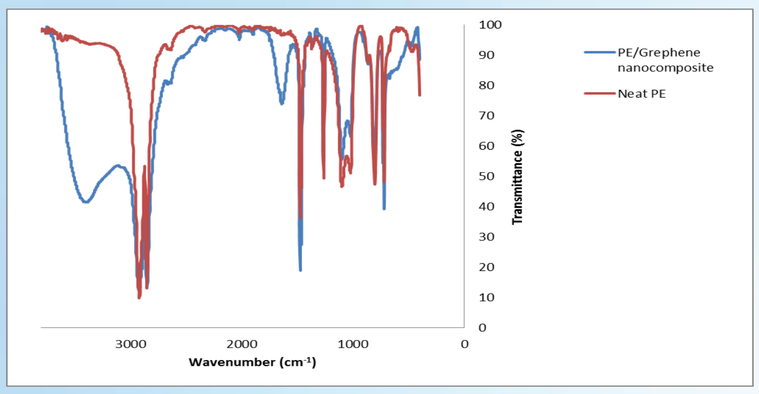

Fig. 1 FR-IR spectrum of neat PE and graphene nanocomposite

Conclusions

Addition of graphene through *in-situ* polymerization of ethylene caused to increase the catalyst activity. The increasing of the graphene the decrease of branching content in the obtained polymer was more significant.

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