The effect of tri ethyl aluminum as masking agent for antioxidant 1010 on Ziegler-Natta catalyst activity in polymerization of poly propylene

Atefeh Iraji[1], Hassan Arabi*[1] , Yousef Jahani[1], Ali Pejouhan[2]

[1]Faculty of Engineering, Iran Polymer and Petrochemical Institute, PO Box 14965/115, Tehran, Iran.

[2]Petrochemical Research & Technology Company, Tehran, Iran

Abstract

This study investigated the use of antioxidant during slurry propylene polymerization using the Ziegler–Natta catalyst. Antioxidant masking using tri ethyl aluminum is the key to reducing the destructive effect of antioxidants containing OH phenolic groups on Ziegler–Natta catalyst performance. Polymer characteristics such as catalyst activity, and oxidative induction time of the products in the presence of different amounts of antioxidant were evaluated. The results shown that the activity of catalyst in presence of masked antioxidant has not decreased. The oxidative induction time (OIT) results indicated that masked antioxidant during PP polymerization did not affect OIT of the products.

Keywords: oxidative induction time, antioxidant, Ziegler–Natta catalyst, aluminum aryloxide, stabilization

Introduction

Generally, polypropylene (PP) is susceptible to degradation reaction. Its properties decrease during polymer processing and over its service life that could restrict its application. In order to prevent or retard degradation process, addition of antioxidant (AO) to PP is promoted [1]. Conventionally, antioxidants are mixed with PP by extrusion under high temperatures and shear rates, thereby producing pellets [2,3]. Pelletizing consumes a significant amount of PP production energy, about one-third of the total energy[4,5]. The development of PP production without pelletizing unit operation is achieved by adding AOs within PP polymerization [2,4,6]. The direct mixing of phenolic compounds with solid titanium catalyst and co-catalyst during propylene polymerization inhibits the activity of catalyst system due to deactivation of active titanium species. Masking of the antioxidant with triethylaluminium (TEAL) has been found to be effective in reducing Ziegler–Natta catalyst deactivation [4]. It is well-known that TEAL reacts with OH phenolic groups, generating aluminium aryloxide compounds. These compounds easily regenerate with the addition of water and alcohol after polymerization[4,6]. In this study, the effect of different concentrations of AO during propylene polymerization, on the catalyst activity was evaluated. As well as, the values of OIT samples this method were compared with the produced samples by adding of antioxidant in extruder.

Experimental

Materials

Ziegler–Natta catalyst ($MgCl_2$/$TiCl_4$/DIBF) was provided by Maroon Petrochemical Co. (Iran). Extra pure polymerization-grade propylene was obtained from Tabriz Petrochemical Co. (Iran). Hexane as a solvent was provided by Bandar Imam Petrochemical Co. (Iran). It was dried over CaH_2

*H.Arabi, E-mail:H.arabi@ippi.ac.ir

and kept over ٤Å/١٣X type molecular sieves and sodium wires to keep its water content below ٢ ppm. TEAl (triethylaluminum) of ٩٣ % purity and donor [cyclohexyl(dimethoxy)methylsilane] were obtained from Sigma Aldrich. The AO product (Ciba Specialty Chemicals, Switzerland) used were:

AO: Tetrakis (٣-(٣،٣-di-tert-butyl)-٤-hydroxyphenyl) propionyloxy methyl methane (Irganox ١٠١٠)

Polymerization procedure

Polymerization reactions were carried out in a ١ L stainless steel Büchi reactor. Temperature control and heating/cooling cycles were utilized through a circulator model. The reaction mixture was stirred continuously using a controlled speed stirrer (Büchi Magnetic Device) equipped with an anchor blade impeller. Before starting the reaction, the reactor was heated up to ٩٠ °C and then purged with nitrogen to remove oxygen and humidity. The reactor was cooled to ٢٥ °C under nitrogen purging. Afterwards, the reactor was charged with ٥٠٠ mL n-hexane under nitrogen atmosphere. The proportional amount of antioxidant was injected; catalyst was then added to TEAl/donor mixtures diluted in hexane. After ٢٠ min, the pre-contacted catalyst was transferred to the reactor. Immediately after the last injection was done, propylene valve was opened. Reactor heating and continuous propylene feeding were started simultaneously to achieve desired operating conditions. In this case, non-isothermal pre-polymerization was used. The reaction temperature increased from ٢٥ to ٧٠ °C within ٢٠ min. Polymerization runs were carried out at pressure of ٨ bar for ١٢٠ min. Reaction temperature was controlled by circulator (LAUDA RE١٠٥٠G). The polymerization reaction was deactivated using ٤٠ mL ethanol and the product was dried overnight in an oven at ٤٠ °C. For all polymerization runs, the Al/Ti (mol/mol) and Al/Si (mol/mol) ratios were kept constant at ٤٠٠ and ٢٠.

Characterization of polypropylene

Catalyst activity was calculated through the:

$$Catalyst\ activity = \frac{weight\ of\ produced\ PP\ (kg)}{weight\ of\ used\ catalyst\ (g)}$$

(١)

Oxidative stability of products was measured by oxidative induction time (OIT, Mettler Toledo) at ١٩٠°C

Result and discussion

Chemical structure of Irganox ١٠١٠ (AO) is demonstrated in Table ١. As shown in Table ١, AO have four OH phenolic group which reacts with TEAL, generating aluminum aryloxide or masked AO (M-AO). Different amounts of M-AO and unmodified AOs were used during propylene polymerization; the results are shown in Fig. ١. Results indicate that the use of M-AO, due to complete masking of OH phenolic groups didn't affect in activity of catalyst. On the other hand, the use of unmodified AO has caused the decreasing of catalyst activity. In the presence of ٥٠٠٠ ppm of AO, the catalyst activity was decreased to ٣،٥ kg/g. The efficacy of masked antioxidant at ٥٠٠٠ppm concentration was carried out by testing of OIT. The OIT test is the measurement of time taken by sample for initiation of oxidation. The OIT results demonstrated in Table٢ that the thermal stability of samples containing masked antioxidant close to the sample is obtained from extrusion method.

Conclusion

The effect of adding irganox ١٠١٠ during PP polymerization was investigated. Characteristics of products were evaluated. The results showed that the addition of AOs without masking reduces the activity of the catalyst. While the use of masked antioxidant in different concentrations is not reduced the activity of catalyst. The results of OIT were shown that desired performance of masked antioxidant in reactor stabilization method in comparison with the extruder method.

References

١. R. Gensler, C.J.G. Plummer, and H.H. Kausch, Polym.Degrad. Stabil., ٦٧, ١٩٥ (٢٠٠٠).

۲.   R. Oliveira, M. Forrester, and M. Marques, Macromol.Symp., ۲۹۹, ۲۱۵ (۲۰۱۱).

۳.   W. Voigt and R. Todesco, Polym. Degrad. Stab., ۷۷, ۳۹۷ (۲۰۰۲).

٤.   N. Kawamoto, T. Horikoshi, K. Nomura, H. Yokota, Y. Negishi, E. Tobita, and M. Terano, J. Appl. Polym. Sci, ۹۹،۱۳۵۰ (۲۰۰٦).

۵.   H. Yokota, K. Nomura, T. Horikoshi, Y. Negishi, N. Kawamoto, E. Tobita, and M. Terano, Novel energy and cost saving polypropylene stabilization via addition of antioxidant into polymerization system, studied in surface science and catalysis, ۱st ed., Elsevier, Amsterdam, ۱۳ (۲۰۰٦).

٦.   B. Rotzinger and M. Brunner, Polym. Degrad. Stabil., ۹۳, ۳۱٦ (۲۰۰۸).

Table ۲. The OIT result of product in presence ۵۰۰۰ ppm of antioxidant

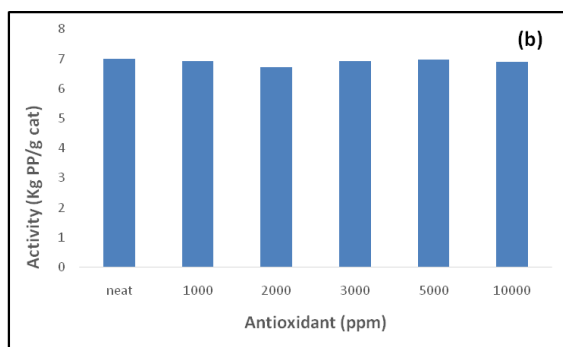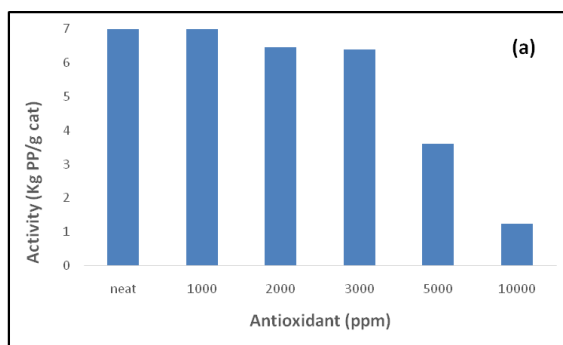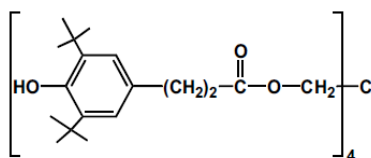| Method	In reactor stabilization	Extruder
OIT(Min)	۱٦،۰٦	۲۱،۳٤

Fig ۱. The effect of different amounts of AOs addition on Ziegler–Natta catalyst activity: (a) AO, (b) M-AO

Table ۱. Chemical structure and formula of used antioxidants.

IUPAC Name	Chemical Structure	Commercial Name	Molecular Weight (g/mole)	Abbreviated
Tetrakis (۳-(۳, ۳-di-tert-butyl)-٤-hydroxyphenyl) propionyloxy methyl methane (Irganox ۱۰۱۰)		Irganox ۱۰۱۰	۱۱۷۸	AO