Improvement of physical properties of polypropylene through functionalization with Ziegler-Natta catalyst

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Polypropylene (PP) has well-balanced physical properties, and features excellent characteristics such as good moldability, currently making it the most common plastic with diverse uses that include packaging film, food containers, automobile parts, and electronic components. In addition, it has low environmental impact due to being lightweight, easy-to-recycle, and halogen-free, and its use is therefore expected to expand to even more fields.

Functionalization is very important to improve properties of PP. Maleic anhydride is the most widely used functionalized PP, which prepared by chemical modification. However, since the tertiary macroradicals formed in the main chain due to the addition of peroxide simultaneously advance the β-scission of the PP main chain, a decrease in the molecular weight of the PP is unavoidable. Functionalization through the copolymerization is also important way to improve PP properties. It is well-known that random incorporation of alkyl side chains in the main chain inhibits the crystallization behavior such as crystallinity and melting temperature, in which a longer side chain offers a stronger inhibitory effect. This leads to decrease physical properties. Random introduction of functional group also decreases crystallization properties, while nucleation effect can be observed through interaction among the functional groups. It is considered that improvement of PP properties without deteriorating the base properties of PP can be achieved to optimize the kind and amount and of functional groups.

In this study, firstly, PP with a small amount of aromatic functional groups was synthesized using Ziegler-Natta catalyst and its crystallization behavior was investigated. In the presence of a small amount of styrene or 1-allylnaphthalene was used as a comonomer during polymerization of propylene. Characterization using ^{1}H NMR showed that less than 0.10 mol% of functional groups was incorporated into PP chain. Base properties such as melting temperature, crystallinity and tensile property were almost same as homo-PP. On the other hand, crystallization rate was significantly affected by a small amount of functional groups. Observation using polarized optical microscopy (POM) showed that this improvement of crystallization rate came from nucleation effect.

Trimethoxy(7-octen-1-yl)silane (OTMS) was used as reactive functional comonomer to obtain more improvement of PP properties. Obtained PP-OTMS were melt-mixed after polymerization. Almost no change was observed in the melting temperature and crystallinity with a small amount of functional groups incorporated into PP chains. On the other hand, crystallization rate after melt-mixing was dramatically enhanced. Nucleation rate and tensile properties were also clearly improved. Crytstallization rate of PP-OTMS without melt-mixing was same as homo-PP. Therefore, it was indicated that these properties were enhanced by reaction between the reactive functional groups. Silica nanocomposite with PP-OTMS showed large improvements of nucleation effect and tensile properties.

This research demonstrated that crystallization rate of PP can be enhanced by a small amount of functional group without disrupting base properties of PP. Dramatic enhancement of crystallization and physical properties can be observed when a small amount of reactive functional groups was incorporated into PP. Moreover, PP nanocomposite with reactive functional group can greatly improve the physical properties of PP through the reaction between reactive functional groups and fillers. Consequently, this research is believed to provide very beneficial to the development of industrial materials.

Key Words: Polypropylene, Functionalization, Copolymerization, Ziegler-Natta catalyst, Nucleation effect