

Metallocene and Ziegler-Natta Catalysts

Sandeep Vinod Vishwakarma and S.G. Kulkarni

Received: 18 March 2021, Accepted: 10 July 2021

Abstract- Fifty years ago, Karl Ziegler and Natta won the Nobel Prize for their discovery of the catalytic polymerization of ethylene and propylene using titanium compounds with aluminum-alkyls as co-catalysts. Polyolefins are constantly growing and are now one of the most important high-consumption polymers. New metallocene/methylaluminoxane (MAO) catalysts have made it possible to synthesize polymers with highly defined microstructure, tacticity and stereoregularity, such as long chain branched or block copolymers with excellent properties. Melt spinning of the fibers of metallocene-catalyzed isotactic polypropylene (PP) and standard equivalent of Ziegler-Natta isotactic polypropylene and therefore the properties of PP and several thermal and mechanical properties of fiber have been investigated. Ziegler-Natta catalysts were prepared by a reaction method which employed $Mg(OEt)_2$ as a precursor. Newly developed metallocene-catalyzed PP possesses higher isotacticity and crystallinity than commercial ones, so the mechanical properties of the final product are guaranteed.

Keywords: Ziegler-Natta, metallocene, polypropylene, catalysts, polyolefins

I. INTRODUCTION

Nonwoven fabric became a particularly important part of the textile industry. Compare to the global market average of 24%, the Indian market will occupy by 12% of the technical textiles manufactured by nonwoven technology. The nonwoven market is projected to grow from USD 40.50 billion in 2020 to USD 53.5 billion by 2025.

S.V. Vishwakarma and S.G. Kulkarni
 DKTE Society's Textile and Engineering Institute, Ichalkaranji-416116,
 Kolhapur, India.

Correspondence should be addresses to S.V. Vishwakarma
 e-mail: sandeeps342@gmail.com

For manufacturing of nonwoven fabric, there are different methods used to produce nonwoven fabrics supported by the web formation method, dry-laid nonwoven, spun-laid nonwoven, wet-laid nonwoven, supported web bonding, mechanical bonding, thermal bonding, and chemical bonding. The bonding types, the fiber type and therefore the manufacturing parameters determine the characteristic feature of the nonwoven. In contrast to standard engineering materials, these fabrics have better specific mechanical properties, strength to weight and stiffness to weight ratios [1]. The official definitions are provided by a professional organization like EDANA (European Disposables and Nonwoven Association) or INDA (International Nonwoven and Disposable Association). Melt-blown nonwoven and spun-laid nonwoven are most generally methods used for production of nonwoven fabrics. Melt-blown nonwovens are usually made through a continuous process. Fibers are spun then directly dispersed into a web by deflectors or are often directed with air streams. This method results in a faster belt speed and cheaper costs. Spun-laid nonwoven fabrics also called spun-bond nonwoven fabrics are produced by extruding molten polymer fibers through a spin net or die consisting of up to 40 holes per inch to create long thin fibers which are stretched and cooled by passing hot air over the fibers as they fall from the die. The approaching web is collected into rolls and subsequently converted to finished products. Spun-blown plays the role of imparting strength to nonwoven fabric and melt-blown is employed for barrier properties of nonwoven fabric. Differing types of polymers are utilized in the assembly of nonwoven fabrics like polyesters, polyethylene terephthalate (PET) and polypropylenes, and they are either within the type of small chips form or in the form of powder. Spun-bond/melt-blown/spun-bond, commonly

called SMS, is a tri-laminate nonwoven fabric. It is made from a top layer of spun-bond polypropylene, a middle layer of melt-blown polypropylene and a bottom layer of spun-bond polypropylene. Polypropylene is a downstream petrochemical product derived from the olefin monomer, propylene. The polymer is produced through a process of monomer connection called addition polymerization normally by using the Ziegler-Natta catalyst system. Ziegler-Natta catalysts are heterogeneous catalysts developed by Karl Ziegler and Natta in 1950, which are utilized in stereospecific catalytic polymerization methods. Isotactic polypropylene resins have been produced from Ziegler-Natta catalysts for more than 45 years. Resins with relatively high molecular mass and relatively wide molecular mass distribution are produced inside the polymerization reactor. Metallocene isotactic PP is a uniform polymer with a relatively narrow molecular mass that is suitable for fiber spinning [2,3].

A. Heterogeneous Catalysts

These are industry-dominating catalysts that are supported titanium compounds (and sometimes vanadium-based) and used for polymerization reactions, usually together with organo-aluminum compounds like tri-ethylaluminium (TEA, $\text{Al}(\text{C}_2\text{H}_5)_3$) as co-catalysts [4].

B. Homogeneous Catalysts

These are the second largest class of catalysts and are supported complexes of Ti, Zr, or Hf. They are generally used in combination with a variety of various organo-aluminum co-catalysts called metallocene/methylaluminoxane (MAO). Traditionally, they include metallocenes but also have multi-dentate oxygen- and nitrogen-based ligands [3].

II. EXPERIMENTAL

A. Manufacturing Process

A.1. Materials

Isotactic polypropylene with metallocene catalyst and

Ziegler-Natta catalyst was used for production of melt-spun nonwoven fabrics by using melt-blown thermal bonding method. The commercial metallocene PP was purchased from Lyondell Basell Industries [5].

A.2. Method

For manufacturing of nonwoven fabrics, there are mainly two methods used: melt-spinning and spun-spinning methods. The melt-extrusion spinning was conducted by using a single-screw extruder (Fig. 1) equipped with a metering-pump and eight-hole spinneret, and its diameter was about 0.5 and 0.6 mm. The spun-extrusion spinning was conducted by using a single-screw extruder with a metering pump and six-hole spinneret, and diameter of 0.4 mm. Nonwoven fabric was produced by using spun-blown or melt-blown methods [6].

A.3 Manufacturing Method

The manufacturing method of nonwoven fabric is completed with spun bonding method (Fig. 2) or melt-blown method and sometimes both are combined to make a nonwoven fabric. Spun bonding method is a spun-bond process that was first patented in 1940s and since then it has become more and more popular all over the world with more progress. The technique itself includes fibers being spun then directly being dispersed into a web by deflectors or air streams. They use no chemicals, and are thermo-bonded. This method is preferred because it is cost effective for manufacturers. Over the past 20 years, it is used to make several household products such baby diapers, adult diapers, medical products, protective apparel and hygiene products. Spun-bonds also are flame-retardant or have antistatic properties, and may therefore be used for increased ultraviolet and gamma radiation protection. Many of their features including: low weight, high strength, high air permeability, hydrophilic properties, and excellent wear and tear properties. In addition, with the advancement of this technique, spun-bonds are now much softer and easier than previous types and weigh on average only 10 g/m^2 to

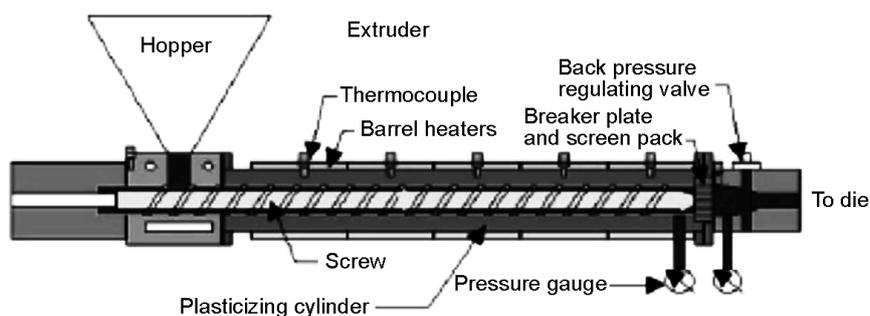


Fig. 1. Extruder.

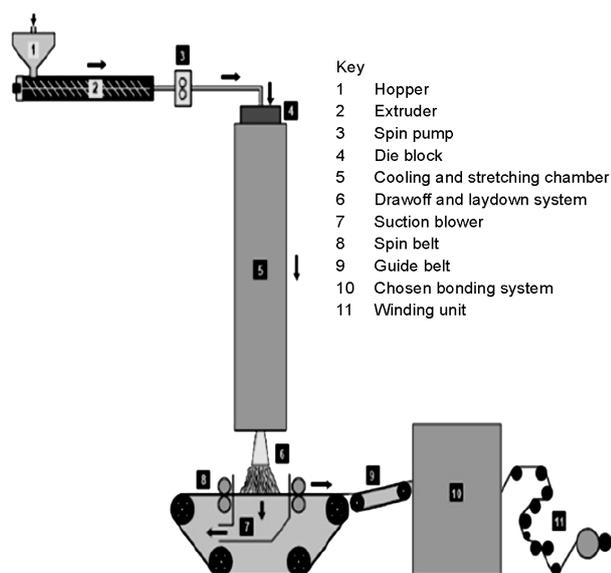


Fig. 2. Schematic of the spun bonding process.

150 g/m² [4,7].

A.4. Melt-Blown Method

The melt-blown process came after spun-bond technology

and is a process by which ultrafine filament (micro-fibers) nonwovens are often produced at low costs. The technique involves blowing hot air onto the molten thermoplastic, which extrudes through a linear die containing many small holes, creating a fine fibered self-bonded nonwoven web (Fig. 3). Its main feature is that the fiber is very thin. As a result, this material is usually used in filters for air, liquids, and particles, or as absorbents in products like wipes, oil absorbents, incontinence products, and feminine hygiene, but also can be utilized in the production of certain electronics, adhesives, and other apparel [7,8].

A.5. Properties of Fiber

The fiber produced from Ziegler-Natta catalyst PP has long starched on the conveyor belt of the machine through a spun-bond machine and fiber produced from melt-blown are finer than the spun-blown it do not required any types of stretching. The properties of the fabric are presented in Table I.

A.6. Catalysts Preparation

The catalyst sample was characterized using scanning electron microscopy (SEM). It had been evident that

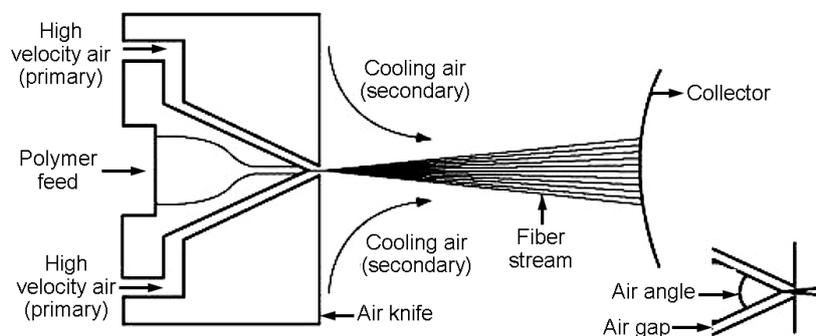


Fig. 3. Melt-blown method.

TABLE I
PHYSICAL PROPERTIES OF POLYPROPYLENE (PP) AND POLYETHYLENE (PE), PREPRINTED WITH PERMISSION FROM [6]

| No. | Properties | Polyethylene | Polypropylene |
|-----|--|--------------|---------------|
| 1 | Density | 0.92-0.95 | 0.9-0.91 |
| 2 | Young modulus (GPa) | 0.3-1.0 | 1.4 |
| 3 | Glass transition temperature (°C) | -125 to -80 | -20 |
| 4 | Limiting oxygen index, LOI (%) | 18 | 17 |
| 5 | Melting temperature (°C) | 112-134 | 160 |
| 6 | Specific heat capacity (J/kg.K) | 1750-2400 | 1900 |
| 7 | Stiffness to weight ratio: tensile (MN.m/kg) | 0.32-1.0 | 1.2-1.5 |
| 8 | Tensile strength (MPa) | 7-49 | 23-36 |

there was no significant change in morphologies upon the immobilization of the catalyst. $\text{TiCl}_4/\text{MgCl}_2$ catalyst was prepared by recrystallization method through reacting MgCl_2 -ethanol adduct with TiCl_4 by the following procedure: 2 g (0.0210 mol) of anhydrous magnesium dichloride was suspended in 100 mL of heptane and 0.1259 mol of ethanol was added dropwise. Then, the solution was stirred for two hours, and 28 mol of aluminum compound was introduced dropwise and heated to 90 °C and hold for 2 h. Thereafter, 0.0255 mol of titanium tetrachloride was added and therefore the mixture was stirred for two hours. Finally, the catalyst obtained was washed with heptane for several times [9].

A.7. Polyethylene and Polypropylene

Currently, polyethylene (PE) is one of the preferred and widely used polymers. The formation of PE occurs by the polymerization of the ethylene monomer in an insertion reaction. Despite the easy structure of PE, its fabrication process is complex and consists of various types of synthetic methods. Due to a number of special features, it is considered as a new polymer with high crystallization rate and flexible chains, which is mostly due to its complete chain structure. Therefore, it is not available in an amorphous state and most of its properties are derived by extrapolating from those of semi-crystalline samples. The properties of various types of PE can vary as a consequence of structural changes resulting from the polymerization technique. Generally, linear low density polyethylene (LLDPE), and high density polyethylene (HDPE) are conventionally synthesized via the catalytic ethylene polymerization reaction at low temperatures and pressures, as compared to the LDPE manufacturing route. Especially, LLDPEs prepared via Ziegler-Natta catalysts have more uneven co-monomer distributions, whereas, a reverse trend is observed for those synthesized by metallocene catalysts. Such differences in co-monomer distributions are mainly attributed to the difference within the available active sites within the two catalysts that manifests itself within the rheological and mechanical properties of the polymers also as their melt miscibility. However, polymer density is often controlled by the ethylene/co-monomer molar ratio, temperature, and therefore the catalyst type. The power to crystallize the substance is suffering from its relative molecular mass, concentration of branches, and their distribution along the backbone of the co-polymer. So as to know the crystallization behavior of the branched molecules, more homogeneous fractions of the co-polymer are required. The processing ability and therefore the properties of the ultimate product depend strongly on the branching of the polymer [10,11].

III. RESULTS AND DISCUSSION

In this study, two different catalyst preparation methods namely reaction and recrystallization were developed and compared so as to clarify the correlation between their nature and polymerization behavior. Throughout this article, we have reviewed the changes and current state of PE and PP manufacturing processes, including role and kinds of catalysts and co-catalysts employed over the years. Although Ziegler-Natta catalysts have been used extensively since their discovery, metallocene catalysts and co-catalyst systems have recently been replaced. More laboratory-scale work is usually recommended to know the complexity of the polymerization process, so more information is available for optimization purposes [10].

A. Effect of Temperature

Based on the polymerization temperature for catalyst Ziegler-Natta and metallocene, it is found that the metallocene catalyst exhibited higher activities than Ziegler-Natta catalyst. It was observed that activities increased with increasing the polymerization temperature from 40 °C to 60 °C. However, activities decreased with increasing the temperature to 70 °C. The dependence of polymerization temperature on isotacticity of PP produced from both Ziegler-Natta and metallocene catalysts was also observed [11].

B. Effect of Pressure

It was observed from the Pipatpratanporn's article that metallocene catalysts are much more active than Ziegler-Natta catalysts. The activity of the metallocene catalyst increases almost linearly with increasing propylene pressure, and considering the activity of the Ziegler-Natta catalyst, it shows that the propylene pressure has a weaker effect. Explanation of the different catalytic responses to

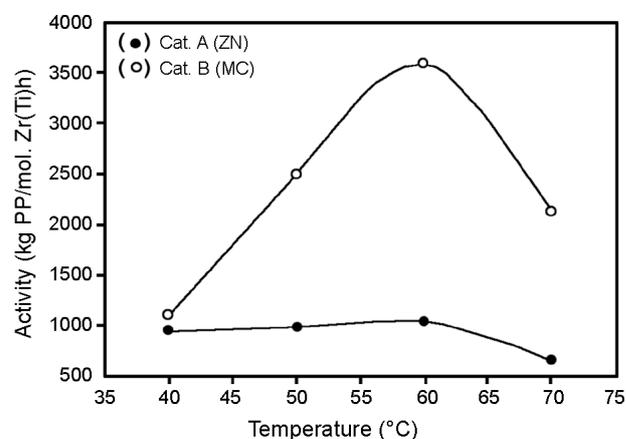
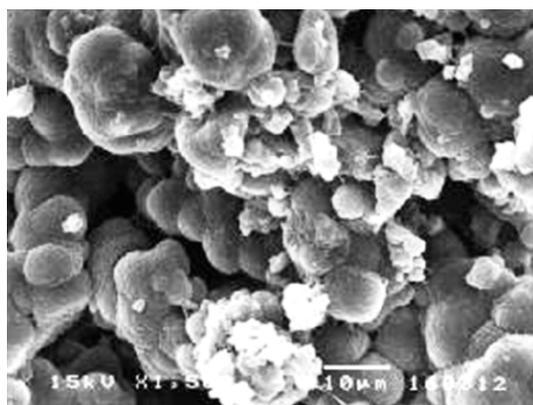
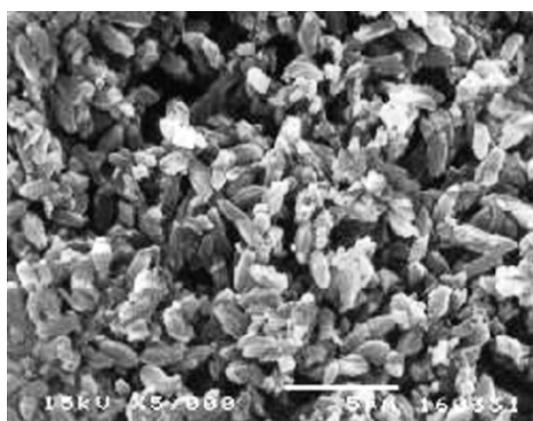


Fig. 4. Effect of polymerization temperature on activities for Ziegler-Natta and metallocene catalysts [10].



(a)



(b)

Fig. 5. (a) Ziegler Natta- based PP and (b) metallocene-based PP.

propylene must lie in the solubility of the propylene in the reaction medium for both catalytic systems [12].

C. Microscopic Structure of Ziegler-Natta and Metallocene-Based PP

T_m of PP produced from the ZN catalyst was high, indicating higher crystallinity. There was no significant change in morphologies (as shown in Figs. 5a and 5b) of PP upon changing the propylene pressures between 40 and 100 psi. It is known that temperature, pressure and also the polymerization time may affect on the fragmentation of heterogeneous catalyst. However, it seems that these effects are pronounced only at a particular level. As reported by Fink group [13] for propylene polymerization, the pressure of 80 bar and temperature of 50 °C were used for 12 h. The activities of the MC catalyst were much higher compared to those of ZN catalysts. However, activities for the MC catalyst essentially decreased when high concentrations of catalyst were used. It is known that at high catalyst concentrations, the coupling reaction of active complex can occur, leading to the catalyst deactivation [14].

IV. CONCLUSION

This paper presents the changes and current status of PE and PP production processes, including the role and types of catalysts and co-catalysts used over the years. Although Ziegler-Natta catalysts have been used extensively since their discovery, they have recently been replaced by metallocene catalysts and co-catalyst systems. We have studied the performance and production mechanism of both PP and PE polymers as well as the prospects for future research [14]. The influence of crystalline properties on the processing ability alongside the mechanical properties of melt spinning fibers are well discussed. Low T_m and high isotacticity of Ziegler/Natta-based PP are some of the advantages that manifest themselves both in terms of fabrication and fiber properties. The newly developed metallocene-based PP is confirmed to be a promising candidate for producing high-performance fibers by the melt spinning process [15].

REFERENCES

- [1] A. Marcindin, M. Hricov, and K. Marcind, "Fiber based on metallocene polypropylene: rheology, mechanical and thermal properties", *Vlakna Text.*, vol. 15, no. 2, pp. 9-18, 2008.
- [2] P. Pipatpratanpor and P. Praserttham, "Impact of process variable on properties of polypropylene derived from the supported Ziegler-Natta and metallocene catalysts", *Iran. Polym. J.*, vol. 16, no. 2, pp. 123-131, 2007.
- [3] A. Shamiri, M.H. Chakarbarti, S. Jahan, M.A. Hussain, W. Kaminsky, P.V. Aravind, and W.A. Yehye, "The influence of Ziegler-Natta and metallocene catalysts polyolefin structure, properties and processing ability", *Materials (Basel)*, vol. 7, no. 7, pp. 5069-5108, 2014.
- [4] R. Xu, P. Zhang, H. Wang, X. Chen, J. Xiong, J. Su, P. Chen et al., "Structure and properties of a metallocene polypropylene resin with low melting temperature for melt spinning fiber application", *Polymers (Basel)*, vol. 11, no. 4, pp. 729, 2019.
- [5] Weiss K., Botzenhardt S., Hofmann M., "Ziegler-Natta and Metallocene Polymerisation of Olefins with Heterogeneous Catalysts", in *Metalorganic Catalysts for Synthesis and Polymerization*, Kaminsky W. Eds. Berlin: Springer, 1999, pp. 97-101.
- [6] P. Pokasermsong and P. Praserttham, "Comparison of activity of Ziegler-Natta catalysts prepared by recrystallization and chemical reaction methods towards polymerization of ethylene", *Eng. J.*, vol. 13, no. 1, pp. 57-64, 2009.
- [7] A. Brochocka, A. Nowak, K. Majchrzycka, M.

- Puchalski, and S. Sztajnowski, "Multifunctional polymer composite produced by melt-blown technique to use in filtering respiratory protective devices", *Materials (Basel)*, vol. 13, no. 3, pp. 712, 2020.
- [8] N. Gobi, S. Evangelin, and R. Kasthuri, "Multilayer nonwoven fabrics for filtration of micron and submicron particles", *J. Text. Eng. Fash. Technol.*, vol. 5, no. 2, pp. 81-84, 2018.
- [9] Y. Nakayama, Y. Sogo, Z. Cai, and T. Shiono, "Copolymerization of ethylene with 1,1-disubstituted olefins catalyzed by ansa-(fluorenyl) (cyclododecylamido) dimethyltitanium complexes", *J. Polym. Sci. Part A: Polym. Chem.*, vol. 51, no. 5, pp. 1223-1229, 2013.
- [10] P.J. Shapiro, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, and W.D. Cotter, "Ziegler-Natta alpha-olefin polymerization catalysts", *J. Am. Chem. Soc.*, vol. 116, no. 11, pp. 4623-4640, 1994.
- [11] J. Cano and K. Kunz, "How to synthesize a constrained geometry catalyst (CGC)-A Survey", *J. Organomet. Chem.*, vol. 692, no. 21, pp. 4411-4423, 2007.
- [12] K. Unverhau, R. Kehr, R. Fröhlich, and G. Erker, "Synthesis of [3] ferrocenophane-bridged Cp-amido zirconium complexes and ansa-zirconocene complexes and their use in catalytic polymerisation reactions", *Dalton Trans.*, vol. 40, no. 14, pp. 3724-3736, 2011.
- [13] S.S. Reddy and S. Sivaram, "Homogeneous metallocene methylauminoxane system for ethylene polymerization", *Prog. Polym. Sci.*, vol. 20, no. 2, pp. 309-367, 1995.
- [14] J.C. Stevens and D.R. Wilson, Olefin Polymerization Process Using Supported Constrained Geometry Catalysts, U.S. Patent 6884857B1, 2005.
- [15] W. Spaleck, M. Aulbach, B. Bachmann, F. Küber, and A. Winter, "Stereospecific metallocene catalysts: scope and limits of rational catalyst design", *Macromol. Symp.*, vol. 89, no. 1, pp. 237-247, 1995.
- [16] J. Okuda, F.J. Schattenmann, S. Wocadlo, and W. Massa, "Synthesis and characterization of zirconium complexes containing a linked amido-fluorenyl ligand", *Organometallics*, vol. 14, no. 2, pp. 789-795, 1995.
- [17] K. Tangjituabun, B. Jongsonjit, and P. Praserttham, "The role of CaO in Ziegler-Natta catalyst for propylene polymerization", *Catal. Lett.*, vol. 109, pp. 147-152, 2006.
- [18] T. Sundell, H. Fagerholm, and H. Crozier, "Isotacticity determination of polypropylene using FT-Raman Spectroscopy", *Polymer*, vol. 37, no. 15, pp. 3227-3231, 1996.
- [19] K. Singha, S. Maity, M. Singha, P. Paul, and D.P. Gon "Effect of fiber Diameter Distribution of Nonwoven fabric on its properties", *Int. J. Text. Sci.*, vol. 1, no. 1, pp. 7-14, 2012.
- [20] A. Alshaiban and J.B.P. Soares, "Effect of hydrogen and external donor on propylene polymerization kinetics with a 4th-generation Ziegler-Natta catalyst", *Macromol. React. Eng.*, vol. 6, no. 6-7, pp. 265-274, 2012.
- [21] G.W. Harding and A.J. van Reenen, "Polymerisation and structure-property relationships of Ziegler-Natta catalysed isotactic polypropylenes", *Eur. Polym. J.*, vol. 47, no. 1, pp. 70-77, 2011.