AIChE Letter: Reaction Engineering, Kinetics and Catalysis

An Atmosphere-Switching Polymerization Process: A Novel Strategy to Advanced Polyolefin Materials

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DOI 10.1002/aic.14248

Significance: *We report on a novel atmosphere-switching polymerization process (ASPP) that produces advanced polyolefin materials with high performance in a single polymerization reactor through unique monomer feeding policies. In the ASPP, each polymer particle is exposed to "atmosphere A" and "atmosphere B" in an alternating manner and time and again. As a result, "polymer A" and "polymer B" are formed within the polymer particle in an alternating manner and time and again too. Two types of polypropylene (PP) in-reactor alloys are prepared: impact polypropylene copolymers (IPCs) with an exceptional stiffness-toughness balance and soft polypropylene alloys (SPPs) with well-defined, high-rubber content sticking-free particles.* © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4468–4473, 2013

Keywords: impact polypropylene copolymer (IPC), soft polypropylene alloy (SPP), atmosphere-switching polymerization process (ASPP), monomer feeding policy, number of cycles, mechanical properties

Introduction

Polyolefins, the world's most common synthetic polymers, continue to develop in terms of properties and processes.[1] One way of preparing high-performance polyolefins is to tailor the connectivity of the monomer molecules in the polymer chains. A recent example is the synthesis of linear olefin block copolymers with alternating semicrystalline and amorphous segments via chain shuttling polymerization of simple olefins.[2] Another attractive and inexpensive way is to prepare multicomponent blends *in situ* directly in reactors. For example, a typical *in situ* polypropylene (PP) blend called impact polypropylene copolymer (IPC) is produced by a two stage polymerization process (TSPP) involving the homopolymerization of propylene in the first reactor and the copolymerization of ethylene and propylene in the second reactor over the same Ziegler–Natta catalyst.[3] The final IPC product is a multicomponent, multiphase polyolefin system consisting of isotactic PP (IPP), amorphous ethylene propylene random copolymers (EPR), and semicrystalline ethylene propylene segmented copolymers (EPS).[3–6] Because of a favorable ratio of polymer properties to process economics, IPC is increasingly used in automobile parts and appliances in replacement of traditional expensive engineering plastics. Nevertheless, it is always challenging to further enlarge the properties window and improve the stiffness-toughness balance of IPC to meet ever-demanding applications.

For thermodynamic reasons IPC tends to phase separate. The chain structures of EPR and in particular those of EPS have strong impact on the phase separation and final mechanical properties of IPC.[4,7–12] However, it is difficult for a conventional TSPP to tune the molecular architecture of the EPR and EPS in an independent manner because of

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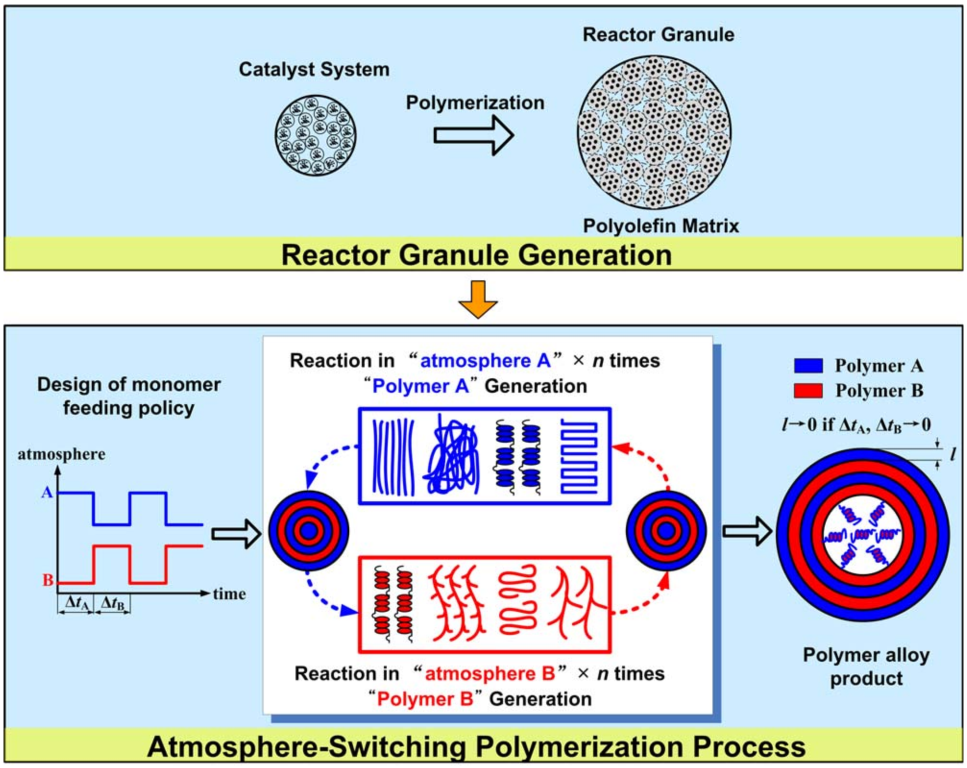

Figure 1. Schematic illustration of the atmosphere-switching polymerization process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the inherent nature of Ziegler–Natta catalysts. Very often the size of the dispersed phase domains is too large and its distribution nonuniform. The stiffness-toughness balance of the corresponding IPC is limited to a narrow range.

Another challenge in polyolefin industry is to prepare PP in-reactor alloys with high EPR contents, especially soft polypropylene alloy (SPP).[13] Indeed it is difficult to achieve a good tradeoff between softness (EPR content) and stickiness (or flowability) of the resulting polymer particles (plant operability). A few strategies for producing PP in-reactor alloys with high EPR content using mixed Ziegler–Natta and metallocene catalysts have been reported.[14,15] However, the preparation of such mixed catalysts and the synthetic procedure are very complex.

This article reports on a new atmosphere-switching polymerization process (ASPP) in a single reactor that allows for the synthesis of IPC with a very wide properties window, on the one hand, and SPP with spherical, uniform, high-rubber content and nonsticky particles, on the other hand. It relies on periodic switching of monomers which can improve the compatibility between EPR and PP by controlling the molecular structures of the EPS.[16,17] Unlike a conventional TSPP in which the homopolymerization of propylene and the copolymerization of ethylene and propylene take place successively and only once, in the case of ASPP they proceed periodically and many times.

With ASPP, a wide range of monomer feeding policies can be designed to prepare PP in-reactor alloys. In this work, four periodic monomer feeding policies are designed to prepare IPC and their impact on the mechanical properties of IPC is assessed. Another monomer feeding policy is designed to show the advantage of ASPP to synthesize SPP.

Atomsphere-Switching Polymerization Process

Figure 1 depicts the ASPP. The first step is the reactor granule generation which is a prerequisite for ASPP. The homopolymerization of an olefin or its copolymerization with a small amount of comonomer is carried out first to generate granules (polymer particles), owing to the replication ability of the fourth generation of spherical Ziegler–Natta catalysts. Each polymer particle will behave more or less like a microreactor in which further polymerization is possible, with its own mass- and heat transfer. In the second step, ASPP is implemented based on the polymer particles generated in the first step.

In the case of a conventional TSPP, each polymer particle goes through the reaction environments "atmosphere A", and "atmosphere B" only once, respectively, and the corresponding polymers are "polymer A", and "polymer B", respectively. The homogeneity of the final product depends on the kinetics of polymerization and/or diffusion of monomer(s) inside polymer particles, on the one hand, and the residence time distribution of polymer particles, on the other hand. For a given polymer particle, its compositional heterogeneity is expected to aggravate with slow diffusion of the monomer(s) or fast kinetics of polymerization. A broad residence time distribution is expected to bring about large compositional heterogeneity among polymer particles. Moreover, when a

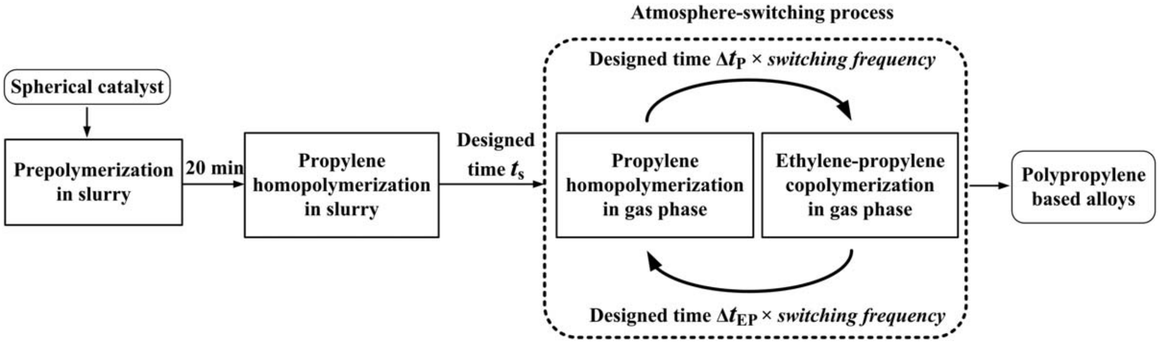

Figure 2. An ASPP for manufacturing polypropylene based alloys. t_s represents time of slurry propylene polymerization.
Δt_P, and Δt_{EP} represent retention time of propylene, and ethylene/propylene mixture per pass in the gas phase, respectively.

conventional TSPP is used to prepare IPC, only a small amount of EPS, a good compatibilizer of the IPC, is formed, because of the fact that polymer particles go through atmosphere "propylene" and atmosphere "ethylene-propylene" only once, respectively.

In the case of the ASPP, each polymer particle is exposed to "atmosphere A" and "atmosphere B" in an alternating manner and time and again. In either reaction environment "atmosphere A" or "atmosphere B", as the monomer(s) diffuses into and through the porous polymer particle, it polymerizes on active sites present on the surface of the catalyst fragments. As a result, the corresponding "polymer A" and "polymer B" are formed on the same polymer particle in an alternating manner and time and again too. If t_{all} is the overall atmosphere-switching reaction time, Δt_A and Δt_B are the retention times of "atmosphere A" and "atmosphere B" per pass, respectively, each particle will go through each different reaction environment n times with $n = t_{all}/(\Delta t_A + \Delta t_B)$. This n is called number of cycles. Since Δt_A and Δt_B depend on the number of cycles and can be much shorter than the overall reaction time, the amounts of "polymer A" and "polymer B" formed per pass can be extremely small, and, hence, "polymer A" and "polymer B" formed inside the polymer particle are expected to be mixed in a very intimate manner, even if they are very different in nature. In other words, the ASPP allows the retention time per pass being short enough to generate different polymer chains within the same shell or in different ones. Even in this latter case, these shells are so thin that segregation of different polymer phases is minimized. As expected, when the ASPP was used to prepare IPC in a previous work, [16] the size of the dispersed EPR phase domains decreased with increasing switching frequency (herein number of cycles). Furthermore, a large amount of EPS could be formed, owing to the fact that polymer particles were exposed to atmosphere "propylene" and atmosphere "ethylene-propylene" time and again. As a result, the compatibility of the PP matrix and the EPR dispersed phase was largely improved.

The ASPP is also very different from the well-known multizone circulating reactor (MZCR) process in terms of the relative motion between polymer particles and monomer atmosphere. In the case of the ASPP, atmospheres pass through the reactor which holds the polymer particles, whereas in the case of MZCR the polymer particles recirculate between its riser and downer.[18] In this latter case since polymer particles move downward in the downer as a packed moving bed, it can be a problem for PP in-reactor alloys with high EPR content to flow in such a dense phase.

Figure 2 shows an ASPP developed for manufacturing IPC and SPP. For IPC, four monomer feeding polices are designed in terms of the pressure, monomer feeding rate, copolymerization time, and sequence times of monomer feeding. For SPP, another monomer feeding policy is designed. Detailed experimental methods and reaction conditions are provided in supplementary materials.

Results and Discussion

Remarkable widening of the properties window of IPC

Figure 3 shows the mechanical properties of IPCs produced by four different monomer feeding policies. The notations *a*1 and *a*20 denote the IPCs produced by policy *a* with a number of cycles of 1 (like a conventional TSPP) and 20, respectively. In other words, polymer particles are exposed to atmosphere "propylene" and atmosphere "ethylene-propylene" in an alternating manner 1 or 20 times, respectively. When *a* and *b* are compared, it is seen that the latter significantly outperforms the former both in terms of flexural strength (stiffness) and impact strength (toughness). This implies that an increase in the monomer feeding rate leads to an increase in the impact toughness of the IPC. This could be ascribed to an increase in EPR content with increasing feeding rate. However, it is surprising that the values of the flexural modulus of the IPCs obtained by *b* are higher than those obtained by *a*, considering the fact that their EPR contents are also higher. A possible reason is that the molar mass of the IPP involved in the IPC would increase with increasing monomer feeding rate. This is more or less confirmed. For example, the weight-average molar masses of the IPP in the IPCs obtained by *b*1 is 35.5×10^4 g/mol, which is slightly higher than that obtained by *a*1 (31.1×10^4 g/mol). More details are given in supplementary materials. It is concluded that upon increasing monomer feeding rate, a better tradeoff is found between the stiffness and toughness of the IPC.

When *c*1 and *d*1 are compared, it is seen that the IPC obtained by *d*1 shows higher impact strength but lower

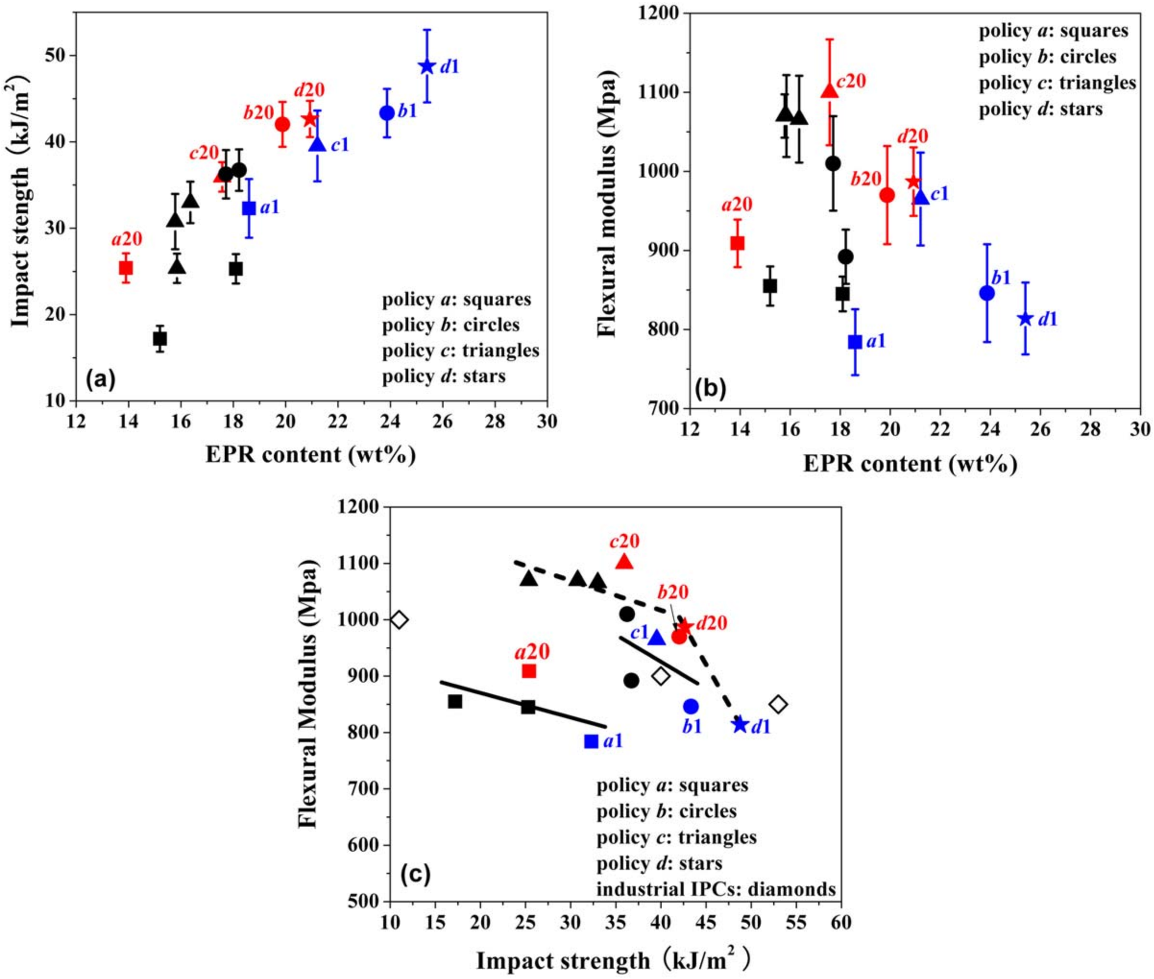

Figure 3. Mechanical properties of IPCs produced by ASPP via four monomer feeding policies.

(a) impact strength (Izod, kJ/m^2, 23°C) vs EPR content; (b) flexural modulus vs EPR content, and (c) flexural modulus vs impact strength (Izod, kJ/m^2, 23°C). The blue dots (*a*1, *b*1, *c*1, *d*1) indicate the IPCs produced by conventional TSPP with a number of cycles of 1. The red dots (*a*20, *b*20, *c*20, *d*20) indicate the IPCs produced by ASPP with a number of cycles of 20. The open diamonds indicate three industrial IPC grades from Sinopec, China. Policy *a*: $P = 0.4$ MPa, $F = 6$ SLM, $t_{EP} = 20$ min; policy *b*: $P = 0.4$ MPa, $F = 10$ SLM, $t_{EP} = 20$ min; policy *c*: $P = 0.3$ MPa, $F = 8$ SLM, $t_{EP} = 20$ min; policy *d*: $P = 0.3$ MPa, $F = 8$ SLM, $t_{EP} = 30$ min. P is the pressure, F is the monomer feeding rate whose unit is standard liter per minute (SLM), t_{EP} is the overall copolymerization time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flexural modulus. These results indicate that when a conventional TSPP is used to produce IPC, an increase in the copolymerization time leads to an increase in the impact toughness, but a decrease in the stiffness of IPC as a result of higher EPR content. Interestingly, ASPP is able to overcome this dilemma. For example, the impact strength of *d*20 is slightly higher than that of *c*1, whereas the values of their flexural modulus are almost the same. In other words, the IPCs prepared by ASPP exhibit a better toughness-stiffness balance. It is very interesting to note that while the impact strength of the IPCs obtained with more cycles such as *b*20, *c*20 and *d*20 are close to those of the IPCs prepared under fewer cycles such as *b*1, *c*1 and *d*1, the values of their flexural modulus are significantly higher. This clearly shows that an increase in the number of cycles leads to a better balance between stiffness and toughness.

Figure 3c plots the flexural modulus-impact strength window for all the IPCs reported in this article. Typical values of three industrial IPC grades from Sinopec, China, are also shown for comparison.[19] These three industrial IPCs are produced by conventional TSPP, including Hypol process and Amoco process. It is seen that the ASPP developed in this work significantly expand the properties window provided that the monomer feeding policy be appropriate.

Nonsticky soft polypropylene alloy particles

To show the ability of ASPP to produce SPP, Figure 4 compares the flexural modulus and particle morphology of SPPs obtained by another monomer feeding policy of ASPP with those of IPCs obtained by policy *a* of ASPP. The EPR contents of SPPs all exceed 35% and are remarkably higher than those of the IPCs because of higher monomer feed rate

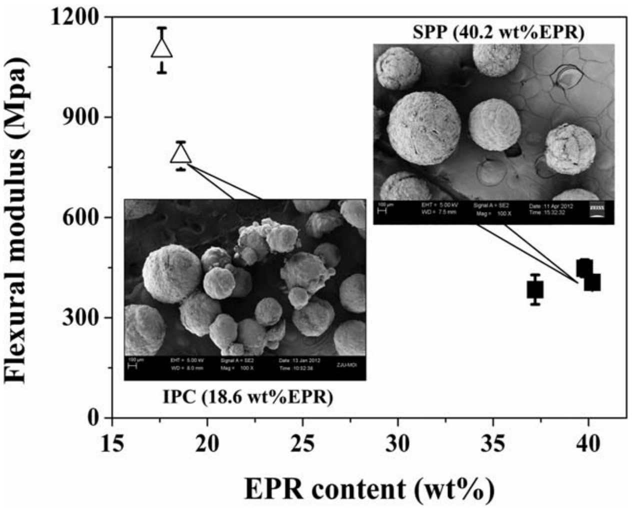

Figure 4. Flexural modulus vs EPR content and particle morphology of SPPs and IPCs. (SPPs: solid squares, IPCs: open triangles).

The SEM micrographs show the particle morphology of IPC prepared by TSPP (number of cycles = 1, $P = 0.4$ MPa, $F = 6$ SLM, $t_{EP} = 20$ min), and that of SPP prepared by ASPP (number of cycles = 20, $P = 0.4$ MPa, $F = 10$ SLM, $t_{EP} = 60$ min).

and longer copolymerization time. Concomitantly the values of their flexural modulus are significantly lower. It is more remarkable to note that while the particles of the IPC with 18.6 wt % EPR prepared by TSPP (policy *a*1 whose number of cycles is 1) are irregular in shape, nonuniform in size and stick to each other, those of the SPP prepared by ASPP (number of cycles = 20) whose EPR is as high as 40.2 wt % remain spherical, relatively uniform in size, and most importantly nonsticky.

Mechanisms responsible for the huge differences between the SPPs obtained by ASPP and those by TSPP, especially in terms of particle characteristics, remain unclear and are the subject of ongoing investigations. Nonetheless it may be speculated that the fact that in the case of ASPP polymer particles do not need to flow and that they are exposed to atmosphere propylene and atmosphere ethylene-propylene in an alternative manner and time and again provide them with greater uniformity in terms of mass and heat transfers as well as reactions, on the one hand, and more intimate dispersion of the EPR in the polymer particles, on the other hand.

Conclusions

This article shows the potential of a novel atmosphere switching polymerization process (ASPP) to manufacture advanced polyolefin materials in a single polymerization reactor using conventional Ziegler–Natta catalysts. In the ASPP, each polymer particle is exposed to “atmosphere A” and “atmosphere B” in an alternating manner and time and again. As a result, “polymer A” and “polymer B” are formed within the polymer particle in an alternating manner and time and again too. Two types of polypropylene (PP) in-reactor alloys are prepared: impact polypropylene copolymers (IPCs) with an exceptional stiffness-toughness balance and soft polypropylene alloys (SPPs) with well-defined, high-rubber content sticking-free particle. In the case of IPCs, an increase in the monomer feed rate or number of cycles leads to a better stiffness-toughness balance. In the case of SPPs, particles with more than 40% rubber phase (EPR) remain spherical, uniform in size and nonsticky. It is hoped that the process reported in this article will trigger new interests in studying or revisiting polyolefins production processes. Work is being undertaken in our laboratories.

Acknowledgments

The authors thank the National Basic Research Program of China (Grant no. 2011CB606001,) and the State Key Laboratory of Chemical Engineering for the Special Funds for Open Research Projects (SKL—ChE-08D03).

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Manuscript received Feb. 27, 2013, and revision received Aug. 7, 2013.