Recent Progress in Polyolefin Materials and Processing

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SUMMARY: In 1998, about 50% of plastic materials production in the world was made up by polyethylene (PE), polypropylene (PP) and other such polyolefin groups. Recently, various types of high-performance polyolefin materials including alloy and blend with other materials have been developed and accepted broadly in the market. For further widespread use, enhanced performance, further cost reduction, and considerations for environmental protection are needed. To find appropriate approaches to these requirements, polyolefin should be investigated in terms of not only materials but also processing.

Introduction

In 1993 the plastics production amounted to 100 million tons in the world. In 1998 it increased up to 140 million tons. Only for five years, the plastics production expanded by as much as 40%. This figure divided by the population of the world, 6 billion indicates that 25 kg of plastics per person was consumed in the world in 1998. Among the total plastics, polyolefins occupy about 50%. In addition, the growth rate of polyolefins is considerably higher than those of other commodity plastics, polystyrene, polyvinylchloride, and so on. Why do polyolefins grow rapidly and greatly? The answer is (1) Light-weight. (2) Practically good enough heat resistance, especially polypropylene can been used even at 130°C. (3) Easy processability. (4) Inexpensive features. This paper describes a recent progress in both the production and processing technology of polyolefins.

Catalyst Development

Catalyst for olefin polymerization has made a great progress during last two decades. In especial, metallocene catalyst opened the new era of polyolefin production¹⁾. Recently, non-metallocene catalyst attracts a great attention^{2,3)}.

Metallocene catalyst is commercially used for polyethylene production. As shown in Figure 1, metallocene LLDPE (m-LLDPE) possesses several outstanding characteristics compared with conventional LLDPE, (ZN-LLDPE) especially in the lower density region. m-LLDPE contains low cold xylene soluble polymer with low molecular weight and high comonomer composition which causes often blocking problem in film application and also becomes

problematic in food packaging applications from the point of view of extraction regulation. In addition, m-LLDPE shows high mechanical strength.

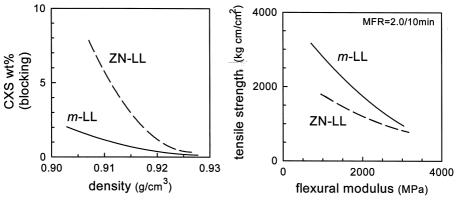


Figure 1. Comparison of m-LLDPE with ZN-LLDPE.

Ziegler-Natta catalyst performance for polypropylene has also been greatly advanced as shown in Figure 2. Since the discovery of titanium-magnesium supported catalyst system, tremendous advancement can be seen. That is, the catalytic activity increases about hundred-fold and stereospecificity increases to a great extent during two decades. Now, atactic polymer is reduced to less than 1%.

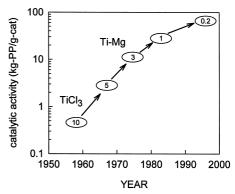


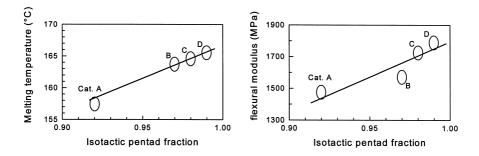
Figure 2. Advance in propylene polymerization catalyst.

As shown in Figure 3, we can control the

properties of polypropylene, e.g., the flexural modulus and the melting temperature by choosing catalyst system.

The progress of catalyst performance has simplified polypropylene production process. In classical solvent process, solvent and deashing agent were necessary to remove atactic polymer and catalyst residue, because of the poor catalyst performance. Therefore, the recovery of the solvent and deashing agent were required, resulting in complicated and expensive production process. The improvement of catalyst performance has simplified the

production process without the atactic part removal and catalyst residue extraction, leading to the reduction of production costs.



Crystal Structure Control

Although catalyst itself is a key to the molecular structure control of polyolefins, the crystal structure control is also important to improve the polymer properties. From such a point of view, we have searched various nucleating agents for polypropylene and found unique polymer type nucleating agent. Isotactic polyvinylcyclohexane (CAP), the melting point of which is 370°C, is extremely effective as a nucleating agent (NA) for polypropylene compared with conventional ones as shown in Figure 4⁴).

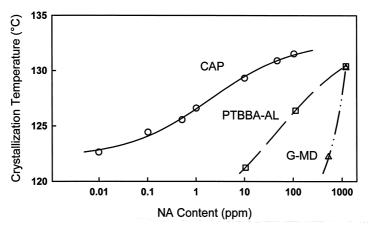


Figure 4. Effect of CAP on Crystallization of Polypropylene. PTBBA-AL: aluminum p-tertbutyl benzoate. G-MD: alkyl dibenzylidene sorbitol derivatives.

Even at a very small content, less than 1 ppm, CAP works as a good nucleating agent.

Figure 5 shows the micro photographs of polypropylenes in which the spherulites of PP are clearly seen in polypropylene without CAP, but they are no longer seen in polypropylene with CAP because of the fine sizes of spherulites.

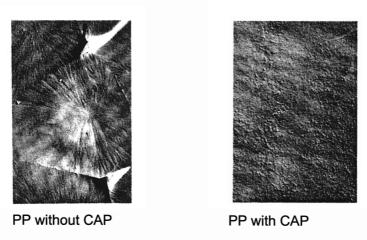


Figure 5. Spherulite size of polypropylene.

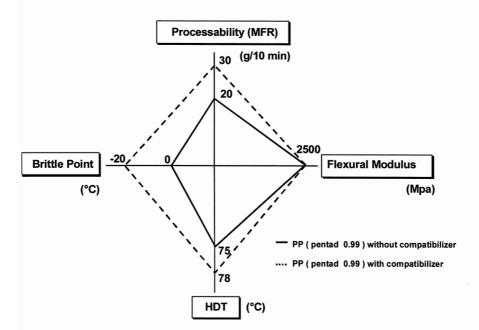


Figure 6. Bumper facia application of polypropylene. (PP/EP rubber/filler/compatibilizer).

Alloys and Blends

Alloys and blends of polyolefins with other polymers or mineral fillers broaden the application field of polyolefins. In a combination of polymers, it is generally known that there are two cases depending on miscibility; one is miscible and the other is immiscible. In the miscible case, the performance of the alloy obtained from A and B polymers demonstrates the additive and constitutive property of both polymers. On the other hand, in the immiscible case which is a common case, the performance of the alloy shows generally very poor properties due to the poor dispersion. However, if suitable compatibilizer is admitted and suitable compounding is carried out, a higher performance than that predicted from the additivity can be achieved successfully. As an example, the bumper facia application of polypropylne, is

shown in Figure 6. While the flexural modulus is kept at the high level, the improvement of processability, impact strength, and heat resistance have accomplished by choosing a suitable compatibilizer and high stereoregular polypropylene.

These efforts lead to an increase in the amount of polypropylene used in each automobile as shown in Figure 7. When an average weight of automobile is taken as 1 ton, as much as 30 kilogram of polypropylene is used, corresponding to about 10% by volume in total materials used for each car.

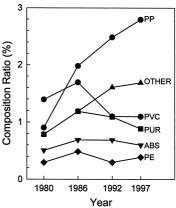


Figure 7. Break-down of plastic materials used in each automobile in Japan.

Processing Technology

A great progress has also been done in processing technology. For example, co-extrusion technology can produce various high-performance film or sheet from a combination of more than two polymers with high oxygen barrier, good heat sealability, easy openability, and so on. Large scale injection molding can produce large-scale processed product and can mold large scale integrated parts at one shot into which individual small parts used to be assembled. Low pressure processing can produce product economically because even cheap machine with low-clamping force and cheap mold can be utilized. Sumitomo Press Mold (SPM) is one of the advanced low pressure processing technologies⁵⁾. These processing technologies have expanded the polyolefin application field.

Conclusion

Recent progresses of the production and processing technology of polyolefins have expanded polyolefin application fields. Now, polyolefines occupy about 50% among the total plastics. For the coming new century, further development should be continued to enhance performance, reduce cost, and meet environmental protection.

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