

Synthesis and Characterization of Polyethylene/Poly(ethylene-co-propylene) Reactor Blends by Gas Phase Copolymerization with Supported Metallocene Catalyst Mei-Zhou Qi (11229011), Zhi-Sheng Fu, Zhi-Qiang Fan*



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Introduction

Recently, metallocene catalysts have found more applications in industrial polyolefin production. A well-known distinct feature of the single-site catalysts is their ability to copolymerize ethylene and α -olefins in a homogeneous fashion. Ethylene-propylene rubber is commercially important materials. The most widely used preparation technology is solution polymerization, whose investment and cost is the highest. Instead, the gas phase polymerization is more desirable since it is solvent-free, environmental and low cost of production. Supported metallocene catalyst can solve the reactor fouling and bad morphology of the prepared polymer.

In this work, metallocene catalyst was supported in spherical polyethylene particles, and metallocene adsorbed on the outer surface of the PE spheres was deactivated with small amount of oxygen. By gas-phase copolymerization of ethylene and propylene with the supported catalyst, polyethylene/poly(ethylene-co-propylene) (PE/EPR) reactor blends were prepared. The results showed large amount of EPR could be filled inside the PE particles without serious agglomeration of the particles.

Experimental



sticky sticky

Digital photos: Al/O₂: **a**: 0.35; **b**: 0.22; **c**: 0.17; **d**: 0.12. From the above table, it can be seen that the catalyst on the surface of PE can be selectively deactivated to produce EPR inside PE particles, obtaining PE/EPR with good flowability. The value of ΔH_m is about half of the original PE (107.4 J/g) because of a decrease in the degree of annealing and/or a reduced diffusion rate.

B. Effect of copolymerization time (t2) on the products



Digital photos: **a**: 5min; **b**: 10min; **c**: 30min; **d**: 40min. As can be seen in **a** and **b**, the particles and NaCl are separated, indiating that the oxygen has already deactivated the catalyst on the surface of PE. However, the particles attach NaCl after increasing copolymerization time, showing that the inner EPR dissolves out.



a: Original PE, the rough surface and the fibrillar structure can be seen at low and high magnification respectively. The hollow structure can be found after incision;

b: Little sticky PE/EPR at Al/O₂=0.19, the smooth surface can be seen and the fibrillar structure can not be found at high magnification. The solid structure can be found after incision;

c: Not sticky PE/EPR at Al/O₂=0.12, a little rough surface can be seen and a little fibrillar structure is still existed. The inner structure is also solid;

d: Polarizing optical microscopy: d1: original PE after incision, the sharp contrast between light and dark indicates the hollow structure; d2-d4: PE/EPR:the gray area represents EPR.

C. Effect of copolymerization pressure on the products



The copolymerization pressure can increase the amount of EPR obviously, meanwhile, the M_w and PDI also increase.

Conclusions

PE/EPR reactor blends could be obtained by gas-phase polymerization after selectively deactivating the catalyst on the outer surface of spheres by oxygen. The results showed that the hollow PE spheres played the role of shell to prevent the products from getting sticky and the resulting products are of good flowability. The content of EPR in PE/EPR could be controlled as high as 50-75 wt%. This new method of gas phase copolymerization may find application in industrial production of EPDM.

 References

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