Studies on the Preparation of New Magnetic Polyolefins Using Nanometer Magnetic Ziegler–Natta Catalyst

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ABSTRACT: Nanometer magnetic particles were prepared through oxidizing Fe^{2+} in basic solution. Initially, using resultant nanometer magnetic powder as support, supported nanometer magnetic Ziegler–Natta catalysts were obtained. Through polymerization *in situ* on the surface of nanometer magnetic particles, a new kind of magnetic polyolefin that is different from both the composite plastics' magnet and the structure plastics' magnet was obtained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2087–2090, 1999

Key words: nanometer magnetic catalyst; Ziegler–Natta catalyst; magnetic polyolefin; new polymer magnetic material

INTRODUCTION

During the past several years, demands for permanent magnets have kept increasing steadily in line with the development of home-use electric applications, audio equipment and, more recently, electronic appliances and measuring and communication equipment.[1] There are obvious trends in the home-use electric appliances and office automation equipment to move toward smaller size, lighter weight, and thinner construction. Ordinary magnets, however, are still unable to fully satisfy the required properties and are not readily amenable to machining. Polymer magnets are beginning to attract attention to overcome such a disadvantage and further meet needs for higher standards. But the polymer magnets of the structural type are still far from practical industrial production. Although polymer magnets of the blend type, such as plastics magnets, have been used, there are many disadvantages. It is difficult to compound the ferrite powders with polymer, especially with polyolefins due to their differences in density and polarity.

In this work, a new preparation method for magnetic polyolefins has been developed, and a new magnetic polyolefin that is different from composite plastic magnets and structural plastic magnets was prepared through coordination polymerization by using nanometer magnetic catalyst. Discussed in this article is the manufacturing method for these new magnetic polyolefins.

EXPERIMENTAL

Materials

Polymerization-grade ethylene and propylene (from the Zhen-hai Petroleum Chemical Plant) were purified by passing through four columns with 4A molecular sieve and a hexane solution containing 10 wt % triethylaluminium before polymerization to remove residual traces of moisture. Petroleum ether (b.p. 90°–120°C) of analytical reagent grade was purified before use. Other chemicals (research grade) were commercially obtained.

H$_2$O$_2$, stirring   OH$^-$, stirring

Fe^{2+} solution ----------------→ ------------------→ magnetic particle

step A   step B   (precipitate)

Scheme 1 Preparation of nanometer magnetic particle.

Preparation of Nanometer Magnetic Particles

Nanometer magnetic particles were prepared through H$_2$O$_2$ oxidizing Fe^{2+} from FeSO$_4$ in basic solution. The procedure of preparation can be shown in Scheme 1.

The particle diameters and particle diameter distribution of the resultant magnetic particles were measured with a Malvern Autosizer 2C instrument.
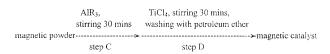
Preparation of Nanometer Magnetic Catalysts

All manipulations were carried in N$_2$. The preparative procedure of catalysts can be divided into the following two steps (see Scheme 2).
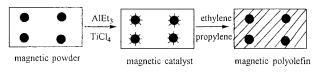
Olefin Polymerization

Polymerization procedures have been described in references 2–5. The coordination polymerization of olefins was conducted at 1 atm. Ethylene or propylene or the mixture of ethylene and propylene were rapidly bubbled through the stirred solution containing magnetic catalysts in a reactor. After polymerization, the resultant product was washed several times and dried in a vacuum oven at 60°C.

Preparation of Magnetic Polyolefin

The preparative procedure of magnetic polyolefin can be described as follows (see Scheme 3).

AlR$_3$,   TiCl$_4$, stirring 30 mins,
stirring 30 mins   washing with petroleum ether

magnetic powder ------------------→ --------------------------------------→ magnetic catalyst

step C   step D

Scheme 2 Preparation of nanometer magnetic catalyst.

Scheme 3 Preparation of magnetic polyolefin.

Table I Influence of H$_2$O$_2$ Quantities Added on the Particle Sizes

VH$_2$O$_2$ (mL)	5	10	15
d (nm)	141.6	160.4	243.4

VFe^{2+} = 30 mL, pH 13, T = 50°C.

RESULTS AND DISCUSSION

The whole procedure of preparing magnetic polyolefin through coordination polymerization *in situ* on the surface of nanometer magnetic particles can be divided into the following four steps: (1) the preparation of nanometer magnetic powder; (2) the preparation of magnetic catalyst; (3) polymerization of olefin; and (4) measurement of magnetic saturation and strength at break of resultant products.

Preparation of Nanometer Magnetic Powders

In recent years, many researchers have discovered and developed the preparation methods of nanometer powders.[6,7] In this work, nanometer magnetic powder (Fe$_3$O$_4$) was obtained through H$_2$O$_2$ oxidizing Fe^{2+} in basic solution. There are many factors affecting particle size, particle size's distribution, and magnetic properties of resultant nanometer magnetic powder.

Influence of H$_2$O$_2$ Quantity Added on Particle Size

As shown in Table I, the H$_2$O$_2$ quantity added obviously affects particle size. It is found that the particle size increases with increasing H$_2$O$_2$ quantities. However, the influence of H$_2$O$_2$ quantities for particle size is far from being understood and is still a challenging research goal.

Influence of pH on Particle Sizes and Particle Size Distribution

Table II and Fig. 1(a–c) show the influence of pH for particle sizes and particle size distribution.

Table II pH Influence on Particle Diameter

pH	9	13	14
d (nm)	114.7	160.7	122.7

VFe^{2+} = 30 mL; VH$_2$O$_2$ = 10 mL; T = 50°C.

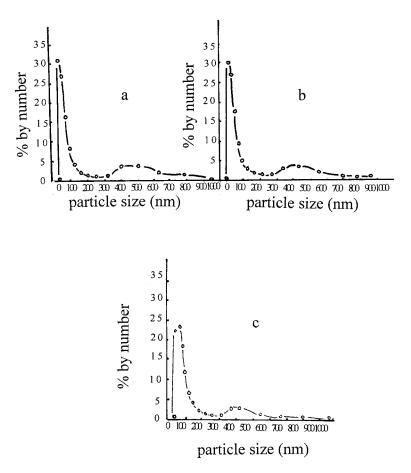**Figure 1** pH influence on particle diameter distributions. VH_2O_2 = 10 mL; VFe^{2+} = 30 mL; T = 50°C; (a) pH 9; (b) pH 13; and (c) pH 14.

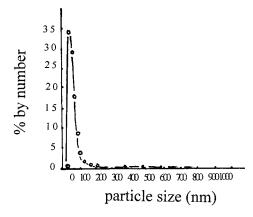Only small differences of the particle size and the particle size distributions were found in Table II and Fig. 1. But, the colors of resultant products are obviously different (pH 9: yellow; pH 13, pH 14: black). pH 13 seems to be better for both particle size distribution and magnetic properties.

However, after selecting appropriate preparation conditions and dilution $[Fe^{2+}]$, nanometer magnetic powder with narrow distribution can be obtained (as shown in Fig. 2).

Figure 2 Nanometer magnetic particles with narrow particle size distribution. VH_2O_2 = 5 mL; VFe^{2+} = 10 mL; pH 13; T = 50°C.

Table III Influence of [Al] on Polymerization Productivity (g/g_{Ti} · h)

[Al] (*M*)	0.02	0.04	0.05	0.07
A (polyethylene)	545	—	580	630
A (copolymer of *E* and *P*)	—	410	530	715
A (polypropylene)	43	67	—	78

[Ti] = 6×10^{-3} (*M*); T = 35°C; t = 20 min.

Table IV   Influence of [Ti] on Polymerization Productivity (g/g$_{Ti}$ · h)

[Ti] (M)	0.001	0.002	0.004	0.0045	0.006	0.007	0.009
A (polyethylene)	2700	3100	900	—	540	—	325
A (copolymer of E and P)	—	—	—	30	320	700	295
A (polypropylene)	—	—	62	80	48	44	30

[Al] = 1.8×10^{-2} (M); T = 35°C; t = 20 min.

Preparation of Magnetic Catalyst and Polymerization

After being aged, the slurry of catalyst obtained by using the procedure described in Scheme 2 can be divided into two phases: solid phase and liquid phase. No Ti^{3+} originating from liquid phase is detected by electron spin resonance or by chemical analysis. A signal originating from solid phases was detected by electron spin resonance which indicates Ti species are supported on magnetic particles.[8] Using this slurry as catalyst, consisting of Ti-supported magnetic particles and solvent, olefins can be polymerized *in situ* on the surface of nanometer magnetic particles, and a new magnetic polyolefin can be obtained due to resultant polyolefin covering nanometer magnetic particles through chemical and physical reactions between nanometer magnetic particle and resultant polymer. Results of polymerization are shown in Tables III and IV.

From Table III, it is found that in reaction conditions: [Ti] = 6×10^{-3} (M), T = 35°C, t = 20 min, with increasing [Al] at step C of Scheme 2, catalytic efficiencies increase, mainly due to two reasons: increasing anchoring points OAlEt$_2$ and eliminating catalyst poison (e.g., trace H$_2$O or trace O$_2$). However, from Table IV, it is found that under reaction conditions: [Al] = 1.8×10^{-2} (M), T = 35°C, t = 20 min, with increasing [Ti] at step D of Scheme 2, catalytic efficiencies first increase, then decrease. The reason is that first with increasing [Ti], polymerization sites increase and catalytic efficiencies increase. After that, with increasing [Ti], monomers become insufficient in the polymerization system and catalytic efficiencies decrease. The preparation procedure of magnetic polyolefins is represented in Scheme 3.

CONCLUSIONS

1. Through H$_2$O$_2$ oxidizing Fe^{2+} in basic solution, nanometer magnetic powders were obtained. Appropriate preparation conditions are pH 13, T = 50°C, VH$_2$O$_2$ = 5 mL and VFe^{2+} = 10 mL.
2. For the first time, using nanometer magnetic powder as a support, nanometer magnetic Ziegler–Natta catalyst was prepared. Through polymerization *in situ* on the surface of nanometer magnetic Ziegler–Natta catalyst, new magnetic polyolefins were obtained.

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