

# Synthesis and Properties of Magnets/Polyethylene Composites

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**ABSTRACT:** Polyethylene-based magnetic composites have been prepared by ethylene polymerization on the surface of NdFeB magnets, which is previously activated by ball milling with catalyst components. The level of magnets has been controlled by catalyst preparation and polymerization parameters such as Al/Ti ratio and polymerization temperature. The coercivity and the residual magnetizability were investigated. It was found that the magnetic properties of magnet powders are largely retained. In addition, in contrast to composites prepared by melt mixing, the adhesion force between magnets and polymer matrix is improved significantly and better mechanical properties are expected. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3412–3416, 1999

**Key words:** magnetic composites; ethylene polymerization; ball-milling procedure; Al/Ti ratio

## INTRODUCTION

Magnetic materials are widely used in various fields. To modify selected physical properties and to reduce cost, magnets are usually blended with polymer materials to obtain composites. The properties of these composites are affected by many factors, such as the complex interplay of the nature, the shape and size of magnets; the nature, crystallinity, and molecular weight of the polymer matrix; the filler content; the dispersion of magnets; and above all, the interfacial adhesion.

The traditional method for preparing composites is melt blending, which is inefficient. Frequently encountered problems are degradation of the magnets by heating, nonuniform dispersion of filler, and poor adhesion of the polymer to the filler, even if coupling agents are employed.

In order to overcome these limitations, Enikolopian<sup>1</sup> and Howard et al.<sup>2,3</sup> developed the polymerization-filling technique. In this technique,

Ziegler-Natta catalysts are anchored on the surface of magnets, where polymerization of olefin monomer takes place. The advantages of this method are very high filler loading (up to 95%) and uniform dispersion of filler. Better mechanical properties are also obtained because of great improvement of interfacial adhesion.<sup>4–6</sup>

There are two methods to generate active sites for polymerization on the filler surface. The transition metal compounds are either physically deposited on the surface and within the pores of the particle<sup>7</sup> or chemically anchored by reaction with some functional groups, such as hydroxyl on the surface of filler.<sup>8</sup> For NdFeB magnets, these methods are useless, because of the small specific area and the lack of a functional group. Ball milling with catalyst components is a feasible way of activating NdFeB surface, but careful operations are needed, because magnet powders size, size distribution, and magnet microstructure may be changed by ball milling, leading to the detriment of magnetic properties. In the present work, an efficient method for catalyst preparation through ball milling was successfully developed without detriment to the magnetic properties. The mag-

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netic properties and the magnet content were also adjustable by these means.

## EXPERIMENT

### Preparation of Catalyst

The melt-spun NdFeB magnets were dried under a vacuum at 50–60°C for 12 h.  $\text{TiCl}_4$  was fixed on the surface of NdFeB magnets through ball milling. The amount of  $\text{TiCl}_4$  added was about 1.22 wt %. Milling rotation rate was 120 rounds/min. After milling the excess reagent was washed off with petroleum ether under nitrogen, and the obtained catalyst was dried under a vacuum at 30°C.

### Determination of Ti Content

The Ti content on the filler surface was determined with a UV-VIS spectrometer at the wavelength of 420 nm. The sample was first dissolved in a mixture of acid solution of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  ( $\text{H}_2\text{SO}_4 : \text{HNO}_3 = 3 : 1$ ), and  $\text{H}_2\text{O}_2$  then was added to oxidize  $\text{Ti}^{3+}$  into  $\text{Ti}^{4+}$ . The interference of Fe and Nd ions was eliminated by the addition of  $\text{H}_3\text{PO}_4$ .

### Polymerization

Polymerization was conducted in slurry under atmospheric pressure, using petroleum ether as solvent. The solvent, monomer gas, cocatalyst ( $\text{AlEt}_3$ ), and supported catalyst (active fillers) were added in the said order. During polymerization the pressure of monomer gas was kept constant.

The polymerization reaction was stopped by adding a mixture of HCl and EtOH. The product was washed and dried in vacuum until constant weight. The degree of filling and catalyst activity was calculated based on weight change. The filling degree of the obtained composites varied in the range of 20 to 95 wt %.

### Properties of Composites

The adhesion between filler and PE was evaluated by the following method. Two samples prepared by different methods (filling-polymerization and traditional melt mixing) were impregnated with mixed acid ( $\text{H}_2\text{SO}_4 : \text{HNO}_3 = 3 : 1$ ) for 1 month. The morphology of samples was observed, and their weight changes were measured.

**Table I** Qualitative Analysis of Supported Fillers

	Change in Color	
	Supported Filler	Unsupported Filler
Dimethyl glyoxime	Red	No change
Chlorophosphonazon(III)	Blue	No change

The coercivity and residual magnetizability were examined by Vibration Magnet Energymeter.

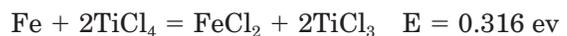
## RESULTS AND DISCUSSION

### Fixation of Catalyst on the Surface of NdFeB

Ball milling is the key step in catalyst preparation and has an important influence on catalytic activity and magnetic properties of the composites. The efficiency of ball milling depends on the microstructure and components of fillers.

The melt-spun NdFeB magnets consist of a two-phase microstructure<sup>9</sup>: small NdFeB grain,  $\approx 30$  nm in size, surrounded by a very thin film (1–2 nm) of an amorphous phase (boundary zone). The mechanical strength of the amorphous phase is weaker than that of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grain. If a mechanical force is imposed on it, the magnet breaks up along the grain boundary. Although the amorphous phase weighs less than 10% of the magnet, it plays an important role in the pinning. The coercivity drops with the decreases of Nd content in the boundary zone. On the other hand, when the amorphous phase is decomposed, the coercivity does drop but not drastically.

According to the microstructure of NdFeB magnets,  $\text{TiCl}_4$  may form a solid phase of transition metal derivatives ( $\text{TiCl}_3$ ) in the amorphous phase, and this process may be accompanied by reduction (Ti) and oxidation (Fe and Nd) of the metals. Table I indicates that some Fe and Nd on the filler surface is oxidized into  $\text{Fe}^{2+}$  and  $\text{Nd}^{3+}$ , respectively, during mechanical mixing. This process can be described by following the equations:



**Table II** Effect of Ball Milling Time on Magnet Particle Size and Ti Content

Milling Time (h)	Particle Size ( $\mu\text{m}$ )	Ti Added (wt %)	Ti Supported (wt %)
0	12.45	0	0
7	1.38	0	0
5	1.3	1.22	0.46
7	1.3	1.22	0.54
9	1.3	1.22	0.65
9.5	—	1.17	0.94
10	1.3	1.22	1.22
11	1.32	1.01	1.01

The content of fixed Ti depends on the amount of the amorphous phase and the surface area. The reaction rate also is one of the key factors determining catalyst concentration.

However, NdFeB and  $\text{TiCl}_4$  react much more slowly without mechanical force. There was no  $\text{TiCl}_4$  fixed on the surface of NdFeB if the magnet was impregnated in  $\text{TiCl}_4$  solution for 2 days. In order to estimate the effect of mechanical force and heat produced during mixing, two different fixation methods were used: (a) NdFeB was mixed with 1.22 wt %  $\text{TiCl}_4$  for 10 h, and no solvent was added. (b) A great amount of petroleum ether (petroleum ether: NdFeB = 4 : 1, weight ratio) and  $\text{TiCl}_4$  ( $\text{TiCl}_4$  : NdFeB = 0.122 : 1, weight ratio) were introduced, and the mixture was milled for 15 h. The other milling conditions were kept constant. The obtained result shows that the  $\text{TiCl}_4$  cannot be fixed on the filler surface in the presence of solvent, while 1.22 wt %  $\text{TiCl}_4$  is anchored using method (a). A possible reason for this is that if the solvent acts as a lubricant and a medium of heat transfer, then not enough energy is provided for the reaction. Thus, friction heat and mechanical force are two essential factors in catalyst preparation.  $\text{TiCl}_4$  is deposited onto the filler surface only in the absence of solvent.

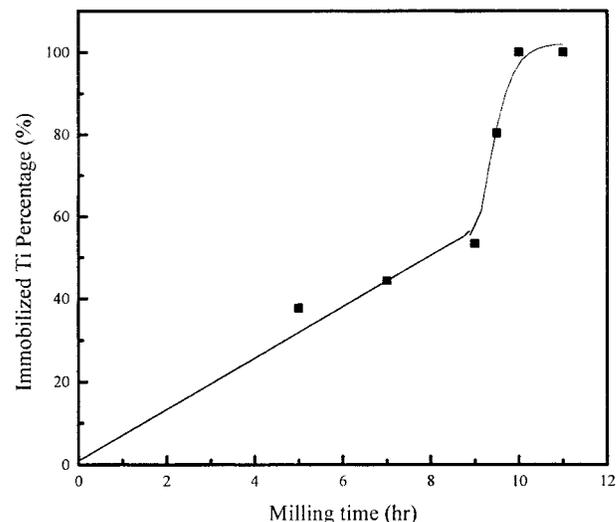
#### Effect of Milling Time on Catalyst Preparation

Milling time is important to the control of magnet particle size, size distribution, and the amount of Ti on the filler surface. Table II summarizes the variation of particle size and fixed Ti content with milling time. A dramatic decrease in the mean particle size was found in the initial 5 h. However, when ball milling exceeds 5 h, both particle size and particle size distribution no longer change

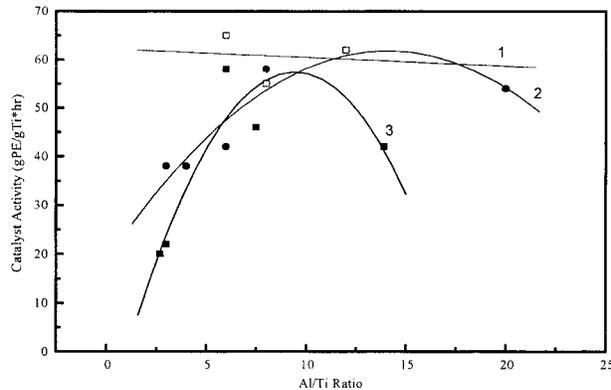
basically. It is clear that the magnet more easily broken up at the beginning of ball milling. Furthermore, after ball milling, the particle size of magnets is 3  $\mu\text{m}$ , which is still much larger than the size of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains. Thus, the magnet grain and the boundary phase may not be destroyed seriously.

As mentioned above, the fixed Ti content depends on the surface area and the amount of the amorphous phase. Therefore, it is expected that Ti concentration increases greatly during first 5 h of milling, but the data in Table II and Figure 1 show that the Ti deposited on the surface enriches throughout the whole mixing of the 10-h interval, and a significant change in fixed Ti quantity is observed in the of 9- to 10-h interval.

This change is attributed to two reasons: the greater surface area because of broken magnet powders and the accumulating friction heat. Initially, the powder is broken along the amorphous phase, and the increased surface area and the amount of boundary grain lead to the increase of Ti concentration. After a certain time, although the fracture of particles becomes difficult, some flaws may be formed at the filler surface and the area also increases. Furthermore, the heat produced by ball milling accumulates during the beginning of the ball milling process because of the poor heat transfer. Then the reaction between  $\text{TiCl}_4$  and the NdFeB magnet is accelerated more and more. In the interval of the 9th to 10th h, the accumulated heat may lead to an increase of the temperature, and the reaction rate is speeded up significantly in this period.



**Figure 1** Ball milling versus percentage of added Ti fixed on the fillers.



**Figure 2** Effect of Al/Ti ratio on the polymerization productivity. 1: Ti = 0.46%, 5 h; 2: Ti = 0.65%, 9 h; 3: Ti = 1.22%, 10 h.

### Ziegler–Natta Polymerization of Ethylene on the Surface of Magnets

One of the main objects of this work was to obtain composite materials with various NdFeB contents, which can be achieved by the variation of the polymerization temperature, changes in ball-milling procedure, and the ratio of catalyst to cocatalyst (Al/Ti ratio) for the polymerization. The Al/Ti molar ratio has a definite effect on the productivity of the catalyst (Fig. 2).

In every system, there is an optimum condition, but in different system, the productivity is affected by Al/Ti ratio to a different extent. However, for the catalyst prepared under 5 h milling, the Al/Ti ratio has little influence on polymerization productivity. It affects the catalyst productivity more and more with the milling time, which increases Ti content. When the filler has mixed for 10 h, a change of Al/Ti ratio (3–8) leads to a variation of productivity from 5 to 65 g PE/g Ti\**h*.

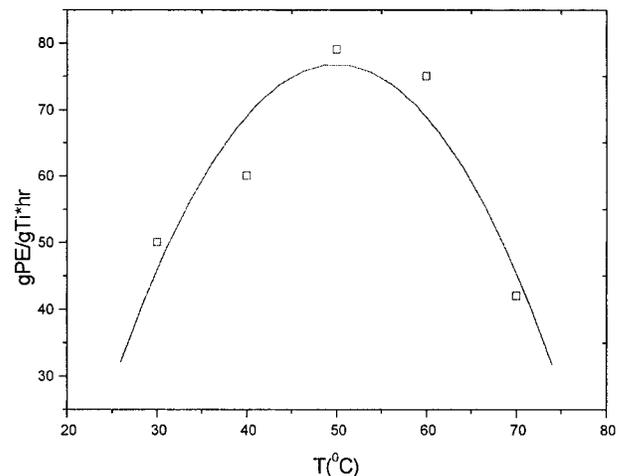
In order to explain this phenomenon, it is worth mentioning that triethylaluminum is used as a reducing agent for the Ti atoms, i.e., from  $Ti^{4+}$  to  $Ti^{3+}$ . However, the Nd and Fe in the NdFeB amorphous phase also can serve as a reducing agent. While the Ti content is low, Fe and Nd can react with the Ti ion, and the role of  $AlEt_3$  is weakened. However, the total amount of the amorphous phase is less than 10% of the magnet weight. As the Ti concentration increases, the quantity of Fe and Nd is insufficient to reduce Ti ions; thus, the  $AlEt_3$  plays a relatively significant role.

Controlling polymerization temperature is an important way of adjusting catalyst productivity. The effect of polymerization temperature on catalyst activity is schematized in Figure 3.

The productivity increases with the temperature in the interval of 30–50°C, but it falls while the temperature increases from 50 to 70°C. This can be attributed to two factors, polymerization rate and monomer concentration, which have adverse influence on polymerization. When the polymerization rate is accelerated because of improved temperature, the ethylene gas dissolved in solvent decreases. Therefore, although risen temperature provides the catalyst active centers with more energy, at the same time the monomer concentration decreases. The interaction of the two factors result in an optimum polymerization temperature.

### Properties of Composites Prepared by Filled Polymerization

Figure 4 shows the effect of NdFeB concentration on the coativity of the composites. The samples were prepared under different polymerization conditions and with various catalysts. Preparation conditions of catalyst had no important influence on coativity. This fact is in accordance with the conclusion that ball milling does not seriously damage the microstructure of NdFeB domain. Nevertheless, the coativity of the composites increases slowly with the decrease in NdFeB content. It may be due to the following reason: at high NdFeB contents, the surface of the magnets could not be packed entirely by the polymer, and the uncovered surface increases with the NdFeB content, resulting in the partial oxidation of the NdFeB magnets in the air, which leads to the damage of the coativity of the composites.



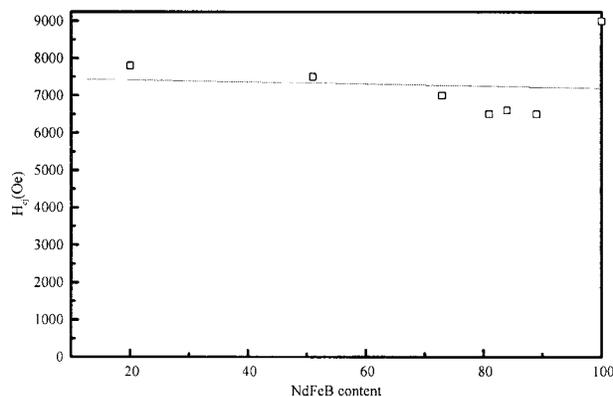
**Figure 3** Effect of polymerization temperature on catalyst productivity.

The effect of NdFeB content on the residual magnetizability of the composites is illustrated in Figure 5. It shows that the residual magnetizability is only relevant to the NdFeB content in the composites. Initially, the residual magnetizability increases steadily with NdFeB content. However, a slight decrease in the residual magnetizability is observed at high filling degree, perhaps because the distance among magnet powders is so short at high filler level that interaction of unorientated magnet powders eliminates part of the residual magnetizability. In a word, ball milling does not damage magnetic properties significantly. The magnetic properties of composites are almost only relevant to the NdFeB content of materials.

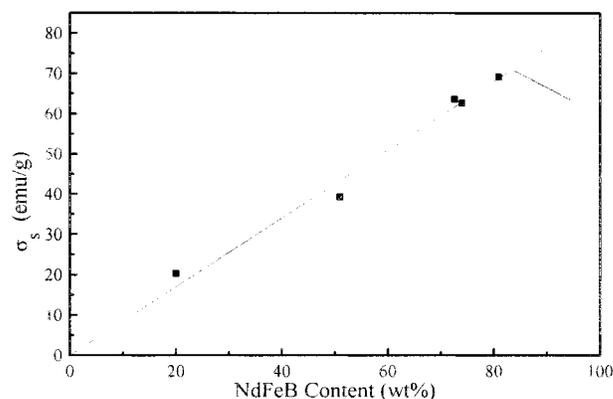
The adhesion between magnets and polyethylene is estimated by the method introduced formerly. It can be observed that NdFeB in the composites prepared by the traditional process is completely dissolved in the mix-acid solution after a week. Comparably, NdFeB in materials synthesized by filling polymerization is not significantly destroyed in a month. It can be concluded that the adhesion between the two phases is greatly improved during filling polymerization. Thus, better mechanical properties and uniform distribution of fillers are expected for these composites.

## CONCLUSION

Through ball milling, titanium tetrachloride can be anchored on the surface of NdFeB magnets, by reacting with Nd and Fe atoms in the boundary zone of a  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grain. These supported catalysts can be used to synthesize magnet/polymer composites.



**Figure 4** Coercivity of the composites versus filling degree.



**Figure 5** Residual magnetizability versus filling degree.

Filler concentration in composites can be adjusted by following methods: the change of Al/Ti ratio, the temperature of polymerization, and the variation of the ball milling procedure. The content of magnet can vary from 20 to 95 wt %.

The magnetic properties only depend on filler content in composites. The coercivity of composites vary slightly with different materials and decreases only a little at high filler concentrations. The residual magnetizability increases with filler degree at first, but it decreases at high NdFeB levels because of interactions among magnet particles. Furthermore, the improved mechanical properties of the composites prepared by filling polymerization are expected because of excellent adhesion force between magnets and polymers.

## REFERENCES

1. Enikolopian, N. S. USSR Pat. 763 379, 1976.
2. Howard, E. G.; Lipscomb, R. D.; Macdonald, R. N.; Glazard, B. L.; Tullock, C. W.; Collette, J. W. *Eng Chem Prod Res Dev* 1981, 20, 421.
3. Howard, E. G.; Lipscomb, R. D.; Macdonald, R. N.; Glazard, B. L.; Tullock, C. W.; Collette, J. W. *Eng Chem Prod Res Dev* 1981, 20, 429.
4. Hindrycks, F.; Dubois, P.; Jerome, R.; Teyssie, P.; Marti, M. G. *J Appl Polym Sci* 1997, 64, 423.
5. Hindrycks, F.; Dubois, P.; Jerome, R.; Teyssie, P.; Marti, M. G. *J Appl Polym Sci* 1997, 64, 439.
6. Wang, Q.; Kaliaguine, S.; Ait-kadi, A. *J Appl Polym Sci* 1992, 44, 1107.
7. Enikolopyan, N. S. *Filled Polymers I: Science and Technology*, Springer-Verlag: Berlin, 1990.
8. Damayanov, D.; Velikova, M. *Eur Polym J* 1989, 15, 1075.
9. Mishra, R. K. *J Magn Magn Mater* 1986, 55, 450.