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Effect of polymer matrices on magnetic properties of plastic magnets

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Plastic magnets were prepared using commercial polyamide (Nylon 12), polystyrene and ethylene–vinylacetate copolymer, and three kinds of ferrite magnetic powders with different concentration levels (20, 35 and 50 vol %). Their magnetic properties and thermal stability are discussed comparing viscoelasticity and thermal properties of the polymers and plastic magnets. Magnetic properties of the anisotropic plastic magnets were largely dependent on the concentration of the magnetic powder and its degree of orientation in the matrix. The degree of the orientation was mainly affected by the interaction between polymer matrix and magnetic powder, and viscoelastic property of the matrix polymer. It was also affected to some extent by the shape of the magnetic particles. The order of the interaction of the polymers to the magnetic powders was as follows: PA > EVA copolymer > PS, and PA-bonded magnets gave the highest magnetic properties among the matrices examined. The decrease in magnetic properties due to the change in the orientation of magnetic powder rarely occurred during thermal treatment.

1. Introduction

Magnetic properties of plastic magnets composed of polymer matrices and magnetic powder are inferior to general casting or sintered magnets, but they have various advantages, e.g. higher producibility, possible production of complicated small and thin shapes with precision, etc. Therefore, they have been widely used in various fields and have played very important roles in the rapid development of electronic instruments, communication instruments, household utensils, audio equipment and so on, and a number of papers and reviews have been published [1–14].

For plastic magnets it is easy to see that the properties of the polymer matrices, especially viscoelasticity, may affect the processability as well as magnetic property. Furthermore, because identical poles in magnetic particles are orientated repulsively in the anisotropic plastic magnets, we have been interested in the effect of polymer matrix as well as the shape and concentration of the magnetic powder on the magnetic properties, and also changes in the magnetic properties during thermal treatment.

In this paper, plastic magnets were prepared using three kinds of polymer matrices (polyamide (Nylon 12), polystyrene and ethylene–vinylacetate copolymer) and three kinds of ferrite magnetic powders with different concentration levels (20, 35, 50 vol %), and their magnetic properties and thermal stability are discussed, comparing viscoelasticity and thermal properties of the polymers and plastic magnets.

2. Experimental details

2.1. Materials

The following commercial powdery or small flake polymers were used as matrices: polyamide (Nylon 12, PA; commercial name Diamide, Dicel Chemical Industry Co. Ltd), polystyrene (PS; commercial name Stylone, Asahikase Co. Ltd), ethylene–vinylacetate copolymer (EVA; VAc: 19 wt %; commercial name Evaflex, Mitsui-Du Pont Co. Ltd).

The commercial magnetic powders used were products of Japan Bengara Industry Co. Ltd and were as follows: strontium ferromagnetic powders: commercial name OP-56, average size 1.00 μm, rich in plate shapes; commercial name OP-71, average size 1.19 μm, rich in block shapes. Barium ferromagnetic powder: commercial name BOP-M, average size 1.33 μm, rich in spherical shapes coagulated with small particles (see Fig. 1).

2.2. Preparation of samples

Weighed amounts of the magnetic powder (20, 35 and 50 vol %) were blended with powdery or flake polymer in an envelope made of polyethylene, added to a double screw-type blender previously warmed (~220° C for PA and PS series, ~100° C for EVA series) and mixed thoroughly at 30 r.p.m. under atmospheric conditions for 30 min. After cooling the blend was taken out and crushed (for PA, PS series) using a stainless-steel hammer or cut (for EVA series) to less than ~5 mm^3.

For the viscoelasticity measurement and thermal

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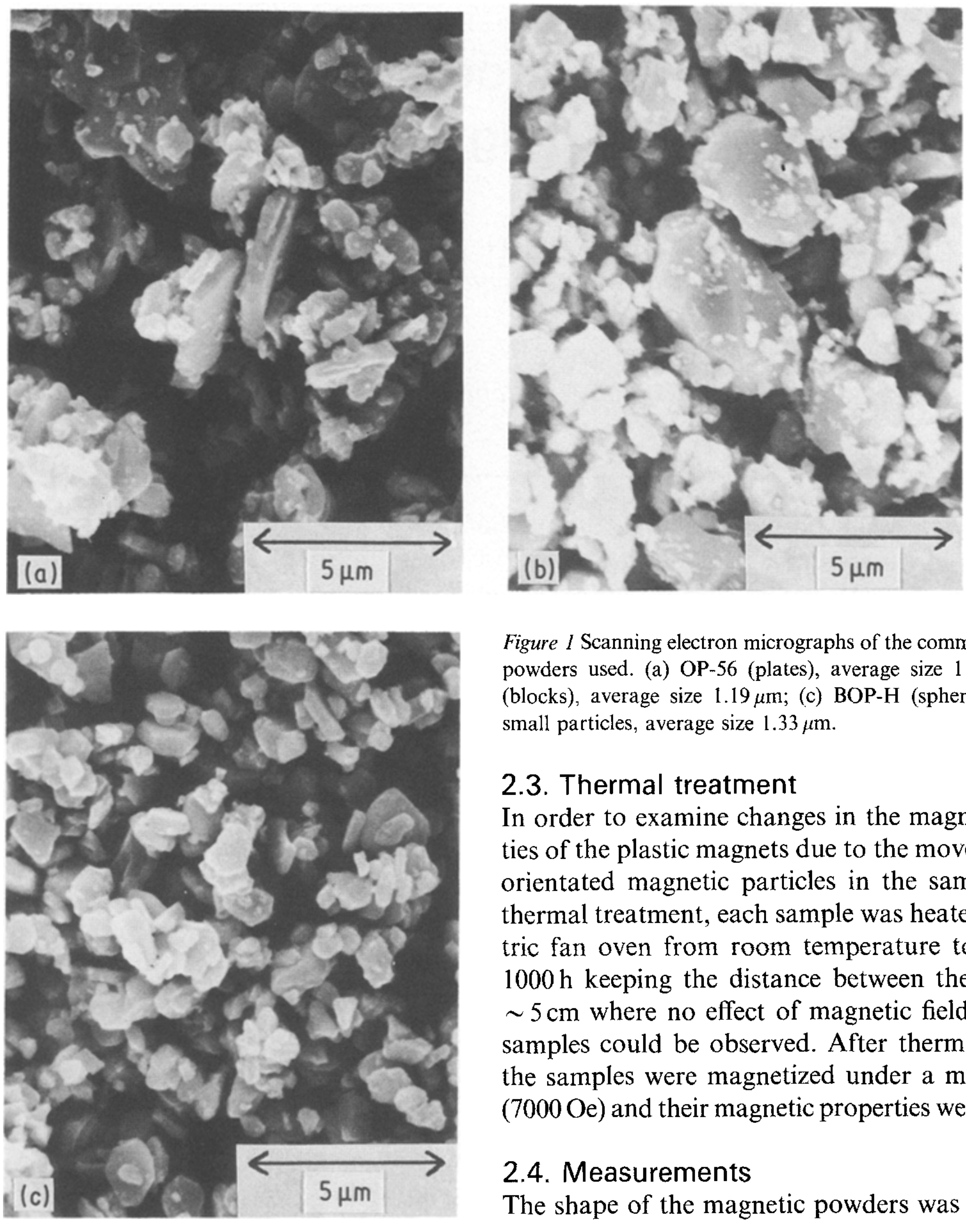


Figure 1 Scanning electron micrographs of the commercial magnetic powders used. (a) OP-56 (plates), average size 1 µm; (b) OP-71 (blocks), average size 1.19 µm; (c) BOP-H (spheres), coagulated small particles, average size 1.33 µm.

analysis, the small blend was crushed or cut to ~ 1 mm^3 and pressed at ~ 150 kg cm^{-2} using a vacuum press under vacuum (~ 2 mm Hg) at constant temperature (PA series ~ 220 to 250° C, PS series ~ 250° C, EVA series ~ 100° C) for 10 min to obtain a 0.2 mm thick plaque, of 40 mm diameter.

For magnetic property measurement, the blend (~ 5 mm^3 size) was moulded using an injection moulding machine (Sanjo Seiki Co. Ltd AV-300) under the following conditions: magnetic field 7000 Oe; previously heated at a constant temperature (PA series 220 to 250° C, PS series 180 to 200° C, EVA series 90 to 100° C) under vacuum (2 mm Hg); injection pressure 70 kg cm^{-2}; cooling period 10 min. During the moulding process, orientation of the magnetic particles occurred and anisotropic plastic magnets were prepared.

After removal of the magnetic force, the central portion of the mould was cut into $9 \times 9 \times 9\,mm^3$ size and each surface was polished with a fine sand paper (no. 800). The anisotropic plastic magnet samples prepared were magnetized by a direct current magnetic flux meter (Riken Electronic Co. Ltd, BHH-3) under 16 kOe at room temperature.

2.3. Thermal treatment

In order to examine changes in the magnetic properties of the plastic magnets due to the movement of the orientated magnetic particles in the samples during thermal treatment, each sample was heated in an electric fan oven from room temperature to 150° C for 1000 h keeping the distance between the samples to ~ 5 cm where no effect of magnetic field from other samples could be observed. After thermal treatment the samples were magnetized under a magnetic field (7000 Oe) and their magnetic properties were measured.

2.4. Measurements

The shape of the magnetic powders was observed by scanning electron microscopy (Japan Electronic Co. Ltd JMS-T20).

Melting properties of matrix polymers were measured by a Laboplastmill (Toyo Seiki Co. Ltd, 18-125) using ~ 90 g sample at a constant screw rotating speed (50 r.p.m.), and heating rate (5 °C min^{-1}), and the torque of the rotating axis was recorded.

Differential scanning calorimetry (DSC) of the plastic magnets was carried out with a calorimeter (Rigaku Electric Co. Ltd Thermoflex DSC 8230) under atmospheric conditions at a heating rate of 5° C min^{-1}, and glass transition temperature (T_g) was measured.

The viscoelasticity of plastic magnets was measured by a viscoelastic spectrometer (Iwamoto Seisakujo Co. Ltd, VES-F) under atmospheric conditions at a heating rate of 2.5° C min^{-1} at 10 Hz, and the storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) = E''/E' were determined (where E = Young's modulus), sample size: 0.2 mm × 5 mm × 10 mm.

Magnetic properties were measured by a direct current magnetic flux meter (Riken Electronic Co. Ltd, BHH-3) recording demagnetization curve (4π I–H curves) at room temperature from which residual magnetic flux density (Br) and maximum energy product ($(BH)_{max}$) were determined. Furthermore, the degree of orientation of the magnetic properties was also calculated using the following equation.

$$P_a(\%) = \frac{M_a}{M_l + M_d + M_w} \times 100$$

where, P_a is the degree of orientation of magnetic property to a direction which is either l, d, or w; M_a is the magnetic property (Br, or $(BH)_{max}$) of a particular direction, where l is the applied magnetic field direction, and d and w are at right angles to l.

3. Results and discussion

3.1. Melt viscosity of matrix polymers

It is well known that a load (torque) is necessary in screws of a laboplast-mill rotating at a constant speed in a melt polymer, which is in proportion to its melt viscosity [15].

As shown in Fig. 2, the torque of the polymer used decreases with increasing temperature but each polymer shows quite characteristic behaviour. In the case of PA, the torque is measurable at ~180° C, where melting of the polymer commences, and it decreases rapidly up to ~200° C and then more slowly. At a temperature higher than ~250° C, measurement of the torque was impossible because of thermal decomposition of the polymer.

In the case of PS, torque is measurable at ~190° C and decreases linearly with temperature, but measurement of the torque was impossible at ~230° C because of degradation of the polymer. In the case of EVA, torque is measurable at a lower temperature (~80° C) than in the previous two polymers and decreases rapidly up to ~100° C and then more slowly.

3.2. Glass transition temperature (T_g)

It is often pointed out that the glass transition temperature (T_g) due to segmental motion of the polymer is affected by added filler, and reflects the interaction between polymer matrix and filler [15].

Representative DSC curves are shown in Fig. 3 and also the T_g of each sample is summarized in Table I. In the case of the PA series, T_g and melting point (T_m) were observed at ~30° C and ~170 to 180° C, respectively. T_g of PA-bonded magnets is slightly higher (3 to 15° C) than that of pure PA. The increase in the T_g suggests that the presence of the fairly strong interaction between polymer matrix and magnetic particles restricts the movement of the matrix surrounding the magnetic particle surface.

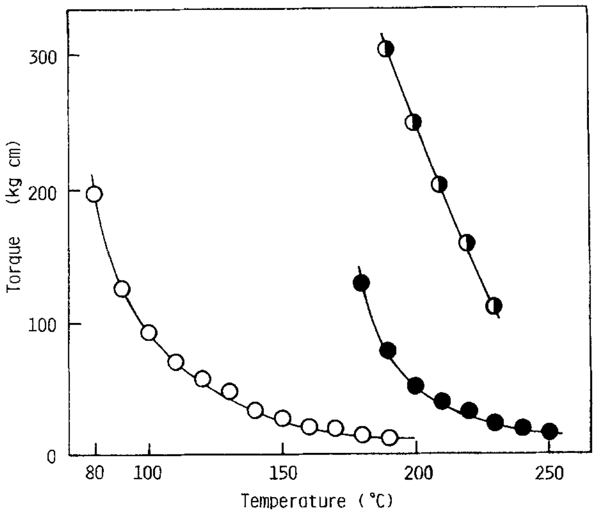


Figure 2 Melt viscosity of polymers. (●) PA, (◑) PS, (○) EVA.

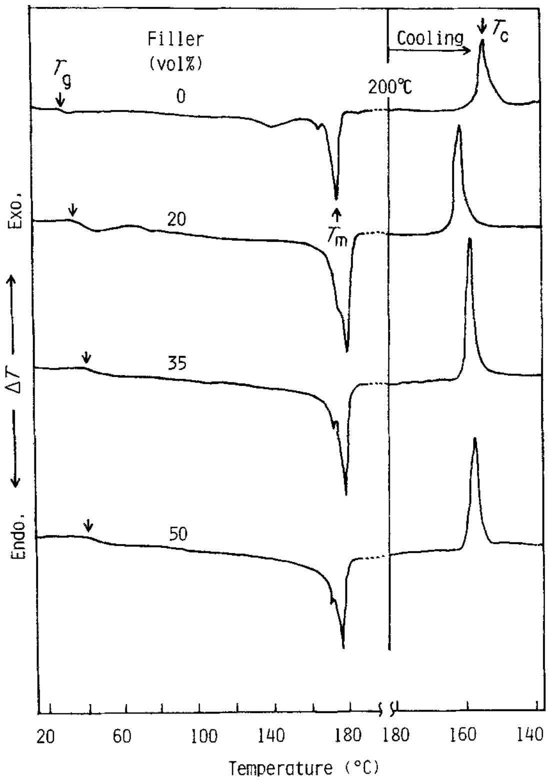


Figure 3 DSC thermograms of PA-bonded magnets (OP-56 series).

In the case of PS series only a small increase in T_g was observed which suggests that interaction between PS matrix and magnetic particles is fairly poor. Neither was any appreciable shift in T_g observed in the case of the EVA series.

3.3. Viscoelasticity

It is generally believed that the adsorption of polymer on the filler surface restricts molecular movement, conformation and orientation of the segment of the polymer [15]. The information on the interaction between polymer matrix and magnetic particles can be

TABLE I T_g of polymers and polymer-bonded magnets obtained by DSC

Polymer	Filler concentration (vol %)	T_g (°C)		
		OP-56	OP-71	BOP-M
PA	0	30	30	30
	20	35	33	41
	35	40	35	43
	50	40	37	45
PS	0	93	93	93
	20	97	95	96
	35	99	96	97
	50	98	97	99
EVA	0	−49	−49	−49
	20	–	−43	–
	35	–	−34	–
	50	–	−50	–

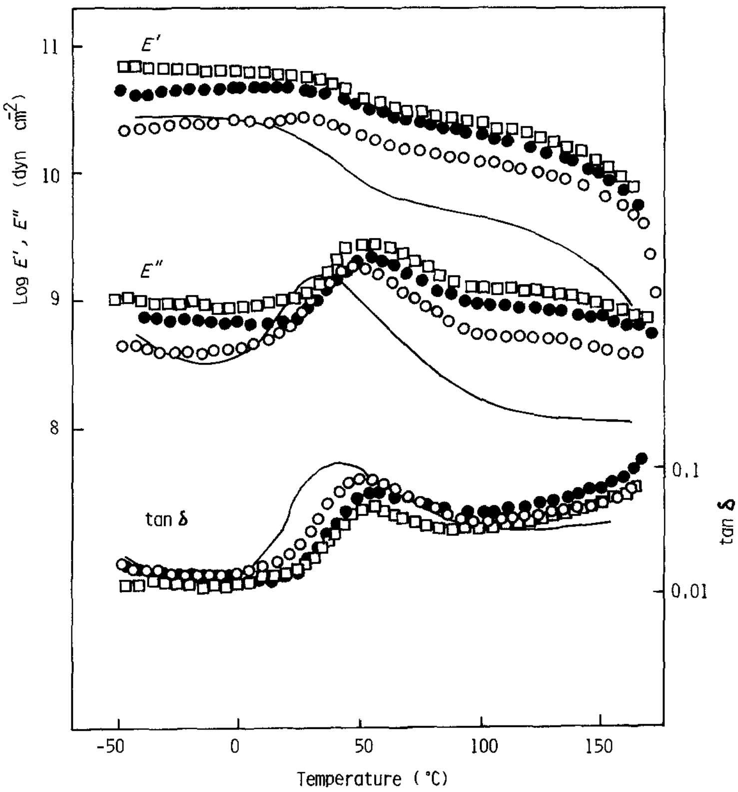


Figure 4 Temperature dependence of dynamic mechanical properties of PA-bonded magnets (OP-56 series). Filler: (——) 0 vol %; (○) 20 vol %; (●) 35 vol %; (□) 50 vol %.

obtained by dynamic mechanical properties of polymer-bonded magnets. Therefore, viscoelastic spectra were measured for all samples prepared and the spectra of the OP-56 magnet series are shown in Figs. 4 to 6 as representative examples. As shown in Fig. 4, PA shows an appreciable decrease in storage modulus (E') at ~ 30 to 50° C, and a maximum peak is observed in loss modulus (E'') at $\sim 35°$ C, and also in loss tangent (tan δ) at a slightly higher temperature, $\sim 40°$ C. Measurement of the mechanical properties above 160° C was impossible because of the breakdown of the sample. Because these changes in viscoelasticity occur near the glass transition temperature (T_g), the results apparently demonstrate that stored energy in the polymer segments is lost as thermal energy.

These E', E'' and tan δ values increase with increasing concentration of magnetic powder, and maximum points in both E'' and tan δ curves shift towards

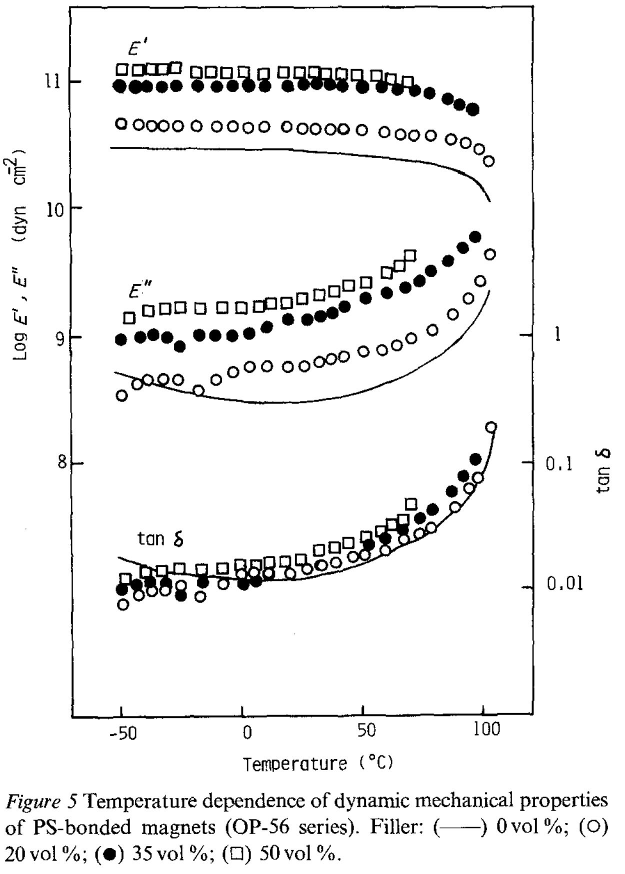


Figure 5 Temperature dependence of dynamic mechanical properties of PS-bonded magnets (OP-56 series). Filler: (——) 0 vol %; (○) 20 vol %; (●) 35 vol %; (□) 50 vol %.

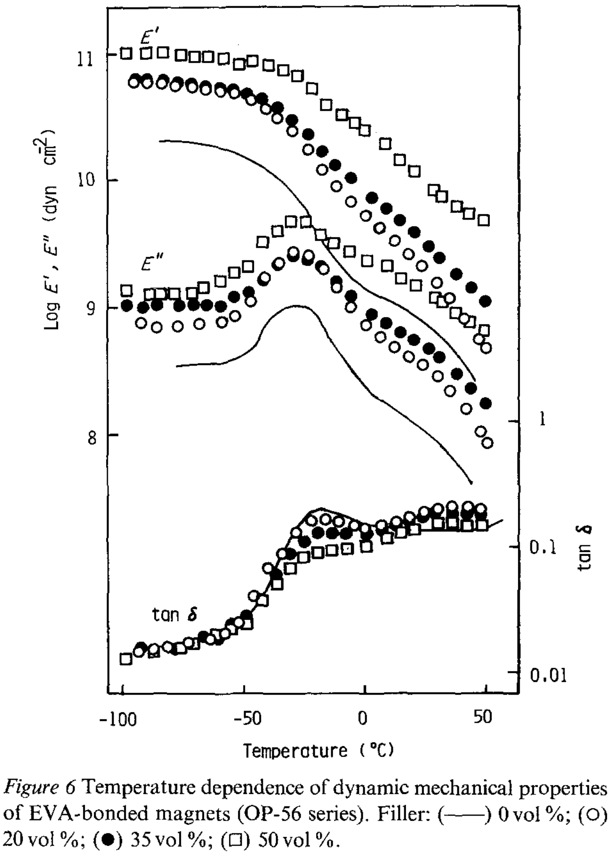


Figure 6 Temperature dependence of dynamic mechanical properties of EVA-bonded magnets (OP-56 series). Filler: (——) 0 vol %; (○) 20 vol %; (●) 35 vol %; (□) 50 vol %.

TABLE II Maximum temperature of tan δ of PA-bonded magnets

Filler concentration (vol %)	Maximum temperature of tan δ (° C)		
	OP-56	OP-71	BOP-M
0	46	46	46
20	52	52	53
35	55	52	53
50	56	55	62

higher temperature. Similar phenomena were also observed in OP-71 and BOP-M series magnets. The maximum points of the tan δ in PA-bonded magnet series are summarized and shown in Table II. These changes in viscoelastic properties in PA-bonded magnets apparently suggest that the presence of the interaction between polymer and magnetic particles restricts the movement of the polymer segments around the magnetic particle surface.

In the case of PS, a decrease in E' due to glass transition and an increase in E'' are observed at ~90 to 100° C, but no maximum peak appears in either E'' and tan δ (see Fig. 5). The elasticity increases with increase in the concentration of magnetic powder, and a remarkable change occurs at ~100° C; measurement of the mechanical properties then became impossible. In the case of PS-bonded magnets containing 50 vol % magnetic powder, the sample piece broke at ~70° C and no measurement was obtained.

In the case of EVA, a decrease in E' due to glass transition and an increase in E'' are observed at ~ −30 to −20° C, and both E'' and tan δ curves show maximum peaks, but measurement became impossible at ~60° C. With increase in the concentration of magnetic powder the elasticity of the plastic magnets apparently increases and maximum peaks in E'' and tan δ curves shift slightly towards higher temperature (see Fig. 6).

3.4. Magnetic properties

As representative examples of anisotropic plastic magnets, demagnetization curves of PA-bonded OP-56 magnetic series are shown in Fig. 7. From these curves the residual magnetic flux density ($Br = 4\pi I$) and the maximum energy product ($(BH)_{\max}$) can be obtained for the applied magnetic field axis (l direction) and two vertical axes (d and w directions).

As shown in Fig. 7, both residual magnetic flux density (Br) and maximum energy product ($(BH)_{\max}$) increase with increasing concentration of magnetic powder. Naturally, Br and $(BH)_{\max}$ in the l-direction were much higher than that in the d and w directions, and from these values the degree of orientation (P%) for each direction can be determined.

It is well known that magnetic properties of the anisotropic plastic magnets are largely dependent on the concentration of magnetic powder. This fact is clearly shown in Fig. 8 where residual magnetic flux density (Br) is plotted against the concentration of magnetic powder for each ferrite series. Similar results are also observed in the maximum energy product (see Fig. 9). However, the tendency of the increase in the magnetic properties (Br and $(BH)_{\max}$) is affected by the kind of polymer matrix used, especially at 50 vol % magnetic powder, and the order of the increase in the magnetic properties is as follows:

$$\text{PA series} > \text{EVA series} > \text{PS series.}$$

Although a remarkable difference in the kind of magnetic powder is not observed, the OP-56 and OP-71 series show similar tendencies, and the BOP-M series gives lower values.

The results mentioned above can apparently be observed when the degree of the orientation (P%) of the maximum energy product ($(BH)_{\max}$) is plotted against the concentration of magnetic powder. In Figs 10 to 12 plots are shown for each PA, PS and EVA series, individually.

In the case of PA-bonded magnets, the degree of orientation (P%) of the maximum energy product for the applied magnetic field axis (l-direction) is ~90% in all magnetic powder concentration levels (see Fig. 10). This suggests that the compatibility between PA matrix and magnetic powder is fairly good.

In the case of the PS matrix series, the degree of orientation (P%) of the maximum energy product decreases with increasing concentration of magnetic powder and this tendency is especially prominent at 50 vol % (see Fig. 11). The results are ascribed to the poor compatibility between the PS matrix and the magnetic powder, i.e. when the concentration of magnetic powder is high, the level of interaction between magnetic particles themselves becomes so strong as to restrict free rotation of the magnetic particles in the

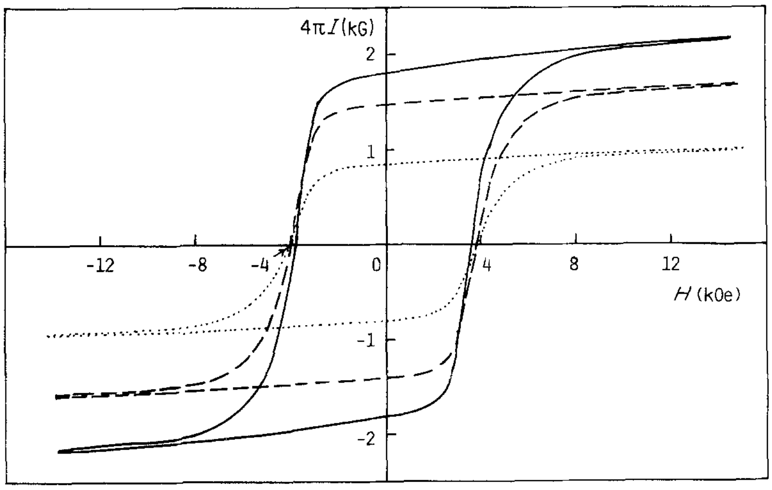


Figure 7 Demagnetization curves of PA-bonded magnets (OP-56 series). Filler: (– – –) 20 vol %; (· · · ·) 35 vol %; (——) 50 vol %.

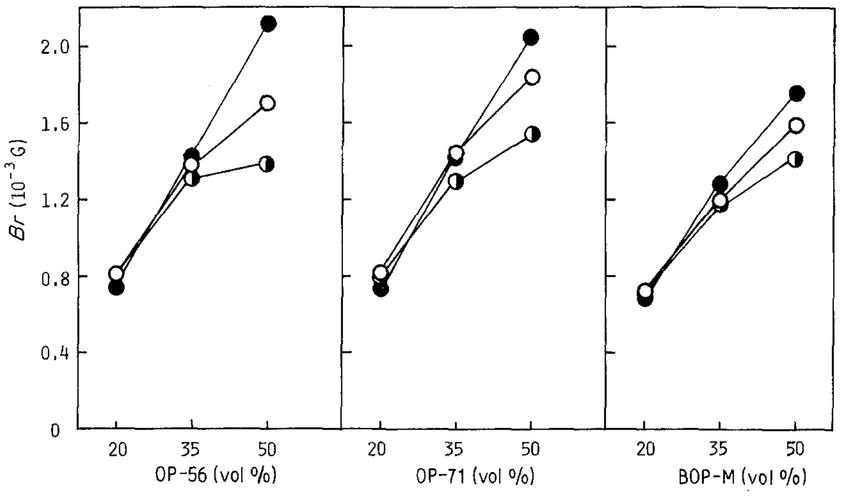
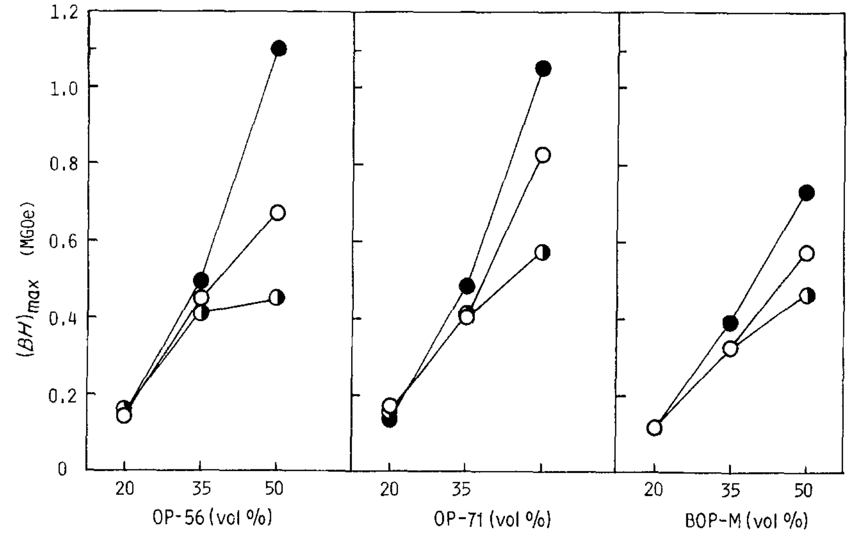


Figure 8 Residual magnetic flux density (Br) of oriented plastic magnets. (●) PA, (◑) PS, (○) EVA.

Figure 9 Maximum energy product ($(BH)_{\max}$) of oriented plastic magnets. (●) PA, (◑) PS, (○) EVA.



matrix. The poor interaction between PS matrix and the magnetic powder can be also assumed from the changes in T_g and viscoelastic properties in the PS-matrix series (see Sections 3.2 and 3.3).

In the case of the EVA matrix series, the degree of orientation (P%) of the maximum energy product is very similar at 20 and 35 vol % magnetic powder, but is much lower at 50 vol %. The results suggest that the compatibility between the EVA matrix and the magnetic powder is inferior to that in the PA-matrix series but slightly better than that in the PS-matrix series.

As mentioned above, it is clearly demonstrated that the degree of orientation of magnetic particles in plastic magnets is remarkably affected by the compatibility of polymer matrix to magnetic powder, i.e. the compatibility of the PA matrix to the magnetic particles is the highest in the polymers examined and the degree of orientation does not change even at high magnetic powder concentration (50 vol %).

Compatibility of the PS matrix with the magnetic particles, however, is the lowest, the degree of orientation changes with increasing concentration of magnetic powder and a drastic decrease in P% occurs at 50 vol %. The compatibility of the EVA matrix to magnetic particles falls inbetween PA and PS matrices, and the degree of orientation of magnetic particles is lower at 50 vol %.

In general it is believed that properties of the surface

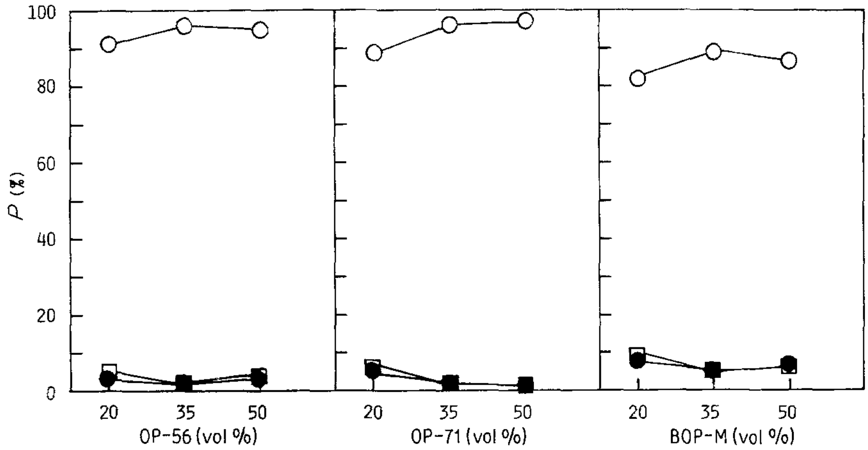


Figure 10 Degree of orientation (P) of PA-bonded magnets. (○) l direction, (●) d direction, (□) w direction.

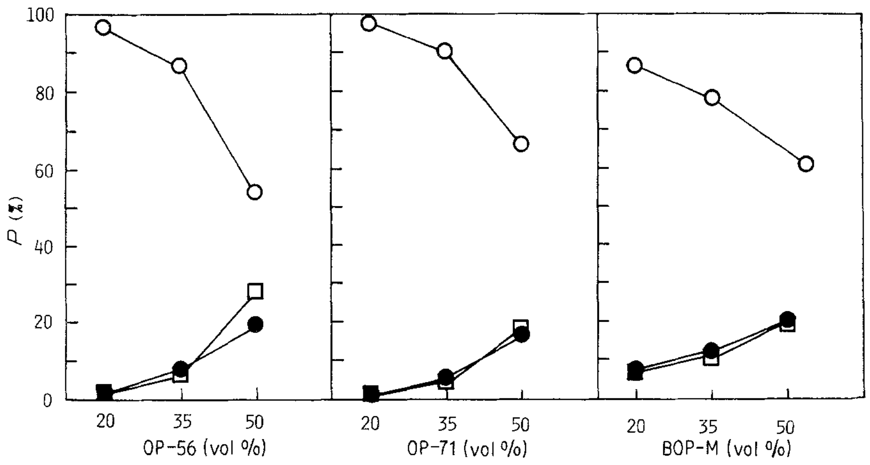


Figure 11 Degree of orientation (P) of PS-bonded magnets. (○) l direction, (●) d direction, (□) w direction.

of metals or metallic compounds are different from those of the inner parts (or bulk state), and the presence of hydroxy groups, water molecules, etc., gives a hydrophillic property to the surface. Therefore, PA, which has hydrophillic groups, shows fairly good compatibility with magnetic particles. On the other hand, hydrophobic PS gives poor compatibility.

Judging from the results mentioned above, the order of the orientation of maximum energy product of the polymer-bonded magnets at 50 vol % ferrite concentration is as follows

$$\underset{(97)}{\text{PA + OP-71}} > \underset{(95)}{\text{PA + OP-56}} > \underset{(87)}{\text{PA + BOPM}}$$
$$> \underset{(85)}{\text{EVA + OP-71}} > \underset{(73)}{\text{EVA + OP-56}} > \underset{(66)}{\text{PS + OP-71}}$$
$$> \underset{(60)}{\text{PS + BOP-M}} > \underset{(53)}{\text{PS + OP-56}} > \underset{(52)}{\text{EVA + BOP-M}}$$

where the numbers in parenthesis are the degrees of orientation (P%). Matrix: PA, Nylon 12; PS, polystyrene. EVA, ethylene vinylacetate copolymer. Ferrite: OP-56, rich in plate shapes; OP-71, rich in block shapes; BOP-M, rich in spherical shapes coagulated with small particles.

3.5. Change in magnetic properties during thermal treatment

The magnetic force of permanent magnets decreases exponentially with time and is very sensitive to heat. Therefore, it is difficult to estimate changes in the magnetic properties during thermal treatment. Thus, in this experiment after thermal treatment for a certain period, plastic magnets were remagnetized and changes in their magnetic properties due to the orientation of magnetic particles was examined.

As representative examples, the differences of the degree of orientation (magnetized direction l) of maximum energy product in OP-56 ferrite 35 vol % series during thermal treatment are shown in Fig. 13. From the figure it is clear that a decrease in the degree of orientation of the maximum energy product has hardly occurred under the experimental conditions. Similar results were also obtained in the case of 20 and 50 vol % ferrite concentrations.

The results apparently indicate that a decrease in magnetic properties due to the orientation of magnetic particles in the plastic magnets does not occur. Therefore, once the position of a magnetic particle is fixed in a plastic magnet during injection moulding under the magnetic field, the movement of that magnetic particle is restricted to its original position by the matrix polymer and by other magnetic particles.

4. Conclusions

From the results obtained in this experiment the following conclusions were obtained.

1. Magnetic properties of anisotropic plastic magnets were largely dependent on the concentration of magnetic powder and its degree of orientation in the matrices.

2. The degree of orientation was mainly affected by the interaction between polymer matrix and magnetic powder, and the viscoelastic properties of the matrix

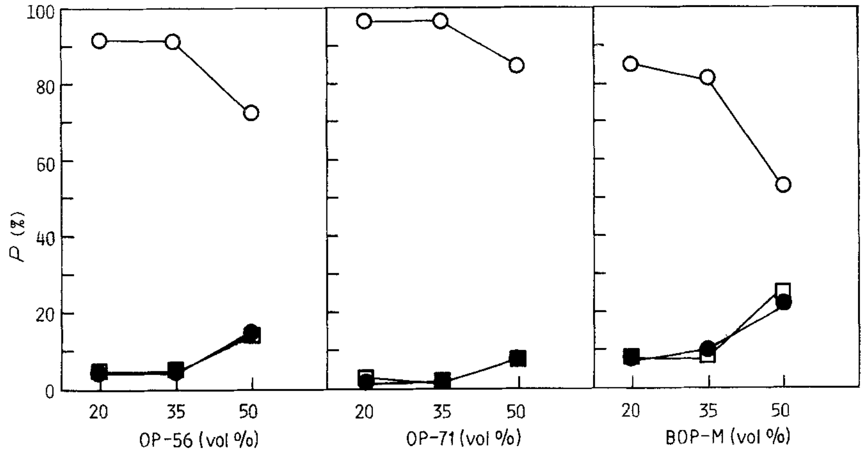


Figure 12 Degree of orientation (P) of EVA-bonded magnets. (○) l direction, (●) d direction, (□) w direction.

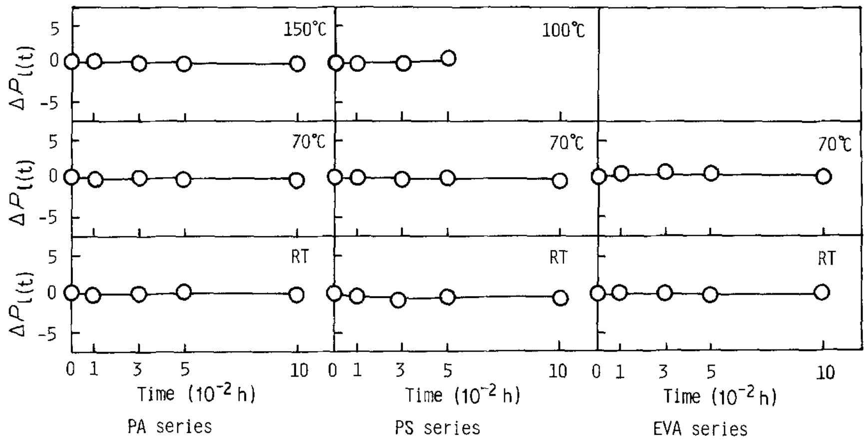


Figure 13 Changes in degree of orientation of maximum energy product of plastic magnets (OP-56 series: 35 vol %) on heating in air.

polymer. The order of the interaction of the polymers to the magnetic powder was as follows: PA > EVA copolymer > PS, and PA-bonded magnets gave the highest magnetic properties among the matrices examined. The shape of the magnetic particles also affects it to some extent.

3. A decrease in magnetic properties due to the change in orientation of magnetic particles was hardly observed during thermal treatment.

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