# Structure and Properties of Polyimide-Bonded Magnets Processed from Prepolymers Based on Diacetyl Derivatives of Aromatic Diamines and Dianhydrides

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**ABSTRACT:** We report a novel method of polyimide (PI) synthesis from prepolymers based on dianhydrides and diacetyl derivatives of aromatic diamines that facilitate the preparation of a melt processable mixture at $300 \pm 10°C$ of the prepolymer and magnetic Nd-Fe-B alloy to provide PI-bonded magnets with enhanced properties. It is shown that chemical structure of the prepolymers strongly influences viscosity behavior via crystallization of the oligoimide in the melt, leading to formation of PI with rigid-rod like structure. This structural ordering of the prepolymers based on diacetyl derivative of diamine used in this study, if not controlled, leads to exponential increase of melt viscosity with time, making it practically impossible to prepare melt processable mixture of the magnetic particles and the PI prepolymers at elevated temperatures. The results obtained demonstrate that appropriate dianhydrides and diacetyl derivatives of diamines that do not lead to crystallization of oligoimides in prepolymer mixture can be used under controlled processing conditions to prepare melt-processable PI-bonded magnets containing rigid-rod like PI structure that significantly increases thermal stability of the magnets. The temperature dependencies of the magnetic properties of the PI-bonded magnets under conditions that they are likely to encounter during their service life were found to be remarkably similar to that of commercial thermoplastic magnets such as injection-molded nylon magnets. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 478–485, 2006

**Key words:** rheology; polyimide resins; rare-earth magnetic alloys; processing; structure and properties

## INTRODUCTION

Polymer-bonded magnets (PBM) composed of thermoplastic polymer matrices and rare-earth magnetic alloys can be produced by traditional polymer processing methods and the magnets offer significant advantages, in terms of shaping and cost, over their metallic or ceramic counterparts.[1–5] Commercial PBM are limited in their application at high temperatures because of the intrinsic tendency of the magnetic rare-earth powders to oxidize in air, especially at elevated temperatures. As reported previously,[6–10] suitable high-temperature polymers can be used with advantage to significantly improve the heat resistance of bonded magnets. For example, thermoplastic poly(p-phenylene sulfide) is a suitable polymer for making bonded magnets, but the glass transition (85°C) and melting (285°C) temperatures of the PPS can limit their applications. In contrast to PPS, thermoplastic polyimide (PI)[11–15] with high thermal stability can be used as binders for PBM, but its relative high processing temperature (300–350°C) coupled with its relatively high melt viscosity presents significant problems that must be overcome during processing. The high melt processing temperature can lead to thermal oxidation of the magnetic rare earth powders such as Nd-Fe-B.

One way to address the high viscosity problem mentioned earlier is to use a two-stage method involving melt impregnation of magnetic particles with PI prepolymer by melting of the dianhydride and diacetyl derivatives of aromatic diamine,[16–20] followed by direct transformation into PI-bonded magnet via direct thermal treatment of a mixture of a dianhydride and diacetyl derivatives of diamines. The PI prepolymer of this method, hereinafter referred to as IDA (Imide based on Di-Acetyl derivatives of diamine), is readily converted to thermoplastic PI having proper-

ties similar to that of pure PI obtained by using diamines and dianhydrides via a traditional two-stage method of synthesis.[20]

As previously reported,[21] the new PI synthesis method used here has been shown to provide a melt-processable mixture of prepolymer and rare earth magnetic alloys (in the form of 75–100-$\mu$m particles), with subsequent chemical transformation of the mixture at 300°C to thermoplastic PI-bonded magnets. The IDA prepolymer based on 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride and diacetyl derivative of 2,2-bis(4-(4-aminophenoxy)phenyl)sulfone diamine after removing of volatile (residue not more than 5%) has a very low melt viscosity of 10–20 Pa*s at 220–240°C, enhancing its magnetic powder impregnation. The purpose of the present study described in this article is to investigate the influence of chemical structure of IDA prepolymer on the rheology and evolution of structure of the pure PI and the PI filled with the magnetic Nd-Fe-B powders. A extensive investigation of magnetic properties of the PI-bonded magnets over a wide range of temperatures is also described to determine their fitness for service in the targeted application areas.

## EXPERIMENTAL

### Magnetic particles

Commercial Nd-Fe-B magnetic powder (MQP-B, Magnequench International, Inc.) was used for this study. The powder is a multimodal mixture of plate-like particles with sizes ranging from 75 to 100 $\mu$m. The average particle size was determined by using two complementary methods described in ref. 8.

### Synthesis of PI prepolymer

The initial diacetyl derivatives of 2,2-bis(4-(4-aminophenoxy)phenyl)sulfone (acBAPS) and 4,4'-oxydianiline (acODA)
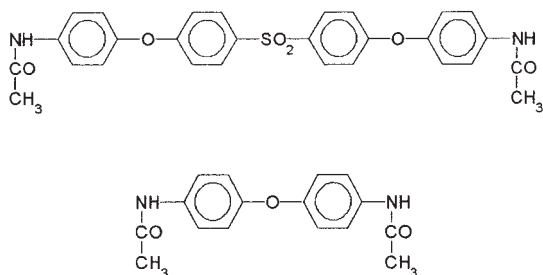
were obtained by a method similar to that described in refs. 17, 20, and 21. The following dianhydrides were used for synthesis of IDA-type prepolymer:
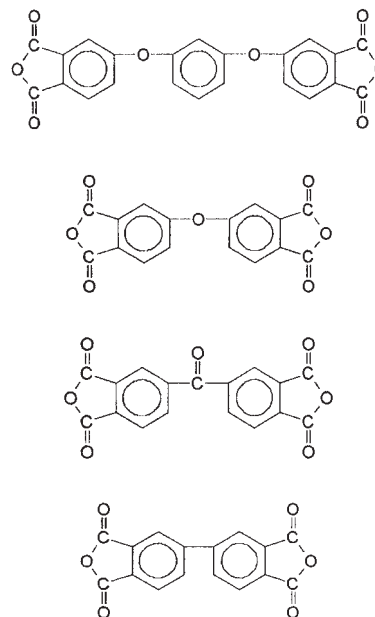
The IDA-type prepolymer was obtained by heating a mixture of dianhydride and diacetyl derivative of diamine in the melt at 275 ± 5°C for 10–15 min, as described in refs.17, 20, and 21.

### PI-bonded magnet sample preparation

A mixture of IDA prepolymer and magnetic Nd-Fe-B powders was prepared by melt-blending the desired relative volume fraction of magnetic particles with the prepolymers. The melt-blending was performed for 10 min at 220°C. Small discs (25 mm diameter × 2 mm thick) were compression-molded under a pressure of 3 MPa at 300 ± 5°C, using a laboratory-scale compression molding press. A mold residence time of about 30 min was used, and the molded sample was allowed to cool in air to ambient temperature under the molding pressure of 3 MPa.
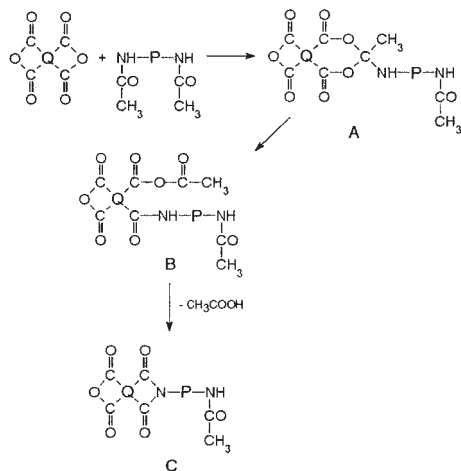
### Measurements

Steady shear rheology

A strain-controlled dynamic rheometer (ARES, Rheometric Inc.) was used to measure the steady shear viscosity of the IDA-type prepolymer under steady shear flows near their melt processing temperature in the cone and plate configurations following standard procedures. The diameter of the plate was 25 mm and the cone angle was 0.1 rad.

Dynamic mechanical and thermal properties

Dynamical mechanical analysis (DMA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) curves were recorded with a comprehensive Perkin–Elmer thermal Analysis 7 system. The

**Scheme 1**

DMA three-point bending measurements were conducted on samples (15 mm length, 5 mm width, and 1.5 mm thick), that were cut from the molded disks, using a Buehler slow speed diamond saw. The DMA experiments were performed at a frequency of 1 Hz and a heating rate of 5°C/min from 25 to 400°C. The TGA measurements were conducted using 5–10-mg samples contained in a platinum crucible, with a heating rate of 10°C under a nitrogen atmosphere. DSC was performed on 8 ± 2 mg samples contained in a platinum crucible, using a heating rate of 10°C/min under a nitrogen atmosphere.

X-ray diffraction and optical microscopy

Wide-angle X-ray diffraction measurements on the as-received and cured IDA prepolymer powder were conducted on an X-ray diffractometer (Model XDS-2000) supplied by Scintag Inc.

An optical microscope (BH-2, Olympus Co.) equipped with automatic video capture system and a heating plate was used to monitor the melting process of IDA-type prepolymer and associated structural evolution or ordering of the prepolymer during chemical reaction. The samples were hot-pressed between two glass slides on a hot plate at 270°C and subsequently used to analyze the prepolymer texture with the aid of polarized light microscopy.

Magnetic properties: reversible and irreversible loss testing

Reversible loss tests were made with samples that are 1 cm × 1 cm × 1 cm cubes. Because the materials were thin (1 mm thick), they were stacked up to 1 cm height, and then cut into cubes. These were then placed into a Walker AMH-1050 hysteresisgraph. This special hysteresisgraph is equipped with a tempera-

ture stage, where the temperature of the sample can be controlled between −50 and +175°C. The coercivity (Hc) and remanence (Br) were measured at several temperatures between these two extremes. By assuming linear behavior within this range, least-square linear regressions were performed on Hc and Br data, and the resulting slopes, i.e., the reversible temperature coefficients for Hc and Br, were obtained.

In this work, the irreversible loss tests were performed using the "long-term irreversible loss test" (L-TILT) protocol. The L-TILT test is designed to measure the time dependent changes as the magnet is kept isothermally at elevated temperatures for up to 1000 h. The test samples were first stacked and machined into shape, using a sample with a permeance coefficient of 2.0. The samples were subsequently magnetized to full saturation, and the magnetic moment was measured using a Helmholtz coil. The magnetic moment, or $B_{di}$, in this testing configuration is very close in value to the Br of the material. Finally, the samples were placed in ovens and heated to designated temperatures (100, 125, and 150°C) and measurements were periodically taken. The data obtained are expressed as the percent of retained magnetic moment as a function of time for each of the temperatures used.

## RESULTS AND DISCUSSION

It has been shown[17,20] that the chemical interaction between diacetyl derivatives of aromatic diamines and dianhydrides of tetracarboxylic acids at 260–280°C results in the formation of a cyclic intermediate (A) that is subsequently transformed into a product containing a noncyclic anhydride group (B), according to the reaction Scheme 1. Acetic acid is extracted from (B) to give the prepolymer (C), containing anhydride, imide, and N-acetyl functional groups.

The procedure for increasing molecular weight of the product is shown by reaction Schemes 2 and 3. The resulting bifunctional substance (C) can interact with each other or with the product containing the noncyclic anhydride group (B). These reactions proceed with



**Scheme 2**

D + D or D + B or D + C
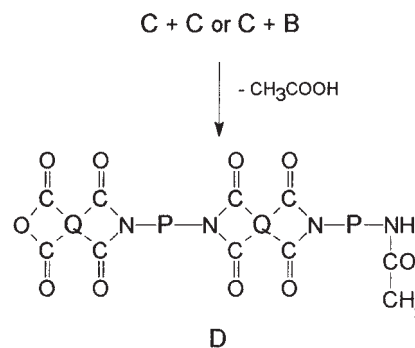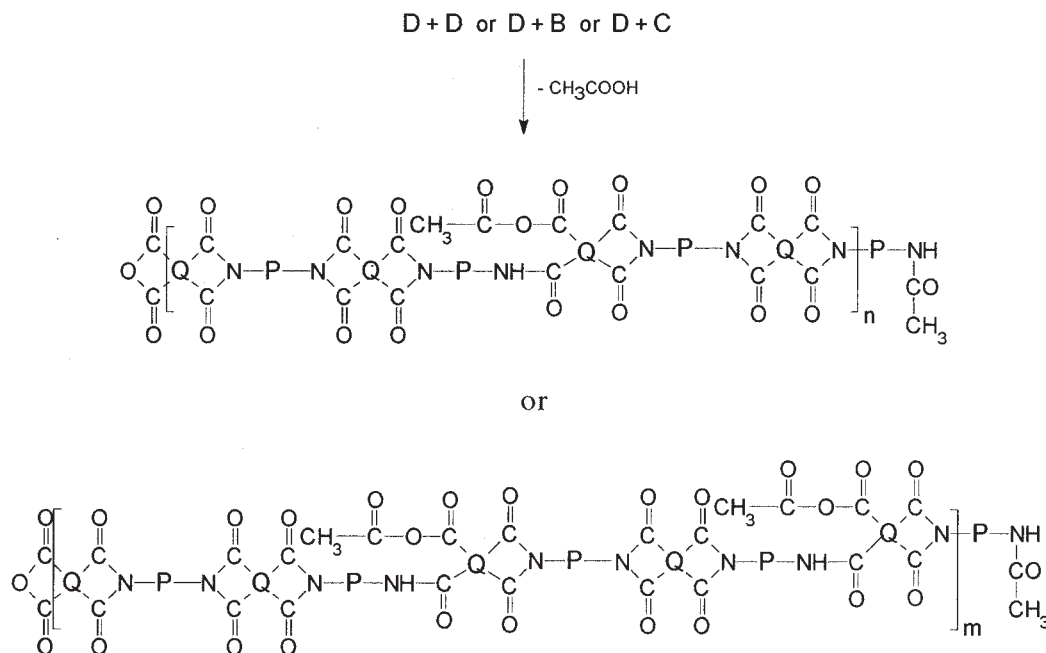


**Scheme 3**

a spontaneous isolation of acetic acid, resulting in formation of dimers (D). The dimer (D) may react with itself or with (B) or (C), followed by thermal imidization or extraction of acetic acid to yield oligomers with different chain lengths according to reaction Scheme 3.

This oligomer formation stage corresponds to the slow increase in melt viscosity of the R-BAPS and ODPA–ODA prepolymers and the very fast increase in melt viscosity of the BPDA–ODA and BTDA–ODA prepolymers at 270°C (see Fig. 1). The observed differences in the rheological behavior of the prepoly-

mers may be attributed to differences in the melt reordering of the rigid-rod like structure of the BPDA–ODA and BTDA–ODA, and the relatively more flexible structure of ODPA–ODA and R-BAPS. This hypothesis is consistent with the XRD and DSC data. For example, the WAXS pattern of the prepolymer samples after curing at 300°C for 1 h shows crystalline peaks at the $2\Theta$ range of 10–30° for the BPDA–ODA and BTDA–ODA PIs (Fig. 2). By contrast, the R-BAPS and ODPA–ODA PIs show typical amorphous WAXS pattern. The DSC scans (Fig. 3) show the melting endotherms for BTDA–ODA and BPDA–ODA at 426
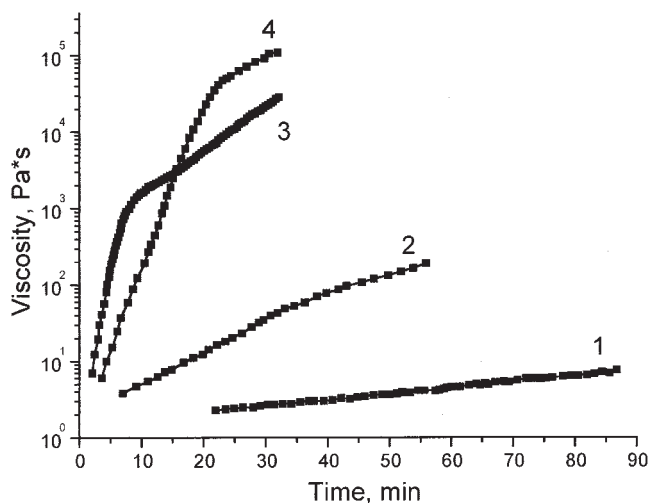


**Figure 1** Time dependence of viscosity at 270°C for IDA prepolymers based on: (1) R-BAPS; (2) ODPA–ODA; (3) BTDA–ODA, and (4) BPDA–ODA.
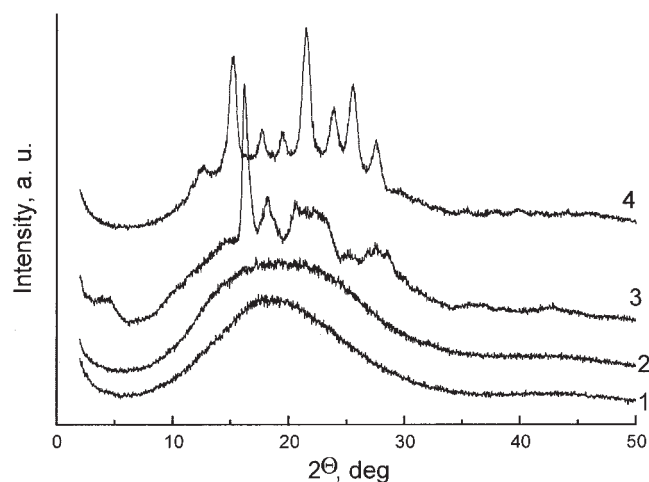
**Figure 2** Wide angle X-ray scattering patterns for IDA-type prepolymers after curing at 270°C for 1 h: (1) R-BAPS; (2) ODPA–ODA; (3) BTDA–ODA, and (4) BPDA–ODA.
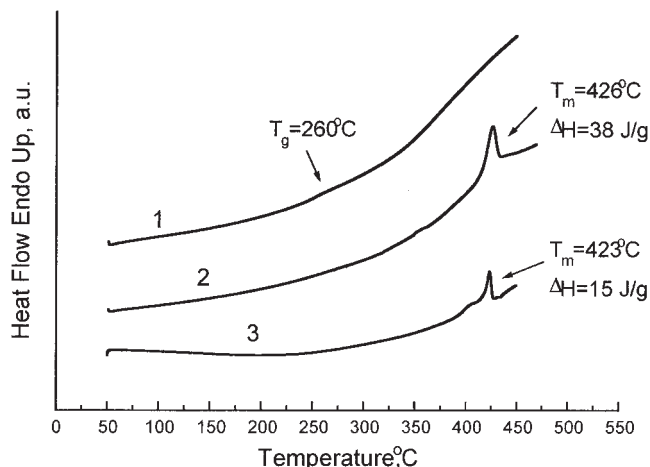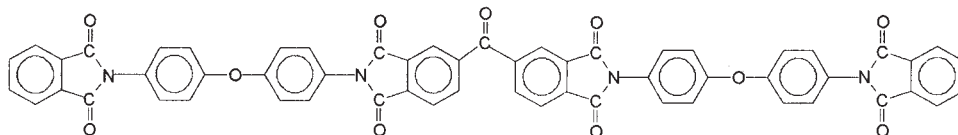
**Figure 3** DSC scans for for IDA-type prepolymres after curing at 270°C for 1 h: (1) ODPA–ODA; (2) BTDA–ODA, and (3) BPDA–ODA.

and 423°C, respectively. These melting endotherms correspond to melting of the observed crystalline structures of these IDA-type PIs.

To confirm the formation or reorganization of the oligoimide structures during the chemical reaction at 270°C of BTDA–ODA prepolymer, we heated samples of BTDA–ODA prepolymer at 270°C for 15, 30, and 60 min, and subsequently determined the WAXS patterns for the heated samples. The WAXS patterns of the BTDA–ODA samples (Fig. 4) show increasing intensity of the peaks with increasing heating times. The data are consistent with the expected increase in the crystalline content with increasing time at 270°C, confirming structural ordering of oligoimides during the chemical reaction of dianhydride BTDA and diacetyl derivatives of diamine ODA.

To further test the hypothesis of oligoimides crystallization, we prepared an oligoimide with the following structure that is similar to that of the repeat unit of the BTDA–ODA PI:



This oligoimide was prepared by the traditional two-stage polycondensation method[13] and was found to show a melting temperature $T_m = 387$°C and melting enthalpy $\Delta H = 23$ J/g. By comparing the WAXS pattern of this oligoimide (see Fig. 4, curve 4) with that obtained from the IDA prepolymer after curing at 270°C for 30 min and 1 h (see Fig. 4, curves 2 and 3), the striking similarity between these WAXS patterns is clearly evident, indicating that the chemical reaction of IDA-type prepolymer do indeed lead to formation of melt reorganized oligoimides structures. As already mentioned, this structural organization leads to a fast increase of melt viscosity of the IDA-type prepolymer that is expected to significantly complicate its mixing with magnetic particles to achieve high volume fraction of these particles in the resulting PI-bonded magnets.

To avoid this problem, IDA-type prepolymers such as R-BAPS and ODPA–ODA having a relatively amorphous structure are preferable (see Fig. 2, curves 1 and 2). These IDA prepolymers are known to have relatively low viscosity after removing the appropriate amount of volatile acetic acid at elevated temperature, as discussed later. Preliminary treatment of IDA prepolymers at 270°C for 1 h decreases the quantity of volatiles by about 5–7%, according to TGA experiments (Fig. 5).

The rheological behavior of IDA-type prepolymers (R-BAPS and ODPA–ODA) after removing of volatiles

at 270°C for 1 h is represented in Figure 6. This figure shows the relatively low viscosities of about 20 and 150 Pa*s for IDA R-BAPS and IDA ODPA–ODA, respectively, at temperatures ranging from 220 to 270°C. Therefore, it is possible to mix IDA prepolymer with magnetic particles to achieve high volume fraction of the particles at these temperatures without significant increase in the melt viscosity. The observed increase in
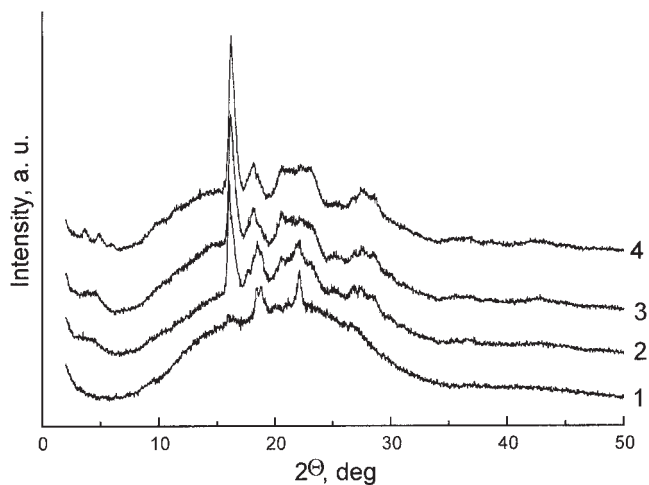


**Figure 4** Wide angle X-ray scattering patterns for IDA-type prepolymer BTDA–ODA after curing at 270°C for 15 min (1), 30 min (2), and 1 h (3), and for oligoimide BTDA–ODA–PA (4).
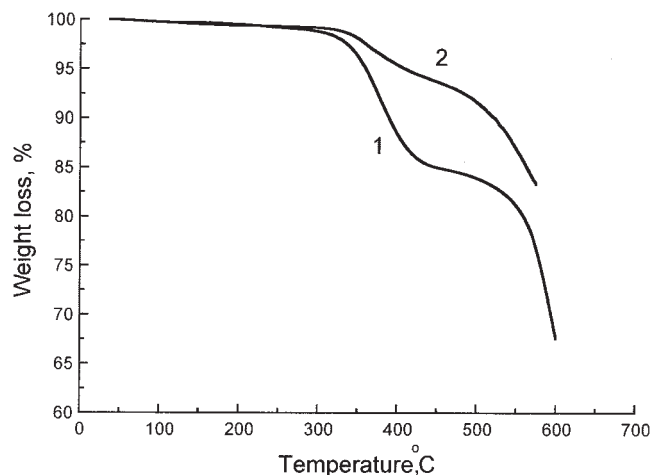
**Figure 5** TGA scans for: (1) as received IDA prepolymer; (2) cured IDA at 270°C for 1 h.



**Figure 7** Temperature dependences of storage (1′, 2′) and loss (1″, 2″) moduli for PI-bonded magnets with 70 vol % magnetic particles prepared from: (1) IDA R-BAPS prepolymer and (2) IDA ODPA–ODA prepolymer.

the viscosity of IDA-type prepolymers at temperatures greater than 270°C is attributed to the final conversion of the prepolymers into PI materials with high thermal stability.

PI-bonded magnets with 70% volume fraction of magnetic particles prepared according to the method described earlier in the experimental section show their high thermal stability (Fig. 7). By the rational modification of the chemical structure of the PI main chain such as by replacing the R-BAPS with the more rigid ODPA–ODA, it is possible to prepare PI-bonded magnets with a $T_g$ (or temperature corresponding to the maximum of the loss modulus $E''$) up to 285°C, a value close to the $T_g$ of these PIs (see Fig. 7). In addition to the excellent thermal stability, it can be seen
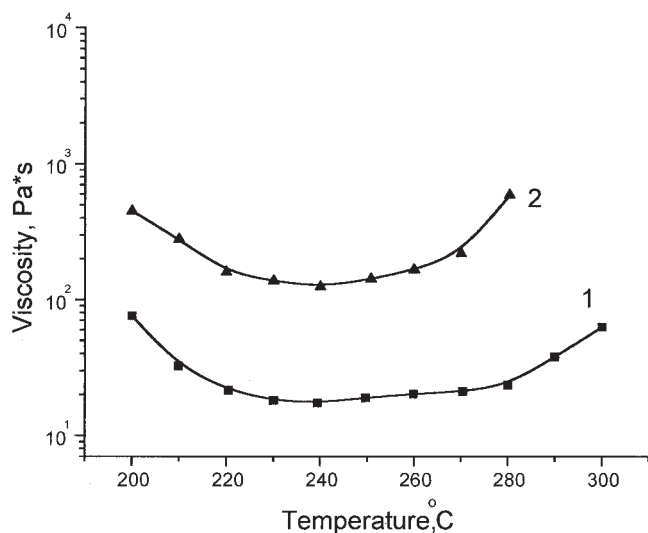


**Figure 6** Temperature dependence of viscosity for IDA-type prepolymers after their curing at 270°C for 1 h: (1) R-BAPS; (2) ODPA–ODA.
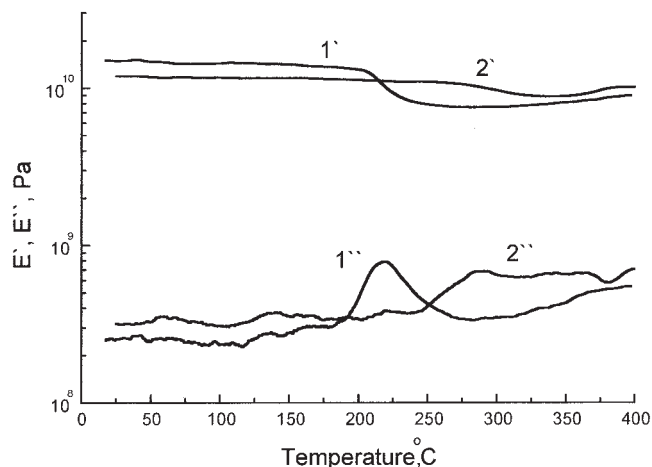
from Figure 7 that the PI-bonded magnets maintain their high stiffness at 10 GPa (as measured by the $E'$) up to a temperature of 400°C.

All magnetic materials exhibit temperature-dependent behavior with respect to their magnetic properties. In general, this behavior is classified as "reversible" and "irreversible" behavior. Reversible properties are analogous to elastic deformation behavior, that is, a magnetized magnet may experience changes in magnetization when the temperature is raised or dropped a small amount. These changes will no longer exist if the temperature is returned to the original value (i.e., "reversible"). At larger temperature changes, however, the magnetized magnet may show significant changes in magnetization that would not return to the original values when the temperature is returned to the original value (i.e., "irreversible"). The magnet in such condition is partially demagnetized. The worst case is when there is actual changes to the structure of the magnet because of oxidation or corrosion reaction. In this work, both reversible and irreversible loss tests were performed as described previously.

Figure 8 shows the reversible temperature data as measured by the hysteresisgraph. Figure 8(a) is the normalized remanance, Br versus temperature of the sample. As already mentioned in the experimental section, the samples were first cooled down from room temperature to −40°C, and then heated up to a maximum temperature of 175°C. Because of this heating procedure, which was done to minimize permanent irreversible loss to the sample, certain experimental complications must be accounted for during the measurement of injection-molded samples. It has been found that when heated this way, the irreversible coefficient of the Br tends to vary significantly due to
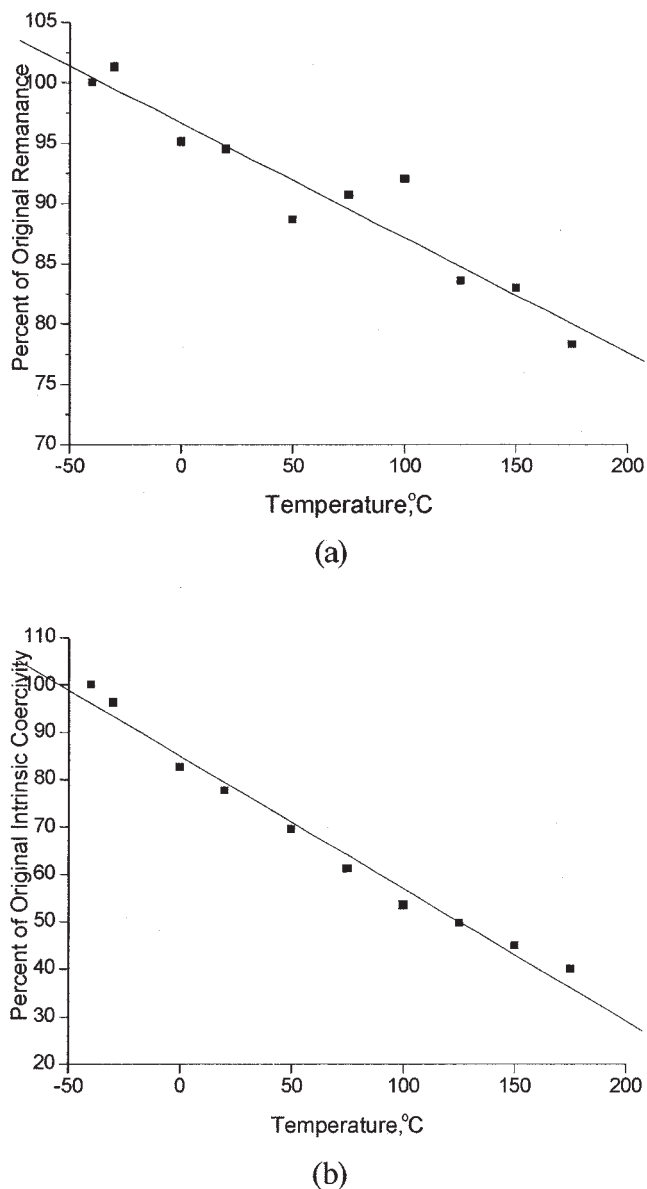
(a)



(b)

**Figure 8** Temperature dependences of magnetic properties of PI-bonded magnets with 70 vol % magnetic particles prepared from IDA R-BAPS prepolymer: (a) is a plot of the percent of original remanance, Br versus temperature of the sample and (b) is a plot of the percent of original intrinsic coercivity, Hci versus temperature of the sample.

moisture out-gassing near 75–100°C. The out-gassing tends to increase the volume of the sample and reduces the amount of air gap between the sample and the pole piece. This tends to cause a jump in the value of Br when this temperature is reached. Notwithstanding this anomaly in the measurement, the calculated value for reversible thermal coefficient of Br for −40 to +175°C is −0.09%/°C, using least-squares linear fit. This value is slightly different from the published value of −0.011%/°C by MagneQuench Inc. (MQI) for room temperature to +100°C, but within the range of error in the measurement capability of the instrument

used in this study. The thermal coefficient of the intrinsic coercivity (Hci) from −40 to +175°C for the samples in this experiment was found to be very similar to the published data by MQI. Figure 8(b) shows a plot of the percent change in Hci, as a function of temperature. The slope, which corresponds to the thermal coefficient of Hci, was found to be −0.3%/°C, using least-squares linear fit. As for the case with the thermal coefficient for Br, the thermal coefficient of Hci is within the measurement capability of the instruments used in this experiment when compared with the −0.4%/°C value published by MQI. The temperature coefficients of Hc and Br are dependent mainly on the chemistry and properties of the rare-earth powder and not the resin. It can be surmised that the resulting reversible loss properties described earlier are similar to the published values, indicating a lack of adverse short term interaction between the resin system used and the rare-earth powder under the experimental conditions of this study.

The irreversible loss properties were also measured. These can be measured in two different ways: (1) S-TILT or short-term irreversible loss test, and (2) L-TILT or long-term irreversible loss test. The S-TILT and L-TILT are performed at constant time with variable temperature, and constant temperature with variable time, respectively. For the designers of magnetic circuits, the L-TILT test is more important because it helps to predict the performance of the material during real long-term use. As a result, the L-TILT tests were performed for four different temperatures up to 1000 h for this work. The results showed that the PI-bonded magnet behaves like typical nylon injection-molded magnets, with no degradation due to rare-earth powder and resin interaction. In the L-TILT tests, the sharp drop in retained magnetic moment in the first few hours is characteristic of the stabilization observed in all magnetic materials, where the "easy" or "soft" domains are reoriented. This behavior is usually exploited by designers who prefer to use more stable magnets in their circuits, with the trade-off being a reduced magnetic output. The slight drop in retained magnetic moment in the L-TILT test (Fig. 9) beyond 700 h is expected due to the normal corrosion behavior of Nd-Fe-B alloys. For large scale industrial evaluation, re-grind studies (recycling of runner materials) should be made, but these initial positive results of this study as compared to standard industrial products are very encouraging.

## CONCLUSIONS

The results of this study show that chemical structure of IDA-type prepolymers has a strong influence on its viscosity behavior, and it can lead to crystallization of the oligomers in the melt into rigid-rod like PI structure. This structural ordering of the IDA-type prepoly-
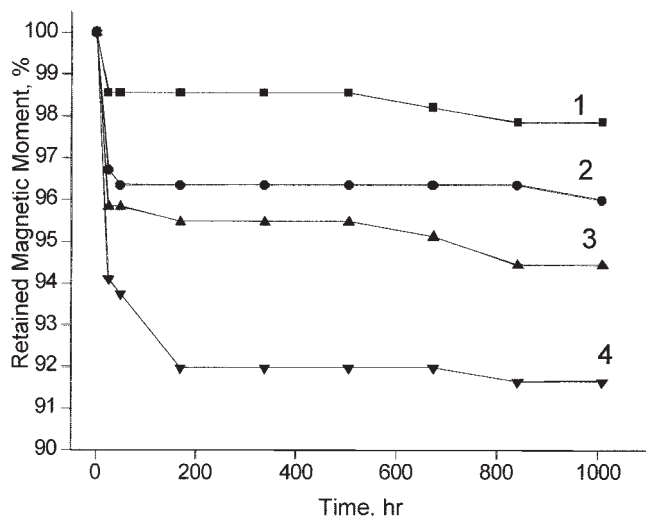
**Figure 9** Long term irreversible loss test of PI-bonded magnets with 70 vol % magnetic particles prepared from IDA R-BAPS prepolymer. Temperatures: 75°C (1); 100°C (2); 125°C (3); and 150°C (4).

mers leads to exponential increase in melt viscosity with time at 270°C, making it impossible to prepare melt processable mixtures of magnetic particles with PI prepolymers at elevated temperatures. This practical difficulty can be avoided by using prepolymers based on dianhydrides and diacetyl derivatives of diamines that do not lead to crystallization of oligoimides during melt processing of PI-bonded magnets. Another benefit of using the prepolymers just mentioned is concerned with the fact that the thermal stability of the PI-bonded magnets can be significantly enhanced by using the special prepolymers based on dianhydrides and diamines having more rigid chemical structure like ODPA–ODA. The temperature dependencies of the magnetic properties of the PI-bonded magnets under typical use conditions were found to be very good and remarkably comparable with that of commercial thermoplastic magnets such as injection-molded nylon magnets. These results suggest that PI-bonded magnets with enhanced benefits can be prepared by tailoring the chemical structure of the PI prepolymer in the bonded magnet to afford magnets with high thermal stability, excellent processability, and magnetic properties.

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