

Polyimide Bonded Magnets: Processing and Properties

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Received 13 May 2002; accepted 14 August 2002

ABSTRACT: We report a new method of polyimide synthesis based on the interaction of dianhydrides with acylated diamines for preparing a melt processable mixture of prepolymer and rare earth magnetic alloy particles in the form of 75–100 μm particles. This mixture can be easily converted to useful thermoplastic polyimide bonded magnets by heating at 300°C. It is shown that the prepolymer based on 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride and the diacetyl derivative of 2,2-bis(4-(4-aminophenoxy)phenyl)sulfone diamine after removing less than 5% by weight of the volatile components can be melted at 220–240°C to give a fluid with a viscosity of 10–20 Pas. This low viscosity of the prepolymer facilitates blending it with

magnetic particles at relatively high volume fractions (up to 85 vol %) that are not possible using conventional methods. The resulting polyimide-bonded magnets exhibit excellent thermal stability and a high storage modulus of 10 GPa at 400°C. Magnetic property measurements showed a $\geq 10\%$ increase in energy products over that of typical commercial bonded magnet materials such as the ones containing thermoplastic poly(phenylene sulfide) or polyamide matrices. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3151–3158, 2003

Key words: rheology; polyimide resins; alloys; processing; properties

INTRODUCTION

In recent years, polymer bonded magnets (PBMs) have seen rapid growth in the market. This is true in spite of the fact that PBMs are magnetically weaker than equivalent fully dense (sintered) metallic magnets. The reason for their popularity is their suitability to very high volume, net shape plastic manufacturing techniques.^{1–10} PBMs are prepared by blending magnetic powder with a thermoplastic or thermosetting polymer binder. The use of a thermoplastic binder is more desirable, because the resulting composite material can be shaped by conventional molding processes, such as injection molding, into magnetic parts with complex shapes. Commercial PBMs have limited applications at high temperatures because of the oxidation of magnetic rare earth powders in air, espe-

cially at elevated temperature. High-temperature polymers can be used to improve the heat resistance of bonded magnets.

As previously reported,^{11–15} thermoplastic poly(*p*-phenylene sulfide) (PPS) is a suitable polymer for making bonded magnets because of its good combination of properties, including good thermal stability, low viscosity, and resistance to chemical environments. The application of the PPS bonded magnets is limited by the glass-transition ($T_g = 85^\circ\text{C}$) and melting temperatures (285°C) of the PPS. Alternatively, polyimides (PIs), because of their well-known high-temperature resistance, are expected to be more attractive polymer binders for PBMs relative to PPS. The presence of aromatic groups in the PI structure confers relatively high thermal stability, making them suitable for application in high-temperature and aggressive environments where other common plastic binders for magnets are not useable.^{16–19} The major difficulty of using commercial thermoplastic PIs in PBMs is their high viscosity at 300–350°C,^{18,20,21} where commercial magnetic rare earth powders can oxidize.

In this article we report the preliminary results of a feasibility study on a useful method for preparing thermoplastic PI bonded magnets by using a two-stage process: melt impregnation of magnetic particles with relatively low viscosity PI prepolymer derived from melting of the dianhydride and diacetyl derivatives of aromatic diamine^{22–25} followed by thermal

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Contract grant sponsor: U.S. National Science Foundation; contract grant number: DMR-9712688.

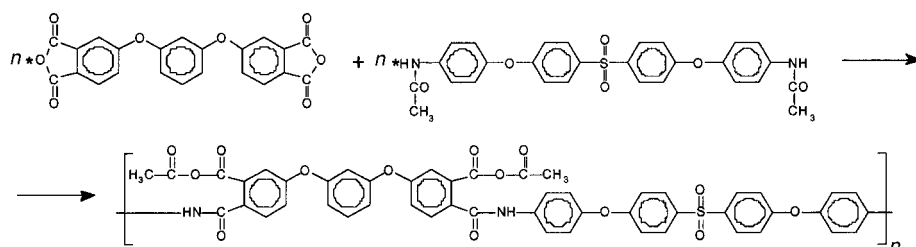
Contract grant sponsor: Russian Fund of Basic Research; contract grant number: 01-03-32415a.

curing at temperatures $\leq 300^\circ\text{C}$. A useful processing window and the structure–property correlations of the PI bonded magnets of this study are also described. In a recent publication²⁶ we showed that PI prepolymer (e.g., imide based on diacetyl derivatives of diamine) prepared by methods similar to the one just described can be readily transformed into thermoplastic PIs by heating it to 300°C .

EXPERIMENTAL

Magnetic particles

Commercial Nd-Fe-B magnetic powder (MQP-B, Magnequench International, Inc.) was used for this study.



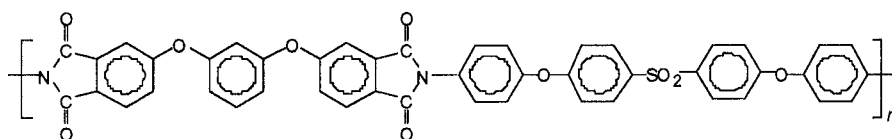
A two-stage polycondensation method described by Svetlichnyi et al.²¹ was used for synthesis of the PI

This powder is a multimodal mixture of platelike particles of $75\text{--}100\ \mu\text{m}$ size. The average particle size was determined by using two complementary methods described elsewhere.¹³

Polymer binder

The imide based on diacetyl derivatives of diamine (hereafter referred to as IDA prepolymer) was obtained by direct thermal treatment (at $270 \pm 5^\circ\text{C}$ for 12.5 ± 2.5 min) of a mixture of a 1,3-bis(3,4-dicarboxyphenoxy)benzene (R) dianhydride and diacetyl derivative of 2,2-bis(4-(4-aminophenoxy)phenyl)sulfone (BAPS) diamine as described in Goykhman et al.²³

R-BAPS:



Sample preparation

A mixture of IDA R-BAPS prepolymer and magnetic Nd-Fe-B powders was prepared by melt blending the desired relative volume fraction of magnetic particles with the prepolymer. The melt blending was performed for 10 min at 220°C . Small disks (25-mm diameter \times 2-mm thickness) were compression molded under a pressure of 3 MPa at $300 \pm 5^\circ\text{C}$ using a lab 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 a molding pressure of 3 MPa.

Measurements

Rheology

A strain-controlled dynamic rheometer (ARES, Rheometric Inc.) was used to measure the steady shear viscosity of the IDA prepolymer under steady shear flows near their melt processing temperature in the cone and plate configuration following the standard

procedure. The experiments were conducted in air. The diameter of the plate was 25 mm and the cone angle was 0.1 rad. To measure the viscosity of the prepolymer/magnetic particles mixtures or composites, we used the parallel plate configuration under small strain oscillatory shear flows. The diameter of the parallel plates was 25 mm and the gap between the upper and lower plate was maintained at 2 mm, giving a flow space of at least 20 times the average particle size of $100\ \mu\text{m}$. The gap size that was used was assumed to be a reasonable size to minimize the effects of reduced particle concentration near the walls of the parallel plates.²⁷ Testing was done using the oscillation mode with a frequency of 1 Hz and a strain of 1%.

Thermal analysis

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

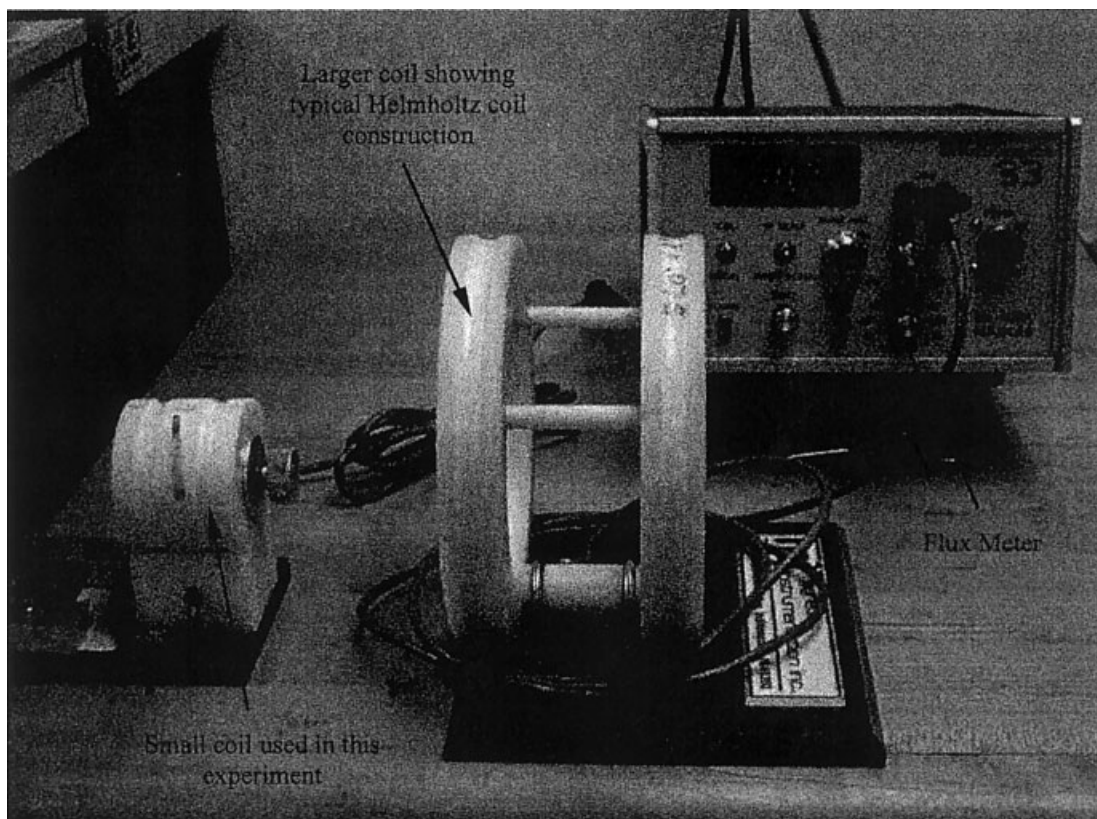


Figure 1 Helmholtz coils and the flux meter used for both tests.

DMA three-point bending measurements were conducted on samples (15-mm length, 5-mm width, and 1.5-mm thickness) cut from the molded disks using a Buehler slow speed diamond saw. The DMA experiments were performed at a scanning rate of 5°C/min from 25 to 400°C and a frequency of 1 Hz. 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 with a heating rate of 10°C/min under a nitrogen atmosphere.

Structural measurements

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. Scanning electron microscopy (SEM, Cambridge S-200 and AMRAY-1200) was performed to examine the polished surfaces of the molded PBM samples.

Magnetic measurements

Samples for magnetic measurements were made using small plates of roughly $1 \text{ cm}^2 \times 1 \text{ mm}$. These plates were then cut into 3-mm squares using diamond abra-

sive blades. Because of the small size of the samples, they could not be tested with a conventional hysteresisgraph (permeameter). As a result, a different approach was needed to obtain the demagnetizing (second quadrant) curve from these materials.

The test methods we used are based on the extraction of fully magnetized samples. One extraction technique uses a Helmholtz coil (Fig. 1). In this method, the intrinsic induction of the samples at the working point is obtained (B_d intrinsic, also called M_d).²⁸ The M_d (G) is obtained from the following equation:

$$M_d = F * C_f / V \quad (1)$$

where V is the volume of the sample (cm^3), F is the measured flux (mx), and C_f is the coil factor that is unique to each Helmholtz coil.

In the second extraction method, we used a simple single-turn coil tightly wrapped around the sample (Fig. 2) and the same flux meter. This technique provides the total (normal) induction at the working point, B_d (G):

$$B_d = F / A \quad (2)$$

where A is the sample area (cm^2) perpendicular to the direction of magnetization. Note that for the same fully magnetized magnet, the equation

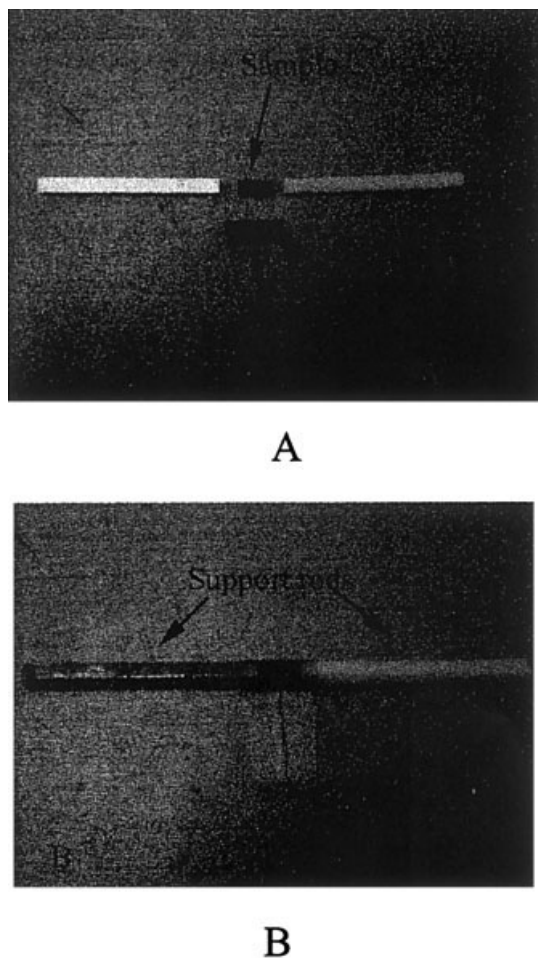
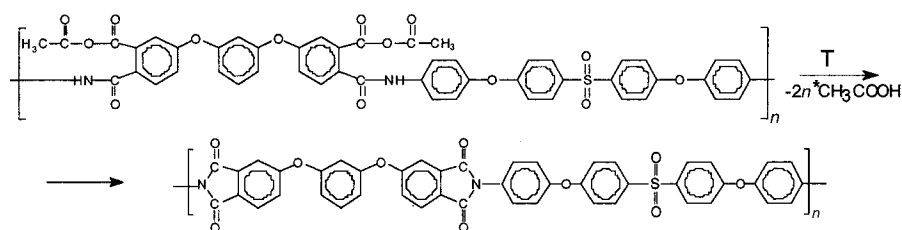


Figure 2 The single coil extraction equipment setup sample (A) outside of the coil and (B) ready for extraction.



As shown in Svetlichnyi et al.,²⁶ the IR spectra of PI formed by this method and heated at 350°C for 1 h was found to be identical to that of PI obtained by the traditional two-stage polycondensation method. The mechanical properties such as the Young's modulus, tensile strength, and deformation at break of the IDA R-BAPS films obtained by this chemical procedure are comparable to that of PI R-BAPS films,²¹ with values of 2.4 GPa, 126 MPa, and 10%, respectively. This confirms our expectation of the formation of thermoplastic PI from IDA R-BAPS at temperatures $\geq 250^\circ\text{C}$.

To minimize the evaporation of acetic acid during the PBM molding process, we subjected the as-received IDA prepolymer to additional heat treatment.

$$B_d = M_d - H_d \quad (3)$$

holds, where H_d is the self-demagnetization of the magnet.²⁹ If the magnet becomes shorter while maintaining its area, then H_d becomes greater. Therefore, $H_d = B_d - M_d$, and H_d approaches zero as the sample becomes infinitely long. At that point (or when there is a return path for the magnet), B_d becomes B_r . By knowing B_d and M_d and therefore H_d , a significant portion of the demagnetizing curve can be obtained.

By varying the length of the magnet, points on the intrinsic and normal demagnetization curve can be obtained. To vary the magnet's length for the limited available samples, we stacked up the 3-mm square samples to provide a change in height. Figure 3 shows a sketch of the experimental procedure and how it relates to the demagnetization curve. From previous experiments it is known that such stacking of magnetized magnets will result in slightly lower values of B , up to 4% lower than the actual value. In this article we use the experimentally obtained values without making any corrections for the effect just mentioned. An example of the second quadrant curve approximated from the technique described above is shown in Figure 4.

RESULTS AND DISCUSSION

The IDA type prepolymer was converted to PI at temperature $>250^\circ\text{C}$ according to the following reaction:

The TGA data showed a weight loss of about 15% of the initial IDA R-BAPS at 300–430°C (see Fig. 5). For the PI obtained by the traditional two-stage method, the weight loss began only at 550°C, primarily because of the chemical decomposition of the polymer (Fig. 5, curve 4). Preliminary treatment of the IDA prepolymer at 270 and 300°C for 1 h decreased the quantities of volatiles by about 7 and 3%, respectively. These results indicate that the additional heat treatment can significantly decrease the amount of volatiles contained in the as-received IDA prepolymer. Therefore, for subsequent experiments the IDA was heat treated at 270°C for 1 h (Fig. 5, curve 2). As shown later, this treatment gave a suitable low viscosity for the IDA

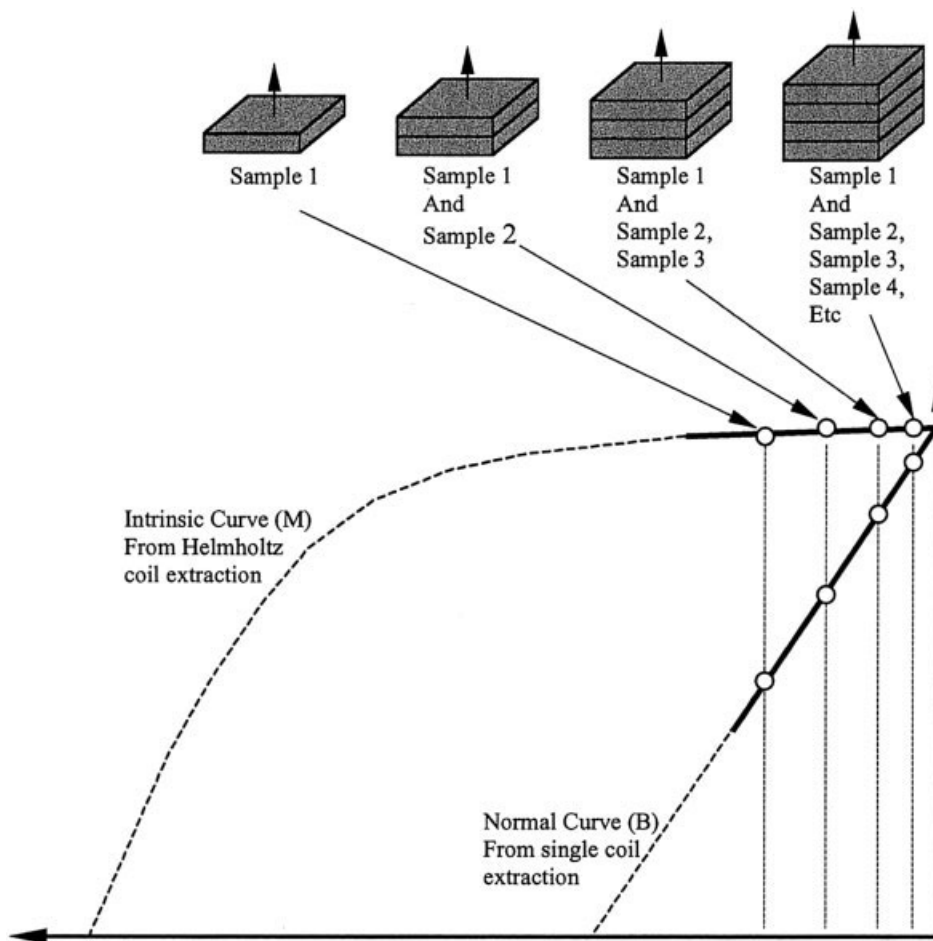


Figure 3 Test samples and their "load line" location on the demagnetization curve.

prepolymer that is desirable for magnetic powder impregnation.

Rheological measurements performed on the IDA prepolymer that was heat treated at 270°C for 1 h showed a very low viscosity of 10–20 Pas for the

prepolymer at 220–240°C (Fig. 6). At 200–220°C the viscosity of IDA decreased following a simple exponential relationship.³⁰ At temperatures greater than 250°C, transformation of the IDA to PI results in a

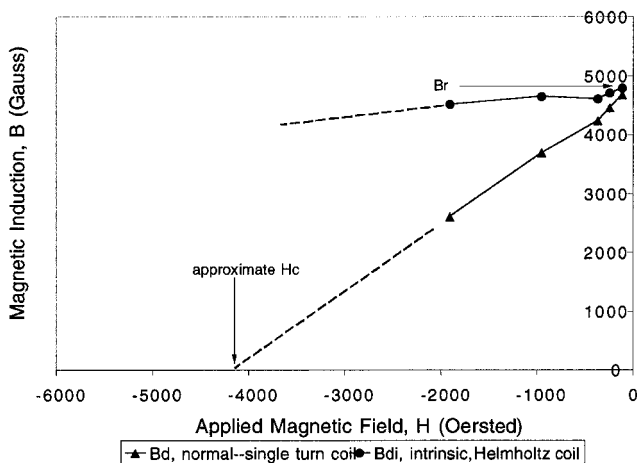


Figure 4 An example of the second quadrant curve approximated for sample 4 (Table I) from the technique described in the text.

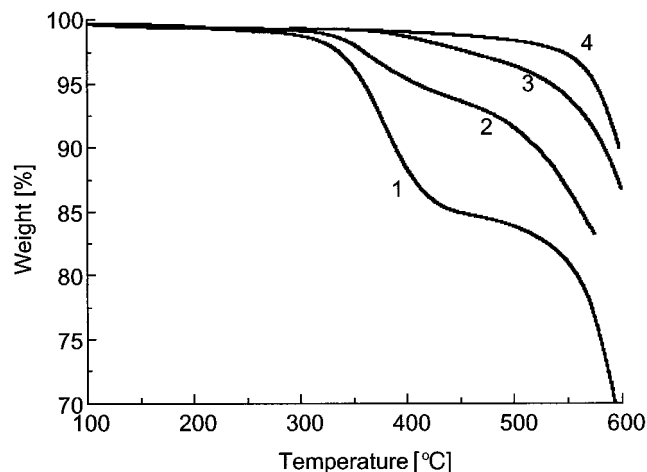


Figure 5 TGA scans for (1) the as-received IDA prepolymer; (2) IDA cured at 270°C for 1 h, (3) IDA cured at 300°C for 1 h, and (4) PI R-BAPS.

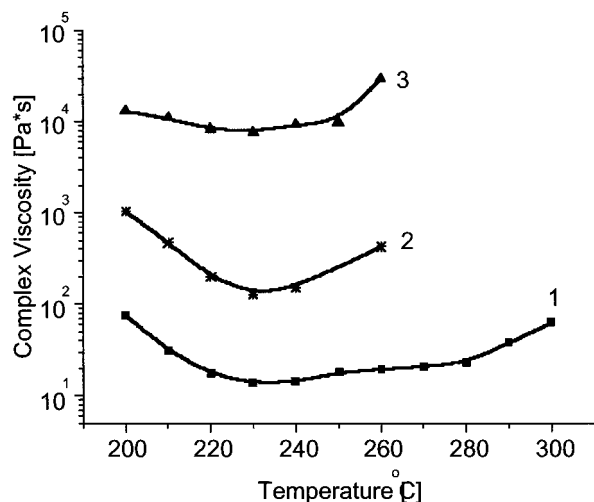


Figure 6 The temperature dependence of the viscosity for (1) IDA prepolymer after curing at 270°C for 1 h and this IDA prepolymer mixture with (2) 30 and (3) 50 vol % magnetic particles.

significant increase in the viscosity of the prepolymer. As expected, blending of IDA with magnetic particles increased the viscosity at all the temperatures we investigated (see Fig. 6, curves 2 and 3). The temperature dependence of the viscosity of IDA containing 30 and 50 vol % magnetic fillers was found to be similar to that of the pure IDA prepolymer already discussed. It is noteworthy that at 220–240°C it is possible to process IDA with magnetic particles to yield magnetic particles encapsulated by the IDA prepolymer for subsequent molding at higher temperatures. This is facilitated by the low viscosity of IDA at 220–240°C and the preliminary heat treatment of the IDA at 270°C for 1 h.

The time dependence of the viscosity of IDA with and without magnetic particles at 220 and 260°C are shown in Figures 7 and 8, respectively. Figure 7 shows no change in the measured viscosity of unfilled IDA and IDA filled with magnetic particles for at least 10 min, a sufficient time period for encapsulating the magnetic particles with the prepolymer. At higher processing temperatures ($220^{\circ}\text{C} \leq T \leq 260^{\circ}\text{C}$) the viscosity behavior of the IDA prepolymer exhibits a strong dependence on time (Fig. 8). For the unfilled IDA prepolymer the viscosity increases slightly over a time period of 40 min. This slight increase in viscosity is due to the chemical reaction discussed earlier. Comparatively, the viscosity of IDA filled with 30 and 50 vol % of magnetic particles increases more dramatically with time. This significant increase in the viscosity at 260°C of the filled IDA with time is possibly exacerbated by the catalytic action of the magnetic particles on the IDA polymerization reaction. This observation implies that lower molding temperatures can be used to achieve 100% conversion of the filled IDA into filled PI. The catalytic mechanism just hypothesized is a matter for future investigation.

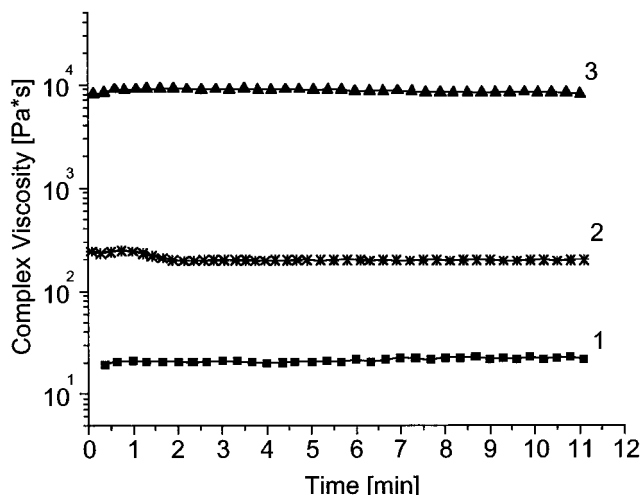


Figure 7 The time dependence of the viscosity at 220°C for (1) IDA prepolymer after curing at 270°C for 1 h and this IDA prepolymer mixture with (2) 30 and (3) 50 vol % magnetic particles.

The rheological characteristics such as the low viscosity of the IDA prepolymer facilitate preparation of the PI bonded magnet containing a high volume fraction of magnetic particles (up to 85 vol %). Figure 9 shows SEM micrographs of the polished surfaces of PBM with 50 and 85 vol %. The figure shows a remarkably uniform distribution of magnetic particles in the PI continuous matrix. In the PBM with 85 vol % magnetic particles, a very thin layer of PI ($<1\mu\text{m}$) is observed between the individual magnetic particles. On a macroscopic scale, this highly filled PBM shows highly dense and closely packed magnetic particles, a morphology that is highly desirable for optimal mag-

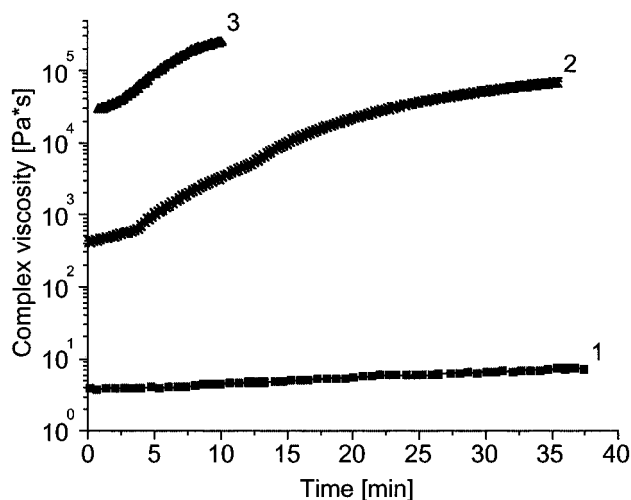


Figure 8 The time dependence of the viscosity at 260°C for (1) IDA prepolymer after curing at 270°C for 1 h and this IDA prepolymer mixture with (2) 30 and (3) 50 vol % magnetic particles.

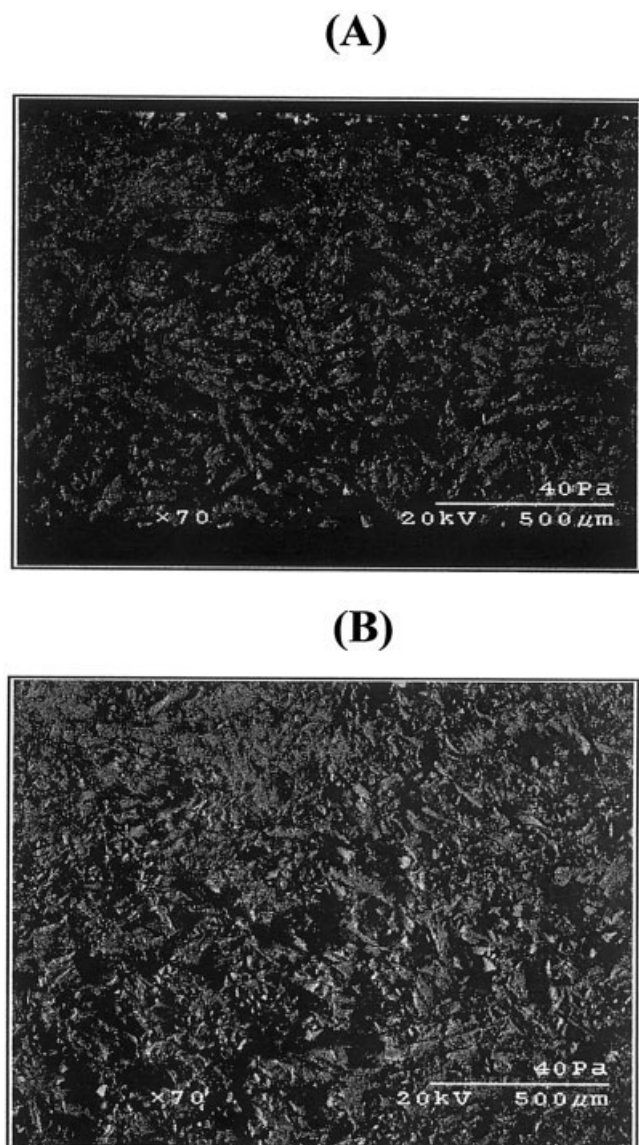


Figure 9 SEM micrographs of the polished surface of the polyimide bonded magnets prepared from IDA R-BAPS with (A) 50 and (B) 85 vol % magnetic particles. Original magnification $\times 70$.

netic properties of the PBM samples, as will be shown later.

The results of the DMA experiments (Fig. 10) show high thermal stability of the polyimide-bonded magnets. As expected, increasing the volume fraction of

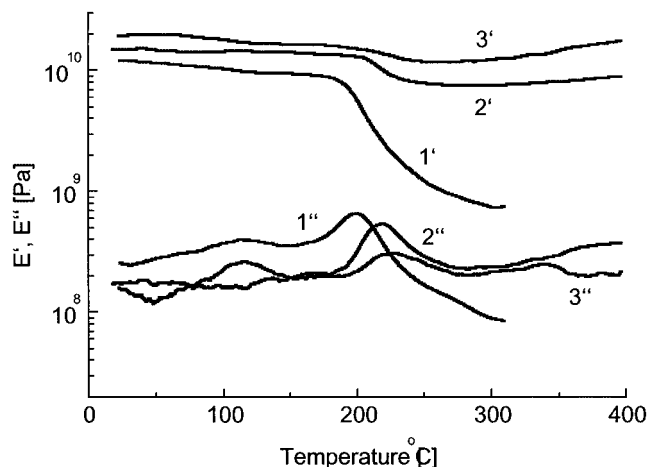


Figure 10 The temperature dependence of the storage ($1'$, $2'$, $3'$) and loss ($1''$, $2''$, $3''$) moduli for polyimide bonded magnets prepared from IDA R-BAPS with ($1'$, $1''$) 50, ($2'$, $2''$) 70, and ($3'$, $3''$) 85 vol % magnetic particles.

the magnetic particles leads to a higher storage modulus of the composites over the temperature range of 20–400°C that we studied. The glass-transition temperature (T_g , temperature corresponding to the maximum in the loss modulus values) is shifted to higher temperatures with an increasing volume fraction of the magnetic particles. For example, the T_g of the 85% volume fraction PBM sample is found to be 230°C, which is 15°C higher than that of the unfilled PI.²¹ This shift of the T_g to higher temperatures is consistent with that reported for fiber-reinforced plastics,³¹ and the Halpin-Tsai³² and Nielsen³³ models and can be explained by a complex shear state of the polymer matrix in the vicinity of rigid particles.

The preliminary results of the magnetic property measurements of the PI bonded magnets are presented in Table I. Typical commercially available injection molded magnets in the industry (Group Arnold, Marengo, IL) have a loading (volume fraction of magnetic materials) of between 65 and 68%. These materials have B_r values ranging from 4800 to 5100 G and energy product values from 5.0 to 5.5 MGOe. Table I also shows the typical properties obtained from various commercially available bonded magnet materials (samples 1–3) based on magnetic Nd-Fe-B powders.

TABLE I
Magnetic Properties at Room Temperature of Polymer-Bonded Magnets

Sample No.	Nd-Fe-B Loading (%)	Binder	B_r (G)	H_c (Oe)	BH_{\max} (MGOe)
1	65–68	Polyamide	4900	4100	5.0
2	65–68	Nylon 12	5100	4200	5.2
3	65–68	PPS	5100	4200	5.5
4	70	R-BAPS	4731	4224	5.0
5	85	R-BAPS	5111	4822	6.16

Figure 4 shows the second quadrant curve approximated from the technique described in the last section. While this technique cannot provide the exact coercivity (H_c) and intrinsic coercivity (H_{ci}) values, by assuming that the material has the typical straight-line demagnetization behavior of rare earth magnetic materials, a linear regression fit can provide an approximate H_c value as depicted in Figure 4. The energy product (BH_{\max}) can be obtained from the equation:

$$BH_{\max} = (H_c \times B_r) / 4 \quad (4)$$

Therefore, the values for B_r , H_c , and BH_{\max} can be approximated from the measured data. The results obtained from two PI bonded magnet samples are shown in Table I (i.e., samples 4 and 5). The data show that it is possible to achieve a $\geq 10\%$ increase in energy product over that of typical, commercial bonded magnet material at room temperature. This is especially significant when one considers that the testing technique used here may produce results that can be up to 4% below the actual value. Experiments are in progress to confirm the effect of temperature cycling on the magnetic properties of the PI bonded magnets via both short- and long-term irreversible loss tests,^{1,11,14} the results of which will be reported elsewhere.

CONCLUSIONS

A new method of PI synthesis of IDA type prepolymer based on the chemical interaction of dianhydrides with acylated diamines yields a processable mixture of IDA type PI prepolymer and magnetic particles that can be subsequently transformed at 300°C to thermoplastic PI bonded magnets. The IDA prepolymer based on R and BAPS monomers after removing the volatile components via heating (volatiles ≤ 5 wt %) can be melted at 220–240°C to yield a fluid with a very low viscosity of about 15 ± 5 Pa s. This low viscosity of the IDA R-BAPS prepolymer makes it possible to blend it with magnetic particles at high volume percentages of 50–80. Overall, the results obtained indicate that PI bonded magnets with 50, 70, and 85 vol % of magnetic particles have excellent thermal stability and maintain a high storage modulus at around 10 GPa at temperatures up to 400°C. This remarkable thermomechanical behavior suggests that the PBM of this study may be suitable for load-bearing applications at high temperatures and in aggressive environments where commercial permanent pure Nd-Fe-B magnets are not useable. The magnetic property data of the PI-bonded magnets at room temperature show a $\geq 10\%$ increase in energy product over that of typical commercially available bonded magnet materials.

The financial support from the U.S. National Science Foundation and the Russian Fund for Basic Research is gratefully acknowledged.

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