Synthesis and Characterization of Magnetorheological Polyimide Gels

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ABSTRACT: Magnetorheological polymer gels (MRPGs) are composite fluids containing ferrous particles suspended in a polymer gel. In addition to modification of the carrier fluid, the polymer gel, which includes crosslinked copolyimide (CCPI) and solvent *N*-octylpyrrolidone, also changes the surface properties of the ferrous particles, thus reducing the particle settling and improving particle redispersion. The viscosity of MRPGs can be easily adjusted by controlling the concentration of CCPI in the carrier medium. High thermally resistant CCPI is synthesized from dianhydride, diamine, diaminobenzonic acid, and crosslinker and has a high glass transition temperature because the crosslinking ratio can be controlled by the molar ratio of diamine to diaminobenzonic acid. The redispersion and rheological properties are also investigated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2402–2413, 2005

Key words: crosslinking; polyamide; viscosity; glass transition

INTRODUCTION

Magnetorheological fluids (MRFs) are suspensions of ferrous particles such as carbonyl iron particles, which are micrometer sized and dispersed in a carrier medium.[1] The carrier fluids can be silicone oil, hydrocarbon oil, or water, depending on the specific application of the MRF. In the absence of an applied magnetic field, MRFs exhibit Newtonian behavior. They exhibit rapid, nearly completely reversible rheological property changes when an external magnetic field is applied (this is known as the on-state). In the on-state ferrous particles are magnetically induced and aggregate to form chain-like or column-like structures parallel to the applied field. These structures restrict the flow of the fluid, thereby altering the rheological properties of the suspension. The stress needed to yield these chain-like structures increases with applied magnetic field, resulting in a field-dependent yield stress.[2] The rheological behavior of MRFs is often described by the Bingham plastic model.[3]

To prevent the particles from settling or aggregating and allowing them to redisperse more easily in the carrier fluid, different additives are used to modify the surface of the carbonyl iron particles or to modify the viscosity of the carrier fluid. Carbonyl iron particles are usually coated with surfactant to reduce settling in MR fluids.[4] Organic polymers are also used to coat the surface of iron particles.[5]

In this research novel magnetorheological polymer gels (MRPGs) are investigated. MRPGs are a new generation of materials used in vibration control and damping devices. Wilson et al.[6] studied MRPGs prepared by suspending iron particles in silicone gel or polyurethane gel. Adjusting the ratio of resin to crosslinker and percentage of diluents can control the off-state rheology of the system.[6] Mei also investigated static shear yield stress, off-state viscosity, and sedimentation properties of similar systems.[7] In this paper, MRPGs with improved redispersion performance and high temperature resistance property are investigated. This MRPG is a composite fluid of magnetic particles suspended in a polyimide gel. Polyimides are thermo-oxidatively stable materials with good chemical resistance. Polyimide gels contain crosslinked copolyimide (CCPI) swollen in excess solvent. It's hard to stop the settling of iron particles completely because of the large difference between the density of iron particles and carrier medium. However, these fluids can be used effectively in different devices if they redisperse quickly and completely. Carlson described earlier work by Rainbow who pointed out that complete suspension stability was not necessary for most MR fluid devices since some devices such as MR dampers are very efficient mixing devices.[8] Therefore, redispersion of iron particles is very important issue in the investigation of MRPGs. Stabilization and redispersion of the carbonyl iron particles in the carrier
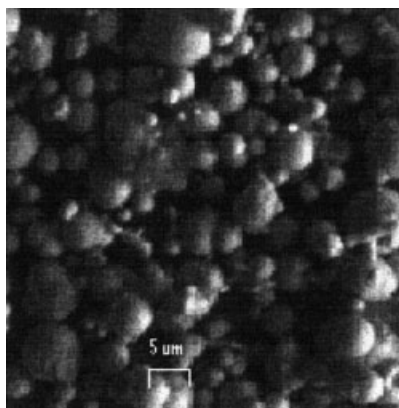
Figure 1   SEM picture of carbonyl iron particles.

medium are attributed to the adsorption of CCPI on the surface of the iron particles, thus sterically preventing the particles from aggregating. One of the features of MRPG is its controllable off-state viscosity. This is achieved through appropriate selection of carrier fluid and weight ratio of CCPI to solvent. CCPI gels are synthesized from dianhydride, diamine, diaminobenzonic acid, and 1–4 butanediol (crosslinker) in the solvent N-octylpyrrolidone.

MRPGS MATERIAL DEVELOPMENT

Materials

The MRPG includes three components: carbonyl iron particles, carrier medium, and additives. Carbonyl iron particles (ISP Technologies, Grade-R-2430) are 99.5% pure iron and are formed by thermal decomposition of iron pentacarbonyl $Fe(CO)_5$. Figure 1 is a scanning electron microscope image of carbonyl iron particles. The average diameter of the ferrous particles is about 5 μm. Each sample contains 81 wt % carbonyl iron particles. The carrier medium includes CCPI and solvent. The solvent is typically chosen based on its viscosity, freezing and boiling points, and vapor pressure. The solvent used is N-octylpyrrolidone (Aldrich Chemical), which has a boiling point of 306°C, viscosity of 9 cP at 20°C, and a vapor pressure of less than 1.3 Pa at 20°C. Claytone APA (CTAPA) (Montmorillonite, Southern Clay Products) is the additive used to improve particle stability.

Synthesis of crosslinked copolyimide

Synthesis of copolyimide from aromatic anhydride, aromatic amine, and crosslinked with carboxylic functionalized aromatic amine has been described previously.[9] The solvent N-octylpyrrolidone (OP) is introduced into a moisture free reactor. 3,5-Diaminobenzonic acid (DABA) (Aldrich Chemical) is dissolved in the N-octylpyrrolidone. The 4,4'-(4,4'-isopropylidene di-

phenoxy)bis(phthalic anhydride) (ISBPA) (Aldrich Chemical) is then added. This compound reacts for 1 h at room temperature to form an anhydride terminated prepolymer. Reactive comonomer 4,4'-methylenedianiline (MDA) (Aldrich Chemical) is then added and mixed for 7 h at room temperature to form high-molecular-weight polyamic acids. Imidization is performed by dehydration of the polyamic acid adding excessive acetic anhydride and N,N-dimethylaniline (Aldrich Chemical) to the reaction mixture and stirred for 2–3 h at 50°C. The temperature is then increased to 110°C for 30 min. This results in formation of linear copolyimide. To synthesize crosslinked polyimide gel, the crosslinker 1,4-butanediol (Aldrich Chemical) is added to the reaction mixture and kept at 170°C for 7 h. The crosslink ratio can be controlled by the stoichiometric ratio of diaminobenzonic acid to the 4,4'-methylenedianiline used in the polymerization reaction.

Figure 2 shows the reaction synthesis of crosslinked copolyimide. It is important to initially react the less reactive diaminobenzonic acid with dianhydride. The anhydride prepolymer formed is extended by adding more reactive 4,4'-methylenedianiline. To get crosslinked copolyimide, 1,4-butanediol should be added to esterize the carboxylic acid group by bridging the two linear copolyimides to form the three-dimensional chain networks. The subscripts of m and n are determined by the stoichiometric ratio of 3,5-diaminobenzonic and 4,4'-methylenedianiline. Two types of crosslinked copolyimides are prepared with stoichiometric ratios of DABA : MDA : ISBPA of 6 : 4 : 10 and 8 : 2 : 10, respectively. Three types of MRPGs are investigated with the weight ratios of crosslinked polyimide to N-octylpyrrolidone to be: 1 to 20, 1 to 30, and 1 to 40, respectively.

To compare the crosslinked copolyimide with that of linear polyimide, a linear polyimide is synthesized by dianhydride ISBPA and diamine MDA using a similar polymerization routine described previously without the crosslinking step.

Synthesis of MRPG

Eighty-one (81) weight % carbonyl iron particles are added to the synthesized CCPI gel and mixed at low shear rate (400 rpm) using a Servodyne Mixer (model 50,003–30, Cole Parmer Instrument) for 30 min. Additives are mixed together and stirred thoroughly at 1200 rpm for 24 h at room temperature.

Instrumentation and methods

Redispersion of MRPG

The redispersability or remixing behavior of MRPG is an important issue. Magnetic particles settle due to the

4,4'-methylenedianiline   3.5-diaminobenzoic acid   N-octyl-pyrrolidone (organic solvent)

4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride)
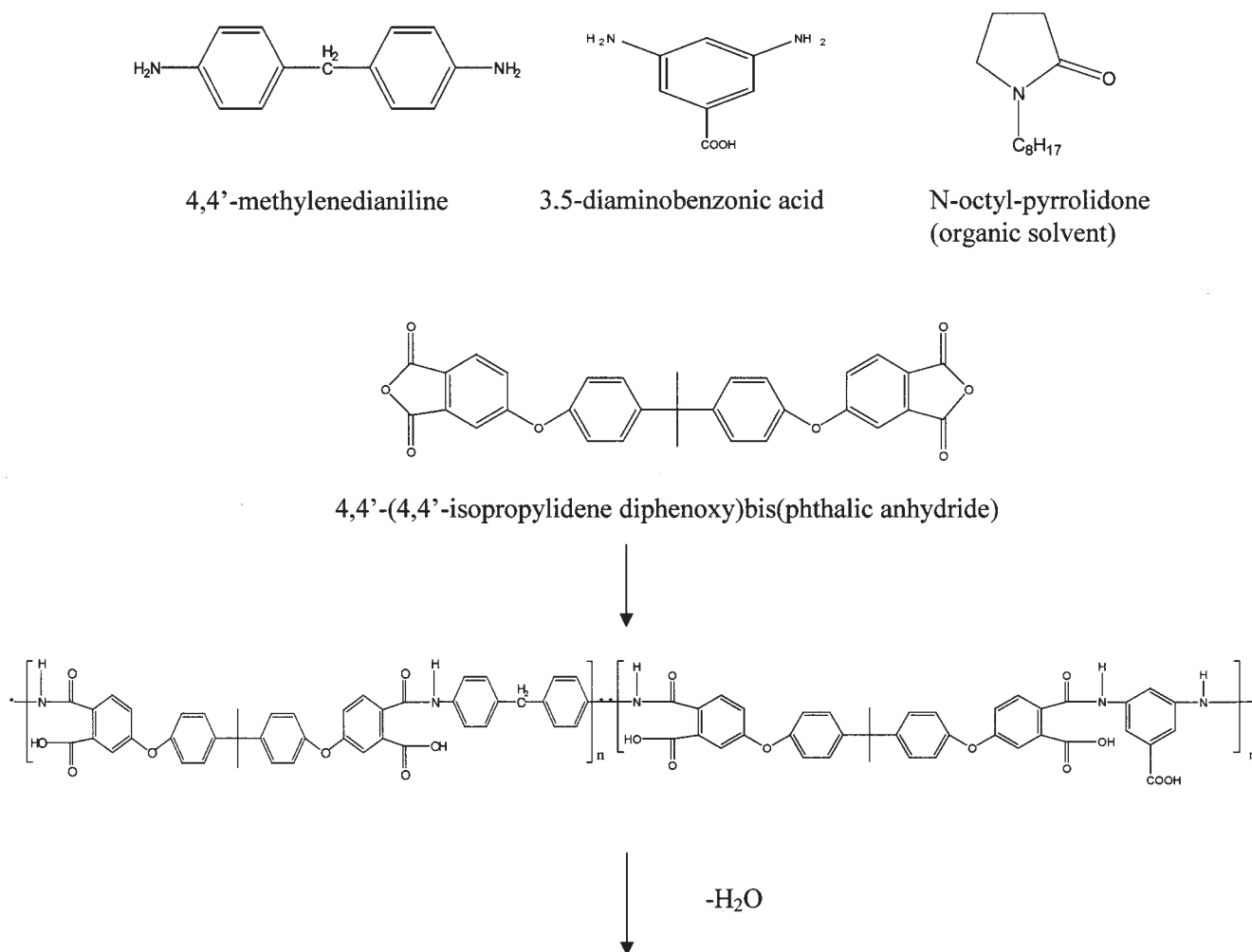
$-H_2O$

Figure 2 Scheme reaction of the synthesis of crosslinked copolyimide.

difference in density between the particles and carrier fluid. However, these fluids can be used effectively in different devices such as dampers if they redisperse quickly and completely.

It is believed that the hardness of the "cake" of carbonyl iron particles formed due to settling and agglomeration is an indication of the redispersability. The harder the cake, the more difficult it is to redisperse the MRPG. A redispersion method has been developed to quanitatively access this property.[10] To accelerate the settling process, the MRPG samples are heated to 70°C for 24 h and then 25 °C for 2 h. This thermal cycling is repeated three times. During thermal cycling the particles settle and form a cake. The settled hardness after thermal cycling is measured using a micromechanical testing instrument (Perkin-Elmer DMA-7e). The test is carried out by depressing the probe into the settled iron cake by increasing the force at rate of 10 mN/min and the displacement of the probe is measured. Larger displacement of the probe indicates easier MRPG redispersion. For instru-

ment sensitivity, measurements of the position are precise to ±50 nm. Measurements of the force are precise to 0.001 mN.

Magnetorheological rheometer

A magnetorheological rheometer (MCR300, Paar Physica) was used to investigate fluid rheology.[11] The measurement system includes three parts: the mechanical drive system, the electronics for data processing, and a corresponding software package. Unlike a conventional rheometer, the magnetic field applied to the MRPG is generated by a built-in copper coil. The magnetic field is perpendicular to the gap filled with MRPG. The magnetic field (B) in the gap depends on the current in the coil and the material in the gap through which the flux flows. Two parallel disks with 20-mm diameter and a 1-mm gap were used for this study. Approximately 0.314 mL of sample was placed in the gap between the two plates.
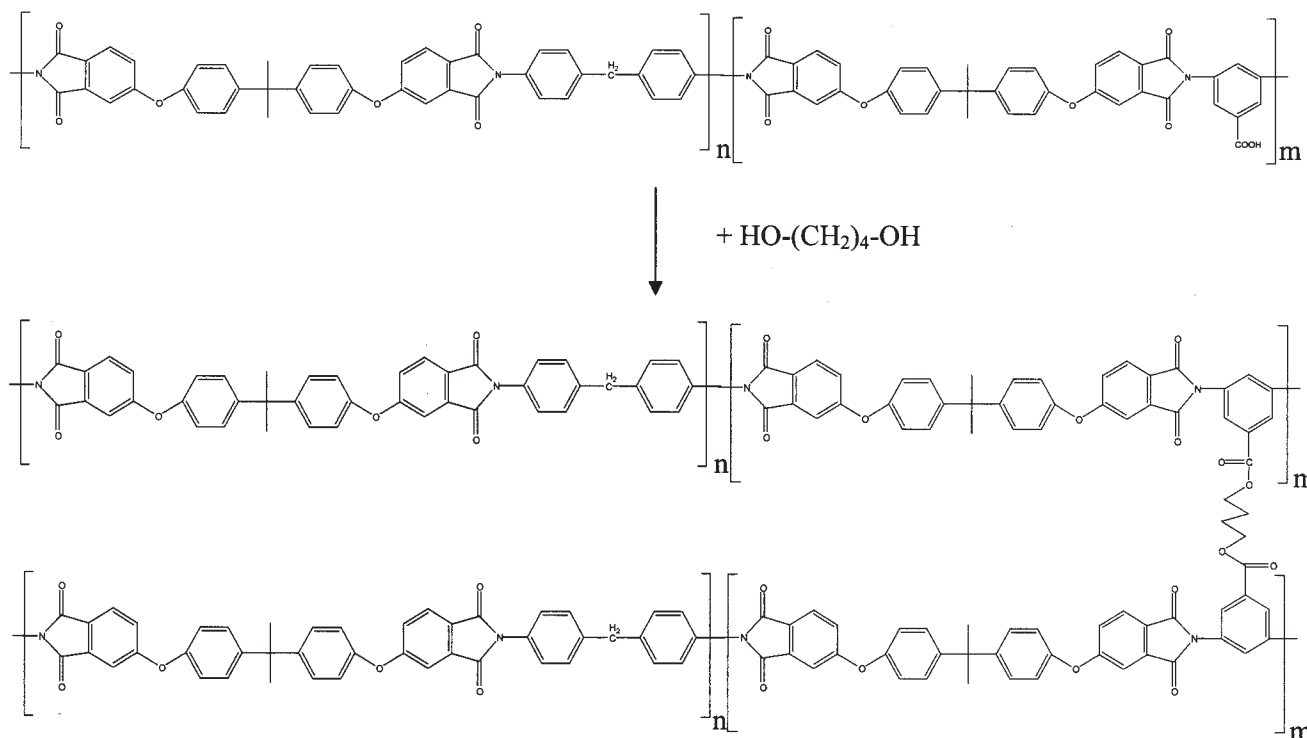
Figure 2 (*Continued from the previous page*)

Stepscan DSC measurement for T_g

Stepscan DSC is used to separate reversible from irreversible phenomenon. In the case of polymers with residual solvent, stepscan DSC is an effective means for measurement of the glass transition temperature (T_g) because it allows separation of the thermal transition due to the T_g from evaporation of the solvent. The glass transition temperature (T_g) of the synthesized linear and crosslinked polyimide is measured using stepscan DSC. Stepscan DSC is a modified temperature modulated DSC technique for the characterization of thermal properties of materials, including T_g.[12] A series of short heating and isothermal steps was used to separate reversible from irreversible phenomena. Two signals are obtained: one is the thermodynamic C_p, which reflects the reversible behavior of the material such as glass transition temperature, and the other is the isoK baseline, representing the irreversible or kinetic behavior. Sample preparation for stepscan DSC involves washing the polyimide gel with methanol. The polyimide is then dried in vacuum for 24 h at room temperature. Table I gives the parameters used for stepscan DSC measurement of T_g.

RESULTS AND DISCUSSION

Redispersion of MRPG

Agglomeration results from the attractive van der Waals forces when particles approach one another.

For a suspension of solid particles in a liquid there is very high surface energy because of the presence of individual particles, which have high surface area.[13] Therefore, processes accompanied by decreasing surface energy, such as aggregation of particles, easily occurs in this system. To prevent agglomeration, and hence stabilize the MRPG system, iron particles must be stabilized through forces of repulsion. Polymer gels can provide polymeric stabilization including sterical and depletion stabilization. Steric stabilization is achieved by polymer molecules adsorbing or attaching to the surface of magnetic particles and depletion stabilization is due to the molecules in free solution. In a sterically stabilized system, each iron particle is coated with physically or chemically adsorbed surface layers that hinder the particles' approach to each other to distances where van der Waals force dominate. The thickness of the adsorbed layer is determined by the length of the polymer chain. The long polymer chains in solution assume numerous configurations, which

TABLE I
Step Scan DSC Parameters

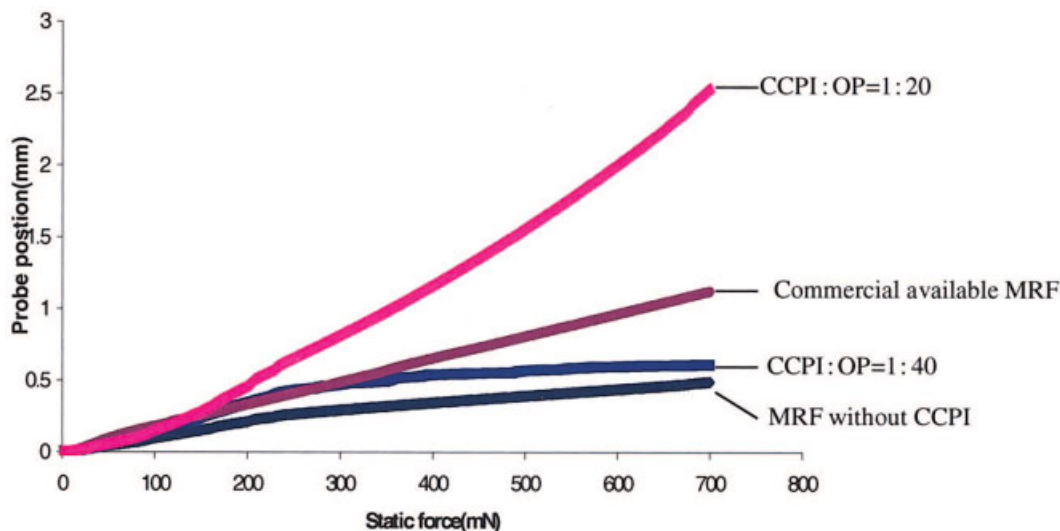|	
Heating rate	5 °C/min
Isothermal hold time	0.7 min
Sample weight	3–5 mg
Start temperature	130 °C
End temperature	295 °C
Repeat times	60 cycles

Figure 3 Redispersion behavior affected by different weight ratios of crosslinked polyimide.

results in repulsion between particles. In depletion stabilization, close approach of iron particles must be accompanied by mixing of the polymer molecules and the solvent in the interparticle regions and driving the polymer molecules out of these interparticles regions. Work must be done to make the polymer molecule leave the interparticle region and this corresponds to repulsion force between particles.

Redispersion is the remixing of magnetic particles, which have agglomerated because of Van der Waals forces. Figure 3 shows the redispersiblity as a function of crosslinked copolyimide concentration. Probe displacement for an applied force is used as the measure of dispersibility (Fig. 3). To investigate how the crosslinked PI affects the MRPGs redispersibility, the redispersion behavior of a MRF sample only containing solvent (N-octylpyrrolidone) and iron particles with the weight ratio of 19 : 81 is also shown. Each sample has the same amount of carbonyl iron particles, 81 wt % (the total weight ratio of carrier medium plus additives is 19 wt %). Carrier medium contains solvent and CCPI polyimide in which the stoichiometric ratio of DABA : ISBPA : MDA is 6 : 4 : 10 and solvent OP. CCPI : OP = 1 : 20 indicates that the weight ratio of CCPI to solvent (OP) is 1:20.

From Figure 3, the MRF (not containing any crosslinked PI) is difficult to redisperse, indicating that the hardness of settled iron particles cake is highest. By increasing the concentration of crosslinked PI, the slope of the each curve increases and the improvement in redispersability is achieved. The reason might be that crosslinked PI forms a spatial network coating on the surface of iron particles allowingt the aggregated iron particles to separate easily.

The crosslink ratio of CCPI can also affect the redispersion of MRPG. Two kinds of CCPI are synthesized

with stoichiometric ratios of DABA : MDA : ISBPA of 6 : 4 : 10 and 8 : 2 : 10, respectively. The crosslink ratio is determined by the stochiometirc ratio of DABA to MDA. The subscripts of m to n in Figure 2 are 6 : 4 and 8 : 2 for these two cases, respectively. The redispersion behavior of these two MRPGs is shown in Figure 4. These two samples have equal weight ratios of iron particles, 81 wt %. At low static force (less than 370 mN), there is no significant difference in redispersion behavior between the two MRPGs. However, at higher static force the hardness of the MRPG, which has higher crosslink ratio of CCPI (DABA : MDA = 8 : 2), is lower than that of MRPG with lower crosslink ratio (DABA : MDA = 6 : 4). Consequently, it is easier to redisperse the MRPG with higher crosslink ratio. This is probably because more highly crosslinked PI forms a more stable coating on the surface of the iron particles and prevents agglomeration.

For instrument sensitivity, measurements of the position are precise to ±50 nm. Measurements of the force are precise to ±0.001 mN.

Particle settling

Sedimentation of iron particles under gravity causes severe problems with the operation of devices utilizing magnetic fluids. However, settling may be tolerated, to some extent, if the particles are easily redispersed. Sedimentation is a direct consequence of the greater density of iron particles than that of the carrier medium. When the particles size is sufficiently small (<1 μm), the gravitational force is opposed by a diffusional force associated with thermal Brownian motion. However, the yield stress of MRPG decreases when reducing the size of the iron particles.
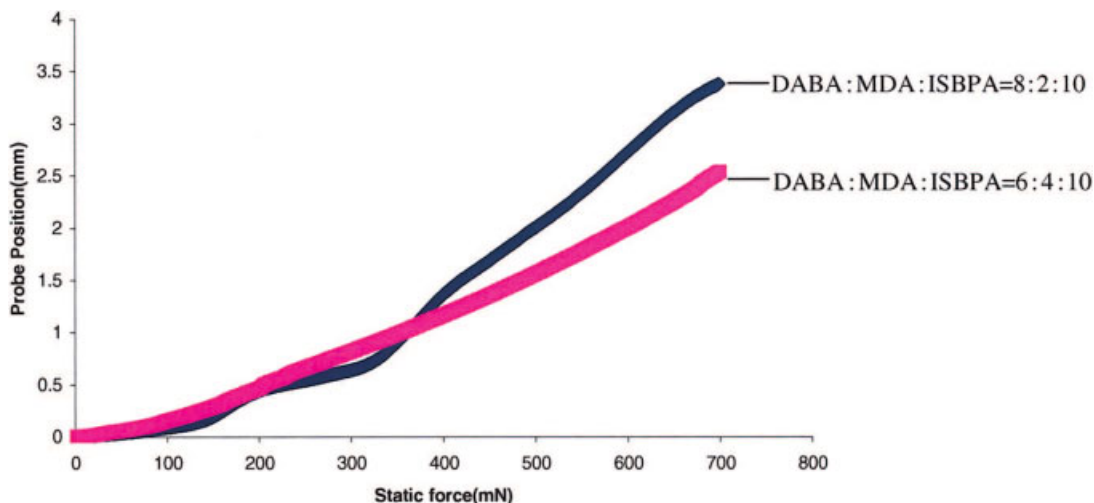
Figure 4 Redispersion behavior affected by different crosslink rate polyimides.

Particle settling is investigated by observing the formation of a clear layer of carrier medium above the iron particles. The interface is easily distinguishable for the settled system. The height of the clear liquid layer is measured as a function of time. The ratio of the volume of the clear liquid to the total volume of MRPG is an indication of the settling rate.

One type of organic clay, Claytone APA (CTAPA) (montmorillonite), is used as an antisettling agent, thixotropic agent, and rheology modifier and to improve redispersion. Montmorillonite is produced by reacting organic cations, such as a quaternary ammonium chloride, with smectite clay. The reaction that occurs is an ion exchange reaction where the positively charged quaternary ammonium chloride replaces the sodium cation on the clay surface. During the reaction as the clay is being converted to organic

clay it changes from being hydrophilic in nature to being oleophillic. CTAPA is a modified montmorillonite and is designed for use in systems containing aromatic solvent or aromatic-oxygenated solvent blends that display medium to high polarity. CTAPA can form networks, which can be easily broken by the shear stress and can also reform easily after the shear stress is removed. It is believed that the organic clay provides network structure to prevent the magnetic particles from settling.[10] Therefore, addition of 1 wt % CTAPA further improves dispersion stability.

The particle settling rate is shown in Figure 5. An increase in polymer from CCPI : OP = 1 : 40 to 1 : 20 reduces the settling. This indicates that the dispersion stability is improved with increasing the concentration of CCPI. A criterion for achieving good particulate dispersion is to ensure that the polymer coats the
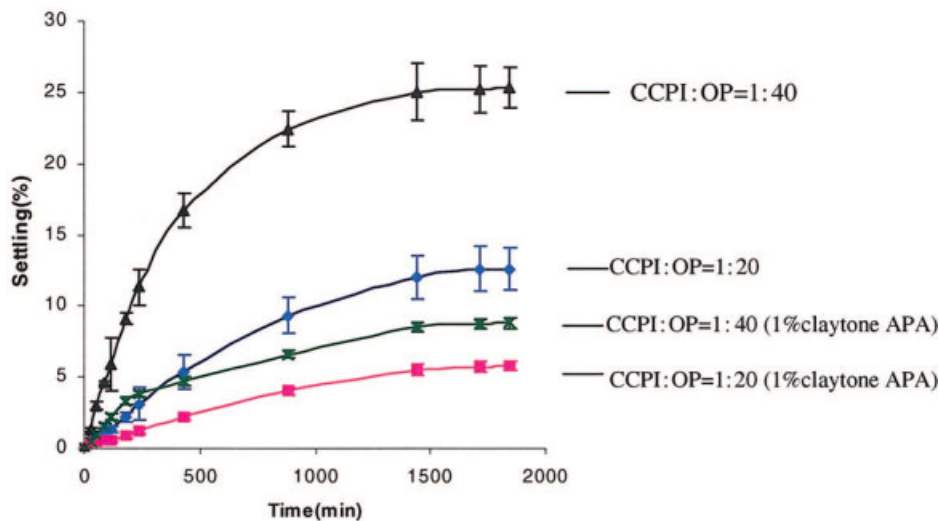

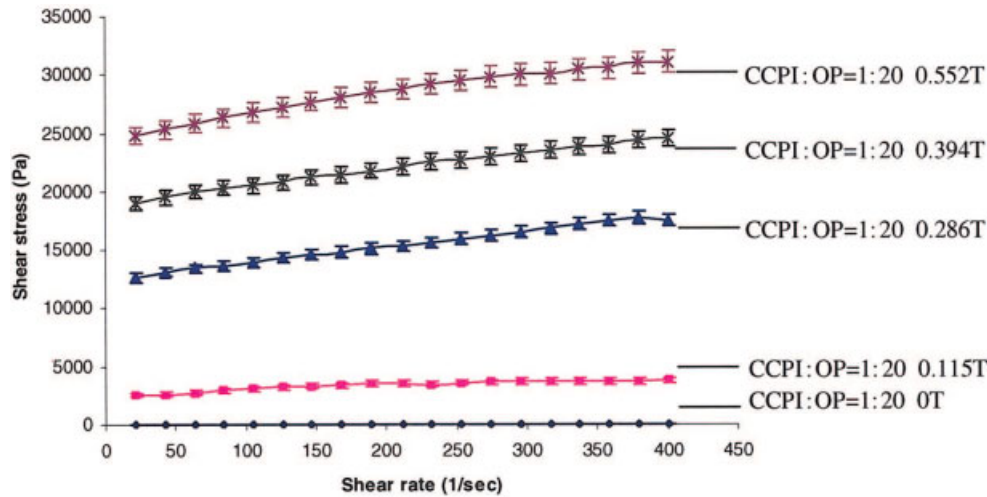**Figure 5** Settling curves for the MRPGs

Figure 6   The dependence of shear stress of MRPG on the shear rate at different applied magnetic field density.

particle surface homogeneously. If the particle coating is complete, settling, which is due to gravity attractive forces, should be reduced. The stability of magneto-rheological (MR) suspensions has been studied by Rankin et al. using the gravity yield parameter, Y_G.[14]

$$Y_G = \tau_0^G/[gR(\rho_p - \rho)], \tag{1}$$

where τ_0^G is the yield stress of the carrier medium, g is the acceleration of gravity, R is the particles radius, ρ_p is the iron particle density, and ρ is the density of the carrier medium. Larger values of Y_G indicate better stability of MR suspension. Larger values of Y_G also indicate a better ability of the medium to suspend the particle. If Y_G is greater than a critical value, $Y_{Gcritical}$ (for each particulate material and particle, a critical viscoplastic yield stress can be defined), the carrier medium will prevent a particle from settling. But the medium having larger value of Y_G has very high off-state viscosity so that it will increase the MR suspension response time to the magnetic field and MR fluid applications are limited.

Shear yield stress

A change in rheological behavior results from polarization induced in the suspended particles by application of an external magnetic field. These induced dipoles cause the particles to align "head to tail" in chains and form columnar structures, parallel to the applied field.[16] These chain-like structures hinder the flow of the fluid, thereby increasing the apparent viscosity of the suspension. The pressure needed to yield these chain-like structures increases with applied magnetic field, resulting in a field-dependent yield stress. Thus, behavior of this type of controllable fluid in the postyield region is often represented as a Bingham plastic having variable yield strength, as follows,

$$\tau = \tau_y + \eta\gamma, \ \tau \geq \tau_y, \tag{2}$$

where τ is the total shear stress, τ_y is field-controllable shear yield stress, η is the plastic viscosity of MRPG, and γ is the shear strain rate. In the preyield region, MR suspension behaves as a viscoelastic solid and therefore the shear below the yield stress (at strains on the order of 10^{-3}) is given by

$$\tau = G\gamma, \tag{3}$$

where G is the complex material modulus and γ is the shear strain. The complex modulus is also field dependent.

The effect of applied magnetic field on shear yield stress of the polyimide MRPG is investigated using the MR rheometer described earlier. The results of the shear stress versus strain rate under different applied magnetic flux densities for the MRPG are shown in Figure 6.

Figure 6 indicates that MRPG exhibits typical Bingham plastic behavior. When the shear stress is higher than the yield stress, the shear stress is a linear function of the shear rate applied. Using the Bingham model, the dynamic yield point is determined for each curve by extrapolating the shear stress to zero shear rate and finding the intersection with the vertical axis. For an increase of magnetic flux density, an increase of shear yield stress can be observed and the predicted yield stress is 2.6 kPa at 0.115 T. However, at a magnetic field strength of 0.552 T the yield stress increases to about 24 kPa.

In Figure 7, dynamic yield stresses of two different MRPGs and one commercially available MRF are shown as functions of the applied magnetic flux density B. The yield stress increases significantly with an increase of magnetic flux density. The numerical and analytical model was developed by Ginder et al.[17]
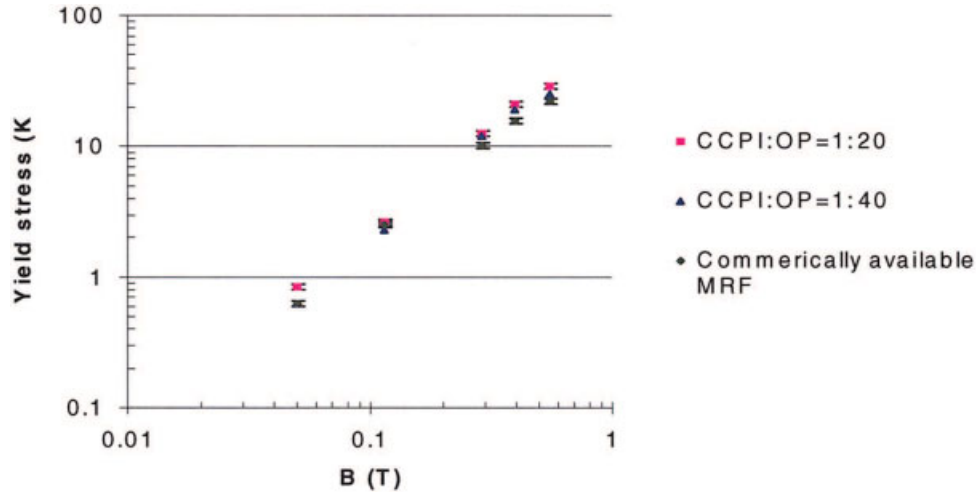
Figure 7 The dependence of dynamic yield stress of MRPGs on applied magnetic field.

$$\tau_y \propto \phi \mu_0 M_s^{\frac{1}{2}} B^{\frac{3}{2}}, \tag{4}$$

where $\mu_0 = 4\pi \times 10^{-7}$ T-meter/ampere is the permeability in free space, ϕ is the volume fraction of carbonyl iron particles, M_s is the local saturation of magnetization, and B is the magnetic induction related with the external field H_0 by the equation

$$B = \mu_0(H_0 + M_s). \tag{5}$$

Therefore, the yield stress measured increases with a $B^{3/2}$ dependence and agrees with the model provided by Ginder et al.[17] This subquadratic dependence of flux density is a consequence of local saturation of magnetization in the contact region of each particle.

This numerical model agrees well with the experiments shown in Figure 7. The slope of log-log plot curves between yield stress and magnetic field for MRPG and commercial available MR fluid is about 1.59.

In Figure 7, the CCPI : OP = 1 : 20 system shows a slightly higher yield stress than the CCPI : OP = 1 : 40 system. It is speculated that this may occur because of improved dispersion stability at higher polymer concentrations.

Apparent viscosity

The apparent viscosity is defined as the slope of shear stress/shear rate curve. An important feature of MRPGs is that the off-state viscosity can be controlled by
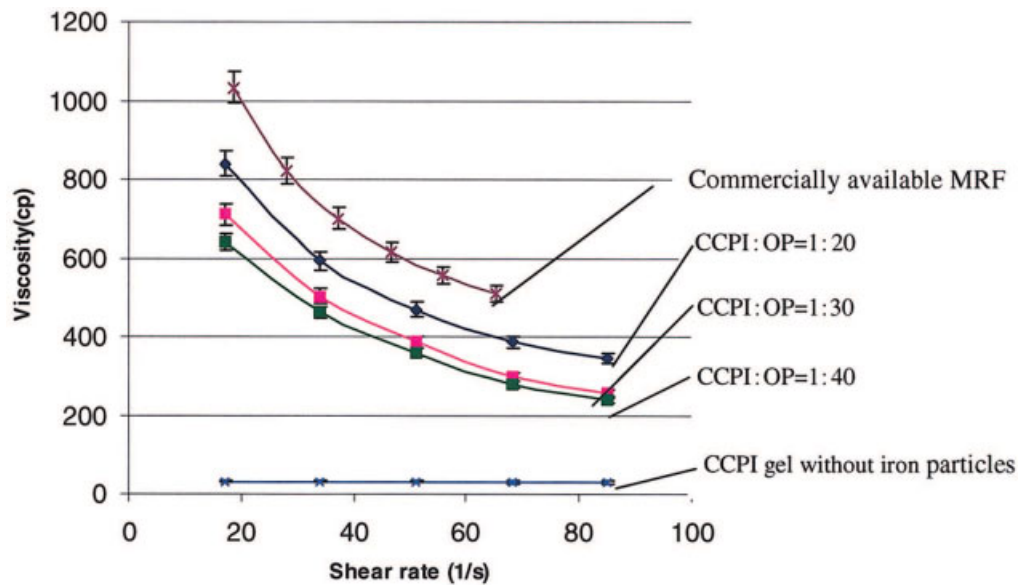

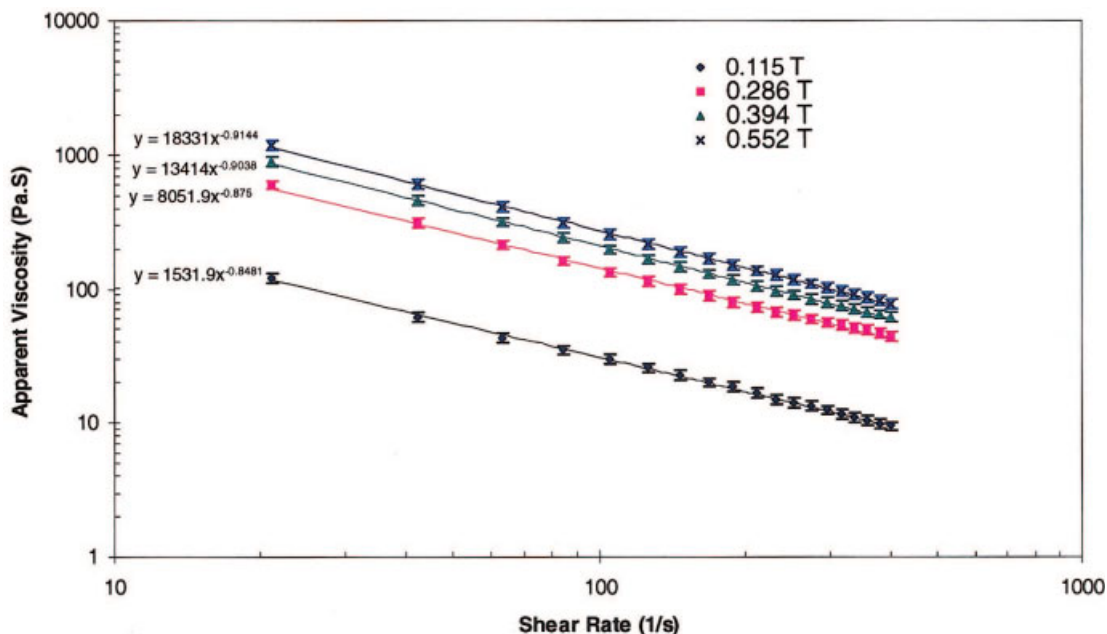**Figure 8** Apparent viscosity of MPRGs as a function of shear rate.

Figure 9   Log-log plot of apparent viscosity versus shear rate for various magnetic fields.

the concentration of CCPI in the solvent. Figure 8 shows the off-state viscosity at room temperature. A typical viscosity-shear rate curve for the crosslinked copolyimide gel is also shown in the same figure. The gel (no magnetic particles) remains Newtonian in this range of shear rates. This is because the presence of solvent reduces the number of chain entanglement per unit volume.[18] The viscosity of the carrier medium (containing 5% polymer) is about 28 cp. When iron particles are added the material demonstrates non-Newtonian behavior and higher viscosity. Rakesh described earlier work by Frankel and Activos who pointed out that the increase in viscosity due to particulate addition is caused by energy dissipation in the thin liquid film between neighboring spheres as they move past each other.[18] The viscosity also increases with the amount of polyimide in the solvent so that the off-state viscosity of MRPG can be controlled.

Figure 6 shows the experimental plot of the shear stress versus shear rate for MRPG for the "on" and "off" states. Apparent viscosity (η_{app}), which is derived by the ratio between shear stress and shear rate, decreases with increasing shear rate and is shown in Figure 9. The phenomenon of the decreasing apparent viscosity with increasing shear rate is known as shear-thinning behavior and is due to the presence of micrometer-size particles. At higher shear rates the apparent viscosity decreases, ultimately reaching a constant value. This shear thinning phenomenon can be represented by the equation

$$\eta_{app} \propto \dot{\gamma}^{-\Delta}, \tag{6}$$

where Δ is a constant, which may vary slightly with different field. The analytical and experimental results show that the range of Δ is from 0.68 to 0.93.[19] Figure 9 is a log-log plot of η_{app} versus γ for MRPG (CCPI : OP = 1 : 20) with various magnetic fields at room temperature. The linear relation in this log-log plot indicates that the apparent viscosity is proportional to the power function of shear rate described by eq. (6). The values of Δ increase slightly with increasing magnetic field from 0.84 to 0.91 in the range of magnetic field investigated.

FTIR analysis of polyimide

The chemical structure of crosslinked copolyimide is studied by Fourier transform infrared spectroscopy (FTIR). The CCPI polymer gel is precipitated in pure methanol and washed five times at room temperature. The precipitated CCPI is kept in a vacuum to dry at room temperature for 3 days. The IR spectrum for CCPI is given in Figure 10. The carbonyl C = O stretching band group absorbs at 1778 and 1721 cm^{-1} and it exhibits a deformation band at 628 cm^{-1}. The cyclic imide(= C-N-) stretching band absorbs at 1361 cm^{-1} and its rocking band at 547 cm^{-1}. The aromatic C = C stretching bands appear at 1599 and 1505 cm^{-1}. The FTIR spectra agree with the chemical structure of CCPI shown in Figure 2. The degree of imidization is estimated by the absorbance ratio of 1778 cm^{-1} band (C = O stretching in imide ring) to the 1505 cm^{-1} band (C = C stretching in benzene ring in DABA and MBA). The degree of imidization shown in Figure 10 is about 57%, which corresponds to the degree of imidization of other polyimide system reported by other research groups.[20]
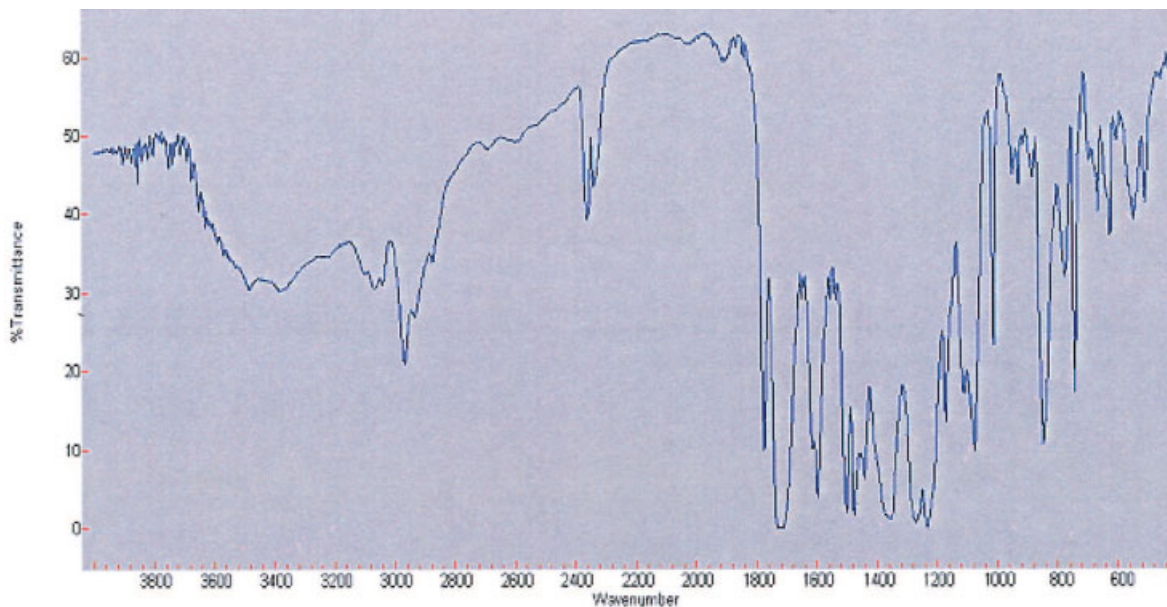
Figure 10 FTIR spectra for crosslinked copolyimide after the imidization process.

Glass transition temperature

CCPI has good thermo-oxidative stability and temperature resistance. The glass transition temperature of linear polyimide and crosslinked copolyimide are investigated using step scan DSC.

The step scan DSC approach allows separations of reversible and irreversible (kinetic) phenomena. By heating over small temperature increments (2.75°C) and then holding for a short time interval (0.7 min), the thermodynamic heat capacity reflects the revers-

ible component of the transition. Irreversible (kinetic) effects are shown by changes in the isoK baseline. Therefore, the glass transition temperature can be determined from the Cp results. The isoK baseline data, which reflect the irreversible process, are also shown in Figures 11 and 12. The T_g of crosslinked copolyimide is about 207°C, while linear PI's T_g is ~192°C. The T_g difference between crosslinked and linear polyimide is about 15°C. The glass transition temperature is indicative of the temperature at which large segmental
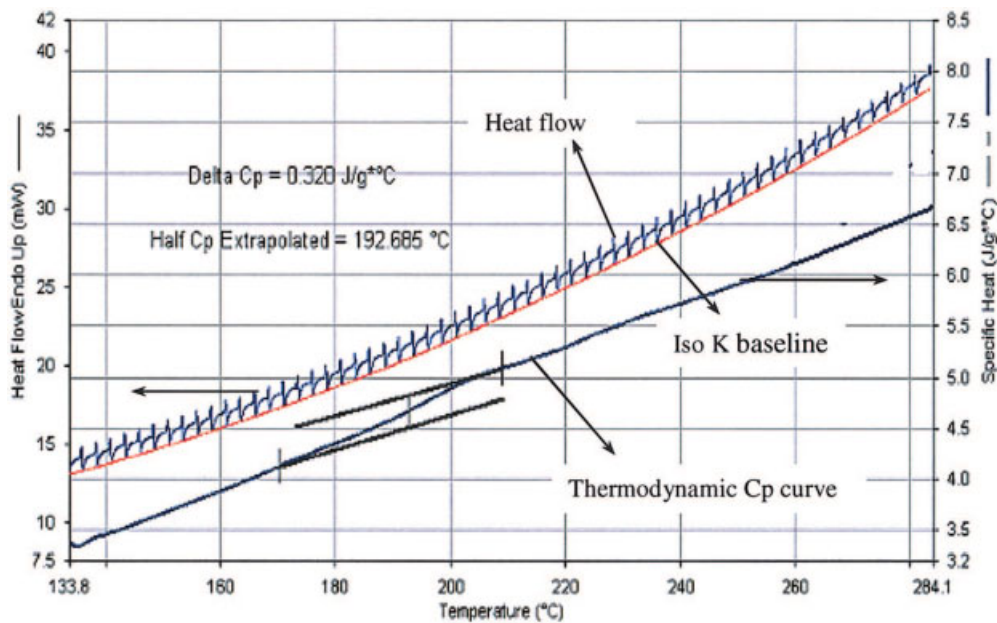

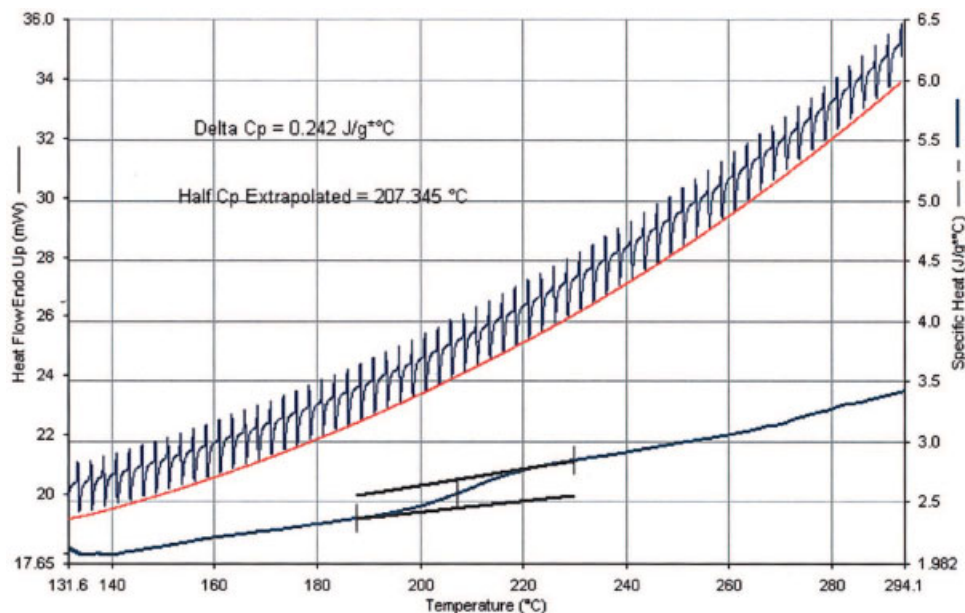**Figure 11** Step scan DSC results on linear polyimide.

Figure 12　Step scan DSC results on crosslinked copolyimide.

chain motion begins. Crosslinking can greatly increase the T_g temperature, since the site of crosslinking can cease the movement of segments and segments can only oscillate around their original positions. To allow the segments between the crosslink sites to move, the temperature should be increased; thus, the glass transition temperature is increased. Therefore, one can conclude that the CCPI has good potential for use in MRPG because of the higher temperature resistance.

The precision of calorimeter of DSC instrument is better than ±0.1% and the temperature precision is better than 0.01°C.

Error analysis

The error measurements are based on two to three reproductive measurements for each parameter. The error analysis is based on "student t distribution" theory.[21]

$$\text{Upper limit} = \bar{x} + \frac{(t_{\alpha/2})S}{\sqrt{n}} \qquad (7)$$

$$\text{Lower limit} = \bar{x} - \frac{(t_{\alpha/2})S}{\sqrt{n}}, \qquad (8)$$

where $\bar{x}$ is the mean value, n is the number of reading taken, $t_{\alpha/2}$ is the t value with $n - 1$ degree of freedom, which can be obtained from the table of critical values of the t distribution with specified confidence interval and $n - 1$ degree of freedom, and s is standard deviation for experimental value.

CONCLUSIONS

A novel magnetorheological polymer gel (MRPG) whose carrier medium contains crosslinked polyimide synthesized from 4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride), diaminobenzonic acid and comonomer 4,4'-methylenedianiline in the solvent octyl-2-pyrrolidinone is investigated. The crosslink rate can be controlled by the stoichiometric ratio of diaminobenzonic acid to comonomer 4,4'-methylenedianiline. The crosslinked polyimide has higher glass transition temperature (T_g) than the linear one. Rheological properties are studied with and without an external magnetic field. Rheological properties of MRPG depend significantly on the carrier medium, the amount of polymer, additives used to stabilize MRPG, and the external applied magnetic field. The viscosity of MRGPs is lower than commercially available MR fluid and it can be controlled by the concentration of crosslinked polyimide in the MRPG. The magnetorheological polymer gel has high yield stress. Redispersion of MRPGs can be greatly improved through suitable control of the amount of crosslinked copolyimide.

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