

Development and Characterization of Magnetorheological Elastomers

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ABSTRACT: A new class of materials termed magnetorheological elastomers (MREs) are developed that respond to externally imposed magnetic fields. Magnetic particles are embedded in viscoelastic solids or liquid elastomeric precursors. This kind of composite demonstrates a unique combination of good magnetic controllability and elastic properties. Polybutadiene (hydrocarbon based) based polyurethane MREs are developed because of their thermooxidative, hydrolytic, and chemical resistance. The structure–property relationships of polyurethane–

MREs are investigated using several characterization techniques. Morphological features such as interdomains of soft and hard segments are identified with tapping-mode atomic force microscopy. The thermal and mechanical behavior is evaluated with dynamic mechanical analysis, differential scanning calorimetry, and stress–strain tests. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2497–2508, 2007

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INTRODUCTION

Magnetorheological elastomers (MREs) are viscoelastic composites that are prepared using conventional elastomeric materials filled with iron or other magnetizable particles. By chemical crosslinking of the elastomer in the presence of an applied magnetic field, a chainlike particle structure aligned along the direction of the field is formed by field-induced interparticle interactions. The resulting viscoelastic solid possesses stiffness and damping that is non-zero even in zero magnetic fields and increases substantially as a field is applied. The field dependence of the mechanical properties, such as the storage and loss moduli as well as anisotropic mechanical and magnetic properties, enables the construction of controllable elastomeric components. These materials exhibit stiffness and damping that can be continuously and rapidly controlled by an applied magnetic field. They are solid under all circumstances and the modulus is nonzero without an applied field.¹ MREs can be used for vibration control in damping and vibration isolation systems including engine mounts and suspension bushings to reduce noise and vibration. Conventional elastomeric components such as hydrobushings and hydromounts contain fluid-filled cavities separated by a channel or orifice, which has

many limitations such as degradation in performance due to aging or loss of fluid. MREs provide an alternative to conventional materials. They provide stiffness controllability, do not need channels or seals to hold or prevent leakage, and are more stable because there is no particle sedimentation. There are challenges related to prevention of rubber aging.²

Composites of magnetic particles in polymeric host media have been produced for some time, although they were initially for structural studies or dielectric applications. In 1981 Rosenweig et al. investigated the structure of a magnetostabilized bed of particles by polymerizing the suspending fluid, thereby “freezing” the particulate structure and permitting optical microscopy and magnetic measurements on the solidified specimens.³ In 1992 Jin et al. cured magnetic metallic particles in silicone elastomers to produce transparent sheets whose conductivity along the field direction is extremely sensitive to pressure, and they used these sheets in touch-screen panels.⁴ In 1990 Behroozi et al. dispersed the highly anisotropic metallic magnetic particles in rigid epoxies to produce highly anisotropic dielectric materials for microwave frequencies.⁵ In 1992 a group at Toyota Central Research and Development dispersed iron particles in liquid silicone and cured them to produce MREs.⁶ After 1996 Jolly et al. at Lord Corporation and Ginder et al. at Ford Motor Company developed the MREs for automotive applications.^{1,7–11} Because of the advantages of natural rubber, the Ford Motor Company has developed chassis elastomers and apparatuses for reducing brake shudder. A suspension

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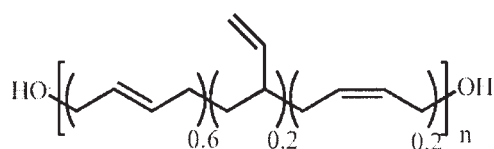


Figure 1 The chemical structure of polybutadiene resins.

bushing in motor vehicles included an MRE with embedded iron particles and an associated magnetic coil.^{9–13}

Suitable matrix materials for MREs include natural rubber, polyurethane (PU),^{9,11,13} silicone, polybutadiene, polyethylene, polyisoprene,^{10,11,13} ethylene-propylene, poly(vinyl alcohol), polyacrylamide, and polystyrene.⁷ These materials are usually nonmagnetic viscoelastic solid materials that can be uniformly mixed with the magnetizable particles and subsequently processed into final solid form through various thermal, chemical, optical, or electrical processes. Recent work has focused on natural rubber because of its easy handling, temperature resistance, durability, and compatibility with other components.⁹ Silicone rubber has some advantages because it can be easily processed from liquid precursors, but it is ill suited for most load-bearing automotive applications because of its low strength and reduced fatigue life.¹

The development of polybutadiene (hydrocarbon-based) based PU MREs is presented, which can be applied as MREs with good performance in a harsh service environment. Polybutadiene resins are selected for investigation because of their excellent thermooxidative, hydrolytic, and chemical resistance. Blend elastomers of polybutadiene PU and silicone are also developed and characterized. The structure-property relationships are investigated using mechanical, thermal, and morphological measurements.

EXPERIMENTAL

Materials

Polybutadiene polyol based PU MREs were prepared by a reaction between hydrocarbon polyol and polymeric 4,4'-diphenyl methane diisocyanate (MDI) iso-

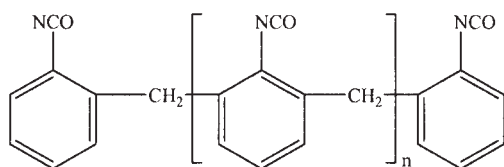


Figure 2 The chemical structure of polymethylene polyphenyl isocyanate (p-MDI).

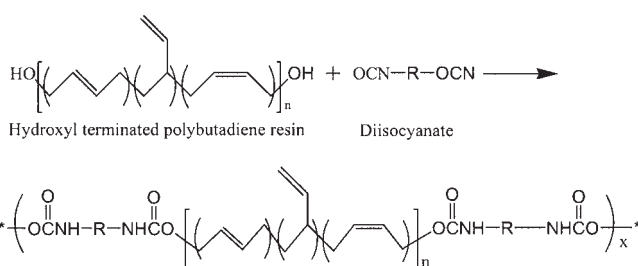


Figure 3 A reaction schematic of polybutadiene-PU.¹⁵

cyanate. The chemical structure and reaction schematics are demonstrated in Figures 1–3. The polyol is hydroxyl-terminated polybutadiene (Poly BD R-45 HTLO, Sartomer Company), which has an average molecular weight of 2800 and a functionality of 2.4–2.6. The isocyanate used is polymethylene polyphenyl isocyanate (p-MDI, Dow PAPI 27), which has a functionality of 2.7 and an equivalent weight of 134. The magnetic particles embedded in the elastomeric matrix are micron-sized (about 3–7 μm) highly magnetically permeable carbonyl iron particles (micropowder iron grade R-2430, ISP Technologies Inc.), which are the most widely used MR materials.⁷

Because of the hydrocarbon nature of the polybutadiene backbone, the PUs derived from it provide high hydrolytic stability, low water absorption, low moisture permeability, and high resistance to aqueous mineral acids and bases. They also have low temperature flexibility, excellent load bearing in both tension and compression, impact resistance, high resistance to degradation by atmospheric oxygen, ozone and chemical resistance, and low toxicity.

The polyether polyol used in the study is VORANOL 220–260 (Dow Chemical). It is a nominal 425 molecular weight homopolymer diol with a functionality of 2.0. This polyol is used in the manufacture of prepolymers and as a chain extender in elastomers. The chemical structure is provided in Figure 4.

MREs were processed by mixing polymer matrices with magnetic iron particles. For the PU system the polyol and isocyanate were added in stoichiometric ratios. Then, 50–70 wt % micron-size carbonyl iron particles were added to the liquid polybutadiene resin (and polyether polyol for the blend) and mixed completely. The p-MDI was added to the mixture and stirred to uniformly disperse the particles in the polymer matrix. The mixture was cured at room temperature for 24 h and then demolded. Characterization was performed after 1 week to ensure

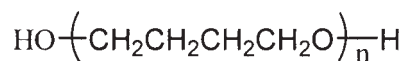


Figure 4 The chemical structure of polyether polyol.

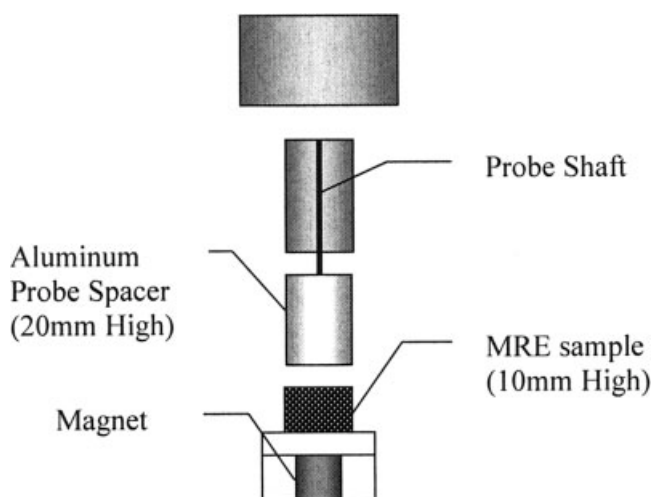


Figure 5 The micromechanical testing device with an accessory for investigating the stress–strain of MREs.

complete cure. PU elastomers with different concentrations of polyether polyol were developed to examine the effect of soft–hard segment modification. A blend of PU/silicone MRE was also developed.

Instrumentation

Microscopy

Optical microscopy and scanning electron microscopy (SEM) were used to visualize the aggregation of micron-sized iron particles along the magnetic field.

Isolation of magnetic effect on mechanical instrument

Characterization of the mechanical properties of polybutadiene–PU–MRE was performed using a micromechanical testing instrument (PerkinElmer, DMA-7e) for dynamic mechanical analysis (DMA). The accessory for magnetic isolation is shown in Figure 5. The 20-mm aluminum probe spacer insured that the magnet was sufficient distance from the measuring

elements so that it did not interfere with force and strain measurements.

Static and dynamic testing

Static testing of the stress–strain relationship of MREs was done by the static scan program of the DMA-7e. Static force scans were run from 0.0 to 6000.0 mN at 500.0 mN/min.

The storage and loss moduli were obtained by the dynamic frequency scan program of the DMA instrument. Frequency scans were run from 0.50 to 45.00 Hz.

Thermal characterization

Differential scanning calorimetry (DSC) was used to investigate the thermal properties of polybutadiene PUs. The step-scan DSC method, which is a modulated temperature DSC technique that operates in conjunction with power-compensation DSC, was used to study the thermal transition. This approach separated the reversible and irreversible reactions by applying a series of short interval heating and isothermal-hold steps over the temperature range of interest. The thermodynamic specific heat (C_p) signal showed the classic stepwise change in the heat capacity, whereas the kinetic or IsoK baseline data set reflected the irreversible or “slow” processes taking place during the experiment.

Atomic force microscopy (AFM) analysis

The microphase structures of segmented PU and the blend of silicone/PU were investigated using tapping-mode AFM (t-AFM). The scans were performed on a Digital Instruments scanning probe microscope using a nanosensor tapping-mode etched-silicon probe type single-beam cantilever. The cantilever had a nominal length of 125 μm and a nominal force constant of 42 N/m, and oscillation frequencies in the range of 315–373 kHz were used. Height as well as phase images were collected.

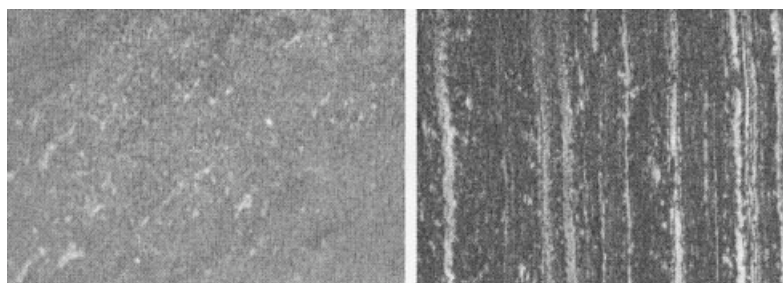


Figure 6 Optical microscopy images of silicone–5 wt % MRE: (left) nonoriented and (right) oriented.

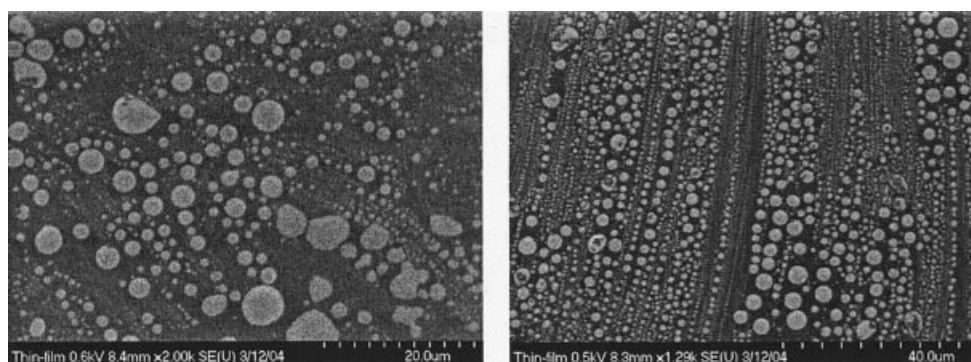


Figure 7 SEM photos of silicone-MRE: (left) nonoriented and (right) oriented.¹⁸

RESULTS AND DISCUSSION

MRE cure conditions

During the elastomer cure process the elastomer was either cured in a magnetic field, forming ordered chains of magnetic particles in the MRE (magnetically oriented MRE or anisotropic), or cured without the influence of a magnetic field, resulting in random orientation of the magnetic particles (nonoriented MRE or isotropic). Curing was done at room temperature. The chainlike columns of iron particles observed using optical microscopy are shown in Figure 6. SEM was used to visualize aggregation of the micron-sized iron particles along the magnetic field (Fig. 7). These images verify that the iron particles in the zero-field cured or nonoriented sample are randomly dispersed in the matrix whereas those in the field-cured or oriented sample are arranged into chains parallel to the direction of the magnetic field.

Static stress-strain of MRE orientation on MR effect

The static stress-strain behavior of oriented MREs and nonoriented MREs under a magnetic field (on state/activated) and without an applied magnetic field (off state) are shown in Figure 8. This difference demonstrates the magnetorheological effect. On-state operations require higher stresses to achieve the same strain as off-state operations. This difference in required stress to achieve a specific strain is referred to as the magnetorheological effect. The data exhibit significant differences in the on-state versus off-state stiffness of the oriented material whereas the non-oriented MRE demonstrates a much smaller effect of stiffness and force range. This reveals that curing the MREs under an applied magnetic field produces a much larger field-dependent stiffness increase than those cured in the absence of a magnetic field. The alignment of magnetic particles in the oriented MRE

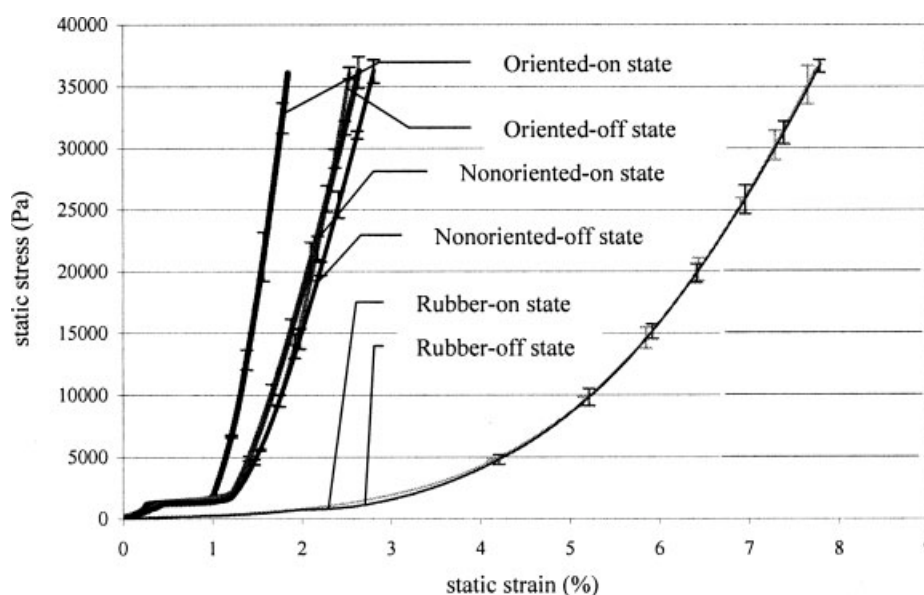


Figure 8 The nonoriented versus oriented static stress of polybutadiene-PU-60% MREs.

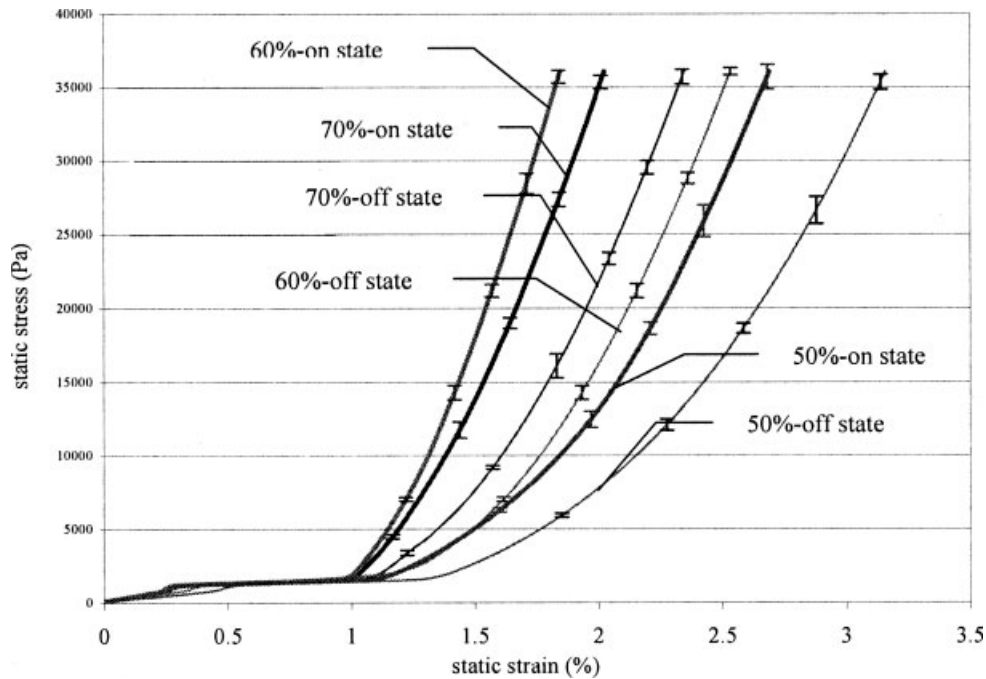


Figure 9 The static stress-strain of polybutadiene-PU-MREs with 50–70 wt % magnetic particles.

sample provides this increased MR effect. Our experimental data also verified Ginder et al.'s conclusions regarding MRE performance mechanisms.¹

Optical and SEM images also confirmed the necessity to align the magnetic particles while curing the matrix. Chain formation and field-dependent mechanical properties are the result of the magnetic forces between particles. When individual particles are exposed to an applied magnetic field, magnetic dipole moments pointing along the field direction are induced, resulting in pairs of particles under magnetic forces that are attracted head to tail (the

north pole of one particle attracts the south pole of its neighbor). During the molding process when the viscosity of the elastomer is low (before reaching its gel point, at which crosslinking occurs), the particles are able to move through the host material and form chains aligned in the field direction by magnetic interactions between particles. Finally the particle structure is locked into place when the liquid precursors cure the solid elastomer. When an external magnetic field is applied, the forces between

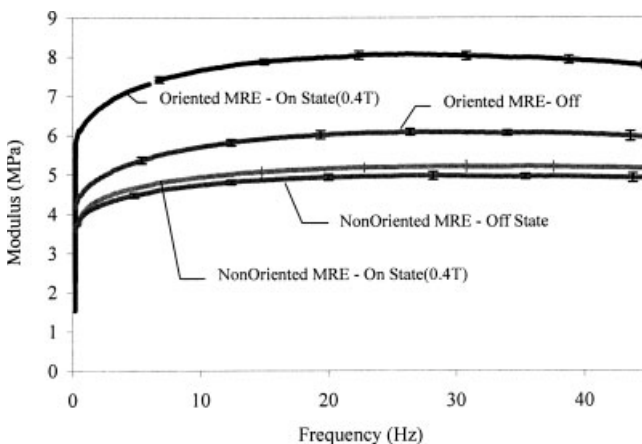


Figure 10 Dynamic storage moduli of polybutadiene-PU-60 wt % MRE.

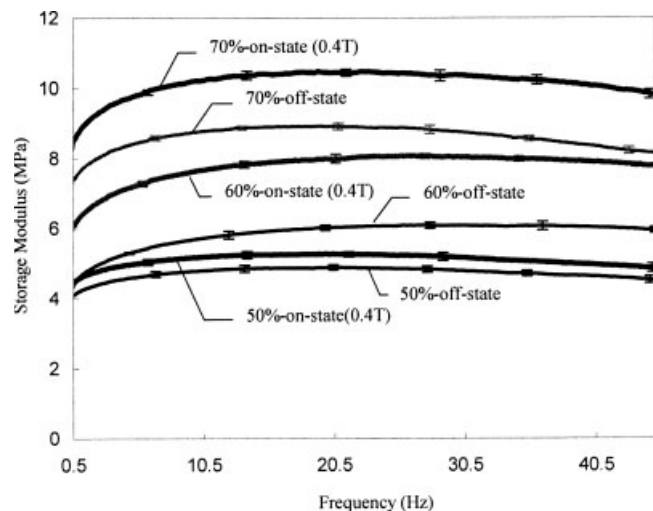


Figure 11 Dynamic storage moduli of polybutadiene-PU-MREs with different particle weight percentages.

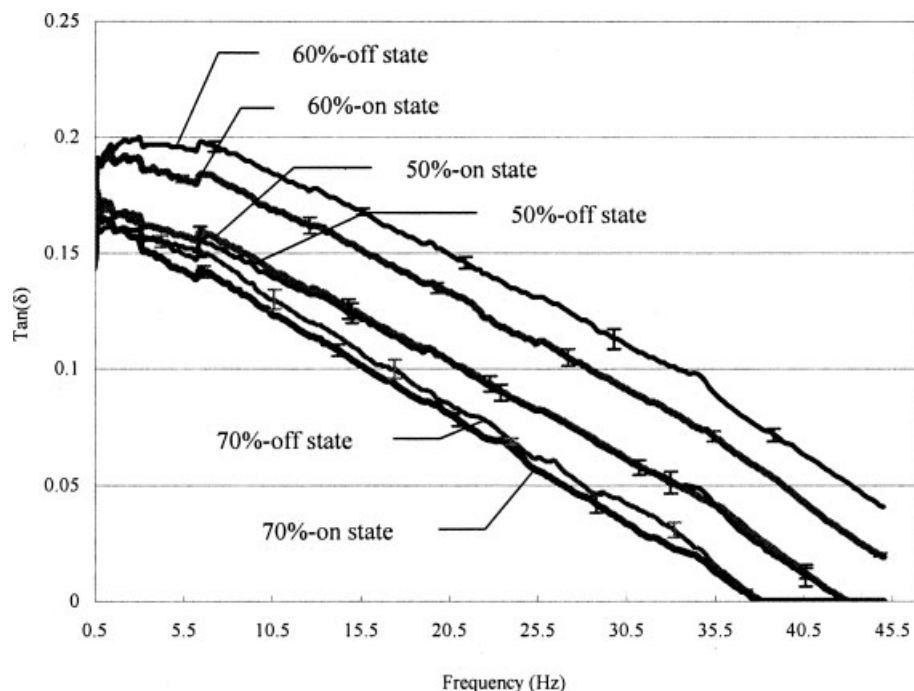


Figure 12 The $\tan \delta$ of polybutadiene-PU-MREs with different particle weight percentages.

particles in these chains will oppose any mechanical deformation that changes the particle chain orientation with respect to the field direction. As a result, the effective stiffness of the elastomer increases in an applied field or on state.¹ Because of the same par-

ticle-particle forces strengthened by the magnetic field, there is also a slight increment of stiffness in nonoriented MREs, even though the particles are not arranged in the chain structure during the curing process.

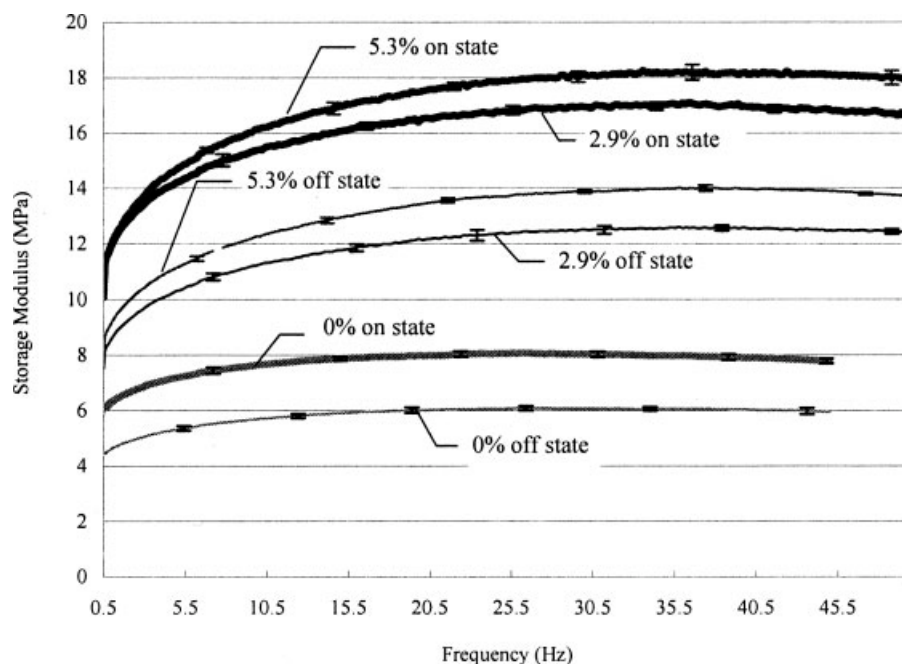


Figure 13 Dynamic storage moduli of PU MREs (60 wt % iron) with different weight percentages of polyether polyol.

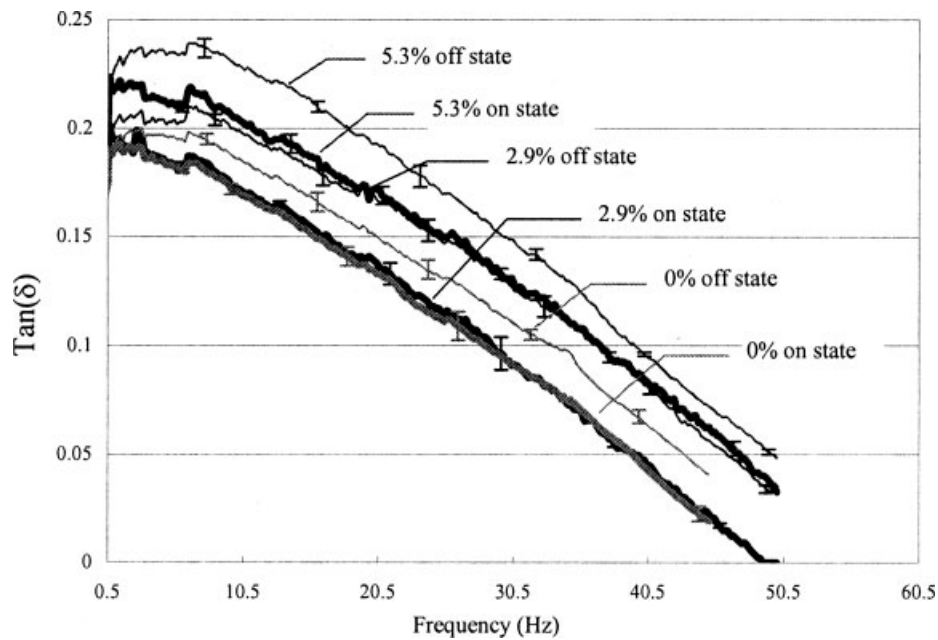


Figure 14 Dynamic $\tan \delta$ of PU MREs (60 wt % iron) with different weight percentages of polyether polyol.

The effect of imposing a magnetic field on the DMA instrument was investigated by testing the behavior of unfilled rubber materials with and without a magnetic field. These data were designated as rubber-on and rubber-off and found to be negligible. The results are shown in Figure 8. The error analyses described in these studies uses the method described in Walpole and Myers.¹⁴

Magnetic particle concentrations

The above results indicated that the significant increase in elastomer stiffness was a result of the activation of the MRE. The MR effect was also influenced by the fraction of magnetic particles in the matrix. The static stress-strain measurements were performed at varying particle concentrations, and the results are provided in Figure 9.

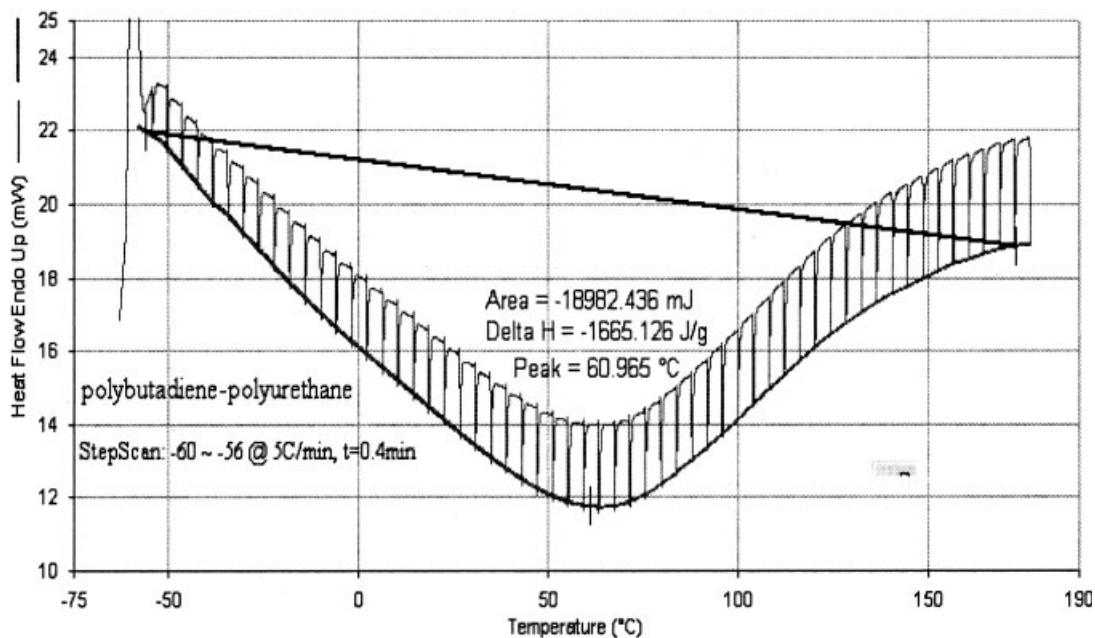


Figure 15 Step-scan data of polybutadiene-PU.

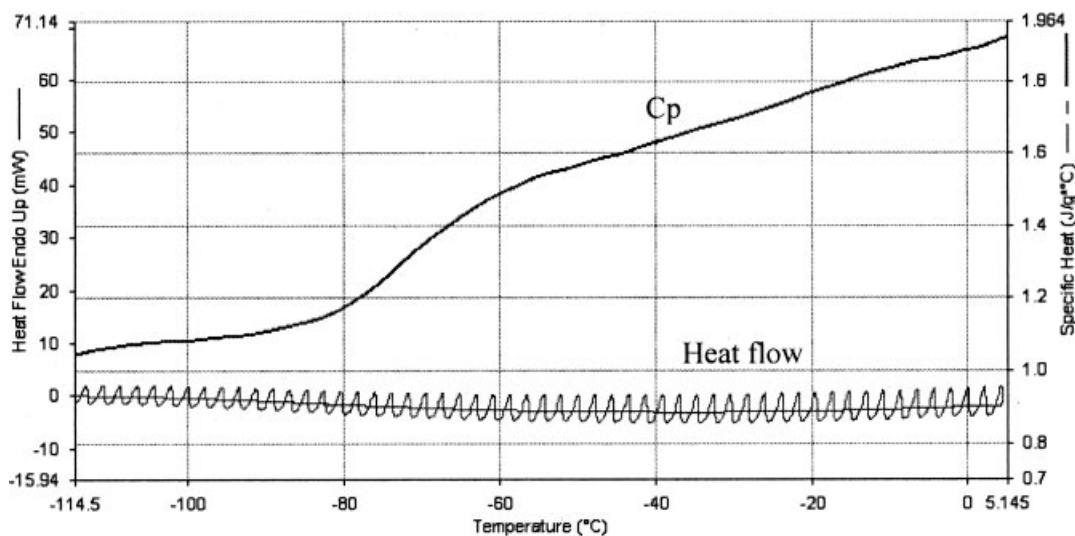


Figure 16 Step-scan DSC results of polybutadiene-PU elastomer.

Figure 9 illustrates the effect of different magnetic particle concentrations on the static compressive stress-strain properties of MREs. The stiffness of MREs increases with the concentration of magnetic particles. The compressive force range is defined as the ratio of the static stress of the on state to that of the off state (or MR effect). The compressive force values for the 50, 60, and 70% iron particle materials were approximately 70, 200, and 60%, respectively. The optimum concentration of iron particles was therefore about 60%. These data demonstrated that the MR effect was determined by the free space that the iron particles had in the polymeric matrix. The

higher concentration of iron particles increased the zero-field stiffness but decreased the dynamic force range increment.

Dynamic testing on MREs

The storage modulus was greatly increased by an applied external magnetic field (on state, Fig. 10). There was an approximate 60% (2 MPa) increment in the on-state storage modulus when comparing the oriented to nonoriented MREs. The MR effect (the increment of modulus between the activated/on-state and nonactivated/off-state MREs) of oriented

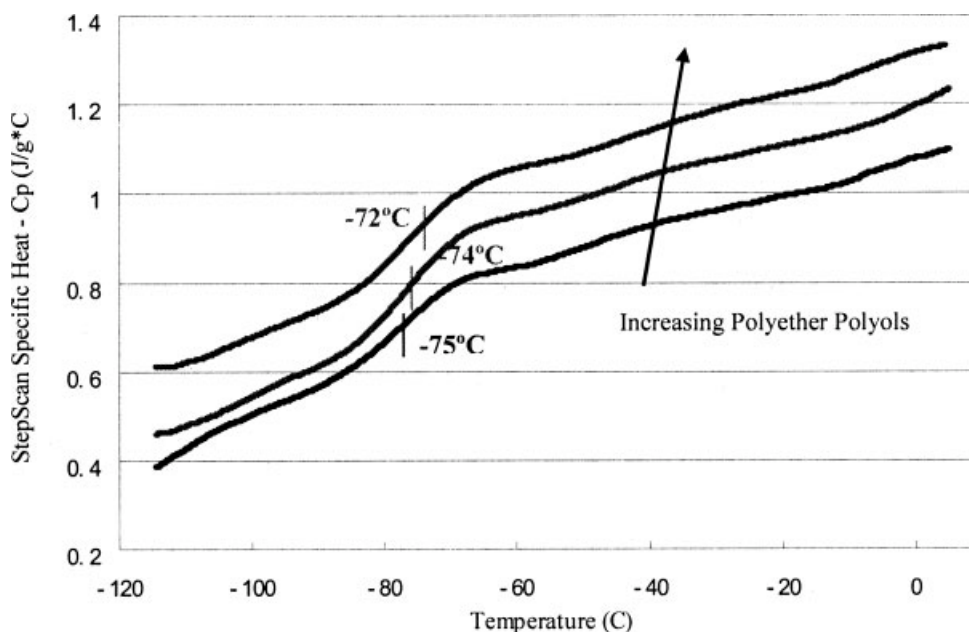


Figure 17 Step-scan DSC of polybutadiene-PU with different contents of polyether polyols.

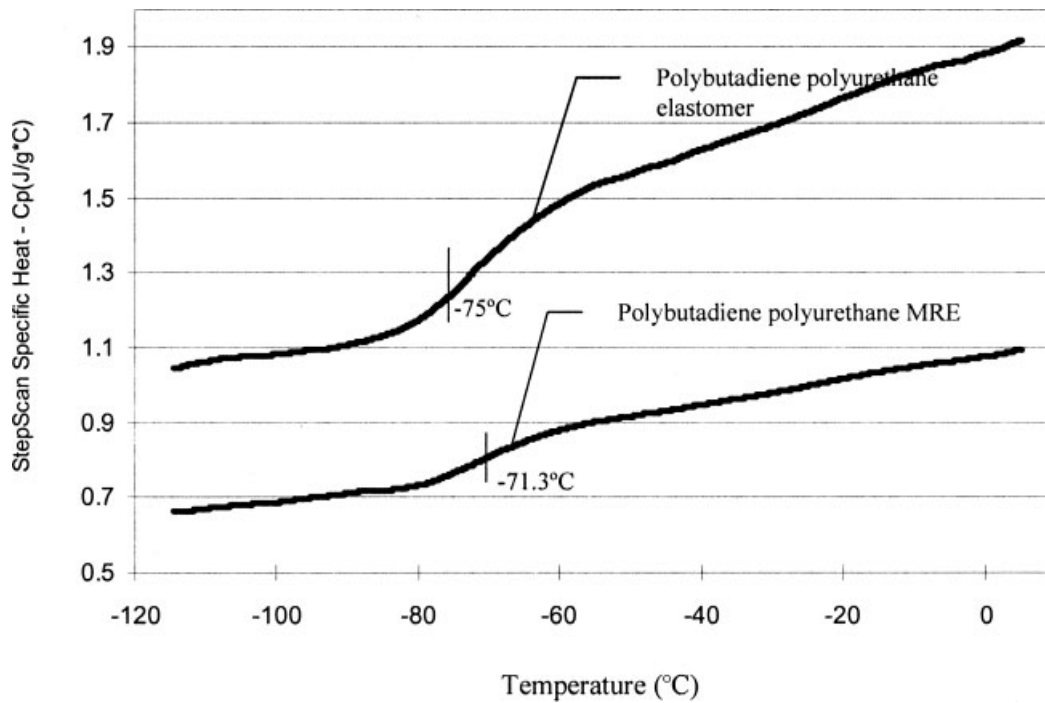


Figure 18 Step-scan data of polybutadiene-PU elastomer and its MRE.

MREs was also much larger than that of nonoriented MREs. The storage moduli of MREs with different iron particle weight percentages are given in Figure 11. The MRE with 60 wt % iron particles had the largest modulus increment compared to MREs with 50 and 70 wt % iron particles. This was consistent with the results of the static measurements. The damping or $\tan \delta$ properties were tested, and the results are provided in Figure 12. The nonactivated MRE with 60 wt % iron particles had good damping compared

to the activated state and MREs with 70 and 50 wt % iron particles.

The mechanical properties of PU elastomers with different polyether polyol contents were also tested (see Figs. 13, 14). Varying the concentration of components in the PU system can change the mechanical properties. The storage moduli and $\tan \delta$ increased with higher polyether polyol content. Adding more polyol to the polybutadiene-urethane system required more $-NCO$ functionality to maintain the

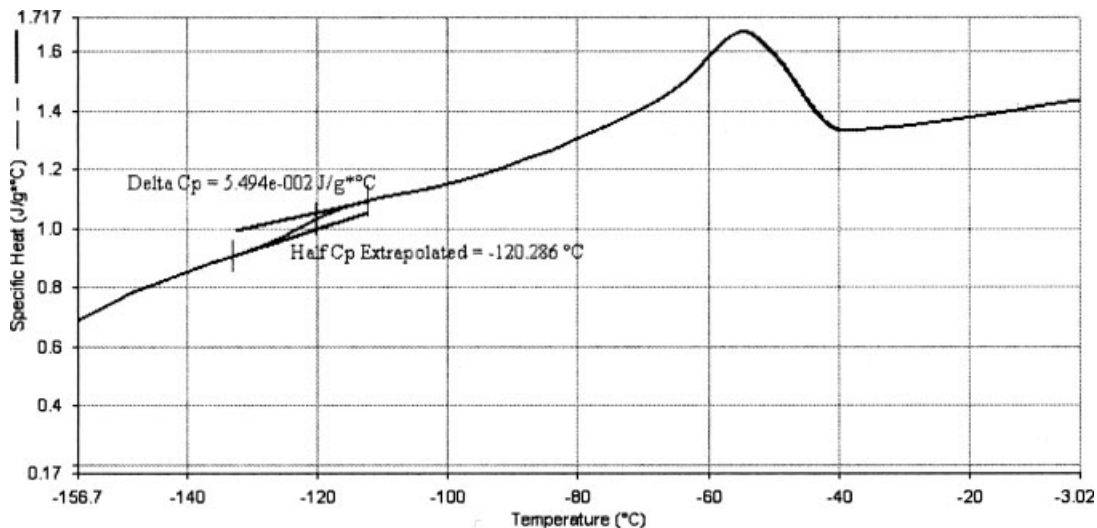


Figure 19 Step-scan DSC of the silicone elastomer.

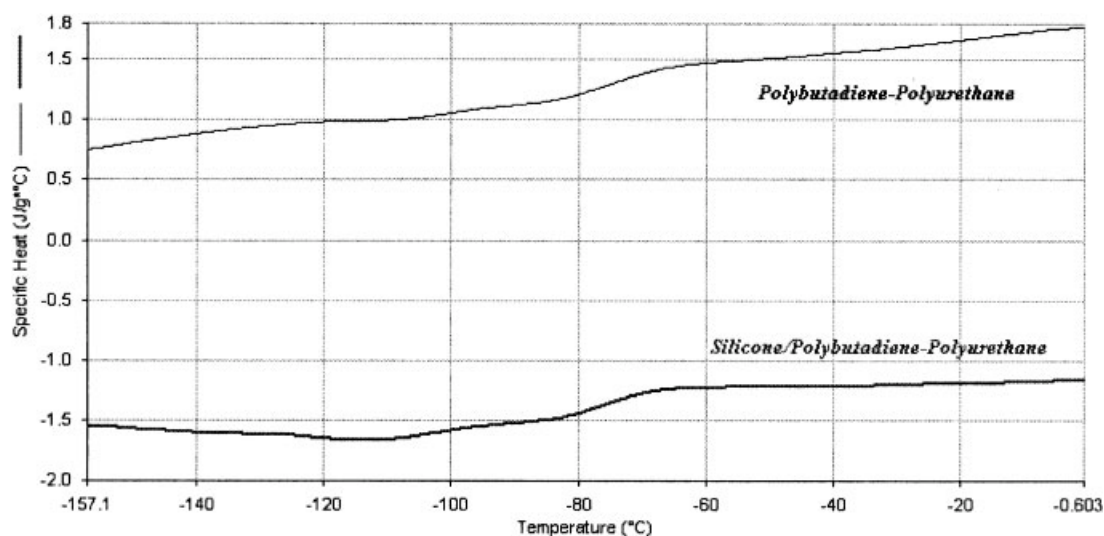


Figure 20 Step-scan DSC of the silicone/polybutadiene-PU blend.

equivalent molar reaction; therefore, the weight percentage of diisocyanate (PAPI 27) was increased. The concentration of the hard segment, which is mainly composed of diisocyanate, also increased, thus making the final PU stiffer.

Thermal characterization

The step-scan DSC results are shown in Figures 15–20. The cure reaction of polybutadiene PU had a wide range of temperatures, and the exothermal heat of the reaction was approximately 1.65 kJ/g (Fig. 15).

Figure 16 shows the IsoK baseline and C_p for the cured polybutadiene-PU elastomer. In the blend of polybutadiene and polyether polyol PU, the contents of polyether polyol range from 0 to 7.5 and 13.2 wt %. The C_p of polybutadiene PU and polybutadiene PUs with different percentages of polyether polyols are combined in Figure 17.

The addition of polyether polyol increases the glass-transition temperatures from -75 to -72°C , which is shown in Figures 16 and 17. The glass-transition temperature of the polybutadiene resin based PU is the same data as in the literature.¹⁵ As the concentration of polyether polyol increases, there is a shift to higher glass-transition temperatures. The

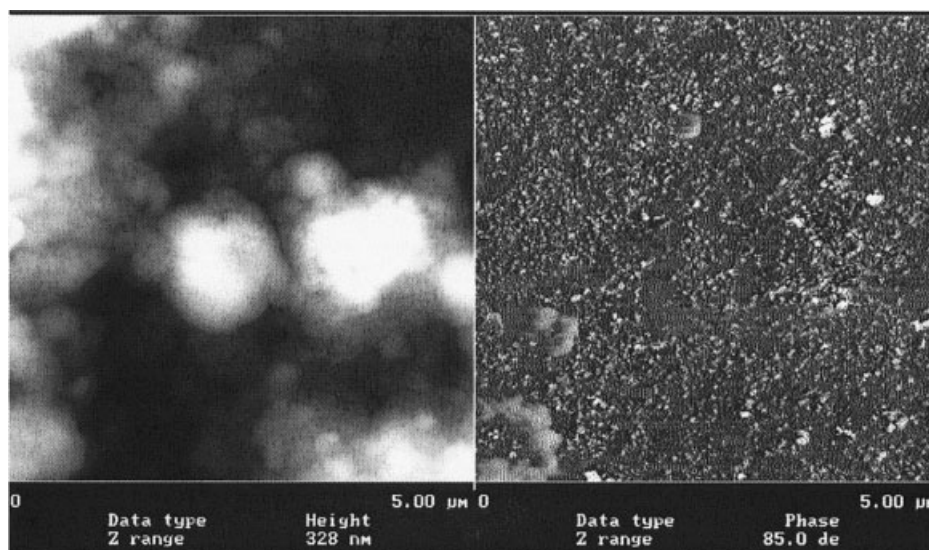


Figure 21 An AFM phase image of the polybutadiene-PU elastomer.

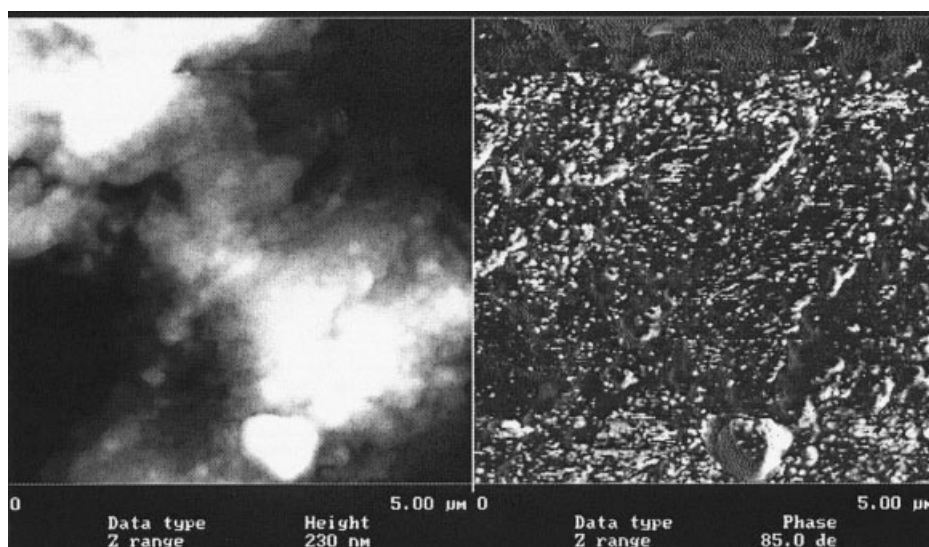


Figure 22 An AFM phase image of the polybutadiene/polyether polyol (5.3 wt %)-PU elastomer.

content of hard segments increases in the system with the addition of polyether polyol and thus increases the transition temperatures.¹⁶

The thermal properties of MRE were also investigated by step-scan DSC. A comparison of MREs and PU elastomers is provided in Figure 18. The inclusion of iron particles caused the glass transition to become narrower and higher, which may have been the result of interfacial interactions between the particle surface and the polymeric matrices.

The elastomer blend of silicone (10 wt %)/PU was also investigated using step-scan DSC. Data for the silicone elastomer, polybutadiene-PU elastomer, and their blend are presented in Figures 19 and 20, in which silicone shows a glass transition at -120.3°C .

Comparing the blend and polybutadiene-PU in Figure 20, the glass transition at around -75°C dominates in the blend. This demonstrates that the blend of silicone (10 wt %) and PU has good compatibility.

AFM analysis

In phase images obtained by t-AFM, a higher modulus material typically induces a higher phase offset and appears lighter as opposed to a softer phase that appears darker. Thus, for the imaged PUs, the microdomains appear lighter whereas darker regions correspond to the softer polyol phase.^{16,17}

Figure 21 shows the microphase of polybutadiene-PU. The existence of brighter areas demonstrated

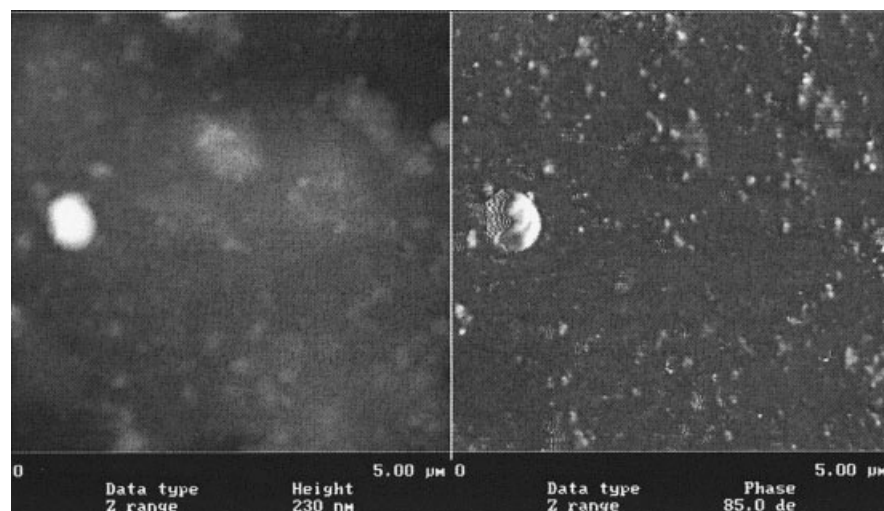


Figure 23 An AFM phase image of the polybutadiene-PU/silicone (10 wt %) elastomer.

that the hard and soft segments did not possess homogeneous features and demonstrated phase separation in the PU elastomer. The image of the polyol blend (polybutadiene and polyether polyols) PU in Figure 22 contains increased brighter areas that are reflected by the hard segments. The microstructure of the blend of silicone and polybutadiene PU (Fig. 23) shows that the less hard segments are dispersed in the soft phase of the polyol and silicone phase. The AFM images show the change of hard segments, which is consistent with the DMA and DSC results showing higher stiffness/modulus and a higher thermal transition temperature with an increasing concentration of hard segments.

The calorimeter precision of the DSC instrument and the temperature precision were better than $\pm 0.1\%$ and better than 0.01°C , respectively.

CONCLUSIONS

Novel MREs with high resistance to environmental degradation combined with excellent mechanical properties were developed in this investigation. A polybutadiene-PU-MRE with high stiffness was obtained at optimum iron particle concentrations (60 wt %) while maintaining good compressive force. In addition, the stiffness was significantly increased under a magnetic field for oriented samples. Silicone/polybutadiene-PU blend MREs were also developed with good compatibility and excellent mechanical and thermal performance.

A significant change in the structure of several MRE matrices was observed using AFM images. Morphological features such as interdomains of soft and hard segments of PU elastomers were identified using these images. The thermal and mechanical be-

havior was evaluated with DMA and DSC. The data demonstrated that the mechanical properties and thermal transition temperatures could be increased by increasing the hard segments. The glass-transition temperature of polybutadiene-PU was -75°C and silicone had a lower glass transition at -106°C .

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