Preparation and Mechanical Characteristics of Poly(methylaniline) Based Electrorheological Fluid

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ABSTRACT: Poly(methylaniline) (PMA) was chemically synthesized and its polymerization was confirmed via an FT-IR. Anhydrous electrorheological (ER) fluid consisting of semiconducting PMA particles dispersed in silicone oil was then prepared, and its mechanical properties such as tensile and compressive stresses were experimentally investigated using a squeeze mode type apparatus that was devised by integrating a motion controller and data acquisition system. The intensity of electric field, electrode velocity, and initial gap were chosen as important test parameters that influence the tensile and compressive characteristics of the ER fluid. The maximum tensile stresses were evaluated at each condition, and a microstructure was also investigated during compressive motion. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1924–1929, 2005

Key words: poly(methylaniline); electrorheological fluid; conducting polymers; tensile stress; compressive stress

INTRODUCTION

Electrorheological (ER) fluid belongs to a class of colloidal suspensions, which exhibit large reversible changes in their rheological behaviors when subjected to external electric fields[1] via ordering of the microstructure into particulate columns. It is regarded that the applied external field induces electric polarization within each particle relative to the suspending medium, and the resulting electrostatic interaction between the particles lead to the formation of aggregates aligned in the direction of the field.[2] One of the salient properties of ER fluid is that it has very fast response characteristics to the electric field. This inherent feature has triggered tremendous research activities in the development of various engineering applications. In general, the working behavior of actuators based on ER fluid is classified by three different modes: shear, flow, and squeeze.[3,4] It is normally assumed that one of two electrodes is free to translate or rotate to the other in the shear mode. Application devices operated under the shear mode include clutches and brakes.[5] In the flow mode, it is assumed that two electrodes are fixed, and the pressure drop can be controlled by the electric field. Thus, vibration dampers can be realized.[6,7] Unlike the former two modes, in the squeeze mode the electrode gap is varied and the ER fluid is squeezed by a normal force. Using this mode, vibration control damper can be devised.[8,9]

Nonetheless, the most important property of ER fluid under the shear mode is the field-dependent yield shear stress, which is normally measured by employing commercially available rotational electrorheometers. However, no commercial test device is available for the measurement of yield shear stress under the flow mode. Therefore, in most of the flow mode-type ER applications, the field-dependent yield shear stress measured from the shear mode electrorheometer has been adopted to determine principal design parameters. However, recent studies[10] reported that the field-dependent yield stress of the ER fluid obtained from the shear-mode rheometer is different from that obtained from the flow-mode test device. The difference, of course, depends upon the type of ER fluid, the range of shear rate, and the operating temperature. Recently, to explicitly demonstrate this, a flow mode test device that is very similar to an ER damper proposed by Kamath et al.[6] was derived, and the field-dependent yield shear stress was evaluated and compared between two modes under various temperatures and shear rates.[11] Note that under the flow mode, the field-dependent yield shear stress is normally obtained by calibrating the field-dependent pressure drop between two chambers.

On the other hand, the principal physical properties of ER fluid under the squeeze mode need to be evaluated in a different sense from the former two oper-

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ating modes. Since the electrode gap vertically varies in a relatively small distance range, ER fluid behaves just like a solid material in tension and compression loading. Therefore, the field-dependent tensile and compressive properties are normally measured under various loading conditions.[12]

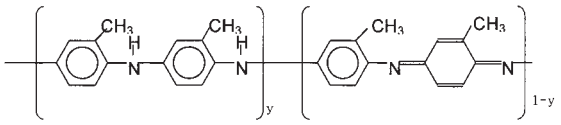
The main contribution of this work is to experimentally show the field-dependent tensile and compressive stresses of an anhydrous dry-base ER fluid composed of PMA particles and silicone oil. Recently, ER materials have been focused on conjugated polymer particles, because their application is particularly interesting due to the fact that such typical drawbacks of conducting polymers (moderate conductivity, powder form, and insolubility) become advantages for ER applications.[13,14] They further provide flexibility, such that their physical and chemical properties can be tailored to maximize the ER effect. Therefore, some semiconducting materials have been used as substrates for anhydrous ER suspensions.[15]

One of the most extensively studied materials in this category is polyaniline (PANI), which has been examined for ER behavior.[16] PANI in its emeraldine base form has advantages with respect to density, conductivity control, and thermal stability.[17,18] Among several polyaniline derivatives from different monomers such as methoxyaniline, ethoxyaniline, and ethylaniline, the PMA was found to show the best ER performances.[19] To undertake this, an experimental apparatus for the squeeze mode is constructed by integrating with a data acquisition system. The electric field strength, the electrode gap, and the initial gap are chosen as three important test conditions under the squeeze mode. In addition, a photomicrostructure is also taken during compressive motion to investigate the change of chain formations of the ER fluid particles.

EXPERIMENTAL

Materials and characterization

The PMA was synthesized from the chemical oxidation polymerization. An ammonium peroxysulfate solution in 1*M* HCl was dropped to a well-stirred reactor containing the monomer in 400 mL 1*M* HCl. During the synthesis, the mixture was stirred for 2 h and the temperature was kept at 0°C, and the pH of the product was then adjusted to 9.0 by adding either NaOH or HCl solution. The synthesized PMA was washed using distilled water to remove the initiator, unreacted monomer, and oligomers, and further washed with ethanol and cyclohexane to make the surface of the synthesized particles hydrophobic.[13] Finally, the synthesized PMA particles were dried to get rid of any trace of water. Characterization for the chemical structure of the synthesized PMA was conducted with FT-IR spectroscopy (Perkin–Elmer System, USA). The mean diameter and shape of the particles were observed using scanning electron microscopy (SEM, *S*-4200, Hitachi, Japan). The ER fluid was prepared by dispersing the synthesized PMA particle (20% by weight) in silicone oil having kinematic viscosity of 30 cS. All tests were undertaken in room temperature. The scheme of the chemical structure of the PMA is as follows:



Scheme 1

Experimental setup

Figure 1 shows an experimental setup for the measurement of tensile and compressive characteristics of the ER fluid under the squeeze mode. The dynamic motion for the movement of the electrode (upper part) is generated and controlled by a dc servomotor, and the speed is reduced at 1/10,000 by the speed reducer. The rotational motion is converted to the vertical motion via the ball screw. The moving velocity of the electrode is accurately controlled by the servo motor associated with the microcomputer, which has both analog to digital (A/D) and digital to analog (D/A) converters. Both A/D and D/A converts have 12 bits, and the program to control the servomotor is written in C^{++} language. The PID (Proportional-Integral-Derivative) controller is adopted to control the required motion and executed with a sampling frequency of 1200 Hz. The initial gap of the electrodes and the movement distance of the upper electrode are measured by linear variable differential transformer (LVDT), and these signals are fed back to the micro-

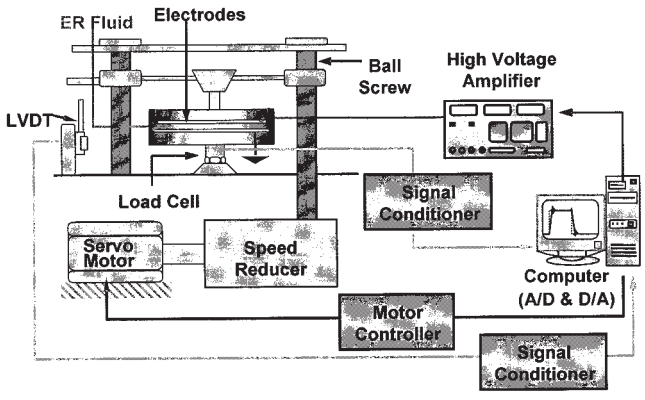


Figure 1 Experimental configuration for the squeeze mode test.

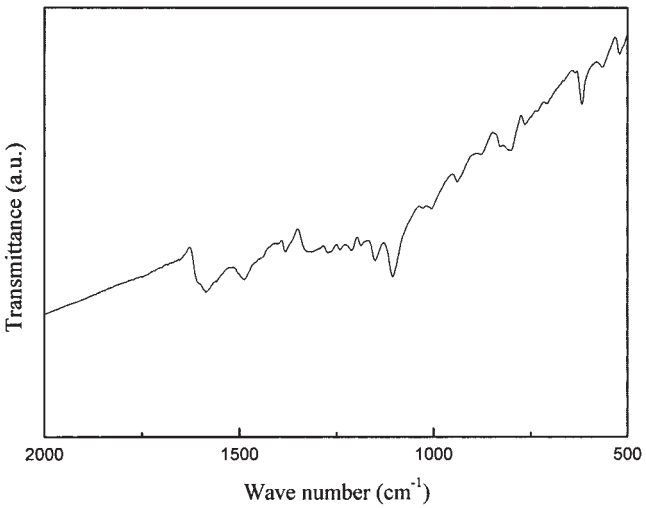


Figure 2 FT-IR spectrum of PMA.

computer through the signal conditioner to be controlled. It is noted that both upper and lower electrodes are made of stainless steel and the diameter is 30mm. The electric field is applied to the ER fluid domain via the high voltage amplifier, which has a gain of 1000. The mechanical properties in tensile and compressive tests are measured by applying the DC electric field strength, which is obtained by considering voltage, electrode gap, time, and moving velocity of the electrode. On the other hand, the load (force) variations of the ER fluid with respect to the field intensity and electrode velocity are measured by the load cell and stored in the microcomputer. The tensile or compressive stress is obtained by dividing the force measured from the load cell to the sectional area of the electrode.

RESULTS AND DISCUSSION

Material characterization

Figure 2 represents the characteristic peaks of the FT-IR diagram for the PMA. The peak at wave number 1590 cm^{-1} is from the C═C stretching (quinoid), that at 1490–1500 cm^{-1} is from C═C stretching (benzoid), and the peaks 1375 and 1450 cm^{-1} are from the methyl group.[16] Figure 3 shows the SEM image of the PMA particle synthesized. The particle shape deviates from the sphere and some agglomerates are observed. The average particle size is assumed to be about 3 μm.

Tensile stress characterization

Figure 4 presents tensile characteristics of the PMA particle based ER fluid at various DC electric fields. The test has been undertaken by moving the electrode (upper) from the initial gap of 1.0mm to 1.2mm for 5 minutes. Thus, the moving velocity of the electrode is 0.04 mm/min. The maximum tensile stress is increased as the electric field increases, as expected.[20] The maximum tensile stress is increased from 0.3 kPa at 0.5 kV/mm to 11.8 kPa at 3 kV/mm. It is also observed from Figure 4a that the maximum tensile

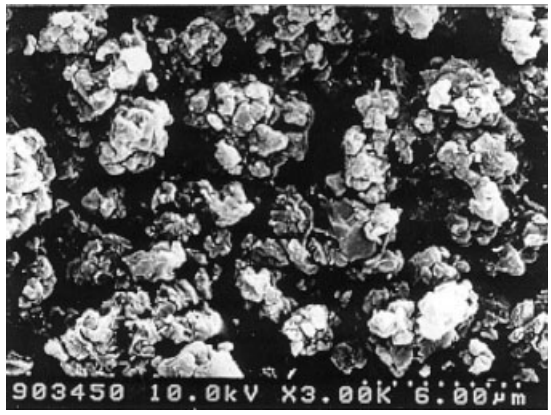
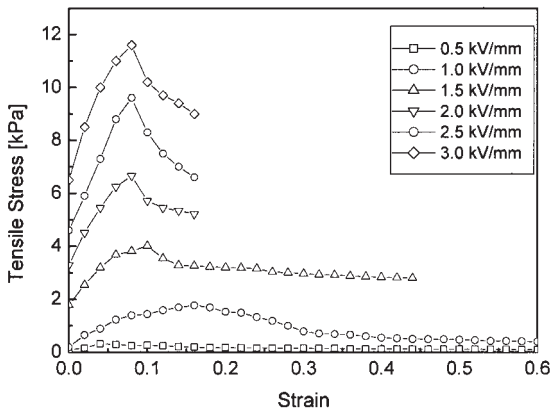
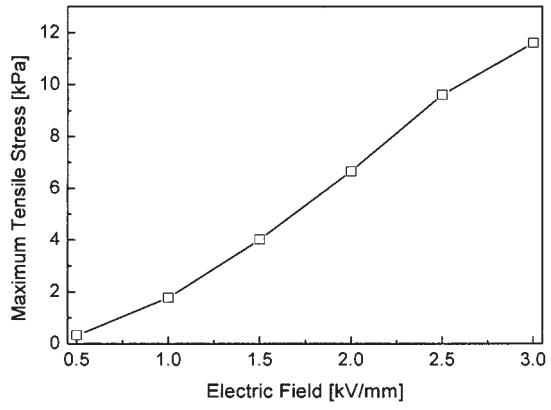


Figure 3 SEM morphology of synthesized PMA particle.

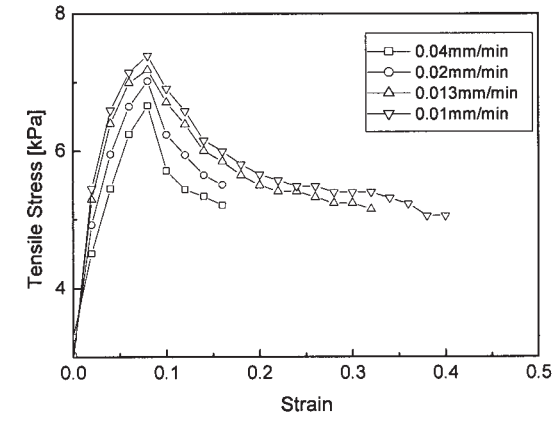


(a) Tensile stress vs. strain

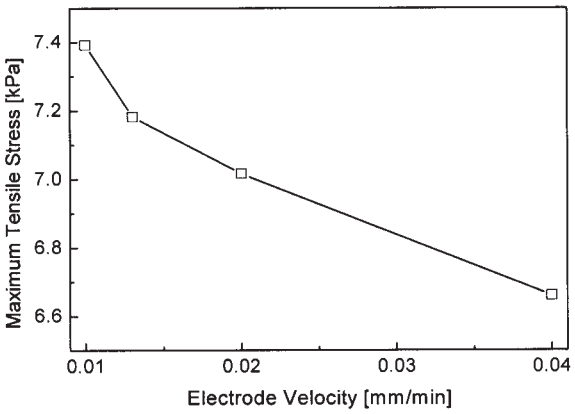


(b) Maximum tensile stress vs. electric field

Figure 4 Tensile characteristics with respect to the electric field: (a) Tensile stress vs. strain; (b) Maximum tensile stress vs. electric field.



(a) Tensile stress vs. strain



(b) Maximum tensile stress vs. electrode velocity

Figure 5 Tensile characteristics with respect to the electrode velocity: (a) Tensile stress vs. strain; (b) Maximum tensile stress vs. electrode velocity.

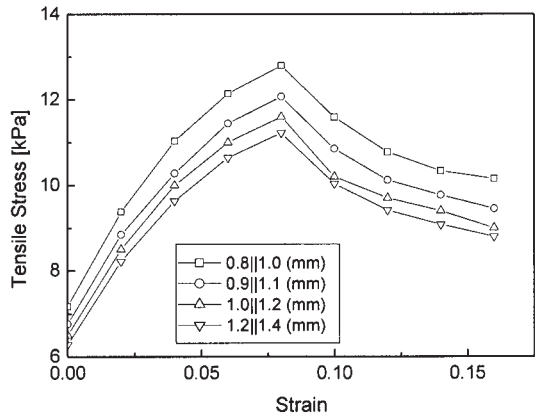
stress always occurs at the strain of 0.07 after 1.5 kV/mm. This implies that the arrangement of the particle clusters between the two electrodes has been well tensioned during the motion. The origin of the maximum stress in Figure 4a is regarded to be related with the basic ER mechanism in which ER fluids in general show a reversible transition from a fluid-like state to a solid-like state under an applied electric field, thus causing a yield stress following a shear stress increase of the fluid above the yield point.[21] Polarized particles behave as electric dipoles, which attract each other to form chains, and the formation of particle chains in the direction of the applied electric field produces the observed rheological changes with enhanced stress. As we increase the tensile stress, at the maximum stress, the two forces of attractive electrostatic interactions by polarized particles and the rupturing force by the tensile stress will be balanced at the critical strain or strain at break. Above this critical strain, even though the rupturing force by the tensile stress becomes larger than the attractive force, the broken structures tend to reform the chains by the applied electric field, depending on the magnitude of the applied tensile stress and particle–particle interaction in the fibrils.[22,23] In addition, this indicates that the contacting area between the ER fluid and the electrodes is well maintained without variation (decrement or increment).

To investigate the effect of the moving velocity of the electrode to the tensile stress of the ER fluid, the electric field of 2.0 kV/mm is applied, while the moving velocity is changed from 0.01 mm/min to 0.04 mm/min; the gap between the upper and lower electrodes is initially set by 1.0 mm and moved to 1.2 mm for all cases. Figure 5 presents tensile characteristics of the PMA particle based ER fluid with respect to the moving velocity of the upper electrode. As expected, the maximum tensile stress is substantially decreased as the velocity is increased. This is, of course, due to the fact that the particle clusters of the ER fluid are more quickly elongated and broken as the velocity is increased.

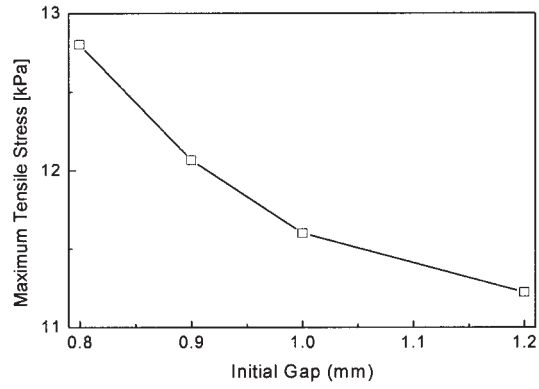
Besides the intensity of the electric field and the moving velocity of the electrode, there is another parameter that influences tensile characteristics of the ER fluid.[24] Figure 6 presents the effect of the initial gap to the tensile stress. For this test, the electric field is fixed at 3.0 kV/mm and the electrode velocity is also maintained to be constant at 0.04 mm/min. The electrode gap initially adjusted at 0.8 mm, 0.9 mm, 1.0 mm, and 1.2 mm moves to 1.0 mm, 1.1 mm, 1.2 mm, and 1.4 mm, respectively. It is noted that the legend in Figure 6 indicates the change from 0.8 mm to 1.0 mm. It is clearly observed that the maximum tensile stress is sharply decreased as the initial gap increases. This is due to the weaker microstructure of the particle chain normally formed for the bigger gaps. This result directly indicates that the initial length of the chain cluster is an important factor to control tensile properties of the ER fluid. It can also be noted that the tensile, compression, and oscillatory squeeze tests using carbonaceous particle based ER fluid were carried out in two different ways, such that either the fluid was placed between the electrodes or the electrodes were immersed inside the ER fluid by Vieira et al.[12] The construction of the load cell and a change of the sample during experiments are especially noteworthy.

Compressive stress characterization

As a second set of experimental tests, compressive characteristics of the PMA particle based ER fluid are investigated. Figure 7 presents the variation of the compressive stress at various DC electric fields. It is observed that the compressive stress is increased with the increment of the electric field. It is also seen that the stress is continuously increased with respect to the strain.



(a) Tensile stress vs. strain



(b) Maximum tensile stress vs. initial gap

Figure 6 Characteristics with respect to the initial gap: (a) Tensile stress vs. strain; (b) Maximum tensile stress vs. initial gap.

To understand the mechanism why the stress is continuously increased, a photomicrostructure is taken during the motion and presented in Figure 8.

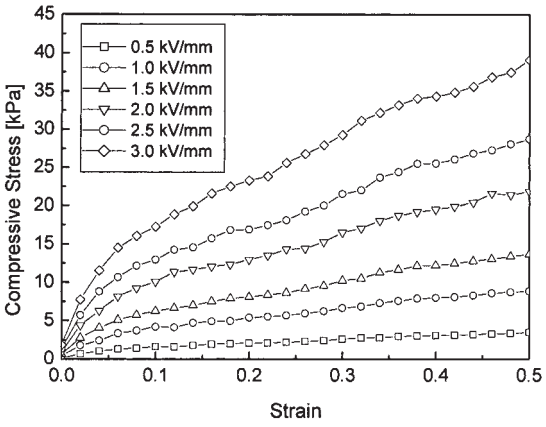
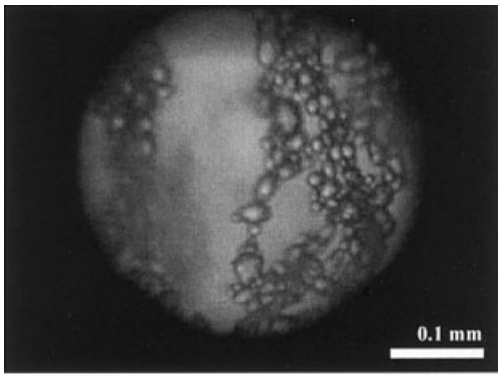
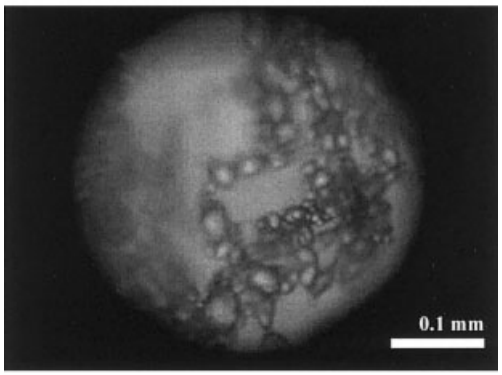


Figure 7 Compressive characteristics with respect to the electric field.



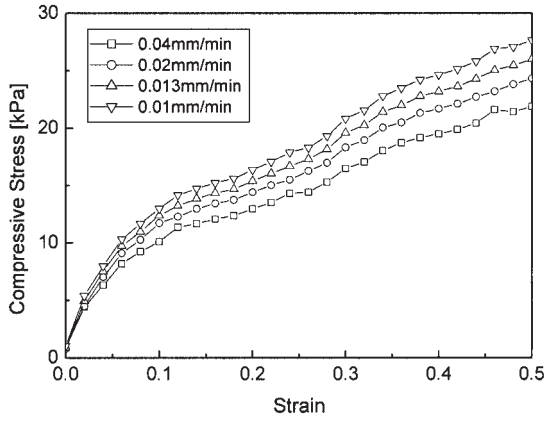
(a) Electrode gap = 1.0mm



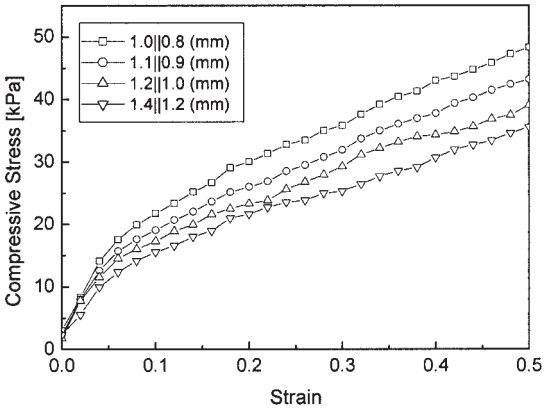
(b) Electrode gap = 0.8mm

Figure 8 Photomicrostructure of the ER fluid during compressive behavior; electrode gap = (a) 1.0mm; (b) 0.8mm.

The photomicrostructure shown in Figure 8a was taken by applying the electric field of 2 kV/mm to the electrodes in which the gap was initially fixed by 1.0 mm. The gap was then continuously decreased with the electrode velocity of 0.4 mm/min, and the photomicrostructure given in Figure 8b was taken when the gap became 0.8mm by applying the electric field of 2 kV/mm. It is clearly observed that the particle clusters (chain) have been compressed by decreasing the electrode gap from 1.0 mm to 0.8 mm. Thus, the resistance to the compressive load becomes stronger, yielding to the higher compressive stress. It may be expected that if the electrode gap is continuously decreased, the original cluster will be broken, and then many small-length clusters will be newly reformed. It is also noticed from Figure 4a and Figure 7 that the PMA particle based ER fluid is more resistant to compressive stress than to tensile at the same level of the electric field. The same characteristic has been ob-



(a) Different velocity



(b) Different initial gap

Figure 9 Compressive characteristics with respect to the electrode velocity and the initial gap: (a) Different velocity; (b) Different initial gap.

served for carbonaceous particle based ER fluid.[12] Similar to the results from the tensile test, the compressive stress is decreased as the moving velocity of the electrode is increased, as shown in Figure 9a. This result has been obtained by applying the electric field of 2.0 kV/mm and changing the gap from 1.2 mm to 1.0 mm. It is also investigated that the larger initial gap leads to lower compressive stress, as shown in Figure 9b. This result is achieved by applying the electric field of 3.0 kV/mm and maintaining the electrode velocity of 0.04 mm/min.

CONCLUSIONS

The semiconducting PMA particle was initially synthesized, and then tensile and compressive characteristics of PMA based ER fluid have been experimentally investigated under the squeeze mode. To achieve this, a squeeze mode type apparatus was devised by integrating with the data acquisition system. Three important parameters that influence the tensile and compressive characteristics of the ER fluid—the intensity of the electric field, electrode velocity, and initial gap—are chosen. It has been evaluated that both tensile and compressive stresses are increased as the electric field increases. It has been also observed that both stresses are decreased by increasing the electrode velocity and initial gap. In addition, the proposed ER fluid exhibits more resistance to compressive than to tensile stress under the same testing conditions. The experimental results presented in this work can be usefully exploited in designing ER application devices operated under the squeeze mode.

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