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ABSTRACT

The recent REACH regulations require the elimination of bisphenol-A and titanium dioxide from commercially available boron-based polymers. This has led to changes in some of the mechanical characteristics, which strongly influence the properties of magnetoactive borosilicate polymers. This work delivers results on the electrical properties and discusses some implications for future research using bisphenol-A and titanium-dioxide-free substitutes.

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INTRODUCTION

When combined with carbonyl iron particles, borosilicate polymers exhibit extraordinary magneto-mechanical and magneto-electrical characteristics similar to, but greatly exceeding, those of conventional viscoelastic polydimethylsiloxane (PDMS)-based magnetoactive polymers (MAPs). Such magnetoactive borosilicate polymers (MBPs) have been documented elsewhere (Guo *et al.*, 2016; Prem *et al.*, 2020; Monkman *et al.*, 2020) but usually contain both bisphenol-A and titanium dioxide. New commercially available materials demonstrate similar viscoelastic-plastic properties (Bartsch *et al.*, 2023) but are by no means identical.

All MBPs exhibit interfacial magnetocapacitance that is simultaneously accompanied by a drastic reduction in electrical resistance (Monkman *et al.*, 2022a). This work considers the electrical characteristics of bisphenol-A-free MBP.

BASE MATERIAL

Boron has three valence electrons and there are various possible configurations for a borosilicate polymer. One variation is shown in Fig. 1 (Schirmer *et al.*, 2021).

Until 2021, commercially available borosilicate compounds contained small amounts of bisphenol-A (Fig. 2), which is now considered toxic and, under EU and US law, withdrawn from domestic use (Gassman, 2022).

Although boron itself is not a problem (BfR, 2022), materials containing bisphenol-A must be substituted (Gassman, 2022). The compounds used in this work are commercially available and contain neither bisphenol-A nor titanium dioxide and only 50 mg/kg boron (up to 1200 mg/kg is permitted) (Wang and Zheng, 2019). Details concerning the chemistry have been published elsewhere and will not be discussed further here (Schirmer *et al.*, 2021).

FABRICATION

Boron silicate polymers can be easily mixed with soft or hard magnetic materials. However, to obtain consistent results, it is necessary to attain a high degree of homogeneity. For this, a pharmaceutical ointment roll mill (for example, exact 50 or similar) may be used.

Figure 3 shows the results of 2, 5, 10, and 20 kneading passes using 5 wt. % carbonyl iron powder (CIP) through a roll mill.

By 20 passes through the roll mill, the process is effectively complete, and a good degree of homogeneity is reached.

MECHANICAL CHARACTERISTICS

One of the most important mechanical attributes is rheopexy (shear hardening). Consequently, simpler alternatives, such as plasticine, are not suitable, and rheoplectic bisphenol-A-free borosilicates are now available (Wang and Zheng, 2019).

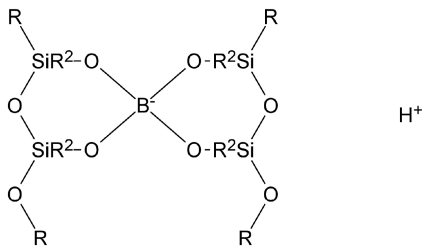


FIG. 1. Borosilicate polymer.

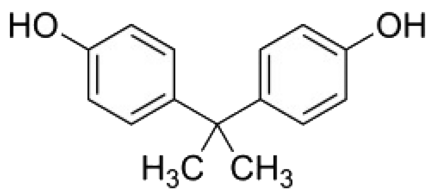


FIG. 2. Bisphenol-A.

Guo and researchers intensively measured both static and dynamic mechanical properties of MBP (probably containing bisphenol-A) (Guo *et al.*, 2016).

For comparison purposes, examples of the storage and loss moduli of the borosilicate polymers used containing ~60% CIP are shown without magnetic field [Fig. 4(a)] and subjected to a 34 mT magnetic flux density [Fig. 4(b)] as measured on a rheometer (TA-Instruments).

More detailed mechanical properties of bisphenol-A-free versions of MBP, including creep and recovery characteristics, have recently been researched by Bartsch and co-workers (Bartsch *et al.*, 2023) and will not be discussed further here.

ELECTRICAL CHARACTERISTICS

As a result of increasing particle alignment in a magnetic field, the distance between the electrically conductive magnetic particles

reduces, which leads to an increase in electrical capacitance (interfacial magnetocapacitance). A two-electrode configuration has an equivalent circuit as shown in Fig. 5.

The test device used comprised two 40 mm diameter electrically conducting discs held 1.6 mm apart by means of a 37.5 mm internal diameter electrically insulating spacer. The complete volume between the electrodes was filled with sample material.

To calculate the expected capacitance, the traditional expression (1) may be employed,

$$C = \epsilon_0 \epsilon_r \frac{A}{d}, \quad (1)$$

where the area A depends on the radius r in question according to the following equation:

$$A = \int_a^b 2\pi r dr. \quad (2)$$

For the sample itself, $a = 0$ and $b = 18.75$ mm, whereas for the spacer, $a = 18.75$ mm and $b = 20$ mm. This gives a quiescent capacitance (without sample) of 6.1 pF plus the contribution from the ABS spacer of about 3.5 pF, given a relative permittivity of around 3, which is, in general, in agreement with values in the literature (Kuzmanić *et al.*, 2023). However, measured values were slightly higher as given in Table I.

Taking the difference between the capacitance of the sample as CIP and that of air, edge effects and any contribution from measuring leads may be eliminated. Thus, the 4 pF difference results in a relative permittivity of pure borosilicate of 3.7, which is in line with previous findings (Monkman *et al.*, 2020).

As soon as the device was placed in a magnetic field, rapid changes in capacitance and resistance were observed. These changes were recorded at a frequency of 1 kHz using a Hameg 8118 LCR bridge programmed in REXX script.

In addition to magnetically induced increases in capacitance, the electrical resistance simultaneously reduces. In the case of an MAP, these changes take place rapidly and, due to the inherent elasticity of the polymer matrix, reverse equally quickly on the removal of the magnetic field (Monkman *et al.*, 2020).

However, in the case of MBP, the viscoelastic-plastic nature of the matrix impedes rapid movement (rheopexy). Consequently,

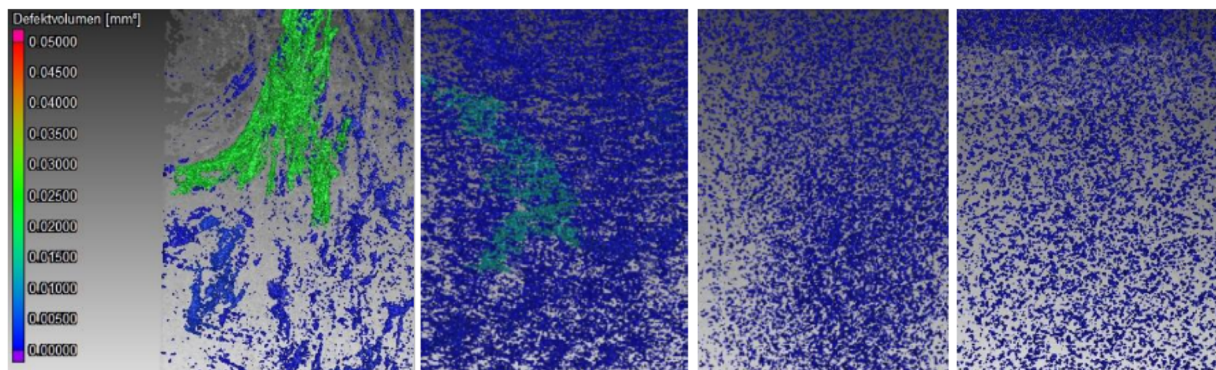
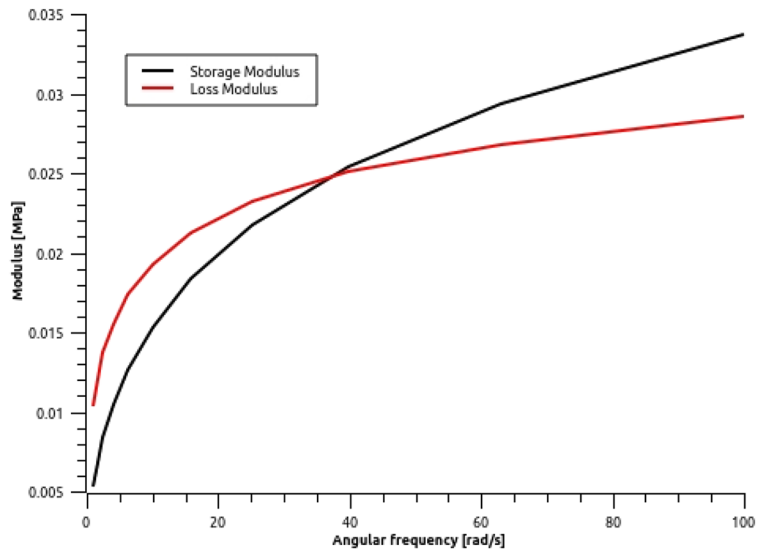
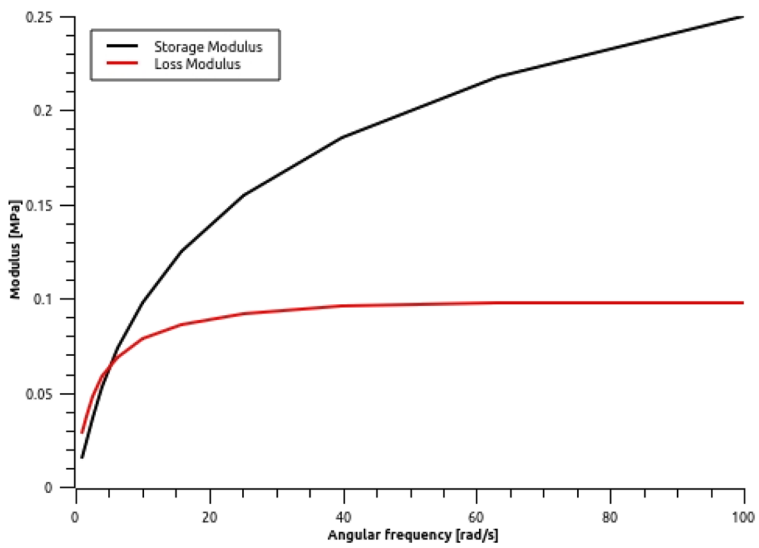


FIG. 3. (a) 2, (b) 5, (c) 10, and (d) 20 kneading passes.



a



b

FIG. 4. (a) Elastic moduli 60% CIP without magnetic field. (b) Elastic moduli 60% CIP with 34 mT flux density.

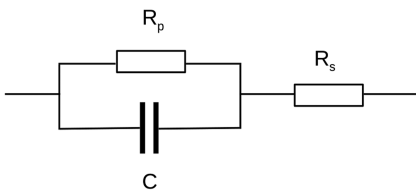


FIG. 5. Equivalent electrical circuit.

TABLE I. Capacitance measurements for MBP samples.

Sample	Capacitance (pF)
Air	14
0% CIP	18
30% CIP	21
45% CIP	25
60% CIP	31

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the final capacitance and resistance are functions of wt. % CIP content and time. Again, this is different for magnetorheological fluids (MRFs) where the almost unrestricted movement of the particles is possible (Horváth *et al.*, 2022).

As described elsewhere (Monkman *et al.*, 2020) and shown in Fig. 6, permanent magnet pairs generating a magnetic flux density of 115 mT were used to obtain the changes in electrical capacitance and resistance as shown in Figs. 7–10.

In each measurement, the magnetic field was removed after a certain time (~10 min). This is clear to see at the transition point visible on all curves.

What is interesting is the increase in capacitance and simultaneous reduction in resistance following the application of the magnetic field [Fig. 8(a)], whereas for the series CR, both C and R rise and fall with one another [Fig. 8(b)].

Apart from the case with the lowest (30%) CIP content shown in Fig. 7(b), all CR cases tend to return toward the *status nascendi* following the removal of the magnetic field.

This is consistent with previous results carried out on MBP containing bisphenol-A and titanium dioxide (Monkman *et al.*, 2020).

On application of the magnetic field, 60% of samples show a moderate increase in capacitance and a simultaneous decrease in resistance [Fig. 9(a)]. Clearly, the most significant changes are those derived from the parallel CR model.

However, as the parallel circuit resistance reduces, as shown in Fig. 9(a), the series circuit resistance increases, as shown in Fig. 9(b).

Increasing the magnetic field to 420 mT provides a much greater effect as can be seen for the parallel CR values shown in Figs. 10(a)–10(c).

In all the parallel curves, the initial drop in resistance is not so clearly visible because the initial electrical resistance is in the GΩ to TΩ range. It is also impossible to apply a step magnetic field with permanent magnets in such a short time to make such changes observable. The situation is not improved with electromagnets as an inductance does not allow rapid step-like changes in flux density (which is proportional to current flow I),

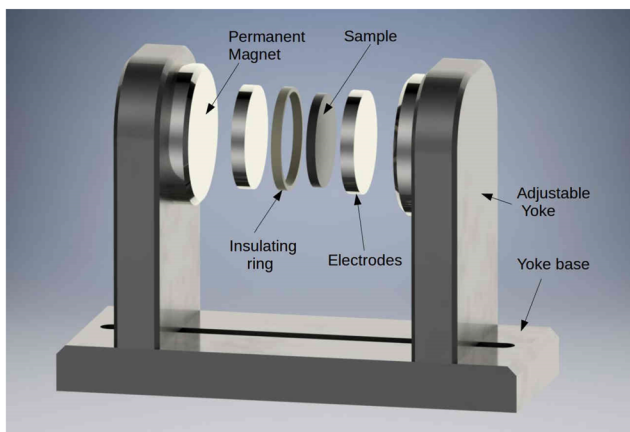


FIG. 6. Permanent magnet field generation (with an exploded view of sample and electrodes).

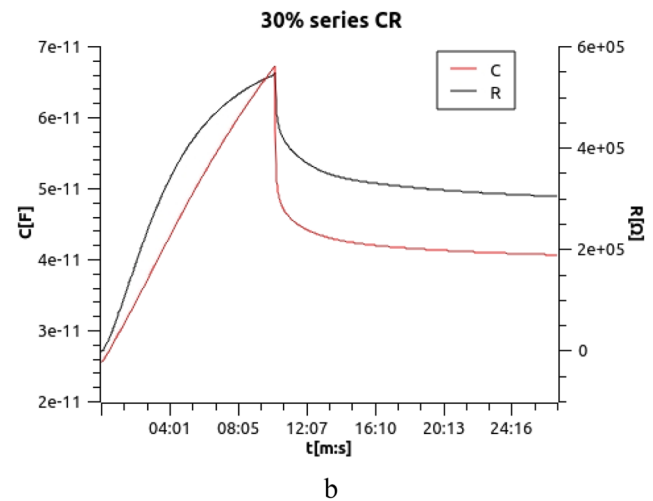
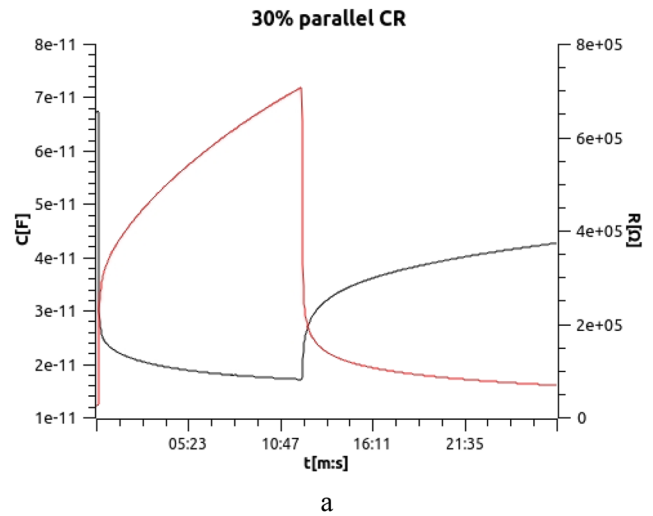


FIG. 7. (a) Parallel C and R versus t for 30% CIP at 115 m. (b) Series C and R versus t for 30% CIP at 115 mT.

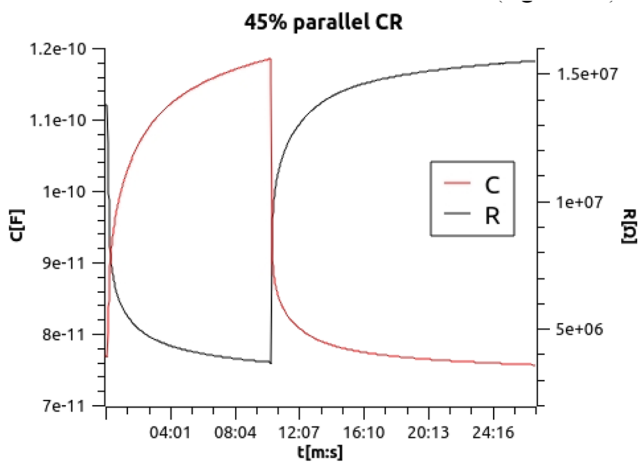
$$I_{rise} = I_0 \left(1 - e^{-\frac{t}{R}} \right), \tag{3}$$

$$I_{fall} = I_0 e^{-\frac{t}{R}}. \tag{4}$$

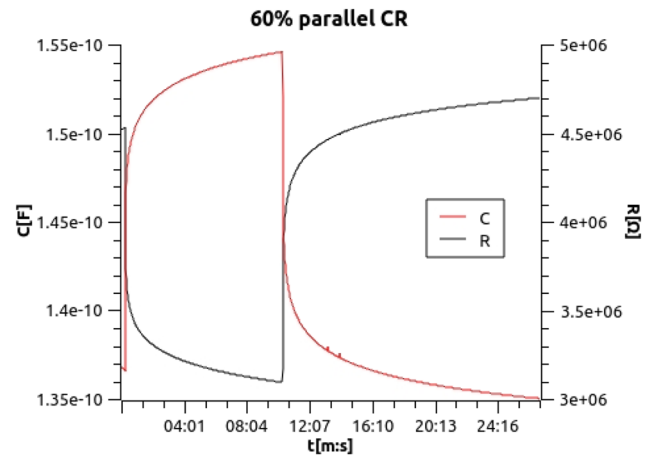
In principle, the rise and fall time constants of such a circuit are given by the quotient L/R in (3) and (4), respectively.

The greater the required magnetic field, the larger the coil inductance L must be. This is proportional to the square of the number of windings, whereas the electrical resistance is directly proportional to the wire length. Consequently, the L/R time constant increases with the coil size. The usual way to overcome this problem is by using a much higher voltage with an additional forcing resistance to reduce the time constant in (3).

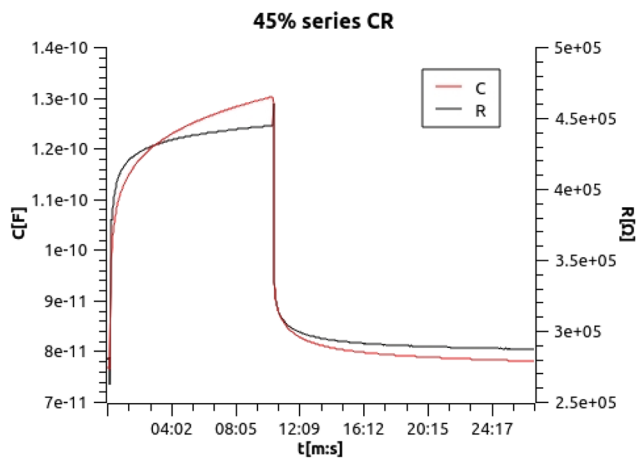
However, a current limit must also be included to prevent the maximum permitted inductor current from being exceeded. Switch-off may be further expedited by introducing a diode and flywheel



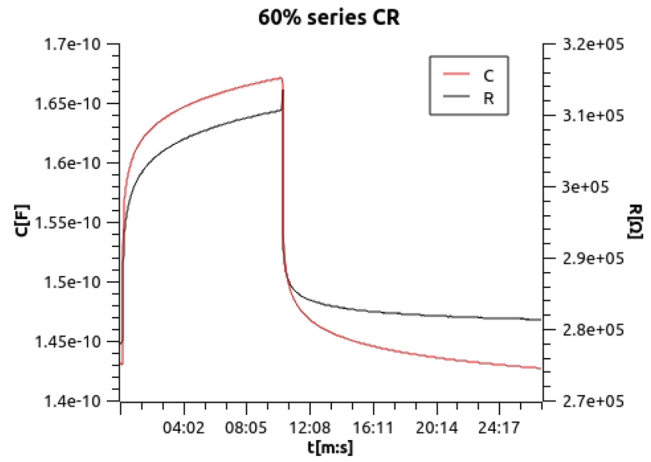
a



a



b



b

FIG. 8. (a) Parallel C and R versus t for 45% CIP at 115 mT. (b) Series C and R versus t for 45% CIP at 115 mT.

FIG. 9. (a) Parallel C and R versus t for 60% CIP at 115 mT. (b) Series C and R versus t for 60% CIP at 115 mT.

resistance in the discharge path to reduce the time constant given in (4). Such systems are common in stepping motor circuits (Acarnley, 1984); however, these are optimistic for switching times under 1 ms in cases where large magnetic fields are concerned (Rao and Monkman, 2023).

Unfortunately, due to the limitations of the instrument used (Hameg 8118) and the time needed for the measuring instrument to react, the curves do not show the initial resistance of the sample.

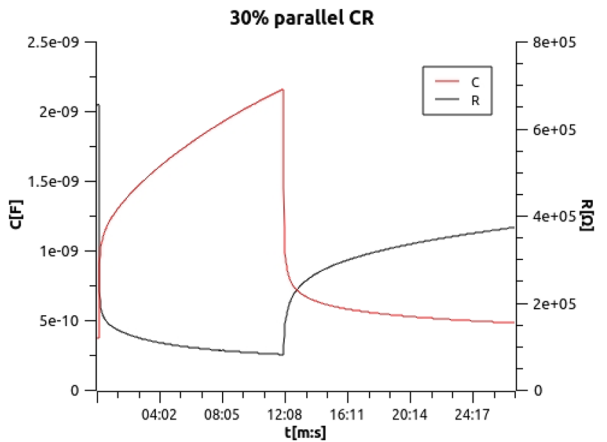
Measurements were conducted on a 4 mm length of 60% MBP placed in an insulating tube of internal diameter 6 mm. A 1000 V Insulation tester (UNI-T UT505A) revealed a resistance >20 G Ω as shown in Fig. 11(a). More precise measurements using a picoammeter (Keithley 414S) and 20 V source revealed a current of 0.01×10^{-9} A, which equates to a resistance of 2 T Ω .

Theoretically, given such reductions in electrical DC resistance, it should be possible to switch high DC voltages magnetically in a similar way to which GaAs can switch high voltages photonically (Monkman *et al.*, 2022b).

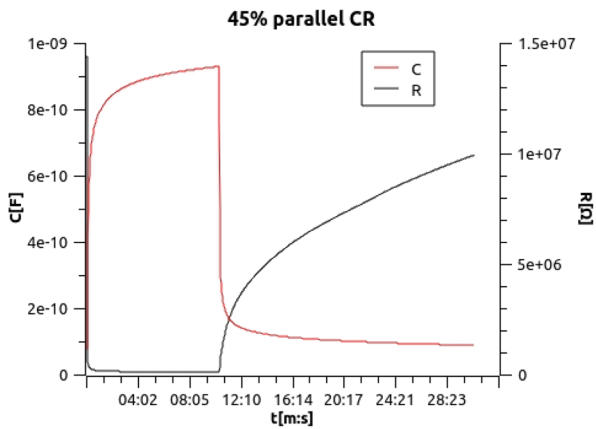
Figure 11(b) shows the result immediately following the application of a magnetic field of around 300 mT. It can be observed from Fig. 11(b) that the resistance rapidly falls to around 90 k Ω .

It is not suggested that this should form a replacement for high-voltage semiconductors, but rather proof of the effects of a magnetic field on MBP at high DC voltages.

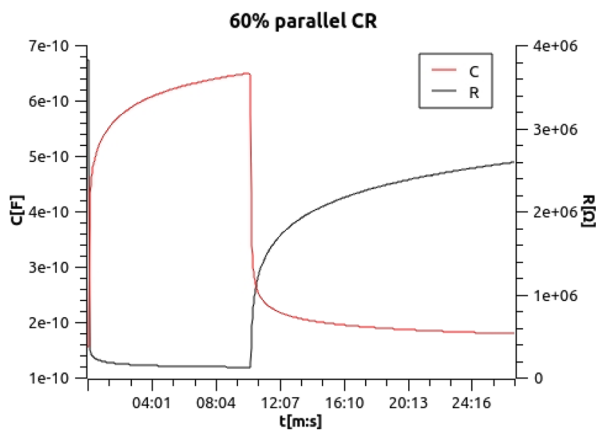
The experiment was repeated with a sample length of ~ 10 mm of 60% MBP and placed in the same insulating tube, with a potential of 5 kV applied to the terminals.



a



b



c

FIG. 10. (a) Parallel C and R versus t for 30% CIP at 420 mT. (b) Parallel C and R versus t for 45% CIP at 420 mT. (c) Parallel C and R versus t for 60% CIP at 420 mT.



a



b

FIG. 11. (a) 1000 V insulation test without magnetic field. (b) Insulation test after magnetic field application.

On the application of a magnetic field, the particles orientate along the flux lines in a similar way to what they do in MRF (Rao and Monkman, 2023), thus creating a temporary conductive path. In the case of an MAP, this is not possible because the elasticity of the polymer matrix prevents the required displacement for adequate electrical contact between particles. Attempts have been made in this respect with predictably negative results (Stepanov *et al.*, 2023). This demonstrates one of the main differences between MAP and MBP.

CONCLUSIONS

Although the mechanical properties of bisphenol-A free differ somewhat from the original versions containing bisphenol-A, the electrical characteristics are very similar allowing almost direct substitution. The ability magnetically to switch to a low resistance mode makes the switching of high voltages, albeit at low currents, possible. The extremely high quiescent electrical resistance allows for very low leakage currents.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Xuyan Loo: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Writing – original draft (equal). **Bhavana Nagaraju:** Data curation (equal); Investigation (equal); Software (equal); Writing – original draft (equal). **Sai Pathivada:** Data curation (equal); Formal analysis (equal); Investigation (equal); Software (equal); Writing – original draft (equal). **Alexander Bartsch:** Formal analysis (equal); Investigation (equal); Project administration (equal); Resources (equal); Visualization (equal). **Thomas Schratzenstaller:** Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Robert Sattler:** Formal analysis (equal); Investigation (equal); Project administration (equal); Resources (equal); Visualization (equal). **Gareth J. Monkman:** Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Original data is available from the Mechatronics Research Unit at the OTH-Regensburg.

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