

PERPUSTAKAAN UMP



0000113723

Electrical Breakdown and Mechanical Ageing in Dielectric Elastomers

Shamsul Bin Zakaria

January, 2016

Supervisor: Anne Ladegaard Skov

PhD Thesis

Danish Polymer Centre, Department of Chemical and Biochemical Engineering,
Technical University of Denmark, Kongens Lyngby

CONTENTS

PREFACE	i
CONTENTS	iii
ABSTRACT	vii
RESUME PÅ DANSK	ix
1 INTRODUCTION	10
1.1 <i>THESIS OBJECTIVES AND OUTLINES</i>	10
1.2 <i>DIELECTRIC ELASTOMERS (DEs)</i>	13
1.3 <i>ELASTOMERS</i>	14
1.4 <i>ELECTRICAL BREAKDOWN</i>	15
1.4.1 Electromechanical breakdown	17
1.4.2 Electrothermal breakdown	17
1.4.3 Partial discharge	17
1.5 <i>OTHER IMPORTANT ELASTOMER PARAMETERS</i>	18
1.5.1 Relative permittivity and dielectric loss	18
1.5.2 Young's modulus and viscous loss	18
1.6 <i>ELASTOMER OPTIMISATION</i>	19
1.7 <i>BREAKDOWN STRENGTH ENHANCING STRATEGIES</i>	20
1.7.1 Filler	21
1.7.2 Mechanical properties	21
1.7.3 Electrode configuration	22
1.7.4 Pre-stretching	23
1.8 <i>Mechanical ageing</i>	25
1.8.1 Macroscopic mechanical ageing	25
1.8.2 Microscopic mechanical ageing	26
2 THE ELECTRICAL BREAKDOWN OF THIN DIELECTRIC ELASTOMERS: THERMAL EFFECTS	33
2.1 <i>INTRODUCTION</i>	33
2.2 <i>METHODOLOGY</i>	34
2.2.1 The samples	34
2.2.2 Rheology, dielectric characterization and thermogravimetric analysis (TGA)	35

2.2.3	Resistivity test	35
2.3	RESULT AND DISCUSSION	36
2.3.1	Experimental data	36
2.3.2	Numerical Prediction of Electrothermal Breakdown	40
2.4	CONCLUSION	45
3	THE BREAKDOWN STRENGTH OF PRE-STRETCHED ELASTOMERS WITH AND WITHOUT SAMPLE VOLUME CONSERVATION	46
3.1	INTRODUCTION	46
3.2	THEORY	48
3.2.1	Sample volume	48
3.2.2	Effective electrode area	49
3.2.3	Polymer morphology	49
3.3	METHODOLOGY	50
3.3.1	Materials	50
3.3.2	Sample preparation	50
3.3.3	Instrumentation	51
3.3.4	Sample parameters	51
3.3.5	Silver deposition and breakdown measurements	53
3.4	RESULTS AND DISCUSSION	55
3.4.1	Volume conservation considerations	55
3.4.2	Young's modulus considerations	57
3.4.3	Sample thickness considerations	57
3.4.4	Electrode area considerations	58
3.4.5	Sample size considerations	59
3.5	CONCLUSION	61
4	THE INFLUENCE OF STATIC PRE-STRETCHING ON THE MECHANICAL AGEING OF FILLED SILICONE RUBBERS FOR DIELECTRIC ELASTOMER APPLICATIONS	65
4.1	INTRODUCTION	65
4.2	METHODOLOGY	67
4.2.1	Materials	67
4.2.2	Sample preparation	67
4.2.3	Pre-stretching of the samples	68
4.2.4	Instrumentation	69
4.3	RESULTS AND DISCUSSION	70

4.3.1	Mechanical ageing	70
4.3.2	Breakdown strength	75
4.3.3	Dielectric properties	76
4.4	<i>CONCLUSION</i>	79
5	MECHANICAL AND ELECTRICAL AGEING EFFECTS ON THE LONG-TERM STRETCHING OF SILICONE DIELECTRIC ELASTOMERS WITH SOFT FILLERS	80
5.1	<i>INTRODUCTION</i>	80
5.2	<i>METHODOLOGY</i>	82
5.2.1	Materials and sample preparation	82
5.2.2	General procedure: films with Co-1 or Co-2	82
5.2.3	General procedure: elastomer synthesis with soft fillers	82
5.2.4	Strain-ageing of samples	84
5.2.5	Instrumentation	84
5.3	<i>RESULTS AND DISCUSSION</i>	84
5.3.1	Properties of different elastomer compositions, before the ageing experiments	84
5.3.2	Properties after ageing experiments: mechanical properties	89
5.3.3	Properties after ageing experiments: breakdown properties	94
5.3.4	Properties after the ageing experiments: figure of merit	97
5.4	<i>CONCLUSION</i>	99
6	POST-CURING AS AN EFFECTIVE MEANS OF ENSURING THE LONG-TERM RELIABILITY OF PDMS THIN FILMS FOR DIELECTRIC ELASTOMER APPLICATIONS	100
6.1	<i>INTRODUCTION</i>	100
6.2	<i>EXPERIMENTAL SECTION</i>	102
6.2.1	Materials	102
6.2.2	Sample preparation	102
6.2.3	Methods	103
6.3	<i>RESULTS AND DISCUSSION</i>	104
6.4	<i>CONCLUSION</i>	117
7	CONCLUSION AND FUTURE WORK	118
7.1	<i>CONCLUSION</i>	118
7.2	<i>FUTURE WORK</i>	120
7.2.1	Electrical breakdown	120
7.2.2	Mechanical ageing	120

7.2.3 Post-curing	120
REFERENCES	121
SYMBOLS AND ABBREVIATIONS	131
LIST OF TABLES	132
LIST OF FIGURES	134
APPENDIX A	139
APPENDIX B	155
APPENDIX C	169
APPENDIX D	187
APPENDIX E	257

PERPUSTAKAAN UMP



0000113723

Electrical Breakdown and Mechanical Ageing in Dielectric Elastomers

Shamsul Bin Zakaria

January, 2016

Supervisor: Anne Ladegaard Skov

PhD Thesis

Danish Polymer Centre, Department of Chemical and Biochemical Engineering,
Technical University of Denmark, Kongens Lyngby

ABSTRACT

Dielectric elastomers (DE) are used in various applications, such as artificial eye lids, pressure sensors and human motion energy generators. For many applications, one of the major factors that limits the DE performance is premature electrical breakdown. There are many approaches that have been reported to increase the breakdown strength of DEs such as compositing and pre-stretching. Some of the techniques, however, affect other parameters related to DEs negatively. For instance, the elastomers with *hard* filler particles (e.g. metal oxides) used as DEs experience difficulties to maintain their long-term mechanical reliability as they are susceptible to Mullins effects as the results of pre-stretching. Therefore, two strategies are developed in this thesis in order to produce DEs with high electrical performance and long-term electromechanical reliability. The first strategy is to study the mechanisms behind the electrical breakdown of DEs and the second strategy is to investigate the long-term electromechanical reliability of DEs. In the first strategy, the electrothermal breakdown in polydimethylsiloxane (PDMS) elastomers was modelled in order to evaluate the thermal mechanisms behind the electrical failures. From the modelling based on the fitting of experimental data, it showed that the electrothermal breakdown of the PDMS elastomers was strongly influenced by the increase in both relative permittivity and conductivity. In addition to that, a methodology in determining the parameters that affect the breakdown strength of the pre-stretched DEs was developed. Breakdown strength was determined for samples with and without volume conservation and was found to depend strongly on the strain and the thickness of the samples.

In order for DEs to be fully implementable in commercial products, the lifetime of elastomer materials needs further investigation. Therefore, in the second strategy, several DE parameters such as Young's moduli, breakdown strengths and dielectric permittivities of PDMS elastomers filled with *hard* filler particles were investigated after being subjected to pre-stretching for various timespans. The study showed that electromechanical reliability when pre-stretching was difficult to achieve with PDMS elastomers filled with *hard* filler particles. Subsequently, the long-term mechanical and electrical reliability was further investigated to the PDMS elastomers filled with the *soft* fillers (e.g. oils). Interestingly, the results also showed that *soft* fillers significantly influence the long-term electromechanical reliability of PDMS elastomers. However, despite the pre-stretched PDMS elastomers filled with *hard* and *soft* filler experience difficulties to maintain their long-term electromechanical reliability, the study paves the way for electromechanically reliable DEs by indicating that simply post-curing PDMS elastomers before use.

Therefore in the last part of this thesis, the effect of post-curing was investigated for PDMS elastomer thin-films as a means of improving the long-term elastomer film electromechanical reliability. The PDMS elastomers were found to contain less than 2% of volatiles but nevertheless a strong effect from post-curing was observed. Furthermore, the determined electrical breakdown parameters from Weibull analyses showed that greater electrical reliability could be achieved by post-curing the PDMS elastomers before usage, and this method therefore paves a way towards more electromechanically reliable DEs.

REFERENCES

- [1] J. E. Mark, *Silicon-Based Polymer Science: A Comprehensive Resource*, American Chemical Society, Oxford University Press, United Kingdom, **1990**.
- [2] P. Brochu, Q. Pei, *Macromol. Rapid Commun.* **2010**, *31*, 10–36.
- [3] S. J. Dünki, Y. S. Ko, F. A. Nüesch, D. M. Opris, *Adv. Funct. Mater.* **2015**, *25*, 2467–2475.
- [4] F. B. Madsen, L. Yu, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polymer* **2014**, *55*, 6212–6219.
- [5] B. Kussmaul, S. Risse, G. Kofod, R. Waché, M. Wegener, D. N. McCarthy, H. Krüger, R. Gerhard, *Adv. Funct. Mater.* **2011**, *21*, 4589–4594.
- [6] F. B. Madsen, I. Javakhishvili, R. E. Jensen, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polym. Chem.* **2014**, *5*, 7054–7061.
- [7] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, *RSC Adv.* **2015**, *5*, 49739–49747.
- [8] C. Tugui, G. T. Stiubianu, M. Iacob, C. Ursu, A. Bele, S. Vlad, M. Cazacu, *J. Mater. Chem. C* **2015**, *3*, 8963–8969.
- [9] S. M. Ha, W. Yuan, Q. Pei, R. Pelrine, S. Stanford, *Smart Mater. Struct.* **2007**, *16*, S280–S287.
- [10] S. M. Ha, M. Wissler, R. Pelrine, S. Stanford, G. Kovacs, Q. Pei, *Proc. SPIE* **2007**, *6524*, 652408–652408–10.
- [11] P. Brochu, H. Stoyanov, X. Niu, Q. Pei, *Smart Mater. Struct.* **2013**, *22*, 055022.
- [12] F. Carpi, G. Gallone, F. Galantini, D. De Rossi, *Adv. Funct. Mater.* **2008**, *18*, 235–241.
- [13] F. B. Madsen, L. Yu, P. S. Mazurek, A. L. Skov, *Unpublished* **2015**.
- [14] S. Vudayagiri, S. Zakaria, L. Yu, S. S. Hassouneh, M. Benslimane, A. L. Skov, *Smart Mater. Struct.* **2014**, *23*, 105017.
- [15] G. L. Wang, Y. Y. Zhang, L. Duan, K. H. Ding, Z. F. Wang, M. Zhang, *J. Appl. Polym. Sci.* **2015**, *132*, 42613.
- [16] S. Vudayagiri, M. D. Junker, A. L. Skov, *Polym. J.* **2013**, *45*, 871–878.
- [17] F. Carpi, D. De Rossi, R. Kornbluh, R. Pelrine, P. Sommer-Larsen, *Dielectric Elastomers as Electromechanical Transducers: Fundamentals, Materials, Devices, Models and Applications of an Emerging Electroactive Polymer Technology*, Elsevier Ltd, Oxford UK, **2008**.

- [18] S. Rosset, L. Maffli, S. Houis, H. R. Shea, *Proc. SPIE* **2014**, *9056*, 90560M–1–90560M–12.
- [19] W. Noll, *Chemistry and Technology of Silicones*, Academic, New York, **1968**.
- [20] M. A. Brook, H. U. Saier, J. Schnabel, K. Town, M. Maloney, *Ind. Eng. Chem. Res.* **2007**, *46*, 8796–8805.
- [21] R. M. Villahermosa, A. D. Ostrowski, in *Proc. SPIE 7069, Opt. Syst. Contam. Eff. Meas. Control* (Ed.: S.A. Straka), International Society For Optics And Photonics, **2008**, pp. 706906–706906–10.
- [22] J. Rothka, R. Studd, K. Tate, D. Timpe, *Outgassing of Silicone Elastomers.*, ArlonSilicone Technology Division, ISC., **2000**.
- [23] S. Zakaria, L. Yu, G. Kofod, A. Ladegaard, **n.d.**
- [24] M. Kollosche, H. Stoyanov, H. Ragusch, S. Risse, a. Becker, G. Kofod, *2010 10th IEEE Int. Conf. Solid Dielectr.* **2010**, 1–4.
- [25] A. L. Skov, S. Vudayagiri, M. Benslimane, *Proc. SPIE* **2013**, *8687*, 86871I–86871I–8.
- [26] M. Benslimane, H.-E. Kiil, M. J. Tryson, *Proc. SPIE* **2010**, *7642*, 764231–764231–11.
- [27] X. Zhao, Z. Suo, *Phys. Rev. Lett.* **2010**, *104*, 1–4.
- [28] D. Gatti, H. Haus, M. Matysek, B. Frohnapfel, C. Tropea, H. F. Schlaak, *Appl. Phys. Lett.* **2014**, *104*, 052905.
- [29] K. H. Stark, C. G. Garton, *Nature* **1955**, *176*, 1225–1226.
- [30] A. Dorfmann, R. W. Ogden, *Int. J. Solids Struct.* **2004**, *41*, 1855–1878.
- [31] A. M. Stricher, R. G. Rinaldi, C. Barrès, F. Ganachaud, L. Chazeau, *RSC Adv.* **2015**, *5*, 53713–53725.