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Reutilizing and retesting of parallel plate sensors in dielectric thermal analysis[1]

John Q. Whitley[a], Robert P. Kusy[a,b,*]

[a]Dental Research Center, University of North Carolina, Chapel Hill, NC 27599-7455, USA
[b]Biomedical Engineering, University of North Carolina, Chapel Hill, NC 27599-7455, USA

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Abstract

One of the advantages of dielectric thermal analysis (DETA) is that the parallel plate sensors are disposable, thereby eliminating potentially time-consuming clean-up procedures. Nonetheless, sometimes the reusing of parallel plate sensors is desirable, for example, when the test material is limited, further processing is intended, or cyclic testing is required. In this experiment, multiple-run and single-run methodologies were performed, the former without unloading the ram, and the latter after unloading the ram, removing the specimen, and cleaning the sensor. A dummy biomedical membrane was cast from a tetrahydrofuran solution of highly plasticized poly(vinyl chloride). After running each DETA experiment at a heating rate of 3°C min^{-1} from −20 to + 80°C at 1, 10, and 100 Hz, no significant differences were observed for permittivities, loss factors, tan deltas, ion conductivities, or the membrane thicknesses at room temperature. When calibrated, sensor areas varied by ±1%, and thermistor values varied by ±0.5%. From comparative graphs, box-plots, and statistical analyses, the data confirm that parallel plate sensors can be reutilized for retesting with these biomedical membranes.

Keywords: DETA; Membrane; Quality assurance; Poly(vinyl chloride); Loss factor; Permittivity

1. Introduction

To design and fabricate optimal amperometric and potentiometric biosensors requires some understanding of their fundamental biocompatibility, mechanical properties, and electrical characteristics [1–3]. If these biosensors should fail in one of these regimes, then the product is rendered useless. Consequently, being able to differentiate a good

* Corresponding author.

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product from one that is likely to fail can be valuable to the patient into whom one of these has been inserted or in a diagnostic instrument within which many of these may be used to assay various analytes.

Although in recent years some countries have increasingly turned towards disposable products in order to obviate potential time-consuming clean-up procedures and governmental regulations, there are occasions in which recycling is not only desirable but required. For biosensors this occurs because some ingredients are quite expensive, batches are very small, and membrane specimens are limited. Thereby when a new batch is made, one would like to make comparable measurements using the same apparatus. Sometimes additional processing is required in situ, too, as for example when chemical reactions following a masking procedure are used to modify the local properties and characteristics. To test the electrochemical fatigue of a biosensor product, as an outcome of multiple assays, repeated hydration-dehydration cycles, or stepwise aminated chemical reactions, it would be desirable to eliminate as much error as possible by retaining the identical components.

In the present work the precursor of one biomedical membrane, a so-called dummy membrane, is cast from a highly plasticized poly(vinyl chloride) solution. Having eliminated composition as a variable, the membrane is evaluated by dielectric analysis (DETA) in order to measure its capacitive and conductive properties. After comparing the multiple-run and single-run methodologies, the data analyses confirm that these biosensors may be removed and reinserted, or recycled and run multiple times, without significantly having the instrument parameters or dielectric properties change.

2. Materials and methods

2.1. Test material

A poly(vinyl chloride) (PVC; Polysciences) high molecular weight polymer (MW = 110 000) was mixed with a polar low molecular weight (MW = 251) plasticizer, *o*-nitrophenyl octyl ether (o-NPOE; Fluka). The composition chosen was the standard of the art, that of 200:100 parts of plasticizer/polymer [4]. By using this composition, one obtains a polymer solution in which a structural solute (the polymer) is dispersed in a solvent (the plasticizer). Such a phase inversion results in a very compliant biomaterial, after it is diluted with HPLC-grade tetrahydrofuran (THF; Mallinckrodt) and cast into 0.25 mm thick membranes by evaporating the THF [5]. This biomedical membrane is denoted a "dummy" because it lacks any explicit charge carriers that an ionophore might offer [6].

2.2. DETA instrumentation

The unhydrated membrane was run in a TA Instruments' DEA 2970 using gold-coated ceramic parallel plate sensors. Prior to each test the DETA was calibrated two or more times to determine the "geometry" (A) factor and the "resistance temperature detector" (RTD) or thermistor factor, which corresponded to the electrode plate area (mm^2)

between the two capacitive/conductive plates and the resistance (Ω) observed at 0°C for the platinum thermometer on the bottom parallel plate, respectively. Thereafter the membrane was inserted into the instrument and the "thickness" (d) of the membrane, which corresponded to the plate spacing, was measured (mm) at a ram force of 200 N. After purging with dry nitrogen at a flow rate of 1.0 l min^{-1}, the apparatus with sample was cooled down to −20°C by the Liquid Nitrogen Cooling Accessory. Using a rate of 3°C min^{-1}, the samples were heated to +80°C, while exposing one of the parallel plates to an alternating electric frequency (f) of 1, 10, and 100 Hz. The 2000 System Controller monitored the current in the opposing parallel plate as well as the phase angle shift (δ) between the applied voltage and the measured current. From these two measurements, the dissipation factor (tan δ), the capacitance (C), and the resistance (R) or conductance (R^{-1}) were computed. By knowing A, d, and f, the permittivity (e') and the loss factor (e'') were derived, and the ionic conductivity (σ) was calculated from e'' [7].

2.3. Methodology

In all, seven quantities were monitored: A, RTD, d, e', e'', σ, and tan δ under two experimental conditions, the multiple-run and the single-run methodologies (Table 1). In the multiple method, for one test the dummy membrane was run six times without lifting the ram and unloading the membrane. Consequently, the same A and RTD were used to compute parameters of each successive run. In the single method, the membrane was tested eight times for a total of eight runs, after unloading the force, removing the membrane, and cleaning the parallel plate sensors with THF between tests. Comparative

Table 1

Test methodologies

Methodology	Test no.	Run no.
Multiple-run[a]	1	1
Multiple-run		2
Multiple-run		3
Multiple-run		4
Multiple-run		5
Multiple-run		6
Single-run[b]	2	7
Single-run	3	8
Single-run	4	9
Single-run	5	10
Single-run	6	11
Single-run	7	12
Single-run	8	13
Single-run	9	14

[a]In this methodology the membrane was run six times without lifting the ram and unloading the membrane, thereby resulting in one test.

[b]In this methodology after each run the force was unloaded, the membrane was removed, and the parallel plate sensors were cleaned with THF, thereby resulting in eight tests.

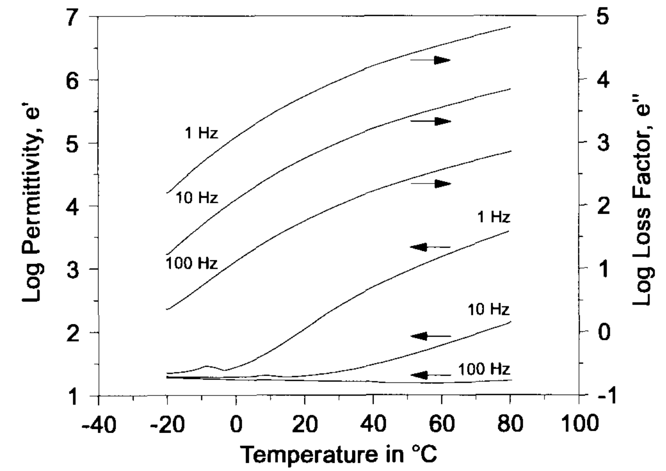

Fig. 1. Typical influence of temperature and frequency on the permittivity (e') and loss factor (e'') of a dummy biomedical membrane composed of 200 parts *o*-nitrophenyl octyl ether (o-NPOE) and 100 parts poly(vinyl chloride) (PVC).

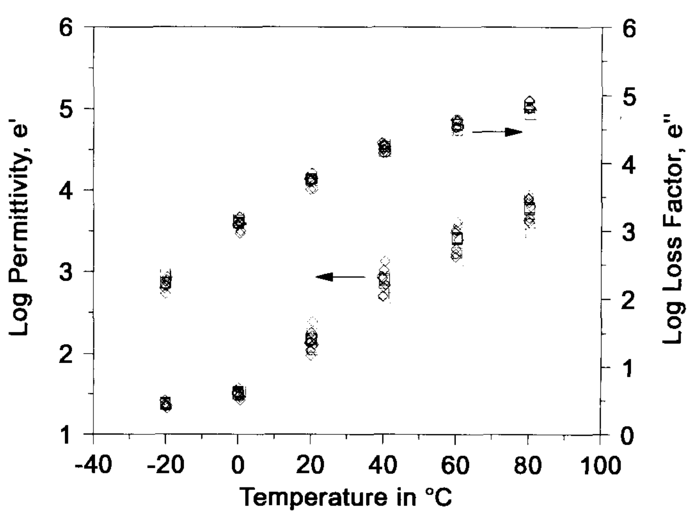

Fig. 2. Comparison of the permittivity (e') and the loss factor (e'') at 1 Hz, after dielectric analyses of 9 tests via the multiple-run (□) and the single-run (◇) methodologies.

graphs, box-plots [8], and Student's t-tests were used to analyze these 9 tests or 14 runs by analyzing those data sets at six nominal temperature intervals: –20, 0, 20, 40, 60, and 80°C.

Table 2

Summary of the results for multiple- and single-run methodologies at 1 Hz

Quantity	Methodology	Student's t analyses[a]	Temperature in °C –20	0	20	40	60	80
e'	Multiple		23.96[b]	32.53	143.5	713.5	2237	5177
			(0.43)[c]	(1.26)	(21.3)	(148.3)	(503)	(1245)
	Single		23.43[d]	30.20	133.3	693.1	2350	5659
			(1.43)[c]	(1.95)	(24.6)	(177.5)	(765)	(1576)
		t-value	1.26	1.07	–0.33	–0.67	–1.04	–1.31
		DF	11	12	12	12	12	12
		P	0.23	0.30	0.74	0.51	0.31	0.21
		Significance	Same	Same	Same	Same	Same	Same
e''	Multiple		196.5	1399	5924	16990	35430	62470
			(27.0)	(90)	(498)	(1530)	(3050)	(6810)
	Single		156.1	1178	5160	16310	37490	70750
			(21.1)	(143)	(675)	(1660)	(4520)	(8810)
		t-value	1.89	1.66	1.01	–0.07	–1.52	–2.44
		DF	11	12	12	12	12	12
		P	0.08	0.12	0.32	0.94	0.15	0.03
		Significance	Same	Same	Same	Same	Same	Uncertain
σ in $p\Omega\ cm^{-1}$	Multiple		109.29	778.4	3295	9446	19700	34730
			(11.56)	(43.8)	(274)	(689)	(1240)	(3640)
	Single		91.74	690.8	3038	9490	21760	41430
			(14.56)	(104.2)	(489)	(1087)	(2510)	(4960)
		t-value	1.89	1.67	1.01	–0.07	–1.53	–2.44
		DF	11	12	12	12	12	12
		P	0.08	0.12	0.32	0.94	0.15	0.03
		Significance	Same	Same	Same	Same	Same	Uncertain
Tan δ	Multiple		8.20	42.87	42.01	24.65	16.55	12.61
			(0.76)	(1.97)	(3.45)	(3.43)	(3.10)	(2.16)
	Single		7.24	40.10	38.20	23.02	15.80	12.31
			(1.40)	(6.02)	(7.14)	(5.07)	(3.77)	(2.24)
		t-value	1.21	0.93	1.04	0.58	0.35	0.21
		DF	11	12	12	12	12	12
		P	0.24	0.36	0.31	0.56	0.73	0.83
		Significance	Same	Same	Same	Same	Same	Same

[a]Where DF and P represent the degrees of freedom and the probability for pooled variances, respectively.
[b]Mean of six multiple-run values.
[c]Value represents ± one standard deviation.
[d]Mean of eight single-run values (except for –20°C where there were only seven single-run values).

Table 3
Summary of the initial membrane thicknesses for all tests[a]

	Test no.								
	1	2	3	4	5	6	7	8	9
Thickness in mm	0.251	0.245	0.235	0.235	0.231	0.224	0.250	0.240	0.253

[a]Mean of all values = 0.240 ± 0.010 mm.

3. Results

A graph of e' and e'' as a function of temperature and frequency (Fig. 1) indicates the typical molecular motion in this dummy membrane under the influence of an alternating electrical field. That this was a typical result is evidenced by the combined results of multiple-run (□) and single-run (◇) methodologies (Fig. 2). The values of e', e'', σ, $\tan\delta$, and their corresponding t-tests for the two methodologies were tabulated at one representative frequency (1 Hz) and six temperature intervals (–20, 0, 20, 40, 60, and 80°C) (Table 2). The initial values of membrane thicknesses (d) were recorded for each run (Table 3). When a box-plot was used to detail the A and RTD factors for the 9 tests (one before each test as the membrane was placed in the DETA; cf. Table 1) and once after the final run, the variability of the methodologies differed by ±1% and ±0.5% from the mean values, respectively (Table 4 and Fig. 3).

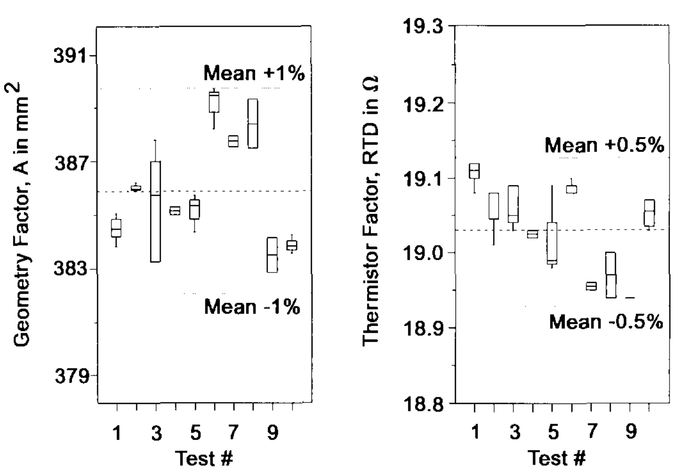

Fig. 3. Box-plots (cf. Ref. [8]) of the geometry factor (A) and the thermistor factor (RTD), after making a total of 41 measurements for the 9 tests and once after all tests were completed (cf. Table 4).

Table 4

Summary of parallel plate geometry (A) and thermistor (RTD) factors for all tests

Factor	Statistics[a]	Test no. 1	2	3	4	5	6	7	8	9	Final[b]
A in mm^2	Mean	384.50	385.96	385.44	385.17	385.22	389.15	387.78	388.44	383.52	383.89
	SD	0.41	0.25	2.11	0.21	0.60	0.79	0.28	1.29	0.93	0.23
	n	10	4	5	2	3	3	2	2	2	8
RTD in Ω	Mean	19.11	19.06	19.06	19.03	9.09	19.09	18.96	18.97	18.94	19.05
	SD	0.01	0.04	0.03	0.01	0.01	0.01	0.01	0.04	0	0.02
	n	10	4	5	2	3	3	2	2	2	8

[a]Mean reported for n determinations along with its standard deviation (SD).
[b]Measured after test no. 9. All other factors were measured before their test number.

4. Discussion

The DETA technique is extremely sensitive, having proven itself to be capable of measuring glass transition temperatures where other techniques cannot detect differences [9]. Consequently, the requirement of reproducibly placing a biosensor membrane, or any thin film for that matter, between the parallel plate sensors is not a trivial matter. For example, in the field of dynamic mechanical spectroscopy, which represents a less sensitive mechanical analog to DETA, a certain lack of reproducibility has been reported both within as well as between instruments as a result of different clamping forces and different operating principles, respectively [10].

Against this backdrop, it would not be surprising if the potential advantages of reusing parallel plates were not to materialize here either. These membranes are very compliant, oftentimes being referred to as liquid membranes, since the dynamic mechanical moduli at 20°C and 11 Hz are quite low, ca. 3×10^5 Pa [11]. However, the d values showed that a ram force of 200 N was not sufficient to cause creep of the membrane either during a run or after 14 runs, since the d of the first and last values differed by only 0.5% (Table 3). Moreover, the A factor, which has an inverse linear effect on the values of e', e'', and σ (i.e. for example the Y-axes of Figs. 1 and 2), changes these values by only ±1% (cf. Fig. 3, left and Table 4); and the RTD factor, which can shift the absolute temperatures (i.e. for example the X-axes of Figs. 1 and 2), presents an error of only ±0.5%. (cf. Fig. 3, right and Table 4). Overall, there appears to be no large or systematic changes as a function of run methodology (Fig. 2); consequently, neither $\tan\delta$ nor σ will change, since they are equal to e''/e' and $8.85e''f$ pF m^{-1}, respectively. Finally, if Student's t-tests are evaluated at 20°C increments from −20 to +80°C for e', e'', σ, and $\tan\delta$, the data are not significantly different. That is, they are likely to be from the same population (i.e. probabilities $P > 0.05$) in 22 of the 24 analyses, the only two exceptions occurring at 80°C for e'' and σ. For these two exceptions, the t-values and the degrees of freedom (DF) are such that, within the limits of $0.05 > P > 0.001$, one cannot distinguish whether the two methodologies are the same or different; that is, the significance is uncertain (Table 2) [12]. Suffice to say, the present evidence shows that parallel plate sensors can be reutilized for rerunning these biomedical membranes.

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