Effects of plasticization on the dielectric properties of poly(vinyl chloride) membranes[1]

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Abstract

Electrode bodies and biosensors are engineered from membranes that often contain poly(vinyl chloride) (PVC) as the structural component. Citroflex B-6 (CF), dibutyl sebacate (DBS), dioctyl sebacate (DOS), epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), ortho-nitrophenyl octyl ether (o-NPOE), and propylene glycol dioleate (PGDO) were used to plasticize the PVC membranes. After adding tridodecylamine (TDDA) and potassium tetrakis-4-chlorophenyl borate (KTpClPB) as neutral charge carriers and negative sites, respectively, the dielectric properties of the plasticized PVC membranes were measured with a TA Instruments' DEA 2970. Using parallel plate sensors, the plasticizers were scanned at $3°C min^{-1}$ from -100 to $+100°C$ at seven log frequencies: $-1, 0, 1, 2, 3, 4,$ and 5. Generally, increasing the amount of plasticizer in the membrane improved the ionic conductivity (σ) and lowered the temperature of the tan δ peak. A positive linear correlation existed between the log σ and the log(phr ratio) for a given temperature and frequency. The slopes and intercepts of the log σ versus log(phr ratio) lines were linear functions of the log frequency but non-linear functions of temperature. The positive slope of the log σ versus log(phr ratio) lines was greatest at about $0°C$ and 10^{-1} Hz, and the peak values of the slopes diminished as they shifted to higher temperatures and frequencies. The intercepts of the log σ versus log(phr ratio) lines increased monotonously and tended to converge at the highest temperatures and frequencies. In the final analysis, the traditional phr ratios, which are associated with 200 parts of plasticizer per 100 parts of polymer, were not necessary since sufficient performance was achieved for all plasticizers at lower phr ratios.

Keywords: Dielectric properties; Membranes; Plasticizers; Poly (Vinyl Chloride); Biosensors

1. Introduction

The study of the charge storage capacity of materials began in the middle of the eighteenth century. At that time, the work of Faraday was recognized for the quantitative nature of the research and the naming of "dielectric" materials [1]. In the middle of the nineteenth century, Maxwell's analysis of electromagnetic field made possible the Clausius–Mossotti determination of an internal electric field for polar materials [2,3]. Lorenz and Lorentz clarified the effects of an internal field on different materials, beginning the study of structure-property relationships for dielectric materials [4]. In 1912, Debye composed what remains the definitive equation for polarized gases and established the dielectric constant's dependency on the dipole moment of the molecules [5]. In 1949, Onsager modified Debye's equation to include polar liquids, which essentially completed the basic precepts of dielectric materials [6].

In 1938, Fuoss began research on the electrical properties of poly(vinyl chloride)-tricresyl phosphate materials [7]. By 1945, Mead and Fuoss had begun to investigate the addition of electrolytes to plasticized PVC, thus establishing the use of polymers as conductive materials [8]. The ion-selective electrode (ISE) application of poly(vinyl chloride)(PVC) began in 1970 with Frant's measurements of the potassium ion [9]. By 1978, Hill et al. were making ISEs using the valinomycin-containing PVC membranes for in vivo studies of myocardial K^+ ion concentrations [10].

Since the first of the sensor applications, the PVC membranes have been plasticized to 200 parts per hundred resin (phr), which is five to ten times the amount of plasticizer used in typical PVC applications [11]. These highly plasticized membranes act virtually as a liquid that, with proper additions, allows proton transport. Those additions can be in the form of an ionophore with negative sites, aminated sites on the PVC, or a combination of the two. The ion being measured is the basis for whatever ionophore is chosen. Examples of ionophores are the valinomycin used in K^+ measurements and the tridodecylamine (TDDA) used in this work for H^+ measurements. The species of plasticizer used in ISE membranes has also been varied, but the traditional value of plasticization has been used without regard for these changes. The high level of plasticization results in the plasticizer leaching out of the membrane. For in vivo applications such as biosenors, plasticizer leaching can be a serious health risk, as when the electrode fails due to formation of a plasticizer film on the electrode's surface [12].

Due to the risk of infection associated with synthetic organic materials, natural derivatives have been proposed for use as plasticizers [13]. With changes in plasticizer species and membrane applications, the effectiveness of the traditional plasticizer ratio must be reconsidered. In this work, dielectric analysis was used to evaluate the electrical effects of changes in plasticizer species and concentration. Seven plasticizers were studied at a variety of plasticizer levels ranging from the neat polymer to at least the traditional value of 200 phr. The permittivity (ε'), loss factor (ε''), tan δ, and ionic conductivity (σ) were measured using seventy different membranes. The tan δ peak and σ were indicative of the glass transition temperature (T_g) and the mobility of charge carriers, respectively. As expected, the tan δ peak occured at lower temperatures with increased plasticization. When the log σ was plotted against a measure of the quantity

of plasticizer in the membrane, that is the log(phr ratio), a positive linear correlation was found for a given temperature (T) and frequency (f), independent of the plasticizer species. From these measurements, the ionic behaviour of membranes, ISEs, and biosensors can be predicted so that, when coupled with mechanical properties, a better understanding of structure-property relationships will be achieved.

2. Materials and methods

2.1. Membrane preparation

The membranes were composed of a 50/50 blend of low and high molecular weight (MW) PVCs (MW = 77,300 and 193,600, Scientific Polymer). The 50/50 blend was chosen for ISE applications because the blend provided a good combination of strength and processability [14]. To the PVC blend, one of seven plasticizers was added: Citroflex B-6 (CF, Morflex), dibutyl sebacate (DBS, Kodak), dioctyl sebacate (DOS, Aldrich), epoxidized linseed oil (ELO, Viking Chemical), epoxidized soybean oil (ESO, Union Carbide), *ortho*-nitrophenyl octyl ether (o-NPOE, Fluka), and propylene glycol dioleate (PGDO, Viking Chemical). The DBS, DOS, and o-NPOE are synthetic organics and were included because of previous use in ISE applications [10,15,16]. The CF, ELO, ESO, and PGDO were derivatives of natural products and likely to be biocompatible. These seven plasticizers also facilitated analysis of the effects of molecular weight and polarity on plasticization. Four plasticizers (CF, DBS, DOS, and o-NPOE) had low MWs, and three plasticizers (ELO, ESO, and PGDO) had high MWs (Table 1). The o-NPOE was the only polar plasticizer. Tests were performed on membranes using at least four plasticizer levels for each of the seven plasticizers for evaluation of the effects of plasticizer species and amount. In addition to the plasticizer, a proton-selective ionophore, tridodecylamine (TDDA, Fluka) at 2.5 wt% and a salt, potassium tetrakis-4-chlorophenyl borate (KTpClPB, Lancaster) at 1.7 wt% were added as neutral charge carries and negative sites, respectively. The ratio of 1.5:1 of

Table 1
List of the seven plasticizers, calculated MWs, phr ratios at the traditional plasticization level of 200 phr, and viscosities.

Plasticizer	MW	phr Ratio at 200 phr	Viscosity (μ)/cps[a]
CF	514	3.4	
DBS	314	5.6	–
DOS	427	4.1	16.7
ELO	1490	1.2	763
ESO	1470	1.2	329
o-NPOE	251	7.0	11.9
PGDO	1040	1.7	106

[a] Viscosities in centipoise are from Simon and Kusy [13].

TDDA:KTpClPB has been established as optimum for ion-conductive membranes [17]. Membranes were prepared by dissolving 1.1 wt% PVC in tetrahydrofuran (THF, Mallinckrodt) and adding the appropriate amounts of plasticizer, netural charge carriers, and negative sites. Approximately 10 ml of the mixture was evaporated under a hood for five to six days in a 2.5 cm diameter glass ring mounted on a glass side. The ring was covered with weighted filter papers, which provided control of the evaporation rate. The dry membranes were at least 125 microns thick.

2.2. "phr" Ratio

The phr ratio accounts for the MW of the plasticizer used in a membrane and provides a useful reference point in discussions of plasticization. The phr_{exp} defines the percent mass ratio of the plasticizer to the PVC in grams for a given membrane, or

$$phr_{exp} = \frac{mass\ of\ plasticizer}{mass\ of\ PVC} \times 100 \tag{1}$$

The phr_{min} for a given plasticizer represents the minimum plasticizer ratio necessary for complete plasticization. This occurs when all polar groups on the PVC backbone are shielded from each other by a monolayer of plasticizer [18]. The phr_{min} is based on the MW of the plasticizer and the MW of one helical unit of PVC (MW = 875)

$$phr_{min} = \frac{MW\ of\ plasticizer}{875} \times 100 \tag{2}$$

Finally

$$phr\ ratio = \frac{phr_{exp}}{phr_{min}} \tag{3}$$

2.3. Test appratus

Dielectric property tests were performed on a TA Instruments Dielectric Analyzer 2970 (DEA) using parallel plate sensors. The membranes were tested under a ram pressure of 200 N while purging the test section with nitrogen gas at $1.0\ l\ min^{-1}$. The temperature of the system was ramped from $-100°C$ to $100°C$ at a rate of $3°C\ min^{-1}$. An alternating electric field was applied to the membranes at frequencies ranging from 10^{-1} Hz to 10^5 Hz at decade increments. Four principle dielectric quantities permittivity (ε'), loss factor (ε''), tan δ, and ionic conductivity (σ), were monitored to analyze the effects of plasticizer content. The ε', or dielectric constant, is the ratio of the capacitance of a condenser filled with a dielectric material versus the capacitance of the same condenser in a vacuum [19]. The ε' represents the transmission of the electric field through the membrane, and ε'' the energy loss due to alignment of dipoles or movement of ions. The tan δ can be defined as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{4}$$

which peaks as transitions in the molecular mobility occur. In this work, the peak was assumed to be representative of the glass transition temperature (T_g). Note that the T_g must be below the operating temperature of the electrode for ion transmission to occur. The σ of the material was calculated according to

$$\sigma = \varepsilon'' 2\pi f \varepsilon_0 \qquad (5)$$

where f is frequency (Hz) and ε_0 permittivity in a vacuum (8.85×10^{-12} farad m^{-1}) [19]. The σ was indicative of the molecular mobility of the system and thereby of the ease of ion transmission across the membrane. Since valinomycin–K$^+$ and TDDA–H$^+$ are ionic molecules, the increased ion transmission capability, or σ is the key parameter in successful biosensors. Note that, by detailing the tan δ and σ in this paper, both ε' and ε'' are implicitly available from Eqs. (4) and (5).

3. Results

3.1. phr Ratio dependence

In unplasticized PVC, the peak of the tan δ occurred at 88°C at 10Hz (Fig 1 and Table 2). Electrical measurements of the T_g are known to be slightly higher than the value found with mechanical testing [20]. Using dynamic mechanical analysis, Simon and Kusy found that the T_g of the same 50/50 blend of unplasticized PVC was 77°C at 11 Hz [21].
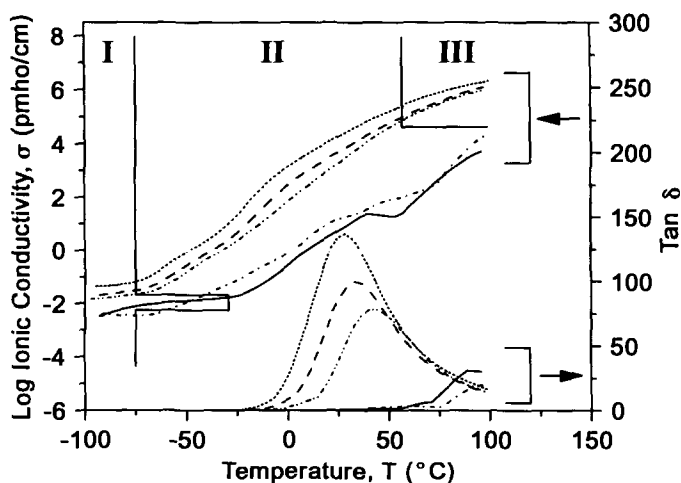

Fig. 1. Typical plot showing the effects of phr ratio on log σ and tan δ versus temperature (T). The graph shows the 10 Hz data for ESO-plasticized PVC membranes at phr ratios of 0.00 (——), 0.25 (– · –), 0.75 (– ·· ··), 1.25 (— —), and 1.75 (····).

Table 2
Measured values of $\log \sigma$ and $\tan \delta$ for unplasticized PVC membranes. All temperature values are within $\pm 2°C$.

phr Ratio	Dielectric measurement		Log f						
			-1	0	1	2	3	4	5
0.00	Log σ	$-60°C$	-3.93	-2.91	-1.97	-0.94	0.04	0.91	1.84
		37°C	0.30	0.85	1.24	1.48	1.71	2.04	2.71
		90°C	0.99	3.41	3.43	3.45	3.46	3.50	4.04
	Tan δ	max.	1.2	3.5	30.6	[a]	[a]	[a]	[a]
		$T°C$	50	59	88	[a]	[a]	[a]	[a]

[a] Values were outside the test range.

The $\log \sigma$ was separated into three regions of activity, which were designated as Regions I, II, and III. The lines separating the three regions were somewhat arbitrary, as the transition from one region to another occurred over a range of temperatures. For unplasticized PVC, the $\log \sigma$ maintained a relatively constant value up to a temperature of $-25°C$ (Region I). At $-25°C$, the log σ increased at a high rate (Region II) until it was five orders of magnitude higher at 90°C. The $\log \sigma$ typically began to level off at these highest temperatures. Although this effect occurred beyond the measured range for unplasticized PVC, it was observed in the plasticized membranes, which are shown in Region III of Fig. 1 (see also Tables 3–9).

The addition of plasticizer generally increased the σ throughout the range of temperatures tested. As exhibited by the 0.25 phr ratio in Fig. 1, very low levels of plasticization had little effect on the $\log \sigma$ or $\tan \delta$ peak. However, as the phr ratio increased to 0.75 for ESO-plasticized membranes, the $\log \sigma$ increased by an order of magnitude at low temperatures and two or three orders of magnitude at room (23°C) and body (37°C) temperatures. Room and body temperatures were of primary importance, since these are the temperatures at which membranes, ISEs, and biosensors typically operate. By the addition of plasticizer at 0.75 phr ratio, the onset of the high slope Region II was lowered to $-70°C$, and the slope in Region II was increased. The temperature of the $\tan \delta$ peak was reduced by 50°C, and the magnitude of the $\tan \delta$ peak was increased by 75. Further increases in the phr ratios continued to affect both $\tan \delta$ and $\log \sigma$, albeit to a lesser extent.

3.2. Frequency dependence

The $\log \sigma$ and $\tan \delta$ were dependent on the frequency of the applied electric field (Fig. 2). Again, the figure was divided into three arbitrarily defined regions. In the low temperature range wherein $\log \sigma$ was relatively constant (Region I), each order of magnitude increase in frequency increased the σ by an order of magnitude. In the high slope transition region (Region II), the slope was lessened with increasing frequency, approaching a value equivalent to the slope in Region III. The $\log \sigma$ was frequency-

independent in the low slope region (Region III) at high temperatures. The tan δ peak increased in temperature and magnitude with increasing frequency. The relationship between the temperature of the tan δ peak and the test frequency was established by Fuoss as the log (f) was proportional to $1/T$ [22]. A set of ten random samples were found to follow this relationship.

3.3. Plasticizer species dependence

The log σ and tan δ were both influenced by the plasticizer species. At the traditional value of 200 phr, the effects of MW were evident in both the log σ and tan δ measurements (Fig. 3 and Tables 1,3–9). Throughout the range of temperatures tested, the log σ was generally increased by choosing a plasticizer having lower MW. The relative importance of the specific plasticizer species lessened with increasing temperature, where as much as three orders of magnitude difference were observed at lower temperatures (Regions I and II) but as little as only one order of magnitude difference was observed at higher temperatures (Region III). The temperatures of the tan δ peaks decreased as the size of the plasticizer molecules decreased. The magnitudes of the tan δ peaks were not considered relevant but instead indicated a thickness effect due to the presence of more charge carriers in a thicker membrane.

4. Discussion

4.1. General observations

According to Ku and Liepins [20], the magnitude of the tan δ peak is related to the number of active dipoles present. While the number of dipoles was similar in all membranes shown in Fig. 1, the increase in magnitude of the tan δ with increasing plasticization was representative of the release of bound dipoles. The dipoles were relatively immobile in unplasticized PVC, but the addition of plasticizer facilitated the movement of the dipoles. Of particular importance was the fact that neither the log σ nor the tan δ peak was substantially changed by plasticization in excess of 0.75, which showed that the traditional value of 200 phr of plasticizer was unnecessary for achieving the desired effects on log σ and tan δ. In Fig. 3 and Tables 3–9, the lower MW plasticizers had a higher log σ at 200 phr throughout the range of temperatures and frequencies tested (see Table 1 for the appropriate phr ratio of each plasticizer at 200 phr). As the MW decreased, the mobility of the system improved. The smaller plasticizers facilitated translation and rotation of the charge carrier, TDDA, through the plasticized PVC. The effect of MW was particularly important, because it revealed that the usage of phr to describe the level of plasticization was ineffective. Conversely, the use of phr ratio gave a consistent value for the required amount of plasticizer, since the MW of the plasticizer was inherently considered (see Eqs. 1–3). Between the phr ratios of 0.75 and 1.00, all plasticizers achieved the increases in log σ and the magnitude of the tan δ peak, as well as the decreases in temperature of the tan δ peak, which were associated with plasticization (see Tables 2–9). In the high temperature region (Region

Table 3
Measured values of log σ and tan δ for eleven plasticizer levels of PVC membranes plasticized with Citroflex B-6 (CF). All temperature values are within $\pm 2°C$.

phr Ratio	Dielectric measurement		Log f						
			−1	0	1	2	3	4	5
0.25	Log σ	−60°C	−3.34	−2.53	−1.62	−0.67	0.38	1.33	2.64
		37°C	−0.42	0.08	0.66	1.24	1.98	2.76	3.60
		90°C	3.88	4.24	4.08	4.14	4.25	4.63	5.12
	Tan δ	max.	1.9	2.2	a	a	a	a	a
		$T°C$	50	63	a	a	a	a	a
0.31	Log σ	−60°C	−3.03	−2.32	−1.44	−0.44	0.57	1.51	2.57
		37°C	0.75	0.97	1.34	1.85	2.46	3.15	3.82
		90°C	4.47	4.57	4.61	4.64	4.52	4.71	5.11
	Tan δ	max.	11.0	15.9	29.4	a	a	a	a
		$T°C$	57	68	90	a	a	a	a
0.38	Log σ	−60°C	−3.22	−2.42	−1.57	−0.64	0.42	1.35	2.60
		37°C	0.96	1.11	1.39	1.84	2.42	3.10	3.85
		90°C	4.32	4.41	4.45	4.48	4.50	4.68	5.08
	Tan δ	max.	11.6	18.2	30.9	a	a	a	a
		$T°C$	56	63	83	a	a	a	a
0.44	Log σ	−60°C	−3.31	−2.65	−1.84	−0.81	0.30	1.26	2.55
		37°C	0.42	0.66	1.21	1.74	2.35	3.05	3.83
		90°C	2.61	4.06	4.10	4.14	4.18	4.52	5.06
	Tan δ	max.	2.6	3.6	27.2	a	a	a	a
		$T°C$	39	54	90	a	a	a	a
0.50	Log σ	−60°C	−2.93	−2.24	−1.42	−0.45	0.56	1.52	2.66
		37°C	1.67	1.75	1.94	2.33	2.84	3.44	4.15
		90°C	4.69	4.78	4.82	4.69	4.72	4.99	5.23
	Tan δ	max.	16.3	24.0	40.5	a	a	a	a
		$T°C$	50	59	84	a	a	a	a

0.63	Log σ	−60°C	−2.81	−2.05	−1.2	−0.36	0.62	1.56	2.65
		37°C	2.66	2.73	2.56	2.83	3.22	3.73	4.38
		90°C	5.04	5.15	5.20	5.22	5.24	5.29	5.51
	Tan δ	max.	15.1	17.6	28.9				a
		T°C	37	45	68				a
0.75	Log σ	−60°C	−2.79	−2.01	−1.24	−0.42	0.55	1.49	2.62
		37°C	1.33	2.01	2.16	2.43	3.04	3.58	4.29
		90°C	4.87	4.88	4.88	4.91	4.93	5.02	5.38
	Tan δ	max.	6.2	17.8	35.6				a
		T°C	76	68	74				a
1.25	Log σ	−60°C	−2.62; −2.70	−1.82; −1.86	−1.01; −1.06	−0.20; −0.26	0.64; 0.59	1.49; 1.35	2.39; 2.33
		37°C	a; −0.02	2.20; 2.00	2.51; 2.33	2.61; 2.38	2.84; 2.52	3.50; 3.31	4.22; 4.09
		90°C	4.61; a	4.81; 4.86	4.87; 4.96	4.89; 4.99	4.91; 5.01	4.93; 5.04	5.18; 5.20
	Tan δ	max.	2.2; 3.3	9.7; 3.8	34.0; 4.5				a
		T°C	3; 0	79; 14	79; 37				a
2.00	Log σ	−60°C	−2.01	−1.32	−0.36	0.46	1.28	1.91	2.77
		37°C	a	3.39	3.57	3.60	3.65	3.96	4.59
		90°C	5.41	5.67	5.72	5.74	5.75	5.67	5.73
	Tan δ	max.	a	9.8	32.2	115.1			a
		T°C	a	a	65	85			a
3.00	Log σ	−60°C	−1.44; −1.27	−0.75; −0.62	0.03; 0.15	0.88; 0.87	1.71; 1.68	2.48; 2.43	3.26; 3.21
		37°C	4.44; 4.58	4.52; 4.66	4.55; 4.57	4.57; 4.58	4.59; 4.60	4.67; 4.69	5.03; 5.03
		90°C	5.84; 5.80	6.09; 6.06	6.13; 6.09	6.15; 6.11	6.16; 6.12	6.16; 6.12	6.12; 6.15
	Tan δ	max.	21.2; 51.7	49.4; 59.9	63.2; 84.2	a; 133.2			a
		T°C	−3; −8	2; 2	20; 23	a; 70			a
3.40	Log σ	−60°C	−0.79; −0.61	−0.35; −0.18	0.31; 0.44	1.10; 1.21	1.93; 2.04	2.70; 2.81	3.42; 3.55
		37°C	4.92; 5.14	5.10; 5.29	5.12; 5.31	5.13; 5.31	5.13; 5.31	5.14; 5.32	5.30; 5.47
		90°C	6.25; 6.43	6.32; 6.50	6.49; 6.63	6.52; 6.65	6.51; 6.65	6.52; 6.65	6.51; 6.65
	Tan δ	max.	99.9; 116.0	78.7; 86.8	91.7; 103.8	138.0; 169.3	260.6; 343.3		a
		T°C	−22; −23	−14; −13	6; 8	42; 43	88; 85		a

[a] Values were outside the test range.

Table 4
Measured values of log σ and tan δ for ten plasticizer levels of PVC membranes plasticized with dibutyl sebacate (DBS). All temperature values are within $\pm 2°C$.

phr Ratio	Dielectric measurement		Log f						
			−1	0	1	2	3	4	5
0.25	Log σ	−60°C	−2.73; −3.72	−1.96; −2.68	−1.10; −1.75	−0.18; −0.82	0.78;0.23	1.76;1.22	2.82;2.56
		37°C	0.78;−0.68	1.01;−0.23	1.35;0.22	1.81;0.73	2.42;1.42	3.15;2.26	3.93;3.11
		90°C	4.56;[a]	4.61;[a]	4.66;[a]	4.69;[a]	4.57;[a]	4.74;[a]	5.14;[a]
	Tan δ	max.	[a]; 3.2	20.5;[a]	33.1;[a]	[a]	[a]	[a]	[a]
		T°C	[a]; 51	79;[a]	84;[a]	[a]	[a]	[a]	[a]
0.31	Log σ	−60°C	−2.97; −3.46	−2.12; −2.55	−1.30; −1.65	−0.50; −0.74	0.46;0.29	1.42;1.16	2.51;2.11
		37°C	0.37;0.62	0.66;0.74	1.13;0.82	1.56;1.19	2.11;1.74	2.81;2.45	3.61;3.27
		90°C	2.15;0.18	3.81;1.91	3.87;2.77	3.91;2.83	3.96;2.94	4.26;3.60	4.82;4.42
	Tan δ	max.	2.5;6.1	3.3;5.5	[a], 5.3	[a]	[a]	[a]	[a]
		T°C	40,42	56,53	[a], 74	[a]	[a]	[a]	[a]
0.38	Log σ	−60°C	−3.17	−2.29	−1.45	−0.58	0.36	1.26	2.33
		37°C	1.03	1.22	1.44	1.78	2.23	2.87	3.56
		90°C	3.12	4.20	4.26	4.29	4.32	4.48	4.87
	Tan δ	max.	2.4	4.3	23.2	[a]	[a]	[a]	[a]
		T°C	31	47	86	[a]	[a]	[a]	[a]
0.44	Log σ	−60°C	−2.93	−2.09	−1.27	−0.40	0.55	1.48	2.52
		37°C	0.81	1.09	1.27	1.79	2.33	2.99	3.77
		90°C	[a]	3.89	3.92	4.00	4.09	4.51	5.11
	Tan δ	max.	1.8	2.3	[a]	[a]	[a]	[a]	[a]
		T°C	32	48	[a]	[a]	[a]	[a]	[a]
0.63	Log σ	−60°C	−2.94; −2.52	−2.28; −1.68	−1.36; −0.84	−0.48;0.00	0.49;0.87	1.43;1.72	2.57;2.65
		37°C	1.26;1.68	1.62;2.58	1.80;2.70	2.20;2.72	2.57;3.12	3.08;3.66	3.79;4.32
		90°C	[a], 5.18	[a], 5.14	[a], 5.21	[a], 5.24	[a], 5.26	[a], 5.34	[a], 5.60
	Tan δ	max.	2.0;2.8	3.0;3.6	4.9;21.0	[a]	[a]	[a]	[a]
		T°C	24;10	39;26	61;72	[a]	[a]	[a]	[a]

0.75	Log σ	−60°C	−2.53; −2.90	−1.69; −2.05	−0.87; −1.22	−0.03; −0.36	0.80; 0.55	1.66; 1.50	2.73; 2.76
		37°C	0.79; 1.28	1.94; 1.76	2.16; 1.98	2.49; 2.35	3.14; 2.73	3.76; 3.31	4.40; 4.03
		90°C	5.04; 0.33	5.11; 4.03	5.09; 4.08	5.13; 4.11	5.15; 4.14	5.20; 4.41	5.50; 5.00
	Tan δ	max.	1.8; 1.8	2.0; 2.5	a, 4.6	a	a	a	a
		T°C	15; 22	30; 39	; 60	a		a	a
1.50	Log σ	−60°C	−1.67; −1.72	−0.90; −0.92	−0.05; −0.06	0.80; 0.79	1.65; 1.62	2.45; 2.43	3.33; 3.34
		37°C	a, 4.14	4.17; 4.26	4.24; 4.32	4.27; 4.35	4.31; 4.39	4.64; 4.70	5.12; 5.14
		90°C	6.07; 6.07	6.13; 6.13	6.22; 6.23	6.26; 6.27	6.27; 6.28	6.28; 6.29	6.27; 6.34
	Tan δ	max.	4.8; 8.1	8.7; 10.9	16.2; 16.9	48.5; 55.1	a	a	a
		T°C	−23; 3	16; 12	59; 28	80; 71	a	a	a
2.50	Log σ	−60°C	−0.78; −1.18	−0.40; −0.55	0.31; 0.21	1.01; 1.06	2.00; 1.93	2.86; 2.78	3.72; 3.64
		37°C	5.21; 5.16	5.43; 5.33	5.49; 5.38	5.51; 5.40	5.53; 5.41	5.56; 5.45	5.72; 5.64
		90°C	6.37; 6.36	6.45; 6.46	6.61; 6.59	6.64; 6.62	6.65; 6.63	6.65; 6.63	6.66; 6.64
	Tan δ	max.	29.0; 22.2	36.1; 29.3	39.5; 37.8	59.8; 60.6	a	a	a
		T°C	−22; −18	−17; −16	0; 4	51; 37	a	a	a
3.50	Log σ	−60°C	a, −1.57	a, −0.87	a, −0.05	a, 0.83	a, 1.73	a, 2.61	a, 3.49
		37°C	5.54; 5.13	5.80; 5.39	5.84; 5.44	5.85; 5.46	5.86; 5.47	5.87; 5.49	5.94; 5.85
		90°C	6.57; 6.33	6.63; 6.46	6.80; 6.65	6.83; 6.68	6.83; 6.69	6.84; 6.70	6.84; 6.70
	Tan δ	max.	33.1; 20.0	103.4; 48.3	143.4; 57.6	166.2; 76.7	284.0; a	a	a
		T°C	−23; −23	−21; −16	−5; −1	24; 25	79; a	a	a
5.60	Log σ	−60°C	5.91; 5.65	6.21; 5.99	6.30; 6.06	6.31; 6.07	6.31; 6.07	6.31; 6.07	6.31; 6.09
		37°C	6.83; 6.67	6.87; 6.74	7.04; 6.96	7.10; 7.00	7.10; 7.00	7.10; 7.00	7.10; 7.00
		90°C	a, 8.8		a	a			a
	Tan δ	max.		28.3; 22.3	71.0; 73.6	167.0; 155.7	325.4; 277.6	a	a
		T°C	a, −18.1	−16; −11	−8; −5	9; 8	48; 64	a	a

a Values were outside the test range.

Table 5
Measured values of log σ and tan δ for nine plasticizer levels of PVC membranes plasticized with dioctyl sebacate (DOS). All temperature values are within ±2°C.

phr Ratio	Dielectric measurement		Log f						
			−1	0	1	2	3	4	5
0.30	Log σ	−60°C	−3.29; −2.73	−2.43; −1.94	−1.62; −1.11	−0.76; −0.20	0.32; 0.72	1.26; 1.68	2.57; 2.64
		37°C	0.32; 0.98	0.81; 1.16	1.00; 1.67	1.45; 2.22	2.02; 2.77	2.71; 3.40	3.52; 4.10
		90°C	−0.43; 4.73	1.70; 4.79	2.83; 4.68	2.97; 4.71	3.09; 4.74	3.60; 4.91	4.43; 5.26
	Tan δ	max.	2.5; 2.7	3.9; 15.8	2.9; 29.1	[a]			[a]
		T°C	39; 38	52; 71	77; 83	[a]			[a]
0.39	Log σ	−60°C	−2.61	−1.78	0.95	−0.08	0.75	1.65	2.64
		37°C	1.31	1.83	1.82	2.45	3.02	3.61	4.27
		90°C	5.20	5.26	5.33	5.36	5.38	5.43	5.55
	Tan δ	max.	1.9	9.9	20.2	[a]	[a]		[a]
		T°C	26	64	73	[a]	[a]		[a]
0.47	Log σ	−60°C	−2.83	−2.00	−1.15	−0.26	0.65	1.55	2.50
		37°C	0.80	1.11	1.51	1.96	2.68	3.37	4.08
		90°C	4.52	4.62	4.75	4.83	4.88	5.06	5.42
	Tan δ	max.	1.5	2.2	[a]	[a]	[a]		[a]
		T°C	30	49	[a]	[a]	[a]		[a]
0.55	Log σ	−60°C	−2.62; −2.57	−1.81; −1.76	−0.97; −0.91	−0.09; −0.03	0.79; 0.85	1.68; 1.74	2.60; 2.67
		37°C	0.87; 1.34	1.82; 2.16	2.01; 2.28	2.57; 2.50	3.16; 3.04	3.72; 3.65	4.34; 4.31
		90°C	5.12; 4.77	5.19; 4.85	5.29; 4.92	5.34; 4.95	5.36; 4.97	5.41; 5.04	5.62; 5.39
	Tan δ	max.	1.4; 2.6	1.7; 3.0	12.1; 21.0	[a]	[a]		[a]
		T°C	21; 17	36; 33	75; 85	[a]	[a]		[a]
0.61	Log σ	−60°C	−2.21; −2.62	−1.42; −1.81	−0.62; −0.98	0.19; −0.12	1.03; 0.76	1.82; 1.64	2.83; 2.61
		37°C	1.44; 0.11	2.87; 2.00	2.95; 2.29	3.10; 2.60	3.58; 3.15	4.06; 3.70	4.61; 4.31
		90°C	5.42; 5.29	5.48; 5.35	5.57; 5.45	5.62; 5.49	5.64; 5.51	5.67; 5.54	5.76; 5.71
	Tan δ	max.	3.0; 1.1	7.6; 1.5	11.2;[a]	27.7;[a]	[a]		[a]
		T°C	6; 16	43; 29	52;[a]	83;[a]	[a]		[a]

0.78	Log σ	−60°C	−1.92; −1.95	−1.18; −1.22	−0.39; −0.43	0.43; 0.38	1.30; 1.25	2.17; 2.11	3.12; 3.03
		37°C	−0.20; −0.11	3.61; 3.05	3.67; 3.51	3.71; 3.56	3.76; 3.61	3.96; 3.85	4.48; 4.46
		90°C	5.35; 5.21	5.70; 5.61	5.67; 5.62	5.69; 5.64	5.70; 5.64	5.71; 5.66	5.74; 5.69
	Tan δ	max.	3.0; 2.2	3.6; 2.5	27.7; 21.9	84.1; 74.9	a	a	a
		T°C	−22; −19	−4; −1	49; 50	69; 70	a	a	a
0.92	Log σ	−60°C	−2.08; −2.07	−1.28; −1.27	−0.47; −0.46	0.35; 0.35	1.20; 1.19	2.05; 1.94	3.02; 2.90
		37°C	a	2.91; 2.21	3.17; 2.81	3.25; 2.97	3.65; 3.38	4.30; 4.11	4.81; 4.68
		90°C	5.74; 5.49	5.80; 5.56	5.89; 5.66	5.94; 5.68	5.95; 5.70	5.97; 5.71	6.07; 5.82
	Tan δ	max.	2.3; 1.7	2.7; 1.8	12.1; 16.6	a; 55.9	a	a	a
		T°C	0; 1	16; 17	56; 79	a; 89	a	a	a
1.86	Log σ	−60°C	−2.44; −2.36	−1.63; −1.54	−0.80; −0.70	−0.03; 0.14	0.84; 1.01	1.70; 1.85	2.65; 2.82
		37°C	0.21; a	2.40; 2.43	2.63; 2.95	2.81; 2.90	3.08; 3.27	3.67; 3.88	4.31; 4.50
		90°C	2.21; 5.30	4.77; 5.36	4.85; 5.43	4.88; 5.46	4.89; 5.48	4.93; 5.50	5.28; 5.72
	Tan δ	max.	1.5; 2.1	2.3; 2.5	21.3; 28.2	39.0; a	a	a	a
		T°C	9; 0	25; 18	71; 68	85; a	a	a	a
4.12	Log σ	−60°C	0.26; 0.21	0.45; 0.41	0.64; 0.80	1.26; 1.36	2.01; 1.98	2.91; 2.88	3.88; 3.85
		37°C	4.91; 4.82	5.08; 5.00	5.12; 5.03	5.13; 5.04	5.14; 5.05	5.07; 5.08	5.25; 5.26
		90°C	5.90; 5.82	6.24; 6.18	6.26; 6.29	6.27; 6.31	6.28; 6.32	6.29; 6.32	6.30; 6.26
	Tan δ	max.	49.8; 40.9	70.8; 59.9	102.2; 93.8	154.7; 140.7	a	a	a
		T°C	−27; −27	−17; −17	6; 9	48; 54	a	a	a

[a] Values were outside the test range.

Table 6
Measured values of log σ and tan δ for four plasticizer levels of PVC membranes plasticized with epoxidized linseed oil (ELO). All temperature values are within ±2°C.

phr Ratio	Dielectric measurement		Log f						
			-1	0	1	2	3	4	5
0.75	Log σ	-60°C	-2.98	-2.22	-1.38	-0.37	0.67	1.72	2.90
		37°C	1.60	2.84	2.88	2.92	3.14	3.69	4.33
		90°C	5.45	5.52	5.55	5.57	5.48	5.49	5.60
	Tan δ	max.	5.9	47.4	101.4	143.0	[a]	[a]	[a]
		T°C	2	49	65	85	[a]	[a]	[a]
1.25	Log σ	-60°C	-2.37; -2.50	-1.65; -1.77	-0.87; -0.96	0.05; -0.02	1.04; 0.98	2.05; 2.02	3.15; 3.16
		37°C	4.31; 4.28	4.34; 4.17	4.37; 4.19	4.38; 4.21	4.41; 4.23	4.56; 4.41	4.89; 4.79
		90°C	6.08; 6.00	6.13; 6.04	6.17; 6.08	6.19; 6.10	6.20; 6.11	6.21; 6.12	6.15; 6.14
	Tan δ	max.	121.8; 120.8	102.5; 106.5	134.9; 128.0	155.1; 155.0	[a]	[a]	[a]
		T°C	7; 9	18; 18	41; 42	65; 71	[a]	[a]	[a]
1.75	Log σ	-60°C	-2.26; [a]	-1.52; [a]	-0.73; [a]	0.15; [a]	1.04; [a]	2.08; [a]	3.24; [a]
		37°C	4.36; 4.93	4.40; 4.96	4.43; 4.98	4.44; 4.99	4.46; 5.00	4.60; 5.03	4.86; 5.11
		90°C	6.07; 6.20	6.03; 6.23	6.07; 6.25	6.09; 6.27	6.10; 6.28	6.11; 6.28	6.14; 6.29
	Tan δ	max.	155.1; [a]	98.3; 192.4	115.6; 243.9	144.3; 259.5	[a]	[a]	[a]
		T°C	5; [a]	14; 6	35; 28	64; 58	[a]	[a]	[a]
2.00	Log σ	-60°C	-2.11; [a]	-1.39; [a]	-0.61; [a]	0.27; [a]	1.24; [a]	2.25; [a]	3.37; [a]
		37°C	4.82; 5.01	4.73; 5.05	4.75; 4.93	4.77; 4.95	4.78; 4.96	4.86; 5.00	5.09; 5.18
		90°C	6.05; [a]	6.13; [a]	6.18; [a]	6.19; [a]	6.20; [a]	6.20; [a]	6.21; [a]
	Tan δ	max.	123.9; [a]	127.1; 151.7	177.5; 200.1	267.5; 266.7	[a]	[a]	[a]
		T°C	3; [a]	10; 4	32; 26	62; 57	[a]	[a]	[a]

[a] Values were outside the test range.

Table 7
Measured values of log σ and tan δ for five plasticizer levels of PVC membranes plasticized with epoxidized soybean oil (ESO). All temperature values are within $\pm 2°C$.

phr Ratio	Dielectric measurement		Log f						
			−1	0	1	2	3	4	5
0.25	Log σ	−60°C	−4.49; −3.93	−3.43; −3.06	−2.55; −2.35	−1.23; −1.12	0.00;0.04	1.06;1.10	2.41;2.36
		37°C	0.83;0.85	0.93;0.96	1.44;1.44	1.77;1.75	2.13;2.13	2.73;2.78	3.51;3.57
		90°C	0.60;0.68	2.26;3.17	3.33;3.58	3.38;3.66	3.41;3.69	3.55;3.81	4.25;4.36
	Tan δ	max.	1.4;1.3	2.8;2.9	[a],3.7	[a]	[a]	[a]	[a]
		$T°C$	32;33	45;46	[a],58	[a]	[a]	[a]	[a]
0.75	Log σ	−60°C	−2.97;3.53	−2.16; −2.68	−1.33; −1.84	−0.37; −0.78	0.62;0.29	1.66;1.37	2.93;2.56
		37°C	3.75;1.29	3.82;2.23	3.85;2.32	3.88;2.40	3.92;2.71	4.16;3.44	4.61;4.12
		90°C	5.67;5.03	5.75;5.22	5.84;5.16	5.86;5.18	5.87;5.20	5.88;5.21	5.92;5.36
	Tan δ	max.	6.0;2.2	48.1;21.2	78.1;57.3	145.1;[a]	[a]	[a]	[a]
		$T°C$	−9;8	21;51	41;63	70;[a]	[a]	[a]	[a]
1.25	Log σ	−60°C	−2.68	−1.90	−1.10	−0.19	0.77	1.79	2.98
		37°C	4.05	4.13	4.16	4.17	4.19	4.33	4.69
		90°C	5.67	5.84	5.94	5.95	5.96	5.97	5.99
	Tan δ	max.	44.0	81.2	99.8	156.5	[a]	[a]	[a]
		$T°C$	6	11	33	68	[a]	[a]	[a]
1.75	Log σ	−60°C	−2.13; −2.07	−1.52; −1.29	−0.72; −0.48	0.15;0.35	1.10;1.26	2.10;2.14	3.24;3.26
		37°C	4.68;4.82	4.62;4.90	4.65;4.93	4.67;4.94	4.68;4.96	4.77;4.86	5.00;5.05
		90°C	5.94;[a]	6.08;6.12	6.16;6.19	6.17;6.21	6.18;6.21	6.18;6.16	6.19;6.16
	Tan δ	max.	77.7;90.9	100.8;110.5	136.4;145.8	209.2;246.9	[a]	[a]	[a]
		$T°C$	−5; −6	6;5	27;25	64;57	[a]	[a]	[a]
2.00	Log σ	−60°C	[a], −2.45	[a], −1.68	[a], −0.88	[a],0.00	[a],0.97	[a],1.99	[a],3.12
		37°C	4.93;4.44	4.99;4.50	5.01;4.52	5.02;4.53	5.03;4.55	5.05;4.66	5.18;4.92
		90°C	6.04;[a]	6.16;[a]	6.17;[a]	6.18;[a]	6.19;[a]	6.19;[a]	6.20;[a]
	Tan δ	max.	[a],41.5	196.2;88.9	247.9;133.6	310.6;[a]	[a]	[a]	[a]
		$T°C$	[a],2	1;10	23;32	58;[a]	[a]	[a]	[a]

[a] Values were outside the test range.

Table 8
Measured values of $\log \sigma$ and $\tan \delta$ for four plasticizer levels of PVC membranes plasticized with *ortho*-nitrophenyl octyl ether (o-NPOE). All temperature values are within $\pm 2^\circ$C.

phr Ratio	Dielectric measurement		Log f						
			-1	0	1	2	3	4	5
0.41	Log σ	-60°C	-2.78	-2.01	-1.26	-0.36	0.56	1.47	2.73
		37°C	0.80	1.43	1.50	2.03	2.75	3.65	4.34
		90°C	1.87	2.84	2.88	2.92	3.03	3.37	4.11
	Tan δ	max.	0.9	18.8	a	a	a	a	a
		T°C	29	68	a	a	a	a	a
0.76	Log σ	-60°C	-2.80	-1.95	-1.08	-0.22	0.64	1.46	2.51
		37°C	0.78	1.63	1.87	2.32	2.87	3.40	4.11
		90°C	4.73	4.91	5.01	5.05	5.08	5.17	5.37
	Tan δ	max.	0.9	1.9	a	a	a	a	a
		T°C	21	38	a	a	a	a	a
1.55	Log σ	-60°C	-2.04	-1.17	-0.28	0.55	1.31	1.84	2.53
		37°C	0.50	3.43	3.88	3.93	3.97	4.08	4.51
		90°C	5.44	5.88	5.96	6.01	6.03	6.04	6.05
	Tan δ	max.	3.06	3.1	9.5	32.9	a	a	a
		T°C	-21	-6	45	61	a	a	a
7.15	Log σ	-60°C	-2.40; 0.70	0.75; 0.62	1.06; 1.22	1.84; 1.99	2.67; 2.81	3.36; 3.50	3.94; 4.06
		37°C	5.01; 5.28	5.43; 5.69	5.96; 6.04	6.15; 6.16	6.09; 6.18	6.10; 6.19	6.13; 6.21
		90°C	6.45; 6.51	6.94; 6.98	7.08; 7.18	7.16; 7.22	7.15; 7.25	7.16; 7.27	7.16; 7.27
	Tan δ	max.	10.8; 16.0	18.9; 26.5	24.1; 32.9	30.6; 40.8	40.1; 52.9	a	a
		T°C	-46; -44	-36; -34	-22; -20	-3; 0	28; 30	a	a

a Values were outside the test range.

Table 9
Measured values of log σ and tan δ for five plasticizer levels of PVC membranes plasticized with propylene glycol dioleate (PGDO). All temperature values are within ±2°C.

phr Ratio	Dielectric measurement		Log f						
			−1	0	1	2	3	4	5
0.50	Log σ	−60°C	a	−3.16	−2.04	−1.04	0.01	1.06	2.46
		37°C	−0.65	1.81	2.05	2.16	2.39	3.10	3.80
		90°C	a	4.94	5.03	5.06	5.07	5.09	5.20
	Tan δ	max.	2.8	2.0	29.4	a	a	a	a
		T°C	2	21	67	a	a	a	a
1.00	Log σ	−60°C	−2.67; −2.38	−1.89; −1.62	−1.11; −0.83	−0.30; −0.01	0.47; 0.85	1.46; 1.81	2.70; 3.00
		37°C	3.66; 3.76	3.78; 3.88	3.82; 3.92	3.85; 3.94	3.69; 3.97	3.97; 4.23	4.44; 4.69
		90°C	5.41; 5.45	5.73; 5.64	5.86; 5.76	5.88; 5.78	5.81; 5.79	5.82; 5.80	5.85; 5.85
	Tan δ	max.	6.3; 9.6	38.1; 23.2	46.9; 32.9	110.9; 83.9	a	a	a
		T°C	−12; 3	16; 13	36; 34	66; 72	a	a	a
1.50	Log σ	−60°C	−2.00	−1.22	−0.42	0.37	1.20	2.10	3.16
		37°C	4.39	4.49	4.52	4.53	4.55	4.65	4.95
		90°C	5.66	5.91	6.03	6.05	6.06	6.07	6.11
	Tan δ	max.	42.8	65.8	88.9	116.9	a	a	a
		T°C	0	5	24	61	a	a	a
1.70	Log σ	−60°C	−2.31; −2.38	−1.53; −1.60	−0.74; −0.81	0.09; 0.03	1.00; 0.93	1.97; 1.91	3.13; 3.06
		37°C	4.94; 4.84	5.08; 4.96	5.09; 4.98	5.10; 4.98	5.10; 4.98	5.13; 5.02	5.29; 5.21
		90°C	6.19; 6.12	6.28; 6.23	6.41; 6.37	6.43; 6.38	6.43; 6.39	6.43; 6.39	6.43; 6.39
	Tan δ	max.	111.1; 125.1	83.8; 88.6	116.2; 123.0	172.8; 167.9	268.4; 268.6	a	a
		T°C	−4; −2	0; 0	14; 16	49; 51	82; 84	a	a
2.00	Log σ	−60°C	a	a	a	a	a	a	a
		37°C	4.75	4.88	4.81	4.82	4.83	4.90	5.11
		90°C	5.92	6.08	6.18	6.20	6.21	6.21	6.22
	Tan δ	max.	38.6	71.7	103.8	138.4	a	a	a
		T°C	0	4	18	56	a	a	a

a Values were outside the test range.
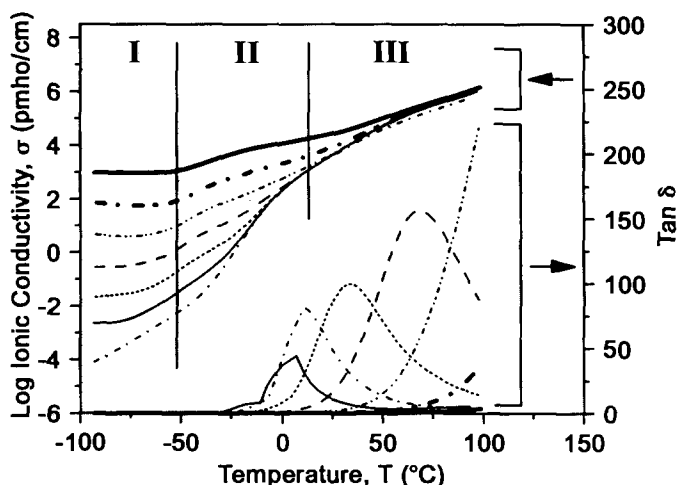
Fig. 2. Typical plot showing the effects of frequency (f) on $\log \sigma$ and tan δ versus temperature (T). The graph shows the data for an ESO-plasticized PVC membranes at a phr ratio of 1.25 for the frequencies 10^5 Hz (——), 10^4 Hz (—·—·), 10^3 Hz (–··–··), 10^2 Hz (— —), 10^1 Hz (····), 10^0 Hz (——), and 10^{-1} Hz (–·–·).
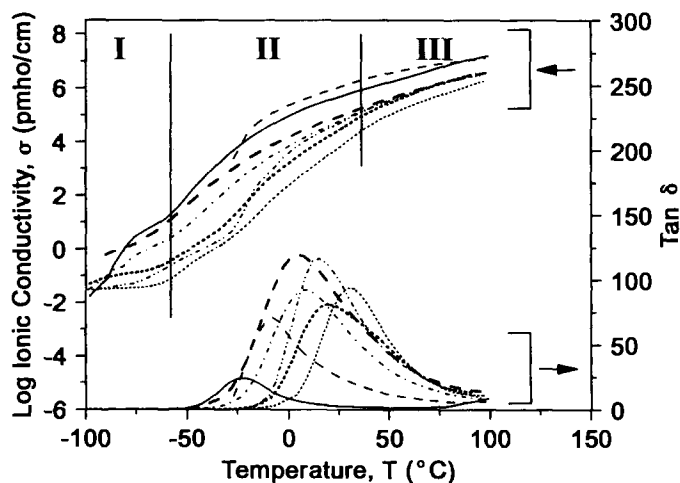

Fig. 3. Electrical properties of plasticized PVC membranes at 200 phr for seven plasticizers. The graph shows the 10 Hz data for CF (–·–·), DBS (— —), DOS (——), ELO (·····), ESO (– – – –), o-NPOE (——), and PGDO (–··–··). Note that the phr ratios will differ (see Eq. (3)), since the MWs of each plasticizer differ (Eq. (2)), as Table 1 shows.

III of Fig. 2), the $\log \sigma$ was noted to be independent of the frequency. Region III represented a region where the plasticization and temperature were great enough to facilitate fully the mobility of ions within the membrane. Again in Region III of Fig. 3, the increase in temperature increased the mobility of the system enough

that the effects of plasticizer species were substantially reduced. Finally, in Fig 2 and Tables 2–9, the magnitude of the tan δ peak increased as frequency increased. Dipole activity was greatest when the temperature and frequency were greatest.

4.2. Overall dependence

The log σ was known to be directly dependent on the viscosity of the membrane [19]. Fouss showed that the logarithm of the viscosity (μ) was inversely proportional to the logarithm of the relative concentration of plasticizer within a membrane [22], and Leilich found that the μ of the membrane was directly related to the μ of the plasticizer [11]. Since the μ of the plasticizer increased as MW increased (see Table 1), the log σ should be dependent on the log(phr ratio). Also, the log σ increased substantially at the outset of increased plasticization, but approached a steady value at higher levels of plasticization (see Fig. 1). This relationship was observed throughout the range of frequencies and temperatures tested (see Tables 2–9). Thus, that dependency also indicated a linear relationship between log σ and the log(phr ratio). Graphing the results of each plasticized membrane on a log σ versus log(phr ratio) plot confirmed the linear relationship over the range of temperatures tested (Fig. 4 and Table 10). Note
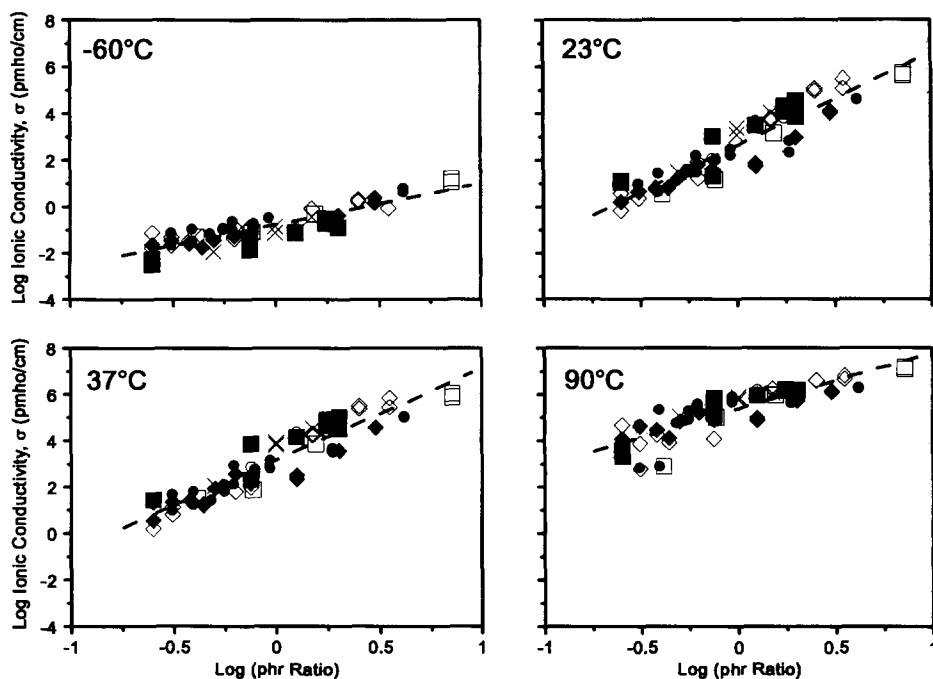
Fig. 4. Typical dependence of log σ versus log(phr ratio) at 10 Hz using all seven plasticizers: CF (◆), DBS (◇), DOS (●), ELO (○), ESO (■), o-NPOE (□), and PGDO (×). Each data points represents one plasticized PVC membrane.

Table 10
Regression data for selected $\log \sigma$ versus log(phr ratio) plots. The probability, p, was $p < 0.001$ for all values, except where noted.

Regression quantity	Temp./ °C	Log f						
		−1	0	1	2	3	4	5
Slope	−90	1.15	1.07	0.80	0.61	0.45	0.35	0.39
	−60	2.24	1.91	1.78	1.35	1.42	1.29	1.00
	−30	3.89	3.28	2.87	2.27	1.87	1.69	1.55
	0	5.09	4.54	3.87	3.04	2.51	1.97	1.62
	23	4.67	4.45	4.00	3.45	2.78	2.16	1.63
	37	4.18	4.13	3.93	3.5	2.89	2.13	1.66
	60	3.94	3.44	3.45	3.33	2.95	2.30	1.65
	90	3.23	2.57	2.43	2.41	2.41	2.08	1.64
Intercept	−90	−3.38	−2.43	−1.53	−0.58	0.49	1.54	2.71
	−60	−2.29	−1.55	−0.77	0.00	1.00	1.89	2.92
	−30	−0.72	−0.20	0.38	0.99	1.72	2.50	3.37
	0	0.97	1.33	1.70	2.14	2.57	3.18	3.90
	23	1.93	2.35	2.61	2.89	3.22	3.69	4.28
	37	2.51	3.02	3.19	3.58	3.64	4.06	4.54
	60	3.77	4.04	4.19	4.27	4.39	4.65	5.04
	90	4.81	5.24	5.36	5.39	5.40	5.47	5.68
Correlation coefficient (r)	−90	0.655	0.694	0.637	0.590	0.519	0.411[a]	0.435
	−60	0.878	0.843	0.882	0.754	0.886	0.887	0.847
	−30	0.920	0.920	0.910	0.927	0.887	0.939	0.936
	0	0.925	0.936	0.938	0.780	0.936	0.929	0.928
	23	0.861	0.927	0.936	0.934	0.922	0.922	0.917
	37	0.805	0.926	0.938	0.936	0.923	0.889	0.915
	60	0.853	0.865	0.912	0.917	0.914	0.905	0.904
	90	0.688	0.814	0.854	0.856	0.863	0.846	0.869
Number of samples (n)	−90	59	63	63	62	63	62	63
	−60	65	66	66	66	66	66	66
	−30	67	67	68	68	68	68	68
	0	71	71	70	71	71	71	71
	23	69	71	71	71	71	71	71
	37	64	71	71	71	71	71	71
	60	60	70	70	70	70	70	70
	90	63	67	68	68	68	68	69

[a] $p < 0.01$.

that all of the plasticizers were plotted on each graph, and a common linear regression analysis was performed for each graph. The slopes of these lines were indicative of the sensitivities of the membranes to plasticization, and the intercepts, at log(phr ratio) = 0, were measures of the ionic mobilities that occurred at the theoretical minimum for complete plasticization (phr ratio = 1). These intercepts increased with increasing temperature. In the low temperature region where $\log \sigma$ was nearly constant (Region I of Fig. 1), the slope of the $\log \sigma$ versus log(phr ratio) line was relatively low, and the

influence of plasticization was minimal. The 23°C and 37°C plots both had high slopes, indicating that the plasticization was important in that temperature domain. These two temperatures typically fell in the high slope region (Region II of Fig. 1) of the $\log \sigma$ versus temperature plot. Recall that the $\log \sigma$ values in this region were increased due to plasticization for two reasons: the onset of the high slope region occurred at a lower temperature with increased plasticization, and the slope increased as plasticization increased. At 90°C the slope of the $\log \sigma$ versus (phr ratio) plot diminished (Region III of Fig. 1). At high temperatures, the specifics of plasticization were less important because all of the available dipoles were already mobilized by the thermal excitation. Table 10 shows the slope and intercept data acquired from similar graphs produced over the full range of temperatures and frequencies tested. Correlation coefficients (r) of these linear regression lines were significant at probabilities (p) of $p < 0.001$ in all cases, except at $-90°C$ and 10^4 Hz, where $p < 0.01$.

4.3. Specific trends

The slopes and intercepts (Table 10) of the selected $\log \sigma$ versus log(phr ratio) plots were linearly dependent on the log(frequency) (Fig. 5). The linear regressions of the dependency of both slope and intercept versus the log(frequency) were significant throughout the range of temperatures tested (Table 11). Both the slopes and the intercepts of the $\log \sigma$ versus log(phr ratio) plots converged at high frequencies, which was indicative of the temperature independence of both quantities at high frequencies. This was consistent with the previous observation that the slopes of the $\log \sigma$ versus log(phr ratio) plots decreased as frequency increased, which indicated that the membranes became less sensitive to phr ratio at high frequencies.

The functional dependencies of the slopes and intercepts versus temperature of selected $\log \sigma$ versus log(phr ratio) plots were not as clearly defined (Fig. 6 and Table 10). The peak observed in the slope of the $\log \sigma$ versus log(phr ratio) plots of Fig. 4 occurred between 23°C and 37°C. The magnitudes of the slopes were higher at lower frequencies and disappeared altogether at high frequencies, which indicated frequency independence of the slope at high frequencies. For those frequencies where the slope reached a peak value, the peak temperature was observed to increase as frequency increased (dashed line in Fig. 6, top). For all frequencies, 23 and 37°C were among the temperatures most sensitive to changes in the phr ratio. As noted previously, the high sensitivity at these temperatures resulted from the two influences of plasticization on the high slope portion of the $\log \sigma$ versus temperature plots (Region II of Fig. 1). The high sensitivities at room and body temperatures are of critical importance, since the phr ratio must be well-controlled to avoid substantial changes in the σ of the plasticized membranes. At high temperatures, the frequency became less sensitive, as indicated by the range of temperatures. The convergence of the intercepts with increasing temperature indicated that the influence of the frequency was diminishing at high temperatures.
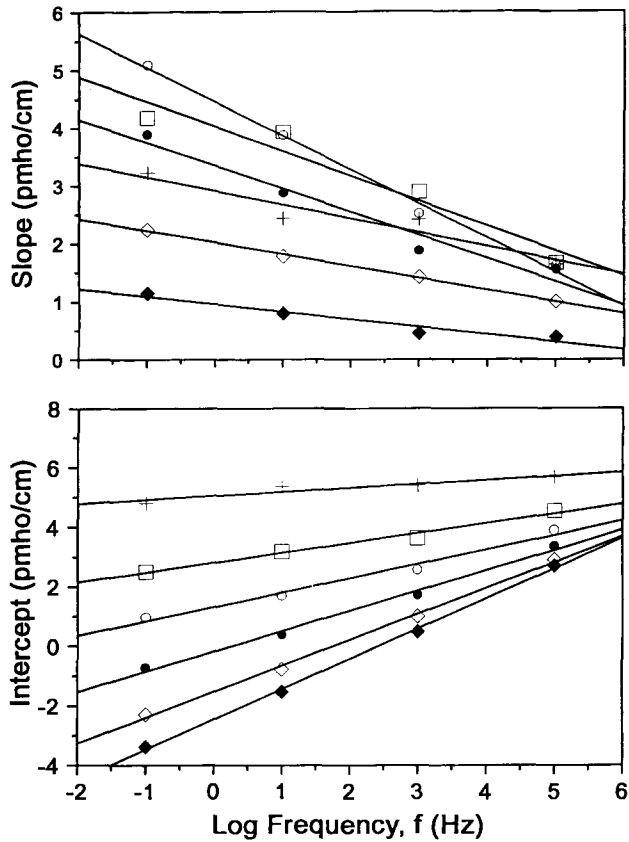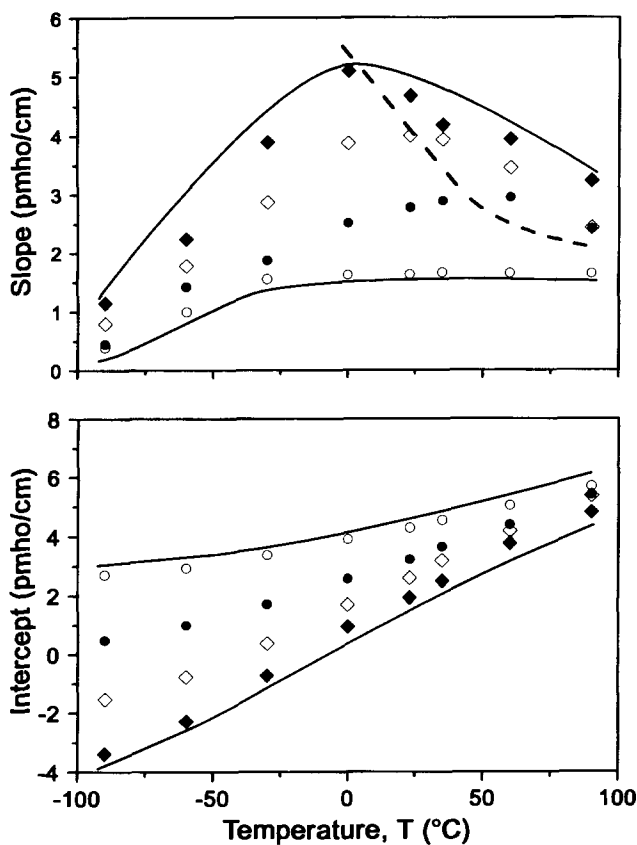
Fig. 5. Dependence of the slopes and intercepts versus the test frequency (f) for the $\log \sigma$ versus log(phr ratio) plots of Fig. 4 and 3–9 at six temperatures (T): $-90°C$ (◆), $-60°C$ (◇), $-30°C$ (●), $0°C$ (○), $37°C$ (□), and $90°C$ (+).

Table 11

Correlation coefficients (r) for slopes and intercepts of $\log \sigma$ versus log(phr ratio) plots versus log frequency (f) as shown in Fig. 5. In all cases, the number of samples was seven, and the probability, p, was $p < 0.001$ for all values, except where noted.

Temperature/ °C	Correlation coefficients (r) for slope vs. Log(f)	Correlation coefficients (r) for intercept vs. Log(f)
-90	0.963	0.999
-60	0.966	0.998
-30	0.978	0.995
0	0.994	0.991
23	0.992	0.990
37	0.967	0.986
60	0.948[a]	0.973
90	0.922[a]	0.896[a]

[a] $p < 0.01$

Fig. 6. Dependence of the slopes and intercepts versus temperature (T) for the $\log \sigma$ versus log(phr ratio) plots of Fig. 4 and Table 3–9 at four frequencies (f): 10^5 Hz (○), 10^3 Hz (●), 10^1 Hz (◇), and 10^{-1} Hz (◆).

4.4. In perspective

The $\log \sigma$ was a function of plasticizer species, phr ratio, frequency, and temperature. The effect of plasticizer species was related to the MW of the plasticizer. However using the phr ratio in lieu of the traditional mass percentage to express the level of plasticization inherently accounted for changes in the plasticizer MW and therefore plasticizer species. Increases in the phr ratio or electric field frequency increased the $\log \sigma$ over the range of test temperatures. The temperature of the system effectively acted as a limiting agent, where substantial increases in $\log \sigma$ could only be attained above certain characteristic temperatures. That limiting temperature was reduced by increasing the phr ratio or the electric field frequency. In biosensor applications, only the frequency and temperature response are fixed. Thus the present functional relationship between the $\log \sigma$ and log(phr ratio) allows the plasticizer species and/or the

amount of plasticizer to be selected and/or reduced, respectively, in many membrane, ISE, and biosensor applications without compromising the electrical properties. Consequently, the mechanical integrity and function of the biosensor should be improved, and the negative effects of plasticizer leaching out during in vivo applications should be reduced.

5. Conclusions

At relatively low phr ratios, the $\log \sigma$ increased substantially as the phr ratio increased. Above phr ratios of 0.75–1.00 (the exact value is plasticizer-species-dependent), the PVC membranes became less sensitive to the amount of plasticizer. The traditional value of 200 phr used in biosensor applications was unnceessary for all plasticizers considered. Increased amounts of plasticizer reduced the temperature at which the $\tan \delta$ peak occurred and increased the magnitude of the $\tan \delta$ peak, which was indicative of an increase in the number of active charge carriers. The $\log \sigma$ increased with increasing phr ratio throughout the range of temperatures considered. When the temperature and frequency increased, the $\log \sigma$ increased. The $\log \sigma$ had a linear dependency on the log(phr ratio) at a given temperature and frequency. The slope and intercept of the $\log \sigma$ versus log(phr ratio) line were linearly dependent on the frequency of the applied electric field at a given temperature. The slope of the $\log \sigma$ versus log(phr ratio) line was maximized in the range of 0–40°C at low frequencies, becoming less sensitive at high frequencies. The intercept of the $\log \sigma$ versus log(phr ratio) line increased with both increasing frequency and increasing temperature.

Acknowledgments

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