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Influence of plasticizer configurational changes on the mechanical properties of highly plasticized poly(vinyl chloride)

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The effects of configurational changes among nine plasticizers were studied using puncture tests. Ion-selective poly(vinyl chloride) (PVC) membranes were plasticized with three citrate-related compounds (Citroflex A-4 (CFA4), Citroflex A-6 (CFA6), and Citroflex B-6 (CFB6)) and six sebacate-related compounds (dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), dioctyl sebacate (DOS), dioctyl azelate (DOZ), and dioctyl adipate (DOA)). The strengths, stiffnesses, and toughnesses of the membranes increased at low PHR ratios (which are defined as the actual concentrations of plasticizer to PVC divided by the minimum concentrations of plasticizer required to isolate all of the PVC polar groups) and then monotonically decreased as plasticizer was added above these ratios. The ductilities increased up to PHR ratios of about 2.0 and decreased above PHR ratios of about 4.0. The citrate-related compounds could not be distinguished according to the mechanical properties. The DMS-, DES-, and DOA-plasticized membranes were generally stronger and stiffer than the DBS-, DOS-, and DOZ-plasticized membranes, but the ductilities were reduced using DMS, DES, and DOA. A nomogram was constructed to predict the strength, based on the plasticizer selection and PHR ratio. The strengths, stiffnesses, and toughnesses of the membranes decreased as the log (ionic conductivity, σ) increased, and the ranking of the configurational differences was similar to those of the mechanical properties *versus* PHR ratio. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Brous and Semon studied 500 different plasticizers for use in poly(vinyl chloride) PVC in 1935[1]. In 1945, Mead and Fuoss added electrolytes to plasticized PVC and initiated the use of polymers as conductive materials[2]. Moore and Pressman added valinomycin to PVC in 1964, creating the first non-glass ion-selective electrode (ISE)[3]. In 1970, Frant and Ross used this type of electrode for measurements of the potassium ion[4]. These earliest ion-selective membranes were plasticized with a 2:1 ratio of plasticizer:PVC by mass, or equivalently 200 parts per hundred resin (PHR)[5]. This ratio was 3–10 times greater than other applications of plasticized PVC[6]. Using these high plasticizer ratios in 1978, Hill *et al.* produced PVC membranes for measurements of myocardial K^+ ion concentrations[7]. In these highly plasticized membranes, the PVC provided a structural framework, and the plasticizer facilitated the diffusion of ionic complexes through the membrane[3]. The plasticizer leached from the highly plasticized membranes and formed a highly resistive surface layer[8]. This layer of plasticizer interrupted ion transport and, due to the toxicity of traditional plasticizers, increased the likelihood of negative reactions during *in vivo* applications.

In two previous works[9,10], three traditional plasticizers and four natural derivatives were investigated at different levels of plasticization. Based on dielectric analyses, the ionic conductivity (σ, the capacity of a membrane to transfer ions) increased substantially as the PHR ratio was increased

from 0 to about 0.75 or 1.0, depending on the plasticizer species[9]. Because less substantial increases were observed above these PHR ratios, the amount of plasticizer could be reduced from the traditional 200 PHR. Subsequent mechanical analysis indicated that stronger and tougher membranes were produced when less plasticizer was used in these membranes[10]. These increases in strength and toughness decreased the likelihood of ISE and biosensor damage during production, insertion, and operation. Furthermore, the reductions in plasticizer deterred the negative biological consequences associated with leaching of the plasticizer. While little difference was observed due to plasticizer selections during the dielectric tests, the mechanical tests indicated that plasticizers having relatively low molecular weights (MWs) improved the strengths and toughnesses of the membranes throughout the range of plasticization.

Using three of the lower MW plasticizers from the previous studies, a third study examined the effects of configurational changes in the plasticizers[11]. In experiments that were modelled after Heijboer's dynamic mechanical analyses of homologous changes in poly(methacrylate)s[12], nine plasticizers from two homologous series were evaluated using dielectric analysis. The first series of three plasticizers constituted biocompatible derivatives of citrate[13], including a compound, Citroflex B-6, which was used in the previous studies[9,10]. The second series of four plasticizers was related to dibutyl sebacate and dioctyl sebacate, both of which were traditionally used in ISEs and sensors[7,14]. The plasticizers in each series were chosen so that the effects of distinct configurational changes could be examined. The σ values of these membranes were linearly

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Table 1 List of the nine plasticizers, molecular weights (MW), and PHR ratios (see equations (1)–(3)) at the traditional plasticization level of 200 PHR

Plasticizer	Symbol	Molecular Weight (MW)	phr Ratio at 200 phr
Citroflex A-4[a]	CFA4	402	4.4
Citroflex A-6[a]	CFA6	486	3.6
Citroflex B-6[a]	CFB6	514	3.4
Dimethyl sebacate[b]	DMS	230	7.6
Diethyl sebacate[b]	DES	260	6.7
Dibutyl sebacate[c]	DBS	314	5.6
Dioctyl sebacate[b]	DOS	427	4.1
Dioctyl azelate[d]	DOZ	412	4.3
Dioctyl adipate[d]	DOA	373	4.7

The bars indicate homologous compounds
[a]Morflex, Inc. (Greensboro, NC)
[b]Aldrich Chemical Co. (Milwaukee, WI)
[c]Eastman Kodak Co. (Rochester, NY)
[d]C. P. Hall Co. (Memphis, TN)

correlated to the amount of plasticizer in each membrane, depending on the plasticizer species, temperature, and frequency. For each of the homologous groups, a nomogram was constructed so that the σ of the membrane could be predicted throughout the range of frequencies (10^{-1}–10^5 Hz) and temperatures (-100–$+100°C$) tested. Thereby plasticizer selection might be tailored to produce optimal results based on a particular application. The current study was intended to complement the dielectric studies of homologous plasticizers by considering the effects of plasticizer selection on the mechanical properties of highly plasticized PVC.

MATERIALS AND METHODS

Membrane preparation

A 50/50 (w/w) blend of low and high MW PVCs (MW = 77 300 and 193 600; Scientific Polymer) was used to prepare a 1.1 wt% solution of PVC in tetrahydrofuran (THF; Mallinckrodt). This blend of PVCs provided a good combination of strength and processability[15]. The appropriate amount of plasticizer was added to each solution. Five millilitres of the mixture were evaporated from a 2.5 cm diameter glass ring under weighted filter papers for at least 5 days, so that clear, non-turbid membranes were produced. The samples were glued to a 1.2 cm i.d., 0.5 cm long section of Tygon tubing. The Tygon tubing was heated prior to attachment of the PVC membrane, so that the stresses imposed on the tubing during shipping would be relieved. Five to nine levels of plasticization were examined for each plasticizer.

Citroflex A-4 (CFA4), Citroflex A-6 (CFA6), and Citroflex B-6 (CFB6) (*Table 1*) were citrate-related compounds. Each compound had three identical groups at its base (shown to the right of the shaded citrate backbones in *Figure 1*) and a different group at the top (shown to the left of the shaded citrate backbones in *Figure 1*). The citrate backbone of each of these compounds (shaded regions of *Figure 1*) had a tetrahedral conformation in free space, when
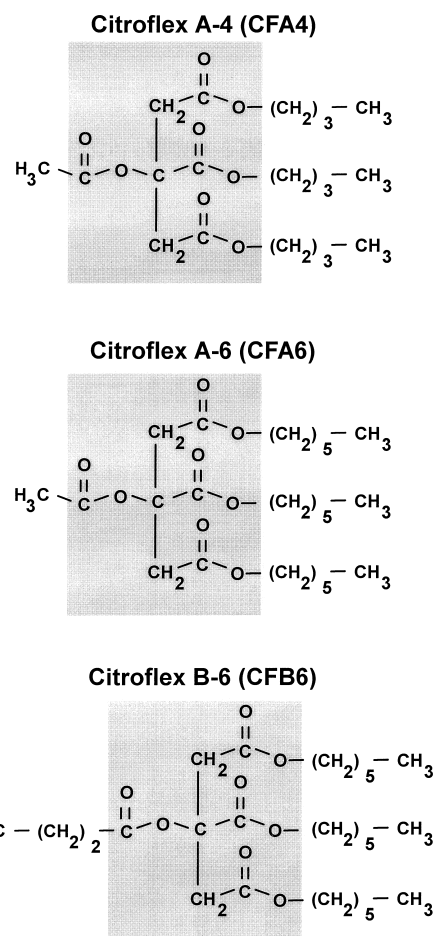

Figure 1 Configurations of the citrate-related plasticizers. The shaded areas represent the citrate base of the compounds, and the bars to the left highlight the homologous compounds

modelled using computational chemistry (Cerius[2] software, Molecular Simulations Inc., San Diego, CA). The group at the top of each molecule had a standard bent chain conformation moving away from the centre of the molecule. The groups at the base also had standard bent chain conformations, but these chains did not move directly away from the centre of the tetrahedron. Instead, these groups spread out at approximately 120° angles from each other in a single plane, forming a triangular structure at the base. Considering the upper two compounds, both the CFA4 and CFA6 had a saturated carbon atom at the top. The CFA4 had four saturated carbon atoms at the base, and the CFA6 had saturated six-carbon-atom chains along the base. These additions decreased the likelihood of entanglements among adjacent PVC molecules in CFA6 compared to CFA4, because of the larger hydrodynamic volume of the CFA6. Considering the lower two compounds, three saturated six-carbon-atom chains formed the bases for both CFA6 and CFB6. The CFB6 had a saturated three-carbon-atom chain substituted at the top. This longer chain length decreased the likelihood of PVC entanglements, since the hydrodynamic volume of the CFB6 would be greater than that of CFA6.

The sebacate-related compounds were based on a binary ester molecule (*Table 1*). Using four sebacates, the changes in the outer chain length and structure were compared: dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), and dioctyl sebacate (DOS) (*Figure 2*). The DMS, DES, and DBS constituted an homologous series of aliphatic one-, two-, and four-carbon-atom chains, respectively. The DOS had two branched, eight-carbon-atom 2-ethylhexyl end-groups. Three structures were used to evaluate the effects of inner chain length: DOS, dioctyl azelate (DOZ), and dioctyl adipate (DOA) (*Figure 2*). The

Figure 2 Configurations of the sebacate-related plasticizers. The shaded areas represent the ester groups of the compounds, and the bars to the left highlight the homologous compounds

aliphatic chains between the esters of these plasticizers were varied as eight-, seven-, and four-carbon-atom chains, respectively. The increased chain lengths in either the inner or outer chains were likely to decrease PVC entanglements and to reduce the bulk strength of the membranes.

PHR ratio

The amount of plasticizer in a given membrane was described by the PHR ratio. This ratio normalizes the actual concentration, or PHR_{exp}, by the minimum concentration required for the isolation of all polar groups on the PVC from each other by a monolayer of plasticizer, or PHR_{min}[6]. The PHR ratio is defined as

$$PHR\ ratio = \frac{PHR_{exp}}{PHR_{min}} \quad (1)$$

The PHR_{exp} is given by the percentage by which the mass of plasticizer differs from the mass of PVC

$$PHR_{exp} = \frac{mass\ of\ plasticizer}{mass\ of\ PVC} \times 100 \quad (2)$$

The determination of the PHR_{min} is based on the MW of the plasticizer and the MW of one helical unit of PVC (MW = 875) as follows

$$PHR_{min} = \frac{MW\ of\ plasticizer}{875} \times 100 \quad (3)$$

Using equations (1)–(3) and the MW of each plasticizer (*Table 1*, column 3), the PHR ratios were calculated at the traditional plasticizer level, or 200 PHR (*Table 1*, column 4).

Test procedure

Using a blunt probe (0.3 cm o.d.) on an Instron mechanical tester (Canton, MA), membranes were deflected until fracture by testing each membrane at 1.0 cm min^{-1} and room temperature (23°C). Full-scale load settings of nominally 10 N were measured using a 4900 N load cell in conjunction with a 50 × amplifier. Five mechanical properties were derived from the force–deflection curves: the maximum force recorded (strength), the ratio of force at rupture to ductility (secant stiffness), the slope of the linear region of the force–deflection curve (tangent stiffness), the area under the force–deflection curve (toughness), and the deflection at rupture (ductility). Toughnesses were determined from the charts using a Summagraphics digitizer (Fairfield, CT). The means and standard deviations of these properties were determined for each plasticizer at each level of plasticization. From these values, the effects of PHR ratio and configuration were examined.

RESULTS

Strength

In general, the membranes were stronger at low levels of plasticizer (PHR ratio less than 1.0) than neat PVC (*Tables 2–10*). The strengths decreased monotonically as plasticizer was added above the initial peaks.

Among the citrate-related compounds, the CFB6-plasticized membranes had the highest mean recorded strength (9.63 N) at a PHR ratio of 0.31 (*Tables 2–4*). At a PHR ratio of 1.0, which equalled the minimum ratio required to isolate all polar groups of the PVC from each other by a monolayer of plasticizer, the CFA4- and CFA6-plasticized membranes had higher strengths (5.7 N) than the CFB6-plasticized membranes (4.5 N). Throughout the rest of the
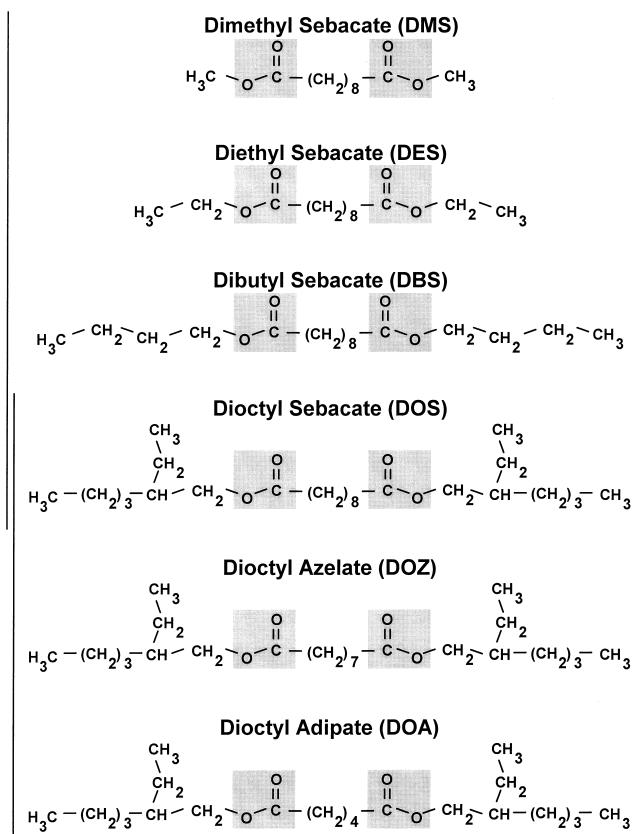
Table 2 Mechanical properties of PVC membranes plasticized with Citroflex A-4 (CFA4)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430 [c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.54 ± 0.00(1)	7.4 ± 1.6	1040 ± 190	1740 ± 220	32 ± 14	7.3 ± 2.1
0.97 ± 0.02(2)	5.7 ± 0.5	450 ± 20	790 ± 50	37 ± 5	12.7 ± 0.6
1.57 ± 0.07(2)	4.2 ± 1.0	290 ± 40	460 ± 40	28 ± 9	14.4 ± 1.6
1.96 ± 0.00(1)	2.8 ± 0.3	180 ± 20	280 ± 30	18 ± 2	15.3 ± 0.9
2.98 ± 0.10(2)	1.5 ± 0.5	100 ± 20	170 ± 30	10 ± 6	14.6 ± 2.9
4.43 ± 0.00(1)	0.8 ± 0.4	50 ± 13	94 ± 11	5.2 ± 4.4	14.3 ± 3.8

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Values in parentheses represent the number of solutions used to make the membranes
[c]Three membranes were tested

Table 3 Mechanical properties of PVC membranes plasticized with Citroflex A-6 (CFA6)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430[c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.49 ± 0.04(2)	7.6 ± 1.8	840 ± 210	1560 ± 550	39 ± 10	9.0 ± 0.8
1.04 ± 0.04(2)	5.7 ± 0.9	460 ± 50	750 ± 20	33 ± 9	12.3 ± 1.8
1.49 ± 0.02(2)	3.1 ± 0.6	230 ± 40	380 ± 80	19 ± 4	13.2 ± 0.6
2.07 ± 0.01(2)	2.6 ± 0.4	180 ± 20	300 ± 30	15 ± 3	13.7 ± 1.5
3.01 ± 0.01(2)	1.8 ± 0.4	120 ± 20	190 ± 10	11 ± 4	14.5 ± 2.3
3.64 ± 0.02(2)	1.1 ± 0.3	82 ± 15	140 ± 10	6.7 ± 3.4	12.9 ± 2.2

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Values in parentheses represent the number of solutions used to make the membranes
[c]Three membranes were tested

Table 4 Mechanical properties of PVC membranes plasticized with Citroflex B-6 (CFB6)[ab]

PHR ratio[c]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[d]	950 ± 430[d]	1480 ± 700[d]	18 ± 8[d]	6.0 ± 0.2[d]
0.31 ± 0.03(3)	9.6 ± 3.6	1250 ± 540	2190 ± 1090	42 ± 15	7.7 ± 0.7
0.57 ± 0.02(3)	8.0 ± 0.9	750 ± 70	1280 ± 20	48 ± 4	10.7 ± 0.3
0.83 ± 0.07(3)	6.0 ± 0.7[e]	470 ± 80[e]	820 ± 150[e]	43 ± 10[e]	12.8 ± 1.9[e]
1.03 ± 0.02(3)	4.5 ± 0.8	350 ± 60	630 ± 110	29 ± 6	12.7 ± 1.0
1.30 ± 0.04(2)	3.6 ± 1.3	270 ± 80	470 ± 120	24 ± 9	13.0 ± 1.4
1.55 ± 0.01(3)	3.3 ± 0.9	240 ± 70	400 ± 130	22 ± 5	13.9 ± 1.0
2.01 ± 0.02(2)	2.0 ± 0.4	150 ± 30	280 ± 50	14 ± 3	13.8 ± 1.5
2.97 ± 0.03(2)	1.6 ± 0.4	120 ± 10	210 ± 40	11 ± 5	14.0 ± 3.5

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Data reproduced from Ref. 10 with permission
[c]Values in parentheses represent the number of solutions used to make the membranes
[d]Three membranes were tested
[e]Six membranes were tested

Table 5 Mechanical properties of PVC membranes plasticized with dimethyl sebacate (DMS)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430[c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.56 ± 0.08(2)	8.4 ± 1.1[d]	1300 ± 150[d]	2200 ± 310[d]	30 ± 9[d]	6.4 ± 0.9[d]
1.11 ± 0.00(1)	7.7 ± 0.7	1100 ± 200	1700 ± 60	31 ± 9	7.1 ± 1.3
3.01 ± 0.00(1)	3.3 ± 0.7[d]	290 ± 80[d]	530 ± 170[d]	20 ± 4[d]	11.1 ± 0.7[d]
5.11 ± 0.00(1)	1.9 ± 0.4	130 ± 6	200 ± 20	12 ± 6	13.8 ± 2.9
7.57 ± 0.00(1)	0.6 ± 0.2	61 ± 15	110 ± 20	2.7 ± 1.1	9.2 ± 0.7

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Values in parentheses represent the number of solutions used to make the membranes
[c]Three membranes were tested
[d]Four membranes were tested

Table 6 Mechanical properties of PVC membranes plasticized with diethyl sebacate (DES)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430[c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.65 ± 0.03(2)	7.8 ± 1.6	930 ± 220	1400 ± 190	38 ± 6	8.4 ± 1.0
1.11 ± 0.00(1)	4.9 ± 0.9[d]	420 ± 100[d]	750 ± 60[d]	29 ± 2[d]	11.5 ± 1.0[d]
3.18 ± 0.00(1)	1.9 ± 0.9	100 ± 25	170 ± 10	16 ± 14	17.1 ± 5.8
4.49 ± 0.30(2)	0.9 ± 0.4	54 ± 11	97 ± 9	7.6 ± 5.4	16.4 ± 4.9
6.73 ± 0.00(1)	0.6 ± 0.3	39 ± 11	72 ± 10	4.6 ± 3.4	14.9 ± 3.6

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Values in parentheses represent the number of solutions used to make the membranes
[c]Three membranes were tested
[d]Four membranes were tested

Table 7 Mechanical properties of PVC membranes plasticized with dibutyl sebacate (DBS)[ab]

PHR ratio[c]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[d]	950 ± 430[d]	1480 ± 706[d]	18 ± 8[d]	6.0 ± 0.2[d]
0.28 ± 0.01(2)	6.4 ± 1.3[e]	1130 ± 170[e]	1770 ± 110[e]	22 ± 14[e]	5.8 ± 2.0[e]
0.57 ± 0.07(2)	6.3 ± 1.1[e]	580 ± 80[e]	980 ± 170[e]	40 ± 12[e]	10.9 ± 1.7[e]
0.75 ± 0.00(1)	4.5 ± 0.2[e]	350 ± 10[e]	720 ± 50[e]	36 ± 3[e]	12.8 ± 0.3[e]
1.06 ± 0.08(2)	4.5 ± 0.5	320 ± 50	550 ± 70	33 ± 4	14.3 ± 1.0
1.55 ± 0.07(2)	3.8 ± 0.9	250 ± 60	380 ± 60	27 ± 7	15.0 ± 1.1
2.03 ± 0.01(2)	2.9 ± 0.4[e]	170 ± 20[e]	270 ± 20[e]	24 ± 3[e]	16.9 ± 1.8[e]
2.52 ± 0.01(2)	1.8 ± 0.8[e]	100 ± 30[e]	170 ± 20[e]	16 ± 11[e]	16.5 ± 4.3[e]
3.02 ± 0.04(2)	1.5 ± 0.6[e]	92 ± 11[e]	160 ± 20[e]	13 ± 9[e]	16.2 ± 5.2[e]
3.57 ± 0.03(2)	1.6 ± 0.5[e]	91 ± 11[e]	140 ± 20[e]	14 ± 7[e]	17.8 ± 5.2[e]

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Data reproduced from Ref. 10 with permission
[c]Values in parentheses represent the number of solutions used to make the membranes
[d]Three membranes were tested
[e]Four membranes were tested

Table 8 Mechanical properties of PVC membranes plasticized with dioctyl sebacate (DOS)[ab]

PHR ratio[c]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[d]	950 ± 430[d]	1480 ± 700[d]	18 ± 8[d]	6.0 ± 0.2[d]
0.34 ± 0.02(3)	6.6 ± 1.3	870 ± 110	1280 ± 100	30 ± 13	7.8 ± 2.1
0.68 ± 0.02(2)	4.4 ± 0.5	370 ± 50	690 ± 60	30 ± 5	11.8 ± 1.2
0.92 ± 0.00(2)	4.6 ± 1.4[e]	360 ± 90[e]	540 ± 80[e]	31 ± 10[e]	12.9 ± 1.2[e]
1.22 ± 0.01(2)	2.9 ± 0.1	230 ± 7	450 ± 10	21 ± 2	12.8 ± 0.8
1.92 ± 0.05(2)	1.9 ± 0.3[e]	130 ± 9[e]	250 ± 10[e]	13 ± 3[e]	13.8 ± 1.3[e]
2.48 ± 0.04(3)	1.2 ± 0.0[e]	99 ± 2[e]	200 ± 3[e]	8.2 ± 0.7[e]	12.7 ± 0.5[e]
4.15 ± 0.01(2)	0.9 ± 0.3[e]	65 ± 10[e]	120 ± 10[e]	6.9 ± 3.2[e]	14.6 ± 2.9[e]
5.65 ± 0.00(2)	1.2 ± 1.3[e]	74 ± 50[e]	131 ± 93[e]	11.7 ± 14.2[e]	14.7 ± 4.6[e]

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Data reproduced from Ref. 10 with permission
[c]Values in parentheses represent the number of solutions used to make the membranes
[d]Three membranes were tested
[e]Four membranes were tested

range of plasticization, all the membranes plasticized with citrate-related plasticizers had similar strengths.

Among the sebacate-related compounds, the DMS-plasticized membranes had the highest mean strength (8.4 N) at a PHR ratio of 0.56 (*Tables 5–10*). At a PHR ratio of 1.0, the DMS-plasticized membranes retained their highest strength (7.7 N). At this PHR ratio, the DOA-plasticized membranes had the next highest strength (5.6 N), and membranes plasticized with other

sebacate-related materials had strengths of about 4.8 N. The strengths of the membranes were greatest throughout the range of plasticization when DMS was selected as the plasticizer. The other plasticizers formed membranes with similar strengths throughout the range of plasticization.

Stiffness

Like the strengths, the secant stiffnesses of membranes plasticized to PHR ratios less than 1.0 were higher than for

Table 9 Mechanical properties of PVC membranes plasticized with dioctyl azelate (DOZ)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430[c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.55 ± 0.03(1)	6.6 ± 0.9	850 ± 130	1200 ± 140	28 ± 10	7.8 ± 1.6
0.98 ± 0.00(1)	4.6 ± 0.6	410 ± 60	690 ± 10	27 ± 4	11.1 ± 1.1
2.02 ± 0.00(2)	1.9 ± 0.2	160 ± 10	290 ± 10	11 ± 2	11.7 ± 1.5
3.08 ± 0.30(2)	1.1 ± 0.0	89 ± 4	180 ± 10	6.7 ± 0.4	12.1 ± 0.4
4.25 ± 0.00(1)	0.9 ± 0.2	69 ± 8	130 ± 6	5.6 ± 3.0	12.6 ± 2.7

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where indicated
[b]Values in the PHR ratio column represent the number of solutions used to make the membranes
[c]Three membranes were tested

Table 10 Mechanical properties of PVC membranes plasticized with dioctyl adipate (DOA)[a]

PHR ratio[b]	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	5.7 ± 2.5[c]	950 ± 430[c]	1480 ± 700[c]	18 ± 8[c]	6.0 ± 0.2[c]
0.57 ± 0.04(2)	8.0 ± 1.5	750 ± 160	1200 ± 140	48 ± 7	10.8 ± 1.2
1.03 ± 0.00(1)	5.6 ± 1.0	430 ± 90	680 ± 40	36 ± 3	13.0 ± 0.4
1.99 ± 0.00(1)	2.5 ± 0.4	170 ± 20	290 ± 20	16 ± 2	14.1 ± 0.4
3.04 ± 0.02(2)	1.9 ± 0.5	110 ± 20	180 ± 20	14 ± 7	16.0 ± 3.4
4.69 ± 0.00(2)	1.3 ± 0.4	72 ± 18	110 ± 10	10 ± 6	17.5 ± 4.3

[a]For each PHR ratio, the means and standard deviations are shown for tests on five membranes, except where noted
[b]Values in parentheses represent the number of solutions used to make the membranes
[c]Three membranes were tested

neat PVC (*Tables 2–10*). Above these levels, the secant stiffnesses decreased monotonically as the PHR ratio increased.

Among the citrate-related plasticizers, the peak secant stiffness was 1300 N m^{-1} when CFB6 was used at a PHR ratio of 0.3 (*Tables 2–4*). At a PHR ratio of 1.0, the secant stiffness was 460 N m^{-1} for CFA6, 450 N m^{-1} for CFA4, and 350 N m^{-1} for CFB6. Membranes plasticized with the citrate-related materials had similar secant stiffnesses throughout the rest of the range of plasticization.

The peak secant stiffness for a sebacate-plasticized membrane was 1300 N m^{-1} when DMS was used at a PHR ratio of 0.56 (*Tables 5–10*). At a PHR ratio of 1.0, the mean secant stiffness was greatest using DMS (1100 N m^{-1}) (*Table 5*). At this level, the DES-, DOA-, and DOZ-plasticized membranes had secant stiffnesses of about 420 N m^{-1} (*Table 6* and *Tables 9 and 10*), and the mean secant stiffnesses of the DOS- and DBS-plasticized membranes were 360 N m^{-1} and 320 N m^{-1}, respectively (*Tables 7 and 8*). Using the sebacate plasticizers, the DMS-plasticized membranes had the highest secant stiffness throughout the range of plasticization. Membranes plasticized with the other plasticizers generally had secant stiffnesses that were similar to each other throughout the range of plasticization. The tangent stiffnesses were approximately 1.7 times the secant stiffnesses, and the trends for tangent and secant stiffnesses were similar throughout the range of plasticization.

Toughness

The toughnesses were above that of neat PVC for PHR ratios below about 2.0 (*Tables 2–10*). Beyond these ratios, the toughnesses decreased as more plasticizer was added.

Among the citrate-related plasticizers, the CFB6 had the greatest toughness (48 N mm) at a PHR ratio of 0.6 (*Tables 2–4*). At a PHR ratio of 1.0, the CFA4-plasticized membranes had the greatest mean toughness at 37 N mm, followed by 33 N mm and 29 N mm for CFA6- and CFB6-plasticized membranes, respectively. When the citrate-related plasticizers were used, systematic changes in the toughness could not be established with regard to configuration.

Among the sebacate-related plasticizers the DOA-plasticized membranes had the highest mean toughness (48 N m) at a PHR ratio of 0.6 (*Tables 5–10*). At a PHR ratio of 1.0, the toughnesses ranged from 36 N mm for DOA-plasticized membranes to 27 N mm for DOZ-plasticized membranes. Using the sebacate-related plasticizers, the configurational differences of the plasticizers did not cause systematic changes in the toughnesses of the membranes.

Ductility

The ductilities increased with plasticizer additions up to PHR ratios of about 2.0 (*Tables 2–10*). Above this PHR ratio, additional plasticizer did not change the ductilities of the membranes.

At a PHR ratio of 1.0, the CFA4-, CFA6-, and CFB6-plasticized membranes possessed ductilities of about 12.5 mm (*Tables 2–4*). Throughout the range of plasticization, the mean ductilities of the membranes having the citrate-related plasticizers were similar.

Among the sebacate-related plasticizers, the membranes showed some systematic changes in the mean ductilities according to the configurational differences. At a PHR ratio of 1.0, the ductilities ranged from 14.2 mm for DBS-plasticized membranes to 7.1 mm for DMS-plasticized membranes (*Tables 5–10*). Among the plasticizers with a fixed eight-carbon-atom inner chain, the ductilities were greater throughout the range of plasticization in the order DMS-, DOS-, DES-, and DBS-plasticized membranes. Among the plasticizers with dioctyl end-groups, the ductility increased throughout the range of plasticization in the order DOZ, DOS, and DOA.

DISCUSSION

General trends

When the properties were plotted using the values for individual membranes, a band of properties was evident (*Figures 3 and 4*).

For both citrate- and sebacate-related plasticizers, the strengths, stiffnesses, and toughnesses of the membranes increased at low PHR ratios and then decreased monotonically as the PHR ratio increased. These peaks at low PHR ratios were similarly observed in Brous and Semon's studies of PVC[1] and were attributed to anti-plasticization. When small amounts of plasticizer were added to a polymer, the plasticizer allowed some of the polymer molecules to move into lower energy conformations. In these preferred conformations, the molecules became less mobile and thereby increased the bulk strength of the polymer. These same effects caused the increases in stiffness and toughness as well. When plasticizer was added beyond the anti-plasticization level, the polymeric molecules moved more during deformation and consequently decreased the strength of the polymer with increasing PHR ratio.

For the citrate-related plasticizers, the ductilities of the membranes increased up to PHR ratios of approximately 1.0, after which they remained relatively unchanged (see *Figure 3*). In contrast, for the sebacate-related plasticizers, the band of ductilities showed a distinct decrease at the highest PHR ratios that were investigated (see *Figure 4*). In separate studies, Walter[16] and Ghersa[17] found similar peaks in the ductilities of PVC using the plasticizers dioctyl phthalate (DOP) and tricresyl phosphate (TCP), respectively. These additions caused peaks at different concentrations; this was attributed to the compatibility of the plasticizers. In the present study, the citrate- and sebacate-related materials had similar compatibilities to PVC, since the ductilities were maintained up to PHR ratios of approximately 4.0 for all the plasticizers. At higher PHR ratios, the sebacate-plasticized membranes had lower ductilities, which may have been caused by a phase separation of excess plasticizer from the PVC. In previous work on the dielectric properties[11], this phase separation was observed above PHR ratios of 3.0 for DMS- and DES-plasticized membranes. At PHR ratios between 3.0 and 4.0, the ductility remained constant, indicating that any occluded regions were not large enough and/or not numerous enough to influence the mechanical properties.

Influence of molecular structure

Membranes plasticized with citrate-related compounds had similar mechanical properties, without regard to the particular species of plasticizer (see *Figure 3*). The similarity among these materials indicated that the tetrahedral conformation of plasticizer produced a consistent plasticizing medium regardless of chain length. This phenomenon most likely revealed that the full length of the carbon chains was not effective. That is, the groups at the so-called base (see *Figure 1*) most likely attained a bent conformation when incorporated into the membrane. In this way, the full lengths of the chains of CFA6 or CFB6 could not prevent entanglements among the PVCs and, compared to those plasticized with CFA4, could not increase the strengths, stiffnesses, and toughnesses of the membranes. Moreover, the group at the so-called top of the tetrahedron did not obstruct PVC entanglements by its extension from the CFA6 molecule to the CFB6 molecule.

In contrast, the sebacate-related materials had some systematic differences according to the configurations of the plasticizers. The sebacate-materials designated by empty symbols were generally in the upper portion of the designated band of strength, and the darker symbols tended to indicate the lower range of strengths (see *Figure 4*, upper left-hand frame). Among the plasticizers with a fixed eight-carbon-atom inner chain (see *Figure 2*), the DMS- and DES-plasticized membranes generally had higher strengths than the DBS- and DOS-plasticized membranes. In the group of dioctyl compounds, the DOA-plasticized membranes had slightly higher values than the DOZ- and DOS-plasticized membranes. In both groups, these trends indicated an increase in strength as shorter chain lengths were selected. A similar trend could be noted in the secant stiffnesses (see *Figure 4*, upper right-hand frame) and tangent stiffnesses (not shown). At PHR ratios below 2.0, the ductilities of the membranes were somewhat lower for the plasticizers having shorter chain lengths; at PHR ratios above 2.0, the distinctions among the configurations were no longer evident. Because the toughnesses were proportional to the strengths multiplied by the ductilities, the contrary effects between the strengths and ductilities confounded any distinctions that may have been evident in the toughnesses.

Nomograms for prediction of mechanical properties

Using a logarithmic fit (bold lines in *Figures 3 and 4*), the strengths of the citrate- and sebacate-plasticized membranes were correlated to the PHR ratios. These fits were statistically significant at $p < 0.001$. For the citrate-related plasticizers, individual membranes varied slightly from the fitted curve without regard to configuration. For the sebacate-related plasticizers, the DMS-, DES-, and DOA-plasticized membranes were generally above the specified curve, in accordance with the configurational influences discussed in the previous section. Using these logarithmic curve fits, a nomogram (*Figure 5*) could be produced[18] which relates the strength and log (PHR ratio). By making the transformation to log (PHR ratio), a straight line through the relation point (designated by a plus sign) correlates a given log (PHR ratio) to its associated strength value.

As an example, consider that the traditional 200 PHR values of plasticization for the citrate-related compounds have equivalent PHR ratios ranging from 3.4 using CFB6 to 4.4 using CFA4 (see *Table 1*). After the logarithmic transformation to 0.53 and 0.64, respectively, the average strengths of traditionally plasticized membranes can be determined in *Figure 5* (black area) to range from 3.1 to 3.5 N. If the PHR ratios were to be lowered to 2.0 (log (PHR ratio) = 0.31), the mean strength increases to 4.3 (thin line in *Figure 5*), which is a 20–40% improvement over the traditional values.

Note that the ranges of applicability must be limited to the ranges of the curves shown in *Figures 3 and 4*. That is, the strengths of citrate-plasticized membranes can be predicted for PHR ratios from 0.5 to 4.5, and the strengths of sebacate-plasticized membranes can be predicted for PHR ratios from 0.5 to 7. Notice also that although the relation points were separated, the difference between citrate- and sebacate-plasticized membranes were small throughout the applicable range of plasticization. At a PHR ratio of 0.5, the citrate-plasticized membranes were 0.1 N stronger, and at a PHR ratio of 4.5 the sebacate-plasticized membranes were 0.2 N stronger. Considering the scatter among individual

membranes, any such changes were not substantial enough to influence the selection of plasticizers. Using the proper curve fits, similar nomograms might be produced for any of the mechanical properties.

Trade-off between electrical and mechanical properties

Using the citrate-related plasticizers, the strengths, stiffnesses, and toughnesses of membranes decreased as log (ionic conductivity, σ) increased (*Figure 6*). For the
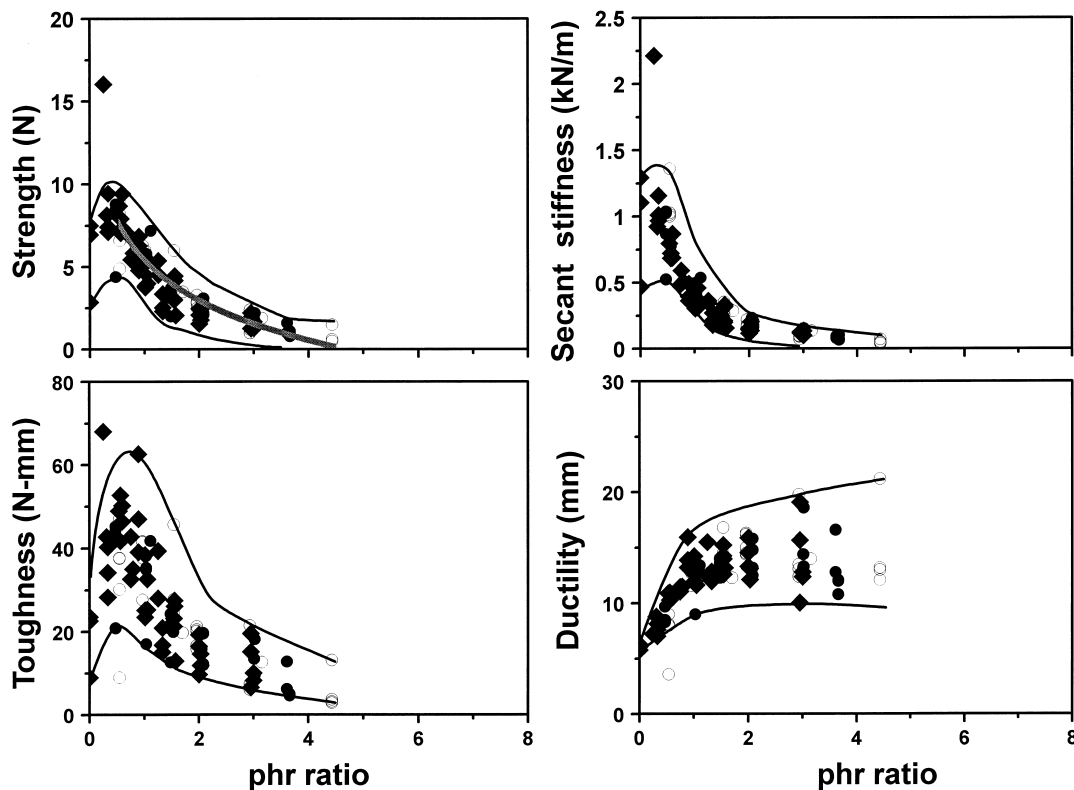

Figure 3 Strength (N), secant stiffness (kN m^{-1}), toughness (N mm), and ductility (mm) plotted *versus* PHR ratio for three plasticizers: CFA4 (○), CFA6 (●), and CFB6 (◆). Each data point represents one plasticized PVC membrane
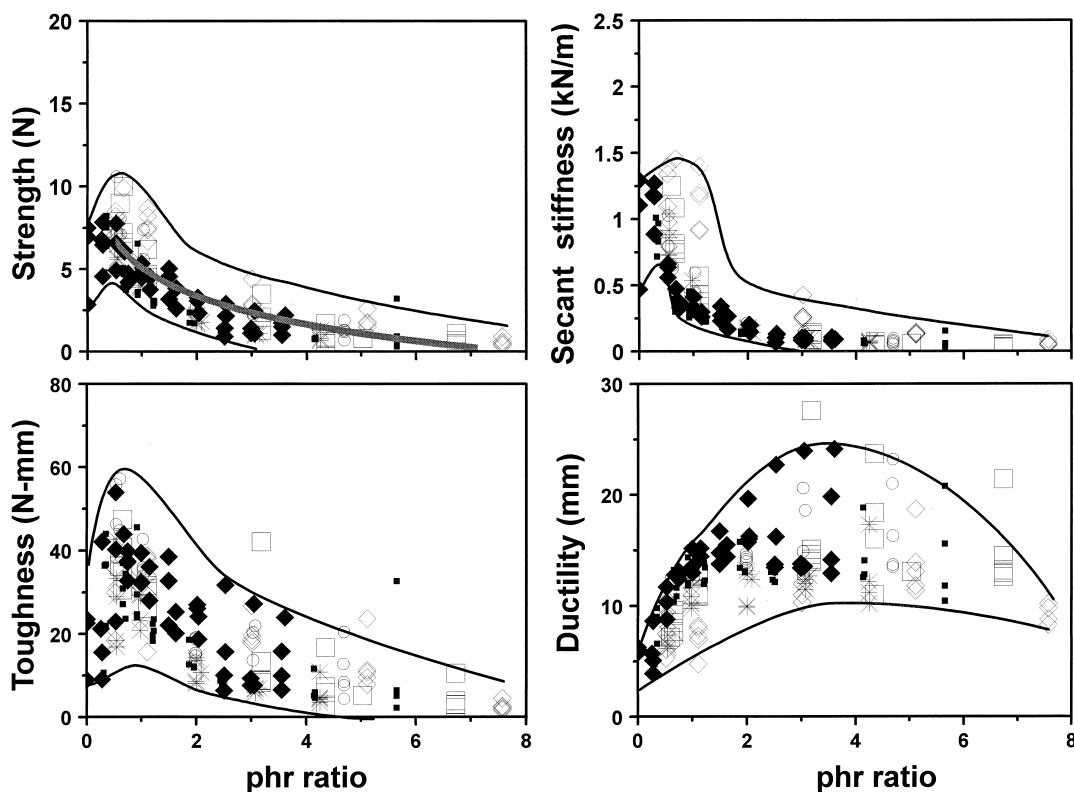
Figure 4 Strength (N), secant stiffness (kN m^{-1}), toughness (N mm), and ductility (mm) plotted *versus* PHR ratio for six plasticizers: DMS (◇), DES (□), DBS (◆), DOS (■), DOZ (*), and DOA (○). Each data point represents one plasticized PVC membrane
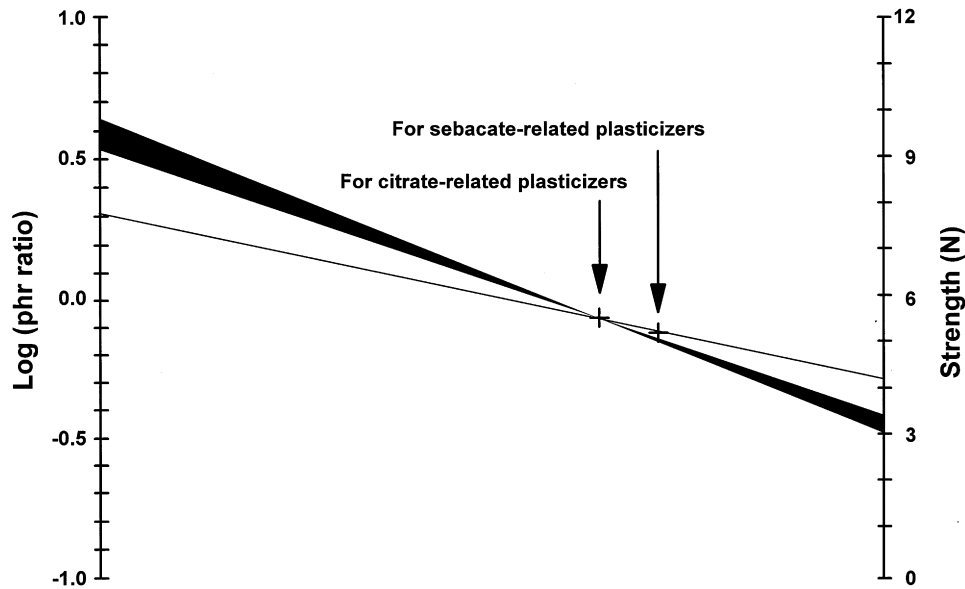
Figure 5 Nomogram relating strength (N) to log (PHR ratio) for citrate-plasticized membranes at PHR ratios from 0.5 to 4.5, and for sebacate-plasticized membranes at PHR ratios from 0.5 to 7.0. A straight line drawn from a given log (PHR ratio) through the appropriate relation point, (+ , which is based on the plasticizer selected) intersects the average strength for those membranes
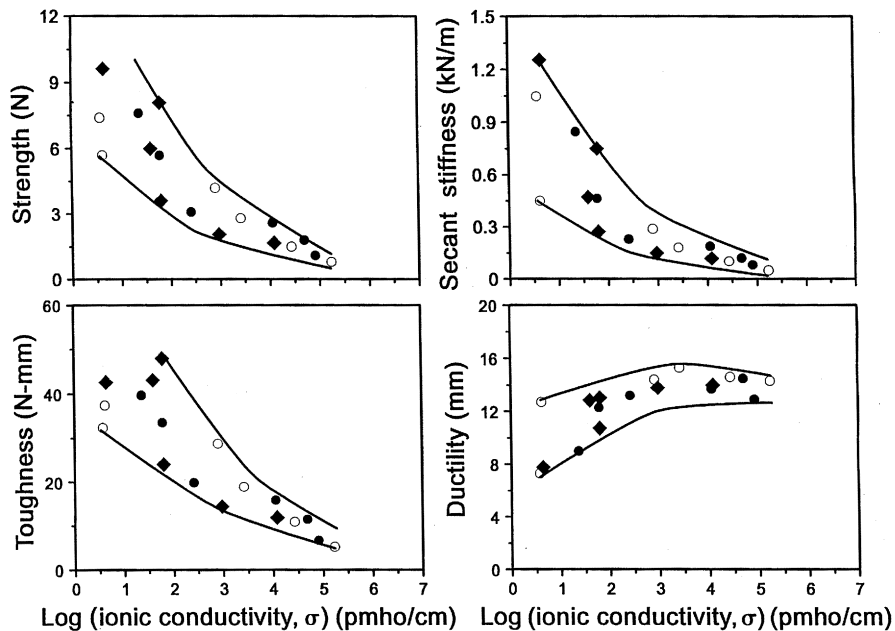

Figure 6 Mean values of strength (N), secant stiffness (kN m^{-1}), toughness (N mm), and ductility (mm) plotted *versus* mean value of log (ionic conductivity, σ) (pmho/cm) for the three plasticizers in *Figure 3*

same materials, the ductility increased slightly as log σ increased, reaching a steady value at a log σ value of approximately 2 pmho cm^{-1}. In previous work[9,11], log σ was linearly correlated to log (PHR ratio), and therefore the mechanical properties *versus* log σ plots represent transformations of the mechanical properties *versus* PHR ratio plots. As such, the trends of the mechanical properties *versus* log σ (*Figure 6*) are similar to *Figure 3*, once antiplasticization has occurred. For each of these four properties, as well as tangent stiffnesses, the scatter along the axes of the mechanical properties decreased as log σ increased. Since the mechanical properties changed most quickly at low PHR ratios, the scatter at low values of log σ (and thereby low PHR ratios) might be expected. At higher PHR ratios, the excess plasticizer causes smaller changes in

the mechanical properties; accordingly the scatter of the mechanical properties decreased at higher values of log σ. No distinctions could be made among the configurations of citrate-related plasticizers despite the increased scatter of the data.

For the sebacate-related plasticizers, the mechanical properties exhibited similar trends to the citrate-related plasticizers when the mechanical properties were plotted *versus* log σ (*Figure 7*). Again, the strengths, stiffnesses, and toughnesses decreased as log σ increased, and the ductility increased until log σ reached about 2 pmho cm^{-1}. Once again, the configurational differences in the plots of strength, stiffness, and ductility *versus* PHR ratio (see *Figure 4*) were maintained in the plots of the mechanical properties *versus* log σ. The DMS-, DES-, and
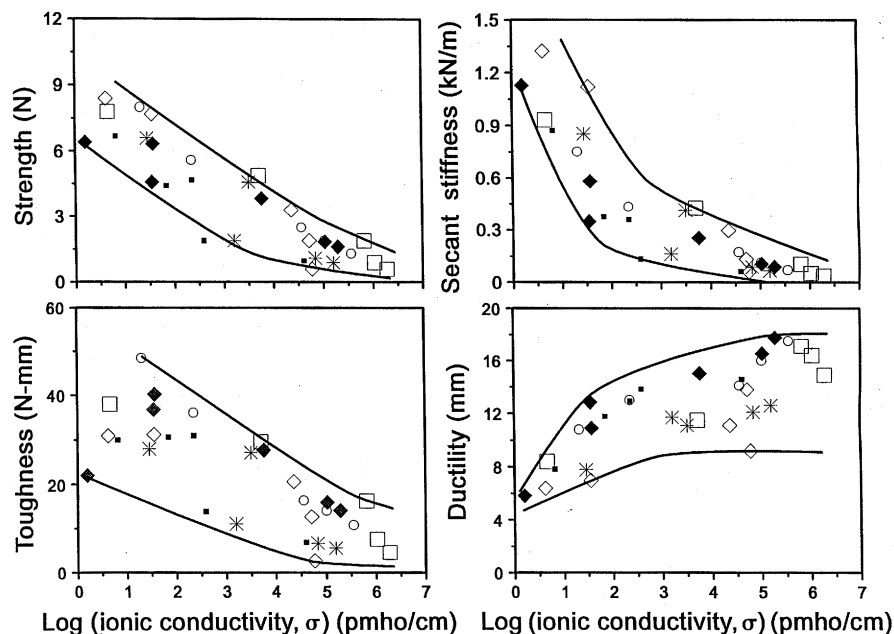
Figure 7 Mean values of strength (N), secant stiffness (kN m^{-1}), toughness (N mm), and ductility (mm) plotted *versus* mean value of the log (ionic conductivity, σ) (pmho cm) for the six plasticizers in *Figure 4*

DOA-plasticized membranes generally had higher strengths and stiffnesses and lower ductilities than the DBS-, DOS-, and DOZ-plasticized membranes. The shorter outer-chain lengths of DMS and DES compared to DBS and DOS, and the shorter inner-chain length of DOA compared to DOS and DOZ facilitated more entanglements among the PVC molecules, which improved the strengths and stiffnesses of the membranes.

Implication of configurational studies for electrodes and biosensors

According to the mechanical properties, any of the citrate-related plasticizers were acceptable for ISE and sensor applications, since the configurational differences between these plasticizers were not distinguishable. These biocompatible plasticizers are preferable to any of the sebacate-related plasticizers when measurements are taken *in vivo*. Note that the leaching characteristics of these plasticizers have been evaluated when they were used in blood serum bags[19]. These studies showed that CFB6, with its longer branches, was more stable than the other two compounds. Among the citrate-related compounds, the CFB6 would therefore be the best selection for biosensor applications.

The configurational differences among the sebacate-related plasticizers affected the bulk properties of the membranes. When the mechanical properties were plotted *versus* PHR ratio or log σ, the DMS-, DES-, and DOA-plasticized membranes were stronger and stiffer than the DBS-, DOS, and DOZ-plasticized membranes. Based on these data, the former plasticizers would be selected for use in ISEs and sensors. Note that future considerations of the leaching properties will most likely further influence the selection of the plasticizer, although DOA with its two branched end-groups is provisionally selected over the aliphatic DMS and DES.

CONCLUSIONS

The strengths of the membranes increased at low PHR ratios and then decreased monotonically throughout the range of

plasticization. The stiffnesses and toughnesses of the membranes behaved similarly. The ductilities increased up to PHR ratios of about 2.0 and then decreased above PHR ratios of about 4.0. The citrate-related plasticizers could not be distinguished according to the mechanical properties. Among the sebacate-related plasticizers, DMS-, DES-, and DOA-plasticized membranes were generally stronger and stiffer throughout the range of plasticization than DBS-, DOS-, and DOZ-plasticized membranes. These differences were associated with the shorter outer-chain lengths of the DMS and DES compared to DBS and DOS, and the shorter inner-chain length of DOA compared to DOS and DOZ. Based on a statistically significant logarithmic correlation between the strength and the PHR ratio, a nomogram could be constructed to predict the strengths of the membranes over a range of PHR ratios. The strengths, stiffnesses, and toughnesses decreased monotonically as log σ increased for the membranes. The ductility increased when log σ was below 2 pmho cm^{-1} and thereafter remained relatively constant. The configurational changes in the citrate-related compounds could not be distinguished in plots of the mechanical properties *versus* log σ. The configurational differences that were evident in plots of the mechanical properties *versus* PHR ratio were also evident in plots of the mechanical properties *versus* log σ. The DMS-, DES-, and DOA-plasticized membranes were again stronger and stiffer than the DBS-, DOS-, and DOZ-plasticized membranes. In the final analysis, among the citrate-related plasticizers the CFB6 was favoured. Among the sebacate-related plasticizers, DMS, DES, and DOA were favoured; based on its configuration, DOA was provisionally selected as being the best.

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