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Effects of plasticizers on the mechanical properties of poly(vinyl chloride) membranes for electrodes and biosensors

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In electrodes and biosensors poly(vinyl chloride) (PVC) membranes were plasticized to 200 parts per hundred resin, independent of plasticizer specie. Puncture tests quantified five mechanical properties for at least eight levels of seven plasticizers. Using Citroflex B-6 at a phr ratio of 0.31, the strength and secant stiffness peaked at $9.63\,N$ and $1250\,N\,m^{-1}$, respectively. At a phr ratio of 0.6 the toughness peaked at $48\,N\,mm$. These three properties decreased at higher phr ratios for all plasticizers. Tangent stiffnesses were generally 1.7 times secant stiffnesses. For all plasticizers, ductility increased to a constant value of 15 mm at a phr ratio of two. The molecular structures of the plasticizers influenced the mechanical properties. For a given phr ratio, plasticizers having lower hydrodynamic volumes increased the strengths, stiffnesses, and toughnesses of the membranes. Compared to prior dielectric testing, the strength, toughness, and stiffness increased as the ionic resistivity increased. In electrodes and biosensors phr ratios should be reduced to a minimum of one. © 1997 Elsevier Science Ltd.

(Keywords: biosensors; electrodes; plasticized PVC)

INTRODUCTION

In 1935 Semon *et al.* experimented with over 500 different plasticizers for poly(vinyl chloride) (PVC)[1]. Their research, which plasticized PVC using tricresyl phosphate (TCP) and dioctyl phthalate (DOP), was essential to the development of useful products and established PVC as one of the leading vinyl products[2]. The vast importance of these products was further emphasized by the needs and urgencies of World War II[3]. Plasticization gave polymers impact resistance and avoidance to both brittleness and thermal decomposition. In this period plasticized PVC accounted for at least 75% of commercial materials[3].

The use of polymers as conductive materials was established by Mead and Fuoss in 1945, when they investigated the addition of electrolytes to plasticized PVC[4]. Non-glass ion-selective electrode (ISE) designs began after the discovery of the ion-selective effects of valinomycin by Moore and Pressman in 1964[5]. This latter event led to Frant and Ross' measurements of the potassium ion in 1970[6]. By 1972 PVC-based ISE's were being developed using two parts plasticizer to one part polymer or 200 parts per hundred resin (phr)[7]. This amount was three to 10 times greater than conventionally plasticized PVC[3]. In 1978 ISE's were produced using PVC membranes for *in vivo* studies of myocardial K⁺ ion concentrations by Hill *et al.*[8]. The highly plasticized PVC membranes, which acted as a liquid barrier, were important in the production of ISE's, because the PVC

provided the structural framework of the network and the plasticizer facilitated the transport of ionophore and ion–ionophore complexes through the membrane[9].

The mechanical properties of ion-selective membranes were critical, since failure of electrodes was usually caused by a loss of integrity in the membrane. These failures included puncturing of the membrane during production, storage, transportation, or insertion *in vivo*. Additional mechanical failures were caused by shrinkage of the ion-selective membrane. Such failures led to leakage of fluid under the PVC membrane, causing a short[10]. Consequently, the strength, toughness, and endurance characteristics of membranes were important in biomedical applications.

Technical problems existed with the traditional amount of plasticizer (200 phr) not only from a mechanical properties standpoint but also with regard to electrical properties. The high levels of plasticizers were questioned because excessive plasticizer could migrate into the surrounding tissues from the biosensors. The formation of a plasticizer film on the electrode's surface increased electrical resistance and caused failure[9]. Biocompatibility and toxicity were also concerns, since traditional plasticizers were toxic and could cause permanent damage *in vivo*. Consequently, natural derivatives were suggested as an alternative[11].

In order to find the amount of plasticizer that insured proper ISE function and optimized mechanical properties, puncture tests were used to evaluate the effects of changes in plasticizer levels and species on the mechanical properties of PVC membranes. In addition to three traditional plasticizers, four natural derivative plasticizers were selected in order to avoid the high risk of infection that had been associated with synthetic organic

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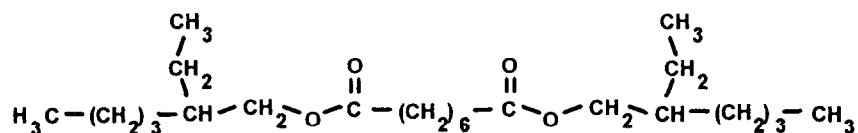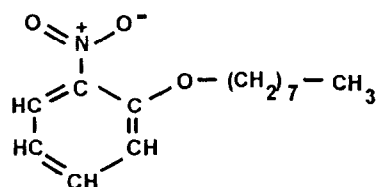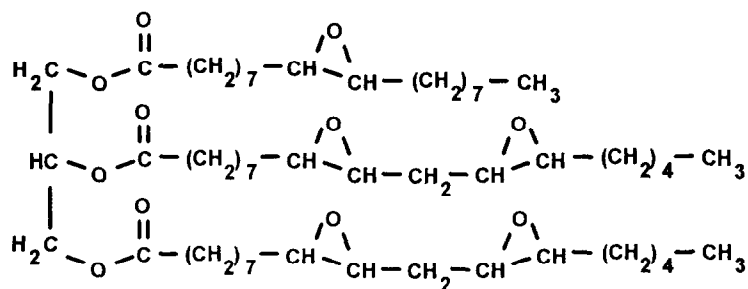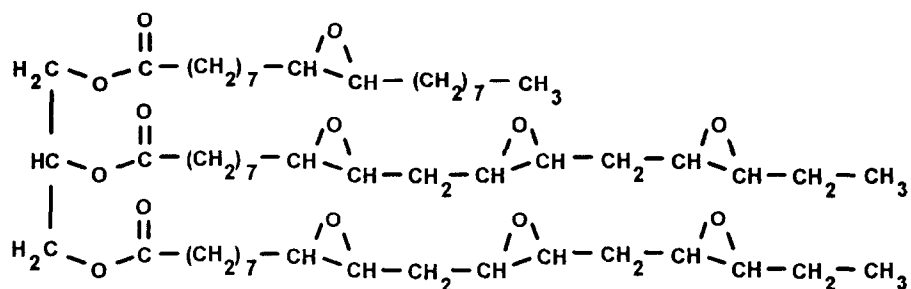
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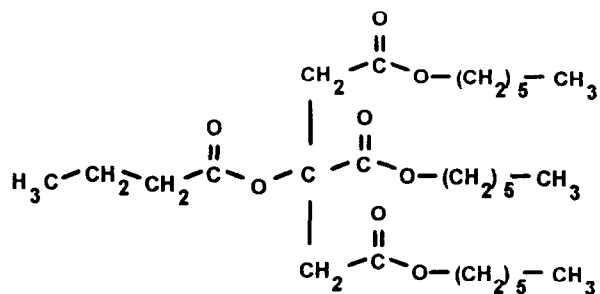
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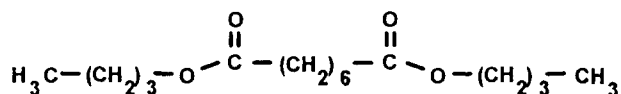
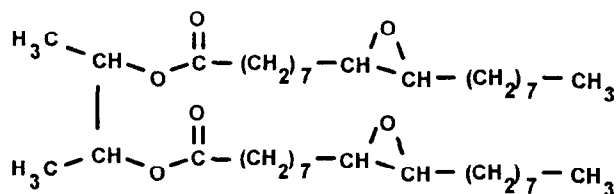**DOS**

o-NPOE

ESO

ELO

PGDO

Figure 1 Molecular structures of the seven plasticizers, which are separated into four groups according to configurational differences

Table 1 List of the seven plasticizers, MW's, and phr ratios at the traditional plasticization level of 200 phr

Plasticizer	Symbol	MW	phr ratio at 200 phr
Citroflex B-6	CF	514	3.4
Dibutyl sebacate	DBS	314	5.6
Dioctyl sebacate	DOS	427	4.1
ortho-Nitrophenyl octyl ether	o-NPOE	251	7.0
Epoxidized linseed oil	ELO	1490	1.2
Epoxidized soybean oil	ESO	1470	1.2
Propylene glycol dioleate	PGDO	1040	1.7
Poly(vinyl chloride)	PVC	135000	—
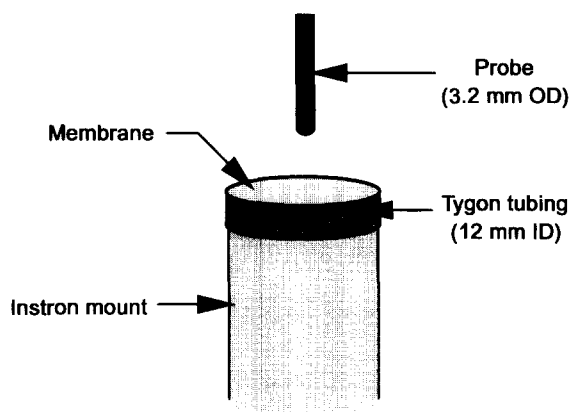
Figure 2 Schematic of the test section of the puncture test apparatus

materials. Results showed that all plasticizers generally reduced the strength, stiffness, and toughness of the membranes but increased the ductility.

EXPERIMENTAL

Membrane composition

The membranes were composed of a 50/50 blend of 77 300 molecular weight (MW) PVC and 193 600 MW PVC. The 50/50 blend provided a good combination of strength and processability[12], which made the blend a proper choice for ISE's and biosensors. One of seven plasticizers was added to the blend at a minimum of eight levels of plasticization. Three plasticizers [dibutyl sebacate (DBS), dioctyl sebacate (DOS), and ortho-nitrophenyl octyl ether (o-NPOE)] were included because of previous use in ISE applications[8,13,14]. The other four plasticizers [Citroflex B-6 (CF), epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), and propylene glycol dioleate (PGDO)] were derivatives of natural products and likely to be more biocompatible. These seven plasticizers facilitated analyses of the effects of molecular structure on mechanical properties. Four had low MW's (CF, DBS, DOS, and o-NPOE), and three had high MW's (ELO, ESO, and PGDO) (*Table 1*). The plasticizers were subdivided into four groups (*Figure 1*). The CF had a tetrahedral configuration with three hexyl ester chains as the base and a butyryl group at the top. The DBS and DOS were members of the homologous series of sebacates; both DBS and DOS had linear configurations. The o-NPOE was unique because of its aromatic structure and its polarity, which was associated with the nitro group. The ESO, ELO, and PGDO were

epoxidized, having higher MW's and viscosities than the other compounds. Both ESO and ELO were trigonal planar with three alkyl groups at the centre, and PGDO had a similar conformation with only two aliphatic branches. The phr ratios at 200 phr also reflected these groupings (*Table 1*).

phr ratio

The phr ratio is used to describe the proportion of plasticizer to PVC in the membrane. The concentration, phr_{exp}, is the normalized ratio of the mass of the plasticizer to the mass of the PVC for a given membrane, or

$$phr_{exp} = \frac{mass\ of\ plasticizer}{mass\ of\ PVC} \times 100 \qquad (1)$$

The phr_{min} for a given plasticizer represents the amount of plasticizer necessary for all polar groups on the PVC backbone to be shielded from each other by a monolayer of plasticizer[3]. The phr_{min} depends on the MW of the plasticizer and the MW of one helical unit of PVC (MW = 875):

$$phr_{min} = \frac{MW\ of\ plasticizer}{875} \times 100 \qquad (2)$$

Finally, the *phr ratio* is defined as:

$$phr\ ratio = \frac{phr_{exp}}{phr_{min}} \qquad (3)$$

Membrane preparation

Membranes were prepared by adding 1.1 wt% PVC to a tetrahydrofuran (THF) solvent and heating the solution for 4 h at 80°C to ensure dissolution of the PVC[15]. The appropriate amount of plasticizer was added to the PVC/THF solution, and 3–5 ml of the mixture evaporated under a hood for 4 days in a 2.5 cm diameter glass ring. Weighted filter papers controlled the evaporation rate. Thickness measurements were made using a Dektak 3030 profilometer. All membranes tested were within the 120 micron limitation of the profilometer. The test samples were secured to a 1.2 cm i.d., 0.5 cm long section of Tygon tubing using a PVC/THF glue. Prior to attachment of the PVC membrane, the Tygon tubing was mounted on a brass tube, turned using a lathe, and heated using a hot air gun in order to relieve the stresses imposed on the tubing during shipping. The tubing was allowed to cool and then cut into the proper segmental lengths. Only clear, non-turbid membranes were used, because turbidity was associated with non-uniform plasticizer distributions. A minimum of five membranes at eight to nine phr ratios were tested for each of the seven plasticizers for a total of about 250 samples.

Test apparatus

The mechanical properties were evaluated by puncture testing on an Instron mechanical tester. The apparatus (*Figure 2*) used a blunt probe to deflect the membranes until puncture. The tests were performed at a crosshead speed of 1.0 cm min^{-1} at room temperature. The Instron used a 4900 N load cell in conjunction with a 50× amplifier, which allowed testing at full scale load settings of nominally 10 N. The mechanical properties were derived from the force–deflection curves (*Figure 3*) as:

Table 2 Mechanical properties of PVC membranes plasticized with Citroflex B-6 (CF). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness ($N m^{-1}$)	Tangent stiffness ($N m^{-1}$)	Toughness (N mm)	Ductility (mm)
$0.00 \pm 0.00(1)$	$16.7 \pm 2.4(3)$	$5.78 \pm 2.54(3)$	$957 \pm 432(3)$	$1480 \pm 706(3)$	$18.3 \pm 8.1(3)$	$6.0 \pm 0.2(3)$
$0.31 \pm 0.03(3)$	$29.0 \pm 18.9(4)$	$9.63 \pm 3.69(5)$	$1250 \pm 542(5)$	$2190 \pm 1090(5)$	$42.7 \pm 15.2(5)$	$7.7 \pm 0.7(5)$
$0.57 \pm 0.02(3)$	$28.6 \pm 2.3(4)$	$8.09 \pm 0.97(5)$	$753 \pm 79(5)$	$1280 \pm 26(5)$	$48.0 \pm 4.2(5)$	$10.7 \pm 0.3(5)$
$0.83 \pm 0.07(3)$	$33.7 \pm 1.7(5)$	$6.00 \pm 0.79(6)$	$474 \pm 83(6)$	$828 \pm 154(6)$	$43.2 \pm 10.9(6)$	$12.8 \pm 1.9(6)$
$1.03 \pm 0.02(3)$	$33.1 \pm 0.9(4)$	$4.51 \pm 0.88(5)$	$356 \pm 68(5)$	$638 \pm 117(5)$	$29.0 \pm 6.3(5)$	$12.7 \pm 1.0(5)$
$1.30 \pm 0.04(2)$	$40.8 \pm 9.1(4)$	$3.62 \pm 1.34(5)$	$274 \pm 81(5)$	$477 \pm 126(5)$	$24.0 \pm 9.9(5)$	$13.0 \pm 1.4(5)$
$1.55 \pm 0.01(3)$	$40.0 \pm 2.1(4)$	$3.35 \pm 0.96(5)$	$243 \pm 78(5)$	$406 \pm 130(5)$	$22.2 \pm 5.7(5)$	$13.9 \pm 1.0(5)$
$2.01 \pm 0.02(2)$	$44.1 \pm 5.6(4)$	$2.07 \pm 0.41(5)$	$151 \pm 32(5)$	$280 \pm 59(5)$	$14.4 \pm 3.8(5)$	$13.8 \pm 1.5(5)$
$2.97 \pm 0.03(2)$	$54.2 \pm 8.5(4)$	$1.68 \pm 0.41(5)$	$120 \pm 13(5)$	$212 \pm 43(5)$	$11.9 \pm 5.3(5)$	$14.0 \pm 3.5(5)$

Table 3 Mechanical properties of PVC membranes plasticized with dibutyl sebacate (DBS). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness ($N m^{-1}$)	Tangent stiffness ($N m^{-1}$)	Toughness (N mm)	Ductility (mm)
$0.00 \pm 0.00(1)$	$16.7 \pm 2.4(3)$	$5.78 \pm 2.54(3)$	$957 \pm 432(3)$	$1480 \pm 706(3)$	$18.3 \pm 8.1(3)$	$6.0 \pm 0.2(3)$
$0.28 \pm 0.01(2)$	$23.6 \pm 4.1(4)$	$6.42 \pm 1.36(4)$	$1130 \pm 170(4)$	$1770 \pm 111(4)$	$22.0 \pm 14.3(4)$	$5.8 \pm 2.0(4)$
$0.57 \pm 0.07(2)$	$25.0 \pm 3.2(4)$	$6.34 \pm 1.17(4)$	$584 \pm 85(4)$	$981 \pm 177(4)$	$40.3 \pm 12.9(4)$	$10.9 \pm 1.7(4)$
$0.75 \pm 0.00(1)$	$25.1 \pm 0.7(4)$	$4.59 \pm 0.25(4)$	$351 \pm 17(4)$	$722 \pm 54(4)$	$36.8 \pm 3.0(4)$	$12.8 \pm 0.3(4)$
$1.06 \pm 0.08(2)$	$29.8 \pm 2.7(5)$	$4.58 \pm 0.57(5)$	$323 \pm 56(5)$	$554 \pm 74(5)$	$33.6 \pm 4.3(5)$	$14.3 \pm 1.0(5)$
$1.55 \pm 0.07(2)$	$35.4 \pm 1.4(5)$	$3.85 \pm 0.99(5)$	$256 \pm 63(5)$	$389 \pm 65(5)$	$27.8 \pm 7.7(5)$	$15.0 \pm 1.1(5)$
$2.03 \pm 0.01(2)$	$38.9 \pm 1.0(4)$	$2.98 \pm 0.44(4)$	$176 \pm 29(4)$	$279 \pm 29(4)$	$24.0 \pm 3.7(4)$	$16.9 \pm 1.8(4)$
$2.52 \pm 0.01(2)$	$37.0 \pm 5.7(4)$	$1.85 \pm 0.87(4)$	$108 \pm 30(4)$	$179 \pm 28(4)$	$16.0 \pm 11.2(4)$	$16.5 \pm 4.3(4)$
$3.02 \pm 0.04(2)$	$48.1 \pm 5.3(4)$	$1.52 \pm 0.65(4)$	$92 \pm 11(4)$	$161 \pm 21(4)$	$13.0 \pm 9.6(4)$	$16.2 \pm 5.2(4)$
$3.57 \pm 0.03(2)$	$45.6 \pm 4.8(4)$	$1.62 \pm 0.50(4)$	$91 \pm 11(4)$	$148 \pm 22(4)$	$14.1 \pm 7.7(4)$	$17.8 \pm 5.2(4)$

Table 4 Mechanical properties of PVC membranes plasticized with dioctyl sebacate (DOS). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness ($N m^{-1}$)	Tangent stiffness ($N m^{-1}$)	Toughness (N mm)	Ductility (mm)
$0.00 \pm 0.00(1)$	$16.7 \pm 2.4(3)$	$5.78 \pm 2.54(3)$	$957 \pm 432(3)$	$1480 \pm 706(3)$	$18.3 \pm 8.1(3)$	$6.0 \pm 0.2(3)$
$0.34 \pm 0.02(3)$	$26.4 \pm 5.3(5)$	$6.69 \pm 1.30(5)$	$874 \pm 118(5)$	$1280 \pm 100(5)$	$30.0 \pm 13.4(5)$	$7.8 \pm 2.1(5)$
$0.68 \pm 0.02(2)$	$26.3 \pm 4.0(5)$	$4.43 \pm 0.55(5)$	$379 \pm 58(5)$	$692 \pm 68(5)$	$30.7 \pm 5.4(5)$	$11.8 \pm 1.2(5)$
$0.92 \pm 0.00(2)$	$26.4 \pm 2.9(4)$	$4.69 \pm 1.46(4)$	$362 \pm 98(4)$	$541 \pm 85(4)$	$31.0 \pm 10.0(4)$	$12.9 \pm 1.2(4)$
$1.22 \pm 0.01(2)$	$35.6 \pm 3.0(5)$	$2.97 \pm 0.12(5)$	$233 \pm 7(5)$	$450 \pm 12(5)$	$21.0 \pm 2.1(5)$	$12.8 \pm 0.8(5)$
$1.92 \pm 0.05(2)$	$41.7 \pm 1.8(4)$	$1.90 \pm 0.32(4)$	$136 \pm 9(4)$	$259 \pm 10(4)$	$13.9 \pm 3.2(4)$	$13.8 \pm 1.3(4)$
$2.48 \pm 0.04(3)$	$51.2 \pm 2.1(4)$	$1.25 \pm 0.04(4)$	$99 \pm 2(4)$	$200 \pm 3(4)$	$8.29 \pm 0.72(4)$	$12.7 \pm 0.5(4)$
$4.15 \pm 0.01(2)$	$70.3 \pm 7.4(4)$	$0.98 \pm 0.37(4)$	$65 \pm 10(4)$	$127 \pm 10(4)$	$6.90 \pm 3.28(4)$	$14.6 \pm 2.9(4)$
$5.65 \pm 0.00(2)$	$88.3 \pm 20.5(4)$	$1.27 \pm 1.33(4)$	$74 \pm 55(4)$	$131 \pm 93(4)$	$11.7 \pm 14.2(4)$	$14.7 \pm 4.6(4)$

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). Note that the toughness was measured with a Summagraphics digitizer.

Statistical analysis

The means and standard deviations were determined for each plasticizer at the different levels of plasticization. These values were plotted *versus* phr ratios in order to determine the effects of plasticizer level. After a logarithmic transformation of the phr ratios, a linear relation was fitted for each of the plasticizer groups. Using the mean values for samples measured at common phr ratios, the correlation coefficients (r) and numbers of values (n) were used to determine the corresponding probabilities (p).

RESULTS

Strength

Membranes plasticized with CF at a phr ratio of 0.31 had the highest peak strength (9.63 N) of all membranes tested (*Tables 2–8*). All plasticizers except PGDO

Table 5 Mechanical properties of PVC membranes plasticized with *ortho*-nitrophenyl octyl ether (*o*-NPOE). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	16.7 ± 2.4(3)	5.78 ± 2.54(3)	957 ± 432(3)	1480 ± 706(3)	18.3 ± 8.1(3)	6.0 ± 0.2(3)
0.49 ± 0.11(3)	25.9 ± 2.8(7)	8.02 ± 0.70(7)	936 ± 152(7)	1590 ± 265(7)	39.6 ± 11.0(7)	8.7 ± 1.4(7)
0.83 ± 0.06(6)	27.1 ± 2.9(14)	7.22 ± 0.92(14)	823 ± 181(14)	1320 ± 230(14)	37.0 ± 10.8(14)	9.0 ± 1.9(14)
1.60 ± 0.04(2)	32.1 ± 3.1(6)	4.82 ± 0.82(6)	338 ± 40(6)	511 ± 45(6)	33.3 ± 6.7(6)	14.2 ± 1.2(6)
2.56 ± 0.04(6)	40.5 ± 11.9(27)	3.17 ± 1.48(27)	212 ± 81(27)	331 ± 113(27)	22.9 ± 13.1(27)	14.9 ± 1.9(27)
4.22 ± 0.05(2)	48.9 ± 2.0(4)	1.26 ± 0.12(4)	93 ± 20(4)	152 ± 15(4)	8.36 ± 0.82(4)	13.9 ± 1.7(4)
5.31 ± 0.05(2)	46.8 ± 11.4(4)	1.72 ± 0.71(4)	80 ± 21(4)	128 ± 22(4)	18.5 ± 9.6(4)	20.7 ± 4.8(4)
61.8 ± 0.07(2)	57.6 ± 7.4(4)	1.24 ± 0.80(4)	65 ± 14(4)	110 ± 9(4)	12.7 ± 13.7(4)	18.1 ± 8.4(4)
7.13 ± 0.05(2)	63.4 ± 8.7(5)	0.85 ± 0.46(5)	54 ± 17(5)	86 ± 8(5)	7.05 ± 4.87(5)	15.0 ± 3.3(5)

Table 6 Mechanical properties of PVC membranes plasticized with expoxidized linseed oil (ELO). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	16.7 ± 2.4(3)	5.78 ± 2.54(3)	957 ± 432(3)	1480 ± 706(3)	18.3 ± 8.1(3)	6.0 ± 0.2(3)
0.27 ± 0.00(2)	35.0 ± 3.9(5)	7.16 ± 1.46(5)	718 ± 236(5)	1160 ± 191(5)	41.7 ± 17.0(5)	10.8 ± 3.4(5)
0.52 ± 0.01(2)	44.0 ± 9.3(6)	4.81 ± 1.97(6)	358 ± 200(6)	624 ± 386(6)	32.9 ± 13.6(6)	14.0 ± 1.6(6)
0.78 ± 0.03(2)	59.9 ± 6.8(6)	2.39 ± 0.91(6)	171 ± 61(6)	300 ± 112(6)	15.5 ± 7.1(6)	13.9 ± 0.8(6)
1.03 ± 0.02(3)	73.5 ± 18.9(6)	1.72 ± 0.36(6)	114 ± 29(6)	203 ± 52(6)	11.9 ± 4.4(6)	15.5 ± 3.8(6)
1.28 ± 0.02(4)	64.6 ± 18.3(5)	1.61 ± 2.34(7)	117 ± 157(7)	221 ± 295(7)	10.7 ± 16.7(7)	12.9 ± 0.9(7)
1.51 ± 0.02(3)	72.0 ± 16.0(6)	0.64 ± 0.60(6)	50 ± 49(6)	942 ± 642(6)	3.8 ± 2.9(6)	12.8 ± 0.5(6)
1.78 ± 0.00(2)	88.3 ± 27.6(4)	1.52 ± 0.97(5)	85 ± 68(5)	153 ± 114(5)	12.6 ± 6.2(5)	18.7 ± 4.3(5)
2.00 ± 0.01(2)	83.8 ± 25.5(4)	1.27 ± 1.22(5)	75 ± 81(5)	127 ± 106(5)	10.2 ± 9.0(5)	16.8 ± 5.1(5)

Table 7 Mechanical properties of PVC membranes plasticized with expoxidized soybean oil (ESO). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

phr ratio	Thickness (μm)	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	16.7 ± 2.4(3)	5.78 ± 2.54(3)	957 ± 432(3)	1480 ± 706(3)	18.3 ± 8.1(3)	6.0 ± 0.2(3)
0.26 ± 0.00(3)	33.2 ± 4.4(5)	6.04 ± 2.09(6)	621 ± 285(6)	1010 ± 494(6)	31.0 ± 11.1(6)	10.1 ± 1.8(6)
0.52 ± 0.03(3)	43.0 ± 4.8(5)	3.70 ± 1.85(5)	300 ± 186(5)	517 ± 323(5)	23.7 ± 10.1(5)	12.9 ± 1.3(5)
0.78 ± 0.03(2)	53.1 ± 10.4(5)	2.32 ± 1.46(5)	176 ± 119(5)	306 ± 232(5)	15.5 ± 10.0(5)	13.4 ± 3.1(5)
1.01 ± 0.01(2)	62.2 ± 15.7(5)	1.90 ± 2.26(5)	147 ± 163(5)	252 ± 254(5)	11.8 ± 14.4(5)	12.3 ± 0.8(5)
1.26 ± 0.00(2)	66.0 ± 19.3(5)	1.25 ± 1.46(5)	95 ± 106(5)	177 ± 180(5)	7.80 ± 9.20(5)	12.6 ± 0.8(5)
1.53 ± 0.02(3)	77.1 ± 22.7(5)	0.64 ± 0.30(7)	43 ± 18(7)	913 ± 44(7)	4.89 ± 3.01(7)	14.2 ± 3.4(7)
1.77 ± 0.03(2)	88.9 ± 26.6(4)	0.67 ± 0.36(5)	47 ± 25(5)	936 ± 36(5)	4.95 ± 3.29(5)	13.9 ± 3.2(5)
2.04 ± 0.03(3)	66.1 ± 8.0(4)	0.69 ± 0.32(8)	58 ± 48(8)	820 ± 34(8)	5.34 ± 3.26(8)	13.8 ± 4.5(8)

Table 8 Mechanical properties of PVC membranes plasticized with propylene glycol dioleate (PGDO). Parenthetic values represent the number of solutions in the phr ratio column and the number of samples in all other columns

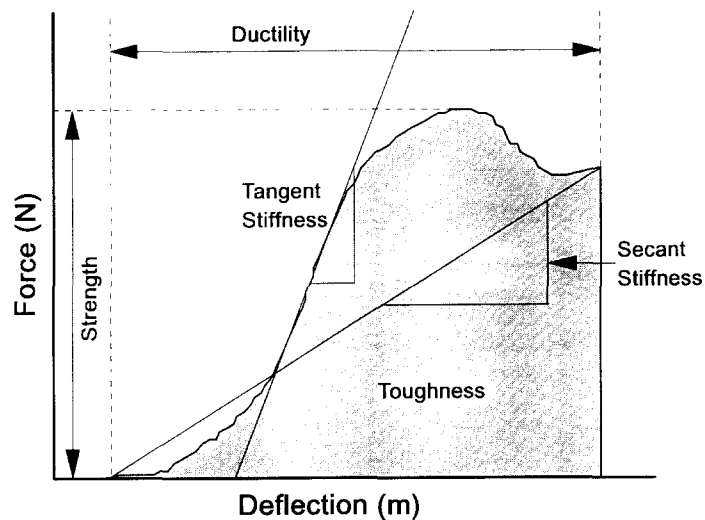| phr ratio	Thickness (μm)	Strength (N)	Secant stiffness (N m^{-1})	Tangent stiffness (N m^{-1})	Toughness (N mm)	Ductility (mm)
0.00 ± 0.00(1)	16.7 ± 2.4(3)	5.78 ± 2.54(3)	957 ± 432(3)	1480 ± 706(3)	18.3 ± 8.1(3)	6.0 ± 0.2(3)
0.26 ± 0.00(2)	32.9 ± 9.2(4)	5.73 ± 2.34(4)	557 ± 220(4)	1040 ± 377(4)	36.2 ± 13.4(4)	10.2 ± 0.6(4)
0.50 ± 0.00(2)	34.4 ± 4.7(4)	4.50 ± 1.38(4)	322 ± 70(4)	542 ± 95(4)	32.6 ± 12.6(4)	13.9 ± 2.5(4)
0.75 ± 0.01(2)	40.2 ± 8.7(4)	3.37 ± 1.48(4)	211 ± 65(4)	338 ± 79(4)	27.1 ± 14.2(4)	15.6 ± 3.1(4)
1.00 ± 0.00(2)	51.5 ± 7.6(5)	2.30 ± 0.76(5)	146 ± 31(5)	269 ± 45(5)	18.3 ± 8.7(5)	15.5 ± 2.5(5)
1.25 ± 0.01(2)	69.1 ± 18.5(5)	2.08 ± 1.07(5)	122 ± 33(5)	232 ± 54(5)	19.3 ± 14.9(5)	16.3 ± 4.9(5)
1.56 ± 0.03(2)	82.1 ± 10.2(4)	1.10 ± 0.44(4)	82 ± 30(4)	162 ± 24(4)	7.1 ± 2.3(4)	13.3 ± 0.7(4)
1.76 ± 0.03(2)	76.5 ± 7.6(4)	0.75 ± 0.13(4)	59 ± 9(4)	127 ± 16(4)	5.0 ± 0.8(4)	12.6 ± 0.9(4)
2.00 ± 0.00(2)	76.4 ± 20.1(4)	0.80 ± 0.48(4)	54 ± 21(4)	109 ± 36(4)	6.0 ± 4.6(4)	13.8 ± 3.1(4)

Figure 3 Typical plot from a membrane puncture test showing the derivation of the mechanical properties from the output
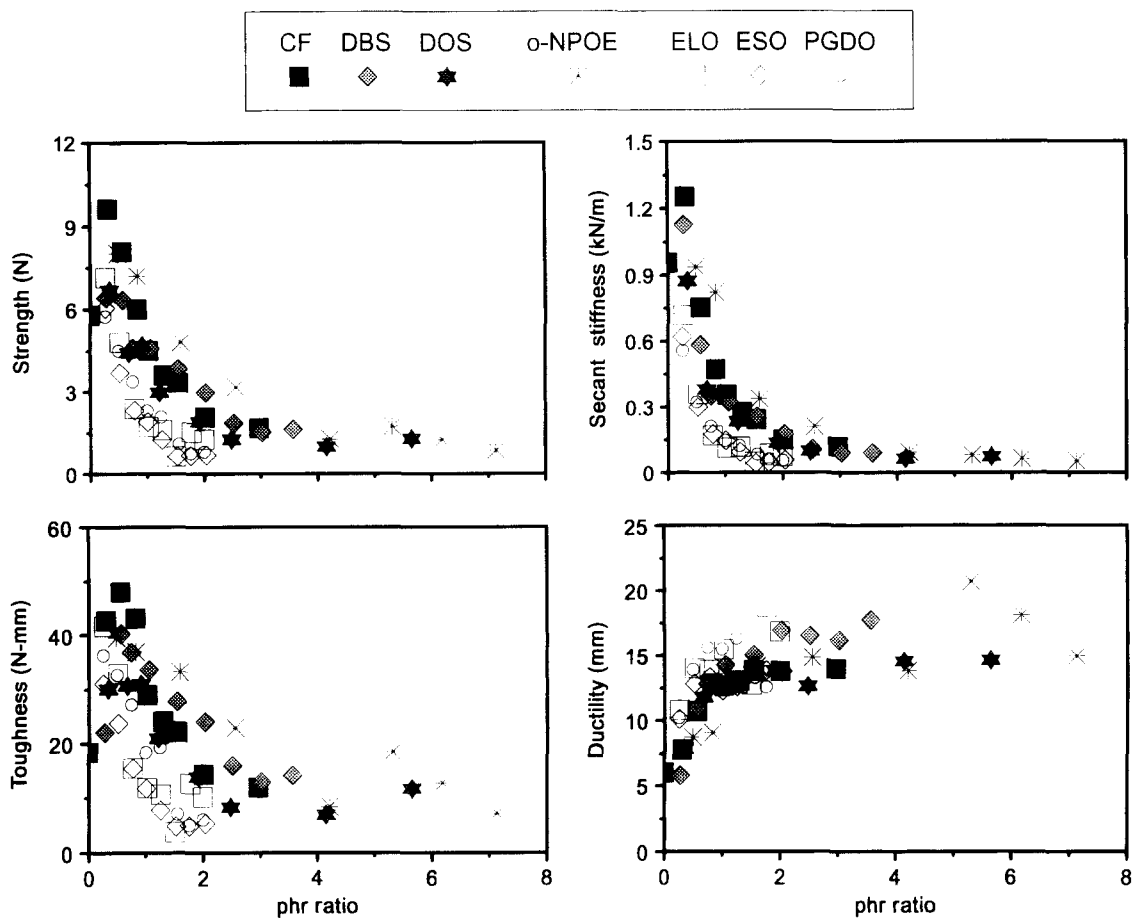

Figure 4 Mean values of strength (N), secant stiffness (kN m $^{-1}$) toughness (N mm), and ductility (mm) plotted vs phr ratio for seven placticizers

increased the strength of the membranes at low levels of plasticization (phr ratio <0.5). Increasing the plasticization of membranes beyond these phr ratios decreased the strength (*Figure 4*). Membranes plasticized with lower MW plasticizers (CF, DBS, DOS, and *o*-NPOE) generally maintained strength values above that of neat PVC up to higher phr ratios than the membranes with higher MW plasticizers (ELO, ESO, and PGDO). Furthermore, the membranes with lower MW plasticizers generally had higher strengths than the membranes with higher MW plasticizers throughout the test range.

At a phr ratio of 1.0, which represented the minimum plasticizer required for complete PVC isolation, the CF, DBS, and DOS membranes had similar mean strengths of 4.5 N; the *o*-NPOE membranes had a mean strength of 6.0 N; and the ELO, ESO, and PGDO membranes had similar mean strengths of 2.0 N. Throughout the range of plasticization, the polarity of *o*-NPOE appears to have increased the strength of the membranes beyond that expected due to the MW of the plasticizer. After logarithmic transformation of the phr ratios, the strength *versus* phr ratio was separated into four groups
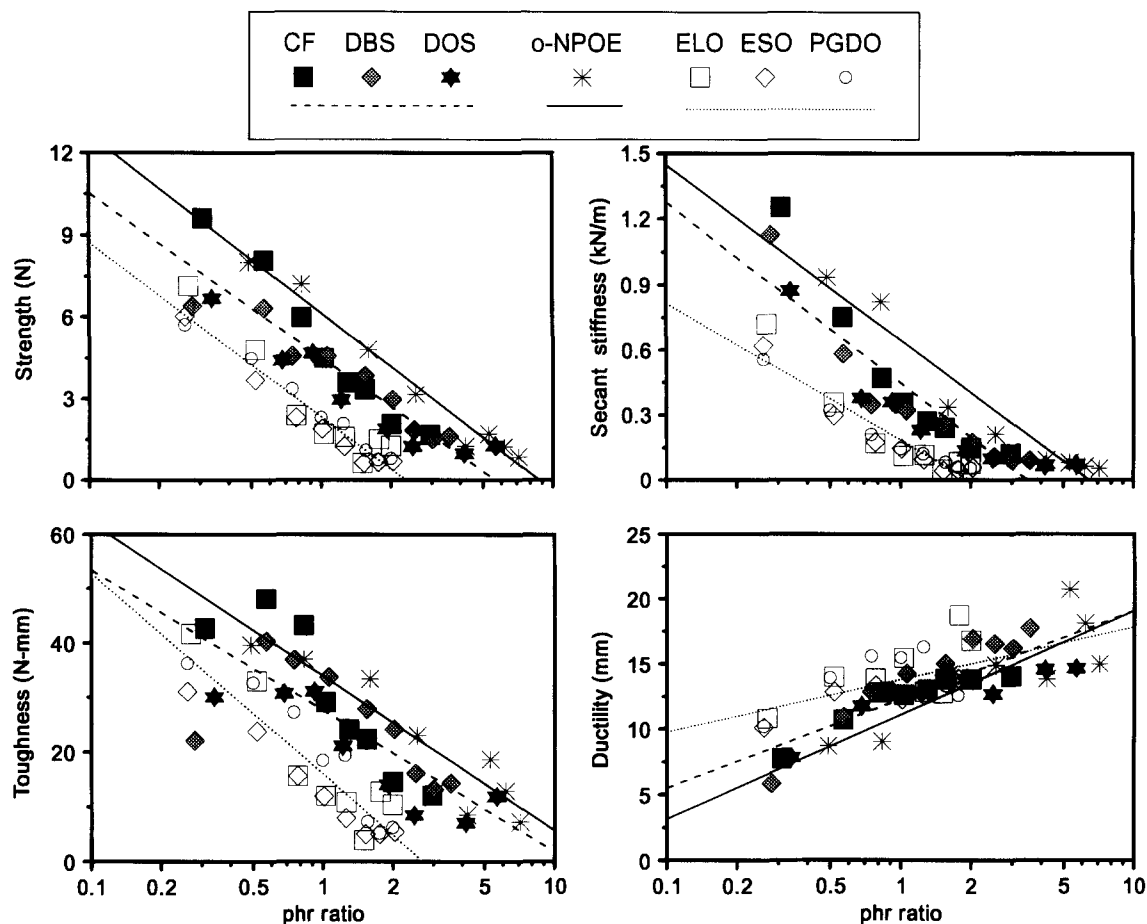
Figure 5 Mean values of strength (N), secant stiffness (kN m^{-1}), toughness (N mm), and ductility (mm) plotted vs log phr ratio for seven plasticizers denoted in *Figure 4*. Linear fits were plotted for four groups: CF (- · · ·); DBS and DOS (– – –); o-NPOE (——); and ELO, ESO, and PGDO (· · · · ·)

Table 9 Statistical data derived from linear regressions of the mean mechanical properties versus the logarithmically transformed phr ratios. The probabilities (P) were $P < 0.001$ (*) unless otherwise noted

Mechanical property	CF			DBS & DOS			o-NPOE			ELO, ESO & PGDO		
	r	n	P	r	n	P	r	n	P	r	n	P
Strength	0.983	8	*	0.953	17	*	0.988	8	*	0.962	24	*
Secant stiffness	0.951	8	*	0.907	17	*	0.965	8	*	0.947	24	*
Tangent stiffness	0.950	8	*	0.929	17	*	0.960	8	*	0.952	24	*
Toughness	0.906	8	<0.01	0.750	17	*	0.941	8	*	0.921	24	*
Ductility	0.924	8	<0.01	0.837	17	*	0.844	8	<0.01	0.574	24	*
Strength[a]	0.970	8	*	0.963	17	*	0.981	8	*	0.951	24	*
Secant stiffness[a]	0.927	8	*	0.899	17	*	0.953	8	*	0.932	24	*
Tangent stiffness[a]	0.931	8	*	0.916	17	*	0.948	8	*	0.933	24	*
Toughness[a]	0.893	8	<0.01	0.858	17	*	0.965	8	*	0.947	24	*
Ductility[a]	0.435	8	>0.10	0.344	17	>0.10	0.158	8	>0.10	0.749	24	*

[a] When normalized per unit thickness

according to molecular structure as noted previously. The data for each group were correlated using linear fits (*Figure 5*), and all four groups were statistically significant with $P < 0.001$ (*Table 9*).

Stiffness

Membranes plasticized with CF had the highest peak secant stiffness of 1250 N m^{-1} at a phr ratio of 0.31 (*Tables 2–8*). For all plasticizers the secant stiffness of the membranes decreased monotonically with increased plasticization, except for low phr ratios (<0.4) using CF

or DBS (*Tables 2* and *3*). Once again throughout the test range, the membranes plasticized with lower MW plasticizers generally had higher secant stiffnesses than those membranes that were plasticized with higher MW plasticizers (*Figure 4*). At a phr ratio of 1.0, the secant stiffnesses were grouped in a manner similar to the strengths. The groups and values were as follows: CF, DBS, and DOS at 350 N m^{-1}, o-NPOE at 800 N m^{-1}, and ELO, ESO, and PGDO at 125 N m^{-1}. As noted in the strength, the secant stiffness also seems to be improved by the polarity of the o-NPOE. The tangent
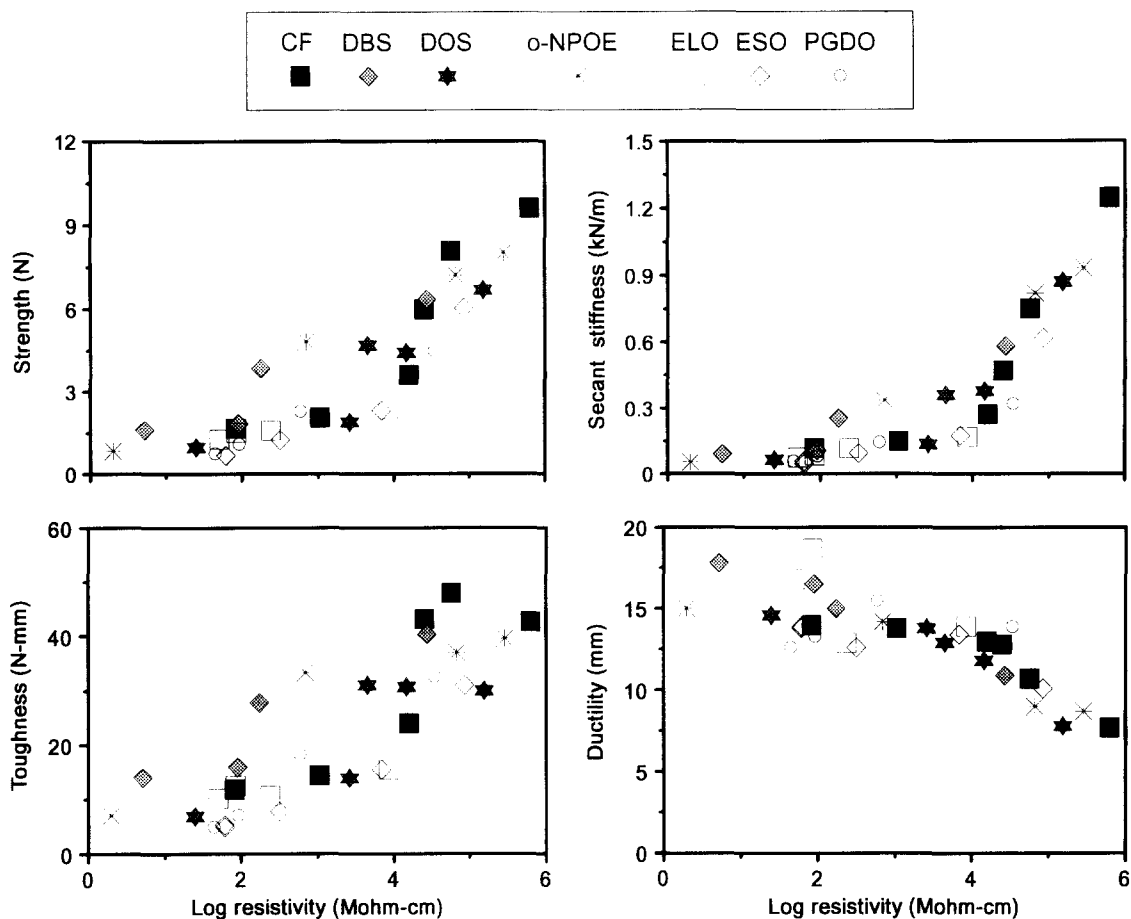
Figure 6 Mean values of strength (N), secant stiffness (kN m⁻¹), toughness (N mm), and ductility (mm) plotted vs mean values of log resistivity (Mohm cm) for seven plasticizers denoted in *Figure 4*

stiffness (not shown) was generally 1.7 times the secant stiffness and had the same apparent trends (*Tables 2–8*). The four groups of plasticizers, which were identified previously, were used for statistical evaluation of the secant stiffness (*Figure 5*) and tangent stiffness. Each of the four groups were significant at $P < 0.001$ using logarithmic transformations of the phr ratios and linear fits (*Table 9*).

Toughness

The peak toughness observed was greatest at 48 N mm for membranes plasticized with CF to a phr ratio of 0.6 (*Tables 2–8*). The toughness increased at low levels of plasticization for all of the plasticizers, but decreased monotonically with further plasticization. The region of increased toughness was below a phr ratio of 0.9 for the low MW plasticizers (CF, DBS, DOS, and *o*-NPOE) and below a phr ratio of 0.3 for the high MW plasticizers (ELO, ESO, and PGDO). Again, the lower MW plasticizers generally produced membranes with higher toughnesses throughout the range of plasticization tested (*Figure 4*). At a phr ratio of 1.0, the low MW plasticizers and high MW plasticizers were again different. CF, DBS, DOS, and *o*-NPOE had toughnesses of about 32 N-mm, while ELO, ESO, and PGDO had toughnesses of about 15 N-mm. Although not evident at phr ratios below 1.5, the polarity of *o*-NPOE generally produced membranes with higher toughnesses. Like the strength and stiffnesses, the toughness *versus* log phr ratio was separated into four groups (*Figure 5*). The CF group was significant

at $P < 0.01$ using a linear fit of the logarithmically transformed data, and the other three groups were significant at $P < 0.001$ using the same analysis (*Table 9*).

Ductility

The ductility increased monotonically, reaching a steady value of 15 mm at a phr ratio of 2.0 for all plasticizers (*Figure 4*). Only DBS fell below the value of ductility for the neat PVC membranes (*Tables 2–8*). At a phr ratio of 1.0, all of the membranes, regardless of the plasticizer specie, had mean ductilities of 12–15 mm. Although the low MW plasticizers generally had lower ductilities at low phr ratios, the differentiation between low MW and high MW plasticizers was not as distinct as with the other four mechanical properties (*Figure 4*). Furthermore, the effect of the polarity of *o*-NPOE was not as evident as in the previously discussed mechanical properties. Although the groups were not as clearly defined, the four groups were used again in regression analyses of the ductility vs log phr ratio (*Figure 5*). The DBS and DOS group as well as the ELO, ESO, and PGDO group were significant at $p < 0.001$ using a linear fit; the CF and *o*-NPOE groups were significant at $P < 0.01$ using the same analysis (*Table 9*).

DISCUSSION

Comparison of observed trends with literature

In early studies of the effects of plasticizer Brous and Semon showed that concentrations of TCP up to 10%

increased the strength of PVC, which was due to antiplasticization of the polymer[1]. Brous and Semon further observed a monotonic decrease in strength as the concentration was increased up to the 60% limit of their tests. Sears and Darby compiled later independent experiments on plasticized PVC by Walter using DOP and Ghersa using TCP[3]. Those experiments not only showed that a peak occurred at *ca* 5 wt% plasticizer but also indicated that the position of the peak varied according to the plasticizer specie. The current study also showed antiplasticization effects on the strength, but the peaks occurred at 15 wt% for CF, DBS, DOS and *o*-NPOE, and at 45 wt% for ELO and ESO. However, these were the minimum values tested for each plasticizer, so that the maxima could have occurred at still lower wt% values. That no maximum was found for PGDO was reasonable because the minimum concentration tested for PGDO was 60% plasticizer, which was most likely beyond the antiplasticization region. Antiplasticization also caused the increases in stiffnesses and toughnesses at the lowest plasticizer ratios, which were contrary to the decreasing trends observed as plasticizer amounts were further increased. The effects of antiplasticization were important in setting limits on the data analyses. The linear fit would no longer be acceptable at very low levels of plasticization, where the effects of plasticization on the mechanical properties were reversed. The low plasticization region was not relevant to present ISE and biosensor applications, since the electrical properties of the membranes declined substantially at phr ratios below 1.0[16]. With regard to ductility, Brous and Semon recorded it as an increase in per cent elongation throughout the range of plasticization that they tested[1]; on the other hand, Walter[17] and Ghersa[18] found peaks in elongation at 60% plasticizer for DOP and 90% for TCP, respectively. Consequently, Sears and Darby suggested that elongation would peak at higher values, when the plasticizer was more compatible[3]. The current study showed no definitive peaks, thereby indicating that the plasticizers were very compatible with PVC. Presumably, additional plasticizer would eventually result in a solution of PVC in plasticizer that would have properties much like a liquid. Indeed, ISE's have been referred to as liquid membranes.

Implementation of thickness normalization

In earlier work[11] the strength, secant stiffness, tangent stiffness, and toughness were linearly dependent on the thickness of the membranes, and the ductility was independent of the membrane thickness. In that work the effects of thickness were based on a fixed membrane constitution. However in the current study, the thicknesses of the membranes were only increased by the amount of plasticizer (note the thickness measurements shown in *Tables 2–8*). In other words, for 5 ml of plasticizer/PVC/THF solution, the amount of PVC was approximately the same. Since PVC was the only structural component of the membrane, no change occurred in the 'structural thickness' of the membranes throughout the range of plasticization. As such the trends in strength, stiffness, and toughness were not affected, when the mechanical properties were first normalized by thickness and then plotted *versus* the logarithmically transformed phr ratios. The ductility became scattered by the thickness normalization, which

was expected since the ductility was not dependent on the membrane thickness[11]. Generally, neither the *r* nor the *P* of the data was improved by thickness normalization (*Table 9*).

Influence of molecular structure

Each of the four groups of plasticizers influenced the mechanical properties in a different manner (cf. *Figure 1*). The CF had the largest antiplasticization effect in the regions tested, probably because of its non-planar conformation. In the antiplasticization region, the CF further inhibited motion of the PVC chains past each other, since its four branches contributed to entanglements. At higher levels of plasticization the low MW of the CF became the dominant factor, and the membranes quickly became similar in strength to the DBS and DOS. DBS and DOS were in the mid-range of strength, bounded by the higher strength *o*-NPOE-plasticized membranes and the lower strength ELO-, ESO-, and PGDO-plasticized membranes. The linearity of the DBS and DOS molecules caused these plasticizers to have less influence than CF in the antiplasticization region. At higher levels of plasticization however, the small hydrodynamic volumes of the DBS and DOS allowed more PVC entanglements, which resulted in higher strengths compared to ELO, ESO, and PGDO. The *o*-NPOE established the upper boundary for strength at phr ratios above the antiplasticization values. The small size of the *o*-NPOE allowed PVC entanglements that were similar to DBS and DOS, and the polarity of *o*-NPOE likely inhibited PVC chain sliding due to the formation of secondary bonds between the Cl groups of the PVC and the nitro groups of *o*-NPOE. The lower boundary for strength was established by the ELO, ESO, and PGDO. These larger molecules had the smallest antiplasticization effects and were the weakest membranes throughout the range of plasticization, because their large sizes decreased the likelihood of PVC entanglements. The stiffnesses and toughnesses behaved similarly to the strengths. The plasticizer groups affected the ductility in a manner opposite to that of the strength, where smaller plasticizers reduced the ductility. These effects on ductility were much less substantial, which was evidenced by the overlap of the linear fits in *Figure 5*.

Trade-off between electrical and mechanical properties

Figure 6 shows each of the means of the mechanical properties plotted vs the means of log resistivity at equivalent plasticizer ratios, the latter of which were taken from previous work[16]. Increasing the strength of a membrane by reducing the amount of plasticizer (*Figure 4*) corresponds to an increase in the log resistivity of the membrane (*Figure 6*). Since no distinctions among plasticizer species were evident in the dielectric results, no distinctions among plasticizer species were evident in this strength *versus* log resistivity plot. Increased secant stiffness also corresponded to increased log resistivity, since each quantity was increased by reductions in the amount of plasticizer. Like the strength plot, the secant stiffness *versus* log resistivity plot did not distinguish among plasticizer species. The tangent stiffness was again similar to the secant stiffness. Increases in the toughness corresponded to increases in log resistivity. Note that the increased scatter on the right portion of the plot was associated with the peak that was observed in the toughness at low phr ratios. Decreases in the ductility

correspond to increases in the resistivity of the membranes, since higher phr ratios correspond to higher ductility and lower log resistivity. The ideal membrane would have not only low resistivity but also high strength, stiffness, toughness, and ductility. Changes in the phr ratio that result in increases in strength, stiffness, and toughness also increase the resistivity, so a trade-off must be made between these quantities. Only ductility can be increased without adversely affecting the electrical properties of the membrane.

Implication of plasticizer studies for electrodes and biosensors

A reduction in the amount of plasticizer from the traditional 200 phr used in electrode and biosensor applications (*Table 1*) would improve the mechanical integrity of the membranes (*Figure 4*). In previous work, however, the ionic resistivity of PVC membranes increased with a reduction in the amount of plasticizer[16]. In that work, the addition of plasticizer beyond a phr ratio of 1.0 did not change the ionic resistivity substantially. A reduction from the traditional 200 phr (cf. *Table 1* for equivalent phr ratios) would substantially increase the mechanical integrity of the PVC membranes, thereby improving the reliability of the electrodes. The reduction in plasticizer to a phr ratio between 1.0 and the traditional value (which depends on plasticizer species) would also decrease the risk of bodily infection or failure of the sensor due to the plasticizer leaching out of the membrane[19].

CONCLUSIONS

The strength of PVC membranes increased due to antiplasticization up to phr ratios of 0.5, dependent on the plasticizer species. The addition of plasticizer beyond these phr ratios decreased the strength of the membranes.

The secant and tangent stiffnesses decreased throughout the range of plasticization tested, except at low levels due to antiplasticization using CF and DBS.

The toughness of the membranes increased with the addition of plasticizer up to phr ratios of 0.9, dependent on the plasticizer species. Plasticization above these phr ratios decreased the toughness of the PVC membranes.

The ductility of the membranes monotonically increased up to a phr ratio of 2.0, above which the ductility was independent of plasticizer amount.

The phr ratio distinguished the plasticizers according to molecular structure. These distinctions were not substantially changed by normalizing the strength, secant stiffness, tangent stiffness, and toughness of the membrane by the thickness of the membrane.

Throughout the range of plasticization, plasticizers having lower hydrodynamic volumes increased the strengths, stiffnesses, and toughnesses of the membranes. The trends were reversed for the ductilities, but the effects on the ductilities were not substantial.

Strength, stiffness, and toughness increased as ionic resistivity increased. Ductility decreased as ionic resistivity increased. As such, useful electrodes and biosensors could be produced using phr ratios between 1.0 and the equivalent of 200 phr, where the particular phr ratio depends on the plasticizer species. Within this range, decreasing plasticization improved the mechanical function, and increasing plasticization improved electrical function.

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