

Mechanical behaviour of a plasticized PVC subjected to ethanol exposure

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Abstract

This paper presents the results of a series of experimental investigations conducted to assess the influence of ethanol exposure at different concentrations on the mechanical properties of a plasticized PVC membrane. Exposure to pure ethanol resulted in a reduction in flexibility, or embrittlement, and the transformation of the PVC membrane from a flexible material capable of undergoing large strain hyperelastic behaviour to a stiffer material with pronounced yield behaviour. Results of X-ray fluorescence measurements indicate the loss of the plasticizer from the PVC membrane as a contributing factor for the alteration in the mechanical properties of the PVC membrane. The experiments also indicate a slower rate of plasticizer leaching during exposure to lower concentrations of ethanol. Exposure of the PVC membranes to 80% and 50% concentrations of ethanol and pure water has a reduced influence on the loss of large strain deformability of the PVC membrane, even after more than one year of exposure. The PVC membranes exposed to a mixture of ethanol and pure water in equal volume proportions indicate that, after longer period, the PVC membranes became softer and exhibit greater deformation under the same external load. This phenomenon can be attributed to the swelling of the PVC membrane.

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1. Introduction

Plasticized PVC is used extensively in geo-environmental applications, particularly as engineered barrier systems for landfills and for containment of other forms of hazardous and toxic wastes [1]. The plasticized PVC membrane constitutes an important component in a multi-barrier containment system that includes alternate layers of impermeable clay and serves as the collector system [1,2]. While the clay layers are intended to provide the main barrier against contaminant migration, on occasions, particularly those involving thermal desiccation of the clay liners, the effluents from the

retained waste can come into direct contact with the PVC membrane. The possibility of direct contact of the PVC membrane with waste leachate is therefore of major concern for the engineering usage of such PVC membrane barriers. In adverse environmental conditions in a landfill, the exposure of the PVC membrane to chemicals can lead to leaching of the plasticizer from the PVC membrane [3]. The evidence of leaching of the plasticizer from plasticized PVCs is also documented in other literatures [4–6]. The plasticizer contributes to a significant increase in the flexibility of an otherwise brittle PVC polymer [7–9]. The work of Pita et al. [10] shows that a monotonically increasing relationship exists between the stress and strain for plasticized PVC with high plasticizer content. When the plasticizer content is lowered, a clear yield-type stress–strain behaviour is observed (Fig. 1). The addition of plasticizers also lowers the glass transition temperature (T_g) of

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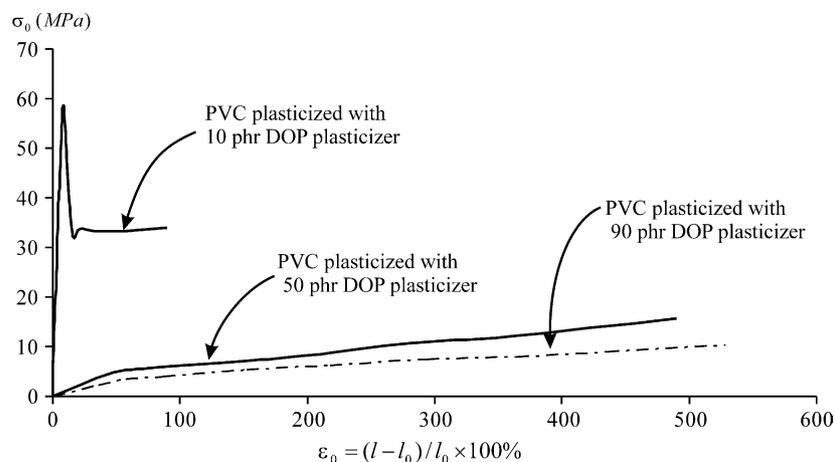


Fig. 1. Stress–strain curve of plasticized PVC with different amounts of DOP plasticizer (in phr) [10].

a rigid PVC polymer, making it more flexible [8,11,12]. The mechanism of the action of a plasticizer in PVC is, however, quite complex [7–9]. Results of spectroscopic examinations presented by Dubault et al. [12] show that the lowering of the glass transition temperature can be attributed to the interaction between the plasticizer and the backbone of the PVC chain. These authors also conclude that changes to the mechanical behaviour (including plastic and yielding behaviour at various temperatures), due to the presence of plasticizer, can be attributed to such interactions.

While additives, such as plasticizers, are favored for the modification of the mechanical properties of a PVC, issues related to the durability of a plasticized PVC can arise from either the loss of additives such as plasticizer from the polymer matrix, or the alteration in chemical composition of the additives or, more adversely, due to the scission of the polymeric chain from within the polymer structure. Polymeric chain scission represents the chemical alteration of the polymer molecule backbone, which directly affects its integrity and subsequently contributes to the failure of the material. Polymer chain scission can materialize more prominently under low-level radiation. The loss of plasticizers is believed to be the dominant process contributing to the aging of plasticized PVC [13,14]. In some cases, while the loss of additives such as the plasticizer may alter the properties of the material, it does not change the integrity of the polymer structure. Plasticizer loss can either take the form of extraction during contact with chemically incompatible media, or migration or volatilization [15–18]. Migration refers to the situation where the plasticizer transfers from one polymer to another (usually an unplasticized one) during contact [17]. Volatilization occurs when the plasticizer is released into surrounding gas usually at high temperatures [13,14,16]. In contrast to the volatilization process at high temperature, the loss of plasticizers in a liquid at

low temperature is considered to be an extraction process [4–6,19]. The extraction of plasticizers from a solid takes place through diffusion [13]. The diffusion process is related to the type of surrounding media, the nature and concentration of the plasticizer, molecular weight of the polymer, the plasticization process and temperature [20]. The diffusive nature of the transport of the plasticizer from within a plasticized PVC creates a non-uniform distribution of its concentration across the thickness of the PVC membrane, with the highest concentration at the center [21,22]. Loss of plasticizer can also be induced by other processes such as biological action [15,23,24], thermal degradation [13] and weathering [25]. Chemical alteration of a plasticizer can also occur when a proper chemical reaction is enhanced under UV dosage [26]. In connection with the use of plasticized PVC membranes as landfill liners, the adverse environments can include exposure to heat, ultra-violet light, bacteria and chemicals [27]. The longevity of the containment provided by a PVC membrane can thus be influenced by any of these actions. Previous investigations have recognized the importance of the loss of additives in determining the longevity and serviceability of the PVC membrane barrier [28]. The alterations manifest in the form of the loss of physical properties of the PVC membrane including its total weight and thickness, and an alteration in the mechanical properties such as an increase in elastic modulus, an increase in tensile strength and the loss of flexibility which results in a reduction in the strain to failure.

In this paper the performance of a plasticized PVC membrane as a landfill liner subjected to chemical exposure will be discussed. While the range and complexity of the contaminants in a waste disposal endeavour can be diverse, this research is directed to the examination of the behaviour of the PVC membrane when exposed to commonplace contaminants such as ethanol and acetone. Previous preliminary experimental

investigations conducted by Haedrich [29] and Contamin and Debeauvais [30] point to a significant loss of elasticity of the PVC membrane during exposure to acetone and ethanol, respectively. The research reported in this paper is an effort to examine the influence of the exposure of a PVC membrane to concentrations of ethanol, in terms of alteration in the mechanical response of the material. The volumetric concentrations were 100%, 80%, 50% and 0% of ethanol in a water–ethanol mixture. The focus of the experimental investigations was to assess the effects of exposure on the loss of flexibility of the PVC membrane and to correlate such findings with the loss of plasticizer from the PVC membrane.

2. Experimental investigations

2.1. Materials and sample preparation

The PVC membrane tested (Solmax 220, manufactured by Canadian General Tower, Inc., ON, Canada) was supplied from Groupe Solmax Inc., QC, Canada. The PVC membrane has a nominal thickness of 0.5 mm and contains PVC resin (50–70% weight content) as a major component along with several types of additives, such as plasticizer, lubricant, pigment and fillers to alter its mechanical behaviour [31]. The chemical composition of a typical PVC polymer is $(\text{CH}_2\text{CHCl})_n$. The plasticizer comprises the major part of the additives, and amounts between 25 and 35% of the total weight. The PVC membrane samples subjected

to chemical exposure were cut from a larger sheet measuring 250 mm \times 180 mm [Fig. 2(a–b)].

2.2. Chemical exposure facility

In the current experimental program, the samples of the PVC membrane were subjected to ethanol exposure at various concentrations through immersion [Fig. 3(a)]. The samples of the PVC membrane measuring 250 mm \times 180 mm were separated by layers of a highly permeable and inert polypropylene geotextile, and placed in a stainless container. The stack of PVC membranes was then dosed with appropriate chemical concentrations. The stainless container was then covered by a stainless cover. To further reduce the possible leakage of the ethanol, a thin strip of silicone glue was used between the cover and the container. When a stack of PVC membranes that were separated by geotextile layers was immersed in a water–ethanol mixture, the geotextile layer allowed the mixture to come into contact with both faces of the PVC membrane. In view of the highly volatile nature of ethanol, the entire exposure facility was stored in a ventilated chamber that was maintained at a relatively constant room temperature. In the exposure facility the samples were kept undisturbed except during situations where the PVC membranes had to be removed manually, which induced some mixing of the water–ethanol mixture inside the container. There is a likelihood that such disturbances can also alter the contact condition between the water–ethanol mixture and the PVC membrane during an immersion sequence; such effects are, however, not

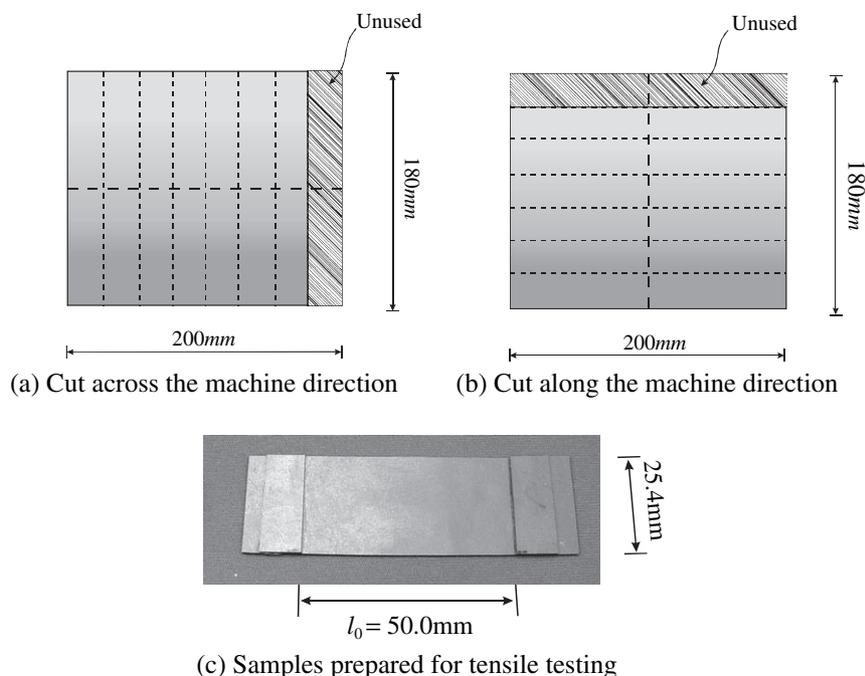


Fig. 2. PVC membrane prepared for the immersion test and the tensile test.

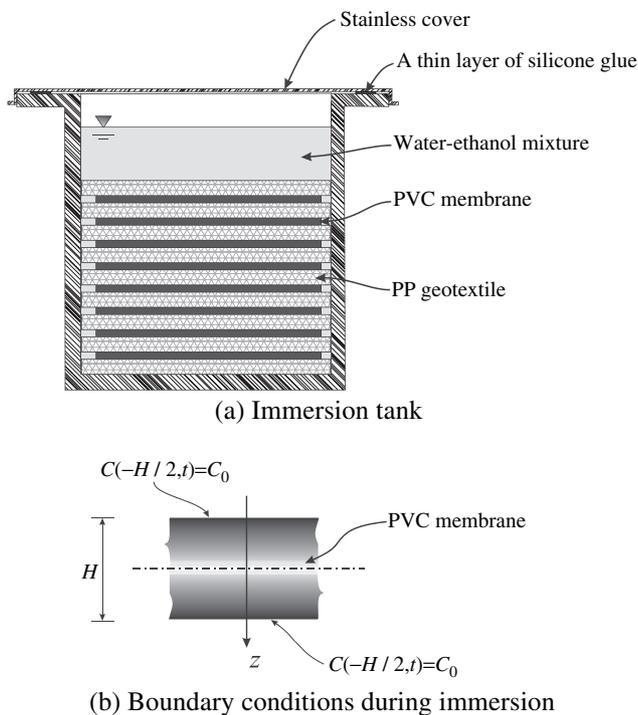


Fig. 3. Immersion test for PVC membranes subjected to chemical exposure.

considered significant from the point of view of the experiment. It has also been noted that *direct contact* between the solid polypropylene geotextile and PVC membrane can induce plasticizer migration between two media [17]. The quantitative analysis of such migration processes is rare due to the absence of the definition of contact conditions between two materials. In the current experimentation, it was assumed that the contact area between the PVC membranes and highly porous geotextile was small (with an area ratio corresponding to the porosity of the geotextile) and that entire surfaces of the PVC membrane were therefore subjected to exposure to the water–ethanol mixture, enabling free diffusion of the plasticizer from the PVC membrane. Furthermore, the chemical interactions between the water–ethanol mixture and the polypropylene were considered not to be important to the examination of the interaction between the PVC membrane and the ethanol.

The process governing the migration of the plasticizer from a PVC membrane subjected to ethanol exposure was considered to be diffusive. The process involves both ethanol migration into the PVC membrane and migration of plasticizer from the PVC membrane [32–36]. Once a chemical comes into contact with the surface of a PVC membrane, the transport of the chemical to the interior of the PVC membrane will take place through a concentration-gradient-dependent transport process. The classical diffusion process was identified by

Fick [37] and the equations governing chemical diffusion within the medium can be obtained through consideration of mass transport [38]. In view of the large lateral dimensions of the chemical dosage area in comparison to the thickness of the PVC membrane, the chemical diffusion within the membrane can be modelled as a one-dimensional process [Fig. 3(b)]. The one-dimensional diffusion of the chemical through the thickness of a membrane is obtained from the solution of the governing partial differential equation

$$D \frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial t}; \quad t \geq 0; \quad z \in [-H/2, H/2] \quad (1)$$

subject to the initial condition

$$C(z, 0) = 0; \quad z \in [-H/2, H/2] \quad (2)$$

and the boundary conditions

$$C(H/2, t) = C_0; \quad C(-H/2, t) = C_0; \quad t \geq 0 \quad (3)$$

where H is the thickness of the PVC membrane. In Eq. (1), $C(z, t)$ is the through-thickness chemical concentration; z is the spatial coordinate; D is a diffusion coefficient and t is time. The linearized form of the diffusion Eq. (1) is simplification of a much more complicated non-linear process where the diffusion coefficient can be altered during the chemical migration process. A further assumption is that the chemical influx is directly related to the loss of plasticizer from the PVC membrane. In practice, when a PVC membrane is used in a waste isolation endeavour, chemical migration to the membrane will take place only through one of its surfaces. In relation to the experimental research that will be conducted, however, it is assumed that the immersed PVC membrane will allow chemical migration to take place from both lateral surfaces as described by the boundary condition (Eq. (3)). The solution to the initial boundary value problem is elementary [38,39] and the through-thickness chemical concentration in the membrane is given by

$$\frac{C}{C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp \left[-(2n+1)^2 \pi^2 \frac{Dt}{H^2} \right] \times \cos \left[(2n+1) \pi \frac{z}{H} \right] \quad (4)$$

The objective of a diffusion analysis is mainly to ascertain the time required for chemical diffusion to take place over a significant portion of the 0.5 mm thick PVC membrane. Theoretically, the elementary diffusion process requires an infinite time for the chemical to completely occupy the membrane. In contrast, only a finite time is required to saturate roughly 90%–95% of the thickness of the membrane. For example, the

time required to achieve 90% saturation of the chemical concentration at the central plane of the membrane is

$$t_{90\%} = \frac{H^2}{4D} \quad (5)$$

The critical parameter needed for the estimation of migration time is the diffusion parameter D . Messadi and Vergnaud [22] conducted tests to determine the diffusion parameters for both pure ethanol and an 80% concentration of ethanol in an ethanol–water mixture. Their results indicated that a plasticized PVC with 38% weight content of DOP plasticizer had a diffusion coefficient $D = 1.0 \times 10^{-8} \text{ cm}^2/\text{s}$ for pure ethanol at 30 °C. Considering Eqs. (4), (5) and this value of D , the time required to dose in excess of 90% of the central plane of a 0.5 mm-thick PVC membrane will be

$$t_{90\%} = \frac{H^2}{4D} = \frac{(0.05 \text{ cm})^2}{4 \times 10^{-8} \text{ cm}^2/\text{s}} \approx 0.7 \text{ days} \quad (6)$$

Similarly, considering the value for the diffusion coefficient for 80% ethanol, $D = 0.21 \times 10^{-8} \text{ cm}^2/\text{s}$ at 45 °C (also given by Messadi and Vergnaud [22]), the time required to saturate in excess of 90% of the central plane of the 0.5 mm-thick PVC membrane will be

$$t_{90\%} = \frac{H^2}{4D} = \frac{(0.05 \text{ cm})^2}{0.21 \times 10^{-8} \text{ cm}^2/\text{s}} \approx 13.8 \text{ days} \quad (7)$$

For immersion tests conducted at room temperature and on a PVC membrane containing plasticizers other than DOP, the time taken for the ethanol to fully penetrate the PVC membrane is considered to be slightly longer. Considering these results, it is reasonable to assume that the effective migration will occur after several weeks. Such a short saturation time can allow for a reasonably complete distribution of the water–ethanol mixture within the PVC membrane and this distribution was observed to be almost uniform within a 1-month immersion period [30]. Results of fast saturation of a PVC membrane by other organic liquids are also available in the literature; for example, in the experiments conducted by Messadi and Vergnaud [22], a 3.5 mm-thick PVC membrane is almost fully saturated by pure ethanol within 5 days of exposure at a temperature of 45 °C. Liquids such as paraffin oil and white spirit can also fully migrate into a 0.5 mm-thick PVC membrane within about 20 days of exposure at a temperature of 37 °C [40]. These experimental investigations enable the choice of the duration of immersion test for the purposes of achieving a satisfactory chemical exposure of the PVC membrane. The criterion for the selection of the exposure period was basically to allow the alteration in the mechanical

behaviour of the PVC membrane. In view of the short duration required for saturation of the PVC membrane by both pure and 80% ethanol, in the current experimental investigations, the exposure time was chosen as 1 week, 2 weeks, 1 month, 2 months, 7 months, and 9 months. In cases where there is a faster migration process, shorter exposure periods of 2 h and 1 day were chosen. At each exposure stage, three exposed PVC membranes measuring 250 mm × 180 mm were prepared; these membranes provided adequate samples for mechanical testing. In cases where no significant alterations in the mechanical behaviour of the PVC membrane were observed during testing further 12 PVC membranes were subjected to ethanol exposure to examine the change in the mechanical behaviour with prolonged exposure. For ethanol concentrations less than 80%, the information concerning the diffusivity characteristics is not readily available in the literature; in these cases, a longer period of exposure was attempted. A stack of 12 PVC membranes was prepared for each ethanol concentration (at 50% and 0%). The choice of the time interval between tests was based on observations concerning the alteration in the mechanical properties of the PVC membrane. For purposes of comparison, tests were also conducted on PVC membranes which were exposed to air. In these tests, a stack of 12 alternate layers of PVC membranes and geotextiles was placed in an open container located in a dark storage area maintained at room temperature. The PVC membranes were kept isolated except when the container was opened for sample removal for testing.

2.3. X-ray fluorescence analysis

A liquid form of the phthalate monomer has been used as the plasticizer in the manufacturing of the PVC membrane used in this experimental research program [31]. The loss of the plasticizer content in the exposed membrane was identified through X-ray fluorescence techniques. The sample of the PVC membrane used for this purpose had a circular shape with a radius of 20 mm. The weight ratio of the oxygen element to the chloride element in the PVC membrane, defined by $R_{O/Cl}$, can be used as an indicator to assess the plasticizer content at any stage of exposure of the PVC membrane to ethanol. Table 1 shows the value of $R_{O/Cl}$

Table 1
The value of $R_{O/Cl}$ for PVC membranes subjected to ethanol exposure

Specimen	$R_{O/Cl}$
PVC membrane as supplied	6.47%
2-month pure ethanol exposure	5.33%
5-month pure ethanol exposure	5.20%
16-month 50% ethanol exposure	5.44%
18-month water exposure	5.55%

determined at different stages of exposure to pure ethanol. The continuous decrease in this ratio is indicative of the loss of plasticizer in the PVC membrane. The exposure resulted in an appreciable loss of plasticizer during the first 2 months. The results of the X-ray fluorescence experiments, however, indicate that the rate of extraction was significantly reduced after a 2-month exposure. The evidence of loss of plasticizer from plasticized PVC exposed to low concentrations of ethanol was also observed in other studies [4–6]. The X-ray fluorescence technique was also applied to examine PVC membranes exposed to 50% ethanol and pure water after 16 months and 18 months, respectively. Both cases, however, reveal noticeable alterations in the $R_{O/Cl}$ value when compared with the corresponding values for the untreated PVC membrane. The PVC membrane exposed to 50% ethanol mixture shows slightly lower value for $R_{O/Cl}$ indicating faster leaching rate of plasticizer.

2.4. Measurement of mechanical properties

The alteration in the mechanical properties of the PVC membrane subjected to various durations of exposure to ethanol was examined through conventional uniaxial tensile testing. The testing facility consists of a servo-controlled MTS Machine with a load capacity of 44,000 N (10,000 lbs). The conventional grips for material testing were considered to be inadequate for providing fixity at the ends of the PVC membrane. Special grips were therefore fabricated for purposes of the current experimental research program. The details of the grips consisting of an upper and a lower set are shown in Fig. 4. During testing, the lower set of grips was fixed and the upper one was moved by the MTS machine in a displacement-controlled mode. The PVC membrane was clamped between the grips and subjected to extension. The rigid connections between the grips and MTS Testing Machine were achieved through the provision of two adaptors. Holes inside the upper and lower connectors of the adaptors fit the grips to the MTS frame. The grips that were originally designed for testing PVC membrane strips of width 200 mm, were used to test strips of width 25.4 mm. In comparison to the peak load capacity of the MTS machine, the forces involved in the uniaxial testing of the PVC membranes were extremely small. Therefore a lower capacity load cell [4400 N (1000 lbs)] was used to measure the applied loads. The steel grips were fabricated in such a way that the PVC membrane could be stretched without development of either an eccentricity or a tilt. The details of the grips are shown in Fig. 5(a–b). The sides of the aluminum plates that come into contact with the PVC membranes were roughed to generate adequate frictional forces. The aluminum plates could slide freely on three steel rods within a steel box and five adjustable

screws were used for alignment. To further prevent slip between the PVC membrane and the roughed sections of aluminum plates, an additional layer of the PVC membrane strip was bonded to each end of the PVC membrane, using a non-reactive LOCTITE® 404 instant adhesive [Fig. 2(c)], which increased the thickness of the ends of the PVC membrane. The ends were then tightly clamped between two faces of the aluminum grips. It was found that without the provision of this additional layer, there was insufficient frictional resistance between the surfaces of the membrane and the grips, which resulted in slippage. If the additional layer was not bonded to the PVC membrane, the slippage was restricted to a limited extent at small strains but became appreciable at large strains, largely due to the progressive loss of friction between layers of membrane as the PVC membrane contracts in the thickness direction. There is the possibility of chemical reactions between the adhesive and the PVC membrane during prolonged tests. The time-scale of such chemical reactions, however, is expected to be much greater than those associated with the duration the tests. Therefore, the influence of the reactivity of the adhesive was not considered in the examination of the experimental results. All PVC membranes used had an initial cross-section area of 25.4 mm × 0.5 mm. The experiments were conducted in a Material Testing Laboratory maintained at a room temperature of approximately 24 °C. These durations of tensile tests were restricted to about 1 h. The temperature variation in the laboratory during this period was less than 1 °C. The duration of the chemical exposure lasted up to 13 months. During this period, the temperature in the storage area varied between 20 °C and 26 °C. The influence of these temperature fluctuations on either the rate of chemical reaction or on the mechanical properties of the PVC membrane was not considered in this study. During uniaxial testing, the displacement of the PVC membrane was initially measured using two LVDTs located on either side of the PVC membrane. Since the PVC membrane was highly deformable in comparison to the rigid steel grips and test frame, a machine stiffness correction to the measured deformations was not considered to be necessary; the relative extension of the grips was found to be quite close to the average of the LVDT values when the displacement was smaller than 30 mm. At larger extensions, the accuracy of the LVDT is significantly reduced. For simplicity and for accuracy, the movement of the grips was therefore taken as the change in the current gauge length l . The initial gauge length was taken as the distance between two edges of the PVC membrane ($l_0 = 50$ mm) as indicated in Fig. 2(c). The stress σ_0 was defined as the magnitude of applied load divided by *initial* cross-sectional area of the PVC membrane. The strain was calculated as the percentage change of the *initial gauge length*. All tests

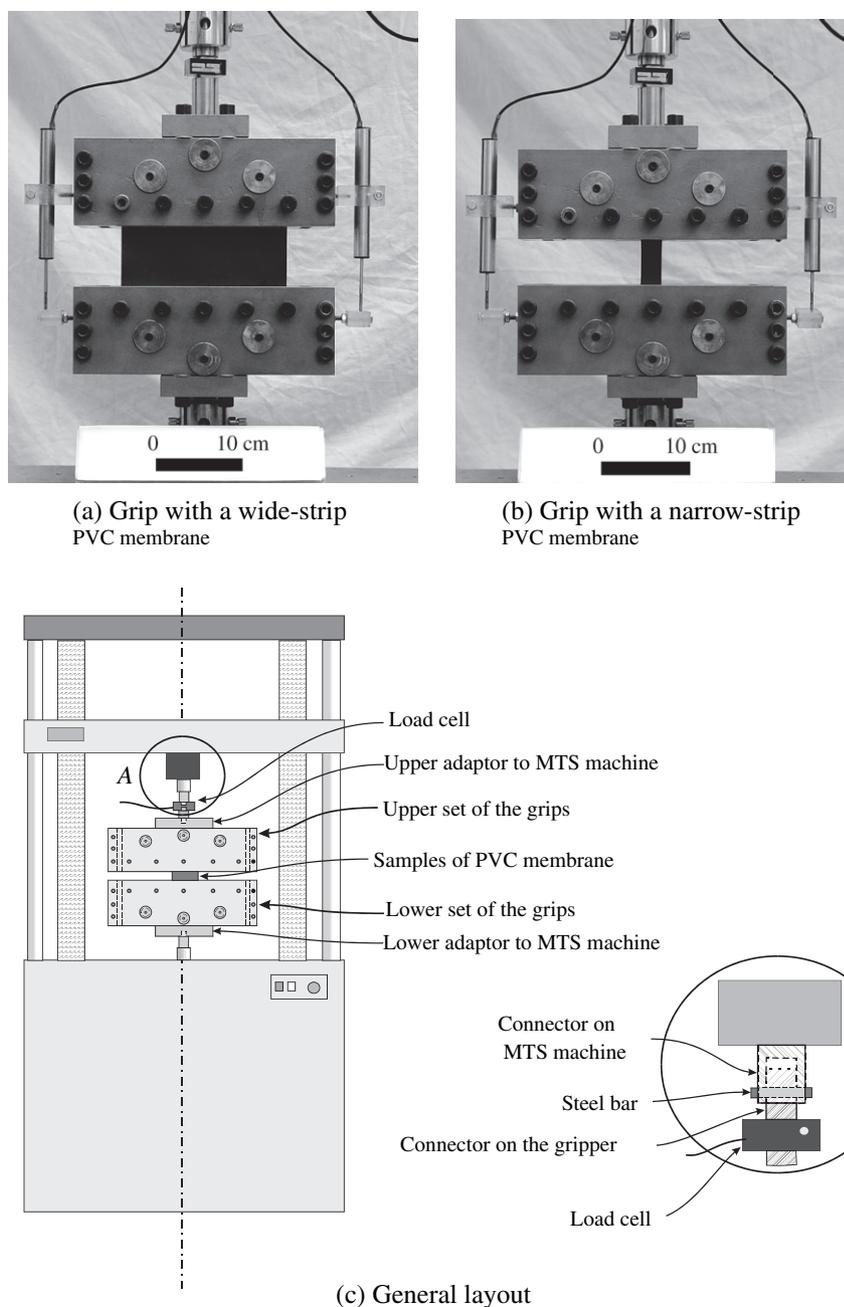


Fig. 4. Tensile testing facility.

were performed at a constant strain rate $\dot{\epsilon}_0$, which was defined as

$$\dot{\epsilon}_0 = \frac{d}{dt} \left(\frac{l - l_0}{l_0} \right) \quad (8)$$

The ASTM Standard D4885-1988 [41] advocates strain rates in the range 1%/min–100%/min. The experiments on the PVC membrane were conducted at three strain rates 4%/min, 40%/min and 160%/min.

PVC membranes are manufactured through calendering techniques [1,31,42]. The objective of a calendering process is either to eliminate or to reduce the development of anisotropy in the deformability and strength characteristics [43]. The development of anisotropy can be minimized through heat treatment and curing processes, which induces thermal relaxation. To determine the possible influences of the calendering process on the mechanical behaviour, uniaxial tests were also performed on PVC membranes, the axes of which were oriented normal to the calendering direction.

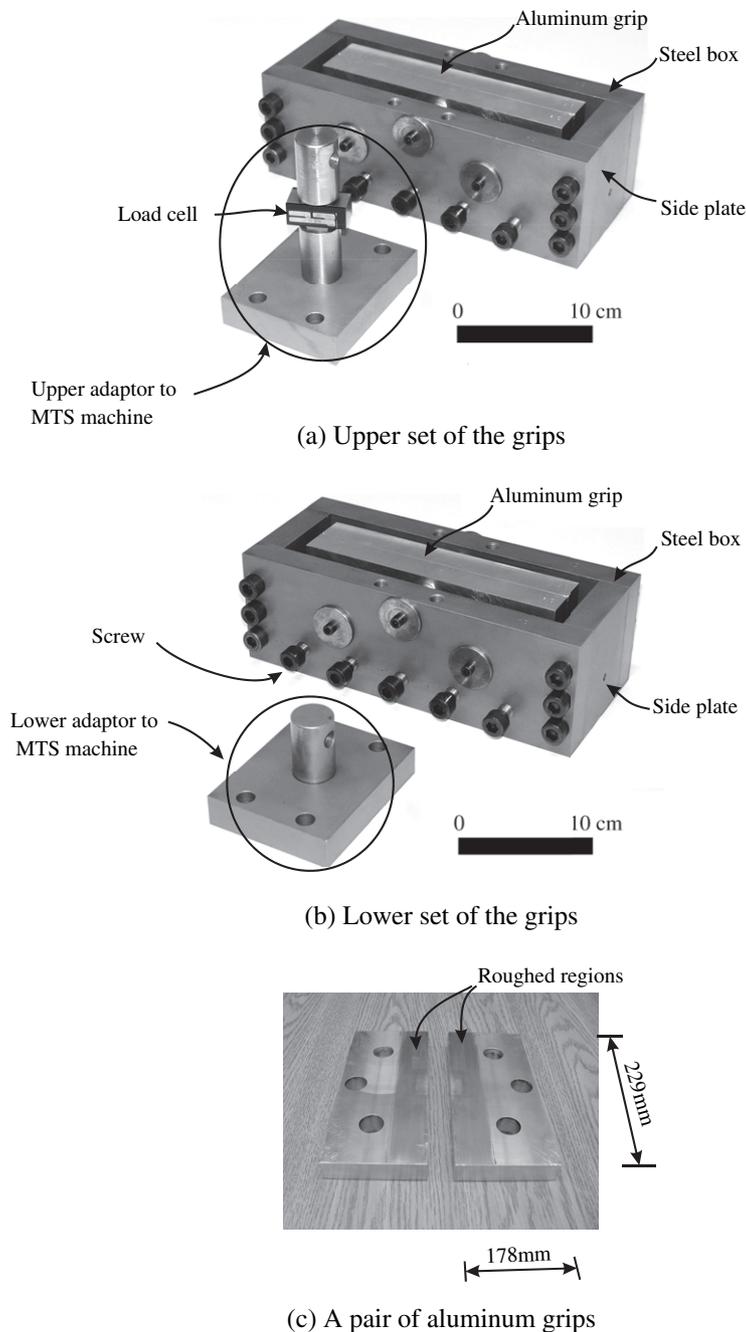


Fig. 5. Design of a set of grips.

Test specimens of PVC membranes were prepared both along the machine direction and across the machine direction [see Fig. 2(a–b)].

3. Experimental results

3.1. PVC membrane as supplied

The results of the uniaxial tests conducted on intact PVC membranes are shown in Figs. 6–8. The untreated

PVC membrane undergoes significant large strains during a tensile test. The PVC membrane exhibits failure at a strain in the range 150%–250%. By examining the continuous stress–strain curve shown in Fig. 6, it is found that the PVC membrane exhibited significant creep during these tests. Experiments were also conducted to identify the unloading behaviour of the untreated PVC membrane. Unlike the typical behaviour of hyperelastic rubber-like materials without fillers, where unloading behaviour closely follows the loading curve, the untreated PVC membrane exhibits significant

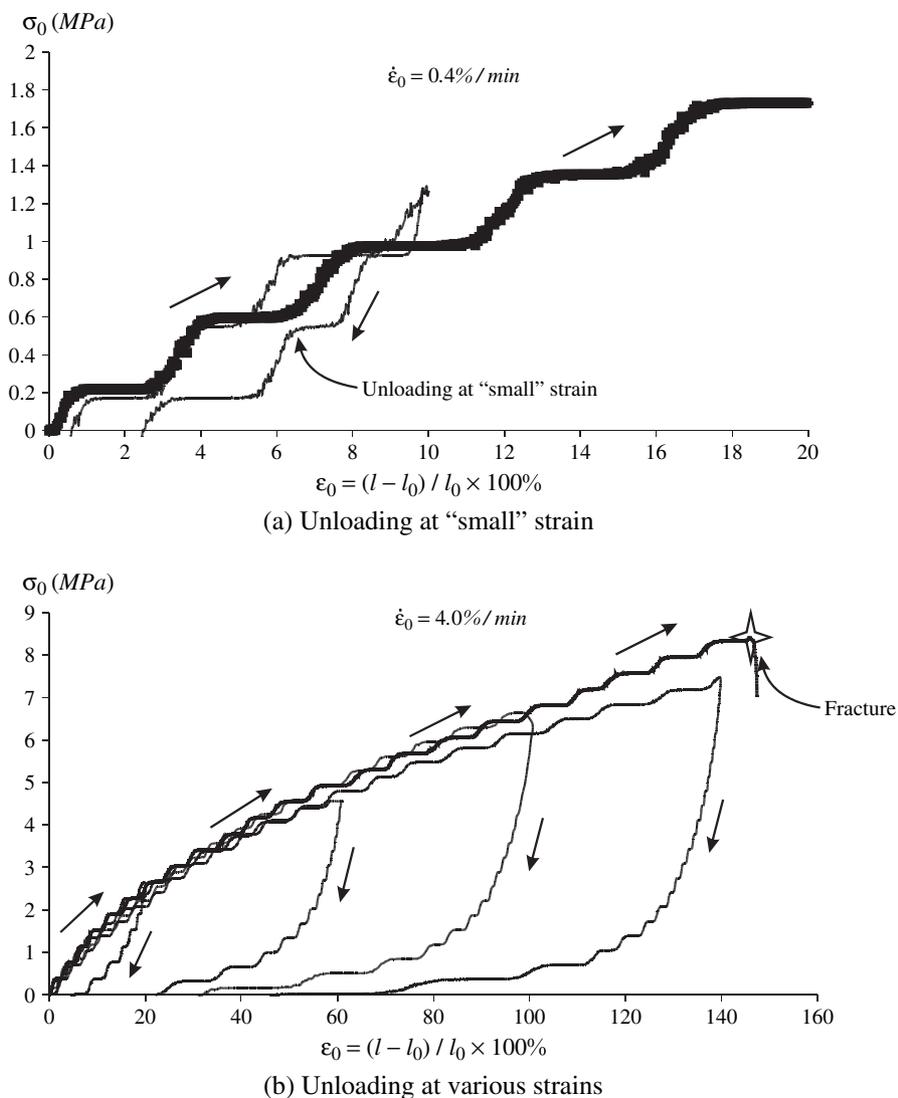


Fig. 6. A continuous stress–strain curve of a PVC membrane as supplied.

irreversible deformations. Fig. 6(b) shows the responses of the untreated PVC membrane, which is loaded to different levels of maximum strain, followed by unloading. It may be observed that, irreversible strain is present over a large range of the strain experienced by the PVC membrane. In order to examine the possibility of the existence of fully reversible behaviour similar to that of a typical rubber-like material, a test was also conducted at a lower strain rate of $\dot{\epsilon}_0 = 0.4\%/min$ and up to a maximum strain level of 10%. The results are shown in Fig. 6(a). The existence of an irreversible strain is still noticeable; the amount of the irreversible component is, however, greatly reduced. This indicates the possibility of fully reversible behaviour of the untreated PVC membrane in situations where the loading rate and maximum strain are considerably restricted. Further results obtained by extracting data from several selective points on a continuous stress–strain curve are shown in Fig. 7(a). The inset figures shown in Fig. 7(a) indicate

that the grips, while providing no slippage at the ends, also restricted the lateral contraction at the gripped boundary during uniaxial stretching. This violates the condition necessary for straining PVC membrane to produce a homogeneous deformation, which is required for any theoretical treatments particularly related to the development of constitutive relationships. To observe the extent to which the end constraints influence the development of homogeneous straining, a grid was marked on the surface of an undeformed PVC membrane with a spacing of 5 mm between the grid lines. As deformation progressed, the horizontal grid lines were used to calculate the real physical gauge lengths for different sections on the PVC membrane [Fig. 7(b)]. These distances were averaged over the width of the PVC membrane. The deformed configurations of the PVC membrane were recorded using a digital camera. The distances were first measured in image *pixels* and then calibrated against the value of image *pixels*

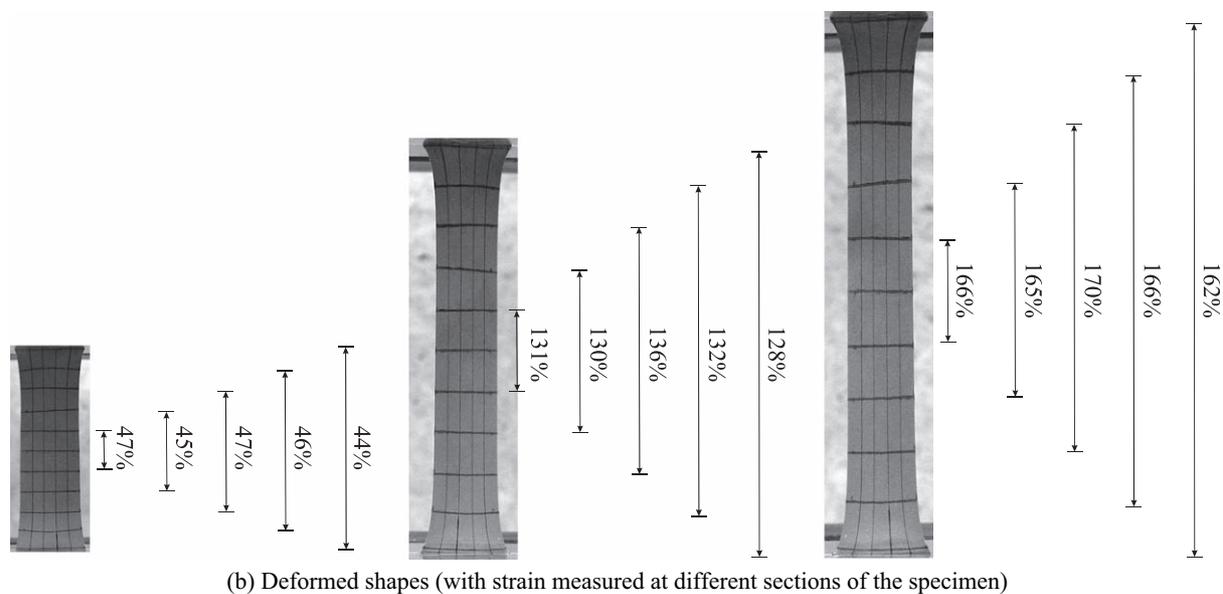
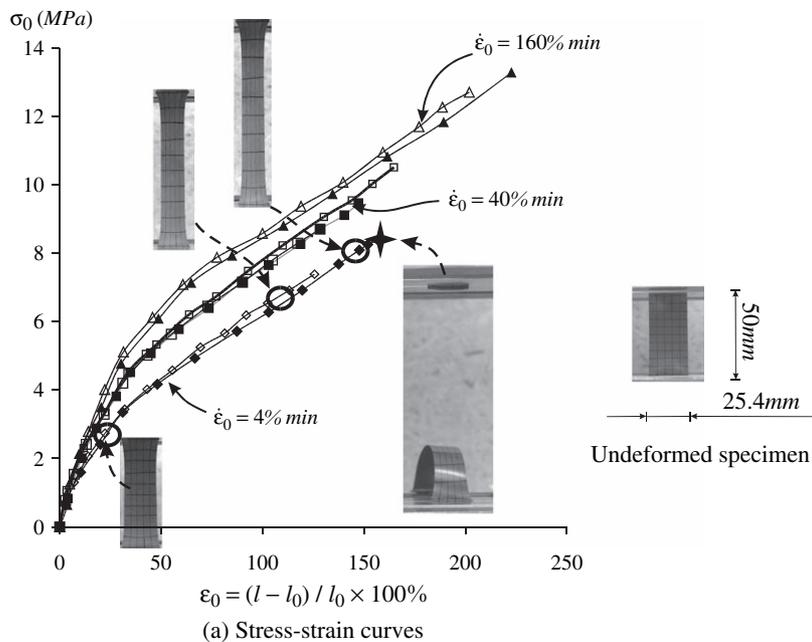


Fig. 7. Tensile behaviour of a PVC membrane as supplied loading at different strain rates.

corresponding to a known physical distance. The known physical distance is chosen as the distance between two grips. The distance between the two grips is directly measured in a displacement-controlled experiment. The strains measured by considering different original gauge lengths are presented in Fig. 7(b). Test results indicate that the effects of the fixity constraints result in an error of 6.8% over an average strain range of $\epsilon_0 = 44\%$ and an error of 2.4% at a larger strain, in the range of $\epsilon_0 = 162\%$. Tests were performed at three different strain rates, 4%/min, 40%/min and 160%/min. To establish the influence of any anisotropy in the deformability of the PVC membrane, tests were conducted on PVC

membranes cut from, both along and perpendicular to the calendering direction. Fig. 8 shows the corresponding stress–strain curves derived from uniaxial tests conducted at three different strain rates. There is some evidence of the influence of manufacturing process on the stress–strain behaviour, but the results are considered to be within the range of experimental error.

3.2. PVC membranes subjected to concentrations of ethanol exposure

Fig. 9 illustrates the typical stress–strain curves for PVC membranes subjected to a 7-month exposure to

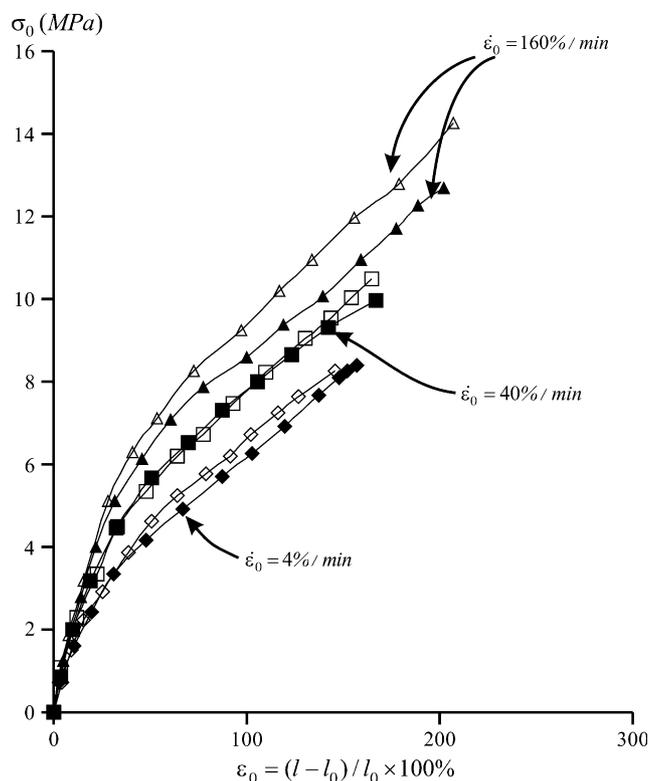


Fig. 8. Tensile behaviour of a PVC membrane as supplied loading at different strain rates in two orthogonal directions (filled symbols represent PVC membrane tested along machine direction, while unfilled symbols represent PVC membrane tested across machine direction).

pure ethanol. The experiments were conducted at a loading rate of $\dot{\epsilon}_0 = 4\%/min$. During the exposure to pure ethanol, the stress–strain behaviour experiences a significant change; PVC membrane has developed a pronounced yield point, and both strain-softening and strain-hardening regions can be observed. The experiments also show that the PVC membrane can continue to sustain appreciable post-yield large strains without failure. When unloading is performed, it is evident that significant irreversible strain is present when the stresses exceed the initial “yield point” or “yield strain” of the PVC membrane. Unloading tests were also conducted up to maximum strains that did not exceed the yield strain. It is assumed that within this small strain range, the unloading behaviour closely follows the loading path. The PVC membrane exposed to pure ethanol basically exhibits an initial linear elastic response followed by a distinct yield point, a noticeable softening behaviour and appreciable post-yield hardening. In order to examine the influence of the rate-dependency on the stress–strain responses, experiments were also conducted at loading rates of $\dot{\epsilon}_0 = 40\%/min$ and $\dot{\epsilon}_0 = 160\%/min$. The influence of the loading rate on the stress–strain response is also noticeable (Fig. 10).

Fig. 11 shows the results of the tensile tests conducted on samples of the PVC membrane subjected to different

periods of exposure to pure ethanol. These results are typical and indicate a significant continued alteration in the mechanical behaviour of PVC membrane. It is observed that the PVC membrane experiences continued alteration in its mechanical response. The influences of the ethanol exposure, include, loss of the hyperelastic characteristics or embrittlement and development of an initial linear modulus and a distinct yield point. The intact PVC membrane exhibits a monotonically increasing hyperelastic behaviour with path dependent partial recoverability of the strain. The PVC membranes subjected to pure ethanol, on the other hand, showed the development of a distinct failure threshold with appreciable irrecoverable deformations. The initial linear modulus and yield stress of the PVC membrane exhibits a continuous increase up to an exposure period of 2 months after which, there is a slight decrease in the peak yield value, which is influenced by further exposure. The rapid alterations in the mechanical behaviour of the PVC membrane within the first 2 months correlate well with the results of the X-ray fluorescence analysis. The rate of alteration of the mechanical response of the PVC membrane tends to stabilize after a 2-month exposure period. This correlates with the reduction in the rate of loss of the plasticizer itself. The experimental results also point to the slight reduction in the initial modulus and yield stress in the stress–strain response between a 2-month and a 7-month exposure period. The reasons for the reduction in the initial linear modulus and yield stress in stress–strain response are not entirely clear. A likely reason could be the swelling-induced alteration in the mechanical response, as the PVC membrane experiences moisture absorption. While there is no conclusive observation of the reduction in the failure strains during the first 9 months exposure, the PVC membrane subjected to 13-month exposure shows significant loss in its ability to experience large strain deformability; the PVC membrane breaks at a strain that just exceeds the yield strain without exhibiting any post-yield hardening. This possibly indicates the significant chemical alteration in the polymer molecule backbone in the last 4 months of exposure period, which directly affects its integrity, and subsequently contributes to the failure of the PVC membrane.

The experiments also investigated the alteration in the mechanical properties of the PVC material subjected to exposure at volumetric concentrations of 80% and 50% [Fig. 12(a)]. The influence of exposure at lower concentrations of ethanol tends to be much less significant than that observed in cases involving exposure to pure ethanol. For this reason, the results of stress–strain data derived from PVC membrane subjected to 80% and 50% ethanol are presented for longer exposure times. The stress–strain curve of the PVC membrane subjected to exposure to an 80%

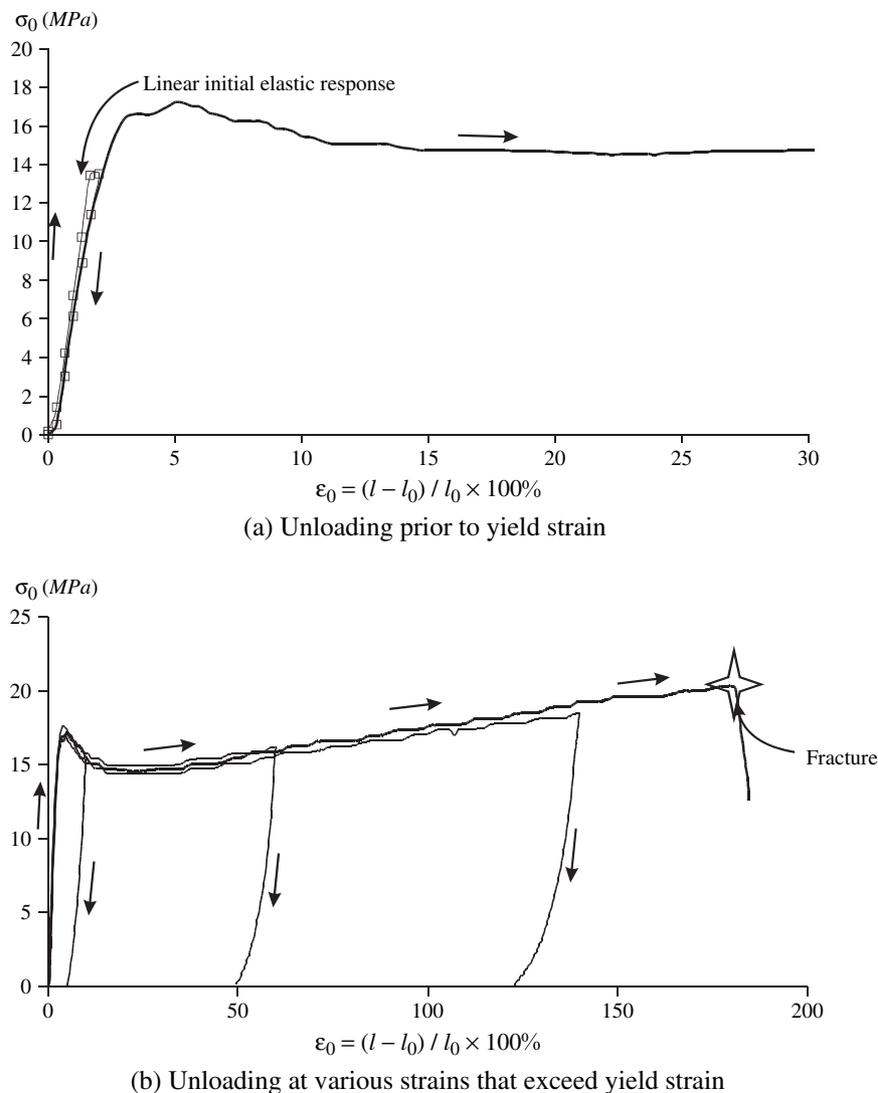


Fig. 9. Continuous stress–strain curves of a PVC membrane subjected to 7-month exposure to pure ethanol ($\dot{\epsilon}_0 = 4\%/min$).

concentration of ethanol indicates a slight “hardening” response after a 7-month period, which results in less deformation under a same external load. A slight increase in the failure strength is also observed in this case. The repeatability of the experiments was also examined [Fig. 12(b–g)]. The PVC membranes that had been subjected to exposure to 80% ethanol were loaded to maximum strains of 60% and 100%, which was further followed by an unloading [Fig. 12(c)]. The experimental results indicate a variability of approximately 3%. It is inferred that the alteration in the stress–strain behaviour of the membrane was primarily due to exposure. The “hardening” response in the stress–strain curve is absent after exposure to 50% ethanol; instead the PVC membrane became softer after 13-month exposure, which can be attributed to the swelling of the PVC membrane indicated previously. For the purpose of comparison, experiments were also conducted on PVC membranes exposed to pure water

and air. The stress–strain curve for the PVC membrane subjected to exposure to pure water after period of 15 months closely follows the response of the PVC membrane subjected to exposure to 50% ethanol, which indicates that similar chemical and physical mechanisms would contribute to the “softening” of the PVC membrane. The results of tests conducted on PVC membranes exposed to air for a period of 21 months indicate no observable changes. The possible influences of the exposure to air (in the absence of ultra-violet light) can be neglected for the purpose of current experimental investigations.

4. Conclusions

The exposure of a PVC membrane to an organic liquid chemical results in two synchronized processes: the first being a fast through-thickness diffusion of the

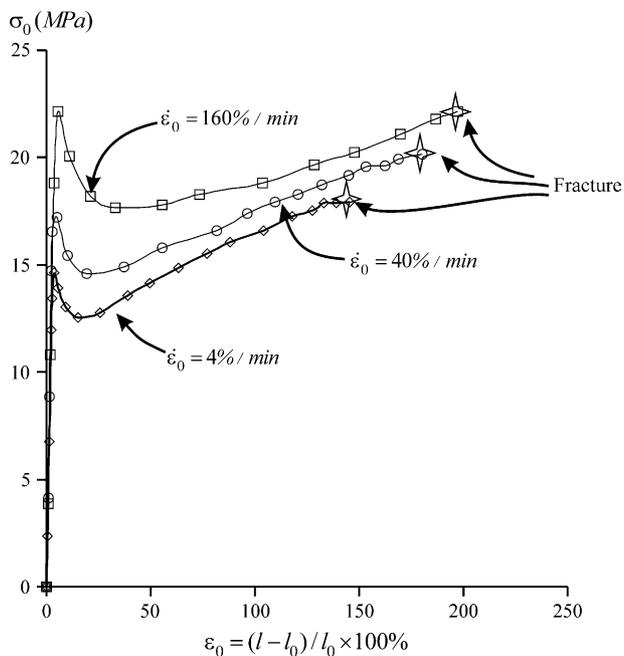


Fig. 10. Rate dependency of the stress–strain curves of a PVC membrane subjected to 7-month exposure to pure ethanol.

liquid into the PVC membrane and second is a relatively slower loss of plasticizer in a diffusive manner. The experiments reported here deal with the examination of the alteration in the mechanical behaviour of a 0.5 mm-thick PVC membrane subjected to exposure to ethanol

at different concentrations. The alteration in the mechanical properties of the PVC membrane subjected to exposure to pure ethanol was a continuing process. These alterations included a progressive loss in the large strain hyperelastic deformability response, the development of embrittlement with an observable initial linear modulus and a distinct yield point. The exposure to pure ethanol up to 13 months results in a complete loss in the large strain deformability capacity of the PVC membrane. The rapid alterations in the mechanical properties of the treated PVC membranes in the first 2 months correlated well with the loss of plasticizer from the PVC membrane, as inferred from the results of X-ray fluorescence techniques. The rate of loss of plasticizer diminished after 2 months, with the resulting reduction in the rate of alteration in the mechanical behaviour. Although the exposure to other concentrations of ethanol reveals leaching of the plasticizer from the PVC membrane over long period, such exposure produced a less significant alteration in the mechanical behaviour. After 7-month period, the PVC membrane exposed to 80% ethanol exhibited a slight “hardening” behaviour. After 13-month period, however, the PVC membrane subjected to exposure to 50% ethanol became softer. The same phenomenon is observed in PVC membranes exposed to pure water for a 15-month period. Both the causes of the “softening” behaviour could be attributed to the swelling of the PVC membrane by moisture migration. In a practical context

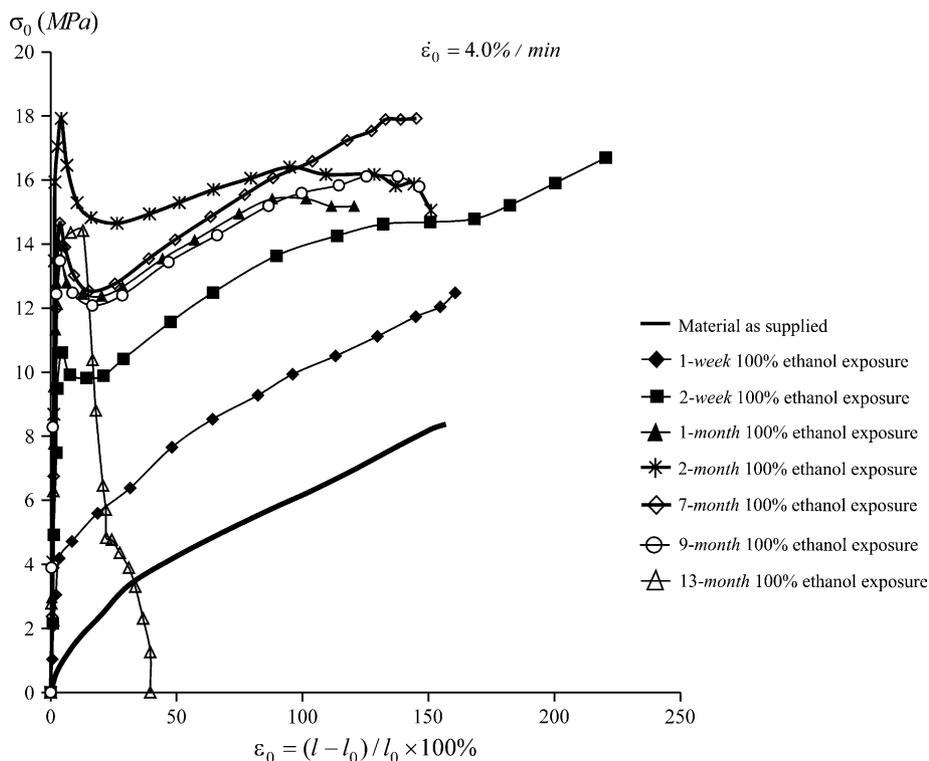
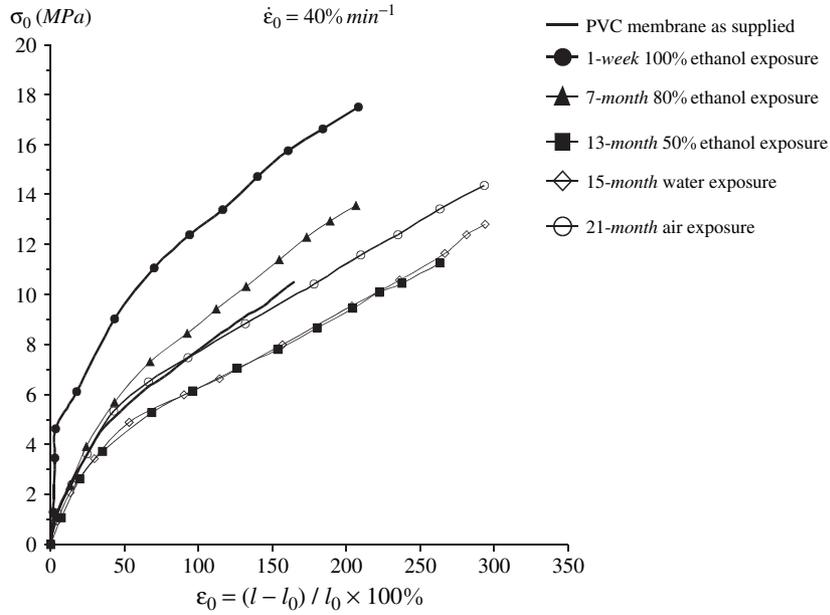
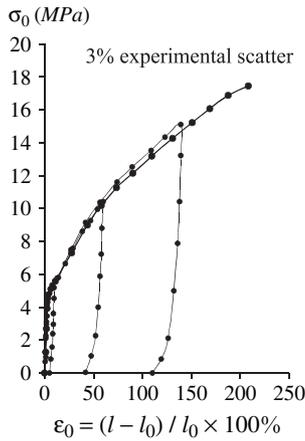


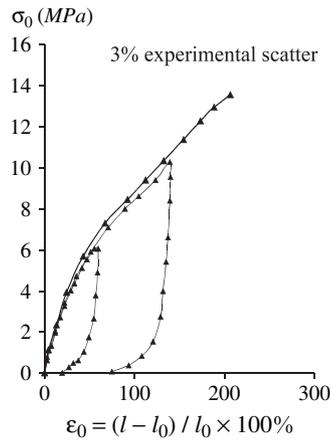
Fig. 11. Tensile behaviours of a PVC membrane subjected to different periods of pure ethanol exposure.



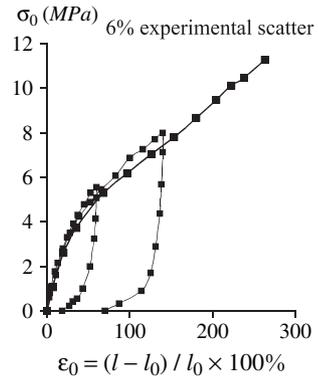
(a) Response of PVC membrane subjected to exposure to concentrations of ethanol



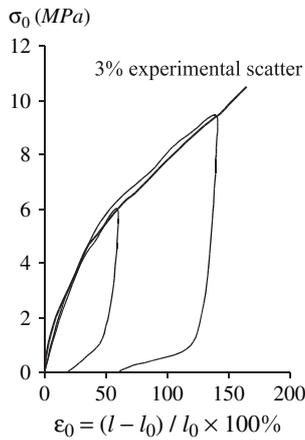
(b) Exposure to pure ethanol



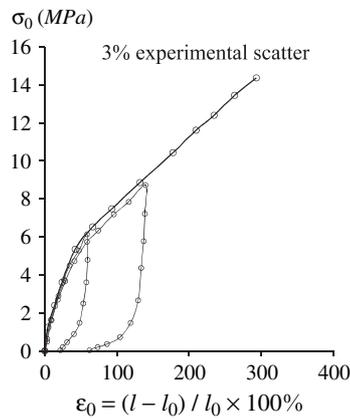
(c) Exposure to 80% ethanol



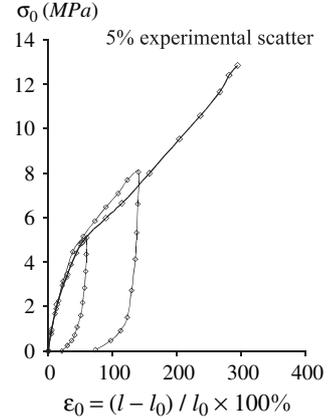
(d) Exposure to 50% ethanol



(e) PVC membrane as supplied



(f) Exposure to air



(g) Exposure to pure water

Fig. 12. Tensile behaviours of a PVC membrane subjected to concentrations of ethanol exposure.

involving landfill application of PVC membranes, the concentration of ethanol can reach a maximum 2–3% [44]. The durability of the PVC membrane barrier resulting from the leaching of plasticizer can pose a problem over the long-term especially when the landfill is subjected to wetting and drying cycles where the leaching of the plasticizer will occur due to prolonged contact with chemicals, whereas swelling is limited due to temperature increases in the landfill associated with its decay.

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