ABSTRACT

To investigate the swelling and mechanical behaviours of protective materials during sorption and desorption with various solvents would be helpful to predict the failure of these materials. However, elastomers with high chemical resistance are usually used as protective materials and in order to reuse these materials after decontamination, studies are imperative to investigate the failure prediction of protective materials. In this article, the effects of various organic solvents on the swelling and elastic properties of polychloroprene (CR) materials as protective substances were systematically studied. Different aromatic (toluene, anisole, and o-dichlorobenzene) and aliphatic (methyl ethyl ketone and ethyl acetate) solvents with various chemical structures, molar volumes and \( R_a \) values (the level of polymer-solvent interaction calculated from the Hansen solubility parameters theory) were considered. The swelling behaviour and the tensile properties of the CR immersed in each solvent for different periods are characterized. The chemical structure and the molar volume of solvents have been found to give better correlations than \( R_a \) values on the swelling rates and maximum equilibrium swelling of CR when \( R_a \) values are close together. It is also shown that the swelling of CR decreases after the leachable additives are completely removed. The elastic property changes are indication of partial degradation of CR after swelling by solvents in the following order: toluene > anisole > methyl ethyl ketone > ethyl acetate. It has also been found that tensile property changes of CR after contact with solvents at low deformation are more prominent than changes at large deformation. In addition, the presence of leachable additives in CR shows reduction in the tensile properties of CR during partial swelling with various solvents.

INTRODUCTION

When a solvent is in contact with an elastomer, the solvent penetrates the material. Depending on the nature of the elastomer and solvent, the extent of the liquid absorbed can be so large that changes are occurred in the dimensions of the samples. A study of the swelling behaviour of elastomers will be helpful for investigating the permanent effect of solvents on the chemical structure of elastomers. The swelling behaviour of any elastomer towards various solvents exhibits differently with time, and this information becomes very useful in the degree of solvent-elastomer interaction and prediction of the solvent degradation effect on elastomers. On the other hand, shrinkage can occur when the elastomer is allowed to dry out.
after swelling with a solvent (deswelling). Swelling normally causes an increase in flexibility and reduction in the mechanical properties of elastomer while shrinkage and inversely deswelling cause reduction in flexibility and an increase in the mechanical properties of rubber. Before and after swelling equilibrium, the overall degree of swelling is affected by the solvent characteristics, whereas during the equilibrium state, the type of cross-linking agent present in the elastomer is important on the degree of swelling [1,2].

Many techniques can be used to determine the swelling properties of elastomers. The methods such as strain-stress measurement [3], sorption (observing the weight changes of an elastomer) [1], and the dynamic swelling method (measuring the length changes of polymer sample) [4] are the most conventional methods for measuring swelling of elastomers. Literature shows that the degree of swelling and deswelling is related to the flexibility and mobility of polymer chains, the molecular size of the solvent, temperature, cross-linking agent type, cross-link density, and molecular entanglement [2,3].

The cohesion energy parameters are most widely used for prediction of the chemical resistance of polymers. These parameters have been developed by Hansen [5] and now called Hansen solubility (cohesion) parameters (HSP). The HSP which is based on an extension of the Hildebrand solubility parameter [6] has been recently confirmed by Panayiotou [7]. Panayiotou proposed a statistical thermodynamics treatment method for comparison of the solubility parameters of polymers and solvents. The following equation is used for comparison of three-dimensional Hansen solubility parameters of a polymer and a solvent:

$$R_a = \left[4(\delta_S - \delta_P)^2 + (\delta_S - \delta_P)^2 + (\delta_S - \delta_P)^2 \right]^{1/2}$$

where, the $R_a$ value represents the level of polymer-solvent interaction and corresponds to the dissimilarity between the polymer and the solvent. $\delta_S$ is the Hansen component parameter for the solvent, and $\delta_P$ is the Hansen component parameter for the polymer. Hansen components containing lower values indicate lower chemical resistance (the solvent diffuses more easily into a polymer) [8]. If the solvent is distributed homogeneously in the elastomer, the solubility parameters will reflect the properties of the whole elastomer. For instance, in Viton (copolymer elastomer), poor correlations in swelling behaviours were found because different segments have different affinities with the solvents, so different qualities of Viton show different chemical resistances [2].

The diffusion of solvents inside elastomers can also cause a reduction in mechanical and physical properties of elastomers and even its degradation over time. While protective materials (especially protective clothing) used several times, the material needs to be decontaminated. The material decontamination is difficult to achieve and it can result in deleterious effect on the mechanical properties of elastomer. However, high chemical resistance elastomers are very important as protective materials for environmental, healthy, and safety considerations; the investigation of the mechanical properties of protective materials during sorption and desorption with various solvents will be helpful to predict the failure of protective materials.

In the present study, the effect of some other physicochemical parameters of solvents (i.e., molar value and chemical structure) on swelling properties of polychloroprene (CR) when $R_a$ values close together will be more focused. Also, the mechanical properties of CR during sorption and desorption with various solvents are investigated and more attention is paid to find the most important parameters which affect the partial degradation of CR. In addition, the effect of leachable additives remained in vulcanized rubber on swelling and mechanical properties of CR are studied. This is important as even any trace amount of leachable additive may affect swelling and mechanicalbehaviours of CR and these are determining factors in prediction of partial degradation rates of protective materials. The results obtained from chemical and mechanical aspects of this research can help to prevent the catastrophic fracture or degradation during swelling or deswelling of protective materials (based on CR) with various solvents.

**EXPERIMENTAL**

**Materials**

The rubber used in this study was polychloroprene...
(CR) sheets with 1.6 mm thickness which were supplied by the Fairprene Industrial Products Company.

The solvents were reagent grades of toluene, anisole, o-dichlorobenzene, methyl ethyl ketone (MEK) and ethyl acetate supplied by Fisher Scientific.

**Methods**

To measure the swelling of CR material, a rectangular band of the material was immersed into a solvent and the length change and weight change were measured. The length change percentage was determined by a dynamic swelling method [4]. In this method, the materials are cut into pieces 5 cm long and 1 cm wide using a cutting die. The samples are immersed in various solvents in test containers that are large enough to allow for free swelling. The swollen samples are taken out periodically from the containers. For the desorption process, the remained samples after maximum swelling time are removed and deswelling starts when the specimens are at maximum swelling. The swelling and deswelling properties of rubber are determined in terms of the length change percentages of the band of material after immersion in a solvent. The following equation is used for length change percentage:

\[
dL_t = \left(\frac{L_s - L_{us}}{L_{us}}\right) \times 100
\]

where \(dL_t\) is the length change percentage, \(L_s\) is the length of rubber during swelling and deswelling, and \(L_{us}\) is the initial length.

Solvent uptake is measured by weight change according to standard method using the following equation [1]:

\[
dQ_t = \left(\frac{W - W_0}{W_0} \right) \times 100
\]

where \(dQ_t\) is solvent uptake change percentage, \(W_0\) and \(W\) represent the weights of dry and swollen (or deswollen) vulcanizates, respectively, and \(M_w\) represents the molecular weight of the solvent.

Weight change and length change are relatively compared using the following equation:

\[
dX = \frac{(X - X_i)}{(X_f - X_i)}
\]

where \(dX\) is the related length change or solvent uptake (or loss) change of specimen and \(X\) is length or weight of the specimens during swelling and deswelling. \(X_i\) and \(X_f\) are the initial and the final length or solvent uptake (or loss) of rubber, respectively, during swelling and deswelling.

The same measurement was repeated after leachable additives had been removed from the vulcanized rubber compounds. For this process, CR samples have been immersed in a poor solvent such as acetone for 24 h and all leachable additives are removed from CR during this time. When acetone is evaporated from the rubber, the swelling test is performed with the selected solvents.

The tensile properties of CR during swelling and deswelling with various solvents were measured by using the uniaxial tensile test. This test conforms to ASTM D412, using a die D for the tensile behaviour of elastomers. The tests were performed on an Instron type machine; model TMS, under a loading rate of 20 mm/min. Related tensile strength change is also compared using eqn (4); where \(X\) is tensile strength of the specimens during swelling, and \(X_i\) and \(X_f\) are the initial and the final tensile stresses at different deformations.

For each measurement, at least four replicated samples are examined and the mean values were recorded.

**RESULTS AND DISCUSSION**

**Swelling and Deswelling Properties of CR in Contact with Various Solvents**

Figure 1 shows an example of the related length and weight change of CR (dX), during swelling and deswelling with MEK which were calculated by eqn (4). The same results were observed with other solvents and after 256 min which maximum swelling of CR occurred for all solvents, deswelling behaviours of material were examined. The results show that no differences between the length and weight changes for CR during swelling and deswelling with various solvents are observed, and
only the length changes have been reported in terms of length change percentages (dL_t) of CR during sorption and desorption with various solvents (eqn (2)).

Figure 2 shows the length change percentage of CR (dL_t), during swelling and deswelling with toluene, o-dichlorobenzene, anisole, MEK, and ethyl acetate at room temperature. It was observed that the swelling and deswelling properties of CR vary with the type of solvent. For instance, with toluene, the swelling is high, while with ethyl acetate, the swelling is low.

The effects of chemical structure, R_a value, and molar volume (M_v) on the swelling properties of CR were investigated. The R_a values were calculated (eqn (1)) using the solubility parameters for CR [9,10]. As it is shown in Table 1, the R_a values of toluene, o-dichlorobenzene, anisole, MEK, and ethyl acetate are 4.346, 3.557, 1.992, 5.616, and 4.703.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical structure</th>
<th>R_a [(MPa)^{1/2}]</th>
<th>M_v [cm^3/mol]</th>
<th>Boiling point (°C)</th>
<th>Vapour pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisole</td>
<td><img src="image" alt="Anisole Structure" /></td>
<td>1.992</td>
<td>108.5</td>
<td>154</td>
<td>10.0</td>
</tr>
<tr>
<td>Toluene</td>
<td><img src="image" alt="Toluene Structure" /></td>
<td>4.346</td>
<td>106.8</td>
<td>110.6</td>
<td>28.4</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td><img src="image" alt="o-Dichlorobenzene Structure" /></td>
<td>3.557</td>
<td>112.8</td>
<td>180</td>
<td>1.2</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td><img src="image" alt="Methyl ethyl ketone Structure" /></td>
<td>5.616</td>
<td>90.1</td>
<td>80</td>
<td>71.2</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td><img src="image" alt="Ethyl acetate Structure" /></td>
<td>4.703</td>
<td>98.5</td>
<td>77</td>
<td>73.0</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of solvents.
(MPa)$^{1/2}$, respectively. Considering the $R_a$ values for each solvent, it was expected that the swelling of CR in contact with anisole and MEK would be the highest and the lowest, respectively. However, the swelling results (Figure 2) show that toluene produced a highest degree of swelling and ethyl acetate produced a lowest degree of swelling in CR. Also, important differences between swelling with toluene and ethyl acetate are shown while the differences between $R_a$ values for these two solvents are small. These differences may be due to uncertainty in the Hansen solubility parameter values for CR obtained in the previous works [9,10].

Regarding these differences and the highest degree of swelling of CR in contact with toluene, among the various solvents, the $R_a$ value for each solvent was recalculated when Hansen solubility parameters of toluene were chosen as the CR solubility parameters. The new $R_a$ values for o-dichlorobenzene, anisole, MEK, and ethyl acetate are 5.61, 5.44, 9.13, and 7.85 (MPa)$^{1/2}$, respectively. Considering the new $R_a$ value for each solvent-polymer interaction, a better correlation with the swelling data was obtained; a high degree of swelling of CR with anisole and o-dichlorobenzene and a relatively low degree of swelling of CR with MEK and ethyl acetate were observed as demonstrated by the swelling results, although it was expected that the swelling of CR in contact with anisole and MEK would be the highest and lowest, respectively. However, the swelling results indicate that the highest degree of swelling occurred with o-dichlorobenzene and lowest degree with ethyl acetate. This variation may be due to an inhomogeneous distribution of solvent on CR because of crystalline regions in the structure of rubber or the presence of additives in rubber compounds.

The molar volumes and chemical structure of solvents are other important parameters that can affect the swelling properties of CR. As it is shown in Table 1, maximum swelling of CR is inversely proportional to the molar volume of the solvents when the $R_a$ values are close together. However, the chemical structure of the solvent can have a greater effect on the swelling properties of CR when the molar volumes of solvents are also close together. For instance, $R_a$ values and molar volumes of o-dichlorobenzene and anisole are 5.61 and 5.44 (MPa)$^{1/2}$, and 112.8 and 108.5 cm$^3$/mol, respectively. Considering these values, it was expected that the equilibrium swelling degree of CR in contact with anisole would be more than that with o-dichlorobenzene, while the swelling results indicate a higher equilibrium swelling in contact with o-dichlorobenzene. Regarding the chemical structure of solvents, o-dichlorobenzene with two chlorine substitution groups of (Cl) in ortho position can easily diffuse more in CR than anisole with a methoxy substitution group (OCH$_3$).

The results also indicate that the swelling rate of CR depends on the chemical structure of the solvent. The results show that the swelling slope (the initial slope of the length change percentages) of CR in contact with o-dichlorobenzene, anisole, MEK, and ethyl acetate are 0.3309, 0.3221, 0.2996, and 0.2706, respectively. The highest swelling slope (or swelling rate) of CR with o-dichlorobenzene and the relatively lowest swelling slope of ethyl acetate are observed. Swelling rate differences can be also described by variations in the chemical structure of solvents as described for o-dichlorobenzene and anisole. As a result, although the $R_a$ value is the first parameter to predict the swelling properties of CR in contact with various solvents, molar volumes and chemical structures of solvents are more effective parameters than $R_a$ values for predicting the swelling property of CR when the $R_a$ values for various solvents are close together.

Different deswelling rates for solvents that were related to variations in the boiling point (B.P) and vapour pressure (V.P) of the solvents were also observed. For example, the rate of toluene loss in the desorption region is higher than the rate of anisole loss and o-dichlorobenzene loss. This difference may cause variations in the mechanical properties of CR.

**Effect of Leachable Additives on the Swelling Properties of CR**

Absorption of the solvent by rubber and extraction of some leachable additives (such as antidegradants, process aids, or tackifires) from the rubber can change the swelling properties of rubber. Figure 3 presents an example of the effect of leachable additives on the swelling properties of CR. Length change percentages of CR have been compared before and after removing the leachable additives. It is observed that swelling
property of CR is changed after removing the leachable additives. However, for CR with a high degree of swelling in solvents, when all leachable additives were removed, no difference in swelling properties before and after removing the additives was observed. A small amount of leachable additives in CR (> 5%), causes a small change in the swelling properties. The increase in the swelling rate of CR in the presence of leachable additives may be due to the increased distance between rubber chain segments caused by additives and replacement of extracted additives by solvents.

Effect of Solvent on the Elastic Properties of CR

The tensile properties of CR during swelling and deswelling with various solvents were investigated. Figures 4 and 5 are examples of the related tensile stress change (d\(\sigma\)) of CR during swelling with toluene and anisole at low deformation and fracture. It was observed that the tensile stress of CR during swelling with various solvents changed more at low deformation than at fracture. This variation may be related to the tendency of polymer chains to form molecular entanglements and physical bonding at low deformation and particularly in low degree of swelling. In addition, a smaller change in tensile stress between low deformation and fracture was observed in partial swelling of CR with anisole (Figure 4), while a relatively larger change in the tensile stress was observed when CR was in contact with toluene. This variation may be related to the improved deswelling rate during the tensile test.

Table 2 shows the tensile properties of dry CR and the properties at maximum swelling and deswelling with various solvents. As shown, the tensile properties of CR decrease after swelling with various solvents. However, a substantial reduction was observed in CR in contact with various solvents. However, a substantial reduction was observed in CR in contact with toluene and anisole. This can be explained by a

### Table 2. Tensile-at-break, elongation-at-break, and tensile modulus of dry, swollen, deswollen CR in contact with various solvents at room temperature.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Tensile-at-break, (\sigma_{\text{max}}) (MPa)</th>
<th>Elongation-at-break, (\varepsilon_{\text{max}}) (%)</th>
<th>Tensile modulus, E (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unswollen</td>
<td>Swollen</td>
<td>Deswollen</td>
</tr>
<tr>
<td>Toluene</td>
<td>10.5(0.3)*</td>
<td>2.07(0.07)</td>
<td>7.28(0.27)</td>
</tr>
<tr>
<td>Anisole</td>
<td>10.5(0.3)</td>
<td>1.82(0.11)</td>
<td>8.11(0.24)</td>
</tr>
<tr>
<td>MEK</td>
<td>10.5(0.3)</td>
<td>3.13(0.09)</td>
<td>8.9(0.29)</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>10.5(0.3)</td>
<td>5.4(0.13)</td>
<td>9.99(0.31)</td>
</tr>
</tbody>
</table>

* Parentheses show the standard deviation.
considerable reduction in the bonding forces between the elastomer segments during swelling with these solvents. A permanent change in the tensile properties of CR was observed after swelling with solvents in the following order: toluene > anisole > MEK > ethyl acetate.

Permanent changes in the tensile properties of CR after deswelling can be described by partial physical or chemical degradation of CR and extraction of leachable additives discussed in the next part.

The highest reduction in the tensile properties of CR was observed at maximum equilibrium swelling with anisole, while the highest degree of swelling of CR was observed in contact with toluene (Figure 2). This also may be due to the deswelling rate of the solvent at maximum equilibrium swelling because the highest degradation of CR after deswelling is obtained in contact with toluene, which produces a high degree of swelling of CR.

Effect of Leachable Additives on the Elastic Properties of Swollen CR
Figure 6 illustrates the effect of leachable additives on the tensile stress of CR during swelling with anisole. No change in the tensile stress of CR at maximum equilibrium swelling with anisole was observed before and after removing the leachable additives. However, the extraction of leachable additives by a poor solvent such as acetone has a minimum effect on the tensile properties of CR; small changes in the tensile stress of CR in partial swelling with anisole were observed. Almost the same results were observed in the tensile properties of CR in contact with other solvents.

The presence of leachable additives in CR during partial swelling with various solvents can cause reduction in the tensile properties of CR while no change in the tensile properties of CR was observed when leachable additives were removed completely by swelling with various solvents. Therefore, permanent changes in the tensile properties of CR after deswelling with various solvents can be described only by physical or chemical partial degradation of CR.

CONCLUSION
Swelling-deswelling and elastic properties of CR under various solvents were investigated. The results indicate that the chemical structure and molar volume of the solvents are more effective predictors than the $R_a$ value of the swelling rate and equilibrium swelling of CR when the $R_a$ values are close together. It is also shown that the swelling properties of CR decrease after removing the leachable additives.

The mechanical test results show that tensile property changes of CR in contact with various solvents at low deformation are more important than the changes at large deformation. Also, permanent changes in the tensile properties of CR after swelling with various solvents show partial degradation of CR. However, the tensile properties of CR in contact with ethyl acetate indicate almost no degradation of CR.
REFERENCES


