Australian Government
Department of Defence
Defence Science and Technology Organisation

Sulfur Mustard Penetration of Thermoplastic Elastomers

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DSTO-TN-0846

ABSTRACT

Resistance to sulfur mustard (HD) penetration was investigated for two commercially available thermoplastic elastomers, Santoprene and Alcryn. To pass the Liquid Agent Vapour Penetration Test (LAVPT), Santoprene sheet needed to be at least 1.03 mm thick while Alcryn sheet needed to be at least 0.73 mm thick. Therefore, to pass the LAVPT, Alcryn sheet could be 29% thinner than Santoprene sheet.

Published by

Human Protection and Performance Division
DSTO Defence Science and Technology Organisation
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Fishermans Bend, Victoria 3207 Australia

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AR-014-282
October 2008

Sulfur Mustard Penetration of Thermoplastic Elastomers

Executive Summary

The resistance to sulfur mustard (HD) penetration of two thermoplastic elastomers, Santoprene and Alcryn, was investigated. Most military style CBR (chemical biological radiological) respirators are fabricated from thermosetting elastomers such as butyl rubber or silicone rubber. Compared to thermoplastic elastomers, these thermosetting elastomers are expensive and difficult to process. Therefore a thermoplastic elastomer that could provide sufficient levels of penetration resistance would have great potential as a replacement for butyl and silcone in CBR respirators.

To pass the Liquid Agent Vapour Penetration Test (LAVPT), Santoprene sheet needed to be at least 1.03 mm thick while Alcryn sheet needed to be at least 0.73 mm thick. Therefore, to pass the LAVPT, Alcryn sheet could be 29% thinner than Santoprene sheet.

A number of compounds, including fluorinated additives, activated carbon and talc powder, were added to the thermoplastic elastomers to improve their resistance to chemical penetration.

Further development of this research is recommended to study: the effect of the inclusion of additives on the mechanical properties of the material; investigation of the thermal properties of component materials and investigation into processing polymer/activated carbon black composites.

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Paul joined DSTO in November 2005 as a member of the Enhanced CB Protection for the Individual research team. His research at DSTO includes the investigation of low cost CB impermeable materials as well as novel moisture vapour permeable materials and design and integration of CBR apparel. In addition he provides S&T advice to IRR and other SOCOMD units, as well as the wider ADF community.

Prior to joining DSTO, Paul studied for his PhD in micro-molding of laminated polymer composites at Swinburne University. He has also worked for the CRC for Microtechnology on the development of manufacturing technology for wire bonding of strain gauges, and on a collaborative project between Swinburne University and Visy Plastics developing new materials that include a significant proportion of recycled material.

He holds a Bachelor of Materials Engineering (Hons) and a Bachelor of Science (Chemistry/Materials Science) from Monash University, where he graduated in 1998.

Contents

1 Introduction

For the last few decades, CBR respirators have generally been manufactured from either butyl rubber (as in the British and Australian S10), or silicone rubber (as in the US M17 and M40). Butyl rubber provides excellent resistance to chemical warfare agents but is less comfortable against the skin, while silicone is more comfortable but has poor penetration resistance to chemical warfare agents, necessitating the use of a protective hood in conjunction with the silicone mask.

In general these thermosetting materials are difficult to process and more expensive when compared to thermoplastics. In the last few decades, there has been a substantial increase in the use of thermoplastic elastomers that have mechanical properties like elastomers at room temperature, but soften and flow at high temperature like thermoplastics, and thus can be processed on high throughput machinery. This offers significant potential for a reduction in cost of manufacture for CBR respirators, or for producing a more capable mask at the same cost.

In addition, the processing flexibility of thermoplastic elastomers allows a variety of post-processing operations that are currently technically difficult, too expensive or too time consuming for masks manufactured from conventional elastomers.

Arguably, the most important characteristic of any candidate replacement material is its resistance to chemical penetration. Sulfur mustard (HD) is used as the standard in CWA penetration testing [1].

This work investigates the HD penetration resistance of two commercially available thermoplastic elastomer mixtures, Santoprene and Alcryn.

A number of compounds, including fluorinated additives, activated carbon and talc powder, were added to the thermoplastic elastomers to improve their resistance to chemical penetration.

2 Methodology

2.1 Materials

2.1.1 Thermoplastic Elastomers

The two thermoplastic elastomer materials used in this investigation were polyolefin based Santoprene (Advanced Elastomer Systems) and Alcryn (Advanced Polymer Alloys). These were selected because polyolefins such as polypropylene (PP) and polyethylene (PE) generally have good resistance to chemical penetration [2], and could thus be reasonably expected to have significant resistance to penetration by HD.

Several other thermoplastic elastomers, such as DuPont ETPV and Daiken were rejected because the MSDS's for these materials state that toxic vapours are produced during processing, and that toxic residues could potentially be present in the material after processing. Due to the end use application (a CBR respirator) involving skin contact, it was decided not to investigate these materials. ETPV also had a strong odour, which would be unacceptable for any respiratory protection device. It may be possible to remove the components that produce the strong odor through further processing, but this was considered beyond the scope of this project.

Other candidate thermoplastic elastomers (TE's) include (1) Geolast (Advanced Elastomer Systems), which was rejected on the grounds that its rubber phase was nitrile rubber, which has generally poor resistance to chemical penetration [3], and (2), Trefsin (Advanced Elastomer Systems), which is a mixture of PP and butyl rubber. This material would have made an excellent candidate since butyl is already common in CBR masks, but is no longer manufactured.

Advanced Polymer Alloys (http://www.apainfo.com, a subsidiary of Ferro Corp.) describes Alcryn as a Melt Processible Rubber (MPR), composed of halogenated polyolefin (greater than 70%) and carbon black (less than 30%). The grade of Alcryn used was 4670BK.

Advanced Elastomer Systems (http://www.santoprene.com, a subsidiary of Exxon Mobil Corp) describes Santoprene as a thermoplastic rubber. It has been described as a blend of polypropylene and finely dispersed, highly vulcanised EPDM rubber [4]. However its exact composition is a trade secret. The Santoprene grade used was 251-70W232.

2.1.2 Additives

In order to improve the materials' resistance to chemical penetration, a number of additives were used in this work including;

- Fluoroguard PCA (DuPont), a fluorinated oil
- ACTICARB PS1300 (Activated Carbon Technologies), an activated carbon powder
- Zonyl MP1100 (DuPont), a fluorinated additive
- Talcum powder, (PZ Cussons Australia Pty Ltd), a talc clay

The fluorinated oil was processed by bag mixing and compression moulding, since the extruder used in this investigation was not designed to process liquids. Bag mixing consisted of placing the required masses of pellets and oil into a bag and mixing manually. The oil coated pellets were then compression moulded.

The fluorinated powders, talc clay and activated carbon adsorbents were weighed in appropriate amounts and extruded to improve dispersion. Following extrusion the materials were granulated, and compression moulded.

2.2 Processing

2.2.1 Extrusion Blending

The extrusion was performed in the Industrial Research Institute at Swinburne University, on an Axon Pacific Pty Ltd single screw extruder (Figure 1).

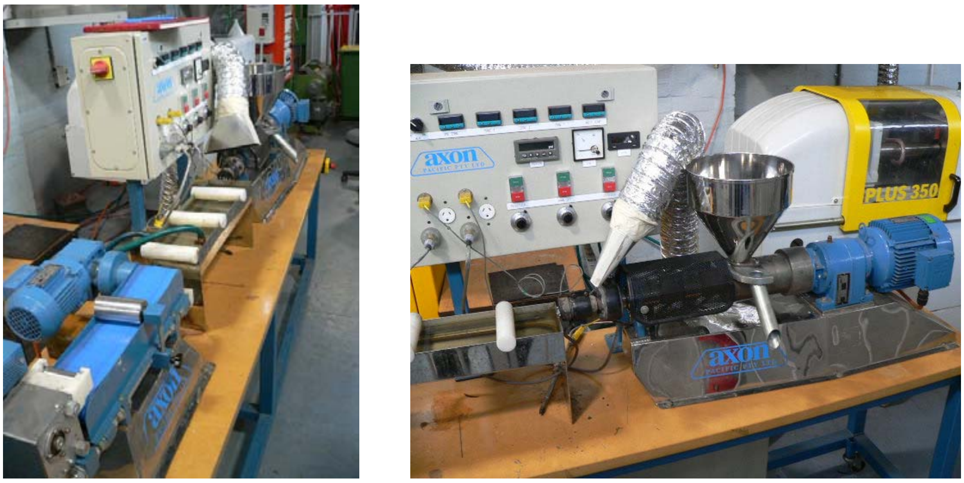

Figure 1: Axon Pacific Pty Ltd single screw extruder

Santoprene and Alcryn were extruded under the following conditions:

Table 1: Extruder zones and temperatures

Extruder Zone	Temperature (^oC)
Die Zone	235
Zone 3 (behind the die)	215
Zone 2 (middle of the barrel)	210
Zone 1 (in front of the materials entry port)	190

The extruder was run at 340 rpm, and the extruded material was water cooled and then granulated before compression moulding.

2.2.2 Compression Moulding

Compression moulding was performed at Swinburne's Industrial Research Institute on a Lab Tech Engineering Company Pty Ltd Model LP S 50 compression moulder (Figure 2).

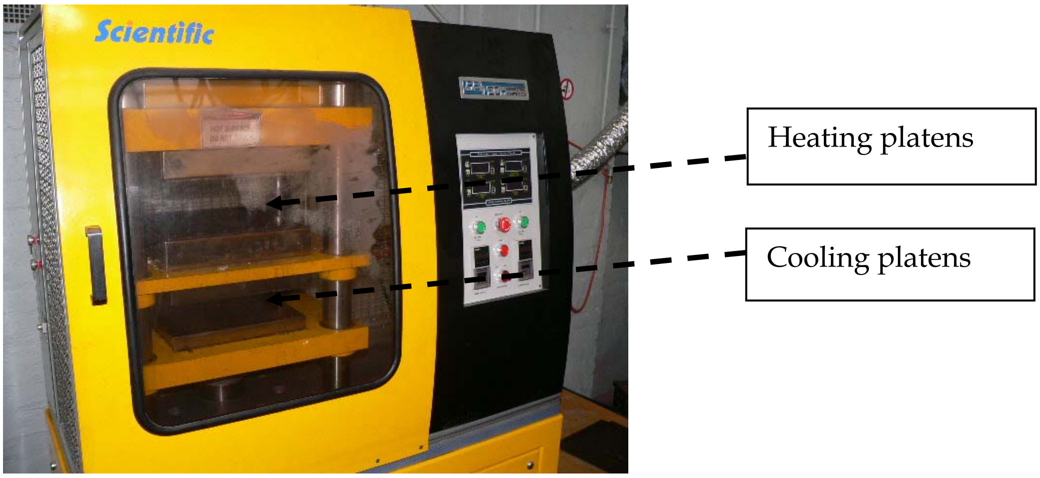

Figure 2: Lab Tech Engineering Company Pty Ltd Model LP S 50 Compression molding machine

This machine has two sets of platens. The top platens are for heating, and are digitally controlled, while the bottom platens are for cooling, which is done by chilled water flowing through internal pipes in the platen block. The material is first pressed in the top set of platens, then removed and inserted into the bottom set of platens for cooling.
Compression moulding was performed using the conditions in Table 2.

Table 2: Processing parameters for compression moulding

Processing parameter	Processing parameter units
Temperature	210 °C
Pre heating time	3 minutes
Pre press time	3 minutes
Full press time	3 minutes
Cooling time	3 minutes

Different materials were used as spacers during compression molding to produce a stable thickness. These materials, which included folded sheets of aluminium foil, folded sheet of Teflon coated fabric, and steel sheet, were placed between the platens during molding.

2.3 Penetration Testing & Analysis

Samples were tested for their resistance to HD penetration using the Liquid Agent Vapour Penetration Test (LAVPT), as previously described [5].

Following agent penetration testing, the concentration of HD in diethyl phthalate (DEP) was determined using a Varian 3400 gas chromatograph (GC) with a pulsed flame photometric detector (PFPD), as previously described [6]. The detection limit of the GC for HD was equivalent to 0.12 $\mu g.cm^{-2}$.

3 Results & Discussion

3.1 Introduction

The materials were compression moulded as supplied, or were mixed with the additives (Section 2.1.2) and then compression moulded. After compression moulding the HD penetration resistance of the materials were measured and the data plotted to investigate how additive loading or sheet thickness affected HD penetration resistance.

It was hypothesised that the different additives would improve penetration resistance in different ways. For talc and activated carbon additives, improvements in resistance to penetration would be gained by increasing the tortuosity of the materials, which would increase the amount of time required for the chemical agent to pass through (Figure 3). Alternatively, the adsorbent particle could adsorb the chemical agent directly, preventing it from passing any further through the material (Figure 3).

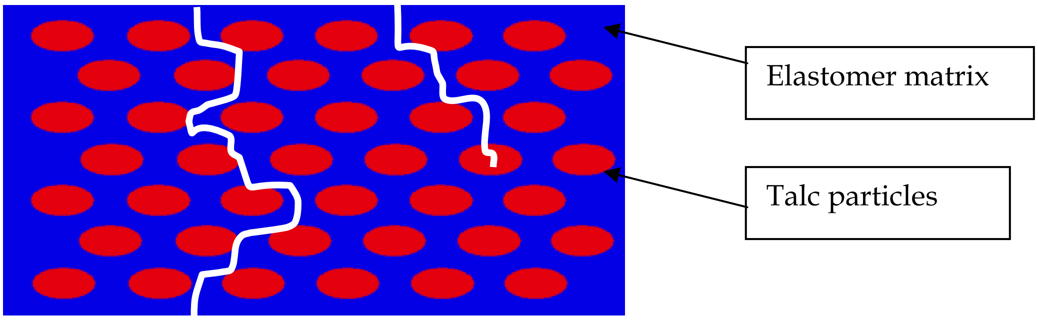

Figure 3: Matrix of elastomer with talc particles. The white lines represent increase in penetration distance due to tortuosity (left), and adsorption on talc particle (right)

For the fluorinated additives, it was expected that they would self-segregate to the surface due to their low surface energy, and form a continuous fluorinated layer, which would increase penetration resistance due to the high chemical resistance of fluorinated polymers (Figure 4).

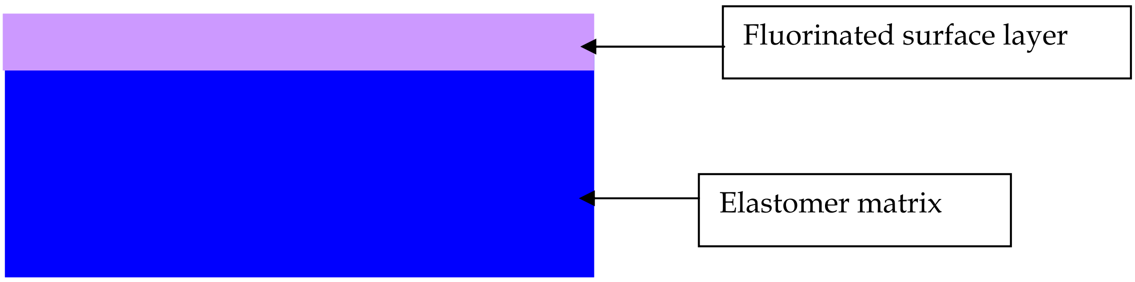

Figure 4: Representation of material with fluorinated surface layer

3.2 Santoprene

3.2.1 Sheet Thickness

The influence of sheet thickness on HD penetration through Santoprene is shown in Figure 5. Each data point is plotted individually as a function of the measured thickness of each individual sample. At thicknesses of 0.5 mm and below, HD penetration is quite high, around 15 - 20 μg/cm². As thickness increases above 1.25 mm, the penetration concentration drops to below 2 μg/cm².

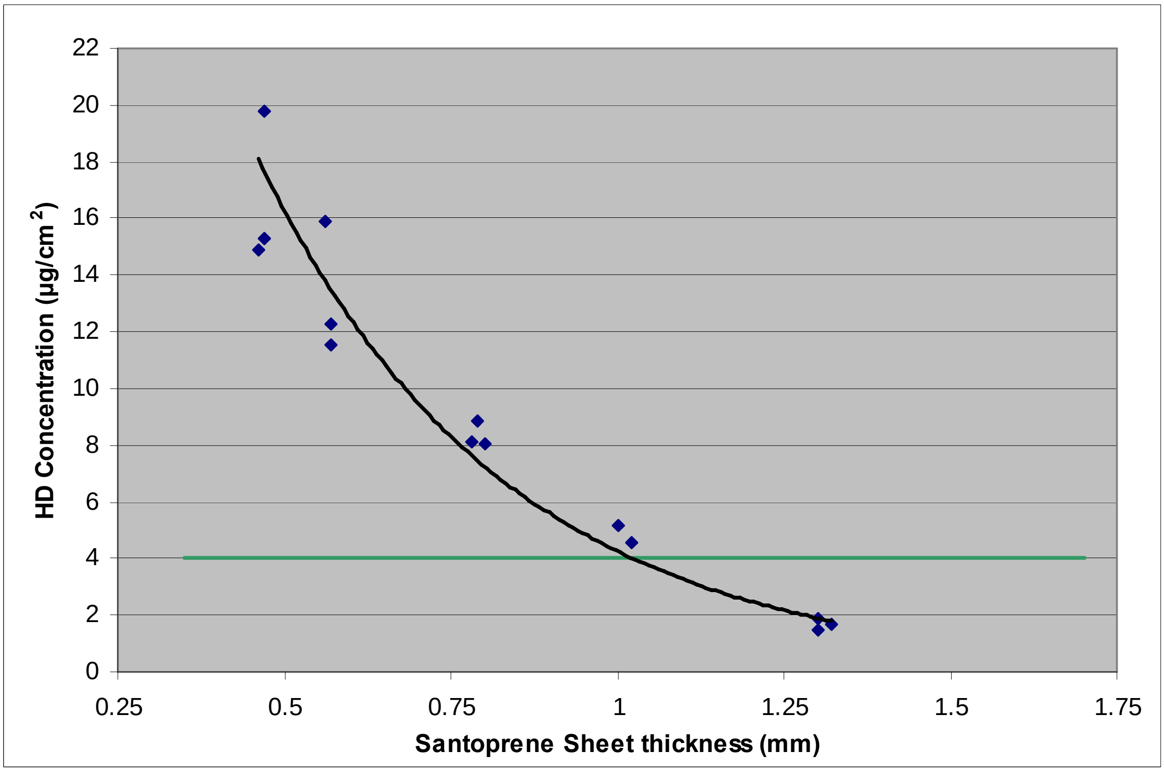

Figure 5: Influence of sheet thickness on HD penetration of Santoprene (green line shows HD penetration pass value of 4 μg/cm²)

Using an exponential curve fit for the HD penetration vs. results of sheet thickness on a log scale (y-axis log), HD concentration can be expressed as:

$$[HD] = 62.1e^{-2.7d} \qquad \text{Equation 1}$$

Where: [HD] = HD penetration concentration in μg/cm², and d = sheet thickness in mm. R^2,which is a measure of how reliable the curve fit is, is 0.97 (the optimal R^2 is 1).

This equation can be used to calculate what thickness is required to pass the HD penetration test. Solving for an [HD] value of 4 μg/cm² gives d = 1.03 mm.

3.2.2 Blending with Talc Powder

An analysis of variance (ANOVA) was performed on the effect of talc powder concentration on HD penetration through Santoprene (Table 3). The Santoprene sheets used were approximately 0.65 mm thick.

Table 3: Summary Statistics and ANOVA of HD penetration through Santoprene/talc blends

SUMMARY

Groups	Count	Sum	Average	Variance
0 wt% talc powder	5	75.82824	15.16565	5.097222
5 wt% talc powder	5	59.90092	11.98018	0.840028
10 wt% talc powder	5	52.73952	10.5479	2.351241

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	55.87028	2	27.93514	10.11106	0.002668	3.885294
Within Groups	33.15397	12	2.762831			
Total	89.02424	14				

Table 3 ANOVA clearly demonstrates that the variability between sample groups is much larger than the variability within the sample groups. Therefore, it can be reasonably concluded that talc concentration has a significant effect on HD penetration.

The effect of talc concentration is shown in Figure 6. Each value is the average of 5 replicates, and the error bars represent ± 1 standard deviation. Based on mean penetration levels, incorporation of 10 wt% talc powder into Santoprene could potentially reduce HD penetration by up to 25%.

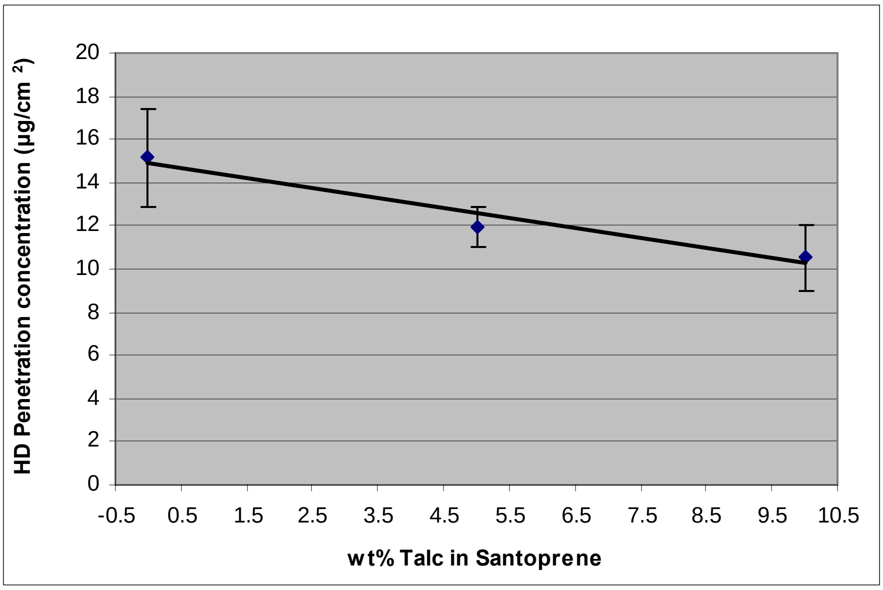

Figure 6: Influence of talc on HD permeation of Santoprene

Using a linear curve fit for the HD penetration data in Figure 6 gives HD concentration expressed as:

$$[HD] = -0.5c + 14.9 \qquad \textit{Equation 2}$$

Where: [HD] = HD penetration concentration in µg/cm^2, and c = wt% talc. The R^2 value is 0.98.

Preliminary tests were conducted to include 20 wt% talc powder into Santoprene. However, the talc powder increased the viscosity of the Santoprene to a level that was difficult to process, so further investigations were discontinued.

It is likely that the mechanical properties of the Santoprene were affected by the addition of talc powder. Specific changes were not investigated but it is likely that inclusion of talc powder would decrease the elasticity of Santoprene (depending on how much talc was added).

3.2.3 Blending with DuPont Zonyl MP1100 Fluoroadditive

Figure 7 shows the results from permeation testing on an extrusion blended mixture of Santoprene and Zonyl MP1100 fluorinated additive. The sheets were approximately 200 µm thick. Four multiples were taken for each experiment, the results were averaged, and the error bars are ± 1 standard deviation.

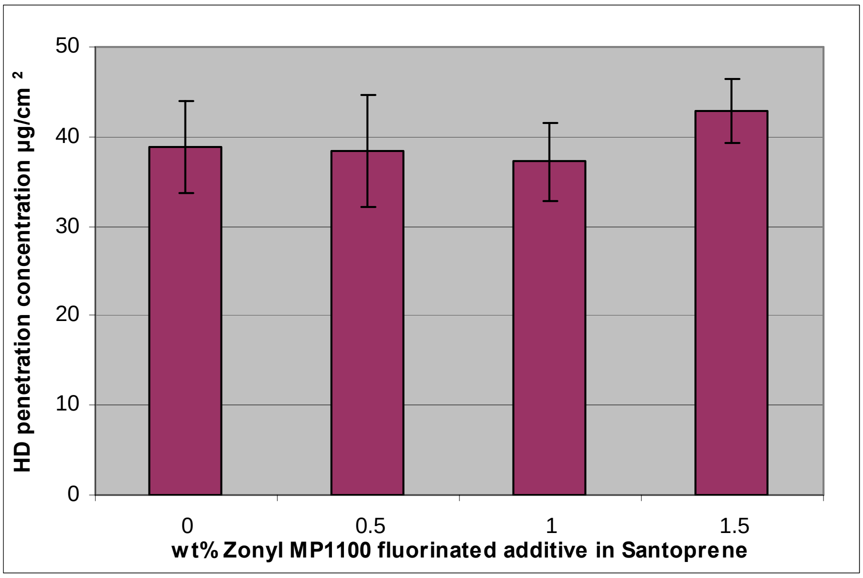

Figure 7: HD Penetration for blends of Santoprene and Zonyl MP1100 Fluoroadditive

Table 4 presents an analysis of the data in Figure 7. The p-value of 0.18 indicates that the variability between the groups is not significantly larger than the variability within the groups.

Table 4: Summary Statistics and ANOVA of HD penetration through Santoprene/Fluoroadditive blends

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	6	233.0412	38.8402	25.90386
Column 2	6	230.4089	38.40149	39.47609
Column 3	6	226.968	37.828	24.38138
Column 4	6	262.504	43.75067	11.93079

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	134.0254	3	44.67515	1.757271	0.187719	3.098391
Within Groups	508.4606	20	25.42303			
Total	642.4861	23				

The addition of Zonyl MP1100 fluorinated additive caused no discernible increase in penetration resistance. One possible explanation for the lack of change in penetration is that the fluorinated additive did not migrate to the surface as intended. Since the thermal properties of the fluorinated additive were unknown, the selected processing temperature may not have been high enough to melt the additive and provide it with sufficient mobility to migrate to the surface.

These results emphasise the importance of processing conditions, and in any future study, an investigation of the thermal properties of the materials should be conducted in order to optimise the processing temperature.

3.2.4 Blending with DuPont Fluoroguard PCA

DuPont Fluoroguard is a fluorinated oil that was combined with Santoprene. It was used for similar reasons as the Zonyl MP1100, to improve chemical resistance through the development of a continuous fluorinated surface layer. However, compression moulding sheets of Santoprene/Fluoroguard was not successful as the moulded sheets contained numerous pockmarks or holes, which seemed to be a consistent feature regardless of Fluoroguard loading or moulding conditions (Figure 8). These features may be where the Fluoroguard liquid congregated during processing.

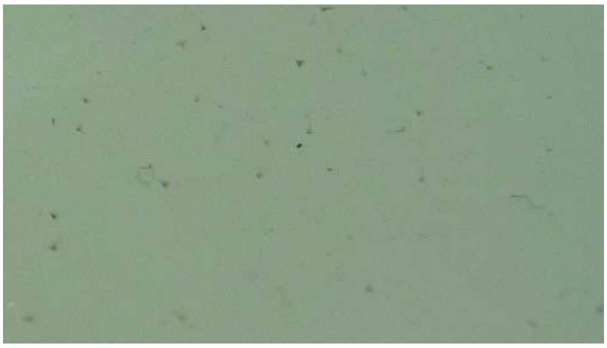

Figure 8: The surface of compression moulded Santoprene/Fluoroguard blend. The dark spots are pits/holes in the surface.

3.3 Alcryn

3.3.1 Sheet Thickness

HD penetration was significantly affected by Alcryn sheet thickness (Figure 10). All results are single point measurements without error bars (as there are no duplicates). Alcryn sheet passed the HD permeation test at approximately 0.75 mm. HD permeation levels decrease to near negligible levels at or above approximately 1.5 mm thickness.

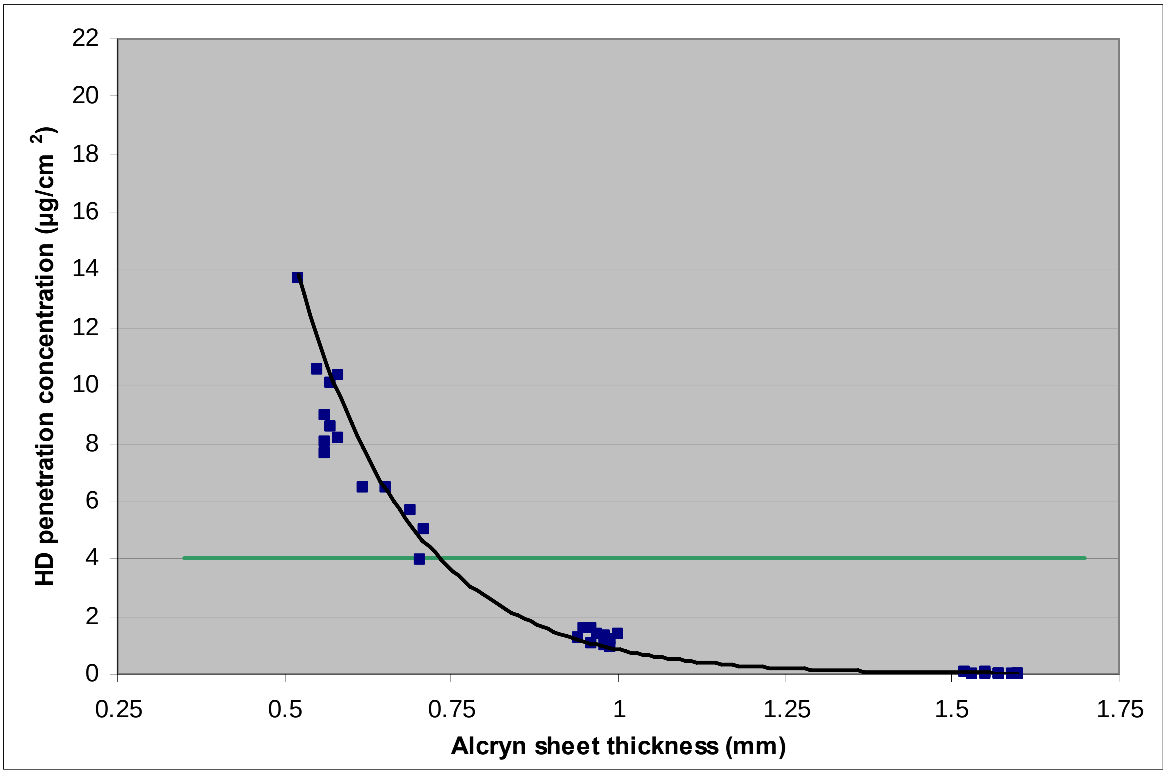

Figure 9: Influence of sheet thickness on HD permeation of Alcryn. The green line is the HD penetration pass value of 4 µg/cm^2.

By fitting a exponential model to the data in Figure 9, HD penetration concentration can be expressed as:

$$[HD] = 287.2e^{-5.8d} \qquad \textit{Equation 3}$$

Where: [HD] = HD penetration concentration in µg/cm^2 and d = sheet thickness in mm. R^2 for this equation is 0.99.

This equation can be used to calculate what thickness is required to pass the HD penetration test. Solving for an [HD] value of 4 µg/cm^2 gives d = 0.73 mm.

3.3.2 Blending with Talc Powder

Figure 10 shows how sheet thickness influences the penetration resistance of the Alcryn/10 wt% talc powder blend.

At higher thicknesses, it was difficult to determine the influence of the talc since the penetration concentration of unmodified Alcryn is already close to the detection limits.

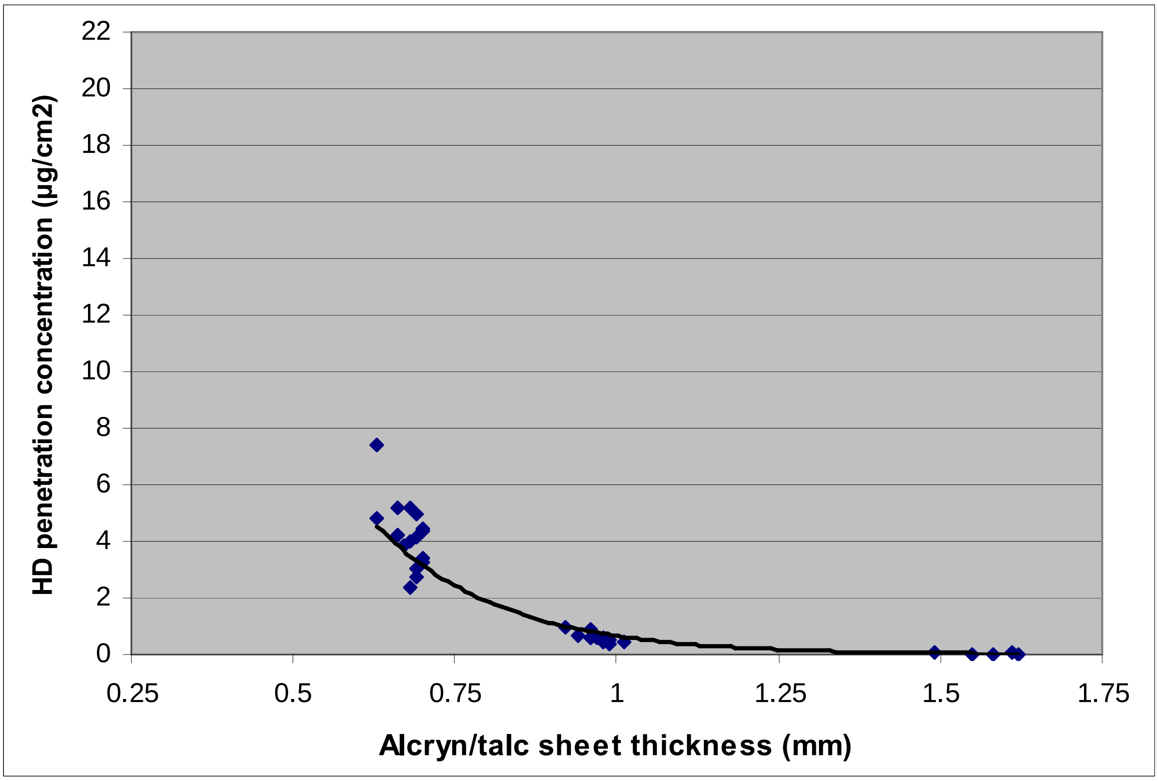

Figure 10: Influence of sheet thickness on HD penetration of Alcryn/talc (10 wt%) blends. The green line is the HD penetration pass value of 4 µg/cm^2.

By fitting an exponential equation to the data in Figure 10, HD concentration can be expressed as:

$$[HD] = 123.8e^{-5.2d}$$ *Equation 4*

Where: [HD] = HD penetration concentration in µg/cm^2 and d = sheet thickness in mm. R^2 for this equation is 0.95.

This equation can be used to calculate what thickness is required to pass the HD penetration test. Solving for an [HD] value of 4 gives d = 0.67 mm.

Based upon the logarithmic model, the addition of 10 wt% talc powder to Alcryn results in an improvement in penetration resistance of up to 8%.

3.3.3 Blending with Activated Carbon

Due to the issues mentioned in Section 2.2.3 and 2.2.4, blending Alcryn with fluorinated additives was not attempted. However, blending activated carbon and Alcryn was attempted, but was difficult to process. The inclusion of the activated carbon raised the viscosity of the material dramatically and the extruder was not able to force the material through the barrel.

However, despite the processing difficulties, it seems a reasonable hypothesis that if the talc powder was effective in improving penetration resistance then activated carbon powder should be effective as well. Despite processing difficulties, this is still an interesting area for research.

4 Conclusions

The resistance to HD penetration of two commercially available thermoplastic elastomers, Santoprene and Alcryn, was investigated. Based on curve fits, Santoprene sheet needed to be at least 1.03 mm thick to pass the HD penetration test, whilst Alcryn could pass while being approximately 0.73 mm thick, a reduction in thickness of up to 29%.

The inclusion of talc powder into both materials provided a clear improvement in resistance to HD penetration. Attempts to extrapolate this result to Alcryn blends including activated carbon failed due to the resulting blend being too viscous to process on the available extruder.

The Zonyl MP1100 fluorinated powder did not prove effective at increasing permeation resistance. This was attributed to poor melting and mixing of the additive and poor mixing behaviour. Additional moulding trials are required to fully explore the possible benefits of the blend.

Mixtures of Fluoroguard oil and Alcryn were also mechanically difficult to process. Bag mixing was possible but compression moulded sheets of Fluoroguard/elastomer blend suffering extensive “pinholing” which rendered them unsuitable for chemical protection.

5 Recommendations

For further development of this research, the following directions could be pursued:

(1) testing to determine how the inclusion of talc powder (and other additives) affects the mechanical properties of the material.

(2) investigation of thermal properties of component materials, with the goal to optimisation processing temperature and mixing.

(3) investigation of processing of polymer/activated carbon black composites

6 References

1. *Operational Requirements and evaluation criteria for general service masks in the timeframe 1985-2005*

2. *Barrier Polymers*, in *Encyclopedia of Polymer Science and Technology*. 2005, John Wiley and Sons. p. 198-262.

3. Crone, H.D., ed. *Protection against toxic chemicals*. 1990, Materials Research Laboratory.

4. Margolis, J.M., *Elastomeric materials and processes*, in *Modern plastics handbook*, C.A. Harper, Editor. 2000, McGraw-Hill. p. pp3.1-3.51.

5. Gray, B. and G. Long, *The effect of adsorbed water on the protective capacity of the MK IV NBC suit*. 1993, MRL-TN-645, DSTO Materials Research Laboratory.

6. Lancaster, P., *Gas chromatographic analysis of sulfur mustard in diethyl phthalate* 1998, DSTO-TR-0703, Aeronautical and Maritime Research Laboratory.

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
DOCUMENT CONTROL DATA

1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)

2. TITLE

Sulfur Mustard Penetration of Thermoplastic Elastomers

3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)

Document	(U)
Title	(U)
Abstract	(U)

4. AUTHOR(S)

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5. CORPORATE AUTHOR

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506 Lorimer St
Fishermans Bend Victoria 3207 Australia

6a. DSTO NUMBER	6b. AR NUMBER	6c. TYPE OF REPORT	7. DOCUMENT DATE
DSTO-TN-0846	AR-014-282	Technical Note	October 2008

8. FILE NUMBER	9. TASK NUMBER	10. TASK SPONSOR	11. NO. OF PAGES	12. NO. OF REFERENCES
2006/110109	07/076	ARMY	13	5

13. URL on the World Wide Web

http://www.dsto.defence.gov.au/corporate/reports/DSTO-TN-0846.pdf

14. RELEASE AUTHORITY

Chief, Human Protection and Performance Division

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CBR IPE
chemical penetration
protective clothing
sulfur mustard resistance

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Resistance to HD penetration was investigated for two commercially available thermoplastic elastomers, Santoprene and Alcryn. To pass the Liquid Agent Vapour Penetration Test (LAVPT), Santoprene sheet needed to be 1.03 mm thick while Alcryn sheet needed to be 0.73 mm thick. Therefore, to pass the LAVPT, Alcryn sheet could be 29% thinner than Santoprene sheet.