

# NOVEL NYLON/HALOGENATED BUTYL RUBBER BLENDS IN PROTECTION AGAINST WARFARE AGENTS

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## BIOGRAPHICAL NOTE



Dr. Marek Gnatowski received his Ph.D. and Engineering degree in polymer chemistry and technology from Warsaw University of Technology. He has 36 years of experience in industrial research and development, consulting, and process control, including 25 years experience in North America in fields related to polymeric materials. This includes over 20 years work on polymer blends for a variety of applications. He is the author of three book chapters in Plastics Waste Management, 10 papers in scientific journals, 13 conference presentations, 11 patents and 3 patent applications pending. Dr. Gnatowski has held the position of technical director of Polymer Engineering Company Ltd. in Burnaby, BC, Canada for over twenty years. The main focus of his research activities has been the response of natural and synthetic polymers to environmental exposure.

## ABSTRACT

Novel thermoplastic material was designed for making warfare agent resistant equipment. Nylon 12/chlorobutyl blends were selected and evaluated. The evaluation included microstructure, resistance to hydrocarbon and halogenated solvents, mechanical properties, and resistance to sulfur mustard penetration and reemission. It was found that nylon/chlorobutyl rubber blends made by dynamic vulcanization show elastomeric behaviour, have good mechanical properties, and are resistant to warfare agent penetration and reemission. The material is also thermoplastic and could be processed by injection moulding or extrusion.

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## INTRODUCTION

Humans and their resources can be exposed to a variety of hostile and aggressive environments due to exploration of new frontiers such as the deep underwater regions of the earth or outer space. Humans can also face natural or man made disasters, or war. In all of these situations protection of humans and their resources, such as food, drinking water, or equipment becomes an urgent and important issue. More recently, a potentially increasing problem could be exposure to toxic chemicals, biological agents, or radioactive materials due to, for example, accidents in chemical manufacturing and storage, or intentional attack. For this reason, development in protective equipment against chemical, biological, and nuclear contamination continues to be an urgent challenge.

Polymers or composites that contain polymers are frequently used as materials in the design and manufacturing of a variety of protective equipment due to favorable properties such as:

- Light weight
- Wide range of mechanical properties (including elastomeric)
- Resistance to wear
- Wide range of coefficient of friction
- Easy moulding
- Resistance to hostile and aggressive environment (if properly designed and selected).

Properties such as being light weight, the elastomeric behavior, and the extremely low modulus of elasticity (stiffness) that are offered by polymers are not generally available in other materials such as metals, or ceramics and glasses. Also, easy mouldability of articles by injection moulding, extrusion, or compression moulding generally favours polymeric materials, in particular thermoplastics. Some disadvantages of polymers could be their frequently limited chemical resistance. For this reason, during selection or designing of polymeric materials that are expected to be exposed to chemical attack, caution has to be taken. Commercially available polymers that are known for their resistance to chemical warfare agents (CW) are listed in table 1 along with some other common plastics and rubbers.

Table 1. Properties of selected commercial polymeric materials

Material		Resistance to			Mechanical Behaviour		Processing Friendly
		CW <sup>d</sup>	Water*	Oil and Fuels	Engineered Plastic	Elastomer	
Butyl, Halogenated Butyl Rubber	(C,B) IIR	4	4	1	1	4	2-3
Natural Rubber (polyisoprene)	NR	1	1-3	1	1(3) <sup>c</sup>	4	2-3
Chloroprene	CR	1-2	2-3	4	1	4	2-3
Nitrile Rubber	NBR	1-2	3	4	1	4	2-3
Santoprene (PP/EPDM)	TPE	1	3	1-2	1	4	4
Polyurethane Elastomer	PU	1-2	2-3	3-4	1	4	3-4
Polyamides (Nylons)	PA	3-4	3 (1) <sup>a</sup>	4	4	1	3-4
Aromatic Polyesters (PBT, PET)	PET, PBT	4	4 (2) <sup>a</sup>	4	4	1	3-4
Polyvinyl Alcohol (PVOH)	PVA	2-4	1	4	3	1	1-3 <sup>b</sup>
Polystyrene	PS	1	4	1	2-3	1	4
HDPE	HDPE	1	4	3-4	2-3	1	4

4 – excellent    3 – good    2 – acceptable    1 – unacceptable

<sup>a</sup>. immersion in hot water

<sup>b</sup>. requires modification

<sup>c</sup>. ebonite

<sup>d</sup>. CW – chemical warfare agent

\* long term exposure

Please note that the only common elastomers that have good resistance to chemical warfare agents are butyl or halogenated butyl rubber. These rubbers are thermoset materials and require a vulcanization process to crosslink them as part of a final cure. Unfortunately, manufacturing goods from these rubbers requires, in most cases, a moulding process with a long production cycle, and they can not be welded. Also, some limited absorption of chemical warfare agents in the final products has been observed. Thermoplastics, that have excellent resistance to chemical warfare agent penetration and absorption, are primarily hard engineering resins such as crystalline polyamides or aromatic polyesters. As a rule of thumb, we can expect that the softening of a polymeric material will lead to an increase in chemical diffusion, and the absorption of chemical compounds such as chemical warfare agents. This means that designing a new, softer elastomeric material that is resistant to warfare agents is a challenge, particularly when this material is required to be moulded as a thermoplastic resin. Another challenge is to obtain this new thermoplastic using commercially available source materials.

### NYLON/HALOGENATED BUTYL RUBBER BLEND

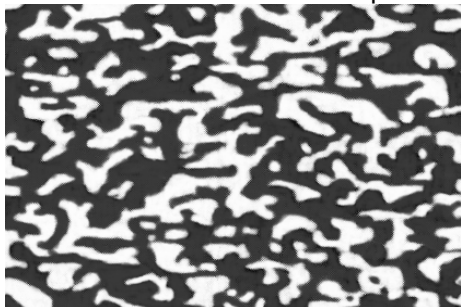
A natural approach seemed to be to combine the properties of an elastomer, such as butyl rubber, with one of the engineered thermoplastic resins that has excellent resistance to warfare agents and good melt processing, such as a nylon. Butyl rubber, when vulcanized and crosslinked, has reasonable mechanical properties, good warfare agent resistance, and is commercially available. Among nylon resins, polyamide 12 has received attention due its excellent mechanical and barrier properties and relatively low processing temperature, in the range of 190° – 220° C. This resin is also commercially available and is used extensively in the food packaging industry.

This mixing approach instantly creates challenges. Nylons and butyl or halogenated butyl rubbers are expected to be incompatible on mixing due to their chemical differences. They have different polarities, solubility parameter values, and surface energies. To obtain suitable rubber properties, including warfare agent resistance, the vulcanization process has to be employed to facilitate crosslinking. Also, a significant quantity of rubber has to be incorporated into the new material to obtain suitable elastomeric characters and properties. A larger quantity of crosslinked rubber in the blend could create a problem in obtaining material with thermoplastic moulding capability and good mechanical properties.

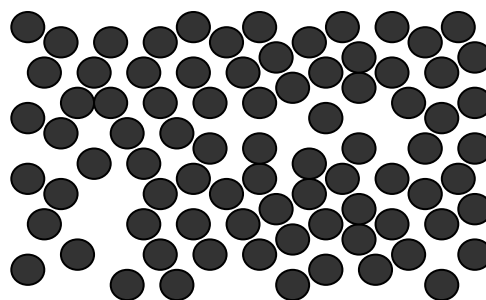
Nylon/butyl rubber blending was conducted in our laboratory using a Brabender batch blender equipped with roller blades, or a twin screw extruder.

The dynamic vulcanization process was employed during the blending of nylon 12 with butyl or halogenated butyl rubbers. Dynamic vulcanization is a process where rubber is vulcanized during blending with thermoplastic resin. During the mixing process, the rubber component becomes crosslinked and suspended in the form of very small particles in thermoplastic resin as shown in schematic form in figure 1a and b, and as SEM photomicrographs in figure 2a and b. This allows for the addition of a significant quantity, well over 50%, of the rubber component into the thermoplastic resin blend which would still maintain flow despite rubber vulcanization. The microstructure of this blend is also responsible for the peculiar properties of this material as will be discussed further in this paper.

Figure 1. Schematics of rubber dispersions

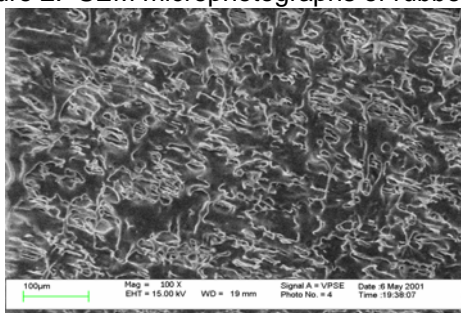


1a. Dispersion of rubber in thermoplastic resin made by blending without vulcanization

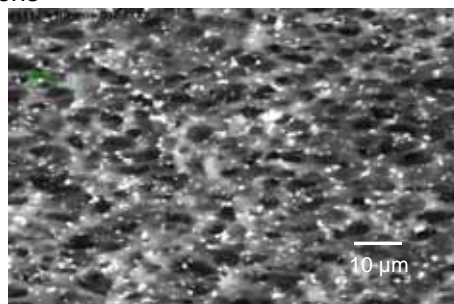


1b. Dispersion of rubber in thermoplastic resin made by the dynamic vulcanization process

Figure 2. SEM microphotographs of rubber dispersions



2a. SEM of dispersion of rubber in thermoplastic resin made by blending without vulcanization



2b. SEM of dispersion of rubber in thermoplastic resin made by the dynamic vulcanization process

The finely dispersed rubber phase in nylon would be very difficult to achieve without good compatibility of both blend components. In the case of our nylon/rubber blend, this was most likely done through the generation of a compatibilizer in the polymer grafting reaction shown in figure 3. The presence of grafted polymers can be seen in the infrared spectrum of the non-vulcanized butyl rubber extracted from the nylon 12 blend by hexane. The weak polyamide absorption band at  $1640\text{ cm}^{-1}$  appears in the rubber spectrum as shown in figure 4.

Figure 3. Grafting reaction – molecule of butyl rubber to nylon

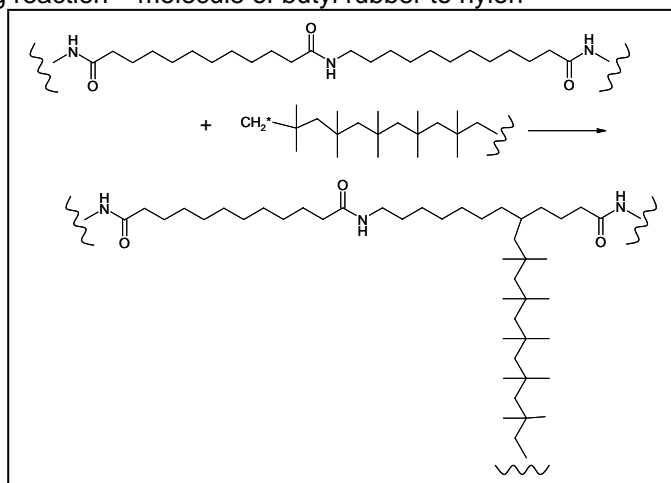
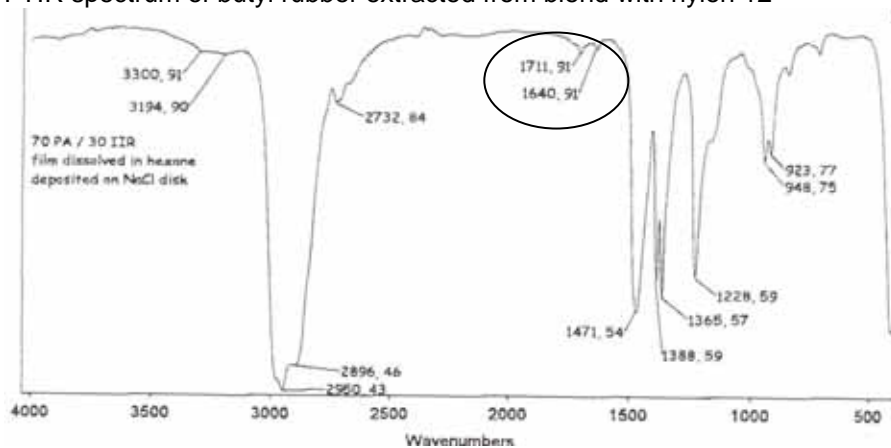


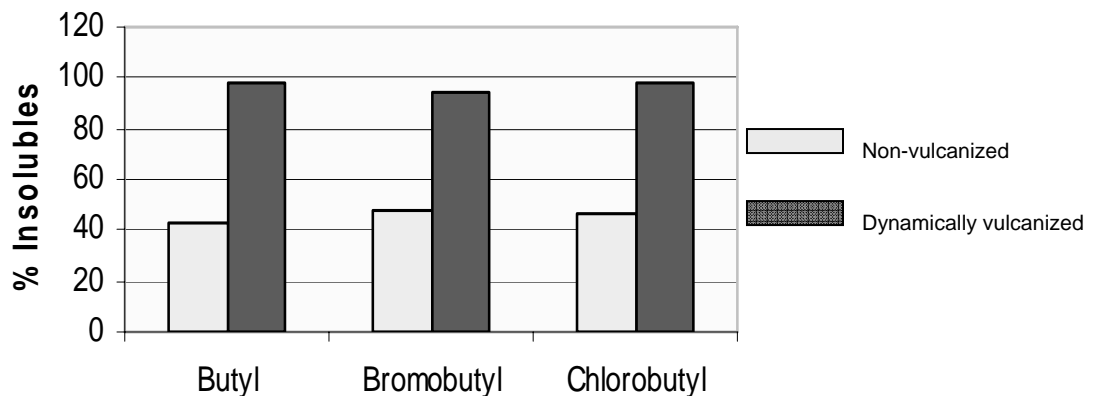
Figure 4. FTIR spectrum of butyl rubber extracted from blend with nylon 12



### VULCANIZATION AND CHEMICAL RESISTANCE

Full crosslinking of the butyl or halogenated butyl rubbers blended with nylon 12 using the dynamic vulcanization process can be confirmed by comparison of insoluble content after extraction of the blend with hexane (figure 5).

Figure 5. Percent of insoluble matter in non-vulcanized and vulcanized rubbers blended with nylon



Comparison of tensile strength and elongation at break for a series of blends of nylon 12 with butyl and halogenated butyl rubbers confirmed that the most favorable mechanical properties in tension had a dynamically vulcanized blend containing chlorobutyl rubber (figures 6 and 7). For this reason, work described further will focus on nylon 12 and vulcanized chlorobutyl rubber exclusively.

Figure 6. Tensile strength of nylon/halogenated butyl rubber blends made with and without vulcanization

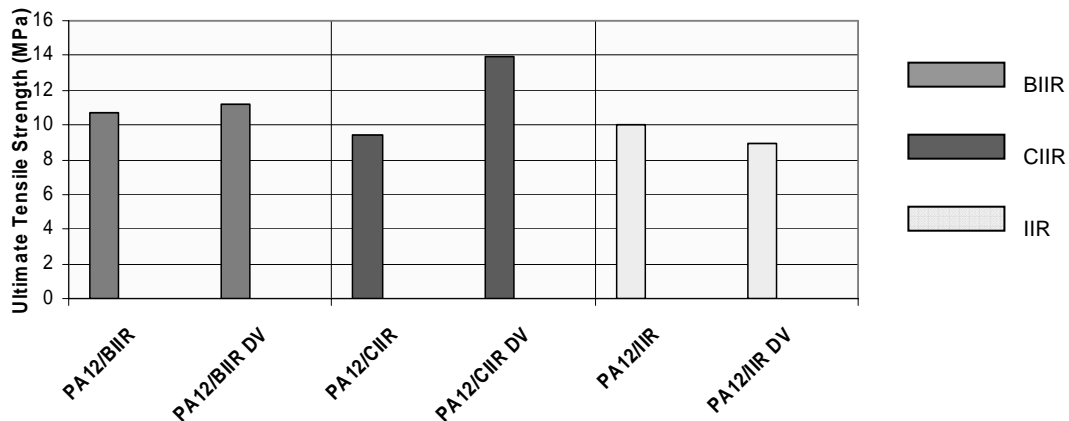
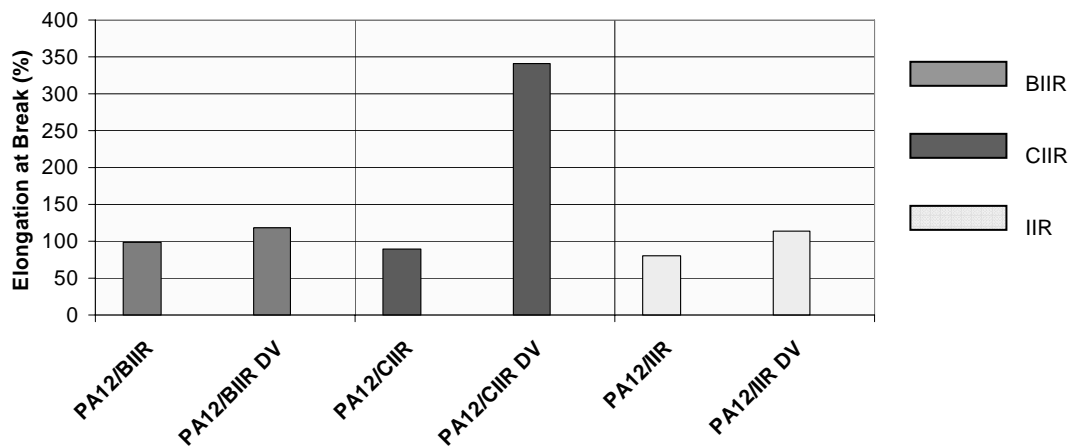
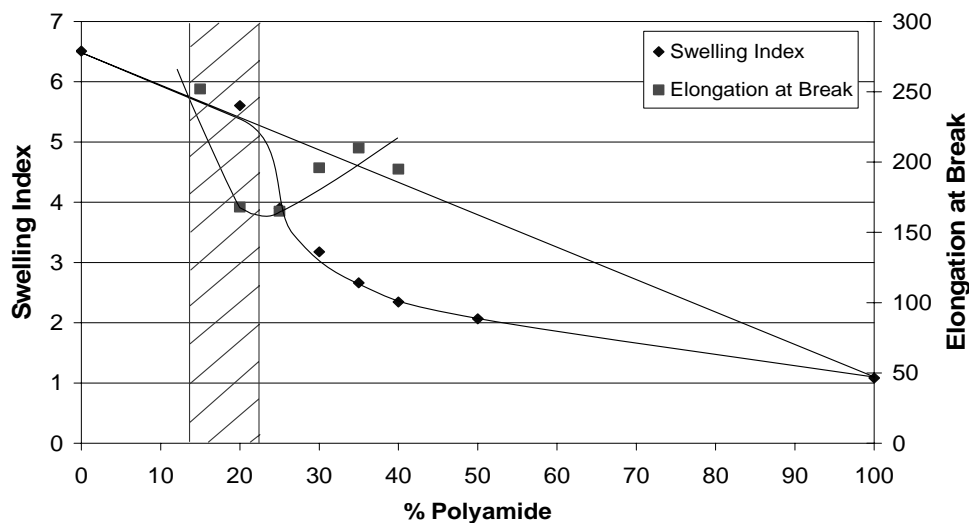


Figure 7. Elongation at break of nylon/halogenated butyl rubber blends made with and without vulcanization



Very interesting data were obtained from testing of the swelling index in hexane and  $\text{CHCl}_3$  of dynamically vulcanized blends containing variable ratios of nylon to rubber. Nylon 12 is insoluble in both of these solvents, while the rubber component of the blend is swollen. It was found that the swelling index for the blends was significantly smaller than expected value based on the proportion of the vulcanized rubber present (figure 8). This also indicated that the blends had significantly improved hydrocarbon resistance regardless of a large content of butyl rubber. This phenomenon was most likely not related to different degrees of crosslinking. An explanation of this phenomenon can be found after looking once more at the microscopic blend structure (figure 2b), where rubber particles can be seen coated by rigid, strong thermoplastic nylon resin. The nylon network seemed to resist rubber expansion and limit solvent diffusion. We can call it the “caging effect”. The “caging effect” seems to be highest around the expected phase reversal point with 15%-20% nylon, where the blends elongation at break also reached a minimum value. This phenomenon may be useful in designing other similar thermoplastic polymeric blend systems with improved chemical resistance.

Figure 8. Swelling index and elongation at break for dynamically vulcanized blends in  $\text{CHCl}_3$ .



### MECHANICAL PROPERTIES

The mechanical properties of the blends were also peculiar. The results obtained were strongly dependent on the method of specimen preparation, and even the flow pattern within the same mould has an effect as can be seen in figures 9-13.

Figure 9. Tensile strength and elongation at break of nylon/chlorobutyl rubber samples injection moulded, compression moulded, and extruded

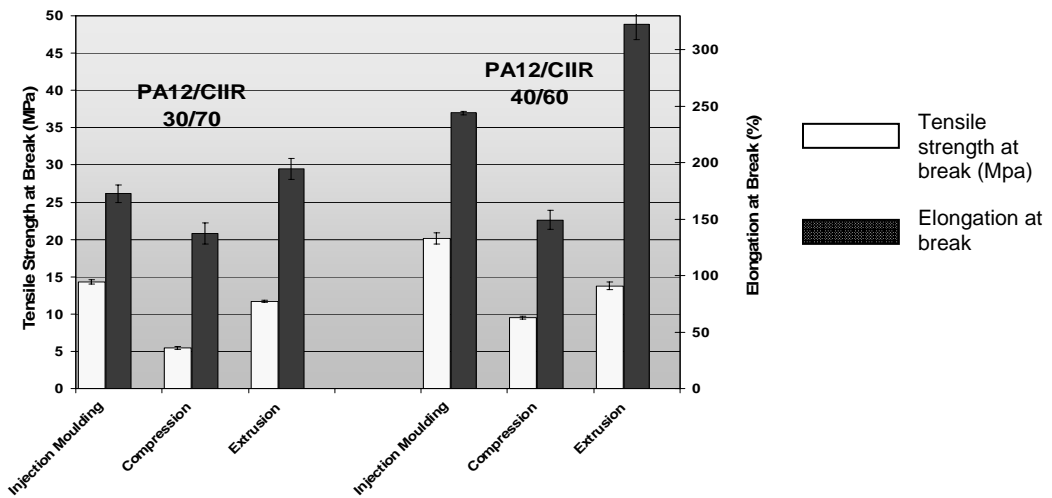


Figure 10. Modulus of elasticity of nylon/chlorobutyl rubber samples injection moulded, compression moulded, and extruded

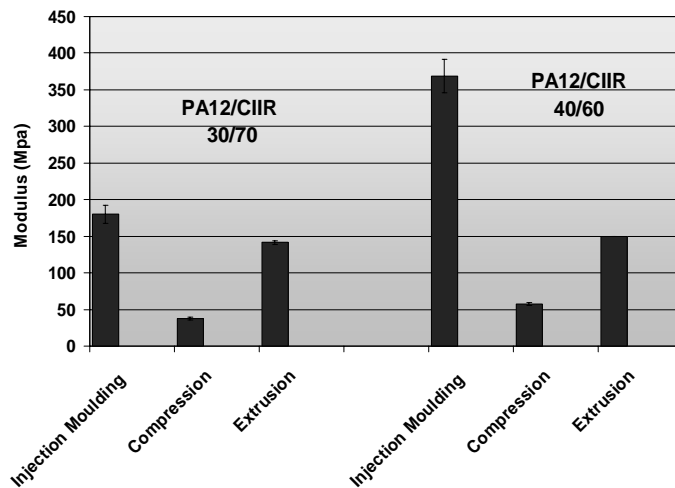


Figure 11 Shore D Hardness of nylon/chlorobutyl rubber samples injection moulded, compression moulded, and extruded

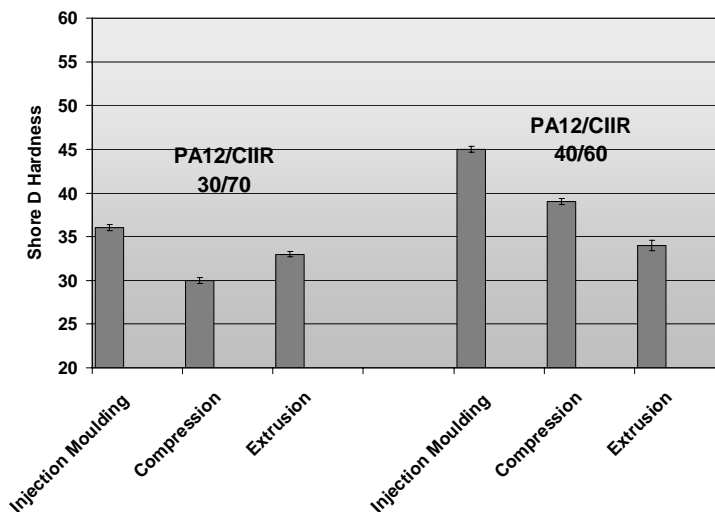


Figure 12. Comparison of tensile strength and elongation at break for injection moulded specimens “as moulded” and cut from impact bar

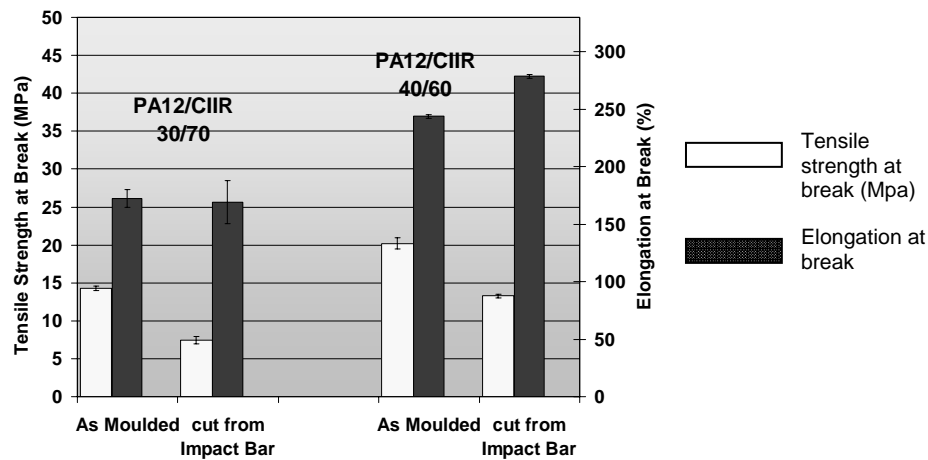
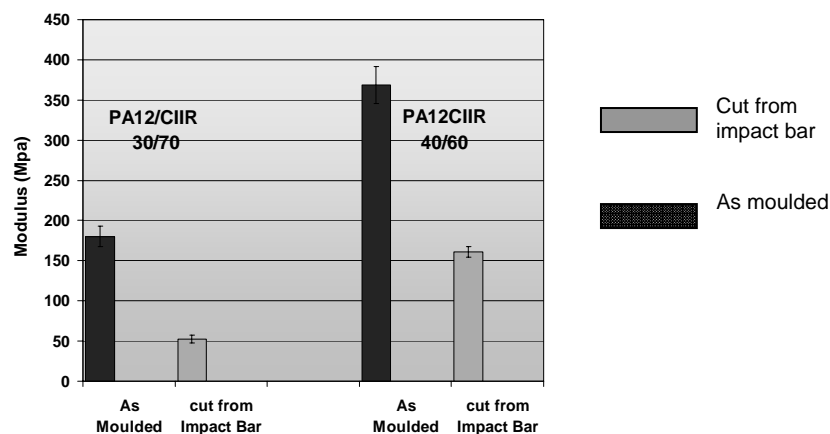


Figure 13. Comparison of modulus of elasticity for injection moulded specimens “as moulded” and cut from impact bar



With respect to tensile strength, the best result for PA/CIIR = 40/60 blends, 20.2MPa was obtained in the case of injection moulded specimens (ASTM D638M type M-III), and the lowest value was for the compression moulded material (9.5 MPa). Extruded sheeting tested in the machine direction showed intermediate results with 13.8 MPa. An identical trend was observed for PA/CIIR = 30/70 blends with the best tensile strength (14.3 MPa) also obtained for the injection moulded specimens. Compression moulded material showed only approximately 50% tensile strength for injection moulded samples as was recorded for 40/60 blends.

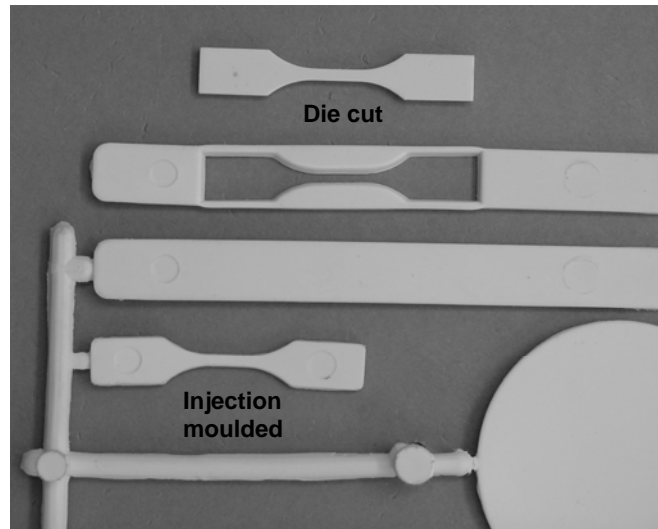
Elongation at break also varied with the highest values (323%) obtained for extruded sheeting tested in the machine direction, and the lowest result (149%) for compression moulded samples of the 40/60 PA/CIIR blend.

A reversed trend to elongation at break was observed for tensile modulus of the discussed blends. For example, for blend with nylon to rubber ratio 30/70, the larger modulus value (180.1 MPa) and the larger durometer hardness (36 Shore D) were recorded for injection moulded specimens. Compression moulded samples of the same material showed modulus of 37.6 MPa and Shore D durometer hardness under 30.

An experiment was conducted to confirm that the blend flow and structure orientation, not the material thermal and shear history, during moulding of specimens were responsible for the variability in mechanical properties. The same size of moulded and die cut specimens were taken from the same injection moulded sample (figure 14). The cavities of the mould for these specimens had different thermoplastic material melt flow patterns. Testing conducted for tensile strength, elongation at break, and tensile modulus showed an identical trend as observed earlier for specimens moulded using different techniques. For example, blend

PA/CIIR = 30/70 had tensile strength for injection moulded specimens of 14.3 MPa vs. 7.4 MPa for specimens die cut from the neighbouring impact bar with less restricted flow within the cavity. Surprisingly, elongation at break was very similar for these two sets of specimens, in the range of 170%. Higher tensile strength was also associated with significantly higher tensile modulus, in the range of 180.0 MPa vs. 37.6 MPa respectively for the same tested specimens.

Figure 14. Specimens M-III (ASTM D638M) injection moulded and cut from impact bar

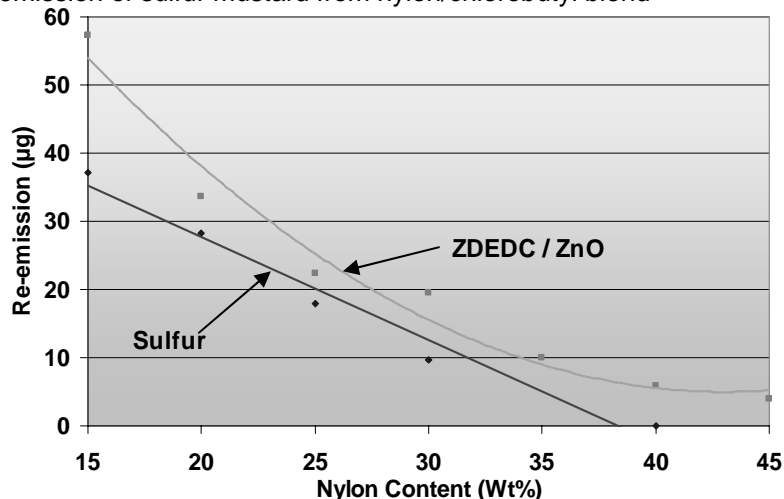


This variability of mechanical properties is likely related, as was mentioned earlier, to blend microstructure and its orientation to the melt flow during moulding. An increase in material stress during flow seemed to cause increased melt microstructure orientation resulting in increased tensile strength and tensile modulus reflecting material stiffness.

#### WARFARE AGENT RESISTANCE

Testing of injection moulded blend samples with different ratios of PA to CIIR, at a thickness of 1.5 mm, for resistance to warfare agents<sup>1</sup> showed no signs of sulfur mustard gas penetration for 24h. Further evaluation of CW agent re-emission (figure 15) showed a decrease from 38  $\mu\text{g}$  to 0  $\mu\text{g}$  with an increase in nylon content from 15% to 40% when sulfur was used as a vulcanizing agent. A larger value of re-emission was found for ZDEDC/ZnO vulcanization. This indicates that vulcanization of rubber and the type of vulcanizing agent seem to be an important factor in designing chemical resistant PA/CIIR blends. Regardless of the vulcanization method used, nylon chlorinated butyl rubber elastomeric blends showed very low levels of re-emission of warfare agents in comparison to other materials used recently for manufacturing protective equipment.

Figure 15. Re-emission of sulfur mustard from nylon/chlorobutyl blend



<sup>1</sup> Testing procedure is described in the presentation “Nylon 12 Nanocomposite Thin Films” by Dr. Cecilia Stevens, et.al.

It can be expected that, in the near future, developments in new special polymeric materials, an example of which is described in this paper as a nylon 12/chlorobutyl blend, will bring revolutionary changes to warfare agent resistant protective equipment with respect to decreased protection efficiency, a reduction of the burden on personnel, and a reduction in the manufacturing costs.

## **Conclusions**

1. Nylon can be blended with butyl or halogenated butyl rubber to obtain material with thermoplastic elastomer properties
2. Properties of the blends depend on nylon/rubber ratio, mixing conditions, and vulcanizing agent used
3. Mechanical properties also depend on moulding conditions and mould geometry
4. Nylon-chlorobutyl blends show significantly better resistance to hydrocarbon and chlorinated hydrocarbon solvents than can be expected from the rubber content in the blend
5. Nylon-chlorobutyl thermoplastic elastomers show excellent resistance to penetration and reemission of warfare agents