The optimal choice to protect your most important asset: Acrylonitrile Butadiene Styrene (ABS) used in the manufacture of Above-The-Neck safety equipment

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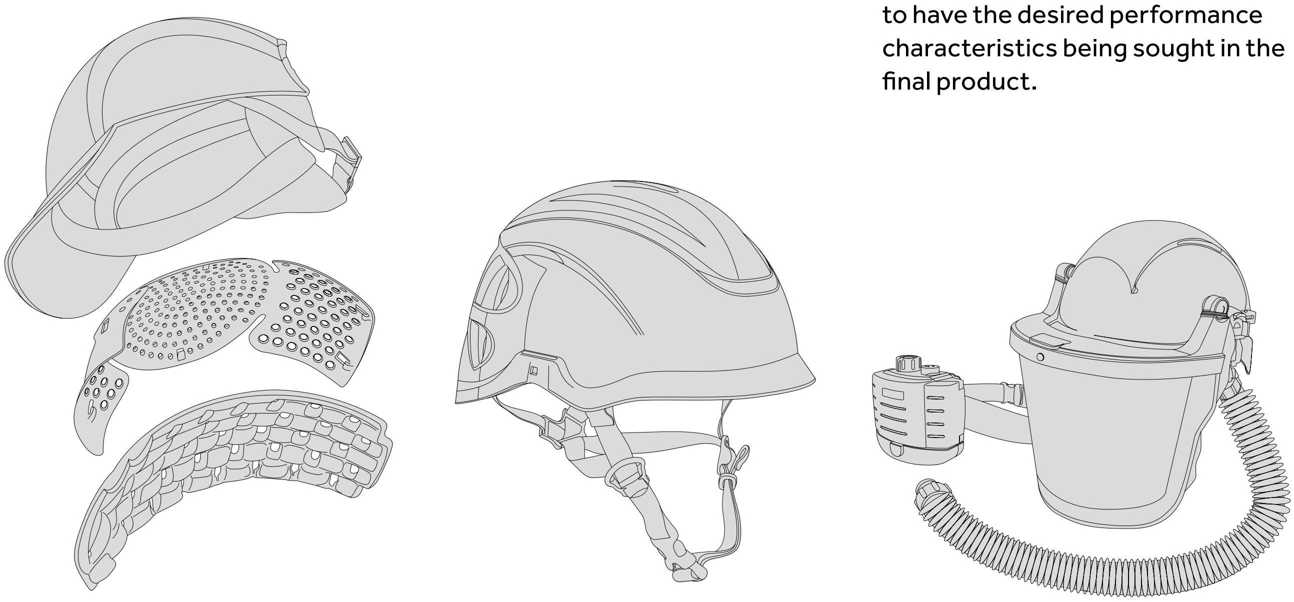
Background

The aim of this paper is to validate Centurion Safety Products rationale for transitioning their Above-The-Neck product portfolio to Acrylonitrile Butadiene Styrene (ABS).

Currently the protective shells at the heart of the head protection product range are made from either semi-crystalline High Density Polyethylene (HDPE) or amorphous Acrylonitrile Butadiene Styrene (ABS).

Entry level products are often manufactured using less expensive, easier to handle HDPE, whereas premium products are manufactured from a specific engineering grade of ABS.

Currently there is confusion within the marketplace regarding polymer choice and rationale. This is exacerbated by the fact that both the HDPE and ABS polymer families have thousands of respective grades with significantly different properties. Not all grades of ABS or HDPE can be expected to have the desired performance characteristics being sought in the final product.



Cap Protection Systems | Helmet Protection Systems | Respiratory Protection Systems

Figure 1
ABS product types

What is ABS?

ABS is a terpolymer; a long chain of units chemically bonded together, made from three distinct monomers, which is a basic unit that is repeated to form a polymer material. The chemical compound make up of ABS is illustrated in Figure 2.

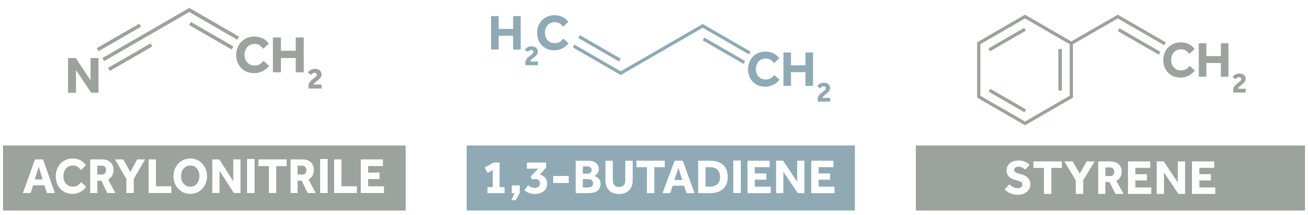


Figure 2
Chemical makeup of ABS plastic

$(C_8H_8.C_4H_6.C_3H_3N)n$, which in simplistic, generic terms means that one of each of the monomer units are bonded together in a repeating sequence.

Each monomer in the ABS earns its place in the formulation by bringing a set of performance characteristics;

1. **Acrylonitrile** brings heat and chemical resistance, tensile strength
2. **Butadiene** (rubber) brings impact strength, toughness and good performance at low temperatures
3. **Styrene** brings the glossy appearance, process-ability, and rigidity.

The particle distributions of the "Butadiene" phase is manipulated which can have a significant additional effect on material properties, i.e. increasing the size of the particles can increase toughness, increasing the polymer chain length produces a stronger material. All of these factors are balanced against the 'manufacturability' of the plastic material, i.e. materials with excessively long polymer chain lengths provide good physical properties. However these material types with long chains have very low melt flow rates, which make them difficult to melt process. The properties of the resulting polymers can be manipulated by changes in the ratios of these monomers. Typical ratios for ABS are acrylonitrile 20: butadiene 25: styrene 55%. (Figure 3)

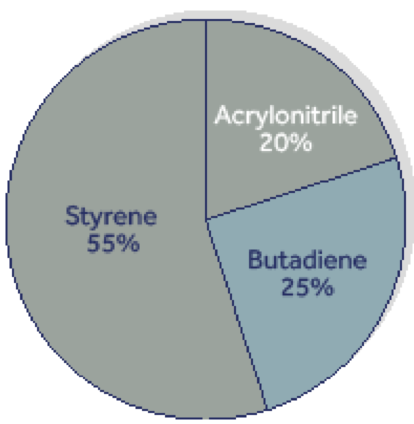


Figure 3
Molecular Mix

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How do we create products with ABS?

The processing conditions of the ABS material can be manipulated to optimise desired characteristics, i.e. moulding at high temperatures will improve gloss and heat resistance of the resulting moulded parts, whereas moulding at lower temperatures will increase the impact strength of the product.

The consistent strength of the material is a function of its amorphous (non crystalline) character post processing and the long butadiene chains criss-cross with shorter poly (styrene-co-acrylonitrile) chains. This creates a complex **'matrix'** which is strong and uniform in all directions (figure 4). This contrasts with some other polymers (such as HDPE) which tend to form a semicrystalline structure with **"chains"** that have a flat zig-zag configuration folded every 5-15 nm, which can form planar lamellar to give some mechanical strength (figure 5).

A few of these chains, for example in HDPE, tend to interconnect via an amorphous region which form spherulites, crystallised 'balls' of lamellar which can be a source of brittleness in material.

During optimised ABS melt preparation prior to injection moulding, these long butadiene chains are 'lined up' to give longitudinal strength to the resulting moulded product. The non-Newtonian or viscoelastic nature of ABS means that moulding conditions should be controlled carefully.

This is to ensure shear is kept to a minimum, to avoid excessive injection pressures during the packing phase of the moulding process and to encourage the linear formation of the butadiene chains. All of these molecular traits ensure that ABS has 'evolved' to have superlative performance characteristics, and as such, is an ideal material for structural applications where impact resistance, strength and stiffness are required.

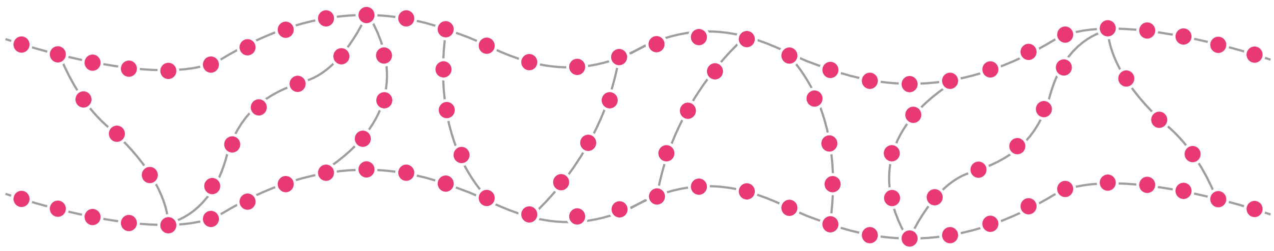

Figure 4
ABS Cross Linked Polymer (Matrix)

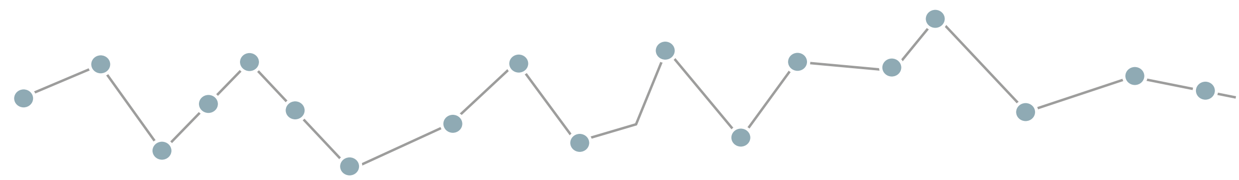

Figure 5
HDPE Linear

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Why specify ABS in Above-The-Neck protection?

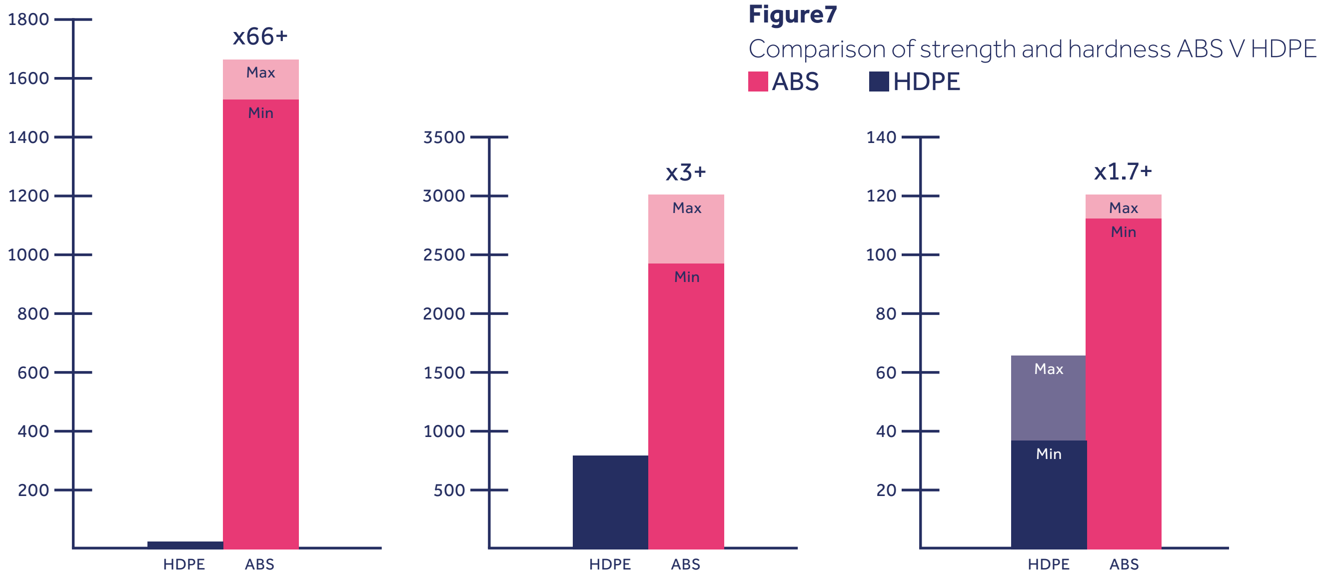
Whilst ABS has superior properties, it can be challenging to process. The high impact tolerant grades of ABS in terms of impact and strength tend to have lower melt flow indexes, ~1.8g/10mm, compared with HDPE at up to ~26g/cc via ISO 1133, which can contribute to challenges during injection moulding of this material, especially into thin wall sections of complex shapes. However, once this has been mastered, the moulded parts benefit from ABS characteristics as highlighted in Figure 6. Like many things, the challenges (in processing) are well worth the performance rewards.

Figure 6
Material comparison ABS V HDPE

Test method	Description	High Impact ABS	HDPE
Compressive modulus ASTM D695	Ability of a material to resist compressing under force	1310-1650MPa	19-25MPa
Tensile Young's modulus ISO 527	Defines the relationship between stress and strain, i.e. a rubber band will have a low modulus	2400-3000MPa	800MPa
Hardness ball indentation ISO2039-1	Defines the force required to create an indentation by 5mm steel ball	110-120N/mm	35-65N/mm

Figure7

Comparison of strength and hardness ABS V HDPE



COMPRESSIVE STRENGTH

The higher the number, the more pressure that must be applied to the material to deform it.
This measurement gives a very strong indication of the excellent performance of ABS to maintain the integrity of the shape it is moulded into. In the protective shell part of head protection, this type of characteristic would be important for product properties such as maintaining low lateral deformation under stress with time.

The higher the number, the less the material will stretch when under stress. This measurement gives a very strong indication of the excellent performance of ABS to resist structural deformation under stress. There are specific applications where a low Youngs modulus is an excellent feature (for example with a rubber band), however, in the protective shell part of head protection applications, a high reading for this characteristic would be optimal for product properties, where the integral shape of the material is critical.

TENSILE STRENGTH

The higher the number, the more force is required to produce an indentation in the test material.
This measurement gives a very strong indication of the excellent performance ABS to maintain its structural integrity when exposed to a projectile (in this case a steel ball). In the protective shell part of the head protection application, a high reading in this area is extremely beneficial as the primary focus of industrial head protection is to prevent injury to the user from objects falling from above.

HARDNESS

Figure 7, Chart 1 shows a selection of relevant material properties in the manufacture of safety equipment involved in impact protection. Considering the various environments in which the product can be used, it makes common sense to choose a material that requires a high level of force to cause an indentation, and that requires a high pressure to 'distort' the structure, i.e. Youngs and the Compressive modulus. With such good material properties, it is not surprising that many industries advocate up to 20% of recycled ABS into virgin material, without substantive loss of performance; and that ABS is the largest selling engineering thermoplastic globally.

The great dimensional stability of ABS makes it an excellent choice for a moulded material produced in high quantities; as this drives consistency of product produced.

The amorphous nature of ABS contributes to its relatively flat stress response to temperature, i.e. the material properties and therefore performance are relatively independent of temperature within a wide temperature envelope. This seems to be particularly significant for low temperatures, where ABS maintains its strength.

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CRYSTALS

It has already been noted that HDPE contains crystalline phases, and it is well reported for many materials, that defects can form at the boundary of such crystals.

Environmental stress, and cracking of HDPE, is a well-known phenomenon. This is described as an external or internal crack in a plastic, which is caused by the tensile stresses being less than its short term mechanical strength. This type of cracking typically involves brittle cracking. It has another name: ‘slow crack growth’, which is the more sinister side of this phenomenon, where cracks can appear and catastrophically impact plastic performance many months after the product was moulded. The phenomenon has been of such concern in the past that a standard test ASTM D883 was developed. There are instances involving cracking of stressed samples (stress can be caused at the interface of two components, even when they are not in use), generally (although not always) in the presence of surface wetting agents, such as alcohols, soaps and surfactant type of substances. It is postulated, in the literature, that these cracks are generally thought to initiate at microscopic imperfection/ crystal boundaries and propagate through crystalline regions of the polymer structure. Over the years, polymer chemistry has explored this issue and this work has resulted in specific grades of HDPE that are reported to have some resistance to Environmental Stress Cracking; there are however many that do not. Resistance to Environmental Stress Cracking of particular grades of HDPE have been completed using the ASTM D1693 standard and the exposure of Igepal, a surfactant, which accelerates the formation of stress cracks in these materials.

As ethylene is the most cost effective raw material associated with polymer production, it is hardly surprising that it is used to manufacture lower cost plastics such as HDPE, the lower cost making it a popular choice. Improvements in synthetic routes, using Ziegler or single site metallocene catalysts, have also improved the manufacturing controls over the polymerisation and therefore chain lengths. Choosing the grade of HDPE can be challenging, as measurement of strength and quality can be difficult due to the impact on performance of the material associated with the heterogeneous spherultic crystalline features within the material, i.e. non-uniform molecular nature of the material.

ABS in the head protection market

What might matter to end users of head protection?

a. the product 'does what it says on the tin'
b. the product lasts a 'reasonable' length of time
c. the product is comfortable to wear
d. the product is perceived as stylish on site

Both ABS and HDPE have quite different properties, that can be leveraged to produce Above-The-Neck protection products of a huge variety. There are examples of both ABS and HDPE shells out in the marketplace that comply with their performance marketing literature, so from a material perspective, it is possible to achieve what the standards are demanding.

European manufacturers tend to suggest that products will sustain performance claims for five years from manufacture. Centurion, particularly confident in its majority ABS range, typically states five years in storage plus five years in use.

It is commonly advocated by manufacturers to clean product with 'warm soapy solution'. Soaps are, by their nature, surface-active. Whether this practise increases the risk of environmental stress cracking in certain HDPE products found in the market remains to be sufficiently addressed.

The perceived comfort of the product is a function of a number of factors: weight and style/design being two of the most important. The strength and 'toughness' of ABS has already been highlighted.

These material properties allow shells of thinner wall thickness and therefore lighter weight to be moulded: affording comparative, and in specifical case studies, superior protection to HDPE shells, i.e. Centurion Concept wall thickness at the crown is 3.4 mm compared with that of an old Centurion HDPE 1100/1125 shell of 5.1 mm. Or, the other alternative, is that the wall thickness and shell design are kept the same and the performance claims of the ABS variant are superior. Centurion have a great case study whereby they produce and sell the same helmet in two different polymers i.e. Reflex (made from HDPE) and Reflex Plus (made from ABS). The performance differences are shown in Figure 8.

Figure 8
Comparison of Reflex and Reflex Plus products

Specification compliance	Reflex	Reflex Plus
Base material	HDPE	ABS
EN 397 (1 metre drop height) @ -30°C	PASS	PASS
EN 397 (1 metre drop height) @ -40°C	FAIL	PASS
ANSI type I (1.12 metre drop height) @ -30°C	FAIL	PASS
Shell weight (g)	~ 240	~ 272

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So which material would you specify to protect your most important asset?

The material properties of ABS allow for the often robust environments to which safety helmets are exposed, whilst providing a protective shell of a weight that is comfortable to wear for 8-12 hours at a time. The superior temperature range and impact performance offered by ABS, makes it a clear choice for a premium product that aims to exceed standards written a long time ago.

There clearly are moulded products for which specific HDPE grades are entirely appropriate; for example when the product is stretched or stressed in a linear fashion. However, the protective shell of a helmet can be ‘attacked’ from any angle, and therefore more robust materials are preferable. When it comes to protecting worker’s most important asset, our recommendation is to spend the little bit extra to exceed standards and maintain peace of mind for all.

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Mandy achieved a Biochemistry/Microbiology degree and used this to start her professional training as a biochemist, working in R&D for Rhone Poulenc, initially as a lab technician and then progressing to become team leader of a multidisciplinary team, whilst completing her PHD thesis with the University of Essex.

Since joining Centurion, Mandy has optimised the technical and operations departments and was instrumental in spearheading the delivery of the award-winning Nexus range.

Mandy is the current chair of TC 158, the European Technical Committee for all head protection. Focussed on individual head protection applications ranging from industrial helmets, to equestrian, to canoeing, etc.

Mandy is also the chair of PH6. This is the UK mirror group of TC158, which takes its lead from TC158 and discusses at a national (UK) level, areas that are being considered in TC158 and ensuring UK representation on the European stage.

Mandy is also a committee member of PH2, the UK committee for eye and face protection.

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