



PVC: confronting the environmental challenge

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PVC (polyvinyl chloride), when compounded with plasticisers, is a versatile soling material available in a range of hardnesses. It is relatively inexpensive, easy to mould, bonds well with PU adhesives and has a good range of general properties. Since the 1960s, PVC has been second only to vulcanised rubber in usage and is injection moulded to produce sole units for a wide range of everyday and casual footwear. It can also be blended with other polymers to provide oil resistance in industrial footwear and used for all-moulded footwear such as boots and beach shoes.

ENVIRONMENTAL PRESSURES

Starting in the 1970s, the use of several of the materials employed in the synthesis or compounding of PVC has been questioned on environmental grounds. Concerns over health and the environment led to European Directive

91/338/EEC (now incorporated into REACH Annex XVII), which restricted the use of cadmium to stabilise or colour PVC. Most PVC products on the EU market will now be free of cadmium, although it is still possible to find cadmium-containing materials sourced outside the European Union.

Vinyl chloride monomer (VCM), the chemical building block for PVC, is generally recognised as a carcinogen and, as a result, it is recommended that the production of PVC is closely monitored to ensure the safety of operatives. This also means that the quantity of the monomer residual in the final product must be carefully controlled, especially in packaging for the food industry. It has in fact been suggested that specifying food-grade PVC for use in apparel may allay concerns over the potential risks from VCM.

There are ongoing concerns about plasticisers used to impart flexibility to PVC. It has been shown that these may

be harmful to health and restrictions have been placed on the use of certain phthalate-based plasticisers. Currently, three phthalates have been restricted for all toys and childcare articles and a further three are restricted in toys and childcare articles intended to be mouthed. While footwear is not explicitly included in these requirements, several retailers have adopted a precautionary stance and are removing these phthalates from their children's products. Under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), certain phthalate plasticisers will be prohibited from use in the EU/EEA from 2015. This will include some of those used in footwear.

PERCEIVED RISKS FROM WASTE

Some environmentalists object to PVC merely because it contains the chemical element chlorine. This view stems from the knowledge that certain

man-made substances containing chlorine are toxic and persist in the environment, as was discovered with some pesticides. There is concern that low levels of highly toxic dioxins are generated when waste containing chlorinated materials, especially packaging, is burned. However, dioxins can arise from many materials and can be formed irrespective of whether PVC is present or not. Moreover, properly controlled incinerators working at high temperature reduce the risks of dioxin being formed. This negative view of certain chlorine-containing materials, such as PVC, has to be countered by the benefits of others, most notably sodium chloride (common salt). Indeed, chlorine itself is widely used to kill harmful organisms in water.

POSITIVE ASPECTS

PVC does however have positive attributes to offset this negative image.

- Its manufacture requires less raw materials and fuel than other plastics.
- The chlorine used is generated as a by-product in the manufacture of alkalis (such as sodium hydroxide) from salt.
- It is the only major use of chlorine which leaves it in a more inert form than the salt from which it came.
- It is recyclable and easy to separate from mixed plastics waste, though separation is more difficult with composite or bonded PVC materials as found in footwear.

COMPOUNDING AFFECTS PROPERTIES

PVC polymer is hard and rigid so it must be compounded with plasticisers to produce a softer and more flexible material at ordinary temperatures. Most are high boiling-point liquids whose molecules penetrate between and lubricate the PVC polymer chains. This allows the chains to slip over each other more easily, so enabling the material to be flexed and then slip back into place as it is straightened again. They typically comprise 35-50% by weight of a PVC soling compound and are generally phthalate esters, sometimes extended with a proportion of secondary plasticisers such as chlorinated paraffins. However, C10-C13 chloroalkanes have been identified as SVHCs (substances of very high concern) under the REACH regulation.

Other compounding ingredients include stabilisers, processing aids, pigments and fillers, together with blowing agents for cellular compounds if required. These are chemicals which mop up damaging degradation products such as hydrogen chloride, caused by heat when the PVC is being compounded, processed and moulded. They also provide longer-term protection in service against the effects of heat, light and oxidation.

Fillers are mainly used to add bulk. They are often relatively cheap substances which can have the side effect of hardening the material, thus countering the softening effect of plasticisers. The range of minerals employed is similar to those used in compounding rubber although they do not usually have the reinforcing effect in PVC that some do in the latter. Examples include calcium carbonate, silica, clays and carbon black.

The density of the final compound is therefore reduced by plasticisers and increased by fillers. PVC resin itself has a specific gravity of 1.4 and the range encountered in compounded solid (compact) PVC solings materials is



PVC remains popular not only for low cost unit soles but also for all-moulded boots and sandals.

mainly between 1.15 and 1.35, with the lowest density ones virtually unfilled. Modern blown PVCs with a uniform microcellular structure do however offer specific gravities down to around 0.75.

PVC blends also contain one or more secondary polymers such as nitrile rubber and polyurethane at up to 30 parts per hundred of PVC polymer. PVC/nitrile blends generally have higher resistance to petroleum oils than PVC/polyurethane blends but a lower resistance to animal fats so, at times, blends of all three are used.

The amount of plasticiser contained in a PVC or PVC blend compound controls not only its hardness but most physical and wear properties as well. Its type determines specialist properties such as low temperature and oil resistance. Resistance to wear, flex cracking and slip are all dependent on hardness and, therefore, on plasticiser content. Soft materials perform the best and the typical hardness range is 50-80 IRHD (international rubber hardness degrees).

Adhesion performance is influenced more by the type than the quantity of plasticiser. Some plasticisers migrate into adhesive films more rapidly than others, but generally there are few adhesion problems with PVC soles provided the proper preparation is given (such as wiping with MEK solvent), and a polyurethane-based adhesive is used.

MIXING AND PROCESSING

PVC and other compounding ingredients are usually blended together in a heated internal mixer such as a 'Banbury'. This comprises a closed chamber within which a rotor revolves at speeds of 20-100 rpm. This process is followed by further mixing in an extruder/pelletiser. Alternatively, it can be done in what is known as a 'twin screw compounding extruder' where the pre-mix is fed in at one end and delivered as a complete compound at the other in the form of small granules.

Injection moulding temperatures for PVC are typically in the range of 160-180°C whilst the mould is kept at 30-50°C by water cooling. This allows a short in-mould time of one to two minutes and a rapid and economical rate of production. Too low a temperature will cause 'cold flow', visually poor mouldings and performance problems such as delamination. Overheating must also be avoided to prevent degradation. Up to 10 percent of the weight of the moulded material can comprise sprues and similar waste. This can be granulated and blended with virgin polymer without causing problems, so eliminating it as sheer waste. The proportion thus treated must nevertheless be limited as repeated heating can cause degradation in PVC.

ADDITIONAL PROPERTIES

Plasticised PVC is suitable for unit soles, direct moulded-on soles and all-

moulded footwear. It is tough and durable in most respects, although it is relatively easily cut and sensitive to temperature, which limits its usage.

It softens with heating and stiffens with cooling, so is prone to flex crack in extremes of cold. It will also melt in extremes of heat that might be found in certain industrial situations such as foundries and the laying down of tarmac roads. As stated earlier, the softer grades are the most abrasion, flex crack and, subject to the correct tread pattern being used for wet conditions, slip resistant. The hardness spectrum among sole materials in general is 30-95 IRHD; PVC is generally best used between 50-80 IRHD.

ALTERNATIVES TO PVC

Alternatives are available for any company seeking to reduce its usage of PVC solings. The closest, from a manufacturing perspective at least, are TR (thermoplastic rubber) and TPU (thermoplastic polyurethane). While there is no single material capable of doing everything PVC does, alternatives can be chosen according to need and depending on which properties are seen to be the most important.

TR has generally better slip and cold flexing resistance than PVC, but poorer wear resistance. Particular care is also needed with the adhesive bonding process when sole attaching. Grades of TR with better wearing properties have however now been developed.

TPU possesses good properties. While it was once confined to hard solings such as in sports boots, it is now available in softer, rubbery grades and also microcellular versions. It is also much more expensive than PVC.

TPO (thermoplastic polyolefin) materials can be used for all-moulded boots and leisure footwear, but adhesion difficulties have limited their use in everyday footwear.

TR - ADVANTAGES AND DISADVANTAGES

This is a good alternative material for sole units, sharing the economy of PVC and benefiting from more rubbery aesthetics, better grip and lower density. However, the weight advantage may be offset or lost by the need to increase the thickness of certain areas of the sole to ensure adequate durability and structural stability. For example, the wearing thickness needs to be 1mm greater than for PVC and the internal ribbing/lightener bars by up to 2mm. TR is stiffer than PVC, even though it is often softer. It is usually also less abrasion resistant making it generally unsuitable for heavy-duty wear. On the other hand, it does have better cold flex crack resistance.

Greater care is needed with the adhesion process than with PVC, particularly where solvent-based primers and adhesives are used due to its inherent sensitivity to solvent. Halogenation priming, gentle application of primers and adhesives, and thorough drying of both are all essential.

TR is a difficult material to direct injection mould on to leather uppers without special adhesives and is, therefore, rarely practised. Like PVC, it can be blown (made cellular), but not quite to the same degree due to its lower wear resistance.

TPU - ADVANTAGES AND DISADVANTAGES

TPU is generally regarded as a premium quality material and its price reflects this, being relatively expensive. This is its chief disadvantage as otherwise its performance-related physical properties are generally very good. It is suitable for unit soles, and is available in a range of hardnesses with good aesthetics and similar or slightly



PVC compound is supplied in granular form.

TR and TPU compared

	TR		TPU	
	Compact	Cellular	Compact	Cellular
Form	Direct moulded and unit soles		Unit soles and wear surface of dual density soles	Unit soles
Density range	0.9 - 1.1	0.8 - 1.0	1.15 - 1.25	0.7 - 1.0
Wear resistance*	Moderate - good	Fair - good	Excellent	Good - excellent
Hardness**	Soft - hard	Soft	Medium - very hard	Medium
Crack resistance***	Good - best at low temperature		Good including harder grades	Good
Slip resistance	Potentially very good but limited tread life - wet grip can be low at heel on soft compounds		Potentially good on softer grades with long tread life Hard grades can be slippery	Potentially good with long tread life
Other properties	Sensitive to oils or solvents and stiff relative to hardness High friction can melt surface in vigorous use		Oil-resistant versions available	Local density depends on proximity to injection point
Other comments	Cheaper lighter alternative to vulcanised rubber but not tough enough for heavy duty use and prone to flow lines - thin coring ribs can collapse		Expensive but performance and appearance very good - can be blended in any ratio with PVC	High cost only partly offset by expansion to medium density.
Applications	Casual and fashion footwear, children's shoes, winter boots, slippers		Women's top-pieces (hard grades), industrial and premium casual shoes (soft grades)	Premium casual shoes

* Assessment given is based on resistance to loss of substance by normal abrasive wear.

** The following arbitrary ranges have been used: Very soft (<45 IRHD); Soft (45 - 54 IRHD); Medium (55 - 74 IRHD); Moderately hard (75 - 84 IRHD); Hard (85 - 95 IRHD); Very hard (>95 IRHD). IRHD—International Rubber Hardness Degrees and similar to Shore A.

*** Purely mechanical forms of cracking are considered here, not cracking due to chemical attack.

lower density compared to PVC.

Wear resistance and flexing endurance are usually good or excellent and attractive cellular versions, which save weight and cost, are also available. It is suitable for heavy-duty footwear such as workboots and hiking boots, and is usually oil resistant. However, its slip resistance is only moderate. Unlike PVC or TR, it is quite commonly used as the wearing surface on dual-density soles, usually in conjunction with a lightweight microcellular PU midsole. This mitigates the high cost factor while taking advantage of its tough nature.

One drawback is that TPU, if polyester-based, is potentially vulnerable to hydrolysis in exactly the same way as pure polyester PU. This breakdown is due to attack by moisture and humidity, promoted by warmth, over a period of several years, depending on the storage and service climate. It is a point that must be watched.

THE FUTURE FOR PVC

The use of PVC remains widespread and highly significant. At present, there is no substantiated environmental



Injection moulding PVC is both rapid and economical.

reason why its use for footwear solings should not continue as these are relatively longer-life products which are stable on disposal. When taking into account cost, ease of use and performance compared to the

alternatives currently available, PVC is in fact hard to beat. While its long-term future—like that of anything else in life—cannot be guaranteed, there is still some way to go before this ubiquitous soling material can be written off. 