Raising the softening point of PVC

Poly acrylonitrile-styrene-acrylate (ASA) is currently being developed as a Vicat/HDT modifier for PVC. Dr. Chris DeArmitt of BASF AG describes some of the advantages that ASA can offer and outlines work currently underway.

PVC is the world's third most important thermoplastic in terms of volume sales. The reasons for the success of PVC include its versatility, extraordinary stability to weathering and competitive price. Addition of plasticizer allows hardness and flexibility to be tuned over a wide range. Rigid PVC contains no plasticizer and is used in a wide range of applications including pipes, gutters and window profiles.

Polymers are readily attacked by UV light and must be stabilized in order to allow them to be used in outdoor applications. Even when property-stabilized, most polymers still suffer from colour change and a loss of properties, in particular gloss, strength and elongation to break. The exceptional durability of PVC has ensured it an important position in the building and construction industry, for example where it accounts for half of all plastic material used.

Despite the many positive attributes of PVC, there are some limitations. One problem is that coloured PVC can discolour after prolonged periods outdoors in sunlight. Another is that it has a relatively low softening point so that it cannot be used in some applications where high temperatures would cause softening and distortion. Fortunately, PVC can be blended with a wide range of additives to improve stability, cost, stiffness and softening point. These include modifiers that can raise the softening point of PVC, as defined by Vicat or heat distortion temperature (HDT).

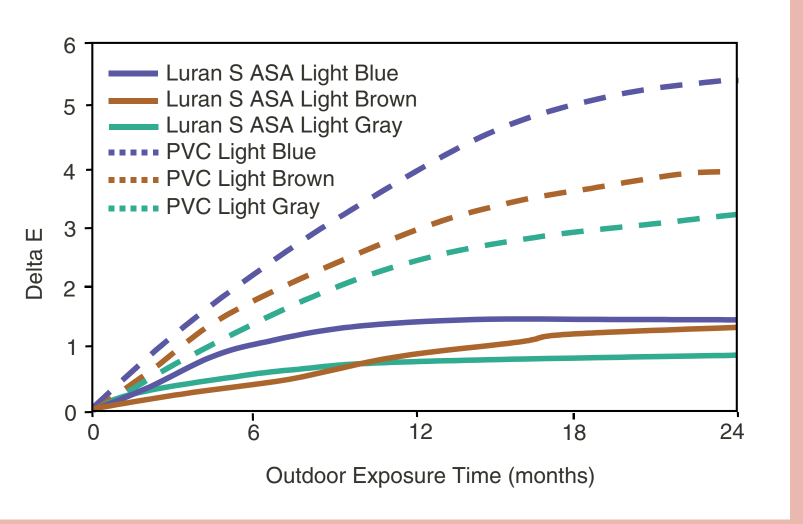

Figure 1: Outdoor ageing of PVC and ASA in Ohio, USA.

Existing solutions

Extruded profiles of PVC are extensively used for window frames and conservatories. These have gained popularity in the US and Europe alike, but there are some limitations. One chief concern is that as one moves closer to the equator, temperatures increase and it is no longer advisable to use PVC windows due to its relatively low softening point. Even in milder climates, PVC is not used in darker colours because such colours increase heating under sunlight so that the PVC may soften. A recent trend is the environmentally-driven move from lead and tin based stabilizers for PVC to calcium-zinc variants. These new additives can lead to lower softening points for PVC compared to the previously used stabilizers.

There are various ways to increase the HDT of PVC. One option is to add fillers but this is rather ineffective as fillers can only raise the HDT to approach the glass transition temperature (Tg) of amorphous polymers like PVC. A more effective approach is to blend the PVC with another polymer having a higher softening point. This other polymer must have a similar polarity (solubility parameter) to the PVC in order to get a good mixture and mechanical properties. This requirement makes the range of suitable polymers very limited. Poly(α-methylstyrene-co-acrylonitrile) can be added to make a blend with PVC. It has a Tg higher than that of PVC and is compatible with PVC in the sense that the two polymers blend without deterioration of mechanical properties. The drawback of this technology is that it increases the HDT but tends to embrittle the PVC as shown by a loss of impact strength. Rubber can be added to regain the impact strength but this adds unwanted complexity in terms of feeding, storage and added investment costs.

High heat ABS can also be blended with PVC to give an increase in HDT without sacrificing impact strength. High heat ABS is a copolymer of styrene, acrylonitrile and α-methylstyrene that contains butadiene rubber particles. This is a good approach for indoor applications, but the butadiene rubber is unstable to heat and UV light, gradually losing its elastomeric performance and tending to yellow over time.

Heat deflection enhancer

The ideal solution would be an additive that has excellent UV stability and can act like ABS in elevating HDT without a sacrifice of impact strength. It is not easy to find a polymer with sufficient UV resistance to match PVC in outdoor applications. Poly acrylonitrile-styrene-acrylate (ASA) is one such polymer. ASA has a proven track record and has been used outdoors for many years.

ASA is similar to ABS but rather than the UV sensitive butadiene rubber contained in ABS, ASA contains acrylate rubber to provide the impact strength. Acrylates are exceptionally resistant to degradation and yellowing.

The HDT (at 1.8 MPa) of a typical ASA grade (around 90°C) is above that of PVC (about 70°C) and so the blend has a higher softening point than PVC alone. Because the ASA contains impact modifier in the form of rubber particles (see Figure 2), the HDT can be increased without sacrificing the impact strength of the PVC.

Furthermore the enhancement of HDT is linear compared with the amount of ASA added, so it is straightforward to add just the right amount without devoting a lot of energy to testing different formulations. Different grades of PVC vary in their HDT and the same is true for ASA. The effect of the ASA will be most pronounced when the HDT of the PVC is low and that of the ASA is as high as possible. There is a special high-heat version of ASA where copolymerization with α-methylstyrene monomer boosts the Vicat/HDT to 105°C. This grade is available now and it is possible to improve the HDT even further if required.

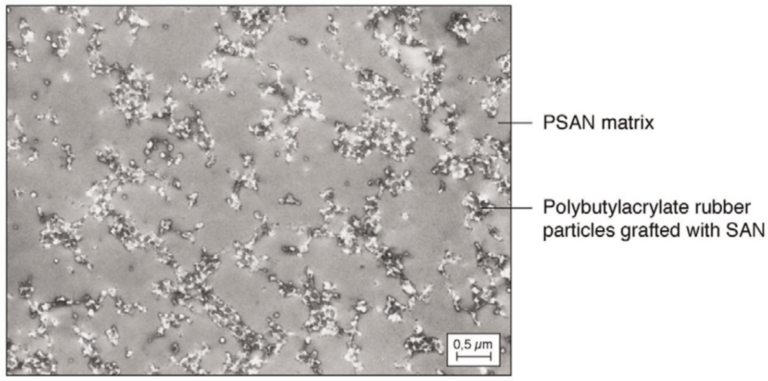

Figure 2:TEM of an ASA containing an emulsion produced impact modifier.

The ASA has been tested by several compounders in Europe and the USA Work is ongoing with several companies to develop this solution. The acceptance of ASA with PVC has been good because it is long established that ASA has excellent UV stability, in fact it is often used as a cap layer on PVC to protect coloured PVC from discolouration. When used as a cap layer it is vital that processing scrap can be re-ground and re-extruded. This has been done routinely for many years with no problems due to the excellent miscibility of ASA and PVC.

The use of high-heat ASA as an additive for PVC is taking off rapidly. Indeed through its use some companies are now finding it possible to enter new markets.

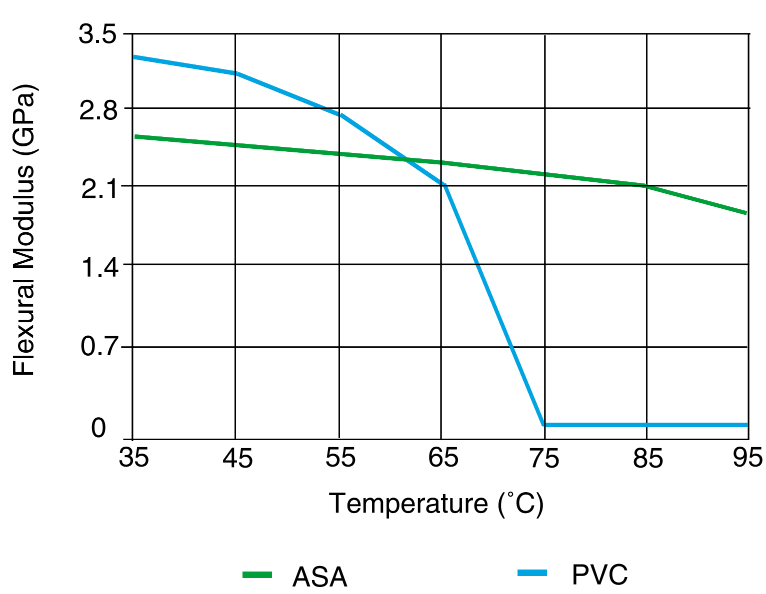

Figure 3: Stiffness of a standard ASA compared to rigid PVC at elevated temperatures.

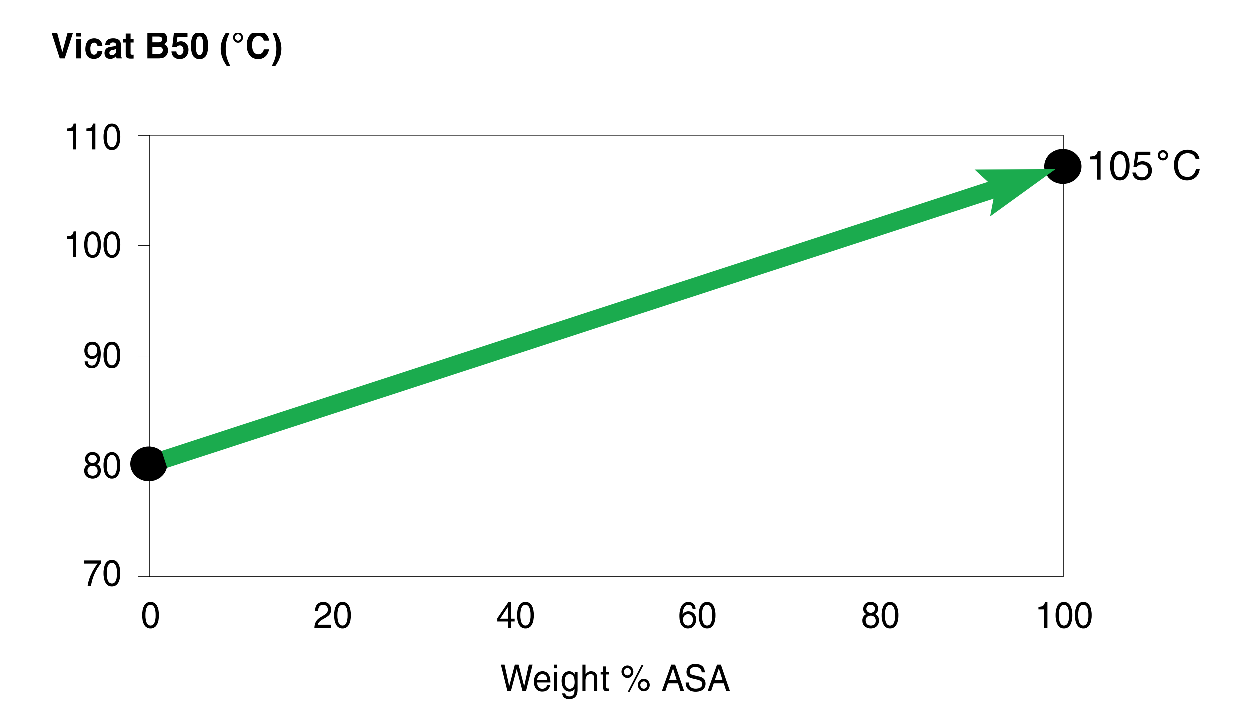

Figure 4:ASA increases the softening point of PVC.

Others find that they need a boost in HDT due to the ongoing changeover to calcium-zinc based stabilization packages. Indeed, other companies have found that they can remove reinforcements such as metal inserts, which avoids complexity and reduces system costs.

As well as using the ASA in a blend with PVC, another approach is to co-extrude the ASA and PVC in such a way that only the ASA is exposed to the high temperatures. For example, it is possible to co-extrude a window profile where the outdoor side is ASA. This gives two advantages; the added stability of coloured ASA and the enhanced stability to warpage and distortion at high temperatures. Normally, only a very thin layer of ASA is used to provide the colour stability. When the added high temperature resistance is needed then a thicker layer of ASA is used to mechanically reinforce the PVC.

The high-heat grade Luran® S 778TE from BASF is already available and is being used in its current form. Luran® S 778TE is presently supplied in pellet form because that is the form required for the majority of uses for neat ASA. However, the PVC industry generally prefers a powder form and work is being undertaken to investigate that possibility.

Conclusion

PVC is a widely used polymer that has an attractive property - price balance. Furthermore, it may be readily tuned using a variety of additives to meet the requirements in a given application. In some instances the softening point of rigid PVC is too low to allow its use, or if it is used it may need to be reinforced using a rigid insert.

Like PVC, ASA has a long-established reputation as a polymer well-suited to outdoor use. In fact, ASA is often used as a cap layer for PVC to prevent colour shift, especially yellowing, on exposure to sunlight. From this application as a cap layer, it has already been established that the ASA is compatible with PVC and can be reground and recycled with PVC without difficulty.

It has now been shown that ASA can also be blended with PVC resulting in an increase in HDT. The HDT of PVC is approximately 70°C while ASA is up to 105°C. Blends have intermediate HDT values and the relationship is linear to the amount of ASA added. A high-heat ASA such as Luran® S 778TE has an HDT of 105°C and is therefore very effective as an additive to enhance the HDT of rigid PVC. This solution has already been implemented by some companies and work is ongoing with several compounders requiring such an additive.

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