Multilayer Structures

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Introduction

Multilayer structures are becoming common in many domestic plastic products but in many cases the end user is unaware of the complexity of the product they are using. One example where the multi polymer structure is obvious is the tooth brush where the strong main body has an inlay of soft touch polymer in contrasting colour. On the other hand, how many people are aware that the squeezy bottle for their tomato sauce bottle contains at least 5 layers. Other common multilayer products, but normally out of sight, are central heating pipes with can have either a base of PB or crosslinked PE and an EVOH oxygen barrier in the centre of the structure or the plastic fuel lines in cars where there as many different structures as there are car manufacturers.

All the above examples are from an end product enhancing basis but there are other reasons for multilayer structures such as cost savings by using internal recycled or scrap polymers and light weighting by using foamed cores.

In many multilayer structures the additional barrier polymer is of a different type to the main structure and as such will not stick to the base polymer in the solid state - in the melt phase there is a natural adhesion. A typical example is for the tomato sauce bottle where the base polymer is a PP and the barrier is an EVOH. To get the required solid phase adhesion and avoid peeling and delamination a maleic anhydride grafted PP adhesive is used on either side of the EVOH layer. To give some idea of the relative thickness of the layers for the tomato sauce bottle a typical PP based structure will be in volume ratio: Inner 10%, Regrind 45%, Inner Adhesive 2.5%, EVOH 5%, Outer Adhesive 2.5%, Outer 35%. Note that the regrind layer is high for this structure because the forming process is blow moulding which has extra material in the top and tail and must be recycled to provide economy for the process. Note also that the regrind also contains EVOH so the true usage will be higher than that just for the barrier properties.

One particular product

To look at just one multilayer product in more detail, the central heating pipe in Britain and Europe uses the flexibility asset of the plastic pipe to reduce installation times and also allow the benefit of long unbroken underfloor runs. See picture below:
In the current absence of international pipe standards there are several different structures and sizes - typical British and European styles are illustrated below together with an example of a typical automotive fuel line pipe.

There was a conception in mainland Europe that only the inner layer of a multilayer structure can be accepted as a pressure retaining part and hence for the oxygen barrier protection this must be on the outer surface of the pipe. This is in itself is not the best place to co-extrude very thin layers and coupled with this is the requirement that all the layers must be accommodated in the thickness tolerance. On the other hand, the barrier resistance of the EVOH type material is a function of the relative humidity and placing the layer close to the inner surface will reduce its effectiveness. To give some idea of this, for a typical EVOH copolymer with 30% ethylene there is a reduction factor of 1000 for the oxygen permeability between the values at 0% and 100% relative humidity. Another factor which influences the position of the barrier layer is the possibility of weakening from the fittings where in many cases there is a claw mechanism which cuts into the pipe and which, if cutting through the barrier layer, could reduce the effective tensile strength of the pipe. Each supplier has its own brand of fixings and there are many layer configurations in existence.
The base polymer for central heating pipes can be either PB or PE although some PP copolymers are now being used. Within the PE structures there are two different types, a high molecular grade and medium density grades. Both require cross linking to achieve the desired mechanical properties. For the high molecular grade radiation cross linking is the preferred route, a facility which is only available at a few sites in mainland Europe. For the medium density grades the predominant cross-linking mechanism is through a silane catalyst process which is mixed in as a masterbatch. The process is activated by temperature and care must be taken in the extrusion process not to have slow moving/stagnant areas in the flow path. The actual cross linking is then done by immersing the finished pipe in hot steam for an extended time. Whilst this may make the PB look more attractive there is another phenomenon for this polymer in that there is a post extrusion crystallisation which can take up to 14 days and in doing so reduces the OD and wall thickness of the pipe. With this process, the pipe is retained on large drums during the crystallisation which also adds to the cost of an overall line.

Multilayer die designs for the PB and medium density grade PEs can be similar but those for the high molecular weight grades are usually different due to the very high viscosities of the material which can make the spiral mandrel type die unsuitable. For small pipes, less than 60mm OD, it has also been found difficult for the spiral mandrel to be efficient and a form of cross fed ring distribution system shown below has been shown to be ideal. A typical 5-layer system is show below which uses only 3 extruders. The main inner and outer layers are split into two tubular flow channels in the feed block and then through tubes into the inner and outer layers. The adhesive layer is also split into two layers in the side fed feed block.

The calibration and cooling of the tube from the diehead is similar for both mono and multilayer systems but one aspect that must be considered is the quality control of the
product. As the barrier layer is only of the order of 0.1mm thick an absence of the vital performance layer may not be picked up by normal wall thickness measuring equipment and a more positive control of the extrusion system must be made to ensure continuity. There are also the different reflective properties of the multilayer polymers when using ultra sonic measuring devices and careful calibration of the unit is required.

So, the design and production of multi-layered products is not a straight forward process but good consistent results can be achieved by considering of all the aspects of polymers and polymer processing.

Contact the author if you would like more information.

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