New developments in polyethylene materials for geomembrane applications

KumHoong Lou, Amos Tay & CheeSiong Lim
Borouge Pte Ltd, Singapore

ABSTRACT: Polyethylene (PE) geomembrane comprising of LLDPE and HDPE are the most popular types of materials for geomembrane in use today. A combination of ease of processability, durability, excellent mechanical properties, economical cost and excellent resistance to a wide range of chemicals gives PE geomembrane a distinct advantage over other types of materials in this application. End users from a wide range of industries have come to depend on the reliability of PE geomembrane in many demanding applications. The PE materials currently in use have been developed to successfully meet today's needs. As the environmental awareness increases in line with the performance expectations from end users, a new range of materials might be needed to meet such challenges. This paper will demonstrate how recent developments in the field of PE materials will help expand the performance envelope of the next generation of geomembrane and also highlight key material properties that engineers and designers can focus on to take advantage of the advancement in material technology.

Keywords: PE materials development, bimodal LLDPE, bimodal MDPE, enhanced stress cracking resistance, improved processability

1 INTRODUCTION

Polyethylene (PE) geomembrane comprising of linear-low density PE (LLDPE) and high density PE (HDPE) are the most popular types of geomembrane used today. The PE resins that are currently supplied for geomembrane production have been designed to give converters sufficient ease in processability at a reasonable cost and end users a geomembrane that is durable, easy to install and will function as designed over the expected lifetime. As the environmental demands becomes more stringent, these geomembranes will need to meet even higher levels of performance.

1.1 *Current PE materials used in geomembrane production*

Table 1 below broadly summarises the PE resins in use today with some of their key properties.

Table 1. Categories of PE resins used for geomembranes today.

Polymer type	Density (g/cm^3)	MFR	HLMI	Comments
LLDPE	0.923	0.25	22	Bimodal Process, 1-Butene as comonomer, for blown process
	0.922	-	15	Unimodal Process, 1-Hexene as comonomer, for blown process
	0.920	0.5	-	Unimodal Process using single-site catalyst, 1-Hexene as comonomer, for blown and cast process
MDPE*	0.938	0.12	13	Bimodal Process, 1-Butene as comonomer, for blown

				process
	0.937	-	12	Unimodal Process, 1-Hexene as comonomer, for blown process
	0.937	-	21	Unimodal Process, 1-Hexene as comonomer, for cast process
	0.940	0.25	-	Unimodal Process using single site catalyst, 1-Hexene as comonomer, for blown and cast process

* Refers to the resin and not the final geomembrane (sheet).

1.2 *Historical PE materials trends*

Figure 1 below shows the evolution of PE materials used in the manufacture of geomembranes. HDPE resin was most commonly used in the 1970s as these gave the final product good chemical resistance. Towards the 1980s, to overcome the stress related failures which was quite common, manufacturers switched to medium density PE materials (MDPE) which used 1-Hexene (C6) as comonomer. When the MDPE resin is mixed with carbon black masterbatch (CBMB) it results in a geomembrane that has a density in the HDPE range. Using the MDPE resin gave the HD geomembranes much improved stress cracking performance. Around the same period, LLDPE with C6 comonomer was introduced to fill the gap of a PE geomembrane that is more flexible compared to HDPE geomembrane but with slightly lower chemical, tear and UV resistance. LLDPE was also easier to weld. In the 1990s, the bimodal polymerisation technology was introduced that allowed LLDPE and MDPE resin with 1-Butene (C4) comonomer to be successfully used for geomembranes as well. The bimodal C4 LLDPE and MDPE resin have better balance of processability and higher mechanicals but are generally available at lower cost. Up until this period, polymerisation was achieved through the use of the Ziegler-Natta catalysts. By the early 2000s, the plastic industry perfected the economic polymerisation using metallocene catalysts. Also known as single-site catalysts, it allowed the creation of very pure, and consistent PE resins with excellent mechanical and sealing properties. This allowed metallocene LLDPE (mLLDPE) with C6 and 1-Octene (C8) comonomer to be introduced with far superior mechanical properties. Later, towards 2010, metallocene MDPE (mMDPE) with C6 and C8 comonomer were also introduced.

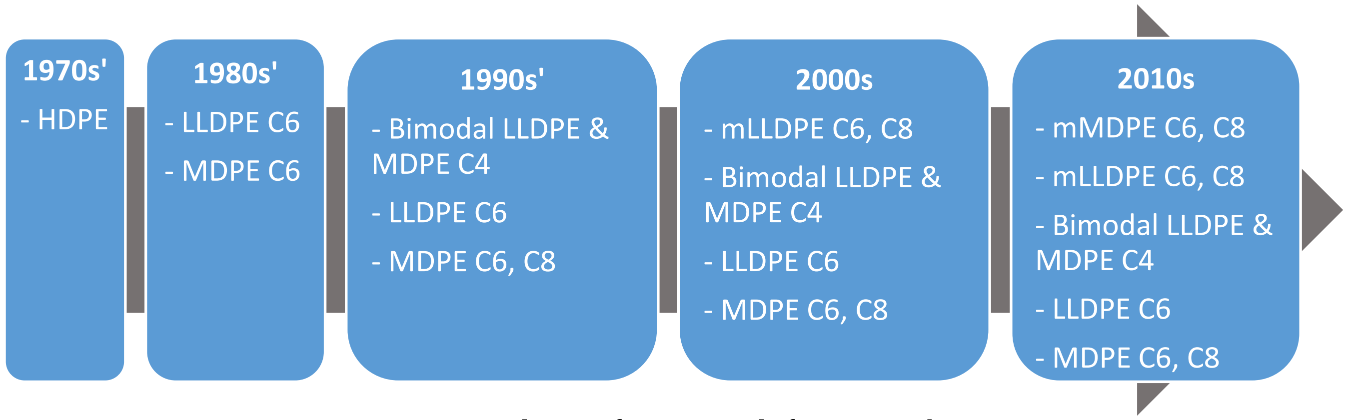

Figure 1. Evolution of PE materials for geomembrane

1.3 *Key PE material properties*

It is well-established in the geomembrane industry that the three most critical PE material properties are melt flow rate (MFR), density and resistance to environmental stress cracking (ESCR). A high MFR makes processing the PE material easier (lower motor load on the machine), but a low MFR is needed to ensure good melt stability as well as good mechanical properties. Hence a balance needs to be struck. Many resin producers, however, have difficulties to produce PE materials (especially LLDPE) with a low enough MFR for geomembrane application due to the polymer design limitations of the technology. The density of the PE material directly affects the tensile properties of the geomembrane and to a large degree its ease in weldability. The puncture resistance of a PE geomembrane is related to its MFR and the type of comonomer used. The ESCR properties of a PE grade will affect the lifetime and durability of a geomembrane in operation. A PE with higher ESCR will be less prone to developing cracks and tears over its operational lifetime from any scratch, folds or point loads.

The suppliers of PE materials have different methods to control/ influence these key properties. MFR is controlled by the ratio of hydrogen to ethylene as well as the residence time in the polymerisation process. Density is mainly controlled by the ratio of comonomer (either 1-butene, 1-hexene or 1-octene) to the main monomer (ethylene) during polymerisation. ESCR is a resultant property of MFR and density, as well as the type of comonomer used. A higher carbon number (C8 versus C6) of the comonomer leads to better ESCR. The higher the carbon number of the comonomer, the longer the side chains and hence the higher the number of tie molecules available to connect the main polymer chains together. Increasing the connections between the main polymer chains improves the polymer's ESCR. Longer side chains reduce the packing efficiency of the polymer chains which reduces the overall material density. Hence lower densities and MFR imply better ESCR. All these parameters in play combine to give the PE materials its processability, weldability, and mechanical properties. But trying to achieve an optimum balance is subjected to the limitations, if any, of the polymerisation technology.

2 RECENT MATERIAL DEVELOPMENTS

The following are newer or less commonly used PE materials that are just recently available and have been originally developed for other applications such as packaging and building solutions but can be adapted for the geomembrane industry to meet more demanding requirements.

2.1 *Bimodal LLDPE/MDPE*

The use of bimodal LLDPE with high molecular weight (low MFR) and very broad molecular weight distribution created from a dual reactor polymerisation system is still quite new in geomembranes. The majority of LLDPE material that is used in the production of geomembrane today are from the unimodal process that have a narrower molecular weight distribution. Figure 2 below shows a comparison between the commonly used unimodal C4 LLDPE compared to the bimodal C4 LLDPE.

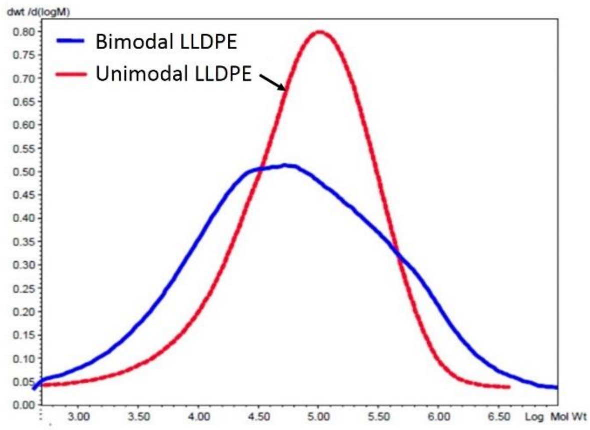

Figure 2. Comparison between the molecular weight distribution between typical unimodal and bimodal LLDPE

The presence of a higher content of low molecular weight fraction in the bimodal resin results in the polymer having good extrudability (high shear thinning index) which means it will be easy to process. The low molecular weight fraction improves the overall processability because they act like lubricants during processing. Having more of the high molecular weight fraction gives the bimodal product better mechanical and ESCR properties compared to the unimodal material. Figure 3 below shows the comparison of the viscosity curves between two bimodal C4 LLDPE with different MFRs, a unimodal C8 LLDPE and two low-density PE (LDPE) with different MFRs.

Viscosity curves gives an indication of the flow properties of the material at different shear rates. Since the primary method of processing PE materials still involve melting and conveying the resin via screw in the barrel of an extruder, these viscosity curves allows us to compare how different types of PE materials behave in the same extruder. As shown in Figure 3, the FB2230 material, which represents a bimodal C4 LLDPE ($MFR_{2.16}$ = 0.25 g/10min), displays the best balance of high melt viscosity at zero shear but also comparable viscosity of a unimodal C8 LLDPE (very commonly used in the production of geomembrane) at high shear rates.

The region with high shear rate represents the material being processed in the extruder through the shear generated by the screw. The part of the curve closest to zero shear represents the point when the melt exits the die. The presence of a high molecular weight fraction in a bimodal C4 LLDPE results in high melt viscosity even at zero shear, enabling a very stable melt when exiting the die. However, despite having a much lower MFR than a typical unimodal C8 LLDPE, the bimodal C4 LLDPE is as easy to be processed as the unimodal C8 LLDPE because of a higher content of low molecular weight fraction in the bimodal material. Figure 3 also confirms a well described effect of MFR on processability and melt stability. Higher MFR helps in processability but reduces overall melt stability, as can be seen from the two LDPE grades with different MFR.

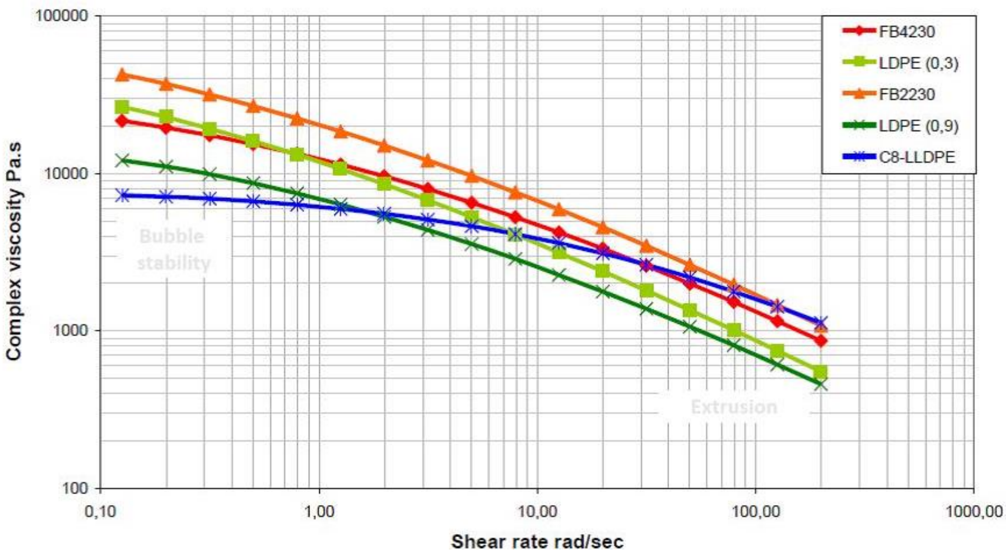

Figure 3. Viscosity comparison between unimodal C8 LLDPE, bimodal C4 LLDPE and other PE materials

The bimodal C4 LLDPE has also been tested to meet the specifications of LLDPE geomembrane according to the GRI GM 17 specification as shown in Table 2 below.

Table 2. Tensile and puncture resistance of the bimodal C4 LLDPE

Property	Test Method	Specifications – 1 mm GRI GM17	Bimodal C4 LLDPE	
			MD	TD
Tensile properties: break strength – N/mm break elongation – %	ASTM D 6693 Type IV	27 800	35 1043	33 888
Puncture Resistance - N	ASTM D 4833	250	369	

Table 3 below compares the stress cracking resistance between bimodal C4 HDPE and unimodal C6 HDPE geomembrane.

Table 3. Stress cracking resistance test according to NCTL* per GRI GM13

Property	Test Method	Specification GRI GM13	Bimodal C4 HDPE geomembrane	Reference unimodal C6 HDPE geomembrane
Stress Crack Resistance	ASTM D5397	500 hr	>1500	649

*Notched Constant Tensile Load

Table 4 below shows that a bimodal C6 MDPE film has significantly improved mechanical properties compared to a bimodal C4 MDPE although both have similar processing behaviour. A bimodal C6 MDPE demonstrates higher resistance to penetration as shown via the dart impact strength and also the total penetration energy test versus a bimodal C4 MDPE.

Table 4. Bimodal C6 MDPE demonstrates better resistance to penetration compared to bimodal C4 MDPE

Property	Units	Test Method	Bimodal C4 MDPE	Bimodal C6 MDPE
MFR (190ºC, 21.6 kg)	g/10 min	ISO 1133	20	20
Density	g/cm^3	ISO 1183	0.931	0.931
Thickness	µm		40	40
Dart impact strength	g	ISO 7765-1	230	480
Instrumented Puncture Test	J	ISO 7765-2	20	28

(Total Penetration Energy)				
Elmendorf Tear Resistance MD TD	N/mm	ISO 6383/2	 50 250	 60 250

Table 5 below shows another comparison between a bimodal C4 MDPE film and bimodal C6 MDPE this time with higher MFR and density. The improvement in puncture resistance is also seen here as well.

Table 5. Bimodal C6 MDPE demonstrates better resistance to penetration compared to bimodal C4 MDPE

Property	Units	Test Method	Bimodal C4 MDPE	Bimodal C6 MDPE
MFR (190ºC, 21.6 kg)	g/10 min	ISO 1133	42	42
Density	g/cm^3	ISO 1183	0.937	0.937
Thickness	µm		40	40
Dart impact strength	g	ISO 7765-1	100	250
Instrumented Puncture Test (Total Penetration Energy)	J	ISO 7765-2	10	18
Elmendorf Tear Resistance MD TD	N/mm	ISO6383/2	 35 200	 35 200

2.2 *Metallocene LLDPE & MDPE*

Metallocene or single-site catalysed PE (mPE) started to gain acceptance in the late 1990s and early 2000s mainly in the packaging industry. The better optical, mechanical and sealing properties compared to Ziegler Natta catalysed PE (ZN-PE) made it an ideal choice as a sealing layer material especially in the flexible packaging industry. However, the use of mPE in the geomembrane industry has been limited, possibly due to:

2.2.1 *Processability*

Metallocene PE has very narrow molecular weight distribution (MWD) and this results in poor melt stability during extrusion, especially in blown process. Besides, the early mPE materials that came into the market were all LLDPE, and there were no dedicated grades with a low enough MFR and high enough density to be used in the HDPE geomembrane industry.

2.2.2 *Cost*

There was a very big price gap between mPE and ZN-PE when mPE was first introduced. This price gap still exists today, though it has narrowed somewhat. Geomembrane producers were reluctant to pay for this high costs or may not be able to pass this cost down to the end user. This is not helped by the fact that gauge reduction is not possible in geomembranes since the thickness is written into the specifications, unlike in the packaging industry where packages were downgauged by using mPE while maintaining or even surpassing mechanical properties, and the entire value chain was able to achieve a certain degree of cost savings.

2.2.3 *New developments in metallocene PE*

Recent developments in metallocene PE have made it possible to overcome the two challenges above. For example, in the last several years, new grades of metallocene LLDPE and MDPE with low MFR were introduced. Some of these materials have a slight degree of long chain branching in order to achieve better processability. These materials were still not really dedicated for the geomembrane industry, but the better mechanical / processing performance balance has made it possible for them to be used successfully in the geomembrane application. With the widespread usage of mPE, mainly in the packaging industry, this had led to better economies of scale in plant production. Coupled with the aggressive marketing from the resin producers, the price gap of mPE and ZN-PE has come down drastically compared to when they were first introduced.

2.3 *Resin pre-compounded with carbon black*

MDPE resin that is supplied precompounded with carbon black is available from several suppliers. However, this has proved less popular among geomembrane suppliers possibly due to the higher cost of the resin and the lack of flexibility if other coloured geomembranes are needed. For niche and specialised application such as geomembrane installed in high altitudes including landfill covers designed for longer periods of operation, using a resin that has been precompounded with carbon black may provide a higher level of safety and better resistance to UV attack especially in these extreme environments. In most geomembrane production, the addition of carbon black additive is achieved via the use of a masterbatch that is added during the extrusion process. Almost all the commercial extruders used by the geomembrane manufacturers consist of single screw extruders. These extruders do an excellent job in melting, converting and conveying the molten resin to the die at sufficiently high outputs. Adding carbon black masterbatch (CBMB) during the geomembrane extrusion process to produce a black geomembrane has been accepted practice for decades and continue to be very popular. However, recently available data on this subject has shed more light on this topic.

In a recently study (S. Deveci et. al. 2018), it was shown that the mixing of CBMB using these single screw extruders can result in pipes exhibiting mechanical results that are different as when produced from precompounded resin especially if extrusion output is not reduced to account for the need to properly mix the CBMB with the natural resin. Pipes extruded via the CBMB and the natural resin route exhibited lower tensile performance compared to pipes extruded using black precompounded resin at the same extrusion output. Although the study was performed on extruded pipes of different thickness, the conclusion is valid for geomembranes as well since the incorporation of CBMB is done in the same way. While the study only detailed the effects of tensile testing, the micrographs showing much poorer CB dispersion with a typical single screw extruder creates doubts on the long term UV protection of the pipe when left exposed for extended periods. These results indicate that while the geomembrane industry has successfully mixed CBMB at the extruder, when producing geomembrane that is exposed to high levels of UV that is in use for an extended period, the use of well dispersed black precompounded resin may be warranted.

3 DISCUSSION

3.1 *Bimodal LLDPE & MDPE geomembrane*

Bimodal LLDPE & MDPE material will extend the performance envelop of current geomembranes through higher stress crack and puncture resistance. Manufacturers benefit from using a material that is easier to process and is more cost effective than the unimodal C6 & C8 materials. Although these material are not the mainstream materials used by geomembrane producers today, there is an opportunity to use these materials more widely as they exhibit mechanical performance close to that of the more expensive metallocene resins but at a lower cost. They therefore offer the best balance of performance versus cost for the industry.

3.2 *Metallocene LLDPE & MDPE*

One practical possibility to overcome the cost issue of these metallocene resins is to incorporate them into a coextruded geomembrane sheet formulation. This can be performed either to resolve current performance shortcomings or to further enhance performance.

To improve poor welding performance of an HDPE geomembrane a formulation as shown in Figure 4 below could be considered.

Figure 4. Introducing mMDPE in the top and bottom layer with ZN-MDPE to improve welding performance

To enhance flexibility and puncture resistance of a LLDPE geomembrane a formulation as shown in Figure 5 below could be considered.

Figure 5. Replacing the middle layer of with mLLDPE to improve flexibility and puncture resistance

In Figure 5 above as well, the use of a combination of ZN-MDPE and ZN-LLDPE layers gives the geomembrane a more superior chemical resistance than just using 100% LLDPE. One disadvantage of doing this is the geomembrane will not be flexible enough even though the middle layer is LLDPE. This will be further improved with mLLDPE as a middle layer, since the typical density of mLLDPE can be much lower than ZN-LLDPE.

4 CONCLUSION

These developments in bimodal LLDPE, bimodal MDPE and metallocene resins demonstrates that the PE materials are continuously being improved and can help geomembrane manufacturers develop geomembranes that better address current and upcoming challenges. These improvements may also allow manufacturers to improve their efficiency that lead to improved product cost competitiveness and help PE geomembranes secure its role as the material of choice in fluid containment & isolation and ground protection application.

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