

Daploy[™] HMS Polypropylene for Foam Extrusion



SHAPING the FUTURE with PLASTICS

BERRY 2001 BOREALIS v. BERRY IPR2016-00235

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About Borealis and Borouge

Borealis and Borouge is a leading provider of chemical and innovative plastics solutions that create value for society. With sales of EUR 4.7 billion in 2009, customers in over 120 countries, and 5,200 employees worldwide, Borealis is owned 64 % by the International Petroleum Investment Company (IPIC) of Abu Dhabi and 36 % by OMV, the leading energy group in the European growth belt. Borealis is headquartered in Vienna, Austria, and has production locations, innovation centers and customer service centers across Europe and the Americas. Through Borouge, a joint venture between Borealis and the Abu Dhabi National Oil Company (ADNOC), one of the world's major oil companies, the company's footprint reaches out to the Middle East, Asia Pacific, the Indian subcontinent and Africa.

Established in 1998, Borouge employs approximately 1,400 people, has customers in more than 50 countries and its headquarters are in Abu Dhabi in the UAE and Singapore.Building on the unique Borstar[®] technology and their experience in polyolefins for more than 50 years, Borealis and Borouge provide innovative, value creating plastics solutions for the infrastructure (pipe systems and power and communication cables), automotive and advanced packaging markets. In addition, Borealis offers a wide range of base chemicals from melamine and plant nutrients to phenol and acetone.

Today Borealis and Borouge manufacture over 4 million tonnes of polyolefins (polyethylene and polypropylene) per year. Borouge is currently tripling its polyolefins manufacturing capacity to 2 million tonnes per year (t/y) by mid-2010 and an additional 2.5 million t/y is scheduled for 2013. The companies continue to invest to ensure that their customers throughout the value chain, across the globe, can always rely on product quality, consistency and security of supply. Borouge and Borealis are committed to the principles of Responsible Care[®] and proactively contribute to addressing the world's water and sanitation challenges through their Water for the World™ initiative.

For more information: www.borealisgroup.com www.borouge.com



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Polypropylene foam

Polymeric foams consume around 3.5 million tonnes of plastics materials annually and account for about 10 % of all polymer usage in Europe. Foamed polymers are used in a wide number of application areas, which range from construction, automotive and household products to food and protective packaging. Among the many benefits of foamed materials are their good mechanical rigidity at low specific gravity, thermal and acoustic insulation, cushioning against mechanical shock and a significant contribution to source reduction in raw material usage.

The foam market is dominated by the amorphous polymers (such as PS, PU and PVC) which have been industrially foamed for more than 50 years.

Polypropylene (PP) foams are a relative late comer to this market. The reasons for this lie in the molecular structure – standard PP's are semi-crystalline materials with a linear molecular structure. They lack the required extensional rheological properties in the melt phase which are required for the production of extruded low density foams with a fine and controlled cell structure. This limitation is resolved by the Borealis Daploy range of High Melt Strength (HMS) PP products. These are long chain branched materials, which combine both high melt strength and extensibility in the melt phase. They open up the possibility of bringing the numerous well-known property benefits of PP into the world of low density polymeric foams. These benefits include a wide mechanical property range, high heat stability, good chemical resistance. PP foams offer significant benefits versus other polymeric foam solutions in terms and sustainability:

- leight weight
- easy recycling
- no "monomer issues"
- single material solutions based on PP possibile

From a fairly recent and small beginning, the global PP foam market is still growing.

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In the case of food packaging, PP foam offers a lightweight packaging solution with excellent grease/fat resistance (no stress cracking) and with no issues related to its monomer. Its high heat stability means products are microwaveable, with good thermal insulation giving them a 'cool touch' during use.



In automotive applications, lightweight foam solutions are helping to improve vehicle performance and fuel efficiency. With increasing pressure for end-of-life vehicle recycling, mono-material solutions are being sought and, with PP becoming a preferred polymer, recyclable foamed PP solutions are a logical next step. PP foams have an excellent moisture barrier and chemical resistance which are important for durability and functionality in the presence of hot oil, grease or fuel. Its high heat stability also opens the possibility for under the bonnet applications. PP foams also have very good cushioning properties, thereby contributing to improved driver and passenger safety.

As a leading PP supplier, Borealis is committed to support the further development of the extruded PP foam market through its Daploy HMS PP products and by offering PP foam solutions.

Figure 1: Some current applications for extruded PP foams

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Daploy HMS-PP

The basic extensional rheological properties of the long branched Daploy HMS-PP products are shown in figure 2, in comparison to those of standard linear PP's. The window in the high melt strength and extensibility area of this graph defines the requirements for a high performance foaming grade. With such long chain branched polymers, it is possible to produce very low density (20 - 50 kg/m³) extruded PP foams which possess a fine and controlled closed cell structure. This is not possible with standard linear PP's or modified materials which fall outside the critical high performance foaming window.



Daploy HMS-PP products can be blended with the full range of standard PP extrusion grades and other polyolefinic products. This offers the opportunity to widely tailor the foam properties to meet the particular demands of the end-use application. Furthermore, Daploy HMS-PP products are specifically designed to be suitable for processing on most types of existing industrial foaming equipment.

Daploy HMS-PP products and their blends are not crosslinked. This means that extruded PP foams produced from them are fully recyclable, an increasingly important environmental demand within the polymer industry.

Figure 2: Extensional rheology curves for linear PP's and Daploy HMS

Foam extrusion process

The first steps in the foaming process (polymer feeding and melting) are common to all extrusion processes. However, three later stages are specific and critical to the process, as illustrated in figure 3.

These three specific steps in the foam extrusion process comprise of (a) dissolving of a blowing agent gas in the polymer melt

- (b) cell nucleation
- (c) cell growth and stabilisation

In order to perform these additional steps, foaming extruders are longer than standard types, typically with an overall L/D ratio>40, in either a single or tandem extruder configuration.



Figure 3: Schematic illustration of processing steps in foam extrusion – direct gas injection/annular die

Polymer-gas solution

A blowing agent is introduced into the polymer melt either by direct gas injection (physical foaming) or by decomposition of an added chemical blowing agent (chemical foaming). In both cases, a key requirement for a uniform and controlled cell structure is a homogenous polymer-gas solution. This is controlled by two factors: the solubility of the blowing agent gas in the polymer and the sorption kinetics. The solubility itself is not the limiting factor

for foaming when using the more common industrial foaming agents: butane and carbon dioxide. With the gas concentrations typically used in foam extrusion, these can be quantitatively dissolved with standard extrusion pressures up to 10 MPa (100 bar). Figure 4 shows the equilibrium solubility curves for the commonly used blowing agent gases in PP.

The achievement of equilibrium solubility is determined by the sorption kinetics and this is therefore a time dependent process. This process can be accelerated by raising the melt temperature and using screw designs which promote good mixing of the polymer melt and injected gas.



Figure 4: Solubility of commonly used blowing agents in PP



Cell nucleation

Control of cell nucleation is crucial to obtaining the desired fine and uniform cell structure of the final foam. It is a complex area with several, often interrelated, factors playing a role. The three main factors which influence the cell nucleation are the pressure drop in the die, the concentration of the blowing agent and the concentration of the external cell nucleating agent.

The rate of pressure drop at the die is determined by the die geometry. Higher rates of pressure drop at the die significantly increase the cell density, irrespective of the concentration of blowing agent gas or external nucleator. High shear rates are also believed to play a role in promoting cell nucleation.

The content of the blowing agent, as well as the one of the nucleating agent, has a direct impact on the cell density. Figure 5 shows an example of the influence of these two factors on cell density in the case of PP foamed with butane and talc as the nucleator.



Figure 5: The effects on cell density of blowing agent and nucleating agent concentrations

Cell growth and stabilisation

Melt temperature is one of the most important process parameters in foam extrusion. In the case of PP foam, depending on the type and concentration of the foaming agent used, the optimum in melt temperature may vary from approximately 130°C to 180°C.

When the melt temperature is too low, foaming is limited because the material solidifies before the cells have the possibility to expand fully. When the temperature is too high, the foam first expands, then collapses again due to lack of stabilisation of the structure. There is an optimum melt temperature window for foaming in which lowest densities are achieved; this temperature is lower than the standard PP melt temperatures (210°C to 240°C) - See also picture 6. The latter part of the foam extruder is dedicated to the melt cooling and intimate mixing of the polymer-gas system.

It is during this part of the process that the Daploy HMS-PP plays its crucial role. Its high melt strength and extensibility help to control cell growth. By a 'strain hardening' mechanism it prevents rupture of the cell walls and coalescence, which would otherwise lead to a polymer containing a few rather large holes in it – far from the desired fine and closed cell structure.

The foam is finally stabilised by a cooling stage before winding. This is either by means of a calibrating mandrel in the case of an annular die or by a conventional roll stack when a flat die is used.



Figure 6: Temperature balance between unsufficient cell growth and collapsing cells.





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Daploy HMS-PP blends and foamability

In order to modify the final foam properties, Daploy HMS-PP's can be blended with standard extrusion grade PP's, as will be described in more detail in the next section.

However, an important consideration is the foamability of such blends. When a long chain branched PP is mixed with a standard PP, it is evident that this will have a 'diluting' effect on the melt strength and extensibility of the blend compared with that of the pure HMS-PP. This effect is shown in figure 7.

It can be seen, however, that quite high levels (approx. 60%) of blend partner can be added before the extensional rheological properties of the blend begin to fall outside the critical high performance foaming window.

This is further verified in figure 8, where the minimum achievable foam density is shown as a function of the HMS-PP content in the blend. A wide range of blend compositions can be used in order to reach low density (<100 kg/m³) PP foams or in order to adjust the extruded foam properties for the end application





Figure 8: Minimum achievable foam density as a function of Daploy HMS-PP content of the blend

Figure 7: Extensional rheology curves for HMS-PP/block copolymer blends

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Providing PP foam solutions

The modification of foam properties is a crucial requirement in order to be able to produce PP foams with properties that meet the technical performance demands of particular end-use applications.

The homopolymer based HMS-PP's can be used pure or in blends with standard homopolymers, providing foams with high stiffness and heat stability. Enhancements in impact strength and toughness of the foam can be achieved by using random or heterophasic (block) copolymers as blend partners. In the case of random copolymers, impact performance is improved at temperatures above approximately 0°C. If good impact performance is required at low temperatures (< 0°C), heterophasic copolymers should be used.

Further interesting property modifications can be made available by using Borealis Borsoft[™] random heterophasic copolymers as blend partners. These are soft PP's (tensile modulus ~400 MPa). The blend with these products provides the opportunity to produce soft PP foams with good impact strength and toughness at low temperatures. Even softer foams can be obtained by blending Daploy HMS-PP's with various polymeric materials such as metallocene LLDPE's, TPO's or EVA's.

Borealis has also developed a random copolymer based HMS-PP. Blends with this product will result in even softer foam and enable their use in a wide range of existing and newly developed applications.

Blend partner	Foam property modifications
Homopolymers	High stiffness Reduced impact
Block copolymers	Low temperature impact Reduced stiffness Improved toughness
Random copolymers	Softer foams Improved toughness
Borsoft PP's	Soft foams Low temperature impact

* For more information and technical data sheets please consult our webpage www.borealisgroup.com

Table 1: Blend partner tγpes and their influence on foam properties using a certain HMS PP product as base resin

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The general description of HMS blends can be further refined to provide more quantitative predictions of PP foam properties. This makes use of various theoretical models for describing foam properties. One of the more important foam properties is the tensile modulus which is determined by three basic parameters:

- Tensile modulus of the compact material
- Foam density
- Foam structure

The tensile modulus of the starting (compact) material is determined by the chosen blend partner and the composition – typically this modulus will be in the range of 750 to 2,000 MPa. The tensile modulus of the foamed material will decrease as the density decreases. The third parameter is foam structure and this relates to factors such as the relative proportions of open and closed cells and cell size.

Figure 9 shows experimental data for tensile modulus as a function of foam density for different Borealis blend partners. The agreement with the theoretical predictions is good and this provides confidence in the ability to use this as a quantitative tool.



For the selection of the right polymer structure – density profile for your specific applications we will be able to provide support with experience of many years in the area of PP foam and a tool developed by Borealis to predict the final properties of a foam.

Figure 9: Experimental data for the tensile modulus of various Daploy HMS-PP blends and theoretical curves

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Basic material data for the Daploy HMS - grades

Daploy HMS grades are PP-based polymers where long chain branching was introduced using a post rector step.

This treatment results in an enhanced melt strength, improved drawability and also high stiffness.

Daploy WB135HMS and WB140HMS are PP-homo based materials whereas WB260HMS is random-copolymer based and allows therefore the production of very soft foams.

Property	Unit	WB135HMS	WB140HMS	WB260HMS	Method
MFR 230/2.16	g/10 min	2.4	2.1	2.4	ISO 1133
Melt Strength	cN	32	36	27	Borealis test method
Melting Temperature	°C	163	163	146	ISO 11357
Crystallisation temperature	°C	128	127	113	ISO 11357
Flexural modulus	MPa	1,900	1,900	850	ISO 178
Tensile modulus	MPa	2,000	2000	900	ISO 527-2
Elongation at break	%	10	10	520	ISO 527-2
Heat deflection temp. A	°C	60	60	50	ISO 75-2
Heat deflection temp. B	°C	110	110	70	ISO 75-2
Vicat A	°C	155	155	130	ISO 306
Charpy impact str. notched +23°C	kJ/m ²	4	3	8	ISO 179/1eA
Charpy impact str. notched -20°C	kJ/m²	1	1	1	ISO 179/1eA

Table 2: Comparison of Daploy foam grades





Figure 10: Shear rheology at 230°C (ISO67211)

Figure 11: Rheotens curves at 200°C



Figure 12: Comparison Daploy WB140HMS vs. WB260HMS

Processing guidelines for PP homopolymer and random copolymer HMS grades

Daploy HMS-PP's and their blends with standard polypropylenes can be processed on all types of conventional foam extrusion equipment.

The final foam density and quality will depend not only on the polymer, blowing agent, processing aids or masterbatches, but also on design and process settings of the machine.

The following tables offer some general process setting guidelines for foaming with Daploy HMS-PP, in the cases of chemical foaming with CO_2 and physical foaming with CO_2 or butane.

Parameter	WB140HMS/ WB135HMS	WB260HMS	Unit
Mass flow	15 - 25	15 - 30	kg/h
CO ₂	0.4 - 1.2	0.4 - 1.2	%
Nucleating agent*	0.15 - 0.30	0.15 - 0.30	%
Extruder temperatures:			
- zone 1	160 - 170	150 - 160	°C
- zone 2	180 - 190	170 - 180	°C
- zone 3	200 - 220	210 - 220	°C
- zone 4	220 - 240	230 -240	°C
- zone 5	220 - 240	215 - 225	°C
- zone 6	220 - 240	165 - 175	°C
- zone 7	180	155 - 165	°C
- cooling extension	175 - 180	145 - 155	°C
- mixer	175	140 - 145	°C
- adapter	175 - 180	140 - 145	°C
- die	165 - 170	140 - 145	°C
Melt temperature	165 -170	140 - 150	°C
Melt pressures:			
- extruder (injection)	50 - 80	70 - 90	bar
- mixer	40 - 65	50 - 70	bar
- die	30 - 50	25 - 40	bar
Screw speed	15 - 25	15 - 25	rpm
Take off speed	2.5 - 4	2.5 - 4	m/min
Foam density	120 - 400	180 - 400	kg/m³

Example for single screw 60 mm, annular die

*Hydrocerol® CF20E

Table 3: Physical foaming of Daploy WB140HMS and WB260HMS with CO₂

Parameter	Range	Unit
Mass flow	3 - 5	kg/h
Foaming agent*	0.5 - 2.5	%
Nucleating agent**	0 - 2	%
Extruder temperatures:		
- zone 1	240	°C
- zone 2	220	°C
- zone 3	180 - 200	°C
- zone 4	180 - 200	°C
- zone 5	180	°C
- zone 6	180	°C
- zone 7	180	°C
- die	175 - 180	°C
Melt temperature	180 - 190	°C
Melt pressures:		
- die	40 - 200	bar
Screw speed	30 - 60	rpm
Take off speed	2.5 - 5	m/min
Foam density	250 - 600	kg/m ³

Example for single screw 30 mm, flat die

*Hydrocerol® CF40E , **Hydrocerol® CT516

Parameter	Range	Unit
Mass flow	80 - 100	kg/h
Butane	4 - 8	%
Nucleating agent* 4 - 1.0	0.4 - 1.0	%
Extruder temperatures:		
- zone 1	190 - 220	°C
- zone 2	220 - 240	°C
- zone 3	175 - 200	°C
- zone 4	175 - 180	°C
- zone 5	140 - 160	°C
- zone 6	140 - 150	°C
- zone 7	140 - 150	°C
- cooling extension	140 - 150	°C
- die	140 - 150	°C
Melt temperature	140 - 150	°C
Melt pressures:		
- extruder (gas injection)	40 - 100	bar
- die	40 - 100	bar
Screw speed	30 - 50	rpm
Take off speed	3 - 5	m/min
Foam density	30 - 120	kg/m ³

Table 5: Physical foaming of Daploy WB140HMS with butane

Table 4: Chemical foaming of Daploy WB140HMS with CO₂

Example for twin screw 60 mm, annular die

* Hydrocerol[®] CT516

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