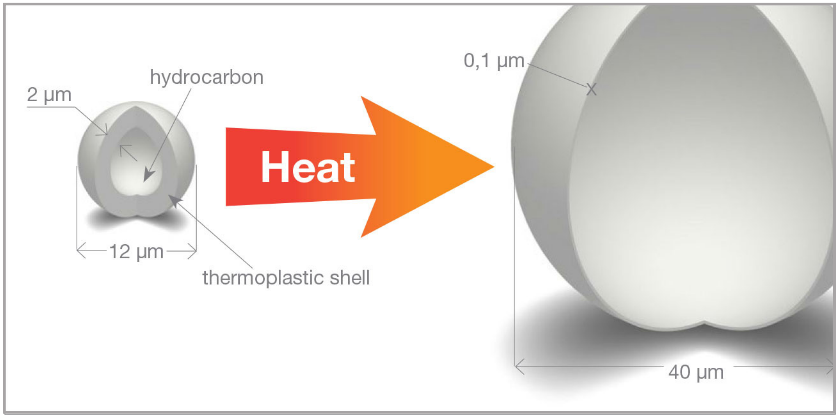
Expancel® Microspheres

an Introduction

Boud Minerals

Introduction to Expancel® Microspheres

Expancel® microspheres are small spherical plastic particles. The microspheres consist of a polymer shell encapsulating a gas. When heated, the internal pressure from the gas increases and the thermoplastic shell softens, resulting in a dramatic increase of the volume of the microspheres. The gas remains inside the sphere.



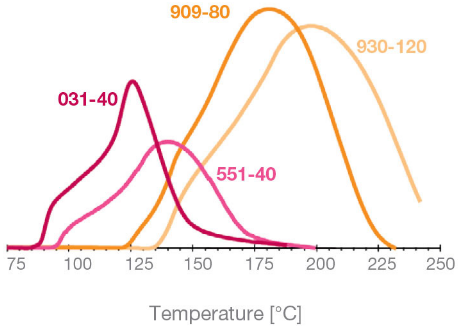
Expansion of Expancel microspheres. This results in a dramatic decrease of the density. Typical values are from 1000 down to 30 kg/m^3 (8.35 to 0.25 lbs/gal).

Properties of Expancel® Microspheres

Thermomechanical properties

Expancel® is available with expansion temperatures in the range of 80 - 190°C (175 - 375°F).

Expancel® can normally be stored for a long time at room temperature without negative effects on the properties; very high temperatures should be avoided.



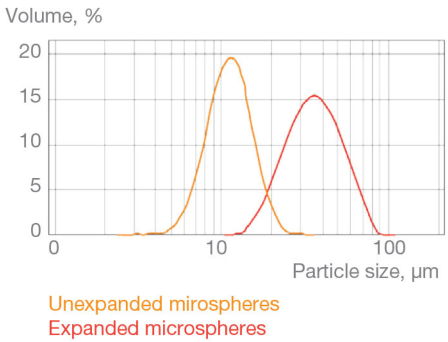
Expansion curves for some Expancel grades.

Elasticity

Expancel® microspheres regain their original volume when the pressure is released. Expancel® can withstand several cycles of loading / unloading without breaking.

This is very important when the microspheres are used in shock absorbent materials but also when pumping the microspheres; alone or in various mixtures.

Illustration of what happens when Expancel DE is first put under pressure and later returned to ambient pressure.



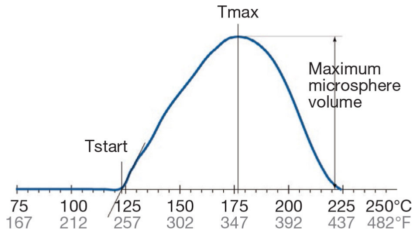
Expansion

The expansion characteristics are measured using Thermo Mechanical Analysis (TMA). The sample is heated at a constant rate (in our analysis 20°C/min, 36°F/min) and the volume of the sample is measured. A graph representing the expansion characteristics of the sample is recorded (figure 1). From this graph, the values are calculated. Typical TMA-graphs of a few grades are shown in figure 2.

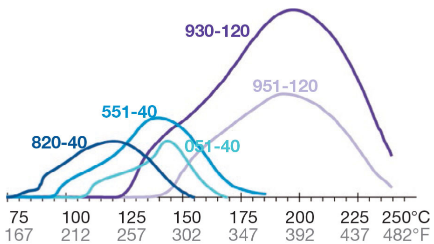
It is important to remember that if T_{max} is 140°C (284°F) this does not necessarily mean that the process temperature should be 140°C.

The expansion process is a delicate balance. The relationship between the softening of the shell, gas tightness of the shell and pressure increase from the gas inside the microsphere are important. The balance is affected by a number of factors such as:

- Polymer composition of the shell
- Type of gas inside the microspheres
- Chemicals in contact with the shell
- Outer pressure
- Free expansion or in a matrix
- Type of matrix
- Heating rate



The graph from a typical TMA analysis.



Typical graphs of some Expancel® grades.

The polymer composition of the shell is important as it determines the glass transition temperature and the gas permeability of the shell. The gas inside the microspheres determines the pressure inside the shell at a given temperature.

Contact with chemicals can decrease the glass transition temperatures and thereby lower T-start of the microspheres. Chemicals might also influence the barrier properties and increase the gas permeability leading to the smaller density reduction.

Inside the matrix the gas permeability can be improved due to its barrier properties. If the microspheres are under pressure from the outside the decrease in pressure between the inside and the outside of the shell can result in a higher T-start and smaller density reduction.

A cross-linking matrix, eg rubber or thermoset, can also prevent some of the possible maximum pressure expansion of the spheres.

Thermal Stability

The thermal stability of different grades of pre-expanded microspheres shows a clear difference. The different thermomechanical behaviour of various Expancel® grades makes it possible to choose an optimal grade for each process and application.

Expancel® Grade		Particle Size	
820	Low	20	Low
642		40	
551		80	
461		100	
920		120	
009		140	High
930	High		

Ranking of thermal stability.

Particle Size

Expancel® microspheres are available in different sizes between 20 and 120 microns after expansion.

The size of Expancel® is measured by laser diffraction, Low Angle Laser Light Scattering (LALLS). The microspheres in any given sample are not all the same size. There is a particle size distribution.

All spheres in this sample have approximately the same relation between diameter and shell thickness. This means that the large microsphere has greater shell thickness - and hence a lower gas permeability - and therefore it will expand slightly better than a smaller microsphere in the same sample. This means that the particle size distribution that is rather narrow for unexpanded microspheres will increase after expansion.

The density of the microspheres has an influence on the particle size. For instance, size 40 microspheres at density 30 kg/m^3 (0.25 lbs / gallon) has about the same size as size 80 microspheres at a density of >100 kg/m^3 (0.83 lbs / gallon).

Chemical Resistance

Expancel® can be used in contact with many chemicals, including solvents, without discoloration or negative effects on expansion or other properties.

High Pressure

Expancel DU has a good resistance to high pressure. The ability of Expancel DE to withstand high pressure varies considerably with density and particle size. Larger microspheres and microspheres with higher density lead to better high pressure resistance.

Closed Cells

Expancel® microspheres are closed cells, which is an important property in many applications.

In a waterborne coating, such as paint, this means that the microspheres have a low water absorption but the coating will have a high water permeability. This is caused by the interface between the microspheres and the surrounding matrix.

In this interface, the moisture transport is quick compared with the moisture transport in the film itself. This allows moisture in the substrate to evaporate.

Gas Tightness

The polymer shell of Expancel® microspheres has been carefully designed to have low gas permeability. This is important in many applications since it keeps the microspheres from leaking gas into the matrix.
Gas leakage into the matrix can produce pinholes in the matrix and an increased density. The degree of gas tightness varies with the grade.

Mechanical Strength

Expancel® microspheres are able to withstand many cycles of loading / unloading without breaking. However as the density of the microspheres decreases this ability will decrease as well.

Some chemicals may also affect the elasticity and mechanical strength.

Surface Modification

Expancel® microspheres can be used to achieve a nice velvet-like surface by adding a small amount to a coating. This can be done on metal, paper, fabrics, etc.

Insulation

Gas-filled closed cells are beneficial in both electrical and thermal insulation applications.

Expancel® microspheres are used in cable filling compounds. In Petrolatum, the relative permittivity was reduced from 2.2 to 1.6 by adding 4% of Expancel DE.

The density was reduced from 900 to 450kg/m^3 (7.5 to 3.8 lbs /gallon).

The thermal conductivity of thermoplastics has been reduced from 0.2 to 0.06 W/m*K (1.4 to 0.4 Btu*ft/h*ft2*ºF). The density was approximately 300 kg/m^3 (2.5 lbs/gallon).

Thermal conductivities of 0.07 W/m*K (0.5 Btu*ft/(h*ft2*ºF) are reported on 1 to 1.5mm (0.4 to 0.6in) thick coatings.

Internal Pressure

Expancel® microspheres can be added to produce an internal pressure in the finished product. This is used in many applications, for example printing blankets and pipe insulation for offshore applications.

Expancel® microspheres are also used to improve the process. They can, for example, be mixed with a filler before adding a binder. Here the microspheres create a pressure in the mold and, together with the binder, fill all the voids between the filler particles.

Another example is injection molding where the pressure is used to counteract the shrinking that occurs when the product is cooled.

Dispersability

Expancel WU is easy to disperse uniformly in an aqueous dispersion, but care must be taken to choose the correct type of dispersing equipment. There are grades that are easier to disperse and there are others that are more difficult.

The grades that are more difficult to disperse may require a rotor / stator mixer like a Silverston mixer, while the grades that are more easily dispersed may only require a simple propeller stirrer for proper dispersion.

Ranking of Dispersability

Expancel® Grade		Particle Size	
642 WU	Difficult	20	Difficult
551 WU		40	
461 WU		80	
007 WUF	Easy	100	
054 WUF	Easy	120	
920 WUF	Easy	140	Easy

Expancel DU can be easily dispersed using general dispersing equipment.

Expancel WE is fairly easy to disperse in an aqueous dispersion using proper equipment.

Expancel DE is very easy to disperse using general dispersing equipment. Care must be taken to avoid dusting because of the extremely low density.

Application Techniques

There are many different processes in which Expancel® microspheres can be used:

Impregnation - a common technique for processing non-wovens

Lamination - Expancel® in a core material will create a lightweight material with resilient properties

Coating - Expancel® in a coating layer will add thickness and improve surface characteristics

Spraying - Spraying is possible

Molding - Expancel DE can be mixed with many thermoset materials to form a moulded product with low density

Matting and anti-slip - Expancel® can be mixed in a coating to modify surface properties like gloss and anti-slip

Injection molding - Expancel DU or MB can be used in injection molding

Extrusion - Expancel DU or MB can be used in extrusion of profiles, cables and hoses

Designation

Every product has its own unique name depending on the composition of the shell, the particle size, the delivery form and if the microspheres are expanded, the density of the microspheres.

The first three to four characters, the grade, are a code for the polymer type and type of hydrocarbon, eg FG = food grade.

The two to four letters indicate the delivery form, eg W = wet; D = dry; U = unexpanded; E = expanded; MB = masterbatch.

The two to three digits after the letter indicate the approximate particle size in microns after expansion.

The final d30 indicates that the true density of the dry product is 30 kg/m^3 (0.25 lbs/gallon). If the product is WE, the density value refers to the density as a dry product.

Delivery Forms

Expancel® microspheres can be delivered in a wide variety of different forms.

Unexpanded products are used when the processing generates enough heat for the spheres to expand and the matrix allows an expansion.

Pre-expanded products are used in processes where no, or not sufficient, heat is generated during production or when, for example, the matrix is cross linking at temperatures lower than the expansion temperature of the microspheres.

Wet microspheres (WU, WUF, WE) are chosen for processes that contain water while the dry versions (DU, MB, DE / DET) are chosen when no water can be present.

The unexpanded microspheres act as foaming agents while the pre-expanded microspheres can be seen as lightweight fillers.

Variety	Description	Solid Content %	Density of Expancel® kg / m³	Density of Expancel® lbs / gallon
WU	Wet, unexpanded	60 to 80	1000 to 1300	8.3 to 10.8
WUF	Wet, unexpanded	60 to 80	1000 to 1300	8.3 to 10.8
DU	Dry, unexpanded	>99	~1000	~8.3
DUT	Dry, treated, unexpanded	>99	~1000	~8.3
MB	Dry, unexpanded mixed with a matrix	62 to 65	1000	8.3
WE	Wet, expanded	15	~ 30	0.25
DE	Dry, expanded	>99	25 to 70	0.21 to 0.58
DET	Dry, treated expanded	>99	25	0.21

Delivery forms of Expancel®

Storage

Expancel® microspheres are very stable when stored in a place with normal temperatures.

Expancel WU(F) must be stored in a cool, well-ventilated area in a way that keeps the microspheres from drying.

If microspheres begin to dry because the bag in the drum is open or punctured, the dispersability will drop rapidly causing problems such as white spots or unevenness in the finished product.

Because of this, it is very important to close a bag when it is opened and only some of the content used.

Expancel DU(T) can be damaged by excessive heat during storage. This heat can cause leakage of the encapsulated hydrocarbon resulting in poor expansion.

Expancel MB must be stored in a cool, well-ventilated area away from direct sunlight.

Expancel WE must be stored in a cool, well-ventilated area in a way that keeps the microspheres from drying. Poor dispersability will result from allowing drying to take place.

Separation can also take place as a result of the large density difference between the microspheres and the surrounding water. This is best prevented by storing the bags lying down flat.

Expancel DE(T) must be stored in a dry, cool, well-ventilated area to control airborne particles.

Recommendations

Form	pH	Grade	Recommended Use
Unexpanded			
WU(F)	Acidic	820	
DU(T), MB	Acidic	642	
	Acidic	551	
	Acidic	461	Low temperature applications
	Acidic	051	
	Alkaline	920	Medium or high temperature applications
	Neutral	031	
	Neutral	007	Very good expansion capacity
Expanded			
WE, DE(T)	Acidic	461	Medium solvent resistance
	Alkaline	920	Excellent solvent resistance

Specification

Product Specification for Expancel® microspheres

Expancel® DE

Dry Expanded Microspheres

Expancel®	Particle Size µm D(0.5)	True Density kg/m³	Solvent Resistance
551 DE 40 d42	30 - 50	42 ± 4	3
461 DE 20 d70	15 - 25	70 ± 6	4
461 DE 40 d60	20 - 40	60 ± 5	4
461 DET 40 d25	35 - 55	25 ± 3	4
920 DE 40 d30	35 - 55	30 ± 3	5
920 DET 40 d25	35 - 55	25 ± 3	5

Expancel® WE

Wet Expanded Microspheres

Expancel®	Est. Particle Size µm D(0.5)	Solid Content	True Density kg/m³	True Volume	Solvent Resistance
461 WE 20 d36	20 - 30	15 ± 2	36 ± 4	4.2 ± 0.45	3
461 WE 40 d36	30 - 50	15 ± 2	36 ± 4	4.2 ± 0.45	3
921 WE 40 d24	35 - 55	10 ± 1.5	24 ± 3	4.2 ± 0.45	5

Expancel® DU

Dry Unexpanded Microspheres

Expancel®	Particle Size µm D(0.5)	Thermomechanical Analysis			Solvent Resistance
		Tstart °C	Tmax °C	Density kg/m³	
551 DU 40	10 - 16	95 - 100	139 - 147	≤ 17	3
461 DU 20	6 - 9	100 - 106	137 - 145	≤ 30	4
461 DU 40	9 - 15	98 - 104	142 - 150	≤ 20	4
051 DU 40	9 - 15	108 - 113	142 - 151	≤ 25	4
031 DU 40	10 - 16	80 - 95	120 - 135	≤ 12	3
053 DU 40	10 - 16	96 - 103	138 - 146	≤ 20	3
093 DU 120	28 - 38	120 - 130	188 - 203	≤ 6.5	5
909 DU 80	18 - 24	120 - 130	175 - 190	≤ 10	5
920 DU 40	10 - 16	123 - 133	168 - 178	≤ 17	5
920 DU 80	18 - 24	123 - 133	180 - 195	≤ 14	5
920 DU 120	28 - 38	122 - 132	194 - 206	≤ 14	5
930 DU 120	28 - 38	122 - 132	191 - 204	≤ 6.5	5
950 DU 80	18 - 24	138 - 148	188 - 200	≤ 12	5
951 DU 120	28 - 38	133 - 143	190 - 205	≤ 9	5

Expancel® FG92 DUX 120

Dry Unexpanded Microspheres

Particle Size D(0.5):	28 - 38μm

Thermomechanical Analysis:

Tstart	122 - 132 °C
Tmax	194 - 206 °C
TMA-density	$\leq$ 14 kg/m^3

Residual Substances:

Acrylonitrile	$\leq$ 30 mg/kg
Methacrylonitrile	$\leq$ 100 mg/kg
Sodium 2-cyanoethanesulfonate	$\leq$ 200 mg/kg
Sulfite	$\leq$ 2000 mg/kg

Expancel® MB

Masterbatch with Unexpanded Microspheres

Expancel®	Grade	Concentration	Carrier	Height of Foaming (mm)	Bulk Density (g/l)
920 MB 120	920 - 120	65 $\pm$ 1	EVA*	90 - 140 (200 °C)	400 - 500
930 MB 120	930 - 120	65 $\pm$ 1	EVA*	100 - 150 (200 °C)	400 - 500
950 MB 80	950 - 80	65 $\pm$ 1	EVA*	90 - 130 (210 °C)	400 - 500
951 MB 120	951 - 120	65 $\pm$ 1	EVA*	100 - 150 (210 °C)	400 - 500

EVA* - Copolymer of ethylene vinylacetate

Expancel® WU

Wet Unexpanded Microspheres

Expancel®	Dry Content %	Particle Size µm D(0.5)	Thermomechanical Analysis Tstart °C	Tmax °C	Density kg/m^3
551 WU 40	71 ± 2.5	10 - 16	95 - 100	139 - 147	≤ 17
461 WU 20	68 ± 2.5	6 - 9	100 - 106	137 - 145	≤ 30
461 WU 40	68 ± 2.5	9 - 15	98 - 104	142 - 150	≤ 20
007 WU 40	71 ± 2.5	10 - 16	91 - 99	138 - 143	≤ 15
031 WUF 40	76 ± 2.5	10 - 16	80 - 95	120 - 135	≤ 12
053 WU 40	71 ± 2.5	10 - 16	96 - 103	138 - 146	≤ 20
920 WUF 40	71 ± 2.5	10 - 16	123 - 133	170 - 180	≤ 17

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