

"EXTRUSION PROCESS OF POLYPROPYLENE FOAM"

1 This invention relates to an improved process
for producing polypropylene foam.

 More particularly, it relates to a process for
producing a highly expanded polypropylene foam having
5 uniform and fine cell structure.

 Since polypropylene has a high crystallinity
and a low melt viscosity and is difficult to cross-link,
it has hitherto been quite difficult to obtain a highly
expanded product therefrom. As such kind of product,
10 radiation-crosslinked foam-sheet is the only one com-
mercially available today.

 However, since polypropylene is superior to
polyethylene in heat resistance, polypropylene is expect-
ed to become useful in the field requiring a heat resist-
15 ance of 100°C or higher, such as heat-insulating material
for hot water piping, if a highly expanded product
can be obtained therefrom with relative inexpensive-
ness by the non-crosslinking extrusion foaming process
similarly to polyethylene.

20 Thus, the present inventors started a study
with the aim of developing a technique for producing
a highly expanded product of polypropylene by the non-
crosslinking extrusion foaming process. In the course
of this study, the present inventors encountered the
25 following two problems: (1) the breakage of cell at

- 1 the foaming and (2) the occurrence of uneven foaming
which results in uneven surface of expanded product.

Since these problems were not found in the
foaming process of polyethylene, the inventors measured
5 the characteristic properties of molten polyethylene and
molten polypropylene, the crystallizing behaviors of
these polymers, etc. to investigate how these two polymers
were different from each other in these properties.
As the result, it was found that they were different
10 in melt tension (melt strength) behavior.

Measurement of Melt Tension:

Using Melt Tension Tester manufactured by Toyo
Seiki, a molten polymer heated to 190°C was extruded
through an orifice having a bore diameter of 2.095 mm,
15 a length of 8 mm and an entrance angle of 45° at a speed of
0.72 cm³/min. The extruded product was passed through a
tension-detecting pulley and wound up a speed of 3m/min.
The tension at this time was detected by means of
differential transformer and recorded by means of a recorder
20 to determine minimum value of tension (M.T.min) and maximum
value of tension (M.T.max). Further, M.T.max/M.T.min was
calculated as a measure of the width of variation of melt
tension.

Thus, it was found that low density polyethylene
25 has a high melt tension and a small width of its variation,
while polypropylene generally has a low melt tension and
a great width of its variation.

Watching this melt tension behavior, the inventors studied the relation between melt tension value and failure in polypropylene foaming process to find that the breakage of cell at the foaming occurred in cases of low melt tension value and that appearance of uneven surface by uneven foaming occurred when width of variation of melt tension was great.

In view of above, polypropylenes having various values of melt tension were prepared and their foaming processings were tentatively carried out. As the result, it was found that a uniform foaming could be effected without breakage of cell and a foamed product free from unevenness of surface could be obtained when a polypropylene having a minimum melt tension not

1 smaller than a definite value and having a small width of variation of melt tension was used.

Thus, this invention provides a process for producing a polypropylene foam having uniform and fine cell
5 structure and a smooth surface characterised by feeding, into an extruder, a polypropylene resin having a minimum value of melt tension of 3 g or more at 190°C and a maximum/minimum ratio of melt tension of ≤ 2.5 :~~or less~~ together with a nucleus-foaming agent, melting and
10 plasticating them, thereafter feeding a volatile foaming agent through the cylinder of extruder, uniformly mixing the materials, and then extruding the mixture while cooling it.

The polypropylene resins usable in this inven-
15 tion are resins composed mainly of polypropylene of which minimum value of melt tension is 3 g or more, preferably 5 g or more, at 190°C and of which maximum/minimum ratio of melt tension is 2.5 or less and preferably 2.0 or less. Said resins include isotactic poly-
20 propylene, ethylene-propylene block copolymer, ethylene-propylene random copolymer and mixtures of two or more kinds of the above-mentioned polypropylene type resins.

Apart from above, a polymeric substance miscible with the above-mentioned polypropylene type resins, such
25 as high- and low-density polyethylenes, polybutene-1, ethylene-vinyl acetate copolymer, ethylene-propylene rubber, styrene-butadiene rubber, ethylene-ethyl acrylate copolymer, ionomer and the like, may be mixed into the above-mentioned polypropylene type resins either alone

- 1 or in the form of a blend of two or more polymers,
so far as polypropylene is the main component in the
resulting mixture.

- It is also possible to add various additives
5 such as inorganic filler, pigment, antioxidant, ultra-
violet absorber, processing aid and the like.

- The reason why a polypropylene resin having
such a specified melt tension is preferably usable in
this invention is that such a resin is small in uneven-
10 ness of viscosity and gives an extruded product having
a melt strength suitable for foaming so that, at the
time of extrusion-foaming, cells can be uniformly formed
without breakage to give a highly expanded product
free from unevenness of surface.

- 15 If a polypropylene resin having a minimum melt
tension smaller than 3 g, which is out of the above-
mentioned range, is used, the foams break at the foaming
so that no foamed product of high expansion ratio can
be obtained. If a polypropylene resin having a maximum/
20 minimum ratio of melt tension greater than 2.5 is used,
unevenness due to uneven foaming appears so that a foamed
product having a smooth surface state cannot be obtained.

- The volatile foaming agents usable in this
invention include aliphatic hydrocarbons such as pentane,
25 butane, propane and the like; fluoro-chlorinated hydro-
carbons such as dichlorotetrafluoroethane, trichloro-
trifluoroethane, trichloromonofluoromethane, dichloro-
difluoromethane, dichloromonofluoromethane, dibromo-

1 tetrafluoroethane and the like; and so on. Among them,
fluoro-chlorinated hydrocarbons are preferable in point
of forming workability, non-toxicity and flame retardancy,
among which a mixture consisting of 90 - 30% by weight
5 of trichlorotrifluoroethane and 10 - 70% by weight of
dichlorotetrafluoroethane is particularly preferable
because it is excellent in impregnation property to
polypropylene and processing stability at the extrusion
foaming and can give a polypropylene foam having fine
10 cells and a high expansion ratio.

From the viewpoint of foaming workability and
quality of foamed product, the amount of foaming agent
added to polypropylene resin is preferably in the range
of 5 - 50 parts by weight per 100 parts by weight of
15 polypropylene resin. If the amount of foaming agent
is less than 5 parts by weight, the plasticizer-like
effect of foaming agent is small, the extruded product
is not easily controllable at the temperature suitable
for foaming and the expansion ratio (the term "expansion
20 ratio" herein referred to means the ratio (density of
resin)/(density of expanded product)) cannot become high.
With increasing the amount of foaming agent, temperature
control becomes easier and expansion ratio increases so that
a foamed product of high expansion ratio becomes obtainable.
25 However, if its amount exceeds 50 parts by weight, a
separation between resin and foaming agent takes place
in extruder and "foaming in die" occurs, so that the
surface of expanded product becomes rough and no good

1 expanded product is obtainable.

As the nucleus-forming agent used in this invention for controlling dispersion and size of cells, there can be referred to inorganic substances such as calcium
5 carbonate, talc, clay, titanium oxide, silica, barium sulfate, diatomaceous earth and the like; carbon dioxide generator by the combination of a bicarbonate or a carbonate of sodium, potassium, ammonium or the like and an inorganic or organic acid such as boric acid,
10 citric acid, tartaric acid or the like; thermal decomposition type chemical foaming agents such as azodicarbonamide, benzenesulfonyl hydrazide, toluenesulfonyl hydrazide and the like; and so on. Among them, finely pulverized products of inorganic substances such as
15 calcium carbonate, talc and the like are relatively preferable in point that they have no restriction as to extrusion temperature.

The amount of said nucleus-forming agent may be appropriately selected from the range of 0.01 - 5 parts
20 by weight per 100 parts by weight of polypropylene resin. In this range, the most preferable amount is 0.1 - 3 parts by weight. In general, an increased amount of nucleus-forming agent gives a smaller diameter of cell. However, if the amount exceeds 5 parts by weight, agglomeration
25 or insufficient dispersion of nucleus-forming substance occurs, so that the diameter of cell becomes greater on the contrary. If the amount is less than 0.01 part by weight, the nucleus-forming action is too feeble to

- 1 decrease the diameter of cell.

As the method for adding said nucleus-forming agent to polypropylene resin, dry blend method, master batch method and the like can be employed.

- 5 Since the process of this invention is a non-crosslinking extrusion foaming process, it has the following merits:

- (1) By attaching various shapes of die to the tip of extruder, a polypropylene foam having the shape of pipe, sheet, rod, etc. can be obtained as a product of continuous length.
- 10
- (2) Polypropylene foam can be integrally coated on copper pipe or the like continuously by extrusion.
- (3) The production process is relatively simple.
- 15
- (4) As compared with crosslinked product, the product of this process can be heavy-gage.
- (5) The cost of production is low.

Further, since the polypropylene foam produced by the process of this invention has a high expansion ratio and fine cells and is excellent in heat-insulating property and heat resistance, it is satisfactorily usable as heat-insulating material, buffer material and the like.

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Hereunder, this invention will be illustrated in more detail with reference to the following illustrative examples which may be modified appropriately unless they exceed the scope of this invention.

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In the examples, melt tension was measured by

the method mentioned on page 2.

Example 1

To 100 parts by weight of a polypropylene (melt index 0.7 g/10 min, specific gravity 0.91) having a minimum value of melt tension (M.T.min) of 5.8 g, a maximum value of melt tension (M.T.max) of 10 g at 190°C and a M.T.max/M.T.min ratio of 1.72 was added 0.5 part by weight of talc (Micro-White[®] #5000S) as a nucleus-forming agent, and the mixture was dry-blended with Henschel mixer to obtain a compound for foaming processing.

An extrusion foaming process was practised by using an extrusion foaming apparatus wherein the first extruder (bore diameter 50 mm ϕ , L/D = 23) having a foaming agent injecting hole on its cylinder was in

1 series connected with the second extruder (bore diameter 40 mm ϕ , L/D = 20) having a cooling oil jacket on its cylinder and its tip was connected with a static mixer (bore diameter 2.54 cm ϕ [1 in ϕ], element number 9).

5 First, the above-mentioned compound was fed at a rate of 6.4 kg/hour to the first extruder of which temperature was adjusted to 200°C. To a region of the extruder where the compound was molten and kneaded, a mixture consisting of 80% by weight of trichlorotri-
10 fluoroethane and 20% by weight of dichlorotetrafluoroethane, as a foaming agent, was injected at a rate of 1.3 kg/hour by applying a pressure of 120 kg/cm². The kneaded mixture was fed to the second extruder through the connecting tube while maintaining its pressure at 30 kg/cm²,
15 after which it was cooled to a temperature of 158°C and then extruded into atmospheric pressure through a pipe-forming die having an inner diameter of 2 mm and an outer diameter of 5 mm and foamed there to obtain a pipe-formed expanded product having a smooth surface and
20 having an inner diameter of 12 mm and an outer diameter of 20 mm. The expanded product thus obtained had a density of 0.029 g/cm³, a cell diameter of 0.4 mm and a good elasticity.

Examples 2 - 4

25 By using various polypropylenes of which melt tension at 190°C fell in the range specified in this invention, extrusion foaming was practised under the same

- 1 conditions as in Example 1 to obtain pipe-formed expanded products.

Dimensions, surface states, densities and foam diameters of the expanded products were as shown
5 in Table 1.

Example 5

To 100 parts by weight of a polypropylene (melt index 0.2 g/10 min, specific gravity 0.91) having a M.T.min value of 7.3 g, a M.T.max value of 9.3 g at
10 190°C and a M.T.max/M.T.min ratio of 1.27, was added 0.5 part by weight of talc (Micro-White [®]#5000S) as a nucleus-forming agent. The mixture was dry-blended by means of Henschel mixer to obtain a foaming processing compound.

- 15 Using the same extrusion foaming apparatus as in Example 1, the compound was fed at a rate of 5.8 kg/hour to the first extruder adjusted to 200°C. Into a region of the extruder where the compound was molten and kneaded, dichlorotetrafluoroethane was injected as a
20 foaming agent at a rate of 1.4 kg/hour by applying a pressure of 100 kg/cm². The kneaded mixture was fed to the second extruder through the connecting tube while keeping the kneaded mixture at a pressure of 25 kg/cm², after which the kneaded mixture was cooled to a temper-
25 ature of 156°C and then extruded into the atmospheric pressure through a pipe-forming die having an inner diameter of 2 mm and an outer diameter of 5 mm and

- 1 foamed there to obtain a pipe-formed expanded product having smooth surface and having an inner diameter of 11 mm and an outer diameter of 21 mm.

The expanded product thus obtained had a density
5 of 0.026 g/cm³, a cell diameter of 0.6 mm and a good elasticity.

Comparative Experiment 1

Using a polypropylene (melt index 0.3 g/10 min, specific gravity 0.91) having a M.T.min value of 4.5 g,
10 a M.T.max value of 16.1 g at 190°C and a M.T.max/M.T.min ratio of 3.58, an extrusion foaming process was practised under the same conditions as in Example 1. As the result, uneven foaming took place, and nothing was obtained other than a product having an uneven surface.

15 The expanded product had an inner diameter of 8 - 12 mm, an outer diameter of 19 - 25 mm, a density of 0.028 g/cm³ and a cell diameter of 0.4 mm.

Comparative Experiment 2

Using a polypropylene (melt index 3.0 g/10 min,
20 specific gravity 0.91) having a M.T.min value of 1.6 g, a M.T.max value of 3.5 g at 190°C and a M.T.max/M.T.min ratio of 2.19, an extrusion foaming process was practised under the same conditions as in Example 1. As the result, the surface was roughened due to the breakage of cells
25 at the time of foaming and cavities were formed due to the coarse and large cells, so that no good expanded

- 1 product was obtained.

Comparative Experiment 3

Using a polypropylene (melt index 0.7 g/10 min, specific gravity 0.91) having a M.T.min value of 1.8 g, a M.T.max value of 8.2 g at 190°C and a M.T.max/M.T.min ratio of 4.56, an extrusion foaming process was practised under the same conditions as in Example 1. As the result, the surface was roughened due to breakage of cells, cavities were formed due to the coarse and large cells and unevenness appeared on the surface due to the uneven foaming, so that no good expanded product was obtained.

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Table 1

	Sample polypropylene				Foamed product		
	M.I. (g/10 min)	M.T.min (g)	M.T.max (g)	M.T.max M.T.min	Inner diameter (mm)	Outer diameter (mm)	Surface state
Example 1	0.7	5.8	10	1.72	12	20	Smooth
"	1.0	4.5	6.8	1.51	11	18	"
"	0.25	8.6	17.7	2.06	10	22	"
"	0.5	10.3	15.9	1.54	11	21	"
"	0.2	7.3	9.3	1.27	11	21	"
Comparative Experiment 1	0.3	4.5	16.1	3.58	8-12	19-25	Unevenness
" 2	3.0	1.6	3.5	2.19	10	17	Roughened surface
" 3	0.7	1.8	8.2	4.56	7-12	17-20	Roughened surface, Unevenness

Table I (Cont'd)

Density (g/cm ³)	Cell diameter (mm)
0.029	0.4
0.036	0.45
0.023	0.4
0.025	0.35
0.024	0.6
0.028	0.4
0.041	Coarse cell, Formation of cavity
0.057	Coarse cell, Formation of cavity



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CLAIMS

1. A process for producing a polypropylene foam which having uniform and fine cell structure and a smooth surface, which comprises feeding a polypropylene resin having, at 190°C, a minimum value of melt tension as defined herein of 3 g or more and a maximum/minimum ratio of melt tension of $\leq 2.5:1$ into an extruder together with a nucleus-forming agent to form a first mixture, melting and plasticating the first mixture thereafter feeding a volatile foaming agent into the cylinder of the extruder and uniformly mixing the first mixture and the foaming agent to form a second mixture, and then extruding the second mixture while cooling it.
2. A process according to claim 1, wherein said polypropylene resin has, at 190°C, a minimum value of melt tension of 5 g or more and a maximum/minimum ratio of melt tension of 2.0 or less.
3. A process according to claim 1 or 2, wherein said volatile foaming agent is a mixture consisting of 90 - 30% by weight of trichlorotrifluoroethane and 10-70% by weight of dichlorotetrafluoroethane.
4. A process according to any one of the preceding claims wherein 5-50 parts by weight foaming agent is used per 100 parts by weight polypropylene resin.
5. A process according to any one of the preceding claims wherein 0.01-5 parts by weight nucleus forming agent is used per 100 parts by weight of polypropylene resin.



- 16 -

6. A process according to any one of the preceding claims wherein the nucleus forming agent is talc.
 7. A process for producing a polypropylene foam according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.
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