(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 031 602 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**
Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 2,18

(48) Corrigendum issued on:
19.07.2006 Bulletin 2006/29

(45) Date of publication and mention of the grant of the patent:
03.05.2006 Bulletin 2006/18

(21) Application number: **99931477.6**

(22) Date of filing: **22.07.1999**

(51) Int Cl.:
C08J 9/18 *(2006.01)* ***B29C 44/00*** *(2006.01)*
C08L 23/12 *(2006.01)* ***B29K 23/00*** *(2006.01)*
B29C 44/34 *(2006.01)* ***C08J 9/232*** *(2006.01)*

(86) International application number:
PCT/JP1999/003916

(87) International publication number:
WO 2000/006636 (10.02.2000 Gazette 2000/06)

(54) **PRE-EXPANDED POLYPROPYLENE RESIN BEADS AND PROCESS FOR PRODUCING MOLDED OBJECT THEREFROM BY IN-MOLD FOAMING**

VOREXPANDIERTE POLYPROPYLENHARZTEILCHEN UND VERFAHREN ZUR HERSTELLUNG EINES FORMKÖRPERS DARAUS DURCH SCHÄUMEN IN DER FORM

PARTICULES DE RESINE DE POLYPROPYLENE PRE-EXPANSEES ET PROCEDE DE PRODUCTION D'UN OBJET MOULE A PARTIR DE CES PARTICULES DE RESINE PAR MOUSSAGE DANS LE MOULE

(84) Designated Contracting States:
BE DE FR GB SE

(30) Priority: **30.07.1998 JP 21551098**

(43) Date of publication of application:
30.08.2000 Bulletin 2000/35

(73) Proprietor: **KANEKA CORPORATION**
Osaka-shi, Osaka 530-8288 (JP)

(72) Inventors:
- **YAMAGUCHI, Takema**
  Akashi-shi,
  Hyogo 673-0003 (JP)
- **IWAMOTO, Tomonori**
  Kobe-shi,
  Hyogo 654-0153 (JP)
- **YAMAGUCHI, Minori**
  Akashi-shi,
  Hyogo 673-0876 (JP)
- **SENDA, Kenichi**
  Hirakata-shi,
  Osaka 573-0084 (JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4
81675 München (DE)

(56) References cited:
EP-A- 0 317 995
EP-A- 0 359 032
EP-A2- 0 224 265
JP-A- 3 254 930
JP-A- 7 138 399
JP-A- 8 020 662
US-A- 4 617 323

- **PATENT ABSTRACTS OF JAPAN vol. 0111, no. 93 (C-430), 20 June 1987 (1987-06-20) & JP 62 018438 A (JAPAN STYRENE PAPER CO LTD), 27 January 1987 (1987-01-27)**

EP 1 031 602 B9

Description

[0001] The present invention relates to a process for preparing cellular moldings of a polypropylene resin from pre-expanded particles of a polypropylene resin suitable for the production of thermal insulation materials, cushioning packaging materials, returnable delivery boxes, automobile bumper cores and so on.

[0002] Polypropylene in-mold foaming products are superior in chemical resistance, heat resistance and distortion restoration rate after compression as compared to polystyrene in-mold foaming products. They are also superior in heat resistance and compression strength as compared to polyethylene in-mold foaming products. For these reasons they are widely used as cushioning packaging materials, returnable delivery boxes, automobile bumper cores, and others.

[0003] In recent years, efforts to improve productivity are being made for the purpose of reducing the cost of industrial products in a wide range of fields, e.g., in the production of molded articles by shortening the molding time. It is strongly demanded to shorten the molding time also in the production of polypropylene in-mold foamed articles to reduce costs.

[0004] Various techniques for shortening the molding time are known in the production of in-mold foamed articles from polypropylene resin pre-expanded particles.

[0005] For example, Japanese Patent Publication Kokai No. 61-103944 discloses a process of the production of in-mold foamed articles using expanded particles of a non-crosslinked polypropylene having a density of 8 to 100 g/liter and a particle diameter of 1 to 5 mm and containing 0.02 to 1 part by weight of organic sodium phosphate per 100 parts by weight of the polypropylene. However, this process requires the incorporation of the phosphorus compound and, therefore, it may exert an unfavorable influence on environment and is also disadvantageous in cost. Further, when performing in-mold molding of the polypropylene expanded particles obtained, this process requires compressing the particles to 50 %.

[0006] Japanese Patent Publication Kokai No. 8-20662 discloses a process for preparing molded articles wherein polypropylene resin expanded particles exhibiting a high temperature side fusion peak, the heat of fusion of which is more than 3.5 cal/g and is not more than 6.0 cal/g, are compressed and filled in a mold in a compression rate of 10 to 60 % and heated with steam to produce a molded article. In this process, however, the molding method is limited to only a specific method and there is a limit in shortening the molding time in general production of in-mold foamed articles.

[0007] EP-A-0 359 032 relates to a method for manufacturing pre-expanded particles of polyolefin resin from strand pellets having a Tm in melting temperature measured by the DSC method, wherein the expansion ratio E of the pre-expanded particles of the resin, the length l and the average diameter d of the strand pellets after having been heated at a temperature (Tm - 5 DEG C) are in the following relational expression: $0.04E + 0.9 \leq l/d < 0.15E + 1.3$.

[0008] It is an object of the present invention is to provide pre-expanded particles of a polypropylene resin which can be molded in a mold in a shortened molding time to give cellular molded articles.

[0009] A further object of the present invention is to provide pre-expanded particles of a polypropylene resin which can be stably molded according to various known in-mold foaming methods in a shortened molding time under a wide rage of molding conditions to give cellular molded articles having excellent properties such as weldability of particles and surface appearance.

[0010] Another object of the present invention is to provide a process for stably preparing polypropylene resin in-mold foamed articles having excellent properties in a shortened molding time.

[0011] The present inventors have found as a result of making intensive study in view of such circumstances, that when performing in-mold foaming by using polypropylene resin pre-expanded particles, the expandability of which measured when heated by steam of a temperature equal to the melting point peak temperature of the base resin thereof measured by differential scanning calorimetry (hereinafter also referred to as "DSC method") is controlled within a specific range, the cooling time in the in-mold foaming can be shortened, and also that when a difference between the expandability when heated by steam of the melting point peak temperature and the expandability when heated by steam of "the melting point peak temperature - 10°C" is controlled to not more than a specific range, the cooling time can be shortened stably even if the molding conditions such as heating pressure of in-mold foaming are changed, and further that pre-expanded particles can be suitably used in various in-mold foaming methods.

[0012] Thus, in accordance with the present invention, there is provided a process for preparing cellular moldings of a polypropylene resin comprising the steps of filling polypropylene resin pre-expanded particles having an expandability of 1.0 to 1.8 in a mold capable of being closed but incapable of being hermetically sealed, and heating said particles to fuse together, said expandability being represented by the equation:

$$\text{Expandability} = \frac{\text{Expansion ratio of polypropylene resin pre-expanded particle after steam heating}}{\text{Expansion ratio of polypropylene resin pre-expanded particle before steam heating}}$$

wherein the expandability is measured by subjecting said pre-expanded particle to said steam heating without imparting an inner pressure thereto, said steam has a temperature equal to the melting point peak temperature of said polypropylene resin measured by differential scanning calorimetry under the conditions that 1 to 10 mg of the pre-expanded particles is heated to 210°C at a rate of 10°C/minute, then cooled to 40°C at a rate of 10°C/minute and heated again to 210°C at a rate of 10°C/minute, and said expansion ratio of polypropylene resin pre-expanded particle after steam heating denotes the value measured after the restoration from shrinking by impregnating the pre-expanded particle with air.

[0013] Further embodiments of the present invention are apparent from the dependent claims.

[0014] Fig. 1 is a view showing a DSC curve obtained when measuring the melting point peak of an ethylene-propylene random copolymer having an ethylene content of 2.1 % by weight by differential scanning calorimetry.

[0015] The polypropylene resin pre-expanded cellular moldings prepared according to the present invention show an expandability of 1.0 to 1.8 when heating the particles by steam of a temperature equal to the melting point peak temperature measured by differential scanning calorimetry of the base resin of the particles, wherein the expandability is represented by the equation:

$$\text{Expandability} = \frac{\text{Expansion ratio of polypropylene resin pre-expanded particles after steam heating}}{\text{Expansion ratio of polypropylene resin pre-expanded particles before steam heating}}$$

If the expandability is less than 1.0, the pre-expanded particles do not sufficiently expand upon conducting in-mold foaming of the particles thus resulting in insufficient melt-adhesion of the particles. Also, the obtained molded articles have a large dimensional shrinkability and such a surface appearance that gaps between the particles are noticeable in the surface thereof, so no satisfactory molded articles are obtained. If the expandability is more than 1.8, satisfactory molded articles can be obtained, but the cooling time in molding becomes long since expandability exhibited at the time of molding becomes large.

[0016] The polypropylene resin pre-expanded particles are preferred to be those showing a difference of not more than 0.2 between the expandability obtained when heating the pre-expanded particles by steam of the melting point peak temperature of the base resin and the expandability obtained when heating the pre-expanded particles by steam of "the melting point peak temperature - 10°C". In case that the expandability difference is not more than 0.2, the molding time does not change largely even if the molding conditions of in-mold foaming of the pre-expanded particles such as heating pressure for molding, gas pressure to be imparted to the beads and compression rate applied upon filling the beads in a mold are changed, so the in-mold foamed articles can be stably obtained.

[0017] In case that the above mentioned expandability of the polypropylene resin pre-expanded particles measured when heating the particles by steam of the melting point peak temperature of the base resin is from 1.0 to 1.5, preferably 1.0 to 1.3, molded articles satisfactory in melt adhesion of the particles and surface appearance of the molded articles can be obtained in a shortened cooling time in molding by a process of the preparation of in-mold foamed articles as mentioned after which comprises imparting an inner pressure to the pre-expanded particles prior to filling them in a mold, filling the particles in a mold capable of being closed but incapable of being hermetically sealed and heating the particles by steam to mold them, or which comprises filling the pre-expanded particles in a mold capable of being closed but incapable of being hermetically sealed in the state of being compressed in a compression rate of 10 to 60 % and heating the particles by steam to mold them.

[0018] Also, in case that the above-mentioned expandability of the polypropylene resin pre-expanded particles measured when heating the particles by steam of the melting point peak temperature of the base resin is from 1.5 to 1.8, preferably 1.6 to 1.7, the polypropylene resin pre-expanded particles can be molded in a shortened cooling time in molding by a process of the preparation of in-mold foamed articles as mentioned after which comprises directly filling the pre-expanded particles in a mold capable of being closed but incapable of being hermetically sealed without performing an inner pressure-imparting procedure such as gas introduction, and heating the particles by steam to give molded articles satisfactory in melt adhesion of the particles and surface appearance of the molded articles.

[0019] As mentioned above, in the production of in mold foamed articles, the moldings can be stably obtained in a shortened period of the cooling time in molding by regulating the above-mentioned expandability, which becomes an index of the secondary expansion force of polypropylene resin pre-expanded particles, within a specific range. Further, since the pre-expanded particles having the optimum expandability can be selected in various processes for preparing in-mold foamed articles, good melt-adhesion of the pre-expanded particles is achieved in the in-mold foaming and in-mold foamed particles having a good surface appearance and a uniform density extending from the surface portion to the inner portion can be obtained. It is assumed that since the pre-expanded particles have only the minimum expandability necessary to give a foamed article true to the mold and, therefore, since the inner pressure of the foamed article does

not rise any more than necessary after heating the particles with steam or the like, the inner pressure dropping speed in the mold is high, so the molding time becomes short, and further since the difference in pressure between the surface portion and the inner portion of the molded article, the density becomes uniform extending from the surface to the inner portion of the molded article.

[0020] An explanation is given below with respect to the expandability when heating pre-expanded particles by steam of the melting point peak temperature measured by differential scanning calorimetry of the base resin of the particles.

[0021] The melting point peak temperature of the base resin measured by differential scanning calorimetry denotes the temperature of a peak showing the melting point in a DSC curve obtained using a differential scanning calorimeter with a sample of 1 to 10 mg of polypropylene resin pre-expanded particles under conditions of elevating the temperature to 210°C at a temperature elevation speed of 10°C/minute, then cooling to 40°C at a temperature dropping speed of 10°C/minute and elevating the temperature again to 210°C at a temperature elevation speed of 10°C/ minute. From the viewpoint of the melt-adhesion of pre-expanded particles in in-mold foaming, it is preferable that the melting point peak temperature of the base resin in the polypropylene resin pre-expanded particles is about 135° to about 160°C.

[0022] The differential scanning calorimeter used in the differential scanning calorimetry may be an ordinary differential scanning calorimeter such as model DSC-2 made by Perkin-Elmer or model SSC5200H made by Seiko Electronic Industries, Ltd.

[0023] As an example that the melting point peak temperature of a base resin has been obtained by the differential scanning calorimetry, in Fig. 1 is shown a DSC curve obtained when the melting point peak temperature was measured using an ethylene-propylene random copolymer having an ethylene content of 2.1 % by weight as the polypropylene resin particles. In Fig. 1, the maximum value of the peak is the melting point peak and the temperature T_M of the melting point peak is the melting point peak temperature.

[0024] The above-mentioned expandability is obtained as follows:

[0025] After placing 100 to 300 cc of pre-expanded particles having a known expansion ratio in a pressure container having at least two ports for steam inlet port and steam outlet port, e.g., a pressure container of autoclave type or an in-mold foaming machine, steam is introduced from the steam inlet port for 5 seconds in the state of the steam outlet port being opened to expel the air in the container, the steam outlet port is closed and the pre-expanded particles are heated for 10 seconds by steam of the above-mentioned melting point peak temperature of base resin obtained by differential scanning calorimetry. After cooling; the pre-expanded particles are taken out, dried at 60°C for 12 hours and treated with air pressure of 2 kg/cm^{2}G at room temperature for 12 hours to impart an inner pressure to the pre-expanded particles. The shrunk pre-expanded particles are restored to the expansion ratio of the particles which expanded at the time of being heated by imparting an inner pressure as mentioned above. The expansion ratio at that time of the pre-expanded particles is defined as the expansion ratio of polypropylene resin pre-expanded particles after steam heatings.

[0026] From the obtained expansion ratio of polypropylene resin pre-expanded particles after steam heating and the expansion ratio of polypropylene resin pre-expanded particles before steam heating, the expandability is obtained by the equation:

$$\text{Expandability} = \frac{\text{Expansion ratio of polypropylene resin pre-expanded particles after steam heating}}{\text{Expansion ratio of polypropylene resin pre-expanded particles before steam heating}}$$

[0027] The polypropylene resin means resins containing not less than 80 % by weight of units of a propylene monomer and less than 20 % by weight of units of other monomers copolymerizable with the propylene monomer.

[0028] Examples of the polypropylene resin used as a base resin of the pre-expanded particles are, for instance, propylene homopolymer, ethylene-propylene random copolymers, ethylene-propylene block copolymers, ethylene-propylene-butene random terpolymers, propylene-vinyl chloride copolymers, propylene-butene copolymers, propylene-maleic anhydride copolymers, and other known propylene-based resins. Polypropylene resins prepared by a stereospecific polymerization method are preferred. These may be used alone or in admixture thereof. Of these, particularly preferable are ethylene-propylene random copolymers and ethylene-propylene-butene random terpolymers which have a high versatility

[0029] The above-mentioned polypropylene resins are preferred to be in a non-crosslinked state, but they may be those crosslinked by a peroxide or radiation.

[0030] The polypropylene resins may be used in the form of a blend with other thermoplastic resins admixable therewith within such a range that the properties of the polypropylene resins are not lost. Such other thermoplastic resins include, for instance, low density polyethylene, linear low density polyethylene, polystyrene, polybutene and ionomer. In general,

the other thermoplastic resins compatible with the polypropylene resin are used in an amount of 5 to 20 parts by weight per 100 parts by weight of the polypropylene resin. In case of using polystyrene, it is preferable that the amount thereof is from 5 to 10 parts by weight per 100 parts by weight of the polypropylene resin.

[0031] The polypropylene resins are usually processed into a desired particulate shape so as to make it easier to use in pre-expansion, for example, by melting the resins in extruder, kneader, Banbury mixer or mixing rolls and forming into particles having a desired shape, such as column, prolate spheroid, sphere, cube or rectangular parallelopiped, and having an average particle size of 0.1 to 5 mm, preferably 0.5 to 3 mm.

[0032] The process for preparing the polypropylene resin pre-expanded particles may comprise impregnating polypropylene resin particles with a volatile blowing agent in a pressure vessel, dispersing the particles into an aqueous dispersion medium, preferably water with stirring heating under pressure to a prescribed expansion temperature, and releasing the aqueous dispersion into a low pressure zone to thereby expand the particles.

[0033] The expandability of the pre-expanded particles varies depending on the molecular weight, molecular weight distribution, molecular structure, crystalline structure, amount of crystals and thermal history of the base resin, or depending on the heating temperature at the time of expanding (expansion temperature), heating pressure (expansion pressure), heating time and the like in the preparation of the pre-expanded particles. Although the expandability of the pre-expanded particles varies depending on factors such as the molecular structure of the base resin, the expandability is increased, in the above-mentioned process for preparing the pre-expanded particles, with raising the expansion temperature. The pre-expanded particles showing an expandability of 1.0 to 1.8 as defined above when heated at the melting point peak temperature can be easily obtained by setting the expansion temperature within the range of from (T_M - 25) to (TM + 10) (°C) wherein T_M is the melting point peak temperature of a base resin, namely a polypropylene resin. When the expansion temperature is selected from the above temperature range, the expandability can be suitably selected within the above range in accordance with the kind of polypropylene resin, the amount of a volatile blowing agent, the desired expansion ratio of pre-expanded particles and the like.

[0034] Examples of the volatile blowing agent are, for instance, an aliphatic hydrocarbon such as propane, butane, isobutane, pentane or hexane; an alicyclic hydrocarbon such as cyclopentane or cyclobutane; a halogenated hydrocarbon such as trichlorotrifuoromethane, dichlorodifluoromethane, dichlorotetrafluoromethane, trichlorotrifluoroethane, methyl chloride, methylene dichloride or ethyl chloride; and the like. These blowing agents may be used alone or in admixture thereof.

[0035] The amount of the volatile blowing agent used is not particularly limited, and is suitably selected according to a desired degree of expansion of the polypropylene resin pre-expanded particles to be produced. In general, the blowing agent is used in an amount of 10 to 60 parts by weight per 100 parts by weight of the polypropylene resin particles.

[0036] In the preparation of the aqueous dispersion of polypropylene resin particles, it is preferable to use, for example, calcium tertiary phosphate, basic magnesium carbonate or calcium carbonate as a dispersing agent, and to use a small amount of a surfactant such as sodium dodecylbenzenesulfonate, sodium n-paraffinsulfonate or sodium α-olefinsulfonate as a dispersing aid. The amounts of such dispersing agent and surfactant vary depending on the kinds thereof and the kind and amount of the polypropylene resin particles used. Usually the amount of the dispersing agent is from 0.2 to 3 parts by weight per 100 parts by weight of water, and the amount of the surfactant is from 0.001 to 0.1 part by weight per 100 parts by weight of water.

[0037] The amount of the polypropylene resin particles to be dispersed into an aqueous dispersion medium such as water is generally from 20 to 100 parts by weight per 100 parts by weight of the dispersion medium in order to achieve good dispersion.

[0038] Usually the polypropylene resin particles are introduced into a pressure vessel with water and a blowing agent to form an aqueous dispersion of the particles, and impregnated with the blowing agent at an elevated temperature, e.g., a temperature higher than the softening point of the polypropylene resin used. The aqueous dispersion of the particles containing the blowing agent is heated under pressure to the expansion temperature in the pressure vessel, and then released from the vessel into an atmosphere of lower pressure through an orifice having openings with a diameter of 2 to 10 mm, thereby expanding the polypropylene resin particles to give the polypropylene resin pre-expanded particles.

[0039] As mentioned above, the heating temperature (expansion temperature) is selected within the range of (T_M - 25) to (T_M + 10)°C according to the kind of polypropylene resin particles used and a desired value of the expandability of the polypropylene resin pre-expanded particles to be produced. On the other hand, the expansion pressure (pressure in the pressure vessel) is selected primarily according to the desired expansion ratio, and is generally from 10 to 50 kg/cm^2G.

[0040] There is no particular limitation in the pressure vessel used, and any vessels can be used so long as they can withstand the pressures and temperatures noted above. A representative vessel is an autoclave type pressure vessel.

[0041] A process for producing in-mold foamed articles will be explained below.

[0042] Molding of the pre-expanded particles is carried out, for example, in accordance with a known in-mold foaming method as disclosed in Japanese Patent Publication Kokoku No. 51-22951 or Japanese Patent Publication Kokai No.

6-59694, by filling the polypropylene resin pre-expanded particles in a mold capable of being closed but incapable of being hermetically sealed, and heating the particles with steam or the like to fuse them together, thus giving cellular molded articles true to the mold.

[0043] In case that polypropylene resin pre-expanded particles having an expandability of 1.0 to 1.5 measured when heating at the melting point peak temperature are used in the process of the present invention for preparing in-mold foamed articles, it is preferable to provide the pre-expanded particles with a gas pressure prior to filling the particles in a mold, or to fill the pre-expanded particles in a mold in the state of being compressed at a compression rate of 10 to 60 %.

[0044] Thus, the polypropylene resin pre-expanded particles having an expandability of 1.0 to 1.5 measured when heating by steam of the melting point peak temperature of the base resin can be molded by imparting a gas inner pressure to the pre-expanded particles, filling the particles in a mold capable of being closed but incapable of being hermetically sealed and heating with steam, whereby the cooling time can be shortened and cellular molded articles satisfactory in melt-adhesion of the particles and surface appearance of the molded articles can be obtained.

[0045] Prior to filling the polypropylene resin pre-expanded particles into the mold, an inner pressure based on a gas pressure can be imparted to the pre-expanded particles by holding the pre-expanded particles under pressure in an inorganic gas or the like. It is preferable from the viewpoint of the moldability in in-mold foaming of the pre-expanded particles that the inner pressure imparted to the pre-expanded particles is from 1.18 to 3.0 atms.

[0046] Examples of the inorganic gas are, for instance, air, nitrogen, helium, neon, argon or carbon dioxide gas. These may be used alone or in admixture thereof. Of these, air and nitrogen are preferable in view of versatility.

[0047] The polypropylene resin pre-expanded particles having an expandability of 1.0 to 1.5 measured when heating by steam of the melting point peak temperature of the base resin can also be molded by filling the pre-expanded particles in a mold capable of being closed but incapable of being hermetically sealed so that the compression rate of the particles is from 10 to 60 % and heating with steam, whereby the cooling time can be shortened and cellular molded articles satisfactory in melt-adhesion of the particles and surface appearance of the molded articles can be obtained.

[0048] The compression rate of polypropylene resin pre-expanded particles is a value obtained by dividing a weight of the pre-expanded particles when filled under atmosphere in a mold of a molding machine by a weight of the pre-expanded particles when filled in the compressed state in the mold, and is represented by the equation:

$$\text{Compression rate} = \left\{ 1 - \frac{\text{Weight of pre-expanded particles when filled under atmospheric pressure}}{\text{Weight of pre-expanded particles when filled in the compressed state}} \right\} \times 100$$

[0049] Further, in case that polypropylene resin pre-expanded particles having an expandability of 1.5 to 1.8 measured when heating by steam of the melting point peak temperature of the base resin are used in the production of in-mold foamed articles, the pre-expanded particles are filled as they are in a mold capable of being closed but incapable of being hermetically sealed without imparting an inner pressure thereto and heated with steam to mold them, whereby cellular molded articles satisfactory in melt-adhesion of the particles and surface appearance of the molded articles can be obtained in a shortened cooling time even if the particles are filled in a mold directly without applying any inner pressure-imparting procedure.

[0050] Also, when in the above-mentioned molding processes are used polypropylene resin pre-expanded particles which show a difference of not more than 0.2 between the expandability measured when heating the particles by steam of the above-defined melting point peak temperature of base resin and the expandability measured when heating the particles by steam of "the melting point peak temperature - 10°C", not only the cooling time in molding is shortened, but also the molding time does not greatly change even if the molding conditions such as heating pressure in molding, gas pressure imparted to the particles and compression rate applied in filling the particles in a mold are changed, so in-mold foamed articles can be stably obtained.

[0051] The present invention is more specifically explained by means of examples and comparative examples, in which all parts are by weight unless otherwise noted. It is to be understood that the present invention is not limited to only these examples.

[0052] Methods of evaluation used in the examples and comparative examples are shown below.

(Expansion ratio of pre-expanded particles)

[0053] In a 100 ml measuring cylinder, about 1 g of dried pre-expanded particles were immersed in ethanol and the volume of the particles was measured by increase of volume. The expansion ratio was calculated according to the following equation.

$$\text{Expansion ratio of pre-expanded particles} = \frac{\text{Density of polypropylene resin}}{\text{Density of polypropylene resin pre-expanded particles}}$$

$$= \frac{\text{Volume of pre-expanded particles (ml)} \times \text{Density of polypropylene resin (about 0.90 g/ml)}}{\text{Weight of pre-expanded particles (g)}}$$

(Bulk density)

[0054] Dried pre-expanded particles were filled in a container having a volume of about 5 liters, and the weight of the particles filled was measured. The bulk density was calculated according to the following equation:

$$\text{Bulk density} = \frac{\text{Weight of pre-expanded particles (g)}}{\text{Volume of the container (liter)}}$$

(Expandability of pre-expanded particles)

[0055] In a wire net basket were placed 200 ml of obtained pre-expanded particles, and the particles were placed with the basket in a 5 liter autoclave type pressure container having a steam inlet port and a steam outlet port. From the steam inlet port, steam of 1.0 kg/cm^{2}G was passed through the container for 5 seconds in the state of the steam outlet port being opened in order to expel the air in the container. The steam outlet port was then closed and the particles were heated by steam of 3.4 kg/cm^{2}G (about 146.5°C) for 10 seconds. The steam outlet port was then opened, and the pre-expanded particles were cooled until the inner pressure of the container became 0 kg/cm^{2}G and taken out of the container. After drying the pre-expanded particles at 60°C for 12 hours, the particles were held at room temperature in air of 2.0 kg/cm^{2}G to impart an inner pressure thereto, thereby restoring the particles from shrinking. The expansion ratio of the pre-expanded particles after steam heating which were restored from shrinking was obtained. The expandability was calculated according to the following equation:

$$\text{Expandability} = \frac{\text{Expansion ratio of polypropylene resin pre-expanded particles after steam heating}}{\text{Expansion ratio of polypropylene resin pre-expanded particles before steam heating}}$$

(Cooling time)

[0056] In molding of pre-expanded particles in a mold, after the steam heating was finished, the time (in seconds) required for the pressure of the molded article surface against the mold surface (molded article surface pressure) to decrease to 0.3 kg/cm^{2}G was measured.

(Density of molded article)

[0057] The length, width, thickness and weight of a molded article were measured, and the density was calculated according to the following equation:

$$\text{Density of molded article (g/liter)} = \frac{\text{Weight of molded article (g)}}{\text{Volume of molded article (liter)}}$$

$$= \frac{\text{Weight of molded article (g)} \times 10^6}{\text{Length (mm)} \times \text{Width (mm)} \times \text{thickness (mm) of molded article}}$$

(Melt adhesion)

[0058] After forming a notch with a knife in the surface of a molded article to a depth of approximately 5 mm, the molded article was split along the line of the notch by bending the molded article. The broken surface was observed and the percentage of broken particles to the whole particles was obtained. Evaluation was made according to the following criteria. A melt adhesion rate of at least 60 % is usually satisfactory for molded articles.

◎ : Melt adhesion rate of at least 80 %
○ : Melt adhesion rate of 60 % to less than 80 %
Δ : Melt adhesion rate of 50 % to less than 60 %
×: Melt adhesion rate of less than 50 %

(Surface appearance)

[0059] The surface of a molded article was visually observed and evaluated according to the following criteria.

◎: There is no irregularity in the surface and there is little gap between particles.
○: There is no irregularity in the surface, but there are slight gaps between particles
Δ: There is no irregularity in the surface, but there are conspicuous gaps between particles.
×: There is an irregularity in the surface, and gaps between respective particles are very large.

Example 1 to 3 and Comparative Example 1 and 2

(Preparation of polypropylene resin pre-expanded particles)

[0060] A pressure vessel was charged with 100 parts of pellets of a base resin (ethylene-propylene random copolymer) A shown in Table 1 (base resin A having an ethylene content of 2.1 % by weight, a melt flow index MI of 7 g/10 minutes, a weight of about 1.8 mg per a pellet and a melting point peak temperature of 146.5°C measured by DSC), isobutane of an amount shown in Table 2 and, as a dispersing agent, 2.0 parts of powdery basic calcium tertiary phosphate and 0.03 part of sodium n-paraffinsulfonate, and 300 parts of water. The resulting aqueous dispersion was heated to a heating temperature shown in Table 2. The pressure inside the vessel at that time was about 16.0 kg/cm^{2}G.

[0061] The pressure inside the vessel was then adjusted to a prescribed expansion pressure of 17.0 kg/cm^{2}G by introducing isobutane to the vessel. Once the prescribed expansion pressure was reached, a valve provided at a lower part of the pressure vessel was opened and, while maintaining the pressure inside the vessel at that pressure, the

aqueous dispersion was released into atmospheric pressure through an orifice plate having openings therein of 4.4 mm diameter, thereby performing expansion to give pre-expanded particles 1 to 5.

[0062] The properties such as expansion ratio and expandability of the obtained pre-expanded particles are shown in Table 2. The expansion ratio of pre-expanded particles when heated by steam of the melting point peak temperature of the base resin can be obtained by the equation of (expansion ratio) x (expandability at melting point peak temperature). For example, in case of Comparative Example 1, the expansion ratio at the melting point peak temperature was 45.0 times.

Examples 4 to 11 and Comparative Examples 3 to 7

[0063] Pre-expanded particles 6 to 18 were prepared in the same manner as in Example 1 except that ethylene-propylene random copolymers B to F shown in Table 1 were used and the preparation was carried out under the conditions shown in Table 2. The properties thereof such as expansion ratio, bulk density and expandability at the melting point peak temperature were evaluated according to the above-mentioned methods.

[0064] The results are shown in Table 2.

Table 1

Base resin (ethylene-propylene random copolymer)	Melting point peak temperature (°C)	Ethylene content (% by weight)
A	146.5	2.1
B	144.0	3.2
C	145.4	3.9
D	141.0	3.9
E	143.0	3.5
F	138.0	4.6

Table 2

	Pre-expanded particles	Preparation conditions			Results of evaluation				
		Kind of base resin	Amount of isobutane charged (part)	Heating temperature (°C)	Expansion ratio	Bulk density (g/liter)	Expandability at melting point peak temperature (A)	Expandability at "melting point peak temperature -10°C" (B)	Difference in expandability (A-B)
Com. Ex. 1	1	A	12.0	143.4	19.3	29.3	2.33	1.75	0.58
Com. Ex. 2	2	A	12.0	141.0	19.0	29.7	1.87	1.50	0.37
Ex. 1	3	A	15.0	138.9	18.5	29.8	1.38	1.28	0.10
Ex. 2	4	A	15.0	136.3	19.3	29.2	1.17	1.10	0.07
Ex. 3	5	A	15.0	131.0	19.2	29.6	1.01	0.98	0.03
Com. Ex. 3	6	B	10.0	143.0	19.0	27.0	1.90	1.34	0.56
Ex. 4	7	B	10.0	141.5	18.8	27.8	1.27	1.14	0.13
Ex. 5	8	C	6.5	142.5	10.0	49.4	1.45	1.23	0.22
Com. Ex. 4	9	C	6.5	144.5	10.2	48.4	1.83	1.55	0.28
Ex. 6	10	C	6.5	143.4	8.7	57.0	1.62	1.35	0.27
Com. Ex. 5	11	C	6.5	145.0	8.5	57.5	2.24	1.75	0.49
Com. Ex. 6	12	C	23.0	138.0	32.1	16.3	1.83	1.54	0.29
Ex. 7	13	C	23.0	136.1	32.4	15.9	1.50	1.27	0.23
Ex. 8	14	C	23.0	134.6	31.9	16.5	1.24	1.15	0.09
Ex. 9	15	D	10.5	140.3	21.0	24.7	1.27	1.05	0.22
Ex. 10	16	E	10.5	142.1	20.3	25.6	1.40	1.10	0.30
Ex. 11	17	B	10.5	143.0	20.9	25.4	1.64	1.24	0.40
Com. Ex. 7	18	F	10.5	138.0	19.4	25.1	1.81	1.25	0.56

Example 12

[0065] The pre-expanded particles 3 obtained in Example 1 were placed in a pressure vessel and compressed by air pressure, and the compressed particles were filled in a block mold having a size of 320 x 320 x 60 mm at a compression rate of 36 %.

[0066] Air in the mold was then expelled by steam of 1.0 kg/cm^{2}G, and in-mold foaming was carried out by heating with steam of 3.3 kg/ cm^{2}G to give an in-mold foamed article having no problem in surface appearance. The cooling time at that time was 80 seconds.

[0067] The obtained in-mold foamed article was evaluated according to the above-mentioned methods with respect to density of foamed article, melt adhesion and surface appearance.

[0068] The results are shown in Table 3.

Examples 13 to 29 and Comparative Examples 8 to 21

[0069] In-mold foamed articles were prepared in the same manner as in Example 12 except that the molding was carried out under the conditions shown in Tables 3 to 5, and were evaluated in the same manner.

[0070] The results are shown in Tables 3 to 5.

Table 3

	Molding conditions				Results of evaluation			
	Kind of base resin	Kind of pre-expanded particles	Compression rate (%)	Heating pressure (kg/cm^2G)	Cooling time (sec.)	Density of molded article (g/liter)	Melt adhesion	Surface appearance
Ex. 12	A	3	36	3.3	80	50	◎	◎
Ex. 13	A	3	36	3.5	85	50	◎	◎
Ex. 14	A	3	36	3.7	90	50	◎	◎
Ex. 15	A	4	38	3.8	70	50	○	○
Ex. 16	A	4	38	4.0	75	50	◎	◎
Ex. 17	A	4	38	4.2	85	50	◎	◎
Ex. 18	A	5	37	4.2	25	50	○	○
Ex. 19	A	5	37	4.5	20	50	◎	◎
Ex. 20	B	7	32	3.2	33	46	◎	◎
Ex. 21	B	7	43	3.2	53	54	◎	◎
Ex. 22	B	7	36	3.5	49	49	◎	◎
Ex. 23	B	7	43	3.5	55	54	◎	◎
Com. Ex. 8	A	1	37	2.6	132	50	◎	◎
Com. Ex. 9	A	1	37	2.8	165	50	◎	◎
Com. Ex. 10	A	1	37	3.0	205	50	◎	◎
Com. Ex. 11	A	2	37	2.8	125	50	◎	◎
Com. Ex. 12	A	2	37	3.0	130	50	◎	◎
Com. Ex. 13	A	2	37	3.3	140	50	◎	◎
Com. Ex. 14	B	6	28	2.9	83	40	◎	◎
Com. Ex. 15	B	6	44	2.9	184	51	◎	◎
Com. Ex. 16	B	6	25	3.2	89	39	◎	◎
Com. Ex. 17	B	6	45	3.2	211	51	◎	◎

Table 4

Molding conditions				Results of evaluation			
Kind of base resin	Kind of pre-expanded particles	Compression rate (%)	Heating pressure (kg/cm^2G)	Cooling time (sec.)	Density of molded article (g/liter)	Melt adhesion	Surface appearance
Ex. 24	C 8	29	3.4	16	75	◎	○
Ex. 25	C 10	23	3.4	17	80	◎	○
Com. Ex. 18	C 9	31	3.4	48	75	◎	◎
Com. Ex. 19	C 11	23	3.4	65	80	◎	◎

Table 5

Molding conditions				Results of evaluation			
Kind of base resin	Kind of pre-expanded particles	Compression rate (%)	Heating pressure (kg/cm^2G)	Cooling time (sec.)	Density of molded article (g/liter)	Melt adhesion	Surface appearance
Ex. 26	C 13	29	3.3	25	25	◎	◎
Ex. 27	C 13	40	3.3	53	30	◎	◎
Ex. 28	C 14	30	3.3	20	25	◎	◎
Ex. 29	C 14	42	3.3	48	30	◎	◎
Com. Ex. 20	C 12	28	3.3	80	25	◎	◎
Com. Ex. 21	C 12	40	3.3	130	30	◎	◎

[0071] From the above Tables, it is found that in case of using polypropylene resin pre-expanded particles having approximately identical bulk density in in-mold foaming, the lower the expandability, the more the cooling time is shortened

Example 30

[0072] The pre-expanded particles 13 obtained in Example 7 were placed in a pressure vessel, held at 25° under an air pressure of 2.5 kg/cm^{2}G for 16 hours and then allowed to stand under atmospheric pressure for 60 to 90 minutes to adjust the internal pressure of the particles to 1.45 atms. The particles were then filled in a block mold having a size of 320 x 320 x 60 mm.

[0073] Air in the mold was then expelled by steam of 1.0 kg/cm^{2}G, and in-mold foaming was carried out by heating with steam of 3.0 kg/cm^{2}G to give an in-mold foamed article having no problem in surface appearance. The cooling time at that time was 15 seconds.

[0074] The obtained in-mold foamed article was evaluated according to the above-mentioned methods with respect to density of foamed article, melt adhesion and surface appearance.

[0075] The results are shown in Table 6.

Examples 31 to 33 and Comparative Examples 22 to 23

[0076] In-mold foamed articles were prepared in the same manner as in Example 30 except that the molding was carried out under the conditions shown in Table 6, and were evaluated in the same manner.

[0077] The results are shown in Table 6.

Table 6

	Molding conditions				Results of evaluation			
	Kind of base resin	Kind of pre-expanded particles	Inner pressure of pre-expanded particles (atm)	Heating pressure (kg/cm^{2}G)	Cooling time (sec.)	Density of molded article (g/liter)	Melt adhesion	Surface appearance
Ex. 30	C	13	1.45	3.0	15	20	◎	◎
Ex. 31	C	13	1.45	3.3	23	20	◎	◎
Ex. 32	C	14	1.45	3.0	12	20	◎	◎
Ex. 33	C	14	1.45	3.3	17	20	◎	◎
Com. Ex. 22	C	12	1.45	3.0	70	20	◎	◎
Com. Ex. 23	C	12	1.45	3.3	75	20	◎	◎

Example 34

[0078] The pre-expanded particles 15 obtained in Example 9 were filled in a block mold having a size of 320 x 320 x 60 mm without imparting an inner pressure to the particles.

[0079] Air in the mold was then expelled by steam of 1.0 kg/cm^{2}G, and in-mold foaming was carried out by heating with steam of 3.0 kg/cm^{2}G to give an in-mold foamed article having no problem in surface appearance. The cooling time at that time was 25 seconds.

[0080] The obtained in-mold foamed article was evaluated according to the above-mentioned methods with respect to density of foamed article, melt adhesion and surface appearance

[0081] The results are shown in Table 7.

Examples 35 to 40 and Comparative Examples 24 to 25

[0082] In-mold foamed articles were prepared in the same manner as in Example 34 except that the molding was carried out under the conditions shown in Table 7, and were evaluated in the same manner.

[0083] The results are shown in Table 7.

Table 7

	Molding conditions			Results of evaluation			
	Kind of base resin	Kind of pre-expanded particles	Heating pressure (kg/cm^2G)	Cooling time (sec_1)	Density of molded article (g/liter)	Melt adhesion	Surface appearance
Ex. 34	D	15	3.0	25	36	◎	◎
Ex. 35	D	15	3.3	35	36	◎	◎
Ex. 36	E	16	2.5	18	36	○	◎
Ex. 37	E	16	3.0	35	36	◎	◎
Ex. 38	E	16	3.3	40	36	◎	◎
Ex. 39	B	17	2.5	30	36	◎	◎
Ex. 40	B	17	2.8	47	36	◎	◎
Com. Ex. 24	F	18	2.2	70	36	◎	◎
Com. Ex. 25	F	18	2.5	97	36	◎	◎

[0084] When the polypropylene resin pre-expanded particles the expandability of which measured when heated by steam of the melting point peak temperature of the base resin thereof is adjusted within a specific range, are used in in-mold foaming, the cooling time can be shortened and in-mold foamed articles having good melt-adhesion of the particles to each other and good surface appearance and having a uniform density extending from the surface to the inner portion can be stably obtained. Also, when a difference between the expandability when heated by steam of the melting point peak temperature and the expandability when heated by steam of "the melting point peak temperature - 10°C" is adjusted

to not more than a specific range, the cooling time can be shortened stably even if the molding conditions such as heating pressure of in-mold foaming are changed. Further, the pre-expanded particles can be suitably used in various in-mold foaming methods.

Claims

1. A process for preparing cellular moldings of a polypropylene resin comprising the steps of filling polypropylene resin pre-expanded particles having an expandability of 1.0 to 1.8 in a mold capable of being closed but incapable of being hermetically sealed, and heating said particles to fuse together, said expandability being represented by the equation:

$$\text{Expandability} = \frac{\text{Expansion ratio of polypropylene resin pre-expanded particle after steam heating}}{\text{Expansion ratio of polypropylene resin pre-expanded particle before steam heating}}$$

wherein the expandability is measured by subjecting said pre-expanded particle to said steam heating without imparting an inner pressure thereto, said steam has a temperature equal to the melting point peak temperature of said polypropylene resin measured by differential scanning calorimetry under the conditions that 1 to 10 mg of the pre-expanded particles is heated to 210°C at a rate of 10°C/minute, then cooled to 40°C at a rate of 10°C/minute and heated again to 210°C at a rate of 10°C/minute, and said expansion ratio of polypropylene resin pre-expanded particle after steam heating denotes the value measured after the restoration from shrinking by impregnating the pre-expanded particle with air.

2. The process of claim 1, wherein said pre-expanded particles to be filled in the mold have an expandability of 1.0 to 1.5, and an inner pressure is imparted thereto before filling in the mold.

3. The process of claim 2, wherein said inner pressure is imparted to the pre-expanded particles by introducing a gas into the pre-expanded particles.

4. The process of claim 1, wherein said pre-expanded particles to be filled in the mold have an expandability of 1.0 to 1.5, and are filled in the mold in the state of being compressed at a compression rate of 10 to 60 %.

5. The process of claim 1, wherein said pre-expanded particles to be filled in the mold have an expandability of 1.5 to 1.8, and are filled in the mold without applying an inner pressure-imparting procedure thereto.

6. The process of any one of claims 1 to 5, wherein said pre-expanded particles have an expandability such that the difference between said expandability measured at the melting point peak temperature of the polypropylene resin and an expandability measured at a temperature of "melting point peak temperature -10°C" is at most 0.2.

Patentansprüche

1. Verfahren zur Herstellung zellulärer Formkörper eines Polypropylenharzes, umfassend die Schritte des Füllens vorexpandierter Polypropylenharzteilchen mit einem Ausdehnungsvermögen von 1,0 bis 1,8 in eine Form, welche geschlossen, aber nicht hermetisch abgedichtet werden kann, und des Erwärmens der Teilchen, um sie miteinander zu verschmelzen, wobei das Ausdehnungsvermögen durch die Gleichung

$$\text{Ausdehnungsvermögen} = \frac{\text{Ausdehnungsverhältnis vorexpandiertes Polypropylenharzteilchen nach Dampferwärmung}}{\text{Ausdehnungsverhältnis vorexpandiertes Polypropylenharzteilchen vor Dampferwärmung}}$$

dargestellt wird,
wobei das Ausdehnungsvermögen gemessen wird durch Unterziehen des vorexpandierten Teilchens einer Dampferhitzung, ohne ihm einen inneren Druck zu verleihen, der Dampf eine Temperatur aufweist, welche gleich der Schmelzpunktpeaktemperatur des Polypropylenharzes ist, gemessen durch Differentialscanningkalorimetrie unter den Bedingungen, dass 1 bis 10 mg der vorexpandierten Teilchen auf 210°C bei einer Geschwindigkeit von 10°C/Minute erwärmt werden, dann auf 40°C bei einer Geschwindigkeit von 10°C/Minute abgekühlt werden und wieder auf 210°C bei einer Geschwindigkeit von 10°C/Minute erwärmt werden, und das Ausdehnungsverhältnis des vorexpandierten Polypropylenharzteilchens nach der Dampferwärmung den Wert, welcher nach der Wiederherstellung nach Schrumpfen durch Imprägnieren des vorexpandierten Teilchens mit Luft gemessen wird, angibt.

2. Verfahren gemäß Anspruch 1, wobei die in die Form zu füllenden vorexpandierten Teilchen eine Ausdehnungsfähigkeit von 1,0 bis 1,5 aufweisen und ihnen vor dem Füllen in die Form ein innerer Druck verliehen wird.

3. Verfahren gemäß Anspruch 2, wobei den vorexpandierten Teilchen der innere Druck durch das Einführen eines Gases in die vorexpandierten Teilchen verliehen wird.

4. Verfahren gemäß Anspruch 1, wobei die in die Form zu füllenden vorexpandierten Teilchen eine Ausdehnungsfähigkeit von 1,0 bis 1,5 aufweisen und in komprimiertem Zustand bei einer Kompressionsrate von 10 bis 60 % in die Form gefüllt werden.

5. Verfahren gemäß Anspruch 1, wobei die in die Form zu füllenden vorexpandierten Teilchen eine Ausdehnungsfähigkeit von 1,5 bis 1,8 aufweisen und ohne das Anwenden eines ihnen einen inneren Druck verleihenden Verfahrens in die Form gefüllt werden.

6. Verfahren gemäß einem der Ansprüche 1 bis 5, wobei die vorexpandierten Teilchen eine solche Ausdehnungsfähigkeit aufweisen, dass der Unterschied zwischen der Ausdehnungsfähigkeit, gemessen bei einer Schmelzpunktpeaktemperatur des Polypropylenharzes, und einer Ausdehnungsfähigkeit, gemessen bei einer Temperatur Schmelzpunktpeaktemperatur - 10°C", höchstens 0,2 beträgt.

Revendications

1. Procédé de préparation de moulages cellulaires d'une résine de polypropylène comprenant les étapes consistant à remplir un moule capable d'être fermé mais incapable d'être scellé hermétiquement par des particules de résine de polypropylène pré-expansées ayant une expansibilité de 1,0 à 1,8, et à chauffer lesdites particules pour les fondre ensemble, ladite expansibilité étant représentée par l'équation :

$$\text{Expansibilité} = \frac{\text{Rapport d'expansion des particules pré-expansées de résine de polypropylène après chauffage par la vapeur}}{\text{Rapport d'expansion des particules pré-expansées de résine de polypropylène avant chauffage par la vapeur}}$$

dans lequel on mesure l'expansibilité en soumettant lesdites particules pré-expansées audit chauffage par la vapeur sans leur conférer une pression interne, ladite vapeur ayant une température égale à la température de pic de point

de fusion de ladite résine de polypropylène mesurée par calorimétrie par balayage différentiel dans des conditions telles que 1 à 10 mg des particules pré-expansées soient chauffées à 210 °C à un taux de 10 °C/minute, puis refroidies à 40 °C à un taux de 10 °C/minute et chauffées de nouveau à 210 °C à un taux de 10 °C/minute, et ledit rapport d'expansion des particules pré-expansées de résine de polypropylène après chauffage par la vapeur signifie la valeur mesurée après la restauration depuis le retrait en imprégnant les particules pré-expansées par de l'air.

2. Procédé selon la revendication 1, dans lequel lesdites particules pré-expansées devant remplir le moule ont une expansibilité de 1,0 à 1,5 et une pression interne leur est conférée avant le remplissage du moule.

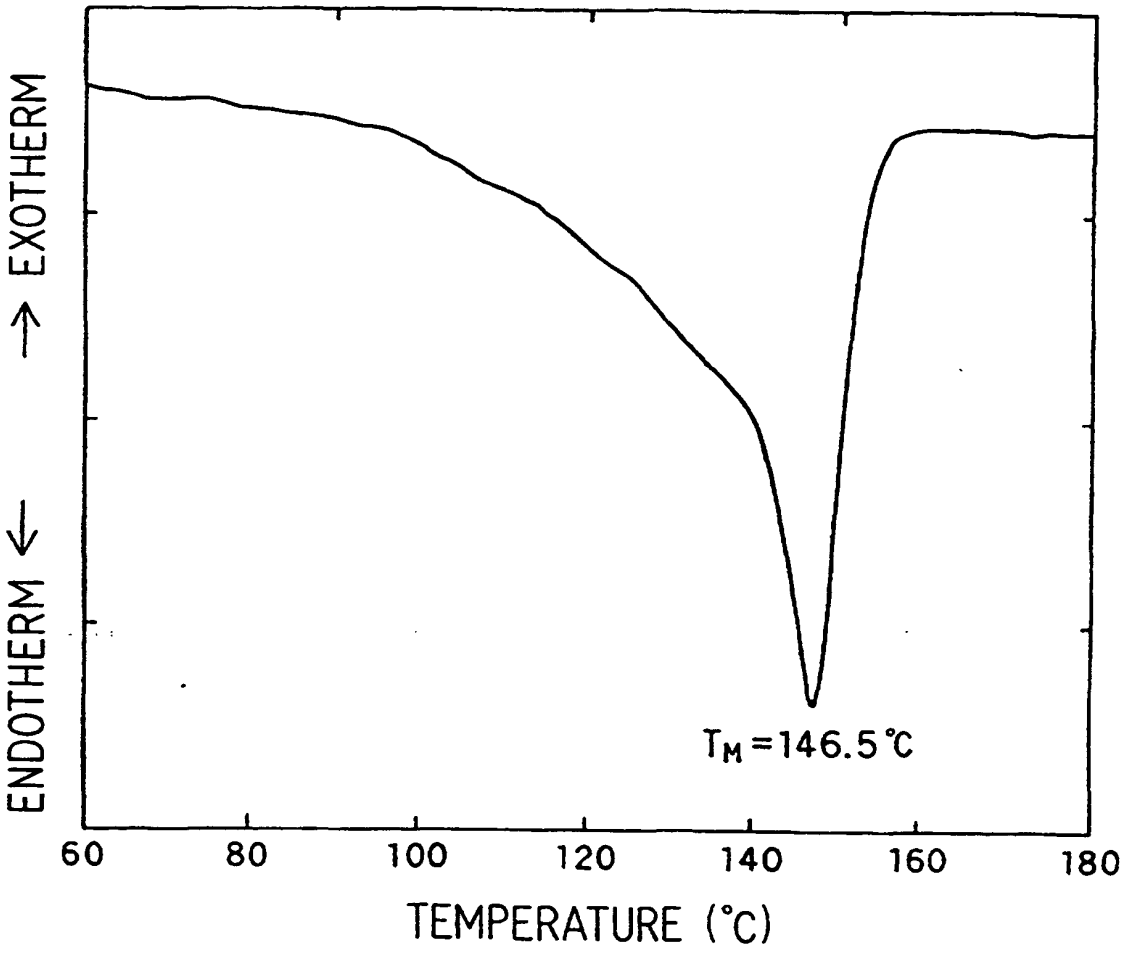
3. Procédé selon la revendication 2, dans lequel ladite pression interne est conférée aux particules pré-expansées en introduisant un gaz dans les particules pré-expansées.

4. Procédé selon la revendication 1, dans lequel lesdites particules pré-expansées devant remplir le moule ont une expansibilité de 1,0 à 1,5, et remplissent le moule dans un état d'être compressées à un taux de compression de 10 à 60 %.

5. Procédé selon la revendication 1, dans lequel lesdites particules pré-expansées devant remplir le moule ont une expansibilité de 1,5 à 1,8 et remplissent le moule sans appliquer le mode opératoire consistant à leur conférer une pression interne.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel lesdites particules pré-expansées ont une expansibilité telle que la différence entre ladite expansibilité mesurée à la température de pic de point de fusion de la résine de polypropylène et l'expansibilité mesurée à une température de "température de pic de point de fusion -10 °C" soit au plus de 0,2.

FIG. 1


→ EXOTHERM
ENDOTHERM ←
T_M = 146.5 °C
60
80
100
120
140
160
180
TEMPERATURE (°C)