

Method for continuous PMI foam production

Field of the invention

5 The present invention relates to a novel process for the continuous manufacture of PMI foam blocks. This process has high flexibility in respect of the size of the blocks. This novel process begins by bonding the ends of individual prepolymerized PMI blocks to one another, preferably by means of hot-plate welding, and then passes the blocks into an NIR heating unit. The PMI polymer here foams continuously during passage through the said unit. The PMI foam is discharged at the
10 end in the form of continuous material and can be cut or sawn into individual pieces of any desired length and shape. This process is advantageous in comparison with the continuous procedure in that the PMI foam material is almost stress-free and has a very uniform, closed-cell pore structure. At the same time, uniform density distribution is achieved over the thickness of the block, since the foaming procedure does not proceed from the outside to the centre of the block, but instead the
15 volume of the polymer is increased uniformly.

Prior art

It is known in the prior art that poly(meth)acrylimide foams (PMI foams) can be produced batchwise
20 in the form of blocks. This process begins by copolymerizing (meth)acrylic acid and (meth)acrylonitrile to give a precursor which is already in appropriate sheet form. The copolymer is then subjected to ring closure to give the imide. A blowing agent present in the reaction mixture provides appropriate foaming on heating. For the purposes of this invention, the term (meth)acrylimide describes either methacrylimides or acrylimides. The same applies to the term
25 (meth)acrylic acid, which comprises both acrylic acid and methacrylic acid. DE 1 817 156 has already described a process by which foamable plastics are produced in sheet form by polymerizing mixtures of methacrylonitrile and methacrylic acid between two glass plates sealed with a flexible bead. A blowing agent, namely formamide or monoalkylformamide, has already been added to the starting mixture. Free-radical generators are moreover present, for example in
30 the form of a two-component mixture of tert-butyl perpivalate and benzoyl peroxide. The foaming of the individual sheets takes place thermally in an oven at a temperature of from 170 to 300°C. It is difficult to achieve uniform polymerization, since the temperature can very easily exceed the intended temperature. It is therefore necessary to monitor temperature variations very precisely and use alternating cooling or heating phases to compensate these. This mostly leads to irregular
35 pores and to stresses within the foam matrix. In particular, disadvantages of this type occur to a greater extent when the thickness of polymer sheets is greater than 30 mm.

EP 1 175 458 describes isothermal production of thick blocks. This is achieved by using at least four different initiators. The initiator described as active at the highest temperature has a half-life

time of 1 h at from 115°C to 125°C and acts primarily during a final conditioning process, rather than during the foaming process. This process, too, comprises batchwise foaming in an oven. Furthermore, although this process can foam relatively thick materials, because the foaming proceeds inwards from the outside, an insulating layer forms at the surface and retards the heating of the centre of the block, and in the case of very thick blocks likewise leads to an irregular pore structure and to stresses in the material.

DE 3 630 930 (Röhm GmbH) describes another process for foaming the abovementioned copolymer sheets made of methacrylic acid and methacrylonitrile. Here, the sheets are foamed with the aid of a microwave field. A factor that has to be considered here is that the sheet to be foamed, or at least the surface thereof, must be heated in advance up to or above the softening point of the material. These conditions naturally also cause onset of foaming of the material softened by the external heating, and it is therefore impossible to control the foaming process solely by using the effect of a microwave field, and additional external control is required from an ancillary heating system. The normal single-stage hot-air process is therefore supplemented by a microwave field in order to accelerate foaming. However, the microwave process has proved to be excessively complicated and therefore irrelevant for practical purposes, and currently remains unused.

Object

In the light of the prior art discussed, it was therefore an object of the present invention to provide a novel process which can foam PMI blocks continuously. In particular, the intention is to permit foaming of the blocks in the form of continuous material.

Another object of the present invention was to provide a process which can in particular foam thick PMI blocks to give a very uniform pore structure. The intention is to carry out the subsequent cooling process in a manner that avoids intrinsic thermal stress in the foam block, by conditioning of the foam.

A further intention is that the process is simple to carry out, saves energy, and requires no major capital expenditure. The process is also intended to be adaptable so as to permit achievement of comparable results with materials having different properties and having different thicknesses.

Other objects not explicitly discussed here can also be derived from the prior art, from the description, from the claims or from the inventive examples.

Achievement of object

The objects described are achieved through a novel process for foaming P(M)I blocks by foaming P(M)I blocks by irradiation with NIR radiation with a wavelength of from 0.78 to 1.40 μm in an infra-red heating unit.

The expression P(M)I here means either polymethacrylimides (PMI) or polyacrylimides (PI). The term NIR radiation means what is known as near-infra-red radiation. According to the invention, PMI blocks are preferred to PI blocks because of low residual monomer content and the markedly lower toxicity of the said residual monomers. These PMI foams are normally produced in a two-stage process: e.g. production of a cast polymer and foaming of this cast polymer. The present invention relates to this foaming of the cast polymer, but the invention is not to be interpreted as restricted to cast polymers, and can also be applied to alternative methods for producing P(M)I blocks.

Production of the cast polymer begins by producing monomer mixtures which comprise (meth)acrylic acid and (meth)acrylonitrile, preferably in a molar ratio of from 2:3 to 3:2, as main constituents. It is also possible to use other comonomers, e.g. esters of acrylic or of methacrylic acid, styrene, maleic acid or itaconic acid or anhydrides thereof or vinylpyrrolidone. However, the proportion of the comonomers here should not be more than 30% by weight. It is also possible to use small amounts of crosslinking monomers, e.g. allyl acrylate. However, the amounts should preferably be at most 0.05% by weight to 2.0% by weight.

The copolymerization mixture also comprises blowing agents which at temperatures of about 150 to 250°C either decompose or vaporize and thus form a gas phase. The polymerization process takes place below this temperature, and the cast polymer therefore comprises a latent blowing agent. The polymerization process advantageously takes place in block form between two glass plates or by means of an in-mould-foaming process. The production of PMI blocks of this type for foaming is in principle known to the person skilled in the art and can be found by way of example in EP 1 444 293, EP 1 678 244 or WO 2011/138060. Acrylimide foams (PI foams) are considered to be analogous to PMI foams in terms of production and processing.

The process of the present invention in particular uses what is known as IR-A radiation, i.e. radiation in the short-wavelength region of NIR radiation. The wavelength of this radiation is from 0.78 to 1.40 μm .

In the process according to the invention it is preferable that the ends of a plurality of P(M)I blocks are bonded to one another prior to the irradiation with the NIR radiation mentioned. The irradiation with the NIR radiation then preferably takes place in a tunnel. It is therefore in particular possible to carry out the entire foaming process continuously.

It is particularly preferable that the ends of the P(M)I blocks are bonded to one another by means of hot-plate welding. An advantage of a welding process, in particular of a hot-plate welding process, in comparison with an adhesive bonding process here is that this joint is preferably no longer discernible in the P(M)I foam blocks subsequently obtained, and production of continuous material by continuous operation of the claimed process actually gives a material with a uniform quality.

It is preferable that the claimed process has the following steps:

- a) hot-plate welding for bonding the ends of P(M)I blocks,
- b) transferring the PMI blocks into an infra-red heating unit, and this transfer in particular takes place continuously,
- c) passage through the infra-red heating unit and irradiation with NIR radiation in the wavelength range mentioned for controlled foaming,
- c1) optional subsequent, uniform cooling to avoid thermal stress due to cooling,
- d) sawing or cutting the foamed P(M)I blocks apart, e.g. to a desired length, and
- e) optionally cooling further and removing the finished block product.

It is preferable that the cooling of the foamed block product takes place in step c1). However, it is also possible as an alternative to delay complete cooling to step e) or to carry out cooling in step c1) to a slightly increased temperature and finally to carry out cooling in step e) to a removal temperature.

It is preferable that the intensity distribution of the NIR radiation in the infra-red heating unit is selected in such a way as to achieve the highest radiation intensity in the centre of the P(M)I block. This can be achieved through individual controllable/regulatable infra-red sources in the infra-red heating unit. Local differences in intensity distribution are thus possible.

A further improvement in the quality of the foam can be achieved by passing the material, between step c) and step d), through an oven in which the PMI foam is conditioned. This oven can likewise have been equipped with NIR lamps. However, it is generally a conventional oven, without any radiation source. In this type of variant, the material in particular passes through the cooling step in step e), irrespective of whether the optional step c1) has been carried out or not.

A major advantage of the claimed process is that it can be carried out in an environmentally compatible manner and with very short cycle times, while at the same time combining a plurality of operations within a process. Surprisingly, it has been found that the non-aggressive heating of the material in step c) can bring about plastic deformability through uniform heat input, while avoiding any adverse effects on the material. Rapid and, in particular, uniform foaming is therefore possible. In particular, correct conduct of the present process avoids the adverse effects that can be observed by way of example on heating in an oven and that affect the subsequent surface of a rigid

foam. The thermal radiation in the NIR spectral region used undergoes no absorption while penetrating the gas phase of the foam cells as they form, and brings about direct heating of the P(M)I, inclusive of the cell-wall matrix that is being formed.

- 5 The claimed process can be carried out with short cycle times, economically and in an environmentally compatible manner. Because the heating by the radiation mentioned can be carried out relatively rapidly, and in particular if the temperature distribution and intensity distribution associated with the NIR radiation are suitable, where the person skilled in the art required little resource to derive this suitable distribution, the heat distribution achieved in the entire
10 workpiece is uniform, avoiding stress. The intensity of the radiation here can be varied within the range mentioned as required by the P(M)I used, and in particular can be varied in relation to the thickness of material used.

- In one particular embodiment of the invention, the individual P(M)I foam blocks are transferred after
15 step d) or e) into a further shaping mould for further processing. To this end, prior to transfer into the shaping mould the individual P(M)I foam blocks can be separated by means of a horizontal saw cut to give slab product. The said shaping mould can by way of example be used to produce, from the foam blocks or from slabs produced therefrom, composite materials with one or two outer layers, for example made of fibre-reinforced thermoplastic or resins. As an alternative, or in
20 addition, the P(M)I foam blocks or slabs produced therefrom can be compacted to some extent or converted to a usage form, for example an open hollow profile. It is also possible by way of example to produce closed hollow profiles from two P(M)I foams thus shaped.

- In one very particular embodiment of the present invention, the shaping mould has equally been
25 equipped with NIR heating technology. Details of this type of shaping process can be found in the provisional application US 61/675,011.

- The present invention also provides, in addition to the process described, P(M)I foam materials produced by the claimed process. A feature of these P(M)I foam materials in comparison with
30 corresponding materials of the prior art is that they exhibit very uniform pore structure and relatively little thermal impairment, e.g. in relation to yellowing.

- In principle, the P(M)I foams produced according to the invention are very versatile. Particular examples of application sectors are automobile construction – for example in the construction of
35 bodywork or in interior cladding – aerospace technology, shipbuilding, construction of rail vehicles, mechanical engineering, medical technology, the furniture industry, in battery boxes, in lift construction, air ducts in air-conditioning systems, or in the construction of wind turbines, e.g. in the form of aerodynamic module in wind-turbine rotor blades.

The PMI foam material produced according to the invention can also comprise the following as required by intended use: fire-protection additives, colorants, inorganic fillers and/or process additives.

5 Example

Continuous foaming of PMI block polymer:

PMI block polymer, in this case ROHACELL RIMA, was foamed continuously at a thickness of 33 mm with a throughput speed of 5 cm/min in a heating section equipped with NIR sources.

10 Surface temperatures were in the region of the foaming temperature at 200°C and the intensity of the IR heating field was about 50% of maximum power.

Surprisingly, the foaming procedure was successfully controlled through appropriate selection of temperature and intensity in such a way that foaming of the block polymer proceeded from the inside outwards.

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Claims

1. Process for foaming P(M)I blocks, characterized in that the P(M)I block is foamed by irradiation with NIR radiation with a wavelength of from 0.78 to 1.40 μm in an infra-red heating unit.
- 5 2. Process according to Claim 1, characterized in that the ends of a plurality of P(M)I blocks are bonded to one another prior to the irradiation with NIR radiation, that the irradiation with NIR radiation takes place in a tunnel, and that the entire foaming process is carried out continuously.
- 10 3. Process according to Claim 2, characterized in that the ends of the P(M)I blocks are bonded to one another by means of hot-plate welding.
4. Process according to any of Claims 1 to 3, characterized in that the process has the following steps:
- 15 a) hot-plate welding for bonding the ends of P(M)I blocks,
b) transferring the PMI blocks into an infra-red heating unit,
c) passage through the infra-red heating unit and irradiation with NIR radiation for controlled foaming,
d) sawing or cutting the foamed P(M)I blocks apart and
20 e) optionally cooling and removing the finished block product.
5. Process according to Claim 4, characterized in that after step c) the P(M)I blocks are uniformly cooled.
- 25 6. Process according to any of Claims 1 to 5, characterized in that the arrangement of the NIR lamps in the infra-red heating unit is such that the highest radiation intensity is achieved in the centre of the P(M)I block.
7. Process according to any of Claims 1 to 6, characterized in that the production of the P(M)I
30 blocks also takes place continuously.
8. Process according to any of Claims 1 to 7, characterized in that PMI blocks are foamed.
9. Process according to Claim 4, characterized in that the material passes, between step c)
35 and step d), through an oven in which the PMI foam is conditioned.
10. Process according to Claim 4, characterized in that the individual P(M)I foam blocks are transferred after step d) or e) into a shaping mould.

11. Process according to Claim 10, characterized in that, prior to transfer into the shaping mould, the individual P(M)I foam blocks are separated by means of a horizontal saw cut to give slab product.

5 12. Process according to Claim 10 or 11, characterized in that the shaping mould has likewise been equipped with NIR heating technology.

13. Process according to any of Claims 1 to 12, characterized in that the P(M)I also comprises fire-protection additives, colorants, inorganic fillers and/or process additives.

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14. P(M)I foam material, characterized in that this has been produced by a process according to at least one of Claims 1 to 13.