METHODS AND APPARATUS FOR PRODUCING FOAMED THERMOPLASTICS MATERIAL AND ARTICLES

The invention concerns a production of foamed thermoplastics materials in which the thermoplastics material to be foamed is mixed with a solvent. The resultant gel is compressed to form a pre-form or precursor which is heated. The use of polyethersulphone (P.E.S.), with acetone and/or butanone is described. In addition to the description of methods of producing foamed thermoplastics materials a description is also made of methods of forming composite, laminated, structures using foamed thermoplastics materials with other laminae.
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DESCRIPTION

TITLE: METHODS AND APPARATUS FOR PRODUCING FOAMED THERMOPLASTICS MATERIALS AND ARTICLES

TECHNICAL FIELD.

The invention concerns methods and apparatus for producing foamed thermoplastics materials and articles.

BACKGROUND ART.

The consistent production of foamed thermoplastics materials (for example foamed polyethersulphone - hereinafter referred to as P.E.S. - polysulphone, polycarbonates and the like) present several problems. One great problem is the production of a suitable preliminary material, precursor or pre-form for the foaming process.

In general a foamed thermoplastics material is formed by heating a pre-form or precursor material leading to a substantial expansion in its volume, and a substantial decrease in its density. To produce consistently high quality foamed thermoplastics material it is necessary that the pre-form material contains no large, visible, random, irregular holes which would lead to irregularities in the size and structure of the cells of the finished, foamed material. Such holes are hereafter referred to as 'voids'.

The known techniques for producing pre-form materials essential comprise soaking granules of a thermoplastics material to be foamed in a solvent for a considerable period of time (say 170 to 350 hours) and then heating the resultant gel to produce a foam of expanded material with a density substantially less than that of the original thermoplastics material. For example when foaming P.E.S.
having an original density of approximately 1370 kgs/m$^3$, a gel formed by steeping granules of P.E.S. in acetone and heating produces an expanded, foamed material with a density of approximately 100 kgs/m$^3$.

The main problem with this method is that air becomes trapped in the gel pre-form material and causes irregularities in the size and structure of the cells in the finished product; the size of holes produced is usually so large that the material is of no use for applications which require a uniform and readily reproducible product.

It is known that if the gel pre-form is allowed to dry for a considerable period of time (two to three months) after steeping, it is possible to produce a finished article having smaller and more regular cells. However large irregular 'voids' still occur in such materials.

DISCLOSURE OF INVENTION

According to one aspect the invention provides a method of producing foamed thermoplastics materials in which the thermoplastics material is mixed with a solvent and the resultant gel is compressed to form a pre-form material which is then heated.

Fillers, reinforcing fibres of glass, carbon and the like, and/or colourants may also be added.

Chemical blowing or foaming agents may be incorporated in the compression stage. These agents do not generate gas until the pre-forms are heated.

The pre-form material produced may be expanded in a mould containing layers of continuous reinforcement material.
e.g. glass - or carbon-fibre reinforced materials.

A random array of reinforcing fibres may be added to
the thermoplastics material during its production to
increase its structural stability.

Compression of the thermoplastics/solvent mix may
be achieved by making use of a press or a two or three
roll compounding mill (for one-off pre-form production),
or of an extruder/die combination (for continuous pre-
form production).

Other aspects of the invention provide foamed
thermoplastics materials formed in accordance with
the above methods and articles made thereof.

Experiments we have performed and which exemplify
methods embodying the invention will now be described
briefly.

The experiments we carried out make use of poly-
ethersulphone (P.E.S.), (a thermoplastics material of
the general formula:

\[ \text{of the three following commercially available grades:} \]

PES 200P (with a reduced viscosity of 0.39–0.43)
PES 300P (with a reduced viscosity of 0.46–0.50)
PES 500P (with a reduced viscosity of 0.34–0.38)

and a normal glass transition temperature (TG) of approx-
imately 222°C. Other grades and copolymers of the above
may be used.

Similar results can be expected from polysulphone
(of the general formula:

\[ \text{and having a normal glass transition temperature of} \]

approximately 174°C, or with polycarbonates.
EXAMPLE I

Granules of P.E.S. 200P were soaked for two weeks in acetone of industrial quality and the resultant gel compressed in a compression moulding press at room temperature. The pressure applied to the gel was such that it was flattened to approximately 1.5 mm in thickness. The flattened material was removed from the press, folded in four, and then returned to the press and pressed again to the same thickness. Folding and repressing to the same thickness was continued until a flat sheet was obtained which to external inspection was free of 'voids'.

A number of these sheets were stacked on one another and pressed in a semi-positive compression mould tool at room temperature so that a sheet of even thickness (approximately 5 mm) was obtained. The sheet was allowed to dry at room temperature for 48 hours.

After drying the sheet was heated in a microwave oven so that it foamed, and the resultant material inspected. The foamed material produced by this method showed a significant improvement over those produced by the known processes but still included 'voids'. Before foaming took place in the microwave oven it was noted that some 'voids' had re-appeared in the pre-form material due, it is thought, to its internal contraction during drying.

EXAMPLE II

The gel material produced by the method of Example I was divided into small charges - (about 12 mm³ to 25 mm³) -and
loaded into a conventional two-roll compounding mill, the rolls of which had been set in motion. The temperature of the rolls at the beginning of the run was approximately 20°C. The material was compounded into a continuous crape, a bank of excess material (the thickness of which could be varied in accordance with the spacing of the rollers) was removed as a crape of reasonably constant thickness. It was found that a thickness of crape less than 3mm was best if the contraction voids thought to be produced on drying were to be minimised.

EXAMPLE III

P.E.S. 200P powder was soaked in acetone for 1.5 hours. The resultant gel was opaque white in colour and was passed to the two-roll mill. As the temperature of the mill rose the crape material first became translucent white and then cleared appearing to be of a similar consistency to that produced in Example I.

EXAMPLE IV

A mixture of 99% w/w P.E.S. 200P powder and 1% SYLOID 72 (a finely divided silica, foam nucleating agent sold by W.R. Grace) was steeped acetone for 1.5 hours and then passed to the two-roll mill as with Example II.
EXAMPLE V

P.E.S. 200P powder was treated with acetone until saturated and the resultant gel split into two. Each half was processed in the two-roll mill. In both cases the opacity of the material cleared as the temperature of the mill rose. The second charge appeared to be of better quality than the first and this is thought to be because the mill rolls had been warmed up whilst processing the first charge.

The crape materials produced by the methods of Examples II to V were heated in a microwave oven and were shown to have excellent foaming characteristics with a low proportion of 'voids'.

It is thought that the remaining voids were again caused by differential contraction of the skin of the crape and its core during drying. It was discovered that this failing was overcome by allowing the crapes formed in accordance with the methods of Examples II to V to dry out for not less than 48 hours (such that the acetone level in them reduced to between 10-13% w/w) and then loading a number of dried crapes into a pre-heated compression moulding tool at 120°C - 180°C (the temperature selected being proportional to the percentage of acetone in the crapes compressing the crapes at a pressure of 6.4 MPa and then holding the pressure while cooling to below the boiling point of acetone (70°C). This produces a pre-form having no visible irregularities, such as voids, and consequently foams from such pre-forms are also free of voids.
It was found that allowing the pre-forms to dry for 30 days reduced the acetone level in them to 6% w/w and final densities of 55 kg/m$^3$, 115 kg/m$^3$ and 200 kg/m$^3$ were obtained for the foamed materials with foaming temperatures of 200°C, 160°C and 130°C respectively. The foamed produced obtained had closed cells and the cells were of a regular dodecahedral shape.

We have found that certain other ketone solvents e.g. butanone may be used either alone or mixed with one another.

In addition to the use of the foaming agent described above, our experiments with other foaming agents in particular that product sold by Messrs. Fisons Ltd. under the Trade Name Genitron AF100 worked well with PES.

Consideration of the results of our experiments led us to formulate various methods of making foamed thermoplastics materials which will now be described with reference to the accompanying drawings, in which:

**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 diagrammatically illustrates one way of making pre-form material embodying the invention.

Fig. 2 diagrammatically illustrates another way of making pre-form material embodying the invention.

Fig. 3 diagrammatically illustrates apparatus for making foamed thermoplastics materials embodying the invention.
Fig. 4 illustrates a method of forming composite foamed/fibre-reinforced thermoplastics materials.

Fig. 5 diagrammatically illustrates one apparatus for effecting manufacture of composite foamed/fibre-reinforced thermoplastics materials; and

Fig. 6 diagrammatically illustrates another form of apparatus for effecting continuous production of a composite foamed/fibre-reinforced thermoplastics material sheet.

MODES FOR CARRYING OUT THE INVENTION

Figure 1 shows a mixing bowl 10 in which powdered P.E.S. 200P is steeped in a solvent, preferably acetone together with a foaming agent (SYLOID 72 for example) and colouring agents and/or fillers as required. As soon as mixing has been completed the content of the bowl 10 is transferred to a member 11 of a compression tool 12 in which it is subjected to pressure by a member 13. When the gel placed in the tool 11 has been compressed to approximately 1.5 mm in thickness member 13 is retracted and the flat sheet removed from press 12. The sheet is folded in four and reinserted in the member 11. After a number of passes the sheet is removed and stored and other sheets prepared in the same way. When a number (say ten), sheets have been prepared in this way they are stacked one on another in member 11 and the stack compressed to a thickness of not more than 5 mm, preferably not more than 3 mm. The compacted stack of sheets is a pre-form material, which may be utilised to form a foamed thermoplastics material article as will be described below.
Figure 2 shows another form of apparatus for preparing a pre-form material embodying the invention. This apparatus comprises a bowl 20 in which powdered P.E.S. is mixed with acetone (and any other suitable filler) in the proportions 500:300 (:5) parts by weight. After thorough mixing in the bowl 20 the resultant gel is passed to a two-roll mill 21 having rolls 22 and 23 as shown which are driven in contra-rotation. There is a build up of compressed material on one of the rolls (say roll 22) and continuous compaction of the material passing through the mill at 24 in the known way. After the mill has been run for 5-10 minutes a knife 25 is used to lift from the roll 22 a sheet of pre-formed material. This sheet of pre-formed material is then placed on one side and a further sheet of pre-formed material prepared in the same way. A number of the sheets prepared in this way are then passed through a further compaction process in a compression moulding tool (as, for example shown in Fig. 1 at 12) or through a further multi-roll mill processing.

It is possible by using multi-roll mill processing to provide continuous production of a pre-form material for example with a multi-roll mill by providing to the input of the mill a continuous supply of the gel material and extracting from the mill the pre-form material.

Figure 3 shows an extruder 30 to be provided with a jacket 31 through which water (which preferably is heated and/or cooled to maintain a temperature of approximately 40°C in the extruder) is passed via conduits 32.

Extruder 30
includes a trough 33 to which a mixture 34 of P.E.S. powder saturated with acetone (or with a mixture of acetone and other agents as discussed above) is fed. Mixture 34 is preferably formed on a continuous basis and passed directly to trough 33.

After passage through trough 33 the mixture falls into a screw 35 and is fed through the extruder to an outlet 36. At the outlet 36 the mixture 34 passes through a die 37 and is then fed to a dryer/extractor 38 (operating at a temperature somewhat less than 70°C).

The pre-form issuing from the dryer 38 is formed on a continuous basis and may be used in accordance with the methods described below. Alternatively it may be thereafter passed directly between a pair of pinch rollers 39 heated to a temperature of approximately 150°C (for example electrically or by heated oil passed thereto via conduits 40) so that the pre-form passed to the rollers 40 emerges as a finished foamed thermoplastics sheet material 41 on a continuous basis. When operating in this way it is thought desirable to provide a pair of spaced, chilled sizing rollers 42 as shown to limit the size of the expanded sheet being produced.

It is preferred that the temperature of the heated pinch rollers when using blends containing high levels of plasticiser (with a volatile content in the blend of 10 to 12%) are of the order of 100 to 120°C. With lower levels of volatiles present in the blend, higher temperatures are required for example with P.E.S./acetone blends having a total volatile content of 3 to 6% temperatures in the range of 160 to 180°C are preferred.
It will be readily appreciated that in place of the extruder 30 other suitable compounding devices may be used.

The pre-form material passed to the pinch rollers 39 from the extruder 30 becomes flexible at a relatively low temperature, approximately 40°C, and this feature of it enables the production of composite structures of foamed P.E.S. with glass or other fibre materials such as illustrated in Figure 4. In such an arrangement a length of P.E.S. pre-form 43 is sandwiched between two layers 44 of glass or other fibre as shown. Heating of the composite material, for example in a microwave oven - or more preferably directly with hot air and/or steam enables the formation of a solid structure. When heated, the P.E.S. expands to completely fill the gap between the two outer layers (Figure 4b).

The three parts may be heated to approximately 40°C and bent as shown in Figure 4g prior to heating in a mould to achieve a non-flat composite structure of a desired shape.

The composites in such an arrangement are coated on their facing surfaces with a P.E.S. solution to enable bonding between the various laminae.

This technique may be used to form composite 'sandwich' constructions in which a layer of any material, for example metal, glass - or carbon-fibre matrices or glass - or carbon-fibre-reinforced thermoplastics material laminates are bonded to the core of foamed thermoplastics material as that core is foamed. This is of particular advantage in
forming various articles.

An example of the technique will now be described with reference to Figure 5.

It is preferred in such cases for the solvent plasticised layer or film used as the interface between the foamed core material and the outer layers be derived from a partially dried solution of P.E.S. in N Methyl-2-Pyrroolidone (N.M.P.) (or N.M.P. diluted with a liquid hydrocarbon such as Xylene or Toluene - preferably the ratio of N.M.P. to hydrocarbon being 2:1 or greater). Solvent mixtures such as Dichloromethane, or Dichloromethane with N.M.P., 1,1,2, Trichloroethane or combination thereof may also be used.

The solution is spray, roll or brush coated as shown at 48 onto the P.E.S. containing layer 46 then partially heat dried (for example with N.M.P. solutions, at temperatures of between 60°C and 200°C for 10 minutes) the drying temperature being dependent on the foaming temperature and solution composition.

Two dried skins 46 are then laid-up in a mould 48 to be used with a P.E.S. pre-form 49 therebetween. The mould 48 is placed between the platens 50 of a heated compression moulding machine (or in an air circulating oven or in a heated autoclave - the moulds in the latter cases being suitably clamped) and the temperature of the heating system utilised is set to operate at the desired foaming temperature (in the range of 100°C and 210°C).
On foaming the pre-form 49 expands and the surface of
the foam contacts the plasticised P.E.S. film 45 which
bonds the foam surface to the layer 46. An extended cycle
time is used to remove any excess solvent from the skin
46 and foamed material.

Multi-layered structures may similarly be produc-
ed such as a film/pre-impregnated foam/pre-impregnated
film sandwich construction. Such materials are useful
for aircraft and ship panels.

The layer 46 may be pre-produced laminated, fibre
re-inforced P.E.S. composite, or a metal such as alumi-
nium, stainless steel, mild steel. If layer 46 is a metal
it is preferably spray, brush or roll coated with a
layer of P.E.S. solution which is dried and then baked
onto the surface of the metal. A typical cycle for
batch production of P.E.S. prepared metal surfaces being
10 minutes at 90°C followed by 10 minutes at 380°C.
The prepared surface of the metal may then be treated in
a similar manner to a normal P.E.S. containing skin.

By using pre-treated metal surfaces such as phos-
phated mild steel or an aluminium surface with a chrom-
ate finish (e.g. I.C.I.'s ALOCROM 1200), the final bak-
ing temperature may be reduced from 380°C to below
300°C.

For skins containing no P.E.S. a curing resin
having a suitable curing temperature may be substitu-
ted for the P.E.S. solution. For example copper may
be bonded to the foamed pre-form with a thermosetting
epoxy resin such as Aruldite MY750 in printed circuit
board applications, in
particularly in "low loss" printed circuit boards for antennae.

Figure 6 discloses a modified form of the apparatus of Figure 3 for use in forming continuous lengths of foamed/fibre re-inforced laminate constructions. Parts of this apparatus common to the arrangement of Figure 3 are given the same reference numerals and will not further be described.

With the arrangement of Figure 6 the pre-form issuing from the dryer 38 is passed to the pinch-rollers 39 which also have fed to them lengths of fibre-reinforced laminates 60 from rollers 61 as shown. The surfaces of the lengths 60 which contact the pre-form passed to the rollers 39 are coated with an adhesive layer, preferably a solution of P.E.S. in N.M.P. diluted with Xylene or Toluene, at coating stations 62. On passing through the heated pinch rollers 29 a continuous length 63 of composite material formed with an inner core of foamed thermoplastics material and outer layers of fibre-reinforced thermoplastics laminates is produced. Sizing rollers 42 again control the thickness of the finished product.

If the pre-form produced in accordance with the above methods is not to be used immediately it is preferred that it is cooled rapidly to a temperature below the boiling point of the volatile plasticiser included in it. For example with P.E.S./acetone pre-forms, the pre-forms, if not to be used immediately, should be cooled to below 70°C. It is essential that pressure be maintained on the pre-form.
during this rapid cooling period.

It is preferred that if the pre-form is to be foamed into a shell or cavity the dimensions of the shell or cavity should be such that the pre-form expands to sixteen times its original volume during foaming.

It will be appreciated that modifications may be made to what has been described above without departing from the scope of the present invention. In particular the arrangement of Fig. 1 lends itself to the incorporation in the P.E.S./solvent mix of chopped glass - or carbon-fibres (3 mm or longer) leading to an increase in the strength of the foamed product finally produced.

With the arrangement of Figure 3 it is possible to replace the extruder shown with a vented extruder and use a higher boil point plasticiser (such as a long-chain aliphatic oxide or epoxy) such that acetone is removed at the vent and plasticisation of the P.E.S. achieved by the second plasticiser. In this way it is possible to produce plasticised P.E.S. which has, to our knowledge, not yet been achieved by a melt processing technique.

Although described with reference to a mix of P.E.S. and acetone it will be seen that other types of thermoplastics materials may be used for example polysulphone and polycarbonates.
INDUSTRIAL APPLICABILITY.

The adoption of the above methods enable the production of a precursor or pre-form material which may be subsequently processed, following the introduction of the solvent to the thermoplastics material, in significantly less time than has been possible until now. Other advantages are that the working temperature for forming the finished material is substantially lower than might be expected and that a consistent and reproducible foamed material is obtained, that is to say, a foamed material is obtained having a consistent, uniform cell structure.

With the arrangement of Figure 3 for example the overall production time from start of process to issuance of finished product can be as little as 15 minutes.

Apart from the above noted advantage of being produced substantially more quickly than might otherwise be the case it is noted that the finished foam products produced by the methods embodying this invention are generally safer than the foamed products formed by conventional techniques in that they appear to have a much higher burning point and are significantly less liable, when alight, to give off toxic gases.

Another advantage that the described processes have is that the temperature used in them is significantly lower than would have been anticipated. The melt temperature of P.E.S. is approximately 300°C and it will be noted that in the processes described the highest temperature used is 180°C.
CLAIMS

1. A method of producing a foamed thermoplastics material in which a thermoplastics material in granular or powder form is mixed with a solvent and the resultant gel is compressed to form a pre-form which is then heated.

2. A method according to claim 1 in which a foaming or nucleating agent is added to the thermoplastics material and solvent as they are mixed.

3. A method of producing foamed P.E.S. materials in which powdered P.E.S. material is mixed with acetone or butanone, in which the resultant gel is compressed to form a pre-form and in which the pre-form is heated.

4. A method according to any one of the preceding claims, in which the gel formed by mixing the thermoplastics material with the solvent is compounded by repeated compression in a compression moulding tool, the compressed material being folded between repeated operations of the moulding tool.

5. A method according to any one of claims 1-3 in which the gel formed by mixing the thermoplastics material with the solvent is compounded by passage through a two-roll mill, the compounded material being extracted from the mill.

6. A method according to claim 4 or claim 5 in which layers of the compressed or compounded material are stacked in a compression moulding tool and the tool is operated to produce the pre-form material.
7. A method according to any one of claims 1 to 3 in which the mix of thermoplastics material and solvent is compressed by passage through an extruder and die.

8. A method of making a foamed thermoplastics article in which a pre-form formed in accordance with the method of any one of the preceding claims is placed in a mould and heated.

9. A method of making a continuous length of foamed thermoplastics material in which a pre-form formed in accordance with the method of claim 7 is dried and passed between a pair of heated pinch rollers.

10. A method of making a composite structure in which a pre-form formed in accordance with any one of claims 1 to 9 is when foamed brought into intimate contact with a surface of a layer which surface has been coated with an adhesive.

11. A method according to claim 10, in which the layer is a fibre-reinforced thermoplastics material in a solvent.

12. A method according to claim 11, in which the layer, the adhesive and the pre-form are of the same thermoplastics material.

13. A method according to claim 12, in which the pre-form material and the layer are of P.E.S., and in which the adhesive is a blend of P.E.S. and N Methyl-2-Pyrrolidone.

14. A method according to claim 13, in which the adhesive is a blend of P.E.S. and N Methyl-2-Pyrrolidone diluted with Xylene or Toluene.
**INTERNATIONAL SEARCH REPORT**

**I. CLASSIFICATION OF SUBJECT MATTER**

According to International Patent Classification (IPC) or to both National Classification and IPC

- Int.Cl. 3: C 08 J 9/14; B 29 D 27/00; B 32 B 5/20;
  C 09 J 3/16

**II. FIELDS SEARCHED**

Minimum Documentation Searched

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Documentation Searched other than Minimum Documentation

to the extent that such Documents are included in the Fields Searched

**III. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>GB, A, 1504559, published March 22, 1978, see claims 1-21, 29, 30, 37, 43, 45, 47, page 4, line 31 - page 5, line 30, page 7, line 45 - page 8, line 6, Union Carbide</td>
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<td>GB, A, 1062684, published March 22, 1967, see claims 1-8, page 2, line 120 - page 3, line 107, Grünzweig &amp; Hartmann</td>
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<td>GB, A, 1569763, published June 18, 1980, see the whole document, Imp. Chem. Ind.</td>
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<td>GB, A, 429316, published May 28, 1935, see examples 1,3, Dynamit-Aachen-Gesellschaft</td>
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  *O* document referring to an oral disclosure, use, exhibition or other means
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**IV. CERTIFICATION**

Date of the Actual Completion of the International Search: November 11, 1981

Date of Mailing of this International Search Report: November 24, 1981

International Searching Authority:
EUROPEAN PATENT OFFICE, Branch at The Hague
P.O. Box 5018 Patentlaan 2
2300 HN Rijswijk (2M), The Netherlands

Signature of Authorized Officer: G.L.M. Kruydenberg

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