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(54) Title: CORE MATERIAL AND PROCESS FOR INJECTION MOLDING

(57) Abstract

A core material for injection molding, comprising a copolymer of a polyvinyl alcohol (PVA) and polyethylene oxide (PEO), as well as a core formed of said core material.

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CORE MATERIAL AND PROCESS FOR INJECTION MOLDING

Field of the Invention

The present invention relates to a core material composed of a water soluble material. The core material of the present invention is useful especially for the preparation of a core for the injection molding of plastic products or parts with a fine structure, e.g., a face fastener (Hook-and-Loop fastener) used in the automotive industrial field, and so forth.

Background of the Invention

For the material for the preparation of core for injection molding of high molecular weight material products or parts with a fine structure, it is needed to satisfy the conditions that it is easy to mold a core having a fine structure in itself, and that after said high molecular weight material products or parts have been molded, the used core can be easily dissolved in water and eliminated.

U.S. Pat. No. 5,242,646 discloses a process for the production of a face fastener composed of a head portion, stem portion and base, and in this process, PVA is used as a core material. However, since PVA is simultaneously melted and decomposed (thermal crosslinking), difficulty has been attended with the formation itself of a core.

As a water soluble core material for the injection molding of a high molecular weight material, there is described an acrylic high molecular weight material having a carboxyl group in Japanese Unexamined Patent Publication No. 60-155212 and EP 0314156. In U.S. Pat. No. 4,990,146 and U.S. Pat. No. 4,870,148, there is described amino group-containing high molecular weight materials soluble in an acid solvent or alkaline solvent. In addition, in Japanese Unexamined Patent Publication No. 1-198609, there is described, as a water soluble core material, a material obtained by addition of a filler to a carboxyl group-containing acrylic high molecular weight material.

However, these water soluble materials have been defective in the insufficiency of heat resistance and fluidity, in forming a core, or has had the drawback that they are poor in water solubility in the case where a used core is to be eliminated by use of water.

Brief Description of the Invention

Therefore, the present invention relates to a core material for injection molding, and the purpose of the present invention is to provide a core material, which has sufficient heat resistance and fluidity in forming a core, thereby facilitating precise formation of a core having a minute structure, and which is easily dissolved in water in the case of used core being dissolved in water and eliminated.

The present inventors studied in various ways for solving the aforesaid problem, and consequently found that a composition comprising a polyvinyl alcohol (PVA) and polyethylene oxide (PEO) satisfies the aforesaid requirements, so as to achieve the present invention.

Accordingly, the present invention provides a core material for injection molding, comprising a copolymer of a polyvinyl alcohol (PVA) and polyethylene oxide (PEO), and the use thereof.

Detailed Description of Preferred Embodiments

In the present invention, there is used, as a water soluble core material to be used in a mold for injection molding or the like, a copolymer of a polyvinyl alcohol (PVA) and polyethylene oxide (PEO). A polyvinyl alcohol (PVA) has a melting point ranging from 170°C to 230°C according to the difference of saponification degrees.

However, any PVA begins to be thermally decomposed at a temperature exceeding 200°C, and at a temperature of 240°C or more, dehydration and crosslinking reaction of PVA proceed, and therefore, PVA has the defect that the water solubility thereof becomes noticeably lowered. As described above, in the case of thermal working of PVA, since decomposition reaction of PVA occurs in parallel with the thermal working thereof, the thermal working of PVA has been

very difficult. On the other hand, polyethylene oxide (PEO) is also known as a water soluble resin. However, PEO is very poor in injection fluidity, as compared with a PVA having a molecular weight in the same degree as that of the PEO, and therefore unsuitable for the production of an injection molded product of a fine shape.

The copolymer of a polyvinyl alcohol (PVA) and polyethylene oxide (PEO) is capable of relatively lowering the hydroxyl group concentration causing a chemical reaction. While a high water solubility is maintained, because the copolymer has a hydroxyl group and ether linkage in the structure thereof, and therefore, the copolymer is more stable than a PVA. In addition, the introduction of an ether linkage gives a low melting point to the copolymer, and therefore, can solve the problem related to the thermal workability of PVA. The PVA portion constituting the above copolymer includes the range from a partially saponified PVA having an acetic group to the fully saponified PVA, according to the extent of the saponification degree.

The molar ratio between the PVA and PEO in the aforesaid copolymer is preferably within the range of 99 to 50 (PVA): 1 to 50 (PEO). Within this range of ratio, there can be obtained sufficient thermal stability and sufficient fluidity at the time of forming a core, as well as sufficient water solubility of the used core, but, when the proportional amount exceeds 50%, the viscosity of the core becomes so high that it becomes difficult to form a core having a fine shape. On the other hand, when the proportional amount is less than 1%, the thermal stability of the core material is so low that thermal crosslinking occurs owing to the heating during the formation of the core, and the water solubility of the used core is likely to be lowered.

The molar ratio between the PVA and PEO in the polymer is more preferably within the range of 95 to 55 (PVA): 5 to 45 (PEO). Within this range, the aforesaid characteristics are emphasized to a greater extent. The molar ratio between the PVA and PEO in the polymer is still more preferably within the range of 90 to 70 (PVA): 30 to 10 (PEO). Within this range, the aforesaid characteristics are emphasized to a still greater extent.

The saponification degree of the PVA in preferably 65 mol-% or more, e.g., within the range between 65 and 99 mol-%. Herein, the saponification degree of 99 mol-% means the maximum value of the actually available saponification degree. When the saponification degree is less than 65 mol-%, the PVA exhibits high hydrophobicity, and the solubility of the PVA in water is liable to be lowered. The saponification degree of the PVA is more preferably 70 mol-% or more, e.g., within the range between 70 and 99 mol-%. When the saponification degree is 70 mol-% or more, especially the water solubility of the PVA becomes high. The saponification degree of the PVA is still more preferably 80 mol-% or more, e.g., within the range between 80 and 99 mol-%. When the saponification degree is 80 mol-% or more, the melting point of the PVA increases, while the water solubility thereof is maintained, and the heat resistance of the PVA is improved in the case of parts or the like being injection molded.

The preferred embodiment of the water soluble core material of the present invention is one having a T_g value ranging from 40°C to 100°C. Because, when the T_g value is less than 40°C, the core material is poor in heat resistance, and unsuitable as a core material to be used in a mold for injection molding. On the other hand, when the T_g value exceeds 100°C, the injection molding of the core itself becomes difficult, and what is more, water solubility of the core material becomes lowered. Therefore, it becomes difficult to use the core material, especially for an injection molded product having a fine shape.

The preferred embodiment of the water soluble core material of the present invention includes a water soluble high molecular weight material in which the MI value of the aforesaid water soluble core material is within the range between 0.1 and 50 (according to ASTM D-1238, at 210°C, under a load of 2160g). The reason why the MI value is limited within the range between 0.1 and 50 in the present invention is that when the MI value is less than 0.1, the fluidity of the core material becomes poor in a mold for injection molding, resulting in the difficulty of the use of the core material, especially for an injection molded product having a fine shape, and on the other hand, when the MI value exceeds 50, the average molecular

weight of the core material becomes relatively lower, resulting in lowering of the heat resistance of the core material.

As concrete commercially available PVA/PEO copolymer, there may be mentioned water soluble PVA/PEO copolymers, "Ax 300", "Ax 2000", and the like produced by Nihon Gosei Kagaku Kogyo K.K. (Japan Synthetic Chemistry Ind. Co., Ltd.). In order to obtain the water soluble core material of the present invention, there may be added to the aforesaid core material an oxazoline compound, polyethylene oxide (PEO), and/or PVA. An oxazoline compound is defined as a high molecular weight material having an oxazoline skeleton in the molecule, and as an oxazoline compound, there may be used, e.g., poly(2-ethyl-2-oxazoline) and the like. The reason why an oxazoline compound, PEO or PVA is herein added is that it thereby becomes possible to improve the fluidity and water solubility of the core material without impairing the heat resistance thereof.

Especially as PVA, there is preferred a one having a hydroxyl group concentration ranging from 70 to 95 mol-%. The reason therefor is that, when the hydroxyl group concentration is less than 70 mol-%, the water solubility of PVA lowers, on one hand, and on the other hand, when the hydroxyl group concentration exceeds 95 mol-%, not only the water solubility of PVA becomes lowered, but also the heat resistance thereof becomes noticeably worsened. The proportional amount of the oxazoline compound, POE or POE to be added is preferably within the range between 5 and 60 parts by weight based on 100 parts by weight of the present water soluble copolymer. Because, when the amount of the added oxazoline compound, PEO or PVA is less than 5 parts by weight, improvement effect expected to be obtained by addition of these substances is poor, and on the other hand, when this amount exceeds 60 parts by weight, the heat resistance of the core material becomes so noticeably lowered that the PVA becomes unsuitable for the production of an injection molded product having a fine shape.

To the water soluble core material of the present invention, there can further be added a polyhydric alcohol compound, filler, pigment and/or dye. Addition of a small amount of a polyhydric alcohol compound can improve the fluidity of the core resin. In addition, since a polyhydric alcohol compound has a hydroxyl group in the

molecule, the boiling point thereof is relatively high, and also in the use thereof in a mold of the present invention, there are not caused the problems such as foaming and bleeding. In addition, the polyhydric alcohol compound is more effective also because it improves the dispersibility of fillers such as inorganic matters or metal oxides and coloring pigments.

A polyhydric alcohol is defined as a compound having at least 2 hydroxyl groups in the molecule, and as a polyvalent alcohol, there can be used, e.g., glycerine, ethylene glycol, trimethylene glycol, tetramethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, 2,3-butanediol, 1,3-butanediol, pentamethylene glycol, and the like.

Fillers are effective for the improvement of the heat resistance, mechanical strength, weighting effect (reduction of cost), fluidity, and solubility of the core material of the resent invention, and as the fillers, there can be used e.g., talc, glass beads, hollow glass beads, magnesium carbonate, mica, alumino silicate, calcium phosphate, zeolite, metal salts, as well as oxides of the metals such as titanium, tin, magnesium, and zinc. The amount of the fillers to be added is preferably within the range between 1 and 150 parts by weight based on 100 parts by weight of the aforesaid water soluble core material, in general, although it is not particularly limited. Within a range other than the aforesaid range, the fillers are poor in the aforesaid improving effects. In addition, it is favorable to improve the compatibility of the fillers such as glass beads with the core material by subjecting them to coupling treatment.

Pigments or dyes are very effective for recognizing the dissolved state of the core material of the present invention, and in its turn, the adhesion of the core material to an injection molded product such as face fastener, by visual observation or the like. For example, by use of a core color different from the color of the injection molded product, adhesion of the core material to the product can easily be recognized. Although the kinds of the pigments or dyes to be used are not particularly limited, there can be used, as the pigments or dyes, carbon black, organic pigments, titanium white, and organic dyes such as azo dyes, acid dyes, basic dyes, thiazole dyes, and naphthol dyes.

The amount of the pigments or dyes to be added is preferably within the range between 0.01 and 5 parts by weight, based on 100 parts by weight of the water soluble core material. When this amount is less than 0.01 part by weight, the aforesaid recognizing effect becomes poor, and on the other hand, when it exceeds 5 parts by weight, on the contrary, the pigments or dyes are adhered to the injection molded product, and time and labor are required to eliminate them, on the contrary.

According to the present invention, there is provided a process for production of a core characterized by melting the present core material at a temperature of at least 50°C, and injection-molding said molten core material into a mold.

Here, the reason why the core material is headed to at least 150°C is because by this method a lower melting viscosity can be obtained, and a fine injection molded article such as a face fastener part having a base portion and a regularly positioned plurality of projections having a leg generating from the base portion and a mushroom-shaped head linked to the end of the leg can be produced with high accuracy in a short time.

As a means for heating, a heater, infrared light, etc. can be used. As a melting temperature, 160-260°C, 190-240°C is preferable. In the former range, a lower melt viscosity is obtained and a core material is not crosslinked by over heating. In the latter range, a more lower melt temperature is obtained, and a core material is neither crosslinked and nor discolored.

For the production of a core, preferably a molten core material is molded into a desired shape in a mold. Fine shaped articles can be easily produced in a short time. Note that to accelerate solidification of a core and to remove the core early and in a short time, a mold is preferably cooled to a predetermined temperature with, for example, cooled air.

As seen from the above, by using the present core material, water soluble core for injection molding, which is excellent in thermoresistance, fluidity and water solubility.

In addition, after that, while maintaining said core in the same mold, a molten material for injection molding can be injection-molded. As a result, a

complicated and fine shaped article such as surface fastener part can be molded in a single step. Note, when the molten material for injection-molded articles is injected, to maintain the shape of the core, the injection is desirably carried out at a temperature lower than the melting temperature of the core.

Note, a process for molding a core and a process for production of a shaped article using said core and described in detail in U.S. Patent No. 5,242,646.

In the following, the present invention will be explained more in detail with reference to working examples and comparative examples.

Table 1

Ax3OO:	Water soluble PVA/PEO copolymer resin, "ECOMATY" produced by Japan Synthetic Chemistry Ind. Co., Ltd.
Ax2OOO:	Water soluble PVA/PEO copolymer resin, "ECOMATY" produced by Japan Synthetic Chemistry Ind. Co., Ltd.
AL03-2:	Polyvinyl alcohol produced by Japan Synthetic Chemistry Ind. Co., Ltd.
GL05:	Polyvinyl alcohol produced by Japan Synthetic Chemistry Ind. Co., Ltd.
KP08:	Polyvinyl alcohol produced by Japan Synthetic Chemistry Ind. Co., Ltd.
KL05:	Poly-vinyl alcohol produced by Japan Synthetic Chemistry Ind. Co., Ltd.
GBI330TE:	Water soluble acrylic resin produced by Berrant Co., Ltd.
PEOX200:	Poly(ethyl oxazoline) produced by Dow Chemical Co., Ltd.
PEO-1:	Poly(ethylene oxide) produced by Sumitomo Seika Co., Ltd.
GB731B:	Glass beads produced by Toshiba Barotini Co., Ltd.
Talc:	"Talc MS-All produced by Japan Talc Co., Ltd.
Carbon:	"Asahi Thermal" produced by Asahi Carbon Co., Ltd.

Table 2

	Ax200	Ax300	AL03-2	GL05	KL05
	PVA/PEO copolymer	PVA/PEO copolymer	PVA	PVA	PVA
Saponification Degree [mol-%]	80	80	99	89	79
Decomposition Temperature (Td) [°C]	318	314	272	303	298
Melting Point [°C]	192	191	224	194	179
Td-Tm	126	123	48	109	119

Examples 1 and 2 and Comparative Examples 1 to 3

A water soluble resin, "ECOMATY", produced by Nihon Gosei Kagaku Kogyo K.K. (Japan Synthetic Chemistry Ind. Co., Ltd.) and a PVA were dried for 24 hours by use of a hot air dryer, whereafter a core was produced at a temperature of 210°C, by use of a core mold No. 6 produced by Sumitomo 3M Co., Ltd. by an injection molding machine of "PS-40" type produced by Nissei Jushi Kogyo K.K. [Nissei Resin Ind. Co., Ltd.]. Subsequently, by use of the thus produced core, there was produced by the aforesaid injection molding machine of "PS-40" type produced by Nissei Jushi Kogyo K.K., a standard face fastener, a product of Sumitomo 3M Co., Ltd., and it was subjected to the following evaluations.

1. Determination of Saponification Degree:

The saponification degree was calculated from the integrated intensity ratio determined by use of a nuclear magnetic resonance device "EX 270", produced by Nihon Denshi K.K. [Japan Electronic Co., Ltd.]

2. Determination of Melting Point (Tm) and Glass Transition Temperature (T_g) of the Core Material:

The temperature of the core material was elevated from -60 to 300°C at a rate of 10°C/min by use of "DSC-2C" manufactured by Perkin Elmer

Ind. Co., Ltd., and the Tm and T_g values were determined from the change of specific heats.

3. Determination of the Decomposition Temperature (Td) of the Core Material:

The temperature of the core material was elevated at a rate of 10°C/min by use of an apparatus for thermogravimetry "951" manufactured by Dupon Co., Ltd., and the decomposition temperature in the air atmosphere was determined.

4. Determination of the Melt Index (MI) of the Core Material:

The melt index (MI) values of the core materials were determined, respectively, by use of a Melt Indexer S-1001 manufactured by Toyo Seiki Ind. Co., Ltd., according to ASTM D-1238 (at 210°C, under a loading of 2160g).

5. Evaluation of Solubility:

Undissolved products in which a face fastener material (1011CH5) is integrated with a core were dipped in water of 23°C or hot water of 70°C for 24 hours. Subsequently, the solubility of each core material was visually judged according to the following criterion,

OK: completely dissolved.

Fair: Almost completely dissolved.

NG: Partially undissolved.

6. Evaluation of Heat Resistance:

Using the under-described high molecular weight materials as fastener members, face fasteners were prepared under the under-described temperature conditions, respectively. Subsequently, a stem line was cut out from each face fastener in the longitudinal direction, and the heat resistances of the core materials were evaluated by microscopically judging the shape and uniformity of the stem

group viewed from the direction of the cross section of the stem line, according to the following criterion.

Polypropylene "6800i" manufactured by Mitsubishi Chemical Ind. Co., Ltd.	210°C
6-nylon "1011CH5" manufactured by Mitsubishi Chemical Ind. Co., Ltd.	250°C
6,6-nylon "1200S" manufactured by Asahi Chemical Ind. Co., Ltd.	280°C

OK: No problem

NG: Partially objectionable

The results are set forth in Table 3.

Table 3

	Example 1	Example 2	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Water Soluble Resin	Ax300	Ax2000	GL05	KL05	1330TE
[parts by weight]	(100)	(100)	(100)	(100)	(100)
T_g [°C]	54	50	68	61	102
MI (210°C, 2160g)	2.9	21.8	2.4	6.4	12.5
Solubility 23°C	OK	OK	NG	Fair	NG
70°C	OK	OK	Fair	OK	Fair
Heat Resistance					
6800J	OK	OK	OK	OK	OK
1011CH5	OK	OK	NG	NG	NG
1200S	OK	OK	NG	NG	NG

Examples 3 to 7 and Comparative Examples 4 and 5

Water soluble resins "ECOMATY" and PVA produced by Japan Synthetic Chemistry Co., Ltd. were dried for 24 hours or more by use of a hot air dryer, the temperature of which had been controlled to 50°C, following which there were added a polyhydric alcohol, oxazoline compound, carbon black, and fillers, so as to be sufficiently mixed so that core materials were prepared. Subsequently, the thus

prepared core materials were evaluated with respect to the following items like in the aforesaid Example 1.

1. Determination of the melt indices (MI) of the core materials.
2. Evaluation of solubility.
3. Evaluation of heat resistance.

The results are set forth in Table 4.

Table 4

	Example 3	Example 4	Example 5	Example 6	Example 7	Comp. Ex. 4	Comp. Ex. 5
Water Soluble Resin	Ax300 (100)	Ax200 (100)	Ax300 (100)	Ax2000 (100)	Ax2000 (100)	KL05 (100)	Ax2000 (100)
Other Resins	KP08 (50)	PEOX200 (30)	PEO-1 (10)				PEOX50 (70)
Polyhydric Alcohols		glycerine (2)	glycerine (1)			glycerine (1)	glycerine (2)
Fillers			talc (15)	GB731B (40)	talc (30)	talc (30)	
Pigment or Dye					carbon (1)		
Melt Index (210°C, 2160g)	0.2	45.1	1.3	18.5	14.2	3.1	54.4
Solubility 23°C	OK	OK	OK	OK	OK	NG	OK
70°C	OK	OK	OK	OK	OK	Fair	OK
Heat Resistance							
6800J	OK	OK	OK	OK	OK	OK	NG
1011CH5	OK	OK	OK	OK	OK	OK	NG
1200S	OK	OK	OK	OK	OK	NG	NG

As mentioned in detail in the foregoing, according to the present invention, by use of PVA and PEO, there can easily be prepared a core having a fine shape due to the excellent thermal stability and fluidity, and the used core can easily be dissolved and eliminated by use of water.

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WHAT IS CLAIMED IS:

1. A core material for injection molding, comprising a copolymer of polyvinyl alcohol (PVA) and polyethylene oxide (PEO).

2. A core material according to claim 1, wherein a molar ratio between PVA and PEO in said copolymer is within a range between 99:1 and 50:50.

3. A core material according to claim 1, wherein a saponification degree of said PVA is within a range between 65 and 99 mol-%.

4. A core material according to claim 1, wherein a glass transition temperature (T_g) of said core material is within a range between 40°C and 100°C.

5. A core material according to claim 1, wherein a melt index (MI) of said core material is within a range between 0.1 and 50.

6. A core material according to claim 1, further comprising an oxazoline compound, PVA and/or PEO.

7. A process for production of a core characterized by melting a core material according to claim 1, at a temperature of at least 150°C, and injection molding said molten core material into a mold.

8. An injection molded article formed using a core according to claim 7.

9. An injection molded article according to claim 8, which is a face fastener.

10. A process for production of an injection molded article characterized by positioning a core according to Claim 1 in a mold, and injecting thereinto a material for injection molded article.

INTERNATIONAL SEARCH REPORT

Interr. al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C33/52 B29C45/44 //B29K29:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 258 (M-1606) ,17 May 1994 & JP,A,06 039844 (RIKEN VINY KOGYO) 15 February 1994, see abstract ---	1-10
A	US,A,3 639 507 (URAM) 1 February 1972 see column 2, line 6 - line 43 ---	1-10
A	MODERN PLASTICS INTERNATIONAL, vol. 23, no. 7, July 1993 page 46 'Vinylalcohol copolymer' ---	1
A	EP,A,0 474 173 (NIPPON GOHSEI KAGAKU KOGYO) 11 March 1992 see page 5, line 50 - page 6, line 4 see page 8, line 5 - line 32 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 June 1995	- 3. 07. 95

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 95/04194

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 242 646 (TORIGOE ET AL.) 7 September 1993 cited in the application see column 5, line 40 - column 6, line 2 -----	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inten ıal Application No
PCT/US 95/04194

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