(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 October 2017 (05.10.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/167197 A1

(51) International Patent Classification:
C08J 9/00 (2006.01) *C08L 33/18* (2006.01)
C08J 9/22 (2006.01)

(21) International Application Number:
PCT/CN2017/078572

(22) International Filing Date:
29 March 2017 (29.03.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/CN2016/077893 30 March 2016 (30.03.2016) CN

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2017/167197 A1

(54) Title: POLYMER COMPOUNDS COMPRISING POLY (METH) ACRYLIMIDE FOAM PARTICLES

(57) Abstract: A polymer compound comprises a thermoplastic resin and poly (meth) acrylimide (P (M) I) foam particles. The polymer compound achieves better mechanical performance than the individual components, and can be widely used in lightweight construction.

POLYMER COMPOUNDS COMPRISING POLY(METH)ACRYLIMIDE FOAM PARTICLES

Field of the invention

The invention relates to a polymer compound comprising poly(meth)acrylimide (P(M)I) foam particles, in particular polymethacrylimide (PMI) foam particles.

Background

Poly(meth)acrylimide foams e.g. polymethacrylimide foams, such as those marketed under the trademark Rohacell® by Evonik Resource Efficiency GMBH, are widely used in composite material for light weight design in the aerospace, automotive, sport and medical device industries, etc. due to their light weight and high mechanical performance.

In the past, the P(M)I foams were supplied in the shape of blocks, which however did not quite fit the processing of parts with complex 3D geometries, and could result in long cycle time, low precision, and material waste.

WO2013/056947 describes a mould shaping process of P(M)I foams which partially solves the above problems, wherein (prefoamed) P(M)I polymer particles are foamed in a mould with the aid of adhesives, which can be a polyamide or a poly(meth)acrylate. The dose of the adhesives can be up to 20% of the P(M)I polymer particles, i.e. up to 16.7% based on the total weight of the P(M)I polymer particles and the adhesive. However this process still results in long cycle time.

To solve the above mentioned problems, the present inventors explored the possibility for the P(M)I foam particles to form polymer compounds with thermoplastic resins and accomplished the present invention.

Summary of the present invention

The present invention provides a polymer compound, comprising:

(1) a thermoplastic resin, which is melt processible at temperatures of less than 400°C, and

(2) poly(meth)acrylimide foam particles, which maintain the particulate form at temperatures of less than 400°C,

wherein

the thermoplastic resin constitutes 20-99%, and

the P(M)I foam particles constitute 1-80%,

based on the total weight of the polymer compound.

It is surprisingly found that the polymer compound of the present invention achieves better compressive and/or bend strength than the individual components, besides the light weight.

The present invention further provides a method for producing the polymer compound of the present invention, which includes a step of physically mixing the poly(meth)acrylimide foam particles and the melt of the thermoplastic resin.

The present invention further provides the use of the polymer compound of the present invention in light weight constructions.

Detailed description of the present invention

There is no limitation to the thermoplastic resin as long as it is melt processible at temperatures of less than 400°C. Melt processible is used in its conventional sense, that the polymer can be processed at the indicated temperatures without substantial degradation of the polymer.

Examples of the thermoplastic resin include polyamides, polyolefins, polyesters and copolymers containing any of the above segments as well as the blend thereof.

Preferably, the polyamide is selected from aliphatic polyamides, more preferably PA6, PA11, PA12, PA46, PA66, PA10, PA610, PA612, PA1010, PA1012 and the blend thereof.

The P(M)I foam particles used in the present invention can be obtained by the granulation of the P(M)I foams which are not in particulate form.

The P(M)I foams are also termed rigid foams, and feature particular robustness. The

P(M)I foams are normally produced in a two-stage process: a) production of a cast polymer, and b) foaming of said cast polymer. In accordance with the prior art, these are then cut or sawn to give the desired shape.

Production of the P(M)I foams begins with production of 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. Other comonomers can also be used, examples being esters of acrylic or methacrylic acid, styrene, maleic acid and itaconic acid and anhydrides thereof, and vinylpyrrolidone. However, the proportion of the comonomers here should not be more than 30% by weight. Small quantities of crosslinking monomers can also be used, an example being allyl acrylate. However, the quantities should preferably be at most from 0.05% by weight to 2.0% by weight.

The copolymerization mixture moreover comprises blowing agents which at temperatures of about 150 to 250°C either decompose or vaporize and thus form a gas phase. The polymerization takes place below this temperature, and the cast polymer therefore comprises a latent blowing agent. The polymerization advantageously takes place in a block mould between two glass plates.

The cast polymer is then foamed at an appropriate temperature in a second step. The production of such P(M)I foams is known in principle to a person skilled in the art and can be reviewed in EP 1 444 293, EP 1 678 244 or WO 2011/138060 for example.

The P(M)I foam particles used in the present invention can also be obtained by the foaming of the P(M)I polymer particles.

The P(M)I polymer particles can be obtained by grinding the cast polymer, for example, in a cutting mill. The grindings are then foamed at an appropriate temperature to produce the P(M)I foam particles.

Preferably, the P(M)I foam particles used in the present invention is obtained by the foaming of the P(M)I polymer particles, where the closed foam cells are not destroyed, compared with the P(M)I foam particles obtained by the granulation of the P(M)I foams.

Preferably, the P(M)I foam particles have a grain size which ranges 0.1-30 mm, more preferably 0.5-10 mm.

Preferably, the P(M)I foam particles have a bulk density of 25-220 kg/m^3, more preferably 50-150 kg/m^3.

In one preferred embodiment of the present invention, the P(M)I foam particles are polymethacrylimide (PMI) foam particles.

Rohacell® PMI polymers and/or foams, commercially available from Evonik Resource Efficiency GMBH, may be mentioned in particular.

There is no limitation to the proportion of the thermoplastic resin and the P(M)I foam particles in the polymer compound of the present invention.

The thermoplastic resin can constitute 20-95%, preferably 20-80%, more preferably 30-70%, and the P(M)I foam particles can constitute 5-80%, preferably 20-80%, more preferably 30-70%, based on the total weight of the polymer compound. But it is also possible that the thermoplastic resin constitutes 1-99%, and the P(M)I foam particles can constitute 1-99%, based on the total weight of the polymer compound.

In one preferred embodiment of the present invention, the thermoplastic resin is melt processible at temperatures of less than 250°C, and/or the P(M)I foam particles maintain the particulate form at temperatures of less than 250°C.

The polymer compound of the present invention may include additives, such as calcium carbonate, glass beads, zinc oxide, and fiber reinforcements such as ceramic fibers, aramid fibers, potassium titanate fibers, glass fibers and carbon fibers, depending on the effect or performance desired.

The polymer compound of the present invention are generally suitable in principle for any type of lightweight constructions, and can in particular be used in mass production by way of example for bodywork construction or for interior cladding in the automobile industry, interior parts in rail vehicle construction or shipbuilding, in the

aerospace industry, in mechanical engineering, in the production of sports equipment, in furniture construction or in the design of wind turbines.

Examples

The PMI foam particles used in the examples were prepared from PMI polymer particles marketed with trademark ROHACELL® Triple F by Evonik Resource Efficiency GMBH. The PMI polymer particles were produced from a fully polymerized copolymer sheet (which had not been prefoamed) with the aid of a granulator. The grain size range of the particles used in the examples, after sieving to keep the fines, was below 1.0 mm. The bulk density of the PMI polymer particles was about 600-700 kg/m^3.

The PMI polymer particles were foamed in an oven at a temperature of 200-240°C for 30-60 mins. The obtained PMI foam particles had a bulk density of 100-150 kg/m^3 and a grain size of 0.5-5 mm.

The PMI foam particles were mixed with the melts of a PA12 (Vestamid® L1600, by Evonik Resource Efficiency GMBH) and a PA12 elastomer (Vestamid® E30, polyether block PA12, by Evonik Resource Efficiency GMBH) respectively to prepare two 50 : 50 (weight) compounds, which were shaped into plates having a thickness of 5 mm.

The plates were tested for compressive strength (ISO 844) and bending strength (ISO 178) as well as density. The result is indicated in the table below.

Examples	**Compressive strength at 10% (MPa)**	**Bending strength at thickness*1.5 (MPa)**	**Density (g/cm^3)**
Vestamid L1600 / PMI (50:50)	6.11	36.7	0.73
Vestamid E30 / PMI (50:50)	6.33	10.4	0.74
Reference material			
Vestamid L1600	6.6	34.7	1.02
Vestamid E30	4	1.79	1.01
Rohacell® 200 WF *	5.02	7.44	0.2

*Rohacell® 200 WF PMI rigid foam, commercially available from Evonik Resource Efficiency GMBH, was selected as reference material, because of its relatively high compression and bending strength,

among the marketed Rohacell® series of PMI foams.

It can be seen that more than 25% weight reduction is achieved for both Vestamid L1600 and Vestamid E30. And the polymer compounds of the examples achieve higher compressive and/or bending strength than the individual raw material.

Claims

1. A polymer compound, comprising:
(1) a thermoplastic resin, which is melt processible at temperatures of less than 400°C, and
(2) poly(meth)acrylimide (P(M)I) foam particles, which maintain the particulate form at temperatures of less than 400°C,
wherein
the thermoplastic resin constitutes 20-99%, and
the P(M)I foam particles constitute 1-80%,
based on the total weight of the polymer compound.

2. The polymer compound according to claim 1, wherein the thermoplastic resin is selected from polyamides, polyolefins, polyesters and copolymers containing any of the above segments as well as the blend thereof.

3. The polymer compound according to claim 2, wherein the polyamide is selected from aliphatic polyamides, more preferably from the group consisting of PA6, PA11, PA12, PA46, PA66, PA10, PA610, PA612, PA1010, PA1012 and the blend thereof.

4. The polymer compound according to any one of the preceding claims, wherein the P(M)I foam particles have a grain size which ranges 0.1-30 mm, preferably 0.5-10 mm.

5. The polymer compound according to any one of the preceding claims, wherein the P(M)I foam particles have a bulk density of 25-220 kg/m^3, preferably 50-150 kg/m^3.

6. The polymer compound according to any one of the preceding claims, wherein the P(M)I foam particles are obtained by:
(1) the granulation of P(M)I foams which are not in particulate form, or
(2) the foaming of P(M)I polymer particles.

7. The polymer compound according to any one of the preceding claims, wherein the

P(M)I foam particles are polymethacrylimide (PMI) foam particles.

8. The polymer compound according to any one of the preceding claims, wherein the thermoplastic resin constitutes 20-95%, preferably 20-80%, more preferably 30-70%, and
the P(M)I foam particles constitute 5-80%, preferably 20-80%, more preferably 30-70%,
based on the total weight of the polymer compound.

9. The polymer compound according to any one of the preceding claims, wherein the thermoplastic resin is melt processible at temperatures of less than about 250°C, and/or
the P(M)I foam particles maintain the particulate form at temperatures of less than 250°C.

10. A method for producing the polymer compound according to any one of the preceding claims, including a step of physically mixing the P(M)I foam particles and the melt of the thermoplastic resin.

11. Use of the polymer compound according to any one of the preceding claims 1-9 in light weight constructions.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/078572

A. CLASSIFICATION OF SUBJECT MATTER

C08J 9/00(2006.01)i; C08J 9/22(2006.01)i; C08L 33/18(2006.01)i

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)

C08J9/- C08L33/-

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 practicable, search terms used)

CNPAT,CNKI,WPI,EPODOC,CA,STN:resin, PMI, acrylimide, polyamide, polyolefin, polyester, PA, foam+, partic+, melt, granulation, light weight, EVON, Ying-N

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TW 201532826 A (EVONIK INDUSTRIES AG.) 01 September 2015 (2015-09-01) abstract, description, page 5, paragraph 2 to page 6, paragraph 4, and page 11, paragraph 5 to page 12, paragraph 1	1-11
X	US 2014309361 A1 (EVONIK ROEHM G.M.B.H.) 16 October 2014 (2014-10-16) description, paragraphs [0022] to [0049], and paragraphs [0091] to [0095]	1-11
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A	CN 1561361 A (ROHM G.M.B.H. CO.KG) 05 January 2005 (2005-01-05) claims 1-13	1-11

☐ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 June 2017	**26 June 2017**
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/078572

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