

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 July 2011 (07.07.2011)

(10) International Publication Number
WO 2011/080221 A2

(51) International Patent Classification:
C08K 3/26 (2006.01)

(21) International Application Number:
PCT/EP2010/070672

(22) International Filing Date:
23 December 2010 (23.12.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
A 2009/10098 31 December 2009 (31.12.2009) TR

(71) Applicant (for all designated States except US): **ARCE-
LIK ANONIM SIRKETI** [TR/TR]; E5 Ankara Asfalti
Uzeri, Tuzla, 34950 Istanbul (TR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ERSOY, Osman**
[TR/TR]; E5 Ankara Asfalti Uzeri, Tuzla, 34950 Istanbul
(TR). **ORAL, Mehmet Ali** [TR/TR]; E5 Ankara Asfalti
Uzeri, Tuzla, 34950 Istanbul (TR).

(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, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, 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, SD, SL, SZ, TZ, UG,
ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report (Rule 48.2(g))



WO 2011/080221 A2

(54) Title: METHOD FOR PREPARING CALCIUM CARBONATE FILLED POLYOLEFIN MIXTURE

(57) Abstract: The mixture prepared according to the mixture preparation method of the present invention comprises a homopolymer, a filler material and a compatibilizer. The mixture is obtained according to a mixture preparation method comprising the steps of melting the homopolymer and the compatibilizer by mixing both at temperatures higher than the melting points thereof and adding filler material to this melted mixture.

Description**METHOD FOR PREPARING CALCIUM CARBONATE FILLED POLYOLEFIN MIXTURE**

- [0001] The present invention relates to a mixture obtained by combining polyolefin materials with filler materials such as calcium carbonate, etc.
- [0002] Filled polyolefin materials are used in various fields, in the production of washing machines, for example in the production of different elements such as cuve, detergent dispenser, pump body and receptacle. Polyolefin, for example polypropylene (PP) material is preferred since it has high chemical resistance and good mechanical strength values and it is cheap. By filling the polypropylene material with filler materials and strengtheners such as talc, calcium carbonate, a cheaper material with more suitable features for utilization purposes can be produced.
- [0003] One of the ways to increase the mechanical strength of calcium carbonate filled PP material is to form a chemical bond between the calcium carbonate filler and the polypropylene matrix. In the current situation, when a tensile force is applied to the calcium carbonate filled PP composite material, tensile force transfer between the polymeric matrix and the calcium carbonate is only provided by the physical relation (friction forces) between the calcium carbonate and the polypropylene matrix. When the tensile force reaches a certain value, gaps occur between the calcium carbonate and the polymeric matrix due to the polymeric matrix lengthening by stretching, and friction forces providing the tension transfer significantly decrease due to these gaps. In case the tensile force further increases, gaps occurring between the calcium carbonate particles and the PP matrix further decrease the strength of the material by combining with the gaps occurring on the surface of other nearest calcium carbonate, and with the gap combining mechanism proceeding fast, the composite material cannot carry the tensile force any more and breaks off.
- [0004] One of the ways to increase the mechanical strength values of the calcium carbonate filled PP material is to form a chemical interaction between the calcium carbonate and the PP matrix. Decreasing filler surface energy by means of modification with substances with low molecular weight (such as

calcium stearate, silane, phosphorus based materials), saturating oligomeric polymers to the filler surface are amongst the most widely known and used methods. However, although mechanical strength values are provided to be increased by applying these methods, due to the low molecular weights of the chemicals applied onto the surfaces of the filler particles, adhesion of the polymeric matrix on to the filler surface is weak..

- [0005] Filler materials are loaded into the polypropylene raw material at process temperatures higher than the melting point during the production in order to obtain a homogeneous mixture. During this process, degradation starts at the organic portion of the mixture after the free radicals are formed due to the effect of the heat and high shear forces, and these radicals react with oxygen, other chemicals and main polymer chain in the environment. Further steps of the degradation causes chain-breaking and/or decrease in the molecular weight, thus causes decrease in mechanical strength values, color distortion and deterioration of fluidity characteristics. In order to solve the degradation problem, chemical stabilizers are required to be added into the mixture during the process of polymeric mixture preparation.
- [0006] Filled polyolefin materials are subjected to heat, water vapor and chemicals (detergent, washing water, dirt dissolved by water during the washing, etc.) according to the utilization area, for example when used as washing machine tubs. As a result of the reactions that the free radicals that can be formed due to the effect of the heat and chemicals may cause, structure of the mixture starts to degrade. Therefore, strength against these factors has to be increased.
- [0007] Chemicals applied in order to form a chemical bond between the surface of the calcium carbonate and the PP matrix generally comprise free radicals. Interaction between chemicals which provide stabilization and which can be added to the formulation in order to eliminate the harmful effects of the free radicals which occur as a result of the chain-breakings which can occur due to the high shear forces during the mixture preparation, to inactivate the acid structures which are the remnants of the catalysts and to protect the mixture against the degradation due to the

operating conditions (high temperature, aqueous solution with detergent, etc.) to which the mixture is subjected to during the application, and the chemicals (compatibilizers) which provide the chemical bonding onto the calcium carbonate surface and chemical bonding with the filled matrix and which comprise free radicals is expectable. Intereaction of the chemical radicals forming a bond between the free radicals of the chemicals used for stabilization and the filled PP matrix eliminates the effectiveness of both chemicals.

- [0008] In the state of the art United States Patent No. 4120844, the process of mixing a polypropylene material composed of a mixture of homopolymer and copolymer with calcium carbonate filler material such as to impact strength properties thereof is explained.
- [0009] In the state of the art British Patent No. 1134422, the process wherein the polymer material is mixed with two different filler materials, one powder based and the other fibrous, such as to increase the flexibility thereof is described.
- [0010] In the state of the art United States Patent No. 6642290, the process of producing syndiotactic polypropylene by using various nucleation agents is described.
- [0011] In another state of the art United States Patent No. 5969027, the process of mixing a polypropylene material composed of a mixture of homopolymer and block copolymer with calcium carbonate filler material such as to impact strength properties thereof is described.
- [0012] The aim of the present invention is the realization of a polyolefin based mixture strengthened with a filler material and the chemical stability of which is increased.
- [0013] The mixture realized in order to attain the aim of the present invention, explicated in the first claim and the respective claims thereof comprises a homopolymer, a filler material and at least one compatibilizer. The mixture is obtained according to a mixture preparation method comprising the steps of melting the homopolymer and the compatibilizer by mixing both at temperatures higher than the melting points thereof and adding filler material to this melted mixture.

- [0014] Thus, a chemical bond is formed between the calcium carbonate filler material and the polymer matrix and increase in mechanical strength values is provided.
- [0015] In the mixture preparation method, first the compatibilizer and the polypropylene are loaded into the double screw extruder and after a homogeneous mixture is provided by melting the compatibilizer and the polypropylene in the double screw extruder, the calcium carbonate is added to this mixture as filler material. After the interreaction between the compatibilizer and the calcium carbonate surfaces is completed, stabilizers are added to the mixture. Thus, interreaction of the stabilizers with the compatibilizer is prevented.
- [0016] A preferred embodiment of the present invention is described in detail below.
- [0017] The mixture prepared according to the mixture preparation method of the present invention comprises a homopolymer or a copolymer, a filler material and at least one compatibilizer.
- [0018] The mixture is obtained according to a mixture preparation method comprising the steps of melting the homopolymer or copolymer and the compatibilizer by mixing both at temperatures higher than the melting points thereof and adding filler material to this melted mixture.
- [0019] In the preferred embodiment of the present invention, a semicrystalline isotactic propylene is used as the homopolymer. Calcium carbonate is preferably used as the filler material. A compatibilizer comprising maleic anhydride is used as the compatibilizer. In the preferred embodiment of the present invention, percentage by weight of the maleic anhydride is between 0.01-10%. Afterwards, stabilizers are also added to the mixture in order to protect this mixture obtained against degradation that can occur at the production and operating conditions.
- [0020] By means of the mixture preparation method of the present invention, calcium carbonate filler material surfaces and polypropylene material are chemically bonded to each other by means of the compatibilizer. Furthermore, by means of the method of the present invention, stabilizers added in order to protect the mixture against the degradation that may

occur at production and operating conditions are prevented from interacting negatively with the said mixture

- [0021] In the preferred embodiment of the present invention, antioxidant stabilizers are used as the stabilizer, which deactivate the radicals (especially peroxy radicals) forming as a result of the degradation and which degrades the hydroperoxides that may occur by the formation of these radicals to alcohol. Moreover, a thiosynergist thermal stabilizer is used, which shows synergistic interaction and which provides long term thermal stabilization (LTTS) when used together with the antioxidant stabilizer.
- [0022] In the embodiment of the present invention, the maleic anhydride filled (grafted) stabilizer and the homopolymer, preferably polypropylene are mixed at a temperature higher than the melting points of both materials. The mixing process is performed in the double screw extruder which can be heated and cooled to a temperature degree higher than the melting points of the polypropylene and the compatibilizer, and which has one or more than one temperature-controlled mixing receptacle and smasher/mixer screw blocks.
- [0023] The temperature of the mixture comprising polypropylene and maleic anhydride grafted compatibilizer loaded into the mixing receptacle of the double screw extruder is increased to 180-220°C range. Thus, melting of the polypropylene and also the ring opening reaction at the maleic anhydride portion of the compatibilizer are provided. Consequently, free radicals form by means of the ring opening reaction at the maleic anhydride. These opened radicals form a chemical bond with Ca^{+2} and CO_3^{-2} ions on the calcium carbonate that will be added to the mixture later. Thus, the mechanical strength of the mixture is increased by forming a chemical bond between the calcium carbonate and the polypropylene.
- [0024] Temperature increase in the mixing receptacle of the double screw extruder is realized by increasing the temperature in the mixing receptacle and by means of the arrangement of the smasher/mixer screw blocks. The polypropylene and the maleic anhydride grafted compatibilizer are melted by means of the force transmitted onto the mixture by means of the

smasher/mixer screw blocks rather than by means of increasing the mixing receptacle temperature. Smasher/mixer screw blocks are arranged such as to increase the temperature to the degree required for the complete melting of the polypropylene and formation of the ring opening reaction in the compatibilizer comprising maleic anhydride. An arrangement having at least seven 30° stagger angles, at least four 60° stagger angles and at least six 90° stagger angles is an exemplary arrangement.

- [0025] In an embodiment of the present invention, the double screw extruder comprises a backward conveying screw element located just after the smasher/mixer screw blocks in order to be sure that the polymeric mixture melts homogeneously and ring opening mechanism is completed. Backward conveying screw element provides the pressure and the temperature of the polymer melt to increase and also prevents the not-melt polypropylene and compatibilizer granules from being conveyed further by filtering them. The not-melt granules are conveyed backwards to the smasher/mixer screw blocks by means of the backward conveying screw element.
- [0026] Afterwards, calcium carbonate is added to this melt polymer mixture. The double screw extruder comprises a side stuffer unit in order that calcium carbonate addition can be performed at the end of the backward conveying screw element. In the preferred embodiment of the present invention, the double screw extruder furthermore comprises a wide pitch, deep threaded, forward conveying screw. Thus initial efficiency of calcium carbonate, thus production capacity is increased. Thus, ions on calcium carbonate surfaces and free radicals in the mixture and forming as a result of the ring opening reaction chemically bond with each other. In this case, the temperature of the mixture is brought to 150-170°C, preferably to 165°C. Thus, the possibility of free radicals of the maleic anhydride grafted polymer chemically bonding to the calcium carbonate surfaces breaking off from the filler surface and entering into ring closing reaction is minimized. After the mixture temperature reaches 165°C and maleic anhydride bonds with the ions on the calcium carbonate, stabilizers are added to the mixture. After this stage, conventional mixture preparation processes,

degassing, forming granules, drying, etc. are implemented.

- [0027] Antioxidant stabilizer is a mixture of a main phenolic antioxidant as the hydrogen donor and a phosphate based secondary antioxidant as the hydroperoxyde decomposer. For example, pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate) is used as the main phenolic antioxidant and tris (2,4-ditert-butylphenyl)-phosphite is used as the phosphate based secondary antioxidant.
- [0028] Dioctadecyl 3,3'thiodipropionate is used as the thiosynergist thermal stabilizer.
- [0029] In another embodiment of the present invention, the mixture comprises calcium stearate which increases the effectiveness of the stabilizer, which has acid binding properties and which reduces the friction between the mixture and the mixers at temperatures higher than the melting point of the polymer.
- [0030] In another embodiment of the present invention, the compatibilizer comprises maleic anhydride grafted homopolymer PP (MA-g-HPP). Although, usage of maleic anhydride grafted homopolymer increases the tensile strength and flexural strength, it also decreases the percentage elongation value during tension and bending and makes the material brittle.
- [0031] In another embodiment of the present invention, the compatibilizer comprises maleic anhydride grafted copolymer PP (MA-g-CPP). Usage of maleic anhydride grafted copolymer increases tensile, bending and impact strengths.
- [0032] In another embodiment of the present invention, the compatibilizer comprises maleic anhydride grafted styrene ethylene butadiene styrene (MA-g-SEBS).
- [0033] In another embodiment of the present invention, the compatibilizer comprises maleic anhydride grafted ethylene propylene diene terpolymer (MA-g-EPDM).
- [0034] Usage of maleic anhydride grafted to an elastomeric polymer such as maleic anhydride grafted styrene ethylene butadiene styrene or maleic anhydride grafted ethylene propylene diene terpolymer increases the

impact strength and elongation during tension and bending, and decreases tension/bending modulus and tensile and bending strength.

[0035] In another embodiment of the present invention, in order to increase the impact strength and percentage elongation during tension and also tensile and bending strengths, maleic anhydride grafted homopolymer or copolymer polypropylene is mixed with maleic anhydride grafted styrene ethylene butadiene styrene or maleic anhydride grafted ethylene propylene diene terpolymer proportionally. In this case, tensile and bending strengths, and also impact and tensile/bending percentage elongation values increase synergistically.

[0036] Various experiments are conducted in order that the effect of the mixture preparation method of the present invention on the parameters aimed to be enhanced can be understood.

EXPERIMENT

- [0037] Experiments are conducted by forming several mixtures with different formulations in order to prove that while the mixture preparation method of the present invention provides the calcium carbonate filler material surfaces and the polypropylene material to chemically bond with each other by means of the compatibilizer, it also prevents the stabilizers from reacting negatively with the mixture in order to protect the mixture against the degradation that may occur at production and operation conditions.
- [0038] The first mixture (K1) used in the experiments comprises polypropylene, calcium carbonate, maleic anhydride grafted polypropylene, antioxidant and lubricant. In the first experiment (D1), the mixture is prepared by mixing the polypropylene, maleic anhydride grafted polypropylene and calcium carbonate at the same time. In the second experiment (D2), a chemical bond is provided between polypropylene and maleic anhydride grafted polypropylene by melting the polypropylene and the maleic anhydride grafted polypropylene and mixing them, then calcium carbonate is added to this mixture, and finally the stabilizer and the lubricant are added, in other words the mixture is prepared according to the mixture preparation method of the present invention. The second mixture (K2) comprises polypropylene, calcium carbonate and maleic anhydride grafted polypropylene, and the rate of maleic anhydride in the maleic anhydride grafted polypropylene is more than in the first mixture. In the third experiment (D3), the mixture is again prepared according to the mixture preparation method of the present invention. The third mixture (K3) comprises polypropylene, calcium carbonate and maleic anhydride grafted styrene ethylene butadiene styrene. In the fourth experiment (D4), the mixture is again prepared according to the mixture preparation method of the present invention. The fourth and the fifth mixtures (K4, K5) comprise polypropylene, calcium carbonate, maleic anhydride grafted polypropylene and maleic anhydride grafted styrene ethylene butadiene styrene. While in the fourth mixture (K4) maleic anhydride grafted polypropylene is more, in the fifth mixture (K5) maleic anhydride grafted styrene ethylene butadiene

styrene is more. The rate of the components used in the mixtures and the results of the experiments are shown in Table 1.

[0039]

Table 1

		Percentage by weight in the mixture					
		D1	D2	D3	D4	D5	D6
		K1	K1	K2	K3	K4	K5
Polypropylene	%	55.6	55.6	54.6	55.6	55.	55.
CaCO ₃		40	40	40	40	6	6
MA-g-PP		3	3	4	-	40	40
MA ratio in the MA-g-PP		0.3	0.3	0.4		3	1
MA-g-SEBS		-	-	-	3	1	3
MA ratio in the MA-g-SEBS					0.3	0.1	0.3
Antioxidant+Lubricant		1.4	1.4	1.4	1.4	1.4	1.4
Mechanical Properties							
Tensile Strength	MPa	21.5	34.9	35.9	29.3	32.	29.
Elongation under maximum load	%	3.90	4.08	4.55	8.79	5.3	8.7
Young's Modulus	MPa	243	302	303	185	278	211
Izod Notched Impact Strength	kJ/m ²	8	1	4	4	9	7
Bending Strength	MPa	36.2	52.3	52.7	38.2	47.	41.
Bending Modulus	MPa	204	224	222	140	219	168
		8	2	0	0	5	3

[0040] By means of the present invention, the chemical bond between the polypropylene and the calcium carbonate is realized by using the ring

opening reaction feature of the compatibilizer comprising maleic anhydride. Thus, mechanical features of the mixture are provided to be improved.

[0041] It is to be understood that the present invention is not limited by the embodiments disclosed above and a person skilled in the art can easily introduce different embodiments. These should be considered within the scope of the protection postulated by the claims of the present invention.

Claims

1. A mixture preparation method used for preparing a mixture comprising a homopolymer or a copolymer, a filler material and at least one compatibilizer, characterized by the steps of
 - melting the homopolymer or the copolymer and the compatibilizer by mixing both at temperatures higher than the melting points thereof and
 - adding the filler material to this melted mixture.
2. A mixture preparation method as in Claim 1, **characterized by** the steps of adding at least one stabilizer and at least one lubricant after the step of adding the filler material to this melted mixture.
3. A mixture prepared by using a mixture preparation method as in Claim 1 or 2, **characterized by** the homopolymer having a semicrystalline isotactic propylene, the filler material having calcium carbonate and the compatibilizer having maleic anhydride.
4. A mixture preparation method as in any one of the above claims, **characterized by** the step of melting the homopolymer or the copolymer and the compatibilizer by mixing both at temperatures higher than the melting points thereof, realized at a temperature between 180-220°C range.
5. A mixture preparation method as in any one of the above claims wherein a double screw extruder comprising one or more than one temperature-controlled mixing receptacle and smasher/mixer screw blocks is used in order to perform the mixing process, characterized by the steps of
 - loading the homopolymer comprising polypropylene and the compatibilizer comprising maleic anhydride,
 - increasing the temperature of the mixing receptacle to the range of 180-220°C,
 - adding the filler material comprising calcium carbonate to the mixing receptacle.
6. A mixture preparation method as in Claim 5, **characterized by** the realization of the steps of
 - decreasing the temperature of the mixture to the range 160-170°C,
 - adding the stabilizers to the mixture after the bonding of the maleic anhydride

with the ions on the calcium carbonate,
after the step of

- adding the filler material comprising calcium carbonate to the mixing receptacle.

7. A mixture preparation method as in Claim 6, **characterized by** the step of
- realizing the processes of degassing, forming granules and drying,
after the step of
- adding the stabilizers to the mixture after the bonding of the maleic anhydride with the ions on the calcium carbonate.
8. A mixture prepared by using a mixture preparation method as in any one of the above claims, **characterized by** the compatibilizer comprising 0.01-10% percentage by weight maleic anhydrate.
9. A mixture prepared by using a mixture preparation method as in any one of the above claims, **characterized by** the compatibilizer comprising the maleic anhydride grafted homopolymer PP.
10. A mixture prepared by using a mixture preparation method as in any one of the claims from 1 to 8, **characterized by** the compatibilizer comprising the maleic anhydride grafted copolymer PP.
11. A mixture prepared by using a mixture preparation method as in any one of the above claims from 1 to 8, **characterized by** the compatibilizer comprising the maleic anhydride grafted styrene ethylene butadiene styrene.
12. A mixture prepared by using a mixture preparation method as in any one of the above claims from 1 to 8, **characterized by** the compatibilizer comprising the maleic anhydride grafted ethylene propylene diene terpolymer.
13. A mixture prepared by using a mixture preparation method as in any one of the above claims from 1 to 8, **characterized by** the compatibilizer comprising the maleic anhydride grafted styrene ethylene butadiene styrene or maleic anhydride grafted ethylene propylene diene terpolymer together with the maleic anhydride grafted homopolymer PP or copolymer PP.
14. A mixture prepared by using a mixture preparation method as in any one of the above claims, **characterized by** the antioxidant stabilizer comprising the mixture of tris (2,4-ditert-butylphenyl)-phosphite and pentaerythritol tetrakis (3-(3,5-di tert-butyl-4-hydroxyphenyl)-propionate).

15. A washing machine comprising components based on the polymer material produced by using a mixture preparation method as in any one of the above claims.