

Polymer Compounding Composition and Recycling Process Thereof

Technical Field

The present invention relates to a polymer compound composition, using of the polymer compound, and a plastic recycling process.

5 **Background**

Plastic has been widely used to replace several other materials due to many of its properties including light weight, strength, durability, mouldability, flexibility, and cheaper cost. A major consequence from increasing consumption of plastic is accumulation of post-consumer plastic waste which could take hundreds of years to decompose.

10 Landfilling is one of the most common alternatives to take care of plastic waste. However, it has led to contamination of chemicals into soil and water.

Recycling of plastic waste has drawn a lot of attentions as a more environmental friendly alternative for taking care of plastic waste. Mechanical recycling requires simple process, but the recycled plastic obtained is usually of a lower physical properties. On the other hand, chemical
15 recycling has an advantage of recovering chemical constituents of the polymer, which can then be used to re-manufacturing plastic or to make other synthetic chemicals.

Chemical recycling of plastic can occur at high temperature, normally 800-1,000°C or above, without catalyst. Also, chemical recycling can occur at much lower temperature in the present of a suitable catalyst.

20 A Chinese patent publication CN101168678A discloses a method for recycling of a plastic waste, specifically polyethylene and polypropylene, using a catalyst containing KDC-1 phosphate modified zeolite and kaolin wherein major products are pyrolysis oil and diesel.

A US patent US7,932,424B2 discloses a method for catalytically cracking waste plastics wherein solid waste plastics are loaded into a horizontal-type reaction vessel including a rotary-
25 vane type agitator in the interior containing a mixture of a granular FCC waste catalyst and a granular Ca compound, the mixture thereby being heated to a temperature range from 350°C to 435°C, wherein the amount of the FCC waste catalyst is 20 to 60 vol% of the capacity of the reaction vessel, and the Ca compound is present in an amount of 15 to 50 parts by mass with

respect to 100 parts by mass of the FCC waste catalyst. The method provides improved selectivity of the oil fraction products in the range of C5-C10.

A US patent US8,344,195B2 discloses a process for producing fuel from a plastic waste material comprising performing pyrolysis of the plastic waste to produce a liquid material, and
5 then mixing the liquid material with a dolomite catalyst in a reactor to perform catalytic cracking.

Object of the present invention is to overcome drawbacks of the prior arts by providing a polymer compound and uses thereof, and a process for recycling of the polymer compound wherein the process is less complex and high selectivity towards lighter hydrocarbon products is
10 achieved.

Summary of the Invention

The object of this invention is achieved by providing a polymer compound comprising:

- (a) 50 to 99 percent by weight of a polymer; and
- (b) 1 to 50 percent by weight of a cracking catalyst.

15 The object of this invention is further achieved by providing a plastic recycling process comprising heating a plastic product produced from the polymer compound according to the present invention to a temperature in the range of 200°C to 1,000°C.

Detailed Description

20 The present invention relates to a polymer compound comprising: (a) 50 to 99 percent by weight of a polymer; and (b) 1 to 50 percent by weight of a cracking catalyst.

The term “polymer” as used herein means a material containing very large molecules which are built up from a series of small basic units (monomers). It can be both homopolymers and copolymers.

25 In an embodiment, the polymer is selected from polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyvinyl chloride, poly methyl methacrylate, and any combination thereof.

In a preferred embodiment, the polymer is selected from polyethylene, polypropylene, and combination thereof, more preferably polyethylene.

In another preferred embodiment, the polymer is polyethylene selected from low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene,
5 and high density polyethylene (HDPE), more preferably high density polyethylene.

The term “high density polyethylene” or “HDPE” as used herein refers to a polyethylene having a mass density in the range of 0.93 to 0.97 g/cm³.

In a further embodiment of the present invention, the polymer is a high density polyethylene having a mass density in the range of 0.93 to 0.96 g/cm³.

10 In another further embodiment, the polymer is a high density polyethylene having a Melt Flow Index in the range of 0.04 to 18 g/10min (190°C, 2.6 kg).

The Melt Flow Index, or MFI, as used herein refers to a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific diameter and length by a pressure applied via
15 prescribed alternative gravimetric weights for alternative prescribed temperatures. The method is described in the similar standards ASTM D1238 and ISO 1133.

Preferably, the polymer compound comprises 70 to 99 wt% of the polymer, more preferably is 80 to 99 wt% of the polymer.

The term “cracking catalyst” as used herein refers to any cracking catalytic materials
20 which may be useful for cracking hydrocarbons.

In an embodiment, the cracking catalyst is an acidic porous solid material. The acidic porous solid material is preferably selected from acidic clay, aluminium oxide, silicon dioxide, zeolite, zirconium oxide, zinc oxide, titanium dioxide, magnesium oxide, layered double oxide, and any combination thereof, more preferably is acidic clay.

25 The acidic clay can be naturally obtained. Preferably, the acidic clay is prepared by treating a non-acidic clay, more preferably a bentonite clay, with an acid chemical.

The term “bentonite” as used herein refers to a class of clay consisting essentially of montmorillonite. There are different types of bentonite, each named after the respective

dominant element, such as potassium bentonite, sodium bentonite, calcium bentonite, and aluminium bentonite.

Further preferably is treating the non-acidic clay with an acid chemical is performed by impregnating or ion-exchanging a non-acidic clay, more preferably a bentonite clay, with an acid
5 chemical solution. For example, the acid chemical can be selected from HCl, HI, HBr, H₂SO₄, (NH₄)₂SO₄, CH₃COOH, BF₃, HNO₃, and HClO₄.

It is favorable that the acidic clay has a proton content of at least 1 micromole per gram.

Preferably, measurement method for determining the proton content of material can be referenced from D.E. Lopez, J.G. Goodwin Jr., D.A. Bruce, Journal of Catalysis, 245 (2007)
10 381-391.

Alternatively, the acidic clay is an iron containing clay, preferably an iron containing bentonite clay.

It is preferred that the polymer compound according to the present invention comprises 1 to 30 wt% of the cracking catalyst, more preferably 1 to 20 wt% of the cracking catalyst.

15 In another embodiment, the cracking catalyst has an average diameter in the range of 1 to 500 micrometers, preferably 100-300 micrometers.

The average diameter as used herein can refer to either primary particle size or secondary particle size, wherein the secondary particle size is the size of agglomerated primary particles.

In a further embodiment, the polymer compound further comprises any additive and/or
20 filler which facilitate modification of chemical and/or physical property of the polymer compound as differently required according to the desired end uses. For example, the polymer compound can further comprise a color pigment such as TiO₂ for white color.

The polymer compound, in an embodiment, is preferably prepared by compounding 50 to 99 wt% of the polymer with 1 to 50 wt% of the cracking catalyst.

25 The term "compounding" as used herein refers to a method of producing a polymer compound including preparing plastic formulations by mixing and/or blending polymers and other ingredients in a molten state.

Any technique for polymer compounding known by persons skilled in the art can be used for the present invention without limitation. In an embodiment, compounding of the polymer and the cracking catalyst is performed by an extrusion technique.

5 The term “extrusion” as used herein refers to a process in which a hot or cold semisoft solid material, such as plastic, is forced through the orifice of a die to produce a continuously formed piece in the shape of the desired product.

It is favorable for the present invention that the extrusion is carried out using a twin screw extruder. Operating condition of the extruder can be varied widely depending on specification of the equipment. In one embodiment, the twin screw extruder is operating, at a
10 screw speed in the range of 130 to 300 rpm.

Further preferably is the extrusion is carried out at an extruder die temperature in the range of 100 to 230°C, more preferably 120 to 210°C.

The polymer compound according to the present invention can be used for producing many plastic products such as bag, bottle, film, and pipe.

15 The polymer compound can be subjected to different plastic forming method including blow molding, injection molding, and rotational molding, for example, in order to produce the desired plastic product.

In one embodiment, the polymer compound is used to produce a plastic film, preferably by film injection method.

20 The film injection method is preferably carried out using a twin screw extruder equipped with a film-injection die.

Also preferably is the film injection method is carried out at a screw speed in the range of 130 to 300 rpm, more preferably 140 to 200 rpm, even more preferably 145 to 180 rpm.

Further preferably is the film injection method is carried out at an extruder die
25 temperature in the range of 100 to 230°C, more preferably 150 to 210°C.

The object of the present invention is further achieved by providing a plastic recycling process comprising: (a) placing a plastic product produced from the polymer compound according to the present invention in a reactor; and (b) heating the plastic product to a

temperature in the range of 200 to 1,000°C, preferably 250 to 800°C, more preferably 350 to 600°C.

The plastic product produced from the inventive polymer compound can be of any type. In an embodiment, the plastic product is bag, film, or combination thereof.

5 In a further embodiment, the plastic product is a freshly produced plastic product.

In a more preferred embodiment, the plastic product is a post-consumer plastic product.

Reducing the size of the plastic product before placing it in the reactor is generally not necessary, unless the plastic product is too large to fit in the reactor or higher volume of the plastic product to be processed in a single reactor is desired.

10 No additional catalyst is required to be placed in the reactor with the plastic product.

The reactor used can be of any type. In one embodiment, the reactor is a batch reactor. In an alternative embodiment, the reactor is a continuous reactor selected from a fixed-bed reactor, a fluidized bed reactor, a moving bed reactor, and a CSTR reactor.

15 The reaction time required for the process depends on several factors including amount of the plastic product raw material, type and size of the reactor used.

In an embodiment, the reactor is a batch reactor and heating the plastic product is carried out for a period of 0.5 to 10 hours, preferably 1 to 5 hours.

20 It is favorable for the present invention that the process is performed in an inert atmosphere. In an embodiment, the process further comprises, prior to heating the plastic product in step (b), purging the reactor with an inert gas, preferably nitrogen, to obtain a substantially inert, oxygen-free atmosphere inside the reactor.

In another embodiment, the process is carried out at a pressure in the range of 0 to 10 bar gauge, preferably 1 to 5 bar gauge.

25 It was surprisingly found by the inventors that the plastic recycling process according to this invention can convert the plastic product produced from the polymer compound according to this invention, using simple equipment, with high selectivity towards light hydrocarbon, specifically methane, ethane, propane, and butane, which can be further utilized as a feedstock in

many industrial processes or they can be further purified and used as raw materials for manufacturing of higher value synthetic chemicals or can be further distilled and used as a transportation fuel.

Example

- 5 The following examples are given for the purpose of illustration only, and are not intended to limit the scope of the invention in any way.

Example 1: Producing of an inventive polymer compound

- A non-acidic sodium bentonite clay was contacted with 2 wt% of ammonium sulfate solution at room temperature followed by drying at 120°C for 3 hours to produce an acid treated
10 bentonite.

- Fine powder of HDPE with MFI of 0.04 g/10 min (ASTM D1238) and density of 0.956 g/cm³ (ASTM D1505) was blended well with 7 wt% of the acid treated bentonite in 100 micron size. The mixture of HDPE and acid treated bentonite was then fed to a twin screw extruder running at a screw speed of approximately 150 rpm and a die temperature of approximately
15 150°C to produce a HDPE compound.

Example 2: Producing of an inventive plastic film

- The HDPE compound produced in Example 1 was then converted to a plastic film by feeding the HDPE compound through a feeder of a twin screw extruder equipped with a film-injection die running at a screw speed of 150 rpm and a die temperature of 170-220°C. The
20 plastic film was produced at a production rate of 500g/45 minutes.

Physical properties of the obtained plastic film are shown in Table 1.

Table 1

Tensile Strength at Yield	MD: 217	TD: 666	kg/cm2	ASTM D882
Tensile Strength at Break	MD: 225	TD: 737	kg/cm2	ASTM D882
Tensile Modulus, 2% Secant	MD: 4189	TD: 3431	kg/cm2	ASTM D882
Elongation at Break	MD: 303	TD: 480	kg/cm2	ASTM D882

MD = Machine Direction, TD = Transverse Direction

Example 3: An inventive plastic recycling process

The plastic film produced in Example 2 was subjected to a recycling process as follow:

- (1) Placing 10 grams of plastic film in a 50 cc 316-stainless steel batch reactor
- (2) Purging the reactor with nitrogen gas 5 times.
- 5 (3) Heating the reactor to 450°C for 2 hours at 2 bar gauge by placing it into the muffle furnace
- (4) Cooling down to temperature below 100°C
- (5) Connecting the heated reactor with GC-FID by 1/8" stainless steel tube in order to analyze the product distribution

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Product distribution results are shown in Table 3.

Example 4: Comparative Example

The same steps as described in Example 1-3 were repeated but the non-acidic sodium bentonite was used without acid treatment.

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Product distribution results are shown in Table 3.

Example 5: Comparative Example

Fine powder of HDPE with MFI of 0.04 g/10 min (ASTM D1238) and density of 0.956 g/cm³ (ASTM D1505) was subjected to a film injection step as described in Example 2 without any cracking catalyst added. Physical properties of the resulted plastic film are shown in Table 2.

20 Table 2

Tensile Strength at Yield	MD: 253	TD: 355	kg/cm2	ASTM D882
Tensile Strength at Break	MD: 340	TD: 726	kg/cm2	ASTM D882
Tensile Modulus, 2% Secant	MD: 4347	TD: 2956	kg/cm2	ASTM D882
Elongation at Break	MD: 858	TD: 766	kg/cm2	ASTM D882

MD = Machine Direction, TD = Transverse Direction

The plastic film was then subjected to the plastic recycling process as described in Example 3. Product distribution results are shown in Table 3.

Example 6: Comparative Example

The plastic film as described in Example 5 was physically mixed with 7wt% of acid treated bentonite as described in Example 1 in a 50cc 316-stainless steel batch reactor and then steps (2) – (5) as described in Example 3 were repeated.

5 Product distribution results are shown in Table 3.

Example 7: Inventive Example

The same steps as described in Example 1-3 were repeated except the reactor was heated up to 600°C instead of 450°C in step (3).

Product distribution results are shown in Table 3.

Table 3

	Example 3	Example 4	Example 5	Example 6	Example 7
Polymer	HDPE	HDPE	HDPE	HDPE	HDPE
Catalyst Type	acidic Bentonite	non acidic Bentonite	no	acidic Bentonite	acidicBentonite
Catalyst Content	7%	7%	0%	7%	7%
Blending Method	Extrusion	Extrusion	no	Physical Mix in Reactor	Extrusion
Furnace Temperature	450°C	450°C	450°C	450°C	600°C
Component	wt%	wt%	wt%	wt%	wt%
Methane	7.6	0.3	-	-	21.6
Ethane	30.6	1.2	-	0.2	37.7
Ethylene	0.5	0.0	-	-	0.5
Propane	31.0	4.3	-	0.5	24
Propylene	2.8	1.1	-	-	1.4
Butane	16.0	3.3	-	1.1	9.3
Tran-2-Butene	0.6	0.0	-	-	0.1
1-Butene	0.4	0.0	-	-	0.1
iso-Butene	0.7	0.0	-	-	0.1
Cis-2-Butene	0.4	0.0	-	0.1	0.1
Pentane	6.5	7.6	4.3	8.3	3.3
Pentene	1.2	3.2	1.7	4.7	1
Hexane+Hexene	1.7	20.2	17.6	19.1	0.8
C7+	-	58.8	76.4	66	-
Total	100	100	100	100	100

It can be seen from the results above that when an acidic porous solid material, such as acidic bentonite, is directly compounded into the polymer, the resulted plastic product can be conveniently converted with high selectivity toward lighter hydrocarbon products in the range of C1 to C4.

Claims

1. A polymer compound comprising:
 - (a) 50 to 99 percent by weight of a polymer; and
 - (b) 1 to 50 percent by weight of a cracking catalyst.
- 5 2. The polymer compound according to claim 1, wherein the polymer is selected from polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyvinyl chloride, poly methyl methacrylate, and any combination thereof.
3. The polymer compound according to claim 1 or 2, wherein the polymer is polyethylene selected from low density polyethylene, linear low density polyethylene, medium density
10 polyethylene, and high density polyethylene.
4. The polymer compound according to any of the preceding claims, wherein the cracking catalyst is an acidic porous solid material.
5. The polymer compound according to claim 4, wherein the acidic porous solid material is selected from acidic clay, aluminium oxide, silicon dioxide, zeolite, zirconium oxide,
15 zinc oxide, titanium dioxide, magnesium oxide, layered double oxide, and any combination thereof.
6. The polymer compound according to claim 5, wherein the acidic porous solid material is acidic clay prepared by treating a non-acidic clay with an acid chemical.
7. The polymer compound according to claim 6, wherein the non-acid clay is a bentonite
20 clay.
8. The polymer compound according to any of the preceding claims, wherein the acidic porous solid material has a proton content of at least 1 micromole per gram.
9. The polymer compound according to any of the preceding claims, wherein the cracking catalyst has an average diameter in the range of 1 to 500 micrometers.
- 25 10. Use of the polymer compound according to any of the preceding claims to produce a plastic product.

11. Use of the polymer compound according to claim 9, wherein the plastic product is bag, bottle, film, or pipe.
12. A plastic recycling process comprising:
- (a) placing a plastic product produced from the polymer compound according to any of claim 1 to 9 in a reactor; and
 - (b) heating the plastic product to a temperature in the range of 200 to 1,000°C.
13. The plastic recycling process according to claim 12, wherein the plastic product is bag, film, or combination thereof.
14. The plastic recycling process according to claim 12 or 13, wherein the process further comprises, prior to step (b), purging the reactor with an inert gas.