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RUBBER PRODUCT MADE OUT OF PYROLYSIS OIL VIA A POLYMERIZATION

Abstract

The present invention relates to a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and an oligomeric product prepared from pyrolysis oil via polymerization being preferably a cationic polymerization.

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Background/Summary

FIELD OF THE DISCLOSURE

[0001] The disclosure relates to the preparation of an oligomeric product or liquid resin prepared via polymerization of pyrolysis oil. The disclosure also relates to a rubber composition comprising of said oligomeric product or liquid resin. In particular, the disclosure relates to the polymerization of the polymerizable components in the pyrolysis oil preferably via polymerization on the oil obtained preferably from the pyrolysis of plastic in order to obtain an oligomeric product that can be further used in rubber applications.

BACKGROUND OF THE DISCLOSURE

[0002] Waste plastics are mostly diverted to landfills or incinerated, with a smaller fraction diverting to recycling. There is however a strong need, influenced by the regulations to limit waste plastic in landfills. On the other hand, waste plastics disposal in landfills is becoming increasingly difficult. There is therefore a need for recycling waste plastic.

[0003] A possible route to recycle plastic is via plastic pyrolysis. However, the pyrolysis plastic oil obtained from plastic pyrolysis generally is generally not easily valorised. The pyrolysis plastic oil contains large quantities of impurities and also large quantities of dienes and of olefins.

[0004] FR3,116,279 relates to a method for producing hydrocarbon resins from a feedstock containing rubber chips, the method comprising at least one pyrolysis step and a resin synthesis step.

[0005] US2016/369015 relates to backbone-modified elastomeric polymers and to polymer compositions comprising such modified polymers, to the use of such compositions in the preparation of vulcanized polymer compositions, and to articles prepared from the same. The modified polymers are useful in the preparation of vulcanized, i.e. cross-linked, elastomeric compositions having relatively low hysteresis loss.

[0006] US2020/377700 relates to a sulphur-crosslinkable rubber mixture, its vulcanizate and a vehicle tire. The sulfur-crosslinkable rubber mixture contains at least the following components at least one diene rubber; and 10 to 300 phr of at least one silicic acid; 1 to 30 phr of at least one silane of a specific formula and 0.5 to 30 phr of at least one silane of a specific formula.

[0007] There is therefore a need for the valorization of those pyrolysis plastic oil. More precisely, there is clearly a need for the valorization of the polymerizable materials present in the pyrolysis plastic oils.

SUMMARY OF THE DISCLOSURE

[0008] The aim of the present disclosure is to provide a valorisation route of the olefins, dienes, and other polymerizable materials that are present in the pyrolysis oil. More precisely, the aim of the present disclosure is to convert the polymerizable components present in the pyrolysis oil into valuable oligomeric products via polymerization. In particular, it was found that it is possible to produce rubber composition from liquid resin prepared from a liquified waste polymer; wherein the liquid resin is an oligomeric product that can be liquid at ambient temperature.

[0009] Surprisingly, the rubber composition comprising such oligomeric product allows, when used

in a tire, an improvement in tire performances at least one of the dispersion of silica, wet traction and rolling resistance. The disclosure aims to the valorization of the olefins and of the dienes present in the pyrolysis plastic oils together with the provision of a rubber composition that allows an improvement for at least one of the dispersion of silica, wet traction, and rolling resistance.

[0010] It has been discovered that the oligomeric products prepared from pyrolysis oil, and especially from pyrolysis plastic oil, are particularly advantageous. Indeed, such oligomeric products present a relatively low viscosity. With a low viscosity, it is easier to handle the oligomeric product making it is easier to mix the oligomeric product with other components and using less mechanical energy to mix the oligomeric product with other components. Another advantage of the oligomeric product lies in its content in aromatics, improving the compatibility of the oligomeric product with certain other constituent of a rubber composition.

[0011] According to a first aspect, the disclosure relates to a rubber composition comprising:

[0012] a) At least one elastomer selected from synthetic and natural elastomers; [0013] b) A curing agent; and [0014] c) An oligomeric product prepared from a liquified waste polymer the oligomeric product having a number average molecular weight, M_n , ranging from 100 to 10 000 g/mol measured using gel permeation chromatography and a polystyrene calibration and wherein the oligomeric product shows a glass transition temperature (T_g) below -20°C . as determined by Differential Scanning calorimetry or a crystallization temperature below 35°C .

[0015] In some embodiments, the content of said at least one elastomer in the rubber composition ranges from 1 to 150 phr; preferably, from 1 to 120 phr; more preferably from 1 to 100 phr; from 50 to 150 phr.

[0016] In some embodiments, the content of said curative agent in the rubber composition ranges from 0.1-25 phr; preferably, from 0.5 to 22 phr; more preferably from 1 to 20 phr, and even more preferably from 5 to 18 phr.

[0017] In some embodiments, the content of said oligomeric product in the rubber composition ranges from 0.1 to 50 phr; preferably, from 0.5 to 40 phr; more preferably from 1 to 30 phr, even more preferably from 5 to 25 phr.

[0018] In some embodiments, the oligomeric product shows an olefinic content of at most 20.0 wt. % as determined by ^1H NMR. With preference, the liquid resin an olefinic content ranging from 0.1 to 20.0 wt. %; preferably from 0.3 to 15.0 wt. %; more preferably, from 0.5 to 10.0 wt. %. from 0.8 to 5.0 wt. %.

[0019] In some embodiments, the oligomeric product shows an aliphatic content ranging from 15 to 100 wt. % as determined by ^1H NMR; preferably ranging from 40.0 to 99.5 wt. %; more preferably ranging from 50.0 to 99.0 wt. %; even more preferably ranging from 70.0 to 98.5 wt. %; and most preferably ranging from 80.0 to 98.0 wt. %.

[0020] In one or more embodiments, the oligomeric product shows an aromatic content ranging from 0.3 to 45.0 wt. % as determined by ^1H NMR; preferably ranging from 0.5 to 40.0 wt. %; more preferably ranging from 0.8 to 30.0 wt. %; and even more preferably ranging from 1.0 to 20.0 wt. %.

[0021] In embodiments, the oligomeric product has viscosity at 30°C . ranging from 10 to 50 000 cps measured using a Brookfield viscometer; preferably ranging from 10 to 50 000 cps; more ranging from 10 to 10 000 cps; even more preferably ranging from 10 to 4 000 cps; and most preferably ranging from 10 to 2 500 cps.

[0022] In some embodiments, the oligomeric product has a number average molecular weight (M_n) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 140 to 1,000 g/mol; even more preferably from 150 to 800 g/mol; most preferably from 180 to 700 g/mol; or from 200 to 650 g/mol; or from 250 to 550 g/mol.

[0023] In some embodiments, the oligomeric product has a weight average molecular weight (M_w) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a

polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 150 to 3,500 g/mol; and even more preferably from 200 to 2,000 g/mol.

[0024] In some embodiments, the oligomeric product has a z-average molecular weight (Mz) ranging from 100 to 100,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 85,000 g/mol; more preferably from 150 to 70,000 g/mol; and even more preferably from 200 to 50,000 g/mol.

[0025] In some embodiments, the oligomeric product has a Mw/Mn ranging from 1.0 to 10.0; preferably from 1.0 to 5.0; more preferably from 1.0 to 4.0; and even more preferably from 1.1 to 2.8.

[0026] In a preferred embodiment, the oligomeric product comprises a comonomer selected from the group consisting of styrene, alpha-methyl styrene, 2-methyl styrene, 3-methyl styrene, 4-methyl styrene, 4-t-butyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2,4-diisopropyl styrene, 2,4,6-trimethyl styrene, 2-ethyl-4-benzylstyrene, 4-(phenylbutyl) styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl anthracene, 4-methoxy styrene, monochlorostyrene, dichlorostyrene, divinyl benzene, Indene, methyl-Indene, and mixtures thereof; with preference the liquid resin (i.e., the oligomeric product) comprises a comonomer being or comprising styrene.

[0027] In embodiments, the oligomeric product comprises a comonomer present at a concentration ranging from 0.01 to 90 mol. % based on the total weight of the liquid resin, preferably from 1.0 to 80 mol. %.

[0028] In some embodiments, the oligomeric product is a wax and/or shows a crystallization temperature (Tc) below 35° C.; preferably ranging from 18 to 32° C.; more preferably ranging from 20 to 30° C.; and even more preferably ranging from 21 to 29° C.

[0029] In embodiments, the oligomeric product is a resin and/or shows a glass transition temperature (Tg) below -20° C. as determined by Differential Scanning calorimetry; preferably ranging from -60° C. to -25° C.; more preferably from -50° C. to -30° C.; and even more preferably from -49° C. to -35° C.

[0030] According to a second aspect, the disclosure provides a tire comprising a rubber composition according to the first aspect, preferably comprising said oligomeric product in a content ranging from 1 to 50 phr.

[0031] According to a third aspect, the disclosure provides a process for the preparation of a rubber composition according to the first aspect comprising the following steps: [0032] a) providing a feedstream containing liquified waste polymer, wherein said feedstream contains at least 0.1 wt. % to at most 80 wt. % of dienes based on the total weight of said feedstream; [0033] c) performing a polymerization reaction on said feedstream under polymerization conditions to obtain a first product stream comprising an oligomeric product and a purified liquified waste polymer; [0034] d) optionally, performing a neutralization reaction by contacting said first product stream with a basic compound to obtain a neutralized product stream and removing said basic compound from neutralized product stream to obtain a second product stream; [0035] g) performing a separation to separate the oligomeric product from the purified liquified waste polymer; and [0036] h) preparing a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and said oligomeric recovered at step g).

[0037] In some embodiments the liquified waste polymer is a pyrolysis plastic oil, with preference, step a) of providing a feedstream containing liquified waste polymer comprises the preliminary steps of preparation of liquified waste polymer including: [0038] a1) of providing a waste plastics stream; [0039] a2) pyrolyzing said waste plastics stream at a temperature of at least 200° C.; [0040] a3) recovering a pyrolizer effluent and separating, into a C1 to C4 hydrocarbons fraction, a fraction having a boiling range higher than 350° C. and a remaining fraction being said pyrolysis plastic oil; [0041] a4) optionally sending the fraction having a boiling range higher than 350° C. into a Fluid Catalytic Cracking (FCC) unit, or a hydrocracking unit, a coker or a visbreaker or blending said fraction having a boiling range higher than 350° C. in crude oil or in a crude oil cut to be further

refined.

[0042] In one or more embodiments, the process further comprises a step b) of drying the feedstream to obtain a dried feedstream wherein step b) is performed before step c) of polymerization so that step c) of polymerization reaction is performed on the dried feedstream. With preference, step b) of drying is performed and comprises a sub-step b1) of decantation and/or centrifugation. More preferably, the first sub-step b1) is followed by a second sub-step b2) of drying using a molecular sieve to reach a water content of less than 0.1 vol. % according to ASTM D95-13 (2018).

[0043] In some embodiments, the feedstream contains at least 75 wt. % of the liquefied waste polymer based on the total weight of the feed stream.

[0044] Step c) comprises performing a polymerization reaction preferably a cationic polymerization or a free radical polymerization or an anionic polymerization.

[0045] In a preferred embodiment, the polymerization reaction is a cationic polymerization; more preferably, the polymerization reaction in step c) is a cationic polymerization performed in the presence of an acidic catalyst; with preference, the acidic catalyst is a Brønsted acid or a Lewis acid.

[0046] In a preferred embodiment, the polymerization reaction in step c) is a cationic polymerization performed in the presence of an acidic catalyst being a Lewis acid chosen among BF_3 , complexes of boron trifluoride, AlCl_3 , SnCl_4 , ZnCl_2 , FeCl_3 and TiCl_3 , alkyl aluminium chlorides, H_2SO_4 or any mixture thereof; with preference, acidic catalyst is or comprises boron trifluoride etherate.

[0047] In embodiments, the process of acidic catalyst is present at a concentration ranging from 0.5 wt. % to 5.0 wt. % based on the total weight of said feedstream and/or the polymerization reaction of step c) is carried out until the dienes of the purified liquified waste polymer is less than 5.0 wt. % based on the total weight of the first product stream.

[0048] In a preferred embodiment, the polymerization conditions of step (c) comprise a contact time ranging from 5 min to 5 hours; and/or a temperature ranging from 5 to 100° C. at atmospheric pressure.

[0049] In embodiments, the polymerization reaction on step c) is performed in the presence of one or more comonomers; with preference, the one or more comonomers comprise a vinyl aromatic and/or the one or more comonomers are present at a concentration from 1.0 to 25.0 wt. % based on the total weight of the liquified waste polymer.

[0050] In some embodiments, the basic compound forms a basic stream; wherein the basic stream and the first product stream are contacted with a weight ratio ranging from 1:1 to 1:1,000.

[0051] In some embodiments, the step d) is performed and the concentration of the basic compound ranges from 0.1 to 50.0 wt. % based on the total weight of said neutralized product stream.

[0052] In a preferred embodiment, step d) is performed and the basic compound: [0053] has a pKa in water ranging from 7.5 to 14; and/or [0054] is selected from LiOH , NaOH , CsOH , $\text{Ba}(\text{OH})_2$, Na_2O , KOH , K_2O , CaO , $\text{Ca}(\text{OH})_2$, MgO , $\text{Mg}(\text{OH})_2$, NH_4OH or any mixtures thereof.

[0055] In embodiments, step d) is performed in continuous mode; and/or the removal of said basic compound from neutralized product stream, to obtain a second product stream, is performed by decantation and/or by centrifugation.

[0056] In embodiments, the process further comprises a step e) of washing the first product stream or the second product stream with a solvent to obtain a washed stream; with preference, the washing is performed at a temperature ranging from 5° C. to 95° C.

[0057] In a preferred embodiment, the solvent is selected from water or an aqueous acidic solution comprising: [0058] one or more organic acids selected from citric acid ($\text{C}_6\text{H}_8\text{O}_7$), formic acid (CH_2O_2), acetic acid (CH_3COOH), sulfamic acid (H_3NSO_3) and any combination thereof; and/or [0059] one or more inorganic acids selected from hydrochloric

acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and any combination thereof.

[0060] In some embodiments, the washing is performed until the pH of said washed stream, is in the range of 5.0 to 9.0; and/or the washing is followed by a decantation and/or a centrifugation to separate the solvent from washed stream.

[0061] In embodiments, the process further comprises a step f) of filtering the stream obtained in the previous step to obtain a filtered stream wherein the filtering is performed to remove solids from the first product stream or from the second product stream or from the washed stream, and/or to coalesce remaining traces of solvent if any; with preference, the filtering step is followed by a dewatering step.

[0062] In embodiments, the step g) of separation is performed via distillation or steam distillation or vacuum stripping or fractional distillation, or any combination.

[0063] In a preferred embodiment, after the separation step g), the purified liquified waste polymer is recovered and blended in the fuel pool; with preference, the purified liquified waste polymer is separated in a naphtha cut having a boiling range of less than 150° C. and a diesel cut having a boiling range between 15° and 350° C. wherein said naphtha cut is incorporated in a naphtha pool, said diesel cut is incorporated in a diesel pool.

[0064] In a preferred embodiment, the liquified waste polymer in the feedstream has a final boiling point of at most 700° C.

[0065] In a preferred embodiment, the feedstream contains from 0.1 to 50.0 wt. % of dienes based on the total weight of said feedstream; preferably from 0.1 to 25.0 wt. %.

[0066] In one or more embodiments, the liquified waste polymer is a pyrolysis oil preferably a pyrolysis plastic oil, or any pyrolysis oil prepared out of waste plastic, rubber, biomass, used tires or any mixture thereof.

[0067] According to a fourth aspect, the disclosure provides an installation for carrying out the process of the third aspect, said installation is remarkable in that it comprises: [0068] a polymerization section; [0069] an optional neutralization section; [0070] a separation section; wherein the polymerization section and the separation section are fluidically connected in series, and wherein the neutralization section when present is placed downstream of the polymerization section and upstream of the separation section.

[0071] With preference, the installation comprises: [0072] a pre-treatment section comprising a pyrolysis unit, one or more separation units, and an optional washing unit; [0073] a drying section comprising a decanter and/or a centrifuge; and/or a molecular sieve; [0074] a polymerization section comprising one or more polymerization reactors; preferably loaded with an acidic catalyst; [0075] a neutralization section a mixing reactor and an optional separation unit comprising at least one selected from a decanter, a centrifuge, and a filter; [0076] a washing section comprising a mixing vessel and a separation unit comprising a decanter and/or a centrifuge; [0077] a filtering section comprising a filter and an optional molecular sieve. [0078] a separation section comprising a separation unit comprising one or more distillation columns.

[0079] With preference, the installation further comprises a mixing unit to prepare the rubber composition from the oligomeric product recovered from the separation section. the disclosure relates to a rubber composition comprising: [0080] a) At least one elastomer selected from synthetic and natural elastomers; [0081] b) A curing agent; and [0082] c) An oligomeric product prepared from a liquified waste polymer the oligomeric product having a number average molecular weight, Mn, ranging from 100 to 10 000 g/mol measured using gel permeation chromatography and a polystyrene calibration and wherein the oligomeric product shows a glass transition temperature (Tg) below -20° C. as determined by Differential Scanning calorimetry or a crystallization temperature below 35° C.

[0083] In some embodiments, the content of said at least one elastomer in the rubber composition ranges from 1 to 150 phr; preferably, from 1 to 120 phr; more preferably from 1 to 100 phr; from

50 to 150 phr.

[0084] In some embodiments, the content of said curative agent in the rubber composition ranges from 0.1 to 25 phr; preferably, from 0.5 to 22 phr; more preferably from 1 to 20 phr, even more preferably from 5 to 18 phr.

[0085] In some embodiments, the content of said oligomeric product in the rubber composition ranges from 0.1 to 50 phr; preferably, from 0.5 to 40 phr; more preferably from 1 to 30 phr, and even more preferably from 5 to 25 phr.

[0086] In some embodiments, the oligomeric product shows an olefinic content of at most 20.0 wt. % as determined by ^1H NMR. With preference, the liquid resin has an olefinic content ranging from 0.1 to 20.0 wt. %; preferably from 0.3 to 15.0 wt. %; more preferably, from 0.5 to 10.0 wt. %; from 0.8 to 5.0 wt. %.

[0087] In some embodiments, the oligomeric product shows an aliphatic content ranging from 15 to 100 wt. % as determined by ^1H NMR; preferably ranging from 40.0 to 99.5 wt. %; more preferably ranging from 50.0 to 99.0 wt. %; even more preferably ranging from 70.0 to 98.5 wt. %; and most preferably ranging from 80.0 to 98.0 wt. %.

[0088] In one or more embodiments, the oligomeric product shows an aromatic content ranging from 0.3 to 45.0 wt. % as determined by ^1H NMR; preferably ranging from 0.5 to 40.0 wt. %; more preferably ranging from 0.8 to 30.0 wt. %; and even more preferably ranging from 1.0 to 20.0 wt. %.

[0089] In embodiments, the oligomeric product has viscosity at 30° C. ranging from 10 to 50 000 cps measured using a Brookfield viscometer; preferably ranging from 10 to 50 000 cps; more ranging from 10 to 10 000 cps; even more preferably ranging from 10 to 4 000 cps; and most preferably ranging from 10 to 2 500 cps.

[0090] In some embodiments, the oligomeric product has a number average molecular weight (M_n) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 140 to 1,000 g/mol; even more preferably from 150 to 800 g/mol; most preferably from 180 to 700 g/mol; or from 200 to 650 g/mol; or from 250 to 550 g/mol.

[0091] In some embodiments, the oligomeric product has a weight average molecular weight (M_w) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 150 to 3,500 g/mol; and even more preferably from 200 to 2,000 g/mol.

[0092] In some embodiments, the oligomeric product has a z-average molecular weight (M_z) ranging from 100 to 100,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 85,000 g/mol; more preferably from 150 to 70,000 g/mol; and even more preferably from 200 to 50,000 g/mol.

[0093] In some embodiments, the oligomeric product has a M_w/M_n ranging from 1.0 to 10.0; preferably from 1.0 to 5.0; more preferably from 1.0 to 4.0; and even more preferably from 1.1 to 2.8.

[0094] In a preferred embodiment, the oligomeric product comprises a comonomer selected from the group consisting of styrene, alpha-methyl styrene, 2-methyl styrene, 3-methyl styrene, 4-methyl styrene, 4-t-butyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2,4-diisopropyl styrene, 2,4,6-trimethyl styrene, 2-ethyl-4-benzylstyrene, 4-(phenylbutyl) styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl anthracene, 4-methoxy styrene, monochlorostyrene, dichlorostyrene, divinyl benzene, Indene, methyl-Indene, and mixtures thereof; with preference the liquid resin (i.e., the oligomeric product) comprises a comonomer being or comprising styrene.

[0095] In embodiments, the oligomeric product comprises a comonomer present at a concentration ranging from 0.01 to 90 mol. % based on the total weight of the liquid resin, preferably from 1.0 to 80 mol. %.

[0096] In some embodiments, the oligomeric product is a wax and/or shows a crystallisation

temperature (T_c) below 35° C.; preferably ranging from 18 to 32° C.; more preferably ranging from 20 to 30° C.; and even more preferably ranging from 21 to 29° C.

[0097] In embodiments, the oligomeric product is a resin and/or shows a glass transition temperature (T_g) below -20° C. as determined by Differential Scanning calorimetry; preferably ranging from -60° C. to -25° C.; more preferably from -50° C. to -30° C.; and even more preferably from -49° C. to -35° C.

Description

DESCRIPTION OF THE FIGURES

[0098] FIG. 1 describes a possible embodiment of the invention. In this possible embodiment, the liquified waste polymer is firstly optionally dried, sent to the cationic polymerization to convert the dienes into oligomeric products. The effluents of the cationic polymerization are then sent to an optional treatment with a basic compound followed by the removal of the basic compound and followed by an optional washing step. After an optional filtering step, the various fractions are separated into various fraction depending on the boiling point. If a heavy fraction can be separated, it is sent to conversion units. The oligomeric product that is converted into resins can also be separated. If a remaining fraction of purified plastic oil fraction is present it can be sent to a hydrotreatment or a cracking or a steam cracking to produce olefins being further polymerized. The oligomeric product obtained can also be further used as valuable resins.

[0099] FIG. 2 presents the calibration curve for maleic anhydride concentration.

[0100] FIG. 3 presents the 1 H NMR olefinic content of treated pyrolysis oil compared to crude pyrolysis oil of examples 2 to 4.

[0101] FIG. 4 presents the olefinic carbon stretching peak areas from FTIR of examples 2 to 4.

[0102] FIG. 5 illustrates the installation to prepare the oligomeric product.

DEFINITIONS AND ANALYTICAL METHODS

[0103] For the purpose of the disclosure, the following definitions are given: The terms “alkane” or “alkanes” as used herein describe acyclic branched or unbranched hydrocarbons having the general formula C_nH_{2n+2}, and therefore consisting entirely of hydrogen atoms and saturated carbon atoms; see e.g. IUPAC. Compendium of Chemical Terminology, 2nd ed. (1997). The term “alkanes” accordingly describes unbranched alkanes (“normal-paraffins” or “n-paraffins” or “n-alkanes” or “paraffins”) and branched alkanes (“iso-paraffins” or “iso-alkanes”) but excludes naphthenes (cycloalkanes). They are sometimes referred to by the symbol “HC-”.

[0104] The terms “olefin” or “alkene” as used herein relate to an unsaturated hydrocarbon compound containing at least one carbon-carbon double bond. They are sometimes referred to by the symbol “HC=”.

[0105] The term “hydrocarbon” refers to the alkanes (saturated hydrocarbons), cycloalkanes, aromatics and unsaturated hydrocarbons together.

[0106] The terms “comprising”, “comprises” and “comprised of” as used herein are synonymous with “including”, “includes” or “containing”, “contains”, and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. The terms “comprising”, “comprises” and “comprised of” also include the term “consisting of”.

[0107] The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of endpoints also includes the recited endpoint values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

[0108] The term “conversion” means the mole fraction (i.e., percent) of a reactant converted to a

product or products. The term “selectivity” refers to the percentage of converted reactants that went to a specified product.

[0109] The terms “wt. %”, “vol. %”, or “mol. %” refers to the weight, volume, or molar percentage of a component, respectively, based on the total weight, the total volume of material, or total moles, that includes the component. In a non-limiting example, 10 grams of a component in 100 grams of the material is 10 wt. % of the component.

[0110] The term “naphtha” refers to the general definition used in the oil and gas industry. In particular, it refers to a hydrocarbon originating from crude oil distillation having a boiling range from 15 to 250° C. as measured by ASTM D2887-22e1. Naphtha contains substantially no olefins as the hydrocarbons originate from crude oil. It is generally considered that a naphtha has a carbon number between C3 and C11, although the carbon number can reach in some cases C15. It is also generally admitted that the density of naphtha ranges from 0.65 to 0.77 g/mL.

[0111] The term “gasoil” refers to the general definition used in the oil and gas industry. In particular, it refers to a hydrocarbon having a boiling point in the range of 250 to 350° C. as measured according to the ASTM D7500-15(2019).

[0112] The term “liquified waste polymer” refers to any hydrocarbon liquid obtained from a waste polymer, preferably obtained from waste plastics. To obtain such liquified waste polymer, processess such as hydrothermal liquefaction or thermal pyrolysis or catalytic pyrolysis or steam pyrolysis or even pyrolysis in the presence of hydrogen of waste polymer can be used. The waste polymers encompass any polymer that is considered as waste such as waste polyethylene (PE), waste polypropylene (PP), waste polyethylene terephthalate (PET), waste polyvinyl chlorine (PVC) but also other polymers originating from waste or used tires for instance. The term “liquified waste polymer” also encompasses “pyrolysis plastic oil”.

[0113] The term “pyrolysis plastic oil” refers to the liquid products obtained once waste plastic have been thermally pyrolyzed. The pyrolysis process shall be understood as an unselective thermal cracking process. The pyrolysis involves the breaking of the polymer chains by heating. Rather than breaking the polymer down to its original monomers, pyrolysis tends to make a range of shorter-chain compounds, similar in many ways to the mixtures of hydrocarbons found in crude oil and oil products. A catalyst is sometimes used to reduce the operating temperature. The plastic being pyrolyzed can be of any type. For instance, the plastic being pyrolyzed can be polyethylene, polypropylene, polystyrene, polyesters, polyamides, polycarbonates, etc. These liquified waste polymers contain paraffins, i-paraffins (iso-paraffins), dienes, alkynes, olefins, naphthenes, and aromatic components. Liquified waste polymers may also contain impurities such as organic chlorides, organic silicon compounds, metals, salts, oxygenates, sulfur and nitrogen compounds, etc. The origin of the plastic is the waste plastic without limitation on the origin or on the nature of the plastic. The composition of the liquified waste polymer is dependent on the type of plastic pyrolyzed. It is however mainly constituted of hydrocarbons having from 1 to 50 carbon atoms and impurities.

[0114] The content in paraffin, naphthene, olefin, and aromatic is determined according to the standardized method UOP990-11. This method uses two-dimensional gas chromatography (GCxGC) coupled with a flame ionization detector (FID).

[0115] The term Diene Value (DV) or Maleic Anhydride Value (MAV) corresponds to the amount of maleic anhydride (expressed as equivalents of iodine) which will react with 100 parts of oil under specific conditions. It is a measure of the conjugated double bonds in the oil. One mole of Maleic anhydride corresponds to 1 conjugated double bond. One known method to quantify the diene is the UOP 326-17: Diene Value by Maleic Anhydride Addition Reaction. The term diene value (DV) refers to the analytical method by titration expressed in g of iodine per 100 g of sample. The term Maleic Anhydride value (MAV) refers to the analytical method by titration expressed in mg of Maleic acid per g of sample. There is a correlation between the $MAV = DV \times 3,863$ since 2 moles of iodine correspond to 1 mole of Maleic Anhydride. For the examples presented, a

particular method was used. The weight % of dienes presented in this application was obtained according to this particular method described in the example section.

[0116] The term bromine number corresponds to the amount of bromine in grams reacted by 100 grams of a sample. The number indicates the quantity of olefins in a sample. It is determined in grams of Br₂ per 100 grams of solution (gBr₂/100 g) and can be measured for instance according to the method D1159-07(2017).

[0117] The term bromine index is the number of milligrams of bromine that react with 100 grams of sample. It is determined in milligrams of Br₂ per 100 g of solution (mg Br₂/100 g) and can be measured for instance according to the method ASTM D2710-20.

[0118] The term boiling point used refers to the boiling point generally used in the oil and gas industry. They are measured at atmospheric pressure. The initial boiling point is defined as the temperature value when the first bubble of vapor is formed. The final boiling point is the highest temperature that can be reached during a standard distillation. At this temperature, no more vapor can be driven over into the condensing units. The determination of the initial and the final boiling point is known per se in the art. Depending on the boiling range of the mixture they can be determined using various standardized methods such as for instance the ASTM D2887-22e1 relating to the boiling range distribution of petroleum fractions by gas chromatography. For compositions containing heavier hydrocarbons the ASTM D7169-20e1 can alternatively be used. The boiling ranges of the distillates can also advantageously be measured using the ASTM D7500-15(2019) or the standard NF EN 15199-1. Due to the nature of the liquified waste polymer, the preferred method for the measurement of the boiling point is the method NF EN 15199-1. Depending on the method, up to 10° C. of difference can be evidenced. Hence, the boiling point expressed here is to be considered with an absolute uncertainty of +/-10° C.

[0119] The molecular weight: Mn (number average molecular weight), Mw (weight average molecular weight), Mz (z average molecular weight) and molecular weight distribution d (Mw/Mn) and d' (Mz/Mw) are determined by Gel Permeation Chromatography (GPC). The GPC was performed as follows.

[0120] Equipment: Agilent 1260 Series Degasser (Part Number G1322A); Agilent 1260 Series Isocratic Pump (Part Number G1310B); Agilent 1260 Series Autosampler (Part Number G1329B); Agilent 1260 Series Thermostatted Column Compartment (Part Number GI 316A); Agilent 1260 Series Multiple Wavelength Detector (Part Number 01365C); and Agilent 1260 Series Refractive Index Detector (Part Number G1362A). [0121] Column set: 1× Agilent ResiPore 50×4.6 mm Guard Column (Part Number PL1513-1300); and 2× Agilent ResiPore 250×4.6 mm 3 um Particle Size Columns (Part Number PL1513-5300). [0122] Software: Cirrus 3.3, ChemStation B04.03[52].

[0123] Solvent: THF Stabilized with 250 ppm BHT [0124] Flow Rate: 0.45 ml/min. [0125]

Column Compartment Temperature: 40° C. [0126] Injection Volume: 5 ml

[0127] Sample Preparation: Weighed approximately 0.06 grams of sample into a vial. Dissolve in 10 ml THF then filter through a 0.45 micron PTFE membrane. Run sample the same day it is prepared.

[0128] Polystyrene calibration standard used.

[0129] The molecular weight averages used in establishing molecular weight/property relationships are the number average (M_n), weight average (M_w) and z average (M_z) molecular weight. These averages are defined by the following expressions and are determined from the calculated M_i:

$$[00001] M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i W_i}{\sum_i W_i / M_i} = \frac{\sum_i h_i}{\sum_i h_i / M_i} M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i W_i M_i}{\sum_i M_i} = \frac{\sum_i h_i M_i}{\sum_i M_i}$$
$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i W_i M_i^2}{\sum_i W_i M_i} = \frac{\sum_i h_i M_i^2}{\sum_i h_i M_i}$$

[0130] Here N_i and W_i are the number and weight, respectively, of molecules having molecular weight M_i.

[0131] The molecular weight distribution (MWD) is then calculated as Mw/Mn.

[0132] The crystallization temperature (T_c) and the glass temperature transition (T_g) were measured using differential scanning calorimetry (DSC), TA Instruments Q2000 equipped with a Liquid Nitrogen Cooling System (LNCS). The software was TA Instruments Universal Analysis 2000 Version 4.5A. We used a temperature ramp with a ramp rate of 10° C./min.

[0133] The particular features, structures, characteristics or embodiments may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0134] It has been found that polymerizing the polymerizable materials in pyrolysis oil and specifically plastic pyrolysis oil containing dienes using a Lewis acid, such as a Friedel-Crafts catalyst leads to the formation of a low molecular weight liquid resin with a low T_{sub.g}, low viscosity, and some aromatic content. Other monomers such as branched mono-olefins, vinyl-aromatics, or other dienes may be combined with the pyrolysis oil to provide additional monomer feeds that can copolymerize to modify properties and compatibility and impart desired functionality to the resin.

[0135] It is one aspect of the present invention to provide a rubber composition comprising of an oligomeric product or liquid resin derived from pyrolysis oil. The liquid resin comprises a low molecular weight pyrolysis oil-based homopolymer or copolymer resin obtained using a Friedel-Crafts catalyst and preferably has a low viscosity and some aromatic content.

[0136] The disclosure relates to a rubber composition comprising: [0137] a) At least one elastomer selected from synthetic and natural elastomers; [0138] b) A curing agent; and [0139] c) An oligomeric product prepared from a liquified waste polymer the oligomeric product having a number average molecular weight, M_n, ranging from 100 to 10 000 g/mol measured using gel permeation chromatography and a polystyrene calibration and wherein the oligomeric product shows a glass transition temperature (T_g) below -20° C. as determined by Differential Scanning calorimetry or a crystallization temperature below 35° C.

[0140] In some embodiments, the content of said at least one elastomer in the rubber composition ranges from 1 to 150 phr; preferably, from 1 to 120 phr; more preferably from 1 to 100 phr; from 50 to 150 phr.

[0141] In some embodiments, the content of said curative agent in the rubber composition ranges from 0.1 to 25 phr; preferably, from 0.5 to 22 phr; more preferably from 1 to 20 phr, even more preferably from 5 to 18 phr.

[0142] In some embodiments, the content of said oligomeric product in the rubber composition ranges from 0.1 to 50 phr; preferably, from 0.5 to 40 phr; more preferably from 1 to 30 phr, even more preferably from 5 to 25 phr.

[0143] In a preferred embodiment, the oligomeric product is used to prepare a rubber composition. Preferably said rubber composition comprises rubbers or elastomers. In said rubber composition preferably comprises 100 phr of the rubber and 0.1-30 phr of the oligomeric product, from 1-30 phr of curing agent, and/or from 0 to 30 phr of coagents or any mixture thereof. Other components such as accelerators and/or activators and/or fillers and/or other additives may be added.

[0144] In some embodiments, the oligomeric product shows an olefinic content of at most 20.0 wt. % as determined by ¹H NMR. With preference, the liquid resin has an olefinic content ranging from 0.1 to 20.0 wt. %; preferably from 0.3 to 15.0 wt. %; more preferably, from 0.5 to 10.0 wt. %. from 0.8 to 5.0 wt. %.

[0145] In some embodiments, the oligomeric product shows an aliphatic content ranging from 15 to 100 wt. % as determined by ¹H NMR; preferably ranging from 40.0 to 99.5 wt. %; more preferably ranging from 50.0 to 99.0 wt. %; even more preferably ranging from 70.0 to 98.5 wt. %; and most preferably ranging from 80.0 to 98.0 wt. %.

[0146] In one or more embodiments, the oligomeric product shows an aromatic content ranging

from 0.3 to 45.0 wt. % as determined by H NMR; preferably ranging from 0.5 to 40.0 wt. %; more preferably ranging from 0.8 to 30.0 wt. %; and even more preferably ranging from 1.0 to 20.0 wt. %.

[0147] In embodiments, the oligomeric product has viscosity at 30° C. ranging from 10 to 50 000 cps measured using a Brookfield viscometer; preferably ranging from 10 to 50 000 cps; more ranging from 10 to 10 000 cps; even more preferably ranging from 10 to 4 000 cps; and most preferably ranging from 10 to 2 500 cps.

[0148] In some embodiments, the oligomeric product has a number average molecular weight (Mn) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 140 to 1,000 g/mol; even more preferably from 150 to 800 g/mol; most preferably from 180 to 700 g/mol; or from 200 to 650 g/mol; or from 250 to 550 g/mol.

[0149] In some embodiments, the oligomeric product has a weight average molecular weight (Mw) ranging from 100 to 10,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 5,000 g/mol; more preferably from 150 to 3,500 g/mol; and even more preferably from 200 to 2,000 g/mol.

[0150] In some embodiments, the oligomeric product has a z-average molecular weight (Mz) ranging from 100 to 100,000 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 120 to 85,000 g/mol; more preferably from 150 to 70,000 g/mol; and even more preferably from 200 to 50,000 g/mol.

[0151] In some embodiments, the oligomeric product has a Mw/Mn ranging from 1.0 to 10.0; preferably from 1.0 to 5.0; more preferably from 1.0 to 4.0; and even more preferably from 1.1 to 2.8.

[0152] In a preferred embodiment, the oligomeric product comprises a comonomer selected from the group consisting of styrene, alpha-methyl styrene, 2-methyl styrene, 3-methyl styrene, 4-methyl styrene, 4-t-butyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2,4-diisopropyl styrene, 2,4,6-trimethyl styrene, 2-ethyl-4-benzylstyrene, 4-(phenylbutyl) styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl anthracene, 4-methoxy styrene, monochlorostyrene, dichlorostyrene, divinyl benzene, Indene, methyl-Indene, and mixtures thereof; with preference the liquid resin (i.e., the oligomeric product) comprises a comonomer being or comprising styrene.

[0153] In embodiments, the oligomeric product comprises a comonomer present at a concentration ranging from 0.01 to 90 mol. % based on the total weight of the liquid resin, preferably from 1.0 to 80 mol. %.

[0154] In some embodiments, the oligomeric product is a wax and/or shows a crystallization temperature (Tc) below 35° C.; preferably ranging from 18 to 32° C.; more preferably, ranging from 20 to 30° C.; and even more preferably ranging from 21 to 29° C.

[0155] In embodiments, the oligomeric product is a resin and/or shows a glass transition temperature (Tg) below -20° C. as determined by Differential Scanning calorimetry; preferably ranging from -60° C. to -25° C.; more preferably from -50° C. to -30° C.; and even more preferably from -49° C. to -35° C.

[0156] The disclosure also provides for a process and an installation for the preparation of a rubber composition including the production of said oligomeric product. Reference is made to FIG. 1 related to the process and FIG. 5 related to the installation. The installation and the process are described herein jointly.

[0157] The process for the preparation of a rubber composition comprises the following steps:

[0158] a) providing a feedstream 1 containing liquified waste polymer, wherein said feedstream 1 contains at least 0.1 wt. % to at most 80 wt. % of dienes based on the total weight of said feedstream 1;

[0159] c) performing a polymerization reaction on said feedstream 1 under polymerization conditions to obtain a first product stream 3 comprising an oligomeric product;

[0160] d) optionally, performing a neutralization reaction by contacting said first product stream 3

with a basic compound to obtain a neutralized product stream **4** and removing said basic compound from neutralized product stream **4** to obtain a second product stream **5**; [0161] g) performing a separation to separate the oligomeric product from the purified liquified waste polymer; and [0162] h) preparing a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and said oligomeric recovered at step g).

[0163] In preferred embodiments illustrated in FIG. **1**, the process for the preparation of a rubber composition comprises the following steps: [0164] a) providing a feedstream **1** containing liquified waste polymer, wherein said feedstream **1** contains at least 0.1 wt. % to at most 80 wt. % of dienes based on the total weight of said feedstream **1**; [0165] b) optionally, drying the feedstream **1** to obtain a dried feedstream **2**; [0166] c) performing a polymerization reaction on said feedstream **1** or on the dried feedstream **2** under polymerization conditions to obtain a first product stream **3** comprising an oligomeric product; [0167] d) optionally, performing a neutralization reaction by contacting said first product stream **3** with a basic compound to obtain a neutralized product stream **4** and removing said basic compound from neutralized product stream **4** to obtain a second product stream **5**; [0168] e) optionally, washing the first product stream **3** or the second product stream **5** with a solvent to obtain a washed stream **6**; [0169] f) optionally, filtering the stream obtained in the previous step to obtain a filtered stream **7** wherein the filtering is performed to remove solids from the first product stream or from the second product stream **5** or from the washed stream **6**, and/or to coalesce remaining traces of solvent if any; [0170] g) performing a separation to separate the oligomeric product from the purified liquified waste polymer; and [0171] h) preparing a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and said oligomeric recovered at step g).

[0172] In a preferred embodiment, the process for the preparation of a rubber composition comprises the following steps: [0173] a) providing a feedstream **1** containing liquified waste polymer, wherein said feedstream **1** contains at least 0.1 wt. % to at most 80 wt. % of dienes based on the total weight of said feedstream **1**; [0174] b) drying the feedstream **1** to obtain a dried feedstream **2**; [0175] c) performing a cationic polymerization reaction on the dried feedstream **2** under polymerization conditions to obtain a first product stream **3** comprising an oligomeric product; [0176] d) performing a neutralization reaction by contacting said first product stream **3** with a basic compound to obtain a neutralized product stream **4** and removing said basic compound from neutralized product stream **4** to obtain a second product stream **5**; [0177] e) washing the second product stream **5** with a solvent to obtain a washed stream **6**; [0178] f) filtering the washed stream **6** to obtain a filtered stream **7** wherein the filtering is performed to remove solids from the washed stream **6**, and/or to coalesce remaining traces of solvent if any; [0179] g) performing a separation to separate the oligomeric product from the purified liquified waste polymer; [0180] h) preparing a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and said oligomeric recovered at step g).

[0181] The disclosure also provides an installation **100** for carrying out a process for the preparation of a rubber composition, said installation is remarkable in that it comprises: [0182] a polymerization section C comprising one or more polymerization reactors **23**; [0183] an optional neutralization section D; [0184] a separation section comprising a separation unit **32** comprising one or more distillation columns.

wherein the polymerization section C and the separation section are fluidically connected in series, and wherein the neutralization section D when present is placed downstream the polymerization section and upstream the separation section.

[0185] In some embodiments, the disclosure also provides an installation **100** for carrying out a process for the preparation of a rubber composition, said installation is remarkable in that it comprises, fluidically connected in the given order: [0186] an optional pre-treatment section A; [0187] an optional drying section B; [0188] a polymerization section C comprising one or more polymerization reactors **23**; [0189] an optional neutralization section D; [0190] an optional washing

section E; [0191] an optional filtering section; and [0192] a separation section comprising a separation unit **32** comprising one or more distillation columns.

[0193] In an embodiment, the disclosure also provides an installation **100** for carrying out a process for the preparation of a rubber composition, said installation is remarkable in that it comprises:

[0194] a pre-treatment section A comprising a pyrolysis unit **11**, one or more separation units (**13**, **16**, **19**) and an optional washing unit **18**; [0195] a drying section B comprising a decanter and/or a centrifuge **21**; and/or a molecular sieve **22**; [0196] a polymerization section C comprising one or more polymerization reactors **23**; preferably loaded with an acidic catalyst; [0197] a neutralization section D a mixing reactor **24** and an optional separation unit **26** comprising at least one selected from a decanter, a centrifuge, and a filter; [0198] a washing section E comprising a mixing vessel **28** and a separation unit **30** comprising a decanter and/or a centrifuge; [0199] a filtering section comprising a filter and an optional molecular sieve **31**; and [0200] a separation section comprising a separation unit **32** comprising one or more distillation columns.

The Feedstream **1** and Step a) of Providing a Feedstream **1** and the Pretreatment Section A

[0201] The feedstream **1** used in the process contains a liquified waste polymer.

[0202] It is preferred that the liquified waste polymer is originated from the pyrolysis of plastic waste **10**, so that the liquified waste polymer is a pyrolysis plastic oil.

[0203] Thus, in a preferred embodiment, step a) of providing a feedstream **1** comprises the preliminary steps of preparation of liquified waste polymer including: [0204] a1) providing a waste stream **10** being preferably a waste plastics stream; [0205] a2) pyrolyzing said waste stream **10** at a temperature of at least 200° C.; [0206] a3) recovering a pyrolyzer effluent **12** and separating said pyrolyzer effluent into a C1 to C4 hydrocarbons fraction **14**, a fraction **17** having a boiling range higher than 350° C. and a remaining fraction being said pyrolysis plastic oil.

[0207] In such cases, the installation **100** may comprise a pretreatment section A comprising a pyrolysis unit **11**, one or more separation units (**13**, **16**, **19**) and an optional washing unit **18**. With preference, the pretreatment section A comprises one or more separation units selected from: [0208] a first separation unit **13** to remove pyrolysis gas comprising a gas-liquid separator [0209] a second separation unit **16** to remove the fraction having a boiling range higher than 350° C. comprising one or more distillation columns; and [0210] a third separation unit **19** to remove particles and gums, comprising a filter and/or a centrifuge

[0211] In some embodiments (not illustrated) the process further comprises a further preliminary step of treatment of the fraction having a boiling range higher than 350° C. and therefore further comprises a step a4) of sending said fraction having a boiling range higher than 350° C. into a Fluid Catalytic Cracking (FCC) unit, or a hydrocracking unit, a coker or a visbreaker; or of blending said fraction having a boiling range higher than 350° C. in crude oil or in a crude oil cut to be further refined.

[0212] In a preferred embodiment, liquified waste plastics comprises mainly pyrolysis plastic oil. Pyrolysis plastic oil is produced from plastic wastes that are pyrolyzed. An example of a pyrolysis process for waste plastics is disclosed in U.S. Pat. No. 8,895,790 or in US 2014/228606 and in W02016/009,333.

[0213] In a waste plastics pyrolyzer, mixed plastics (e.g., waste plastics **10**) are placed in a pyrolysis unit or pyrolyzer. In the pyrolysis unit **11**, the waste plastics are converted via pyrolysis to a pyrolysis product, wherein the pyrolysis product **12** comprises a gas phase (e.g., pyrolysis gases, such as C1 to C4 gases, hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) mainly) and a liquid phase being pyrolysis plastic oil.

[0214] The plastic waste **10** may include post-consumer waste plastics, such as mixed plastic waste. Mixed plastics can comprise non-chlorinated plastics (e.g., polyolefins, polyethylene, polypropylene, polystyrene, copolymers, etc.), chlorinated plastics (e.g., polyvinylchloride (PVC), polyvinylidene chloride (PVDC), etc.), and the like, or mixtures thereof. Generally, waste plastics **10** comprise long-chain molecules or polymer hydrocarbons. Waste tires may also be used. Namely

waste plastics may also include used tires.

[0215] The pyrolysis unit **11** may be any suitable vessel configured to convert waste plastics into gas phase and liquid phase products (e.g., simultaneously). The vessel may be configured for gas phase, liquid phase, vapor-liquid phase, gas-solid phase, liquid-solid phase, or slurry phase operation.

[0216] The vessel may contain one or more beds of inert material or pyrolysis catalyst comprising sand, zeolite, alumina, a catalytic cracking catalyst, or combinations thereof. Generally, the pyrolysis catalyst is capable of transferring heat to the components subjected to the pyrolysis process in the pyrolysis unit. Alternatively, the pyrolysis unit **11** can be operated without any catalyst (e.g., pure thermal pyrolysis).

[0217] The pyrolysis unit **11** may be operated adiabatically, isothermally, nonadiabatically, non-isothermally, or combinations thereof. The pyrolysis reactions of this disclosure may be carried out in a single stage or in multiple stages. For example, the pyrolysis unit **11** can be two reactor vessels fluidly connected in series.

[0218] In a configuration (not illustrated) where the pyrolysis unit comprises two vessels, the pyrolysis process may be divided into a first stage which is performed in a first vessel, and in a second stage fluidly connected downstream to the first stage which is performed in the second vessel. As will be appreciated by one of skill in the art, and with the help of this disclosure, the second stage may enhance the pyrolysis of an intermediate pyrolysis product stream flowing from the first stage into the second stage, to yield a pyrolysis product flowing from the second stage. In some configurations, the first stage may utilize thermal cracking of the waste plastics, and the second stage may utilize thermal or catalytic cracking of the waste plastics to yield the pyrolysis product flowing from the second stage. Alternatively, the first stage may utilize catalytic cracking of the waste plastics, and the second stage may utilize thermal or catalytic cracking of the waste plastics to yield the pyrolysis product flowing from the second stage.

[0219] In some configurations, the pyrolysis unit **11** may include one or more equipments configured to convert mixed plastics into gas phase and liquid phase products. The one or more equipments may or may not contain an inert material or pyrolysis catalyst as described above. Examples of such equipment include one or more of heated extruders, heated rotating kilns, heated tank-type reactors, packed bed reactors, bubbling fluidized bed reactors, circulating fluidized bed reactors, empty heated vessels, enclosed heated surfaces where plastic flows down along the wall and cracks, vessels surrounded by ovens or furnaces, or any other suitable equipment offering a heated surface to assist in cracking.

[0220] The pyrolysis unit **11** can be configured to pyrolyze (e.g., crack), and in some aspects (e.g., where hydrogen is added to the pyrolysis unit), additionally hydrogenate components of the waste plastics stream fed to the pyrolysis unit. Examples of reactions that may occur in the pyrolysis unit **11** include, but are not limited to isomerization of one or more normal paraffins to one or more i-paraffins, selective ring opening of one or more cycloparaffins to one or more i-paraffins, cracking of long chain length molecules to short chain length molecules, removal of heteroatoms from heteroatom-containing hydrocarbons (e.g., dechlorination), hydrogenation of coke generated in the process, or combinations thereof.

[0221] In one or more configurations of the pyrolysis unit **11**, a headspace purge gas can be utilized in all or a portion of the pyrolysis stage(s) (conversion of waste plastics to a liquid phase and/or gas phase products) to enhance cracking of plastics, produce valuable products, provide a feed for steam cracking, or combinations thereof. The headspace purge gas may include hydrogen (H₂), C₁ to C₄ hydrocarbon gases (e.g., alkanes, methane, ethane, propane, butane, isobutane), inert gases (e.g., nitrogen (N_{sub.2}), argon, helium, steam), and the like, or combinations thereof. The use of a headspace purge gas assists in the dechlorination in the pyrolysis unit, when the waste plastics comprise chlorinated plastics. The headspace purge gas may be introduced to the pyrolysis unit to aid in the removal of volatiles entrained in the melted mixed plastics present in the pyrolysis unit.

[0222] A hydrogen (H.sub.2) containing stream can be added to the pyrolysis unit **11** to enrich the pyrolysis unit environment with H.sub.2, assist in stripping entrapped hydrogen chloride in the pyrolysis unit, provide a local environment rich in hydrogen in the pyrolysis melt or liquid, or combinations thereof; for example, via an H.sub.2 containing stream fed directly to the pyrolysis unit **11** independently of the waste plastics **10** stream. In some aspects, H.sub.2 can also be introduced along with stream to the pyrolysis unit **11**, with adequate safety measures incorporated for hydrogen handling with plastics feed.

[0223] The pyrolysis unit **11** may facilitate any reaction of the components of the waste plastics **10** stream in the presence of, or with, hydrogen. Reactions may occur such as the addition of hydrogen atoms to double bonds of unsaturated molecules (e.g., olefins), resulting in saturated molecules (e.g., paraffins, i-paraffins, naphthenes). Additionally, or alternatively, reactions in the pyrolysis unit may cause a rupture of a bond of an organic compound, with a subsequent reaction and/or replacement of a heteroatom with hydrogen.

[0224] The use of hydrogen in the pyrolysis unit **11** can have beneficial effects of (I) reducing the coke as a result of cracking, (II) keeping the catalyst used (if any) in the process in an active condition, (III) improving removal of chloride from stream such that the pyrolysis product from pyrolysis unit **11** is substantially dechlorinated with respect to waste plastics stream, which minimizes the chloride removal requirement in units downstream of the pyrolysis unit, (IV) hydrogenating of olefins, (V) reducing diolefins in pyrolysis product, (VI) helping operate the pyrolysis unit **11** at reduced temperatures for same levels of conversion of waste plastics **10** stream in the pyrolysis unit, or combinations of (I)-(VI).

[0225] The pyrolysis processes in the pyrolysis unit **11** may be low-severity or high-severity.

[0226] Low-severity pyrolysis processes may occur at a temperature of less than about 450° C.; for example, at a temperature ranging from 250° C. to 450° C., preferably from 275° C. to 425° C., more preferably 300° C. to 400° C., and may produce pyrolysis oils rich in mono- and di-olefins as well as a significant amount of aromatics.

[0227] High-severity pyrolysis processes may occur at a temperature equal to or greater than about 450° C.; for example, at a temperature ranging from 450° C. to 750° C., preferably from 500° C. to 700° C., more preferably from 550° C. to 650° C., and may produce pyrolysis oils rich in aromatics, as well as more gas products (as compared with low severity pyrolysis).

[0228] As will be appreciated by one of skill in the art, a high severity pyrolysis process will lead to the formation of more olefins and diolefins. Those olefins and diolefins cannot easily be recovered.

[0229] A pyrolysis product **12** can be recovered as an effluent from the pyrolysis unit **11** and conveyed (e.g., flowed, for example via pumping, gravity, pressure differential, etc.) to a pyrolysis separating unit (i.e. a first separation unit **13**). The pyrolysis product **12** can be separated in the pyrolysis separating unit into a pyrolysis gas **14** stream and a pyrolysis plastic oil further used in step a) of the present disclosure.

[0230] The first separation unit **13** may comprise any suitable gas-liquid separator, such as a vapor-liquid separator, oil-gas separators, gas-liquid separators, degassers, scrubbers, traps, flash drums, compressor suction drums, gravity separators, centrifugal separators, filter vane separators, mist eliminator pads, liquid-gas coalescers, distillation columns, and the like, or combinations thereof.

[0231] In a preferred embodiment, said of pyrolysis plastic oil originates directly from the pyrolysis of plastic wastes without further chemical transformation or separation.

[0232] In a preferred embodiment, the feedstream **1** contains only liquified waste polymer even more preferably only pyrolysis plastic oil. Alternatively, the feedstream **1** contains at least 10 wt. % of liquified waste polymer based on the total weight of the feedstream **1**; preferably at least 25 wt. %, more preferably at least 50 wt. %, even more preferably at least 75 wt. %.

[0233] The feedstream **1** may contain 100 wt. % of said liquified waste polymer based on the total weight of the feedstream **1**; preferably at most 95 wt. %; more preferably, at most 90 wt. %; even

more preferably at most 85 wt. %, and most preferably at most 80 wt. %. When the feedstream **1** contains less than 100 wt. % of liquid waste polymer the rest can be for instance a diluent or other hydrocarbons.

[0234] In a preferred embodiment, the feedstream **1** presents a bromine number of at most 150 g Br.sub.2/100 g as measured according to ASTM D1159-07(2017), preferably at most 100 g Br.sub.2/100 g; more preferably at most 80 g Br.sub.2/100 g, and even more preferably, at most 50 g Br.sub.2/100 g.

[0235] In a preferred embodiment, the liquified waste polymer in the feedstream **1** has a starting boiling point of at least 15° C. and a final boiling point of at most 700° C. With preference, the final boiling point is at most 600° C.; more preferably 560° C., even more preferably 450° C. even more preferably 350° C., the most preferred 250° C.

[0236] In some embodiment, step a) of providing a feedstream **1** comprises one or more sub-steps of pre-treatment of the liquified waste polymer.

[0237] Indeed, depending on the origin of the liquified waste polymer, some pre-treatment may be necessary. Namely, before purifying the liquified waste polymer in the inventive process, the following pre-treatment may be considered either on the liquified waste polymer or on the feedstream **1**.

[0238] In a preferred embodiment, the liquified waste polymer or the feedstream **1** is pretreated in a washing or a desalting unit **18** to remove water-soluble salts before being treated in the inventive process.

[0239] In another preferred embodiment, the liquified waste polymer or the stream **1** is pretreated in a separation unit **19** to extract the particles and gums **20** by filtration, centrifugation or a combination of the two technics before being treated in the inventive process.

The Optional Step b) of Drying the Feedstream **1** to Obtain a Dried Feedstream **2** and the Drying Section B

[0240] In another preferred embodiment, the liquified waste polymer or the feedstream **1** is pretreated in a dewatering unit (i.e., a drying unit) to remove water in said hydrocarbon stream to reach a water content of less than 0.1% vol preferably of less than 0.05% vol according to ASTM D95-13(2018) before being treated in the inventive process, even more preferably said liquified waste polymer may be decanted.

[0241] Preferably, the feedstream **1** is dried before being sent to the polymerization unit. step b) of drying can be performed a sub-step b1) of decantation and/or centrifugation; with preference, the sub-step b1) is followed by a sub-step b2) of drying using a molecular sieve **22** to reach a water content of less than 0.1 vol. % according to ASTM D95-13 (2018).

[0242] In such cases, the installation **100** may comprise a drying section B comprising: [0243] a decanter and/or a centrifuge **21**; and/or [0244] a molecular sieve **22**

Step c) of Performing a Polymerization Reaction on the Feedstream **1** or the Dried Feedstream **2** and the Polymerization Section C

[0245] Step c) comprises performing a polymerization reaction being a cationic polymerization or a free radical polymerization or an anionic polymerization; with preference, the polymerization reaction is a cationic polymerization. Thus, the polymerization section C comprising one or more polymerization reactors **23** loaded with a catalyst; preferably an acidic catalyst.

[0246] In an embodiment, said polymerization is an anionic polymerization. In such case, said anionic polymerization is performed using an organolithium containing anionic initiator and terminated by reaction with a proton donating termination agent selected to form the lithium salt which can be filtered.

[0247] In the embodiments wherein the polymerization reaction is a cationic polymerization, the installation comprises a polymerization section C comprising one or more polymerization reactors **23** loaded with an acidic catalyst.

[0248] In another embodiment, said polymerization is a free radical polymerization. In such case,

said free radical polymerization is performed with an initiator utilized to generate an initial radical leading to monomer propagation followed by a termination via combination or disproportionation. [0249] In preferred embodiments, the polymerization reaction is a cationic polymerization. Thus, preferably, step c) is performed in the presence of an acidic catalyst; with preference, the acidic catalyst is a Brønsted acid or a Lewis acid; preferably a Lewis acid in the form of a transition metal halogenate.

[0250] Friedel—Crafts catalysts are strong Lewis acid catalysts which polymerize monomers via a cationic polymerization reaction mechanism. According to various embodiments of the present invention, examples of Friedel—Crafts catalysts that may be used to polymerize a monomer feed comprising pyrolysis oil include, but are not limited to, boron trifluoride, aluminum trichloride, tin tetrachloride, titanium trichloride, titanium tetrachloride, iron chloride (III), aluminum tri-bromide, dichloromono ethyl aluminum, and complexes thereof, such as boron trifluoride—phenol complex, boron trifluoride—ethanol complex, boron trifluoride—ether complex and the like, especially, boron trifluoride—phenol complex and boron trifluoride—ethanol complex. The Friedel—Craft catalyst may also include a liquid aluminum chloride/hydrochloric acid/substituted aromatics complex, the aromatic being for example o-xylene, mesitylene, ethyl benzene, isopropyl benzene, and the like, such as short or long-chain alkylbenzenes. The alkyl chain may be linear or branched and may vary from 2 to 30 carbon atoms. Acidic liquid AlCl₃, obtained as by-products during the alkylation of benzene or any other substituted aromatics (toluene, xylenes) with branched-chain olefins may also be used. The branched-chain olefins may be produced via the boron trifluoride oligomerization of propylene and fractionation (e. g. C₁₂ olefins or C₂₄ olefins may be alkylated with aromatics).

[0251] The Friedel—Crafts catalysts most preferred are AlCl₃ and BF₃.

[0252] Thus, with preference, step c) is performed in the presence of an acidic catalyst being a Lewis acid chosen among BF₃, complexes of boron trifluoride, AlCl₃, SnCl₄, ZnCl₂, FeCl₃ and TiCl₃, alkyl aluminum chlorides, H₂SO₄ or any mixture thereof. It is understood that BF₃ refers to BF₃ in the gaseous form. A particularly suitable complex of boron trifluoride is boron trifluoride etherate.

[0253] In an embodiment, step c) is performed in the presence of an acidic catalyst being a Lewis acid with an acidic catalyst concentration ranging from 0.5 wt. % to 5.0 wt. % based on the total weight of said feedstream 1,

[0254] In an embodiment, the reaction conditions include a contact time of at least 5 min to at most 5 hours. Preferably, step c) is performed under an inert atmosphere, preferably under N₂ atmosphere.

[0255] The resins described herein may be prepared by a continuous solution polymerization process wherein the Friedel—Craft catalyst, optional comonomers, and a suitable aromatic or aliphatic hydrocarbon solvent, such as, for example, toluene, xylene, or heptane, are continuously added to a reactor vessel to form the desired homopolymer or copolymer. Alternatively, the pyrolysis oil-based polymers may be prepared through a batch process in which all the initiator, monomers, and solvent are combined in the reactor together and mixed. The acid catalyst may also be a solid catalyst.

[0256] Preferably, during a continuous polymerization reaction, the mass flow rate of the catalyst feed is from 0.01 to 20 wt. % based on the total mass flow rate of monomer feed and catalyst feed; preferably, from 0.1 to 5 wt. %, and more preferably from 0.1 to 3 wt. %.

[0257] The reaction temperature of the mixture in the reactor vessel is also preferably maintained at a temperature of about—10 to 50° C., when using BF₃, as the Friedel—Crafts catalyst and about 10 to 60° C., when using AlCl₃.

[0258] The low molecular weight pyrolysis oil-based homopolymers or copolymers resins according to the embodiments of the present invention are liquid resins with a number average molecular weight between 100 and 10,000 g/mol and more preferably 250 and 4,000 g/mol, as

measured via gel permeation chromatography and converted using polystyrene calibration.

[0259] In a preferred embodiment, the cationic polymerization is performed in the presence of an acidic catalyst, being preferably chosen among BF₃, AlCl₃, SnCl₄, and TiCl₃, ion exchange resin, Cl₂AlEt, H₂SO₄ or any mixture thereof.

[0260] In an embodiment, at least one of AlCl₃, and BF₃, may be used to polymerize a monomer feed comprising pyrolysis oil and a comonomer in which the comonomer content of the monomer feed is <90 wt. %, <40 wt. %, <25 wt. %, or <15 wt. %, based on the total moles of the monomer in the monomer feed. Preferably, the polymerization initiator is BF₃.

[0261] In particular, the acidic catalyst can be a solid acidic catalyst. The preferred solid acid catalyst includes molecular sieves such as zeolite or silicalite. The use of a solid acidic catalyst is particularly advantageous. The solid acid catalyst can be easily separated. When a solid acid catalyst is used, the use of a neutralization step d) and step of washing e) may not be required.

[0262] In an embodiment, step c) is performed with a solid acid catalyst being a molecular sieve, preferably selected among the topologies MFI, BEA, FAU, MEL, and the polymerization conditions comprise a Liquid Hourly Space Velocity (LHSV) ranging from 0.5 to 5.0 h⁻¹. In a preferred embodiment, the molecular sieve contains one or more heteroatoms selected from Ti, Sn, Mo, W, Fe, Ni, Co, Cu, Zr, Hf, Nb, and Ta.

[0263] In an embodiment, step c) is performed with a solid acid catalyst being an ion exchange resin, preferably a sulfonic ion-exchange resin such as Amberlyst A15 or A35, and the polymerization conditions comprise an LHSV ranging from 0.5 to 5.0 h⁻¹. Ion exchange resin includes macro-porous polymeric resins having acidic properties for instance having the capability to exchange H⁺ ions. In particular, ion exchange resins can comprise styrene-divinylbenzene copolymers such as for instance Amberlyst resins. In a preferred embodiment, the ion exchange resin is an Amberlyst 15.

[0264] In an embodiment, step c) is performed with a solid acid catalyst being a clay or an activated clay and the polymerization conditions comprise an LHSV ranging from 0.5 to 5.0 h⁻¹.

The Optional Neutralization Step d) and the Neutralization Section D

[0265] When an acidic catalyst soluble is used in step c) to produce the first product stream **3**, it may be required to perform a neutralization step d1) preferably followed by a washing step d2).

[0266] Thus, in some embodiments, the installation **100** comprise a neutralization section D comprising a mixing reactor **24** and an optional separation unit **26** comprising at least one selected from a decanter, a centrifuge, and a filter.

[0267] Step d) is a neutralization step that can be done by adding a base directly on said first product stream **3**. In that case, a basic compound, generally solid is put in contact with said first product stream **3**, the mixture obtained is then agitated during at least 1 second to at most 24 h, preferably during at least 1 minute to at most 12 h. After agitation, the remaining base in form of a solid is separated from the liquid, said liquid being said second product stream **5**.

[0268] The neutralization step can also be done by washing said first product stream **3** with a basic compound **25** being a basic solution. Basic aqueous solutions are preferred, basic aqueous solution containing NaOH and/or NH₄OH are the most preferred type of solution. The basic solutions are put in contact and agitated for at least 1 second to at most 24 h, preferably for at least 1 minute to at most 12 h. Then the mixture is let for separation to remove the second product stream **5** (being the organic phase) from the aqueous phase. The separation can consist for instance in a decantation. The decantation is known per se, it consists in letting the immiscible organic and aqueous phases being separated with the help of gravity.

[0269] The neutralization step can also be done by putting simultaneously or successively one or more basic compound **25**, being preferably a base containing alkali/alkaline earth metals, more preferably a solid base such as LiOH, NaOH, CsOH, Ba(OH)₂, Na₂O, KOH, K₂O, CaO, Ca(OH)₂, MgO, Mg(OH)₂, or any mixture thereof or any strong base alone or in

mixture, and a basic aqueous solution in contact with said first product stream **3**. After agitation of at least 1 second to at most 24 h, the solid, the organic phase being said second product stream **5**, and the aqueous phase are separated.

[0270] In a more preferred embodiment, step d) is performed in continuous mode, namely addition of fresh basic compound is performed on the first product stream **3** at the entry of for instance a mixing reactor **24** while simultaneously, at the exit of the mixing reactor **24** the spent basic compound is removed to obtain the second product stream **5**.

[0271] In a preferred embodiment, the basic compound comprises an alkali metal cation, alkaline earth metal cation, and ammonium quaternary base, being preferably chosen among TMAOH, TEAOH, TBAOH, TPAOH, or any mixture thereof.

The Optional Washing Step e) and the Washing Section E

[0272] The washing step e) comprises washing the first product stream **3** or the second product stream **5** with a solvent **27** to obtain a washed stream **6**. In some embodiments, the washing step e) is performed after the neutralization step d) to remove traces of the basic compound **25**. In such a case, the washing step is performed with a ratio of said second product stream **5**, or optionally of said neutralized product stream **4**, over said solvent **27** ranging from 0.05 to 20.

[0273] For example, the washing is performed at a temperature ranging from 5° C. to 95° C., preferably under atmospheric pressure. The washing can be performed in continuous mode or in batch mode.

[0274] In a preferred embodiment, the solvent is selected water or an acidic water solution, said solution comprising one or more organic acids like for instance citric acid (C.sub.6H.sub.8O.sub.7), formic acid (CH.sub.2O.sub.2), acetic acid (CH.sub.3COOH), sulfamic acid (H.sub.3NSO.sub.3) or inorganic acids being hydrochloric acid (HCl), nitric acid (HNO.sub.3), sulfuric acid (H.sub.2SO.sub.4), phosphoric acid (H.sub.3PO.sub.4) and any combination thereof.

[0275] For example, the acidic solution has a pH ranging from 0.1 to 6.9.

[0276] The washing is preferably performed until the pH of said washed stream **6**, or optionally on said second product stream **5**, or neutralized product stream **4**, is in the range of 5.0 to 9.0, preferably in the range of 6.0 to 8.0, even more preferably in the range of 6.5 to 7.5.

[0277] The washing is preferably followed by a decantation and/or a centrifugation to separate the solvent **27** from the washed mixture **29**, to produce a washed stream **6**.

[0278] In such cases, the installation **100** may comprise a washing section E comprising a mixing vessel **28** and a separation unit **30** comprising a decanter and/or a centrifuge.

The Optional Filtering Step f) and the Filtering Section

[0279] The process can comprise a filtering step f) comprising filtering the stream obtained in the previous step to obtain a filtered stream **7** wherein the filtering is performed to remove solids.

[0280] In the embodiments wherein the preceding step was the washing step e), the process may comprise a filtering step f) comprising filtering the washed stream **6** (i.e., the stream obtained in the previous step) to obtain a filtered stream **7** wherein the filtering is performed to remove solids from the washed stream **6**, and/or to coalesce remaining traces of solvent if any.

[0281] In a preferred embodiment, the filtering comprises a first sub-step of filtering to remove solids and/or to coalesce remaining traces of solvent if any, preferably followed by a second sub-step of dewatering preferably using a molecular sieve to reach a water content of less than 0.1 vol. % preferably of less than 0.05% vol according to ASTM D95-13 (2018) on the filtered stream **7**.

[0282] In such cases, the installation **100** may comprise a filtering section comprising a filter (not represented) and an optional molecular sieve **31**.

The Separation Step g) and the Separation Section

[0283] The process comprises a step g) of performing a separation to separate the oligomeric product **33** from the purified liquified waste polymer **34**.

[0284] In a preferred embodiment said step g) of separation is performed via distillation or steam

distillation or vacuum stripping or fractional distillation or any combination.

[0285] Thus, the installation comprises a separation unit **32** comprising one or more distillation columns.

[0286] The oligomeric product **33** obtained can also be used further converted into valuable as valuable resins. After the separation step g), the oligomeric product **33** may be recovered and mixed with an elastomer, a curing agent, and a filler to obtain a rubber composition or is used as a tackifying resin and mixed with an elastomer to form an adhesive composition.

[0287] If not yet done in a pretreatment section, the process may comprise a step of separating and recovering a fraction having a boiling range higher than 350° C., preferably higher than 300° C. This fraction can be recovered from any of the purified liquified waste polymer **34**, the filtered stream **7**, the washed stream **6**, the second product stream **5**, the neutralized product stream **4**, the first product stream **3**, the dried feedstream, or the feed stream **1**. The fraction having an initial boiling point of at least 350° C., preferably at least 300° C., can therefore be removed and sent into a FCC unit, or a hydrocracking unit, a coker or a visbreaker or blending said fraction having a boiling range higher than 350° C. in crude oil or in a crude oil cut to be further refined.

[0288] With preference, after the separation step g), the purified liquified waste polymer **34** is recovered and blended in the fuel pool; with preference, the purified liquified waste polymer is separated in a naphtha cut having a boiling range of less than 150° C. and a diesel cut having a boiling range between 15° and 350° C. wherein said naphtha cut is incorporated in a naphtha pool, said diesel cut is incorporated in a diesel pool.

Detailed Description of the Curing Step

[0289] In the preparation of a rubber composition, a curable composition is prepared. A curable composition includes a rubber, said oligomeric product, and at least one curing agent. The curable composition may be cured by various methods including but not limited to peroxide cure, peroxide/coagent cure, radiation cure, sulfur, and thiadiazole cure.

[0290] In the present disclosure, the terms “curative agent” or “curing agent” are synonyms and interchangeable. The terms “crosslink” and “cure” as used herein are interchangeable and are understood to mean that chemical bonds have been formed between adjacent chains of the individual polyene molecules. By polyene, it is meant an organic compound that contains at least three alternating double and single carbon-carbon bonds. Examples of suitable crosslinking or curing agents that can be used in the curable liquid rubber compositions are sulfur and peroxides. Either of these types of crosslinking agents may be used at appropriate levels with appropriate coagents, accelerators or activators such as are known and used in the art to increase the speed and completeness of crosslinking. The curing agent can be selected based on the desired curing temperature of the curable composition. Typically, the curing temperature may be between 100° C. and 190° C.

[0291] A curable composition includes a rubber, said oligomeric product, and at least one curing agent.

[0292] Vulcanizing agents that decompose to produce free radicals during the curing cycle may be employed as curing agents in the present disclosure. The free radical generating compound advantageously employed in the present invention may be a ditertiary peroxide, such as tert-butyl peroxybenzoate (TBPB).

[0293] Ditertiary peroxide curing compounds may be used, which peroxides and their homologs and analogs, all correspond essentially to the structural formula: $R_{sub.3}C-O-O-CR_{sub.3}$. These ditertiary peroxide agents contain at least one peroxy group disposed between tertiary carbon atoms, which tertiary carbon atoms are linked to carbon atoms constituting portions of each of the R groups, which R groups may be alkyl (including straight, branched, or cyclic), alkenyl or aryl groups, or mixtures of such groups, and which R groups may be further substituted by non-hydrocarbon groups, for example, ethers, additional peroxy groups, or halogen, such as chlorine, and which organic peroxides do not interfere with either the curing process or the cured elastomeric

product. Each of the R groups may be the same or different from each other.

[0294] Illustrative organic peroxides include diacetyl peroxide, dibenzoyl peroxide, dicapryl peroxide, di-(p-chloro-benzoyl) peroxide, didecanoyl peroxide, di-(2,4-dichlorobenzoyl) peroxide, diisobutyl peroxide, diisonanoyl peroxide, dilauroyl peroxide, dipelargonyl peroxide, dipropynyl peroxide, di(β -carboxypropinoyl) peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, dihydroxy-dimethyl-dioxacyclopentane, t-butyl peroxide, t-butyl peroxy(2-ethylhexanoate), t-butylperoxyisobutylate, O,O-t-butyl-O-isopropylmonoperoxy-carbonate, t-butylperoxypivalate, dimethyl-di(benzoylperoxy)-hexane, t-butyl-peroxy (2-ethylbutylate), di-t-butyl peroxide, dicumyl peroxide, 2,5-bis(t-butylperoxy)-2,5-dimethyl-hexane, t-butyl hydroperoxide, cumyl hydroperoxide, α,α' -bis-(t-butylperoxy) diisopropyl benzene, 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane, and n-butyl-bis(t-butylperoxy)-valerate and the like. Among the foregoing free radical generating compounds mentioned above, dicumyl peroxide (DICUP™), 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane, di-t-butyl peroxide (both available from AKZO Chemicals, Inc. of Chicago, Ill.), 2,5-dimethyl-2,5-di t-butylperoxy-2 hexane (VAROX DBPH 50™), 2,5-dimethyl-2,5-di-t-butylperoxy-3-hexyne (LUPERSOL 130™), tert-butyl peroxybenzoate (TBPB), and α,α' -bis-(t-butylperoxy)-diisopropyl benzene (VULCUP R™) are commercially available and conveniently used. The foregoing organic peroxides may be used alone or in combinations.

[0295] Non-limiting examples of other suitable peroxides are: peroxyketals (such as 1,1'-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane or di(tert-butylperoxy)-cyclohexane); diacyl peroxides (such as dibenzoyl peroxide or dilauroyl peroxide) and peroxyesters (such as tert-butyl peroxyisobutyrate or tert-amyl peroxy-2-ethylhexylcarbonate). In another embodiment, the peroxide may be selected from the group consisting of peroxyketals (such as 1,1'-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane or di(tert-butylperoxy)-cyclohexane); diacyl peroxides (such as dibenzoyl peroxide) and peroxyesters.

[0296] The curable composition may include, as heat-activated crosslinking agents, two or more organic peroxides. For example, the curable liquid rubber composition may include at least two peroxides selected from peroxyketals (such as 1,1'-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane or di(tert-butylperoxy)-cyclohexane); diacyl peroxides (such as dibenzoyl peroxide or dilauroyl peroxide) and peroxyesters (such as tert-butyl peroxyisobutyrate or tert-amyl peroxy-2-ethylhexylcarbonate). "Half-life" is a convenient means of expressing the rate of decomposition of an organic peroxide at a specified temperature. The time required for one-half of the organic peroxide originally present to decompose at any particular temperature is measured. Organic peroxides having a 10-hour half-life from 47° C. to 127° C. are suitable.

[0297] The amount of peroxide present in the curable composition will vary depending upon the type(s) of peroxide used, the reactivities of the curable component(s), the type and reactivity of the accelerator or activator (if present), and the desired curing profile and target cured rubber properties as well as other factors. Typically, however, the curable composition will comprise one or more peroxides in an amount of from 1 to 30 phr (parts per hundred parts of the butadiene homopolymer and any rubber component, if present), or from 1.5 to 20 phr. It is to be understood that this amount refers to the peroxide(s) only. Appropriate coagents may be used in addition to the peroxide. The coagents (if present) are typically present in an amount between 0.1 and 30 phr. The coagents (if present) may be present between 0.2 and 25 phr or between 0.2 and 20 phr.

[0298] The amount of free radical generating compound used in the present invention may be varied depending on the polymer and crosslinking coagent selected. Hence, the required amount of free radical-generating compound required to practice the present invention is a cure-effective amount readily ascertainable by one of ordinary skill in the art. Generally, an amount of from about 0.1 to about 15 parts per hundred parts of the rubber.

Coagents Used in the Curable Composition

[0299] The curable compositions may also include at least one coagent that is adapted for

crosslinking with organic peroxides or other free radical sources. The coagent may contain one or more sites of ethylenic unsaturation (carbon-carbon double bonds) per molecule and may be selected from acrylates, methacrylates, bismaleimides, vinyl esters, allylic compounds, and derivatives thereof. In certain embodiments of the invention, the curable composition includes from 0 phr to 30 phr coagent in total. In other embodiments, the composition may include 0.5 to 15 phr. Non-limiting examples of suitable coagents include metallic acrylates, metallic methacrylates, metallic acrylate salts, metallic methacrylate salts. Zinc acrylate, zinc methacrylate, zinc acrylate salts, and zinc methacrylate salts may be mentioned in particular. Other metal salts of acrylic and methacrylic acids include, without limitation, magnesium, sodium, potassium, calcium, barium, cobalt, copper, aluminum and iron.

[0300] Sulfur can be also introduced as a coagent when crosslinking compositions with organic peroxides. The sulfur content when used as a coagent with peroxide should be low, i.e., not more than 0.5 phr sulfur.

Sulfur in the Curable Composition

[0301] Sulfur can be used as a heat-activated crosslinking agent. Examples of sulfur vulcanizing agents include, but are not limited to, elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. The amount of sulfur vulcanizing agent will vary depending on the type of rubber and particular type of sulfur vulcanizing agent, but generally range from about 0.1 phr to about 5 phr with a range of from about 0.5 phr to about 2 phr being preferred. Sulfur donors may also be used. Each of the accelerators or activators (if present) is typically present between 0.1 and 30 phr. The accelerators or activators (if present) may be present between 0.2 and 25 phr or between 0.2 and 20 phr. Appropriate accelerators or activators may be used in addition to the sulfur. Each of the accelerators or activators (if present) is typically present between 0.1 and 30 phr. The accelerators or activators (if present) may be present between 0.2 and 25 phr or between 0.2 and 20 phr.

[0302] Sulfur donors can be also employed with sulfur to reduce the sulfur content incorporated in the formulation. Non-limiting examples of sulfur donors are thiuram tetrasulfides and morpholine derivatives such as tetramethyl thiuram disulfide; 4,4'-dithiodimorpholine; dipentamethylene thiuram tetrasulfide; and thiocarbamyl sulfenamide.

Accelerators in Curable Composition

[0303] Examples of accelerators that may be used with sulfur as the primary curing agent include but are not limited to: sulfenamides, thiazoles, dithiocarbamates, a thiuram-based compound of N-cyclohexyl-2-benzothiazolesulfenamide (CBS); N-tert-butyl-2-benzothiazyl sulfenamide (TBBS); zinc dimethyl dithiocarbamate (ZDMC), zinc dibenzyl dithiocarbamate (ZBEC); 2-mercaptobenzothiazole (MBT); benzothiazyl disulfide (MBTS). Some primary accelerators, such as thiazole (MBT or MBTS) or dithiocarbamates (ZDMC or ZBEC), can be used in a blend with sulphenamides or instead of sulphenamides. Other non-limiting examples of accelerators are: thiurams such as tetramethyl thiuram disulfide (TMTD) or tetrabenzylthiuram disulfide (TBzTD). Dithiocarbamates as mentioned above or xanthates, for example zinc isopropylxanthate (ZIX) or sodium isopropylxanthate (NaIX) can be also employed.

[0304] In cases where combinations of two or more accelerators are used, the primary accelerator may be used in amounts ranging from 0.5 to 2.0 phr and the secondary accelerator may be used in amounts ranging from about 0.1 to 0.5 phr. Combinations of accelerators have been known to produce a synergistic effect. Preferably, the primary accelerator is a sulfenamide. If a secondary accelerator is used, it is preferably a guanidine, a dithiocarbamate, and/or a thiuram compound.

Activators in Curable Composition

[0305] Examples of suitable activators that can be used with organic peroxides or sulfur as the primary crosslinking agent include but are not limited to: metal oxides, fatty acid metal salts (e.g., metal stearates), fatty acids, and mixtures thereof. Non-limiting specific examples include: zinc oxide, calcium oxide, magnesium oxide, zinc stearate, or stearic acid. Activators may be used in an

amount ranging from about 1 to 4 phr, with a range from about 2 to 3 phr being preferred.

[0306] The cured composition may be obtained by curing a curable composition as disclosed herein by heating the curable composition. The curable composition is curable by heating the curable composition to a temperature of about 100° C. to about 240° C. or a temperature of about 100° C. to about 190° C. To effect curing, the curable composition is held at the temperature for between 5 minutes and 10 hours. As a result of such curing, the curable composition is converted (e.g., by crosslinking reactions) into a solid, elastomeric (rubbery) composition. Typically, curing is achieved by heating the curable composition to a temperature effective to initiate the desired crosslinking reaction involving at least the polymer component. Typically, the time period to achieve adequate cure is between 5 minutes and 10 hours.

Elastomers in the Curable Composition

[0307] Suitable elastomers are those as known and used in the art. For example, suitable elastomers are elastomeric organic high polymers including natural rubber and the various synthetic rubbers which cure, i.e., vulcanize or cross-link. In general, these curable elastomers are polymers of conjugated dienes or polymers, wherein the monomers are linked through carbon-carbon bonds. Representative examples of synthetic rubbery polymers of conjugated dienes include: synthetic polyisoprene, styrene-butadiene rubbers, polybutadiene rubbers (different from the present inventive low viscosity butadiene homopolymer), butyl rubber, bromobutyl rubber, chlorobutyl rubber, the neoprenes, ethylene propylene rubbers, nitrile elastomers, silicone elastomers, thermoplastic elastomers, fluoroelastomers, high styrene butadiene copolymers, vinyl acetate ethylene copolymers, chlorinated polyethylene rubber, chlorosulfonated polyethylene elastomer, polyethylene and reclaimed rubber. Functionalized versions of these elastomers may also be included in the rubber compositions according to the present invention.

[0308] The curable rubber compositions used to prepare tires and other products in accordance with the invention may contain a single diene elastomer or a mixture of several diene elastomers, the diene elastomer(s) possibly being used in association with any type of synthetic elastomer other than a diene elastomer, or even with polymers other than elastomers, for example thermoplastic polymers.

Fillers in the Curable Composition

[0309] Representative reinforcing fillers may be included in rubber compositions according to various embodiments of the invention in amounts ranging from about 5 to 100 parts by weight based on 100 parts by weight of total rubber (phr). Preferably, between about 10 and 50 parts by weight of reinforcing filler is used per 100 parts of rubber.

[0310] Examples of reinforcing fillers that may be included in the rubber compositions according to certain embodiments of the present invention include pyrogenic silica fillers and precipitated finely-divided silicas typically employed for rubber compounding. The silica filler, however, is preferably of the type obtained by precipitation from a soluble silicate, such as sodium silicate.

[0311] For example, silica fillers may be produced according to the method described in U.S. Pat. No. 2,940,830, which is incorporated herein in its entirety for all purposes. The precipitated, hydrated silica pigments may have a SiO₂ content of at least 50% and usually greater than 80% by weight on an anhydrous basis. The silica filler may have an ultimate particle size in the range of from about 50 to 10,000 angstroms, preferably between 50 and 400 and, more preferably, between 100 and 300 angstroms. The silica may have an average ultimate particle size in a range of about 0.01 to 0.05 microns as determined by electron microscope, although the silica particles may even be smaller in size. The Brunauer-Emmett-Teller ("BET") surface area of the filler as measured using nitrogen gas is, preferably, in the range of 40 to 600 square meters per gram, more preferably 50 to 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Vol. 60, page 304 (1930). The silica also may have a dibutyl ("DBP") absorption value in a range of about 200 to about 400, with a range of from about 220 to 300 being preferred.

[0312] Various commercially available silicas and carbon black may be used as reinforcing fillers in various embodiments of the present invention. Suitable types of carbon black include, but are not limited to, super abrasion furnace, intermediate SAF, high abrasion furnace, easy processing channel, fast extruding furnace, high modulus furnace, semi-reinforcing furnace, fine thermal, medium thermal. For example, silicas commercially available from PPG Industries under the Hi-Sil trademark such as, for example, those with designations 210, 243, etc.; silicas available from Rhone-Poulenc, with designations of Z1165MP and Z165GR and silicas available from Degussa AG with designations VN2 and VN3, etc. may be used. The Rhone-Poulenc Z1165MP silica is a preferred silica, which is reportedly characterized by having a BET surface area of about 160-170, a DBP value of about 250-290, and a substantially spherical shape. Suitable examples of carbon blacks include, but are not limited to, N110, N121, N220, N231, N234, N242, N293, N299, S315, N326, N330, N332, N339, N343, N347, N351, N358, N375, N539, N550, N582, N630, N642, N650, N683, N754, N762, N765, N774, N787, N907, N908, N990 and N991.

[0313] In compounding a rubber composition containing a filler, one generally uses a coupling agent. Silane coupling agents are particularly preferred. Such coupling agents, for example, may be premixed or pre-reacted with the filler or added to the rubber mix during the rubber/filler processing or mixing stage. If the coupling agent and filler are added separately to the rubber mix during the rubber/filler mixing or processing stage, it is considered that the coupling agent then combines in situ with the filler. Any coupling agents known to those of skill in the art may be employed in compositions of the present invention. Coupling agents are generally composed of a coupling agent which has a constituent silane component (i.e. moiety) capable of reacting with the silica surface and, also, a constituent component capable of reacting with the rubber. Preferably, the coupling agent is capable of reacting with a sulfur-vulcanizable rubber, which contains carbon-to-carbon double bonds, or unsaturation. In this manner, the coupler (coupling agent) may act as a connecting bridge between the silica and the rubber and, thereby, enhance the rubber reinforcement aspect of the silica.

[0314] The silane of the coupling agent may form a bond to the silica surface, possibly through hydrolysis, and the rubber reactive component of the coupling agent combines with the rubber itself. Usually the rubber reactive component of the coupler is temperature sensitive and tends to combine with the rubber during the final and higher temperature sulfur vulcanization stage. However, some degree of combination or bonding may occur between the rubber-reactive component of the coupler and the rubber during an initial rubber/silica/coupler mixing stage prior to a subsequent vulcanization stage.

[0315] Without departing from the scope of the present invention, and as appreciated by those skilled in the art, inert fillers may be included in the method and curable compositions of the invention. If an inert filler is desired, any known or conventional filler which does not interfere with the vulcanization process described herein may be used, and such fillers are desirable in finely divided form. Suitable fillers include, but are not limited to, the following: silica and silicates, thermal blacks (i.e., furnace, channel or lamp carbon black), clays, kaolin, diatomaceous earth, zinc oxide, cork, titania, titanium dioxide, cotton floc, cellulose floc, leather fiber, plastic fiber, plastic flour, leather flour, fibrous fillers such as glass and synthetic fibers, metal oxides and carbonates and talc. Other examples are calcium carbonate, silicas, carbon black, clays, talc, mica, calcium oxide, aluminas, magnesium carbonate, and the like. The aforementioned fillers may be heat treated or treated with silanes, resins, or cationic species to prevent or reduce decomposition of some peroxides. The amount of inert filler is dictated by its type and the intended end use of the composition and, in general, is from 0 to 200, preferably between 0 and 150 and, more preferably, between 50 and 100 parts by weight for 100 parts by weight of the elastomer or of the blend of elastomers.

Other Additives in the Curable Composition

[0316] Other additives that may be added to the curable compositions of the present invention,

depending upon the intended end-use of the cured composition, include antioxidants, UV stabilizers, antiozonants, plasticizers, mold release agents, tackifiers, anti-tack agents, dispersants, solvents, softening agents, fatty acids such as stearic acid, processing aids, coloring agents and the like. Such additives may be included in the curable composition in order to achieve the final properties desired for particular end-use applications (such as adhesive and sealant applications). A non-exhaustive list of such optional additional components are tackifiers and/or coupling agents; adhesion promoters, such as functionalized liquid rubber resins (e.g., maleinized liquid polybutadiene resins); plasticizers or extender oils, such as paraffinic oil; and/or stabilizers against thermal, thermo-oxidative or ozone degradation. The inventive oligomeric product can serve as a suitable replacement for plasticizers or extender oils.

[0317] Examples of antidegradants that may be in a rubber composition according to various embodiments of the present invention include, but are not limited to, monophenols, bisphenols, thiobisphenols, polyphenols, hydroquinone derivatives, phosphites, phosphate blends, thioesters, naphthylamines, diphenol amines as well as other diaryl amine derivatives, para-phenylene diamines, quinolines, and blended amines. Antidegradants are generally used in an amount ranging from about 0.1 phr to about 10 phr with a range of from about 2 to 6 phr being preferred.

[0318] Examples of a peptizing agent include, but are not limited to, pentachlorophenol, which may be used in an amount ranging from about 0.1 phr to 0.4 phr, with a range of from about 0.2 to 0.3 phr being preferred.

[0319] Examples of processing oils include, but are not limited to, aliphatic-naphthenic aromatic resins, polyethylene glycol, petroleum oils, ester plasticizers, vulcanized vegetable oils, pine tar, phenolic resins, petroleum resins, polymeric esters and rosins. The inventive oligomeric product can also serve as a processing oil. A processing oils may be used in an amount ranging from about 0 to about 50 phr, with a range of from about 5 to 35 phr being preferred.

[0320] The rubber compositions according to embodiments of the present invention may be compounded by conventional means known by those having skill in the art, including a mixer or compounder (such as a Banbury® mixer), mill, extruder, etc. The tires may be built, shaped, molded, and cured by various methods which will also be readily apparent to those having skill in such art.

[0321] To cure the curable rubber compositions of the present invention, any of the usual vulcanization or curing processes known in the art may be used such as heating with superheated steam or hot air in a press or mold. Accordingly, the curable rubber composition may be cured by a process comprising heating the curable rubber composition, which may be molded into a desired form, at a temperature and for a time effective to cure the diene elastomer(s).

[0322] Particular embodiments of the present invention include tires, in particular tire treads, that are intended for passenger-car or light truck tires but the invention is not limited only to such tires. It is noted that the particular embodiments of the tires of the present invention are intended to be fitted on motor vehicles (including passenger vehicles) or non-motor vehicles such as bicycles, motorcycles, racing cars, industrial vehicles such as vans, heavy vehicles such as buses and trucks, off-road vehicles such as agricultural, mining, and construction machinery, aircraft or other transport or handling vehicles.

[0323] The curable rubber compositions disclosed herein may be used for various rubber products such as tires, particularly a tread compound, and in other components for tires, industrial rubber products, seals, timing belts, power transmission belting, and other rubber goods. As such, the present invention includes products made from the curable rubber compositions disclosed herein.

EXAMPLES

[0324] The following pyrolysis plastic oils were used in the examples:

[0325] Pyrolysis Oil 1: it has a boiling point ranging from 50° C. to about 480° C. and a Diene value of about 2.7%. The chlorine content is in the range of about 115 ppm, the silicium content is expected in the range of about 15 ppm. The oxygen content is expected in the range of about 1 wt.

%. The nitrogen is expected in the range of about 1150 ppm wt.

[0326] Pyrolysis Oil 2: A light cut obtained by distillation of a pyrolysis oil (issued from a non-catalytic pyrolysis of mixed waste plastic) and having a boiling point ranging from about 50° C. to about 260° C. The water is expected to be below 100 ppm weight. The Diene value is expected to be in the range of about 4.8%.

[0327] Pyrolysis Oil 3: A light cut of non-catalytic pyrolysis plastic oil (obtained by staged condensation of the pyrolysis effluent) and having a boiling point ranging from <36° C. to about 260° C. This oil has been decanted to assure a water content below 100 ppm weight. The Diene value is expected to be in the range of about 7.8%.

[0328] Pyrolysis Oil 4: it has a boiling point ranging from 40° C. to about 401° C. and a Diene value of about 2.1%. The chlorine content is expected in the range of about 270 ppm, the silicium content is expected in the range of about 12 ppm. The oxygen content is expected in the range of about 0.3 wt. %. The nitrogen is expected in the range of about 1250 ppm wt.

Method Used for Measuring the Diene Content

[0329] Unless otherwise specified, the following method was used to determine the content of dienes in the pyrolysis plastic oils in all the examples.

[0330] The determination of the diene content is performed with the help of the GPC with a UV detector. A given quantity of maleic anhydride is added in the pyrolysis plastic oil and let to react with the dienes via the Diels-Alder reaction. The reduction of the UV active MA peak in the chromatograph is monitored and used to determine diene concentration. In a first step, a calibration curve is prepared. The equipment used are

[0331] Agilent 1260 Series Degasser (Part Number G1322A); Agilent 1260 Series Isocratic Pump (Part Number G1310B); Agilent 1260 Series Autosampler (Part Number G1329B); Agilent 1260 Series Thermostatted Column Compartment (Part Number G1316A); Agilent 1260 Series Multiple Wavelength Detector (Part Number G1365C); and Agilent 1260 Series Refractive Index Detector (Part Number G1362A).

[0332] Column set: 1× Agilent ResiPore 50×4.6 mm Guard Column (Part Number PL1 513-1300); and 2× Agilent ResiPore 250×4.6 mm 3 um Particle Size Columns (Part Number PL1513-5300).

[0333] Software: Cirrus 3.3, ChemStation B04.03[52].

[0334] Solvent: THE Stabilized with 250 ppm BHT Flow Rate: 0.45 ml/min.

[0335] Column Compartment Temperature: 40° C.

[0336] Calibration: polystyrene standards from Agilent EasiCal Standards

i) GPC-UV Calibration of Maleic Anhydride:

[0337] Samples of known concentration of maleic anhydride (MA) in THE were prepared and analyzed using GPC with a UV detector.

[0338] The chromatograph at 240 nm was analyzed for peak area.

[0339] A plot of MA (ppm) versus peak area creates the calibration curve (FIG. 2). The equation of the line can be used to determine the concentration of MA in unknown solutions.

ii) Preparation of Samples for Testing:

[0340] A solution of 6% wt maleic anhydride in toluene is prepared.

[0341] 15 g of MA is added to 200 mL toluene and heated to 55° C. for 4 hours. The solution is then cooled, and the volume is brought to 250 mL.

[0342] The solution is let sit overnight and filtered the following day. This will remove some undissolved MA that has precipitated out.

[0343] Once made, the solution should be used within two weeks.

[0344] The concentration of the MA solution is checked using the equation from the GPC-UV calibration in the following (Equation 1.):

$$[00002] \frac{(0.1586 \times PA + 0.3095)}{\left(\frac{\text{sample M.F.}}{\text{Inj. Vol.}}\right)} = [\text{MA}](\text{ppm}) \quad \text{Eq. 1}$$

where PA is the peak area (15.8-16.6 min) at 240 nm (mV.Math.s), sample M.F is the concentration

of the sample

$$[00003] \left(\frac{\text{sample}(g)}{\text{sample}(g) + \text{THF}(g)} \right),$$

and Inj. Vol is the sample injection volume (uL). The equation $0.1586x + 0.3095$ is the equation of the line from the MA calibration plot.

iii) Preparation of Sample and Diels-Alder (D-A) Reaction.

[0345] Weight out 15 g of sample (pyrolysis oil) and add to a 100 mL round bottom flask (RBF).

[0346] Add 20 mL of the 6% MA in toluene solution and a stir bar to the 100 mL RBF with the sample.

[0347] Mix the solution gently then remove 55-70 mg of the mixture and place into 20 mL vial. Record the exact amount of mixture added.

[0348] Add 9-10 g of THE to the 20 mL vial recording the exact amount of THE added.

[0349] The sample in THE in the 20 mL vial will be used for the initial determination of MA for the diene calculation. Notated as initial in calculations. Run GPC-UV.

[0350] The mixture in the 100 mL RBF is then heated to reflux for 3 hours.

[0351] Upon refluxing, 55-70 mg of the solution is then placed into a second 20 mL vial. Record the exact amount added.

[0352] Add 9-10 g of THE to this second 20 mL vial recording the exact amount of THE added.

This sample is used for the final determination of MA for the diene calculations. Notated as final in calculations. Run GPC-UV.

[0353] Determining amount of reacted and unreacted MA.

[0354] The initial amount of MA is calculated using equation 1 and the initial sample.

[0355] The final amount of MA is calculated using equation 1 and the final sample.

[0356] The results are converted from ppm to % and the amount of MA consumed is calculated using Equation 2:

$$[00004] 1 - \frac{\text{FinalMA}\%}{\text{InitialMA}\%} = \text{MAconsumed} \quad \text{Eq. 2}$$

Determining Diene % of Sample.

[0357] To determine the diene content, it is needed to know the amount (g) of MA used during D-A reaction. [0358] 20 mL of 6% MA in toluene = 1.8 g MA and 16.3 g toluene

[0359] Determine the percentage of C_5H_8 dienes and higher MW dienes.

[0360] Integration of the 240 nm peak area from 13.5-16 min and 16-18.5 min of the pure sample from GPC-UV gives the peak area percentages of the higher MW dienes and the C_5H_8 dienes, respectively.

[0361] The Mw (g/mol) of the higher MW dienes is determined using the Mw (g/mol) from the GPC and normalizing it using the Mw of the C_5H_8 peak and 68 g/mol.

[0362] Use Equation 3 to determine diene percentage.

$$[00005] \left[\frac{\left(\frac{\text{gMA} \times \% \text{C}_5\text{H}_8 \times \text{MAConsumed}}{\text{MwofMA}(\frac{\text{g}}{\text{mol}})} \right) \times \text{MwC}_5\text{H}_8(\frac{\text{g}}{\text{mol}})}{\text{gramsofpyrolysisoilsample}} \right] + \left[\frac{\left(\frac{\text{gMA} \times \% \text{otherdienes} \times \text{MAConsumed}}{\text{MwofMA}(\frac{\text{g}}{\text{mol}})} \right) \times \text{Mwotherdienes}(\frac{\text{g}}{\text{mol}})}{\text{gramsofpyrolysisoilsample}} \right] \quad \text{Eq. 3}$$

Example 1. Production of an Oligomeric Product Using BF.SUB.3

[0363] The purification of pyrolysis oil was prepared through solution polymerization wherein the catalyst and monomers were continuously fed into the reaction vessel and boron trifluoride diethyl etherate is used as the catalyst with the BF.sub.3 weight percentage on the total feed being 1.15+/-0.25%.

[0364] The flow rate of the monomer feed and the Friedel-Craft catalyst is controlled so that the catalyst feed is about 2 to 3 wt. % on the combined mass flow of the monomer. The reaction temperature was maintained at 40° C. throughout the polymerization process and all steps carried out under a nitrogen blanket.

[0365] An initial amount of pyrolysis oil (-10 wt. % of the total) was added as the reaction heel to a round bottom flask (RBF) purged with nitrogen. The heel was then warmed to 40° C. while stirring under nitrogen. The pyrolysis oil feed and Lewis acid catalyst (BF.sub.3—OEt.sub.2) were

each measured out in individual flasks. If a comonomer was used (i.e. styrene) it was measured out and added to the flask with the pyrolysis oil feed. The pyrolysis oil and catalyst were fed into the reactor while maintain a temperature of 40° C. so that the catalyst was added at 2 to 3 wt. % of the monomer and the two feeds finish adding at roughly the same time. Upon completion of the feed additions, the mixture was stirred at 40° C. for 45-60 minutes before cooling to room temperature. The polymerization was carried out under a nitrogen blanket.

[0366] The reaction mixture was then transferred to a separatory funnel and washed three times with ~0.1M NH₄OH, discarding the aqueous phase. The organic mixture was then washed twice more with water and the organic phase transferred to a separate three neck round bottom flask for distillation. During the washings, there is an insoluble tarry like residue that remains on the sides of the reaction flask and separatory funnel. In all cases of purification, the tarry residue was left behind unless otherwise noted.

[0367] The organic mixture was purged with nitrogen while being heated to 230° C. and the volatile organics were collected. Once the temperature reached 230° C. the distillation continued until there were no more volatiles being distilled at which point the nitrogen was replaced by steam. The volatiles collected prior to steam stripping are referred to as the distillate. Oligomeric product and steam condensate were collected until there was minimal oligomeric product being collected. The oligomeric product collected is referred to as oily polymer. The material remaining after steam stripping is a resin/wax product polymerized during purification. The distillate collected is the purified pyrolysis oil with the dienes reduced.

[0368] Table 1 shows the catalyst and comonomer amounts used for polymerization and the final diene concentration of the distillate following purification. The diene content has been reduced to less than 0.5% in all cases and in some instances, removed to undetectable levels, following polymerization.

TABLE-US-00001 TABLE 1 Initial and final diene concentration.

	Poly 1	Poly 2	Poly 3	Poly 4	Poly 5
Origin of the pyrolysis oil	Py Oil 1	Py Oil 2	Py Oil 2	Py Oil 3	Py Oil 3
Initial Diene Percent	2.7	4.8	4.8	7.8	7.8
Styrene (wt. %)	—	—	1.4	—	9.0
BF ₃ , wt. % (on total feed)	0.92	1.16	1.24	1.40	1.28
Final Diene Percent	0.4	0.0	0.3	0.2	0.0

Example 2. Production of an Oligomeric Product Using Aluminum Chloride (AlCl₃) as Catalyst

[0369] Hexanes (−10 wt. % of the total) was added to a RBF purged with nitrogen. The AlCl₃ catalyst, approximately 1.25 wt. % of the total feed, was then added to the hexanes and warmed to 35° C. while stirring under nitrogen. The pyrolysis oil feed was measured out in an individual flask and fed at a rate of 2 mL/min. Upon completion of the feed addition, the mixture was stirred at 35° C. for 50 minutes before cooling to room temperature. The polymerization was carried out under a nitrogen blanket.

[0370] The reaction mixture was then transferred to a separatory funnel and washed three times 25% aqueous isopropanol (IPA), discarding the aqueous phase. The organic mixture was then washed twice more with water and the organic phase transferred to a separate three neck round bottom flask for distillation. The organic mixture was then distilled, and steam stripped as in example 1.

Example 3. Production of an Oligomeric Product Using Amberlyst 15 as Catalyst

[0371] Pyrolysis oil was added to a RBF and stirred under nitrogen while warming to 40° C. Amberlyst 15, approximately 1 wt. % of the total feed, was added as the catalyst in two doses. The initial amount of Amberlyst 15 catalyst (2/3 of the total) was added once the oil reached 40° C. and then stirred at 40° C. for 45 minutes under nitrogen. The remaining 1/3 of catalyst was then added and the reaction stirred for an additional 75 minutes. The mixture was then cooled to room temperature and the catalyst filtered. The organic mixture was then distilled, and steam stripped as in example 1.

Example 4. Production of an Oligomeric Product Using Sulfuric Acid (H₂SO₄)

84.2% 96.3% 94.8%

Example 6. Preparation of a Rubber Composition for Tire Applications

[0379] A model tire tread formulation was used to evaluate the resin and wax products described in Table compared to standard processing oils and Wingtack¹⁰. The formulations were compounded in three stages. The initial stage was compounded in an internal mixer at 15MP155)C for 5 minutes, the second stage completed using an internal mixer at 90-1 0000 for 4 minutes, and the third stage at 60° C. for 5 minutes. The mixing for all samples at each stage was similar and as the stages progressed the compounds became less fragmented.

Initial Stage:

TABLE-US-00005 Component phr Neodymium Butadiene Rubber (Buna CB24) 25.00 Solution Styrene Butadiene Polymer (Buna VSL 4526-2 HM) 103.10 Amorphous Precipitated Silica (Zeosil 1165 MP) 90.00 Tetrasulfidosilane Coupling Agent (Xiameter OFS-6945) 14.40 Processing Oil (Various) 15.00

Second Stage:

TABLE-US-00006 Component phr Stearic Acid 2.30 Antiozonant (6PPD) 2.00

Third Stage:

TABLE-US-00007 Component phr Sulfur 1.30 Zinc Oxide 2.30 Delayed Action Accelerator (TBBS) 1.70 Fast Curing Accelerator (TBzTD) 0.50 Basic Accelerator (DPG) 2.00

[0380] In addition to Wingtack 10 (petroleum based liquid resin), commercial processing oils Sunpar 2280 (paraffinic) and Plaxolene TD346 (treated distillate aromatic extracted, TDAE) were used as comparative examples for the pyrolysis oil products in tire tread formulations. The oil used in the batches are shown in Table.

TABLE-US-00008 TABLE 5 Processing Oil Used in Tire Tread Batches. Batch Processing Oil 1 WT10 2 Sunpar 2280 3 Plaxolene TD346 4 Wax+ 5 Wax 6 Resin 7 Resin-Sty

[0381] Oscillating disk rheometer (ODR) tests were performed to compare the crosslinking behavior of the various batches at 160° C. The results are shown in Table. The working time (ts2) for all of the tire tread formulations remains constant regardless of the processing oil used; however, the use of the resin and resin-sty from the pyrolysis oil increase the cure time (t'90) compared to the standard processing oils and WT10. Delta torque for the resin and resin-sty based formulations are less than that of WT10 while the wax+ and wax are similar.

TABLE-US-00009 TABLE 6 ODR Results and the Effect of the Products on Crosslinking Behavior. Batch 1 2 3 4 5 6 7 ts2 (min) 1.4 1.4 1.4 1.3 1.3 1.1 1.3 t'90 (min) 11.3 11.3 12.6 11.7 12.8 14.5 13.8 MH-ML (dNm) 16.5 17.6 17.7 16.6 16.9 14.9 15.6

[0382] The cured properties of the formulations are shown in Table. The formulations were cured at 160° C. for 25 minutes in a heated press. The resin and resin-sty products are comparable to WT10 as a processing oil in tire tread formulations. The wax and wax+products are comparable to TDAE when used as a processing oil in these formulations.

TABLE-US-00010 TABLE 7 Cured Properties of Tired Tread Formulations with Products. Batch 1 2 3 4 5 6 7 Hardness (Shore A) 63.0 60.7 63.3 62.7 61.3 62.3 60.7 Tensile Strength (psi) 2611.8 2337.1 2652.4 2442.5 2092.0 2659.7 2374.4 Elongation at Break (%) 428.0 360.7 391.6 290.2 245.1 439.4 393.9 Modulus 50% (psi) 260.3 294.3 287.5 280.7 288.6 271.0 266.5 Modulus 100% (psi) 458.9 530.1 511.4 499.5 503.0 479.6 463.2 Modulus 300% (psi) 1697.7 1876.1 1920.2 1798.5 1765.5 1696.4 1702.8 Tear Strength (lbf/in) 239.2 230.8 220.6 207.5 231.9 238.2 237.7 Rebound at RT (%) 26.2 28.0 27.7 32.0 33.7 25.7 25.3 Rebound at 100 C. (%) 62.9 65.3 64.7 63.7 65.4 61.8 62.4 XLD (mol/cm3) 7.55E-05 8.72E-05 8.26E-05 8.04E-05 7.96E-05 7.30E-05 7.42E-05

[0383] Dynamic mechanical analysis (DMA) was used to determine the elastic modulus G' as a function of strain deformation (the Payne effect) and measure tan δ. The elastic modulus as a function of strain deformation is used to evaluate the effectiveness of the silica dispersion; at low deformation, decreased interaction between silica particles results in a lower G' value indicative of better dispersion. Commonly in the industry tan δ is used as a performance indicator; a higher

value of $\tan \delta$ at 0° C. is associated with better wet traction and a lower value of $\tan \delta$ at 600C is associated with better rolling resistance. The results are reported in Table.

[0384] The wax products from pyrolysis oil polymerization improve the dispersion of silica in the formulations relative to the controls and the resin products perform like the standard oils. The resin and resin-sty perform like WT10 and have improved wet traction compared to the standard processing oils in tire tread formulations while the wax products show improved rolling resistance compared to the standard processing oils.

TABLE-US-00011 TABLE 8 DMA Results using Products as a Processing Oil. Batch 1 2 3 4 5 6 7
G' @ 14%, 1.0 Hz, 338.4 332.6 319.3 285.8 303.2 328.1 331.7 100 C. (ML1 + 4) $\tan \delta$ 0° C. 0.440
0.389 0.398 0.323 0.306 0.441 0.416 $\tan \delta$ 60° C. 0.134 0.128 0.121 0.115 0.110 0.147 0.129

Claims

1-31. (canceled)

32. A rubber composition characterized in that it comprises: a) At least one elastomer selected from synthetic and natural elastomers; b) A curing agent; and c) An oligomeric product prepared from a liquified waste polymer the oligomeric product having a number average molecular weight, M_n , ranging from 100 to 10 000 g/mol measured using gel permeation chromatography and a polystyrene calibration and wherein the oligomeric product shows a glass transition temperature (T_g) below -20° C. as determined by Differential Scanning calorimetry or a crystallisation temperature below 35° C.

33. The rubber composition according to the claim 32 is characterized in that the content of said at least one elastomer ranges from 1 to 150 phr.

34. The rubber composition according to the claim 32 is characterized in that the content of said curative from 0.1 to 25 phr and the content of said oligomeric product ranges from 0.1 to 50 phr.

35. The rubber composition according to claim 32 is characterized in that the oligomeric product presents an olefinic content of at most 20.0 wt % as determined by 1H NMR; preferably ranging from 0.1 to 10.0 wt. %.

36. The rubber composition according to claim 32 is characterized in that the oligomeric product presents an aliphatic content ranging from 15 to 100 wt. % as determined by 1H NMR; preferably ranging from 50.0 to 99.0 wt. %.

37. The rubber composition according to claim 32 is characterized in that the oligomeric product presents an aromatic content of less than 50 wt. % as determined by 1H NMR; preferably ranging from 0.1 to 10.0 wt. %.

38. The rubber composition according to claim 32 is characterized in that the oligomeric product presents a viscosity at 30° C. ranging from 10 to 50 000 cps measured using a Brookfield viscometer; preferably ranging from 10 to 10 000 cps.

39. The rubber composition according to claim 32 is characterized in that the oligomeric product presents a number average molecular weight (M_n) ranging from 100 to 700 g/mol measured using gel permeation chromatography and a polystyrene calibration; preferably from 100 to 550 g/mol.

40. The rubber composition according to claim 32 is characterized in that the oligomeric product comprises a comonomer selected from the group consisting of styrene, alpha-methyl styrene, 2-methyl styrene, 3-methyl styrene, 4-methyl styrene, 4-t-butyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2,4-diisopropyl styrene, 2,4,6-trimethyl styrene, 2-ethyl-4-benzylstyrene, 4-(phenylbutyl) styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl anthracene, 4-methoxy styrene, monochlorostyrene, dichlorostyrene, divinyl benzene, Indene, methyl-Indene, and mixtures thereof; with preference oligomeric product comprises a comonomer being or comprising styrene.

41. The rubber composition according to claim 32 is characterized in that the oligomeric product comprises a comonomer present at a concentration ranging from 0.01 to 90 mol. % based on the total weight of the oligomeric product, preferably from 1.0 to 80 mol. %.

42. A process for the preparation of a rubber composition according to claim 32 comprising the following steps: a) providing a feedstream (1) containing liquified waste polymer, wherein said feedstream (1) contains at least 0.1 wt. % to at most 80 wt. % of dienes based on the total weight of said feedstream (1); c) performing a polymerization reaction on said feedstream (1) under polymerization conditions to obtain a first product stream (3) comprising an oligomeric product (33) and a purified liquified waste polymer; d) optionally, performing a neutralization reaction by contacting said first product stream (3) with a basic compound (25) to obtain a neutralized product stream (4) and removing said basic compound from neutralized product stream (4) to obtain a second product stream (5); g) performing a separation to separate the oligomeric product (33) from the purified liquified waste polymer (34); and h) preparing a rubber composition comprising at least one elastomer selected from synthetic and natural elastomers; a curing agent; and said oligomeric recovered at step g).

43. The process according to claim 42 is characterized in that the polymerization reaction in step c) is a cationic polymerization; and/or in that the process further comprises a step (b) of drying the feedstream (1) to obtain a dried feedstream (2) wherein step b) is performed before step c) of polymerization so that step c) of polymerization reaction is performed on the dried feedstream (2).

44. The process according to the claim 43 is characterized in that step b) of drying is performed and comprises a sub-step b1) of decantation and/or centrifugation; with preference, the first sub-step b1) is followed by a second sub-step b2) of drying using a molecular sieve to reach a water content of less than 0.1 vol. % according to ASTM D95-13 (2018).

45. The process according to any one of claim 42 is characterized in that the polymerization reaction in step c) is a cationic polymerization performed in the presence of an acidic catalyst; with preference, the acidic catalyst is a Brönsted acid or a Lewis acid and step d) performed and the concentration of the basic compound ranges from 0.1 to 50.0 wt. % based on the total weight of said neutralized product stream (4).

46. The process according to claim 43 is characterized in that the polymerization reaction in step c) is a cationic polymerization performed in the presence of an acidic catalyst being a Lewis acid chosen among BF₃, complexes of boron trifluoride, AlCl₃, SnCl₄, ZnCl₂, FeCl₃ and TiCl₃, alkyl aluminum chlorides, H₂SO₄ or any mixture thereof; with preference, acidic catalyst is or comprises boron trifluoride etherate.

47. The process according to claim 43 is characterized in that the acidic catalyst is present at a concentration ranging from 0.5 wt. % to 5.0 wt. % based on the total weight of said feedstream (1) and/or in that the polymerization reaction of step c) is carried out until the dienes of the purified liquified waste polymer is less than 5.0 wt. % based on the total weight of the first product stream (3).

48. The process according to claim 42 is characterized in that the polymerization conditions of step (c) comprises a contact time ranging from 5 min to 5 hours; and/or a temperature ranging from 5 to 100° C. at atmospheric pressure.

49. The process according to claim 43 is characterized in that step d) performed and the concentration of the basic compound ranges from 0.1 to 50.0 wt. % based on the total weight of said neutralized product stream (4).

50. The process according to claim 42 is characterized in that it further comprises a step f) of filtering the stream obtained in the previous step to obtain a filtered stream (7) wherein the filtering is performed to remove solids from the first product stream (3) or from the second product stream (5) or from the washed stream (6), and/or to coalesce remaining traces of solvent if any; with preference, the filtering step is followed by a dewatering step.

51. The process according to claim 42 is characterized in that the liquified waste polymer is a pyrolysis plastic oil, with preference, step a) of providing a feedstream (1) containing liquified waste polymer comprises the preliminary steps of preparation of liquified waste polymer including: a1) of providing a waste plastics stream; a2) pyrolyzing said waste plastics stream at a temperature

of at least 200° C.; a3) recovering a pyrolyzer effluent and separating, into a C.sub.1 to C.sub.4 hydrocarbons fraction, a fraction having a boiling range higher than 350° C. and a remaining fraction being said pyrolysis plastic oil; a4) optionally sending the fraction having a boiling range higher than 350° C. into a Fluid Catalytic Cracking unit, or a hydrocracking unit, a coker or a visbreaker or blending said fraction having a boiling range higher than 350° C. in crude oil or in a crude oil cut to be further refined.
