

A PYROLYSIS OIL WITH REDUCED POUR POINT**TECHNICAL FIELD OF THE INVENTION**

5 The invention relates to a composition comprising a pyrolysis oil and a polymeric additive for reducing the pour point, viscosity, or both the pour point and viscosity of the pyrolysis oil. The invention further relates to a method of manufacturing said composition, the use of a polymeric additive for reducing the pour point, viscosity, or both the pour point and viscosity of a pyrolysis oil. The invention further relates to a method for transporting or storing a pyrolysis oil.

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BACKGROUND OF THE INVENTION

Plastic production continues to grow rapidly, and plastic products remain to be a crucial part of our lives due to the versatility of the material and the low cost associated with plastic production. It is estimated that 15 250 million tons of plastic per year are either landfilled or dispersed into the environment. It is also predicted that the use of plastic will continue to increase in the future. The increase in plastic production will also be associated with the increase in associated plastic waste, especially with single-use plastic items. The increase in plastic waste has also brought interest in how to effectively recycle or convert plastic waste back into usable materials.

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One effective way to treat plastic waste is by thermochemically converting plastic waste via a pyrolysis process. Pyrolysis is a thermal cracking process that occurs in the absence of oxygen at temperatures above 400°C. The process breaks down polymer chains into smaller chains and molecules. The pyrolysis process can therefore convert plastic waste material into usable products thereby addressing the plastic waste management issues. There are many types of plastics, but the majority of plastic waste is made up of low-density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET). Of those plastics, polyethylene and polypropylene constitute the greatest portion of plastic waste. The pyrolysis provides a final product termed in the art 'pyrolysis oil'. The main products produced from plastic pyrolysis include 25 liquid oil, wax, solid residues, and gas. All such residues are then processed further as part of existing plastic processing plants or steam crackers used in refineries.

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In the pyrolysis process, the conversion of plastic to usable materials, e.g. oil, gas, and wax, is dependent on several factors. The most influential factors are the reactor design, the process temperature, the type of plastic used, and the type of catalyst. 35

The wax residue comprises those pyrolysis products having alkyl chains of 16 or more carbon atoms. The wax residue is a valuable product in the pyrolysis process. The amount of wax residue produced can greatly influence the final pyrolysis oil properties. The main driver in the amount of wax residue produced is the plastic feedstock being introduced into the pyrolysis process. For example, olefinic plastics such as polyethylene and polypropylene are more linear polymers, which therefore break down into waxy linear 40

alkyl chains when converted in the pyrolysis process. Pyrolysis oils produced from polyethylene and polypropylene can yield over 50wt% wax residue depending on the specific pyrolysis oil process conditions.

Specific process conditions including catalyst types can also influence oil-to-wax ratio. To obtain a lower wax residue content in the final product, certain catalysts can be used. Also, conditions such as residence time in the reactor can be influential. For example, 'fast' pyrolysis leads to the production of waxy hydrocarbon mixtures, whereas 'slow' pyrolysis typically produces more oil than wax. (Materials 2021, 14, 2586).

However, waxy chains can also cause a variety of transportation and storage issues. The waxy chains of 12 or more carbon atoms can begin to crystallize as the pyrolysis oil cools to ambient temperature after the pyrolysis process. Pyrolysis oils also typically have a large quantity of paraffins with waxy chains of 16 to more than 40 carbon atoms. These wax chains are most problematic since the melting point is much higher. The wax crystals can then build up and cause an increase in viscosity, making the thicker oil more difficult to pump or move. If there is enough wax residue in the pyrolysis oil, especially in polyolefin pyrolysis oils, then the wax crystals may cause the entire product to solidify at lower temperatures heading towards ambient temperature. Once solidified, expensive heating must be used to melt the product in order to move or process it further. The wax crystals may also clog equipment such as filters and pipelines, thus increasing servicing costs. Lastly, high wax amounts can lead to paraffin deposition on pipelines in the production lines. As wax builds up, the efficacy and lifetime of the equipment is decreased.

Despite this, wax is a valuable pyrolysis product, and existing plastic processing plants have been designed and built to use the wax residue. However, the wax residue made in the pyrolysis process, especially from increasingly used olefin feedstocks, is making transportation and storage of the pyrolysis oil more difficult and more expensive.

As previously explained, the amount of wax residue varies depending on the plastic feedstock used, and the specific process conditions. And, polyolefin-based pyrolysis oils produced via current or standard pyrolysis processes, tend to produce the most amount of wax, which therefore have the most problems, especially at ambient conditions. The 'pour point' is the lowest temperature at which the pyrolysis oil will still flow, and pyrolysis oils with high wax residue have relatively high pour points (for example, above 50°C), which are usually above standard operating conditions and storage temperatures. This leads to difficulty in processing such pyrolysis oils, as the oil may solidify and become unable to transport. Heat is typically applied to the oil to liquefy it for storage and transportation. This expends heat energy and takes time. Therefore, even slight reductions in the pour point could drastically reduce the amount of heat energy expended and time taken to liquefy or to keep in liquid form the pyrolysis oil for transportation and storage.

One solution for reducing the pour point of the pyrolysis oil is to change the process conditions or the catalysts type to produce pyrolysis oils with lower pour points. But to do this, expensive catalysts need to be employed, the processes must run longer, or special reactors are required. Increasing process times or changing the reactor also increases the cost or decreases the overall efficiency. Furthermore, the valuable

wax product is no longer produced at the same amount, and so cannot be available for subsequent processing set up to expect the wax product. Other solutions have been implemented to isolate the wax by introducing a dewaxing step and reprocessing the oil to crack the wax into smaller molecules. However, these solutions also add costs and decrease efficiency to the process.

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US2012/0310023A1 discloses that oils obtained in pyrolysis of polyolefin containing plastics mixtures are frequently wax-like semisolid products, and that the use of specific catalysts can result in the production of more light and less waxy products.

10 Lee et al. in the Journal of Analytical and Applied Pyrolysis 94 (2012) 209–214 explain that most of the plastic waste consisting of polyethylene is mainly converted in waxy oils. The waxy oils can be problematic because they could result in a breakdown of plant operations, ranging from pipeline blockages to shorter instrument life cycles. Thus, upgrading technology for pyrolysis to produce high-quality oils is needed. The authors demonstrated the efficacy of zeolite catalysts in the catalytic upgrading of the pyrolysis process.

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Hakeem *et al.* in Applied Petrochemical Research (2018) 8:203–210 describe the problem with higher wax contents in pyrolysis oils and propose that catalysis could also be used to reduce the amount of wax in the final products and upgrade the oil to a lower wax quality in order to improve final properties.

20 US2022/081634 discloses the use of a polymeric additive for improving the cold flow properties of a plastic-derived synthetic feedstock composition (see [0008]). Among the disclosed polymeric additives, the polymer can be an ethylene vinyl acetate (EVA) having a weight-average molecular weight from 800 to 13,000 g/mol, preferably from 900 to 12,000 g/mol (see [0060], [0061] and example 1 of Table 1). This document is focused on the treatment of plastic pyrolysis oil with a high wax residue content of alkanes with long carbon chains (high content of waxes having C₁₆ or longer carbon chains - see e.g. [0048], [0086],
25 [0097], [0115], [00127], as well as the two treated pyrolysis oils of the experimental part [0153]).

KR100994244B1 discloses the need to remove the wax from the process and proposes the use of a separation device for wax removal. Therefore, the pyrolysis process will require an additional step to the
30 process.

Jin *et al.* in the Chinese Journal of Chemical Engineering 26 (2018) 400–406 explain that reactor design can help influence the wax quantity in the final pyrolysis oil product. The authors studied falling film reactor in comparison to other reactor types to improve the liquid/wax ratio. The authors showed that the liquid wax
35 ratio in the vertical falling film pyrolysis reactor is slightly higher than that achieved in the tubular reactor, equal to that in the rotary kiln reactor, and slightly lower than that in the medium fluidized bed.

Thus, as exemplified above, the conventional solutions to reduce viscosity and pour point of pyrolysis oils have been to reduce or eliminate production of the wax by changing the reactor design, adding special
40 catalyst, increasing processing times or having an additional dewaxing process step. Although those methods help in producing liquid pyrolysis oils with a lower wax content, it creates additional costs,

maintenance work, increased processing times, which decrease production efficiency and are thus not good industrially viable solutions. Furthermore, the industry looks for high wax residue content pyrolysis oils for cracking processes, without having the transportation and storage disadvantages.

5 However, the properties of the plastic pyrolysis oils strongly depends on the production process, which leads to plastic pyrolysis oils having different wax residue content of alkanes. Therefore, there is still a need to investigate further to find effective and cost-efficient solutions for the treatment of plastic pyrolysis oils from a plastic pyrolysis process in order to keep them liquid, improving the transport and storage of these oils before the cracking process.

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The present invention is therefore directed to provide a pyrolysis oil with a lower pour point, lower viscosity or both lower pour point and viscosity, as well as other objectives.

BRIEF SUMMARY OF THE INVENTION

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According to a first aspect of the invention, there is provided a composition comprising a plastic pyrolysis oil a) and a polymeric additive b) as defined in claim 1.

20 According to a second aspect of the invention, there is provided a method of manufacturing the composition of the first aspect of the invention, the method comprising the steps of:

- providing a plastic feedstock;
- pyrolyzing the plastic feedstock to generate the plastic pyrolysis oil a);
- preparing the polymeric additive b); and
- adding the polymeric additive b) to the plastic pyrolysis oil a).

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According to a third aspect of the invention, there is provided a use of a polymeric additive b) as herein described, to reduce the pour point of a pyrolysis oil, or to reduce the viscosity of the pyrolysis oil, or both.

30 According to a fourth aspect of the invention, there is provided a method of transporting or storing a plastic pyrolysis oil a) comprising the step of adding a polymeric additive b) to a pyrolysis oil to form a composition as defined in the first aspect of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

35 For the purpose of better illustrating the advantages and properties of the claimed pyrolysis oil, object of the present invention, one graph is attached as a non-limiting example:

Figure 1 is a graph showing the viscosity of pyrolysis oil a) and a composition comprising pyrolysis oil a) with a polymeric additive b) over a temperature range of 40 to 80 °C. The reference number 1 on Figure 1
40 corresponds to the curve of the untreated pyrolysis oil (Example 1 of Table 5 below), whereas the reference

number 2 on Figure 1 corresponds to the curve of the pyrolysis oil composition according to the invention (inventive example 2 of Table 5 below).

DETAILED DESCRIPTION OF THE INVENTION

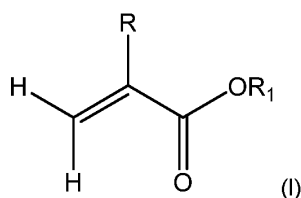
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According to the invention, there is provided composition comprising a plastic pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is an ethylene graft polyalkyl(meth)acrylate A) obtainable by grafting onto an ethylene-based copolymer A1), obtainable by polymerizing a monomer composition consisting of ethylene and a compound selected from the group consisting of vinyl esters,

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acrylates, methacrylates, alpha-olefins or a mixture thereof, based on the total weight of the ethylene-based copolymer A1),

a grafting monomer composition A2) comprising alkyl (meth)acrylates of general Formula (I)



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wherein

R is H or CH₃ and

R₁ is a linear or branched, saturated or unsaturated alkyl group with 1 to 30 carbon atoms, preferably with 7 to 15 carbon atoms.

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The polymeric additive b) reduces the pour point of the pyrolysis oil. The polymeric additive may also reduce the viscosity of the pyrolysis oil. The polymeric additive may also reduce both the pour point and the viscosity of the pyrolysis oil.

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Preferably, the pour point of a pyrolysis oil a) is reduced by at least 1 °C, more preferably by at least 2 °C, even more preferably by at least 3 °C, most preferably by at least 5 °C, by the addition of the polymeric additive as described herein, when compared to the same pyrolysis oil with no polymeric additive.

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The reduction in viscosity is preferably of at least 10 %, preferably at least 20 %, even more preferably 30 %, 40 %, 50 %, or 60 % or more, at a temperature from -20 °C to +80 °C, preferably from -10 °C to +50 °C, when the polymeric additive is added to the pyrolysis oil with a wax residue as described herein, when compared to the same pyrolysis oil with no polymeric additive.

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The polymeric additive b) has a wax inhibition of greater than 1 % relative to the pyrolysis oil a) as determined by the cold finger test measured using CF-15 cold finger device manufactured by PSL with rack temperature set at 5 °C above the Wax Appearance Temperature (WAT) and finger temperature set 20 °C below the WAT for a test period of 24 hours as described in detail in the experimental part of the present

invention. The wax inhibition is preferably greater than 5 %, 10 %, 15 %, 25 % or 30 % (measured according to the cold finger test described above and more detail in the experimental part).

Plastic pyrolysis oil a)

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The term “plastic pyrolysis oil” or “pyrolysis oil” as used herein includes any pyrolysis oil produced from the pyrolysis of plastics or plastic waste. Pyrolysis is a thermal cracking process that occurs in the complete or substantial absence of oxygen, at temperatures above 250°C to convert plastic into energy, in the form of solid, liquid and gaseous fuels. The process breaks down polymer chains into smaller chains and molecules.

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The plastic pyrolysis oil is preferably a plastic waste pyrolysis oil, namely a pyrolysis oil produced from plastic waste. The pyrolysis of plastic waste with a thermal degradation of plastic waste at different temperatures (300–900°C), to produce liquid oil is for example described in Rehan *et al.*, 2017, Int. Biodeterior. Biodegrad. 119, 162–175.

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Preferably, the plastic pyrolysis oil is a plastic pyrolysis oil and/or a plastic waste pyrolysis oil, wherein the plastic and plastic waste are both selected from polyolefins, more preferably polyolefins selected from high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and a mixture thereof; polyethylene terephthalate (PET); polyvinyl chloride (PVC); polystyrene (PS); or a mixture thereof.

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The term “polyolefin pyrolysis oil” and “polyolefin waste pyrolysis oil” as used herein defines an oil produced from the pyrolysis of polyolefins or waste polyolefin respectively, wherein the plastic and plastic waste are selected from high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP).

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Pyrolysis oils having a wax content of at least 1 % by weight typically have problems regarding storage and transportation, due to the high pour point and high viscosity of the pyrolysis oil. The terms “wax residue” or “wax content” include that portion of the pyrolysis oil that comprises linear hydrocarbons containing 16 or more carbon atoms.

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In the context of the present invention, the term “linear hydrocarbons containing 16 or more carbon atoms” used herein means “n-paraffin waxes with C₁₆ or longer carbon chains”, namely, “n-paraffin waxes being a mixture of C₁₆ to C₁₉ n-paraffin waxes, C₂₀ to C₂₉ n-paraffin waxes, C₃₀ to C₃₉ n-paraffin waxes, and n-paraffin waxes with C₄₀ or longer carbon chains”.

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Preferably, the pyrolysis oil a) of the composition of the present invention has a wax residue of 30 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, more preferably of 20 % by weight or less, even more preferably of 15 % by weight or less, most preferably of 12 % by weight or less, most preferably of 10 % by weight or less, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

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Preferably, the pyrolysis oil a) of the composition of the present invention has a wax residue of from 0.01 % by weight to 30 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains, more preferably from 0.01 % by weight to 30 % by weight, more preferably from 0.01 % by weight to 25 % by weight, even more preferably from 0.01 % by weight to 20 % by weight, even more preferably from 0.01 % by weight to 15 % by weight, most preferably from 0.01 % by weight to 12 % by weight, most preferably from 0.05 % by weight to 10 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 30 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 30 % by weight of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 30 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 30 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 30 % by weight, based on the total weight of the plastic pyrolysis oil.

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 20 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 20 % by weight of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 20 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 20 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 20 % by weight, based on the total weight of the plastic pyrolysis oil.

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 15 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 15 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 15 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 15 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 15 % by weight, based on the total weight of the plastic pyrolysis oil.

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 12 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 12 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 12 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 12 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 12 % by weight, based on the total weight of the plastic pyrolysis oil.

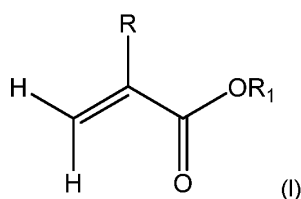
According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 10 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 10 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 10 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 10 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 10 % by weight, based on the total weight of the plastic pyrolysis oil.

According to another preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 10 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 10 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 10 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 10 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 to 10 % by weight, based on the total weight of the plastic pyrolysis oil.

Advantageously, reducing or lowering the pour point or the viscosity or both of a pyrolysis oil makes it easier to transport and store a pyrolysis oil having a wax residue. In this way, the present invention obviates the current requirements to modify the reactor, or to modify the reaction process (for example, by the addition of a catalyst) when processing a pyrolysis oil having a wax residue that it is desired to maintain. In this way, current plastic processing plants designed to expect the use of a wax residue pyrolysis oil can continue to operate without redesign.

Polymeric additive b)

The polymeric additive b) is an ethylene graft polyalkyl(meth)acrylate A) obtainable by grafting onto an ethylene-based copolymer A1), obtainable by polymerizing a monomer composition consisting of ethylene and a compound selected from the group consisting of vinyl esters, acrylates, methacrylates, alpha-olefins or a mixture thereof, based on the total weight of the ethylene-based copolymer A1), a grafting monomer composition A2) comprising alkyl (meth)acrylates of general Formula (I)



wherein

R is H or CH₃ and

R₁ is a linear or branched, saturated or unsaturated alkyl group with 1 to 30 carbon atoms, preferably with 7 to 15 carbon atoms.

Preferably R₁ is a linear or branched, saturated or unsaturated alkyl group with 7 to 15 carbon atoms.

According to the present invention, the polymeric additive b) is one polymer A), or a mixture of one or more polymer A).

Within the context of the present invention, the grafting monomer composition A2) corresponds to the total amount of monomers grafted onto the ethylene-based copolymer A1).

The ethylene-based copolymer A1) in the present invention is obtainable by polymerizing a monomer composition consisting of ethylene, and a vinyl ester or a mixture of ethylene monomer and vinyl esters.

The architecture of the ethylene vinyl ester copolymers is not critical for many applications and properties. Accordingly, the ester-comprising polymers may be random copolymers, gradient copolymers, block copolymers and/or graft copolymers, more preferably random copolymers.

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Preferably, the monomer composition of the ethylene-based copolymer A1) consists of from 55 % to 90 % by weight, preferably from 60 % to 85 % by weight, more preferably from 67 % to 82 % by weight, of ethylene, and from 10 % to 45 % by weight, preferably from 15 % to 40 % by weight, more preferably from 18 % to 33 % by weight, of vinyl ester, based on the total weight of the monomer composition to prepare the ethylene-based copolymer A1).

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In a preferred embodiment of the invention, the weight ratio of ethylene-based copolymer A1) to the monomer grafting composition A2) to prepare the ethylene graft polyalkyl(meth)acrylate A), based on the total weight of the ethylene graft polyalkyl(meth)acrylate B), is from 1:1 to 1:10, preferably from 1:1 to 1:8, more preferably from 1:1 to 1:6.

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According to a preferred embodiment of the invention, the polymeric additive b) further comprises an ethylene-based copolymer B) obtainable by polymerizing a monomer composition consisting of ethylene and a vinyl ester.

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Preferably, the monomer composition of the ethylene-based copolymer B) consists of from 55 % to 90 % by weight, preferably from 60 % to 85 % by weight, more preferably from 67 % to 82 % by weight, of ethylene, and from 10 % to 45 % by weight, preferably from 15 % to 40 % by weight, more preferably from 18 % to 33 % by weight, of a compound selected from the group consisting of vinyl esters, acrylates, methacrylates and alpha-olefins or a mixture thereof, based on the total weight of the monomer composition to prepare the ethylene-based copolymer A1).

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Suitable vinyl esters derive from fatty acids having linear or branched alkyl groups having 2 to 30 carbon atoms. Examples include vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl laurate and vinyl stearate, and also esters of vinyl alcohol based on branched fatty acids, such as vinyl isobutyrate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl isononanoate, vinyl neononanoate, vinyl neodecanoate, vinyl neoundecanoate and vinyl ester of versatic acids. Particularly preferred vinyl esters are vinyl acetate and vinyl propionate. Most preferred vinyl ester is vinyl acetate.

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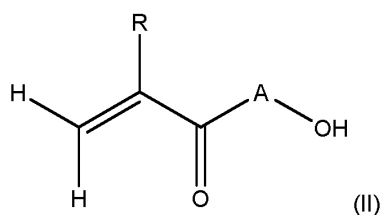
35 Preferably, the ethylene-based copolymer A1) or B) consists of ethylene and vinyl acetate.

Preferably, the ethylene-based copolymers A1) and/or B) according to the invention have a weight-average molecular weight (M_w) from 20,000 to 1,000,000 g/mol, preferably from 45,000 to 500,000 g/mol, more preferably from 60,000 to 400,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 (as described in more detail below).

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According to another preferred embodiment of the invention, the polymeric additive b) comprises an ethylene graft polyalkyl(meth)acrylate A) and an ethylene-based copolymer B), wherein the ethylene-based copolymer B) is from 60 to 95 % by weight and the ethylene graft polyalkyl(meth)acrylate A) is from 5 to 40 % by weight, based on the total amount of the ethylene graft polyalkyl(meth)acrylate A) and the ethylene-based copolymer B).

The grafting monomer composition A2) of the ethylene graft polyalkyl(meth)acrylate A) preferably further comprises hydroxy esters of general Formula (II)



wherein

R is H or CH₃ and

A is a branched or unbranched, aliphatic C₁ to C₄ carbon-based group.

Preferably, the grafting monomer composition of the ethylene graft polyalkyl(meth)acrylate A) comprises 0 to 50 % by weight, preferably 0 to 40 % by weight, more preferably 0 to 30 % by weight of hydroxy esters of general Formula (II), based on the total weight of the grafting monomer composition A2).

Preferably, the hydroxy ester of general Formula (II) is 2-hydroxyethyl methacrylate.

As used herein, the term “(meth)acrylate” refers to esters of acrylic and methacrylic acid, and to mixtures thereof. The term “alkyl (meth)acrylate” refers to esters of (meth)acrylic acid and aliphatic alcohols. The alkyl (meth)acrylates described herein are characterized by the number of carbon atoms in the alkyl chain derived from the alcohol.

The term “C₁ to C₃₀ alkyl (meth)acrylates” refers to esters of (meth)acrylic acid and linear or branched alcohols having 1 to 30 carbon atoms. The term encompasses individual (meth)acrylic esters with an alcohol of a particular length, and likewise a mixture of (meth)acrylic esters with alcohols of different lengths.

Likewise, the term “C₁ to C₆ alkyl (meth)acrylates” or “C₇ to C₁₅ alkyl (meth)acrylates” or “C₁₆ to C₃₀ alkyl (meth)acrylates” refers to esters of (meth)acrylic acid with linear or branched alkyl chain having 1 to 6 carbon atoms or 7 to 15 carbon atoms or 16 to 30 carbon atoms, respectively. The term encompasses individual (meth)acrylic esters with an alcohol of a particular length, and likewise mixtures of (meth)acrylic esters with alcohols of different lengths.

Examples of the C₁ to C₆ alkyl (meth)acrylate monomers, where the linear or branched alkyl group contains from 1 to 6 carbon atoms, are methyl methacrylate (MMA), methyl and ethyl acrylate, propyl methacrylate,

butyl methacrylate (BMA) and acrylate (BA), isobutyl methacrylate (IBMA), hexyl and cyclohexyl methacrylate, cyclohexyl acrylate and or a mixture thereof. Most preferred C₁ to C₆ alkyl (meth)acrylate monomer is methyl methacrylate, butyl methacrylate or a mixture thereof.

- 5 Examples of the C₇ to C₁₅ alkyl (meth)acrylate monomers include (meth)acrylates that derive from saturated alcohols, such as nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, n-dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, n-tetradecyl (meth)acrylate, pentadecyl (meth)acrylate; (meth)acrylates which derive from unsaturated alcohols, for example oleyl (meth)acrylate; cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate having a ring substituent, like tert-butylcyclohexyl (meth)acrylate and trimethylcyclohexyl (meth)acrylate, bornyl (meth)acrylate and isobornyl (meth)acrylate.

- 15 Examples of the C₁₆ to C₃₀ alkyl (meth)acrylate monomers include (meth)acrylates which derive from saturated alcohols, such as hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate, behenyl (meth)acrylate and/or eicosyltetracontyl (meth)acrylate; cycloalkyl (meth)acrylates such as 2,4,5-tri-*t*-butyl-3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-*t*-butylcyclohexyl (meth)acrylate.

More preferably, the alkyl (meth)acrylate of general Formula (I) is isodecyl methacrylate.

- 25 More preferably, the grafting monomer composition of the ethylene graft polyalkyl(meth)acrylate A) consists of alkyl (meth)acrylates of general Formula (I) and hydroxy esters of general Formula (II). Even more preferably, the grafting monomer composition of the ethylene graft polyalkyl(meth)acrylate A) consists of 2-hydroxyethyl methacrylate and isodecyl methacrylate.
- 30 In a preferred embodiment, the polymeric additive b) further comprises a solvent. Preferably, the solvent is selected from hydrocarbon solvents, mineral oils, diesel fuels of mineral origin, naphthenic solvents, natural vegetable and animal oils, biodiesel fuels, esters, higher alcohols, polyfunctional ether-alcohols or a mixture thereof. More preferably, the hydrocarbon solvents are selected from toluene, benzene and xylene, cyclohexane, heptane, octane, nonane, decane, dodecane, or a mixture thereof. Particularly preferred solvents are isodecanol and diethylene glycol.

Preferably, the polymeric additive b) comprises 0 to 90 % by weight, more preferably 10 to 90 % by weight, even more preferably 20 to 80 % by weight, of a solvent, based on the total amount of the polymeric additive b).

Preparation process for polymers for the polymeric additive b) according to the invention

The polymers for use in the polymeric additive b) can be obtained by free-radical polymerization and related processes, for example ATRP (Atom Transfer Radical Polymerization), RAFT (Reversible Addition
5 Fragmentation Chain Transfer) or NMP processes (nitroxide-mediated polymerization). More preferably, the polymers in the polymeric additive b) of the invention are prepared by free-radical polymerization.

Customary free-radical polymerization is described, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator is used for this purpose. The usable initiators
10 include the azo initiators widely known in the technical field, such as 2,2'-azo-bis-isobutyronitrile (AIBN), 2,2'-azo-bis-(2-methylbutyronitrile) (AMBN) and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl peroxy-pivalate, tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, ketone peroxide, tert-butyl peroxoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-
15 butyl-peroxybenzoate, tert-butyl-peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane, tert-butyl-peroxy-2-ethylhexanoate, tert-butyl-peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis(tert-butyl-peroxy)cyclohexane, 1,1-bis(tert-butyl-peroxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl-hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, or a mixture of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned
20 compounds with compounds which have not been mentioned but can likewise form free radicals. Preferred initiator for the preparation of polymers in the polymeric additive b) is tert-butyl-peroxy-2-ethylhexanoate.

Furthermore, a chain transfer agent can be used. It is well-known in the art that a good way to control the molecular weight of a polymer chain is to use chain transfer agents during the polymerization synthesis.
25 Chain transfer agents are molecules with a weak chemical bond which facilitates the chain transfer reaction. During the chain transfer reaction, the radical of the polymer chain abstracts a hydrogen from the chain transfer agent, resulting in the formation of a new radical on the sulfur atom of the chain transfer agent capable of further propagation. Common chain transfer agents are organic compounds comprising SH groups such as n-butyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan, tert-dodecyl mercaptan, butylthiol glycolate, and octylthiol glycolate. A preferred chain transfer agent is selected from n-dodecyl
30 mercaptan, tert-dodecyl mercaptan or a mixture thereof, most preferably n-dodecyl mercaptan.

Preferably, the monomer mixture to prepare the polymer of the present invention may comprise 0.05 to 7 % by weight, preferably 0.05 to 5 % by weight and more preferably 0.1 to 1 % by weight of initiator based on
35 the total weight of the monomer composition to prepare the polymer. The amount of chain transfer agents to prepare the polymer is in the range of 0 to 5% by weight, preferably 0.01 to 5 % by weight and more preferably 0.05 to 4 % by weight, based on the total weight of the monomer composition.

The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The
40 polymerization temperature is not critical. Conventionally the polymerization temperature may be in the range of 0 °C to 200 °C, preferably 0 °C to 140 °C, and more preferably 60 °C to 130 °C.

The polymerization may be carried out with or without solvent, preferably in a solvent. Preferably, the solvent is selected from hydrocarbon solvents, mineral oils, diesel fuels of mineral origin, naphthenic solvents, natural vegetable and animal oils, biodiesel fuels, esters, higher alcohols, polyfunctional ether-
5 alcohols or a mixture thereof. More preferably, the hydrocarbon solvents are selected from toluene, benzene and xylene, cyclohexane, heptane, octane, nonane, decane, dodecane, or a mixture thereof. Particularly preferred solvents are isodecanol and diethylene glycol.

Plastic pyrolysis oil compositions according to the invention

10

Preferably, the composition comprises polymeric additive b) at a concentration of 0.001 % by weight to 1 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition. More preferably, the composition comprises polymeric additive b) at a concentration of 0.005 % by weight to 0.8 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition. Even
15 more preferably, the composition comprises polymeric additive b) at a concentration of 0.005 % by weight to 0.5 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition.

In specific embodiments, the plastic pyrolysis oil a) is a polyolefin pyrolysis oil, wherein the pyrolysis oil is produced at least partially from the pyrolysis of one or more polyolefins. Optionally, the pyrolysis oil a)
20 polyethylene and/or polypropylene pyrolysis oil, wherein the pyrolysis oil is produced at least partially from the pyrolysis of polyethylene and/or polypropylene.

Preferably, the plastic pyrolysis oil a) comprises 30 % by weight or less, more preferably 20 % by weight or less, even more preferably 15 % by weight or less, even more preferably 12 % by weight or less, most
25 preferably 10 % by weight or less, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

Preferably, the plastic pyrolysis oil a) comprises from 0.01 % to 30 % by weight, more preferably from 0.01 % to 20 % by weight, even more preferably from 0.01 % to 15 % by weight, even more preferably from
30 0.01 % to 12 % by weight, most preferably from 0.05 % to 10 % by weight, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 30 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 30 % by weight of C₂₀ to C₂₉ n-paraffin
35 waxes, from 0 % to 30 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 30 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 30 % by weight, based on the total weight of the plastic pyrolysis oil.

40 According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 20 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 20 % by weight of C₂₀ to C₂₉ n-paraffin

waxes, from 0 % to 20 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 20 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 20 % by weight, based on the total weight of the plastic pyrolysis oil.

5

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 15 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 15 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 15 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 15 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 15 % by weight, based on the total weight of the plastic pyrolysis oil.

10

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 12 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 12 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 12 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 12 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 12 % by weight, based on the total weight of the plastic pyrolysis oil.

15

According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 10 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 10 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 10 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 10 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 % by weight to 10 % by weight, based on the total weight of the plastic pyrolysis oil.

20

Preferably, plastic pyrolysis oil a) and polymeric additive b) sum up from 90 to 98 % by weight, based on the total weight of the composition.

25

The composition according to the invention may further comprise an additive c), wherein the additive c) is any of the group comprising scale inhibitors, corrosion inhibitors, oxygen scavengers, biocides, emulsion breakers, antifoam agents, drag reducing agents, hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than polymers A) and B), or a mixture thereof.

30

Preferably, then the amounts of compounds a), b), c) sum up to 90 to 99 % by weight, more preferably sum up to 95 to 98 % by weight, even more preferably sum up to 100 % by weight, based on the total weight of the composition.

35

Any specific embodiments or preferred aspects of the polymeric additive b), polymer A), polymer B) and pyrolysis oil a), as listed herein, apply to the plastic pyrolysis oil composition according to the invention.

Preparation of the plastic pyrolysis oil composition according to the invention

The invention also provides a method of manufacturing a composition as described above, comprising the steps of:

- 5 providing a plastic feedstock;
pyrolyzing the plastic feedstock to generate a plastic pyrolysis oil a);
preparing a polymeric additive b)
adding the polymeric additive b) to the plastic pyrolysis oil a).
- 10 The method for preparing the plastic pyrolysis oil composition according to the invention preferably comprises the step of mixing the pyrolysis oil and the polymeric additive. More preferably, the method comprises the step of mixing for at least 5, 10, 15, 25 or 30 minutes.

- The method may also comprise a step of heating the pyrolysis oil and the polymeric additive, preferably to
- 15 at least 40 °C, even more preferably to at least 50 °C, most preferably to at least 60 °C. The method may comprise heating and mixing the pyrolysis oil simultaneously.

- The method of the present invention is able to reduce the pour point of the pyrolysis oil by at least, or to reduce the viscosity of the pyrolysis oil, or to achieve both, by the addition of the polymeric additive b). The
- 20 resulting pyrolysis oil is thereby easier to transport and store compared to the pyrolysis oil with no polymeric additive. In addition, no modifications to plant design are required to provide a pyrolysis oil having a reduced pour point or viscosity, as this can be achieved by adding the polymeric additive of the present invention after the pyrolysis oil is made.

- 25 In specific embodiments, the method comprises the step of providing a plastic feedstock comprising one or more polyolefins and producing the pyrolysis oil at least partially from said feedstock. The polyolefins may be polyethylene and/or polypropylene.

Use of the polymeric additive b)

- 30 The present invention also extends to the use of a polymeric additive as defined herein to reduce the pour point of a plastic pyrolysis oil or to reduce the viscosity of the pyrolysis oil, or both.

- Preferably, the pour point of a pyrolysis oil is reduced by at least 1 °C, more preferably by at least 2 °C,
- 35 even more preferably by at least 3 °C, most preferably by at least 5 °C, by the addition of the polymeric additive as described herein, when compared to the same pyrolysis oil with no polymeric additive.

- The reduction in viscosity is preferably of at least 10, preferably 20 or 30, even more preferably 40, 50, or 60 % or more, at a temperature from -20° C to +80 °C, preferably from -10° C to +50 °C, when the polymeric
- 40 additive is added to the pyrolysis oil with a wax residue as described herein, when compared to the same pyrolysis oil with no polymeric additive.

Method for transporting or storing a plastic pyrolysis oil

Advantageously, as exemplified in the experimental part, the composition according to the invention has a lower pour point and viscosity in comparison to untreated pyrolysis oils. Pyrolysis oils usually solidify making them difficult to transport. In contrast, pyrolysis oils with lower pour point will remain liquid at lower temperatures, thus making them easier to transport and heat does not need to be applied to the composition before transportation and storage.

Thus, the present invention also extends to a method for transporting or storing a plastic pyrolysis oil a) comprising the step of adding a polymeric additive b) to the pyrolysis oil a) to form the composition described herein.

Preferably, the plastic pyrolysis oil a) comprises 30 % by weight or less, more preferably 20 % by weight or less, even more preferably 15 % by weight or less, even more preferably 12 % by weight or less, most preferably 10 % by weight or less, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

Preferably, the plastic pyrolysis oil a) comprises from 0.01 % to 30 % by weight, more preferably from 0.01 % to 20 % by weight, even more preferably from 0.01 % to 15 % by weight, even more preferably from 0.01 % to 12 % by weight, most preferably from 0.05 % to 10 % by weight, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

By reducing the pour point of the pyrolysis oil comprising a wax residue by at least 1 °C, or by reducing the viscosity of the pyrolysis oil by at least 10 % at 40°C, or doing both, the manufacturer or user of the pyrolysis oil can maintain current transportation or storage conditions of wax residue pyrolysis oils (preferably of 30 % by weight or less, more preferably of 20 % by weight or less, more preferably of 15 % by weight or less, more preferably of 12 % by weight or less, most preferably of 10 % by weight or less, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil), by using their existing plant design, or possibly lower the transportation or storage conditions of high or higher wax residue pyrolysis oils using existing plant design, i.e. reduced OPEX.

The present invention provides a method for transporting or storing a plastic pyrolysis oil a) in liquid form at a temperature in the range -20 °C to +50 °C.

In the context of the present invention, all details provided herein above on the composition, pyrolysis oil and polymeric additive do also apply for the method according to the invention.

EXPERIMENTAL PART

The invention is further illustrated in detail hereinafter with reference to Inventive Examples and Comparative Examples, without any intention to limit the scope of the present invention.

5 Abbreviations

- C₁ AMA C₁-alkyl methacrylate (methyl methacrylate; MMA)
- C₄ AMA C₄-alkyl methacrylate (n-butyl methacrylate; BMA)
- C₁₀ AMA C₁₀ alkyl methacrylate (isodecyl methacrylate)
- DEG diethylene glycol
- 10 EVA 18-150 ethylene-vinyl acetate with 18wt% vinyl acetate and a melt flow index of 150
- EVA 28-025 ethylene-vinyl acetate with 28wt% vinyl acetate and a melt flow index of 25
- EVA 33-025 ethylene-vinyl acetate with 33wt% vinyl acetate and a melt flow index of 25
- EVA 40-028 ethylene-vinyl acetate with 40wt% vinyl acetate and a melt flow index of 28
- EVA 28-150 ethylene-vinyl acetate with 28wt% vinyl acetate and a melt flow index of 150
- 15 EVA 33-400 ethylene-vinyl acetate with 33wt% vinyl acetate and a melt flow index of 400
- HEMA 2-hydroxethyl methacrylate
- IDMA isodecyl methacrylate
- M_n number-average molecular weight
- M_w weight-average molecular weight
- 20 PDI polydispersity index, molecular weight distribution calculated via M_w/M_n
- PP Pour Point
- VA content vinyl acetate content

Methods

- 25 In the present invention, the weight-average molecular weights (M_w) and the number-average molecular weights (M_n) of the EVA (polymer B)) and graft base polymer (Polymer A1) are determined by gel permeation chromatography (GPC) using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 using the following measurement conditions:
- 30 *Column:* the column set consists of a precolumn and 5 SDV columns as disclosed in Table 1:

Table 1

No.	Type	Dimension
Precolumn	SDV 10μ	8 X 50 mm
Column 1	SDV LXL 10μ	8 X 300 mm
Column 2	SDV LinL 10μ	8 X 300 mm
Column 3	SDV 100Å 10μ	8 X 300 mm
Column 4	SDV 100Å 10μ	8 X 300 mm
Column 5	KF-800D	8 X 100 mm

Instruments: Agilent 1100 Series Pump; PSS SECcurity Inline-Degaser; Agilent 1260 Series Autosampler;
35 Agilent 1100 Series RI-Detector; Agilent 1260 Series UV-Detector; Techlab column oven;
Oven temperature: 35 °C;

Standards: poly(methyl-methacrylate) (so called PMMA) calibration standards;

Eluent: tetrahydrofuran (THF);

Flow rate: 1 mL/min;

Injected volume: 100 µL;

5 *Detection:* RI at a temperature of 35 °C and UV at a wavelength of 239 nm.

Viscosity was measured using a Discovery HR20 TA instruments rheometer, using a 2° cone and Peltier plate geometry. The shear rate was 10x1/s (or s⁻¹). The temperature ramp was 1°C per minute.

10 The flow properties of pyrolysis oil compositions were evaluated by measuring the pour point and by evaluating wax deposition using the cold finger test.

Wax content was measured using a Differential Scanning Calorimeter from TA Instruments and analysis via TRIOS software.

15

Determination of wax species was carried out using an Agilent 6890 series High Temperature Gas Chromatograph.

Melt flow index was measured according to ASTM D1238.

20

Pour points (PP) were measured according to ASTM D97 in 1 °C steps. The test involves cooling the pyrolysis oil composition at a defined cooling rate and measuring the temperature at which the composition can no longer be poured from a vessel.

25 The cold finger test in the present invention was conducted to monitor the wax deposition from a pyrolysis oil, by simulating production conditions. Typically, the temperature of the pyrolysis oil composition is higher than the wax appearance temperature (WAT) and the finger temperature is lower than the wax appearance temperature. In the present invention, the cold finger method involves submerging a probe (i.e. the finger) having a certain surface temperature in a pyrolysis oil composition having a defined temperature and determining the amount of wax that is formed on the surface of the finger. The wax appearance temperature of a given pyrolysis oil composition is determined prior to the cold finger test by determining the onset of crystallization by differential scanning calorimetry or similar methods that monitor crystallization. The wax inhibition tests were measured using the CF-15 cold finger device from PSL device with rack temperature set at 64 °C (5 °C above the WAT of an untreated pyrolysis oil, e.g. the Pyrolysis Oil A of Table 4) and
30 finger temperature set at 39 °C (20 °C below the WAT of an untreated pyrolysis oil, e.g. the Pyrolysis Oil A of Table 4) for a test period of 24 hours.

35

From the cold finger experiment, the percentage of wax inhibition is determined by determining the weight of the wax collected on the finger when the pyrolysis oil composition is treated with a paraffin inhibitor compared to the same experiment where no paraffin inhibitor is added.

40

The degree of wax inhibition is calculated according to the following equation (1):

$$\frac{([\text{mass of wax measured after } x \text{ hours in the untreated pyrolysis oil composition}] - [\text{mass of wax measured after } x \text{ hours in the treated pyrolysis oil composition}])}{[\text{mass of wax measured after } x \text{ hours in the untreated pyrolysis oil}]} \times 100\% \quad (1)$$

5

A high degree of wax inhibition calculated according to equation (1) indicates that less wax deposition occurs in the treated pyrolysis oil composition.

Preparation of the polymeric additives b)

10

Table 2 shows the EVA used in the preparation of the polymeric additives.

Table 2: Ethylene-vinyl acetate polymers

	VA content	Melt Flow Index	M _w	M _n
EVA grade	[wt%]		[kg/mol]	[kg/mol]
EVA 12-008	12	008	280	45.1
EVA 18-150	18	150	384	31.5
EVA 28-025	28	25	193	44.5
EVA 33-025	33	25	139	45.9
EVA 28-005	28	5	160	49.7
EVA 28-150	28	150	95	33.7
EVA 33-400	33	400	79	27.3

15

Polymeric additives b)

Table 3 shows the composition of some polymeric additives P1 to P5 according to the invention, as well as some comparative polymeric additives P6 to P8.

Table 3: Preparation of polymeric additives b) according to the invention and comparative polymeric additives

20

			Inventive polymeric additives b)					Comparative		
			P1	P2	P3	P4	P5	P6	P7	P8
Component mixture	EVA-g-PAMA	IDMA	[wt%]	5.1	5.1	5.1	5.1	18		
		HEMA	[wt%]	1.7	1.7	1.7	1.7	6		
		EVA 18-150	[wt%]	1.7	1.7	1.7	1.7	6		
	EVA	EVA 28-025	[wt%]	30.4					100	
		EVA 33-025	[wt%]			30.4				
		EVA 18-150	[wt%]						100	
		EVA 12-008	[wt%]							100
		EVA 28-005	[wt%]				30.4			
		EVA 28-150	[wt%]		15.2					
		EVA 33-400	[wt%]		15.2					
	Solvent	DEG	[wt%]	21.4	21.4	21.4	21.4	0	0	0
		Isodecanol	[wt%]	39.7	39.7	39.7	39.7	70	0	0

Synthesis:

EVA-g-PAMA polymer

The first step is the synthesis of the EVA-g-PAMA emulsifier. 10 g EVA 18-150 were dissolved in 50 g of isodecanol at 100°C. The solution was cooled down to 90°C and 6.67 g of a monomer mixture of 2-hydroxyethyl methacrylate (HEMA) and isodecyl methacrylate (IDMA) in a ratio of 1:3 and 0.21 g tert-butylper-2-ethylhexanoate were added to the heel. Immediately after addition, 33.3 g of the same monomer mixture containing 0.33 g tert-butylper-2-ethylhexanoate were fed into the reaction heel over 210 minutes. Two hours after the feed end, 0.08 g tert-butylper-2-ethylhexanoate were added to the reaction vessel and allowed to stir for one hour. At the end of the reaction, a turbid, viscous solution with a polymer concentration of 50wt% was obtained.

EVA-g-PAMA + EVA

In a second step, the dispersion was created. 16.98 g of the EVA-g-PAMA polymer were added to a mixing vessel, heated to 90°C, and stirred at 200 rpm. As liquid carrier medium C) or solvent, 31.2 g of isodecanol and 21.4 g diethylene glycol were added to the mixing vessel. Finally, 30.4 g EVA 28-025 were charged to vessel and mixed for 5 hours. A milky, white, stable dispersion with a solid content of 38.8wt% was obtained.

Untreated pyrolysis oils

Table 4 below shows the characteristics of some untreated pyrolysis oils, wherein the pyrolysis oils A, B, D and H are polyolefin pyrolysis oils produced from the pyrolysis of polyolefins which include high-density polyethylene, low-density polyethylene and polypropylene.

Table 4: Characteristics of untreated plastic pyrolysis oil (namely, before addition of a polymeric additive of the present invention or a comparative polymeric additive)

Property		Pyrolysis Oil A	Pyrolysis Oil B	Pyrolysis Oil D	Pyrolysis Oil H
Pour Point	[°C]	51	0	18	-2
Wax Appearance Temperature	[°C]	59	48	55	1
Wax Disappearance Temperature	[°C]	71	53	65	10
C ₁₂ -C ₁₅ n-hydrocarbons	[wt%]	12.2	0.4	0.8	3.5
C ₁₆ -C ₁₉ n-paraffins	[wt%]	1.6	0.9	1.5	2
C ₂₀ -C ₂₉ n-paraffins	[wt%]	9.1	0.4	2	3.6
C ₃₀ -C ₃₉ n-paraffins	[wt%]	3.6	0.2	3.7	0
>C ₃₉ n-paraffins	[wt%]	0.5	0	2.2	0
Total C ₁₆ or greater n-paraffins	[wt%]	14.8	1.5	9.4	5.6

Examples of pyrolysis oil compositions

Example 1, Example 10, Example 19, and Example 27 below correspond to untreated pyrolysis oils before the addition of any polymeric additive b) (Reference examples).

- 5 Example 2 was prepared by adding 0.1 g of the polymeric additive P1 to 99.9 g of Pyrolysis Oil A. The two components were mixed using an overhead stirred for 30minutes while being heated on a hot plate set to 65°C. Examples 3 to 6, 11 to 18, 20-26, and 28-33 were prepared in the same way as example 2, except that the components and amounts thereof were adjusted according to Table 5, 6, 7 and 8 below.
- 10 Table 5: Pyrolysis oil compositions according to invention and comparative compositions and pour points and viscosity measurements of said pyrolysis oil compositions in comparison with an untreated pyrolysis oil A)

			Inventive					Comparative		
Example #		1	2	3	4	5	6	7	8	9
Polymer		none	P1	P2	P3	P4	P5	P6	P7	P8
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil A amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	51	36	39	44	44	45	48	48	48
PP Reduction	[°C]	n/a	15	12	7	7	6	3	3	3
Viscosity, 40°C	[cP]	925	13	489	724	210	802	1058	1302	1151
Viscosity Reduction, 40°C	[%]	n/a	98.6	47	22	77	13	-14	-41	-24

- 15 Table 6: Pyrolysis oil compositions according to invention and comparative compositions and pour points and viscosity measurements of said pyrolysis oil compositions in comparison with an untreated pyrolysis oil B)

			Inventive					Comparative		
Example #		10	11	12	13	14	15	16	17	18
Polymer		none	P1	P2	P3	P4	P5	P6	P7	P8
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil B amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	0	-21	-21	-48	-18	-45	-15	-12	-12
PP Reduction	[°C]	n/a	21	21	48	18	45	15	12	12
Viscosity, -10°C	[cP]	6370	5220	3250	3240	4300	5940	6575	7675	9000
Viscosity Reduction, -10°C	[%]	n/a	18	49	49	32	7	-3	-20	-41

Table 7: Pyrolysis oil compositions according to invention and comparative compositions and pour points and viscosity measurements of said pyrolysis oil compositions in comparison with an untreated pyrolysis oil D)

			Inventive					Comparative	
Example #		19	20	21	22	23	24	25	26
Polymer		none	P1	P2	P3	P4	P6	P7	P8
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil B amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	18	12	9	12	12	24	24	27
PP Reduction	[°C]	n/a	6	9	6	6	-6	-6	-9

5

Table 8: Pyrolysis oil compositions according to invention and comparative compositions and pour points and viscosity measurements of said pyrolysis oil compositions in comparison with an untreated pyrolysis oil H)

			Inventive					Comparative	
Example #		27	28	29	30	31	32	33	
Polymer		none	P1	P3	P4	P5	P7	P8	
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	
Pyrolysis Oil H amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	
PP	[°C]	-2	-12	-12	-9	-9	-2	-2	
PP Reduction	[°C]	n/a	10	10	7	7	0	0	

10 Results

Tables 5, 6, 7 and 8 show that treating a pyrolysis oil with the polymeric additives of the present invention improves the cold temperature performance in comparison to the same untreated pyrolysis oil.

Figure 1 is a graph showing the viscosity of pyrolysis oil a) and a composition comprising pyrolysis oil a) with a polymeric additive b) over a temperature range of 40 to 80 °C. The reference number 1 on Figure 1 corresponds to the curve of the untreated pyrolysis oil (Example 1 of Table 5 above), whereas the reference number 2 on Figure 1 corresponds to the curve of the pyrolysis oil composition of inventive example 2 according to Table 5 above. The viscosity plots in Figure 1 show that the polymeric additive lowers the viscosity of the products compared to the untreated pyrolysis oil across a wide temperature range. At 40°C, the untreated pyrolysis oil had a viscosity of approximately 925 cP. By comparison, the pyrolysis oil including 0.1% by weight of polymeric additive 1 had a viscosity of approximately 13 cP.

In contrast, at 45°C, the untreated pyrolysis oil had a viscosity of approximately 595 cP. By comparison, the pyrolysis oil including 0.1% by weight of polymeric additive 1 had a viscosity of approximately 6 cP. At 50 °C, the untreated pyrolysis oil had a viscosity of approximately 254 cP. By comparison, the pyrolysis oil including 0.1% by weight of polymeric additive 1 had a viscosity of approximately 4 cP. At 55 °C, the untreated pyrolysis oil had a viscosity of approximately 34 cP. By comparison, the pyrolysis oil including 0.1% by weight of polymeric additive 1 had a viscosity of approximately 3 cP.

The above experimental data confirms that compositions comprising a pyrolysis oil and treated with a polymeric additive as defined in claim 1 have a much lower viscosity compared to the untreated pyrolysis oil. For instance, the polymeric additives of Table 5 drastically reduce the viscosity of the pyrolysis oil, and in some instances by up to 98% at 40-55 °C. These reductions in viscosity of the pyrolysis oils are a great improvement for transporting and pumping the pyrolysis oils. The untreated pyrolysis oils need to be heated in order to be pumped for the transportation, whereas the compositions comprising the pyrolysis oils treated with a polymeric additive according to the invention do not need to be heated anymore and can be directly pumped for transportation.

Examples 3 to 6 in Table 5 further demonstrate how compositions comprising pyrolysis oil and treated with a polymeric additive b) as defined in claim 1 achieve a reduction in pour point and viscosity when added to Pyrolysis Oil A. Compared to the untreated oil (Example 1), Examples 3 to 6 achieve a 6 to 12°C reduction in pour point and 22 to 77 % reduction in viscosity. In comparison, the comparative examples 7 to 9 in Table 5 only achieve a 3 °C reduction in pour point and viscosity is undesirably increased by 14 to 41 %.

A similar comparison is demonstrated using Pyrolysis Oil B in Table 6. Examples 11 to 15 achieve a reduction in pour point and viscosity when added to Pyrolysis Oil B. Compared to the untreated oil (Example 10), Examples 11 to 15 achieve a 18 to 48 °C reduction in pour point and 7 to 49% reduction in viscosity. In comparison, the comparative examples 16 to 18 in Table 6 only achieve a 12 to 15 °C reduction in pour point and viscosity is undesirably increased by 3 to 41 %.

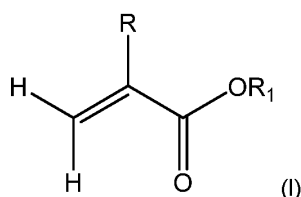
Further comparisons are shown using Pyrolysis Oil D in Table 7. Examples 20 to 23 achieve a reduction in pour point added to Pyrolysis Oil D. Compared to the untreated oil (Example 19), Examples 20 to 23 achieve a 6-9 °C reduction in pour point. In comparison, the comparative examples 24 to 26 in Table 7 cause in increase in pour point of 6-9°C.

A final comparison is shown using Pyrolysis Oil H in Table 8. Examples 28 to 31 achieve a reduction in pour point added to Pyrolysis Oil H. Compared to the untreated oil (Example 27), Examples 28 to 31 achieve a 7 to 10 °C reduction in pour point. In comparison, the comparative examples 32 and 33 in Table 7 do not change the pour point compared to the untreated pyrolysis oil.

Compositions comprising pyrolysis oil and treated with a polymeric additive b) as defined in claim 1 show improved cold flow improvement, reduced pour point, and reduced viscosity.

CLAIMS

1. A composition comprising a plastic pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is an ethylene graft polyalkyl(meth)acrylate A) obtainable by grafting onto an ethylene-based copolymer A1), obtainable by polymerizing a monomer composition consisting of ethylene and a compound selected from the group consisting of vinyl esters, acrylates, methacrylates, alpha-olefins or a mixture thereof, based on the total weight of the ethylene-based copolymer A1),
 5 a grafting monomer composition comprising alkyl (meth)acrylates A2) of general Formula (I)



wherein

R is H or CH₃ and

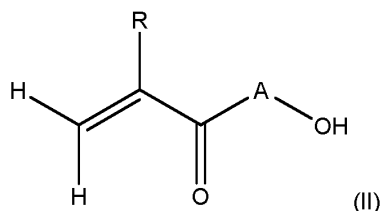
R₁ is a linear or branched, saturated or unsaturated alkyl group with 1 to 30 carbon atoms, preferably with 7 to 15 carbon atoms.

- 15 2. The composition according to claim 1, wherein the monomer composition of the ethylene-based copolymer A1) consists of
 from 55 % to 90 % by weight, preferably from 60 % to 85 % by weight, more preferably from 67 % to 82 % by weight, of ethylene, and
 20 from 10 % to 45 % by weight, preferably from 15 % to 40 % by weight, more preferably from 18 % to 33 % by weight, of a compound selected from the group consisting of vinyl esters, acrylates, methacrylates and alpha-olefins or a mixture thereof,
 based on the total weight of the monomer composition to prepare the ethylene-based copolymer A1).
- 25 3. The composition according to claim 1 or 2, wherein the ethylene-based copolymer A1) consists of ethylene and vinyl acetate.
4. The composition according to any one of the preceding claims, wherein the weight ratio of ethylene-based copolymer A1) to the monomer grafting composition A2) to prepare the ethylene graft
 30 polyalkyl(meth)acrylate P) is from 1:1 to 1:10, preferably from 1:1 to 1:8, more preferably from 1:1 to 1:6.
5. The composition according to any one of the preceding claims, wherein the the polymeric additive b) further comprises an ethylene-based copolymer B) obtainable by polymerizing a monomer composition consisting of ethylene and a vinyl ester.

6. The composition according to any one of the preceding claims, wherein the ethylene-based copolymer A1) and/or the ethylene-based copolymer B) has a weight-average molecular weight from 20,000 to 1,000,000 g/mol, preferably from 45,000 to 500,000 g/mol, more preferably from 60,000 to 400,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

7. The composition according to claim 6, wherein the polymeric additive b) comprises ethylene graft polyalkyl(meth)acrylate A) and ethylene-based copolymer B), and wherein the ethylene graft polyalkyl(meth)acrylate A) is from 5 to 40 % by weight and the ethylene-based copolymer B) is from 60 to 95 % by weight, based on the total amount of the polymeric additive b).

8. The composition according to any one of the preceding claims, the grafting monomer composition A2) to prepare the ethylene graft polyalkyl(meth)acrylate A) further comprises hydroxy esters of general Formula (II)



wherein

R is H or CH₃ and

A is a branched or unbranched, aliphatic C₁ to C₄ carbon-based group.

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9. The composition according to any one of the preceding claims, wherein the composition comprises from 0.001 to 1 % by weight, preferably from 0.005 to 0.8 % by weight, more preferably from 0.005 to 0.5 % by weight of the polymeric additive b), based on the total weight of the composition.

10. The composition according to any one of the preceding claims, wherein the plastic pyrolysis oil a) is a plastic pyrolysis oil and/or a plastic waste pyrolysis oil, wherein the plastic and plastic waste are selected from polyolefins, polyethylene terephthalate, polyvinyl chloride, polystyrene, or a mixture thereof.

11. The composition according to any one of the previous claims, wherein the plastic pyrolysis oil a) comprises 30 % by weight or less, preferably 20 % by weight or less, more preferably 15 % by weight or less, even more preferably 12 % by weight or less, of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

12. The composition according to any one of the preceding claims, wherein the composition further comprises an additive c), wherein the additive c) is any of the group comprising scale inhibitors, corrosion inhibitors, oxygen scavengers, biocides, emulsion breakers, antifoam agents, drag reducing agents,

hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than polymers A) and B), or a mixture thereof.

13. A method for manufacturing a composition as defined in any one of claims 1 to 12 comprising a
5 pyrolysis oil a) and a polymeric additive b), comprising the steps of:
 providing a plastic feedstock;
 pyrolyzing the plastic feedstock to generate the plastic pyrolysis oil a);
 preparing the polymeric additive b) and
 adding the polymeric additive b) to the plastic pyrolysis oil a).
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14. Use of a polymeric additive b) as defined in any one of claims 1 to 12 to reduce the pour point of a plastic pyrolysis oil a) or to reduce the viscosity of the pyrolysis oil, or both.
15. A method of transporting and/or storing a plastic pyrolysis oil a) comprising the step of adding a
15 polymeric additive b) to the pyrolysis oil to form a composition as defined in any one of claims 1 to 12.