

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 25 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 30 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.

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 35 plastic used, and the type of catalyst.

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 40 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

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. 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 a C₁₈–C₃₆ vinyl acetate-acrylate copolymer with a range of weight-average molecular weight from 900 to 9,300 g/mol (see [0068] and example 4 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
25 waxes having C₁₆ or longer carbon chains - see e.g. [0048], [0086], [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 plastic 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 the invention, the present invention relates to a composition comprising a plastic pyrolysis oil a) and is a polymeric additive for reducing the pour point, viscosity, or both the pour point and viscosity of the pyrolysis oil.

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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

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- adding the polymeric additive b) to the plastic pyrolysis oil a).

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.

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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

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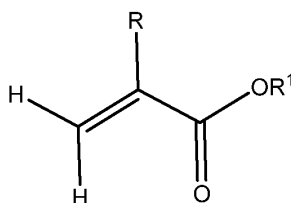
For the purpose of better illustrating the advantages and properties of the claimed composition, object of the present invention, one graph is attached as a non-limiting example:

- Figure 1 is a graph showing the viscosity of an untreated pyrolysis oil A) and compositions according to the invention comprising said pyrolysis oil A) treated with a polymeric additive b) over a temperature range of 40 to 80°C (see also experimental data part).

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DETAILED DESCRIPTION OF THE INVENTION

According to the invention, there is provided a composition comprising a pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is a polymer P) prepared by polymerizing a monomer composition comprising from 50 to 100 % by weight of one or more alkyl (meth)acrylate monomers b1) of formula (I), based on the total weight of the monomer composition,



(I)

wherein R is hydrogen or methyl, and R¹ is a linear, branched or cyclic alkyl residue with 16 to 30 carbon atoms, and

wherein the polymer P) has a weight-average molecular weight from 20,000 to 600,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

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.

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.

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 to +80 °C, preferably at a temperature from -10 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.

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)

5 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.

10 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.

15 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.

20 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).

25 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.

30 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”.

35 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).

40 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 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).

5 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.

10 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.

20 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.

25 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.

30 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.

35 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,

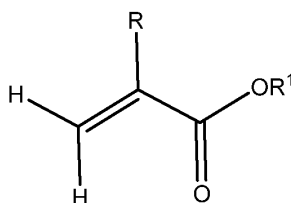
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current plastic processing plants designed to expect the use of a wax residue pyrolysis oil can continue to operate without redesign.

Polymeric additive b

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The polymeric additive b) is a polymer P) prepared by polymerizing a monomer composition comprising from 50 to 100 % by weight of one or more alkyl (meth)acrylate monomers b1) of formula (I), based on the total weight of the monomer composition,



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(I)

wherein R is hydrogen or methyl, and R¹ is a linear, branched or cyclic alkyl residue with 16 to 30 carbon atoms, and

wherein the polymer P) has a weight-average molecular weight from 20,000 to 600,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

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

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Within the context of the present invention, the monomer composition corresponds to the total amount of monomers to prepare the polymer P).

Preferably R¹ is a linear, branched or cyclic alkyl residue with 16 to 24 carbon atoms, even more preferably with 18 to 22 carbon atoms.

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Preferably, the monomer composition to prepare the polymer P) comprises from 60 to 100 % by weight, more preferably from 70 to 100 % by weight, even more preferably from 80 to 100 % by weight, most preferably from 85 to 100 % by weight of one or more alkyl (meth)acrylate monomers b1) of formula (I), based on the total weight of the monomer composition.

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According to a preferred embodiment of the invention, the one or more alkyl (meth)acrylate monomers b1) are selected from the group consisting of C₁₈-C₂₂ acrylate monomers, C₁₆-C₁₈ methacrylate, or a mixture thereof.

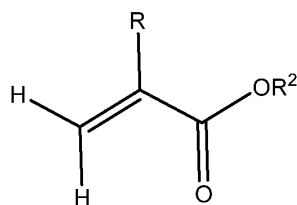
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According to a preferred embodiment of the invention, the polymeric additive is a polyalkylacrylate polymer containing C₁₈-C₂₂ alkyl. In this embodiment, the polymeric additive is formed from C₁₈-C₂₂ acrylate monomers.

According to another preferred embodiment of the invention, the polymeric additive b) is a C₁₈-C₂₂ polyalkylacrylate polymer P) prepared by polymerizing a monomer composition consisting of C₁₈-C₂₂ acrylate monomers; or a C₁₆-C₂₂ polyalkyl(meth)acrylate polymer prepared by polymerizing a monomer composition consisting of from 40 to 80 %, preferably from 50 to 70 % by weight of C₁₈-C₂₂ acrylate and from 20 to 60 % by weight, preferably from 30 to 50 % by weight of C₁₆-C₁₈ methacrylate, based on the total weight of the monomer composition, or a mixture of both.

According to another preferred embodiment of the invention, the monomer composition to prepare the polymer P), in addition to one or more alkyl (meth)acrylate monomers b1), further comprises one or more alkyl (meth)acrylates selected from

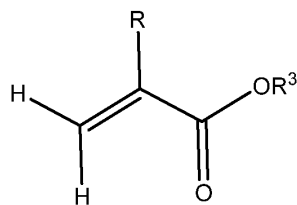
b2) one or more alkyl (meth)acrylate monomers of formula (II)



(II)

wherein R is hydrogen or methyl, and R² is a linear, branched or cyclic alkyl residue with 1 to 6 carbon atoms, preferably with 1 to 4 carbon atoms; or

b3) one or more alkyl (meth)acrylate monomers of formula (III)



(III)

wherein R is hydrogen or methyl, and R³ is a linear, branched or cyclic alkyl residue with 7 to 15 carbon atoms, preferably with 12 to 15 carbon atoms, more preferably with 12 to 14 carbon atoms;

a mixture of both alkyl (meth)acrylate monomers b2) and b3).

According to a preferred embodiment of the invention, the monomer composition to prepare the polymer P) comprises 30 % by weight or less, more preferably 0 to 30 % by weight, even more preferably 0 to 20 % by weight, of one or more alkyl (meth)acrylate monomers b2), based on the total weight of the monomer composition.

According to another preferred embodiment of the invention, the monomer composition to prepare the polymer P) comprises 50 % by weight or less, more preferably 0 to 50 % by weight, even more preferably

0 to 30 % by weight, of one or more alkyl (meth)acrylate monomers b3), based on the total weight of the monomer composition.

5 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.

10 The term “C₁₈ to C₂₂ alkyl (meth)acrylates” refers to esters of (meth)acrylic acid and linear or branched alcohols having 18 to 22 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.

15 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.

20 Examples of the C₁ to C₆ alkyl (meth)acrylate monomers b1) according to formula (I), 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.

25 Examples of the C₇ to C₁₅ alkyl (meth)acrylate monomers b2) according to formula (II) 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
30 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.

35 Examples of the C₁₆ to C₃₀ alkyl (meth)acrylate monomer b3) of formula (III) 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 eicosyltetratriacontyl (meth)acrylate; cycloalkyl
40 (meth)acrylates such as 2,4,5-tri-t-butyl-3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-t-butylcyclohexyl (meth)acrylate.

As an optional component, the polymer may contain further monomer units b4) derived from one or more comonomers or a mixture thereof.

- 5 Preferably, these comonomers b4) are selected from the list consisting of
- hydroxyalkyl (meth)acrylates, preferably hydroxyalkyl (meth)acrylates selected from 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10 decanediol (meth)acrylate;
- 10 aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides, preferably aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides selected from N-(3-dimethyl-aminopropyl)methacrylamide, 3-diethylaminopentyl (meth)acrylate, 3-dibutyl-aminohexadecyl (meth)acrylate;
- 15 nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates, preferably nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates selected from N-(methacryloyloxyethyl)diisobutylketimine, N-(methacryloyloxyethyl)dihexadecyl-ketimine, (meth)acryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl (meth)acrylate;
- aryl (meth)acrylates like benzyl (meth)acrylate or phenyl (meth)acrylate, where the acryl residue in each case can be unsubstituted or substituted up to four times;
- 20 carbonyl-containing (meth)acrylates, preferably carbonyl-containing (meth)acrylates selected from 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, N-methacryloyloxy-formamide, acetonyl (meth)acrylate, N-methacryloyl-2 pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxy-propyl)-2-pyrrolidinone, N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone;
- 25 (meth)acrylates of ether alcohols, preferably (meth)acrylates of ether alcohols selected from tetrahydrofurfuryl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl (meth)acrylate, cyclohexyloxyethyl (meth)acrylate, propoxyethoxyethyl (meth)acrylate, benzyloxyethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, 2-methoxy-2-ethoxypropyl (meth)acrylate, ethoxylated
- 30 (meth)acrylates, 1-ethoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxy-2-ethoxyethyl (meth)acrylate, esters of (meth)acrylic acid and methoxy polyethylene glycols;
- (meth)acrylates of halogenated alcohols, preferably (meth)acrylates of halogenated alcohols selected from 2,3-dibromopropyl (meth)acrylate, 4-bromophenyl (meth)acrylate, 1,3-dichloro-2-propyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-iodoethyl (meth)acrylate, chloromethyl
- 35 (meth)acrylate;
- oxiranyl (meth)acrylate, preferably oxiranyl (meth)acrylate selected from 2, 3-epoxybutyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 10,11-epoxyundecyl (meth)acrylate, 2,3-epoxycyclohexyl (meth)acrylate, oxiranyl (meth)acrylates such as 10,11-epoxyhexadecyl (meth)acrylate, glycidyl (meth)acrylate;
- 40 phosphorus-, boron- and/or silicon-containing (meth)acrylates, preferably phosphorus-, boron- and/or silicon-containing (meth)acrylates selected from 2-(dimethyl-phosphato)propyl (meth)acrylate,

2-(ethylphosphito)propyl (meth)acrylate, 2 dimethylphosphinomethyl (meth)acrylate,
 dimethylphosphonoethyl (meth)acrylate, diethylmethacryloyl phosphonate,
 dipropylmethacryloyl phosphate, 2 (dibutylphosphono)ethyl (meth)acrylate, 2,3-
 butylenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysilane,
 5 diethylphosphatoethyl (meth)acrylate;
 sulfur-containing (meth)acrylates, preferably sulfur-containing (meth)acrylates selected from
 ethylsulfinyethyl (meth)acrylate, 4-thio-cyanatobutyl (meth)acrylate, ethylsulfonyethyl
 (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulfinylmethyl (meth)acrylate,
 bis(methacryloyloxyethyl) sulfide;
 10 heterocyclic (meth)acrylates, preferably heterocyclic (meth)acrylates selected from 2-(1-
 imidazolyl)ethyl (meth)acrylate, oxazolidinyethyl (meth)acrylate, N-methacryloylmorpholine and
 2-(4-morpholinyl)ethyl (meth)acrylate;
 maleic acid and maleic acid derivatives, preferably mono- and diesters of maleic acid, maleic anhydride,
 methylmaleic anhydride, maleinimide, methylmaleinimide;
 15 fumaric acid and fumaric acid derivatives, preferably mono- and diesters of fumaric acid;
 vinyl halides, preferably vinyl halides selected from vinyl chloride, vinyl fluoride, vinylidene chloride and
 vinylidene fluoride;
 vinyl esters, preferably vinyl acetate;
 vinyl monomers containing aromatic groups, preferably vinyl monomers containing aromatic groups
 20 selected from styrene, substituted styrenes with an alkyl substituent in the side chain, such as
 alpha-methylstyrene and alpha-ethylstyrene, substituted styrenes with an alkyl substituent on
 the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as
 monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;
 heterocyclic vinyl compounds, preferably heterocyclic vinyl compounds selected from 2-vinylpyridine,
 25 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine,
 vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-
 vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-
 vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane,
 vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles,
 30 vinyloxazoles and hydrogenated vinyloxazoles;
 vinyl and isoprenyl ethers;
 methacrylic acid and acrylic acid,
 or a mixture thereof.

35 In an embodiment, comonomer b4) is styrene.

The proportion of comonomers b4) in the monomer composition can vary depending on the use and
 property profile of the polymeric additive b). Preferably, the content of comonomer b4) in the monomer
 composition to prepare the polymeric additive b) is in the range from 0 to 20 % by weight, preferably from
 40 0 to 15 % by weight, based on the total weight of the monomer composition.

According to the present invention, the polymeric additive b) is one polymer P), or a mixture of one or more polymer P). Preferably, the polymeric additive b) comprises one or more polymers P) selected from the group consisting of a polyalkylacrylate polymer, a polyalkylmethacrylate polymer, a polyalkyl(meth)acrylate polymer, a polyalkylmethacrylate-styrene polymer, a polyacrylate-styrene copolymer, a poly(meth)acrylate-styrene polymer or a mixture thereof. Variations will be apparent to those skilled in the art.

According to a preferred embodiment of the invention, the polymeric additive b) comprises one or more polymers selected from: a polymer comprising or consisting of monomer units of C₁₈-C₂₂ acrylate, C₁₆-C₁₈ methacrylate, styrene or a mixture thereof; a polymer comprising or consisting of monomer units of C₁₈-C₂₂ acrylate; a polymer comprising or consisting of monomer units of C₁₆-C₁₈ methacrylate; a polymer comprising or consisting of monomer units of styrene; polymers comprising or consisting of monomer units of C₁₈-C₂₂ acrylate, C₁₆-C₁₈ methacrylate, and styrene; and any combinations thereof.

In one embodiment, the polymeric additive b) is a polyacrylate-styrene copolymer containing acrylates with C₁₈-C₂₂ chains. In this embodiment, the polymeric additive b) is a polymer P) prepared by polymerizing a monomer composition comprising from 80 to 95 % by weight, preferably from 85 to 95 % by weight, of C₁₈-C₂₂ acrylate; and from 5 to 20 % by weight, preferably 5 to 15 % by weight, of styrene, based on the total weight of the monomer composition.

Preferably, the amounts of monomers b1), b2), b3) and b4) sum up from 90 to 100 % by weight, more preferably from 95 to 100 % by weight, even more preferably sum up to 100 % by weight, based on the total weight of the monomer composition to prepare the polymer P).

According to the present invention, the weight-average molecular weight of the polymer P) is from 20,000 to 600,000 g/mol, preferably from 20,000 to 550,000 g/mol, more preferably from 22,000 to 500,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 (GPC method as described in more detail in the experimental section below).

Preparation process for polymeric additive b)

The polymers of the polymeric additive b) can be obtained by free-radical polymerization and related processes, for example ATRP (Atom Transfer Radical Polymerization), RAFT (Reversible Addition Fragmentation Chain Transfer) or NMP processes (nitroxide-mediated polymerization). More preferably, the polymers 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 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 peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-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 compounds with compounds which have not been mentioned but can likewise form free radicals. Preferred initiator for the preparation of polymeric additive b) is tert-butyl-peroxy-2-ethylhexanoate.
- 10 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. Chain transfer agents are molecules with a weak chemical bond which facilitate 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
- 15 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 mercaptan, tert-dodecyl mercaptan or a mixture thereof, most preferably n-dodecyl mercaptan.
- 20 Preferably, the monomer mixture to prepare the polymeric additive b) 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 the total weight of the monomer composition to prepare the polymeric additive b). The amount of chain transfer agents to prepare the polymeric additive b) 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
- 25 composition.
- The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The 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.
- 30 The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense. The polymerization is preferably carried out in a nonpolar solvent. These include hydrocarbon solvents, for example aromatic solvents such as toluene, benzene and xylene, saturated hydrocarbons, for example cyclohexane, heptane, octane, nonane, decane, dodecane, which may also be
- 35 present in branched form, or a mixture thereof, such as naphtha. These solvents may be used individually and as a mixture. Particularly preferred solvents are mineral oils, diesel fuels of mineral origin, naphthenic solvents, natural vegetable and animal oils, biodiesel fuels and synthetic oils (e.g. ester oils such as dinonyl adipate), or a mixture thereof.

Plastic pyrolysis oil composition according to the invention

- 5 Preferably, the composition comprises polymeric additive b) at a concentration of from 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 from 0.005 % by weight to 0.8 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition. Even more preferably, the composition comprises polymeric additive b) at a concentration of from 0.005 % by weight to 0.5 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition.
- 10 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) is a polyethylene and/or polypropylene pyrolysis oil, wherein the pyrolysis oil is produced at least partially from the pyrolysis of polyethylene and/or polypropylene.
- 15 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).
- 20 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).
- 25 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.
- 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
- 30 breakers, antifoam agents, drag reducing agents, hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than polymer P), or a mixture thereof.
- Preferably, then the amounts of compounds a), b), c) sum up to 90 to 98 % by weight, more preferably sum up to 95 to 99 % by weight, even more preferably sum up to 100 % by weight, based on the total weight of
- 35 the composition.
- Any specific embodiments or preferred aspects of the polymeric additive b), polymer P) 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

According to the present invention, it is also provided a method of manufacturing the composition of the first aspect of the invention, the method comprising the steps of:

- 5 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).

- 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.

- 15 The method may also comprise a step of heating the pyrolysis oil and the polymeric additive, preferably to 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.

- 20 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 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.

- 35 Preferably, the pour point of a pyrolysis oil 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.

- 40 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 0 to 80 °C, preferably at either 40 °C, 45 °C or 50 °C, or at a temperature from 40 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.

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 at a processing temperature (preferably, 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 examples and comparative examples, without any intention to limit the scope of the present invention.

5

Abbreviations

- CTA Chain Transfer Agent
- Naphtha Shellsol A 150ND solvent from Shell (a C₉-C₁₀ aromatic hydrocarbon solvent with a naphthalene content below 1% m/m)
- 10 PP Pour Point

Methods

15 In the present invention, the weight-average molecular weights (M_w) and the number-average molecular weights (M_n) of the polyalkyl(meth)acrylates (polymeric additives b)) were determined by gel permeation chromatography (GPC) using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 using the following measurement conditions:

Column set: the column set consists of a precolumn and 5 SDV columns as disclosed in Table 1:

20

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; Agilent 1100 Series RI-Detector; Agilent 1260 Series UV-Detector; Techlab column oven;

25

- 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;
- 30 *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 10 1/s (or s⁻¹). The temperature ramp was 1°C per minute.

35

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.

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

Pour points 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.

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 in Table 4) and finger temperature set at 39 °C (20 °C below the WAT of an untreated pyrolysis oil, e.g. the Pyrolysis Oil A in Table 5) for a test period of 24 hours.

- 25 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.

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

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

- 35 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 polymeric additives b)

Preparation of polymeric additive P1:

- 5 1000 grams of C₁₈-C₂₂ alkyl acrylate and 50 grams of n-dodecyl mercaptan (5% relative to the total weight of monomers, namely, the total weight of monomer composition) were charged into a 2L 4-necked round bottom flask. The reaction mixture was stirred using a C-stirring rod, inerted with nitrogen, and heated to 110°C. Once the reactor reached the set-point temperature, 2 grams of t-butylperoctoate were fed into the reactor using the following dosing profile: 0.2 grams in the first 60 minutes, 0.4 grams in the next 60 minutes,
- 10 the set-point temperature was changed to 105°C and the last 1.4 grams were dosed in the next 60 minutes. After the initiator dosing was completed, the reaction was allowed to continue stirring for 1 hour at 105°C. At the end of the reaction, solvent Naphtha was added to reach the polymer concentration as indicated in Table 2 below.
- 15 The polymeric additives P2 to P18 were prepared in the same way as polymeric additive P1 (using the same initiator), except that the weight percentages of monomers and of n-dodecyl mercaptan (n-DDM) were changed according to Table 2, Table 3, and Table 4.

Table 2: Monomer composition, polymer content and weight-average molecular weight of different polymeric additives for pyrolysis oil according to the invention, and comparative polymeric additive examples

			Comparative polymeric additive		Inventive polymeric additive			
	Polymer		P1	P2	P3	P4	P5	P6
Monomer mixture	C ₁₈ -C ₂₂ acrylate	[wt%]	100	100	100	100	100	100
	polymer content	[wt%]	35	35	35	35	35	35
	CTA	[wt% relative to monomer mixture]	5	3.7	0.4	0.3	0.2	0.1
	Weight-average molecular weight	[kg/mol]	7	13	27	39	124	350

Table 3: Monomer composition, polymer content and weight-average molecular weight of different polymeric additives for pyrolysis oil according to the invention, and comparative polymeric additive examples

			Comparative polymeric additive			Inventive polymeric additive		
	Polymer		P7	P8	P9	P10	P11	P12
Monomer mixture	C ₁₈ -C ₂₂ acrylate	[wt%]			68	68	68	68
	C ₁₆ -C ₁₈ methacrylate	[wt%]			32	32	32	32
	C ₁₂ -C ₁₄ methacrylate	[wt%]	100	100				
	CTA	[wt% relative to monomer mixture]]	3.7	0.1	3.7	0.8	0.2	0.15
	polymer content	[wt%]	35	35	35	35	35	35
	weight-average molecular weight	[kg/mol]	13	350	13	24	49	156

5

Table 4: Monomer composition, polymer content and weight-average molecular weight of different polymeric additives for pyrolysis oil according to the invention, and comparative polymeric additive examples

			Comparative polymeric additive		Inventive polymeric additive			
	Polymer		P13	P14	P15	P16	P17	P18
Monomer mixture	C ₁₈ -C ₂₂ acrylate	[wt%]	90	65	90	90	65	65
	styrene	[wt%]	10		10	10		
	C ₁₂ -C ₁₄ methacrylate	[wt%]		35			35	35
	CTA	[wt% relative to monomer mixture]	2.5	2.5	0.4	0.1	2	0.5
	polymer content	[wt%]	35	35	35	35	35	35
	weight-average molecular weight	[kg/mol]	14	13	37	156	22	62

10

After polymerization, the solvent is not removed and therefore the resulting polymer is mixed with the oil of polymerization. The polymer content of the polymeric additive is provided in Tables 2 to 4 for the reproducibility of examples.

15

Untreated pyrolysis oils

Table 5 below shows the characteristics of some untreated pyrolysis oils, wherein the pyrolysis oils A, B, C, D and E are polyolefin pyrolysis oils produced from the pyrolysis of polyolefins which include high-density polyethylene, low-density polyethylene and polypropylene.

Table 5: Characteristics of untreated plastic pyrolysis oils (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 C	Pyrolysis Oil D	Pyrolysis Oil E
Pour Point	[°C]	51	0	48	18	51
Wax Appearance Temperature	[°C]	59	48	52	55	47
Wax Disappearance Temperature	[°C]	71	53	61	65	57
C ₁₂ -C ₁₅ n-hydrocarbons	[wt%]	12.2	0.4	3.7	0.8	1.2
C ₁₆ -C ₁₉ n-paraffins	[wt%]	1.6	0.9	1.8	1.5	1.1
C ₂₀ -C ₂₉ n-paraffins	[wt%]	9.1	0.4	5.5	2	1.7
C ₃₀ -C ₃₉ n-paraffins	[wt%]	3.6	0.2	1.8	3.7	0.6
>C ₃₉ n-paraffins	[wt%]	0.5	0	0.1	2.2	0.05
Total C ₁₆ or greater n-paraffins	[wt%]	14.8	1.5	9.2	9.4	3.45

Examples of pyrolysis oil compositions

Examples 1, 9, 19, 16, and 37 are plastic pyrolysis oils before the addition of any polymeric additive according to the invention (untreated pyrolysis oil).

As shown in Table 5 below, Example 1 is a pyrolysis oil before the addition of the polymeric additive according to the invention.

Example 2 was prepared by adding 0.1 g of polymeric additive P7 to 99.9 g of Pyrolysis Oil A. The two components were mixed using an overhead stirrer for 30 minutes while being heated on a hot plate set to 65°C.

Examples 3 to 8, 10 to 18, 20 to 25, 27 to 36, and 38 to 42 were prepared in the same way as Example 2, except that the component amounts were adjusted according to Tables 6 to 10 below.

Table 6: Pyrolysis oil compositions according to invention and comparative examples with corresponding pour points using Pyrolysis Oil A.

			Comparative			Inventive			
Example #		1	2	3	4	5	6	7	8
Polymer		none	P7	P8	P1	P3	P4	P5	P6
Polymer Mw	[kg/mol]	n/a	13	350	7	27	39	124	380
Polymer	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil A	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	51	51	51	48	45	45	45	45
PP Reduction	[°C]	n/a	0	0	3	6	6	6	6
Viscosity, 40°C	[cP]	925	n.m.	n.m.	951	692	n.m.	351	315
Viscosity Reduction at 40°C	[%]	n/a	n/a	n/a	-2.8	25	n/a	62	66
Wax inhibition	[%]	n/a	0	1	n.m.	n.m.	n.m.	41	32

- 5 n/a: not applicable (baseline) n.m.: not measured
⁽¹⁾ rack temperature 64 °C, finger temperature 39 °C
 Polymer Mw – weight-average molecular weight

Table 7: Pyrolysis oil compositions according to invention and comparative examples with corresponding pour points using Pyrolysis Oil B.

10

			Comparative				inventive				
Example #		9	10	11	12	13	14	15	16	17	18
Polymer		none	P1	P2	P9	P3	P4	P5	P10	P11	P12
Polymer Mw	[kg/mol]	n/a	7	13	13	27	39	124	24	49	156
Polymer	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil B	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	0	-9	-9	-9	-24	-18	-21	-21	-21	-21
PP Reduction	[°C]	n/a	9	9	9	24	18	21	21	21	21
Viscosity, -10°C	[cP]	6370	9864	7673	6879	5088	1760	2772	5460	5276	1645
Viscosity Reduction at -10°C	[%]	n/a	-55	-20	-8	20	72	56	14	17	74

n/a: not applicable (baseline) n.m.: not measured
 Polymer Mw – weight-average molecular weight

15

Table 8: Pyrolysis oil compositions according to invention and comparative examples with corresponding pour points using Pyrolysis Oil C

			Comparative		Inventive			
Example #		19	20	21	22	23	24	25
Polymer		none	P1	P2	P3	P4	P5	P6
Polymer Mw	[kg/mol]	n/a	7	13	27	39	124	380
Polymer	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil C	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	45	45	39	36	36	30	27
PP Reduction	[°C]	n/a	0	6	9	9	15	18
Viscosity, -10°C	[cP]	295	748	460	129	102	66	25
Viscosity Reduction at -10°C	[%]	n/a	-154	-56	56	65	78	92

5 n/a: not applicable (baseline) n.m.: not measured
Polymer Mw – weight-average molecular weight
Example #19 – untreated pyrolysis oil (reference)

Table 9: Pyrolysis oil compositions according to invention and comparative examples with corresponding pour points using Pyrolysis Oil D.

			Comparative			Inventive						
Example #		26	27	28	29	30	31	32	33	34	35	36
Polymer		none	P1	P7	P14	P3	P5	P6	P10	P12	P17	P18
Polymer Mw	[kg/ mol]	n/a	7	13	13	27	124	380	24	156	22	62
Polymer	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil D	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	18	27	18	6	-3	-9	-3	-12	-12	-3	-6
PP Reduction	[°C]	n/a	-9	0	12	21	27	21	30	30	21	24
Viscosity, 40°C	[cP]	146 x10 ³	252 x10 ³	n.m.	188 x10 ³	65 x10 ³	46 x10 ³	57 x10 ³	124 x10 ³	62 x10 ³	132 x10 ³	121 x10 ³
Viscosity Reduction, 40°C	[%]	n/a	-73	n/a	-29	55	69	61	15	65	9	17

10 n/a: not applicable (baseline) n.m.: not measured
Polymer Mw – weight-average molecular weight

Table 10: Pyrolysis oil compositions according to invention and comparative examples with corresponding pour points using Pyrolysis Oil E.

			Comparative				inventive	
Example #		37	38	39	40	41	42	
Polymer		none	P7	P8	P13	P15	P16	
Polymer Mw	[kg/mol]	n/a	13	350	14	37	156	
Polymer	[g]	0	0.1	0.1	0.1	0.1	0.1	
Pyrolysis Oil E	[g]	100	99.9	99.9	99.9	99.9	99.9	
PP	[°C]	55	55	55	54	50	40	
PP Reduction	[°C]	n/a	0	0	1	5	15	

- 5 n/a: not applicable (baseline) n.m.: not measured
Polymer Mw – weight-average molecular weight

Results

- 10 When the polymers are combined with a pyrolysis oil according to the invention, a reduction in viscosity, a reduction in pour point, and a positive wax inhibition are the most desirable outcomes so that the treated pyrolysis oil will flow at a lower temperature (reduced pour point), have lower viscosity for improved handling properties, and reduce the risk of wax build up during the process.
- 15 Table 6 shows that pyrolysis oils, containing the polymeric additives P3 to P6 of the present invention have a lower pour point compared to the untreated pyrolysis oil A, or to the comparative pyrolysis oil compositions Examples 2 to 4 (treated with 0.1% by weight of a comparative additive P7, P8 and P1, respectively). The table also demonstrates that inventive examples provide a viscosity reduction of 25 to 66% compared to the untreated oil (Example 1). Comparative example 4 shows an undesirable increase in viscosity of 3%.
- 20 The data also demonstrates that inventive examples 7 and 8 achieve 41% and 32% wax inhibition, respectively. Comparative examples 2 and 3 achieved 0% and 1% wax inhibition.

- 25 Table 7 provides data on treated and untreated Pyrolysis Oil B. Inventive examples 13 to 18 demonstrate a large reduction in pour point and viscosity compared to untreated Pyrolysis Oil B (Example 9) or treated comparative examples 10 to 12. Inventive Examples 13 to 18 have an 18 to 24°C lower pour point and 20 to 74% reduction in viscosity compared to Untreated Pyrolysis Oil B (Example 9). Comparative examples 10 to 12 demonstrate large increase in viscosity of 8 to 55% compared to the untreated Pyrolysis Oil B (Example 9).

- 30 Table 8 provides data on treated and untreated Pyrolysis Oil C. Inventive examples 22 to 25 demonstrate a large reduction in pour point and viscosity compared to untreated Pyrolysis Oil C (Example 19) or treated

comparative examples 20 and 21. Inventive Examples 22 to 25 have a 9 to 18°C lower pour point and 56 to 92% reduction in viscosity compared to Untreated Pyrolysis Oil C (Example 19). Comparative examples 20 shows no change in pour point and a viscosity increase of 154% compared to the untreated pyrolysis oil. Comparative examples 21 shows a small reduction of pour point of 6°C and an undesirable viscosity increase of 56% compared to the untreated pyrolysis oil C.

Table 9 provides data on treated and untreated Pyrolysis Oil D. Inventive examples 30 to 36 demonstrate a reduction in pour point and viscosity compared to untreated Pyrolysis Oil B (Example 26) or treated comparative examples 27 to 29. Inventive Examples 30 to 36 have a 21 to 30°C lower pour point and 9 to 69% reduction in viscosity compared to Untreated Pyrolysis Oil D (Example 26). Comparative examples 27 and 29 demonstrate large increase in viscosity of 73% and 29%, respectively. Examples 27 to 29 also do not provide a reduction in pour point as large as the inventive examples.

Table 10 provides data on treated and untreated Pyrolysis Oil E. Inventive examples 41 and 42 demonstrate a reduction in pour point of 5 and 15 °C, respectively compared to the untreated Pyrolysis Oil E (example 37). Comparative examples 38 and 39 do not demonstrate any reduction in pour point and Comparative example 40 only provides a 1°C reduction compared to the untreated pyrolysis oil E.

Figure 1

Figure 1 is a graph showing the viscosity of the untreated pyrolysis oil A) and compositions comprising said 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 A) (Example 1 of Table 6 above), whereas the reference numbers 5, 7 and 8 on Figure 1 correspond to the curves of the pyrolysis oil compositions of inventive examples 5, 7 and 8 according to Table 6 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 P3, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 692 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P6, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 315 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P5, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 351 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 P1, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 467 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P6, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 186 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P5, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 196 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 P3, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 165 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P6, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 77 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P5, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 77 cP.

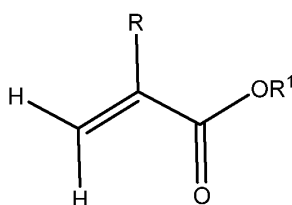
At 55°C, the untreated pyrolysis oil had a viscosity of approximately 34 cP. By comparison, the pyrolysis oil including 0.1% by weight of polymeric additive P3, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 15 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P6, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 9 cP. The pyrolysis oil including 0.1% by weight of polymeric additive P5, based on the total weight of the pyrolysis oil composition, had a viscosity of approximately 9 cP.

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.

Compositions comprising pyrolysis oil and treated with a polymeric additive b) as defined in claim 1 show improved cold flow improvement, reduced pour point, reduced viscosity, and greater wax inhibition. The resulting composition is easier to store and transport. Unlike prior solutions, no adjustment to the pyrolysis process is necessary and no additional treatment prior to transport is required.

CLAIMS

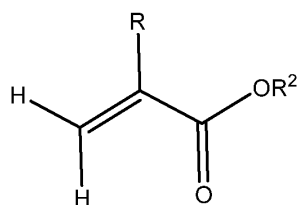
1. A composition comprising a plastic pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is a polymer P) prepared by polymerizing a monomer composition comprising from 50 to 100 %
 5 by weight of one or more alkyl (meth)acrylate monomers b1) of formula (I), based on the total weight of the monomer composition,



(I)

- wherein R is hydrogen or methyl, and R¹ is a linear, branched or cyclic alkyl residue with 16 to 30
 10 carbon atoms, and
 wherein the polymer P) has a weight-average molecular weight from 20,000 to 600,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

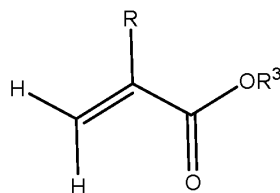
2. The composition according to claim 1, wherein the monomer composition to prepare the polymer P) further comprises
 15 b2) one or more alkyl (meth)acrylate monomers of formula (II)



(II)

- wherein R is hydrogen or methyl, and R² is a linear, branched or cyclic alkyl residue with 1 to 6
 20 carbon atoms; or

- b3) one or more alkyl (meth)acrylate monomers of formula (III)



(III)

- wherein R is hydrogen or methyl, and R³ is a linear, branched or cyclic alkyl residue with 7 to 15
 25 carbon atoms; or

a mixture of both alkyl (meth)acrylate monomers b2) and b3).

3. The composition according to claim 2, wherein the monomer composition to prepare the polymer P) comprises 30 % by weight or less of one or more alkyl (meth)acrylate monomers b2), based on the total weight of the monomer composition.
4. The composition according to claim 2 or 3, wherein the monomer composition to prepare the polymer P) comprises 50 % by weight or less of one or more alkyl (meth)acrylate monomers b3), based on the total weight of the monomer composition.
5. The composition according to any one of the previous claims, wherein the monomer composition to prepare the polymer P) comprises from 60 to 100 % by weight of one or more alkyl (meth)acrylate monomers b1) of formula (I), based on the total weight of the monomer composition.
6. The composition according to any one of the previous claims, wherein the one or more alkyl (meth)acrylate monomers b1) are selected from the group consisting of C₁₈-C₂₂ acrylate monomers, C₁₆-C₁₈ methacrylate, or a mixture thereof.
7. The composition according to any one of claims 1 to 6, wherein the monomer composition to prepare the polymer P) further comprises monomers b4) selected from the group consisting of:
 - hydroxyalkyl (meth)acrylates, preferably hydroxyalkyl (meth)acrylates selected from 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10 decanediol (meth)acrylate;
 - aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides, preferably aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides selected from N-(3-dimethyl-aminopropyl)methacrylamide, 3-diethylaminopentyl (meth)acrylate, 3-dibutyl-aminohexadecyl (meth)acrylate;
 - nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates, preferably nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates selected from N-(methacryloyloxyethyl)diisobutylketimine, N-(methacryloyloxyethyl)dihexadecyl-ketimine, (meth)acryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl (meth)acrylate;
 - aryl (meth)acrylates like benzyl (meth)acrylate or phenyl (meth)acrylate, where the acryl residue in each case can be unsubstituted or substituted up to four times;
 - carbonyl-containing (meth)acrylates, preferably carbonyl-containing (meth)acrylates selected from 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, N-methacryloyloxy-formamide, acetonyl (meth)acrylate, N-methacryloyl-2 pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxy-propyl)-2-pyrrolidinone, N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone;
 - (meth)acrylates of ether alcohols, preferably (meth)acrylates of ether alcohols selected from tetrahydrofurfuryl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl

- (meth)acrylate, cyclohexyloxyethyl (meth)acrylate, propoxyethoxyethyl (meth)acrylate, benzyloxyethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, 2-methoxy-2-ethoxypropyl (meth)acrylate, ethoxylated (meth)acrylates, 1-ethoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxy-2-ethoxyethyl (meth)acrylate, esters of (meth)acrylic acid and methoxy polyethylene glycols;
- 5 (meth)acrylates of halogenated alcohols, preferably (meth)acrylates of halogenated alcohols selected from 2,3-dibromopropyl (meth)acrylate, 4 bromophenyl (meth)acrylate, 1,3-dichloro-2-propyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-iodoethyl (meth)acrylate, chloromethyl (meth)acrylate;
- 10 oxiranyl (meth)acrylate, preferably oxiranyl (meth)acrylate selected from 2, 3-epoxybutyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 10,11-epoxyundecyl (meth)acrylate, 2,3-epoxycyclohexyl (meth)acrylate, oxiranyl (meth)acrylates such as 10,11-epoxyhexadecyl (meth)acrylate, glycidyl (meth)acrylate;
- 15 phosphorus-, boron- and/or silicon-containing (meth)acrylates, preferably phosphorus-, boron- and/or silicon-containing (meth)acrylates selected from 2-(dimethyl-phosphato)propyl (meth)acrylate, 2-(ethylphosphito)propyl (meth)acrylate, 2 dimethylphosphinomethyl (meth)acrylate, dimethylphosphonoethyl (meth)acrylate, diethylmethacryloyl phosphonate, dipropylmethacryloyl phosphate, 2 (dibutylphosphono)ethyl (meth)acrylate, 2,3-butylenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysilane,
- 20 diethylphosphatoethyl (meth)acrylate;
- sulfur-containing (meth)acrylates, preferably sulfur-containing (meth)acrylates selected from ethylsulfinyethyl (meth)acrylate, 4-thio-cyanatobutyl (meth)acrylate, ethylsulfonyethyl (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulfinylmethyl (meth)acrylate, bis(methacryloyloxyethyl) sulfide;
- 25 heterocyclic (meth)acrylates, preferably heterocyclic (meth)acrylates selected from 2-(1-imidazolyl)ethyl (meth)acrylate, oxazolidinyethyl (meth)acrylate, N-methacryloylmorpholine and 2-(4-morpholinyl)ethyl (meth)acrylate;
- maleic acid and maleic acid derivatives, preferably mono- and diesters of maleic acid, maleic anhydride, methylmaleic anhydride, maleinimide, methylmaleinimide;
- 30 fumaric acid and fumaric acid derivatives, preferably mono- and diesters of fumaric acid;
- vinyl halides, preferably vinyl halides selected from vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;
- vinyl esters, preferably vinyl acetate;
- vinyl monomers containing aromatic groups, preferably vinyl monomers containing aromatic groups
- 35 selected from styrene, substituted styrenes with an alkyl substituent in the side chain, such as alpha-methylstyrene and alpha-ethylstyrene, substituted styrenes with an alkyl substituent on the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;
- heterocyclic vinyl compounds, preferably heterocyclic vinyl compounds selected from 2-vinylpyridine,
- 40 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-

vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles;

5 vinyl and isoprenyl ethers;
methacrylic acid and acrylic acid, or
a mixture thereof.

8. The composition according to any one of the preceding claims, wherein the composition comprises
10 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.

9. The composition according to any one of the preceding claims, wherein the weight-average molecular weight of the polymer P) is from 20,000 to 550,000 g/mol, more preferably from 22,000 to
15 500,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

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
20 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,
25 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,
30 hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than polymer P), or a mixture thereof.

13. A method of manufacturing a composition as defined in any one of the preceding claims, wherein the method comprises the steps of:

35 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).

40 14. Use of a polymeric additive as defined in any one of claims 1 to 12 to reduce the pour point of a plastic pyrolysis oil, or to reduce the viscosity of a plastic pyrolysis oil, or both.

15. A method of transporting or storing a plastic pyrolysis oil a) comprising the step of adding a polymeric additive b) to the plastic pyrolysis oil a), to form a composition as defined in any one of claims 1 to 12.