

METHOD AND DEVICE FOR EXTRACTING ADDITIVES FROM PLASTIC-BASED MATERIAL**DESCRIPTION****TECHNICAL FIELD**

The present invention belongs to the technical field of the treatment, decontamination and recycling of plastics.

More particularly, the present invention concerns a method for recycling both additives and polymers from additive-containing plastics or composites by extraction, recrystallization, circulation and floatation, in which a pressurized dense fluid and in particular a supercritical fluid and a temperature or pressure gradient are used. This leads to two streams, the first is made of a condensate of additives and the second one of purified plastic-based material. The present invention also concerns a particular multi-vessel device implemented during said method.

PRIOR ART

The use of flame-retardants (FRs) as plastics additives is essential to ensure safety and compliance with relevant safety regulations. Among all kinds of FRs, halogenated organics, especially brominated flame-retardants (BFRs), have been used extensively because they require the lowest amount for the highest fire retardancy. However, the presence of bromine leads to many challenges whether in regard to their toxicity or their recycling and disposal.

To this extend, incineration has the disadvantage of generating corrosive gases and dioxins as well as difficult treatment due to high incombustibility. Landfilling results in the leaching of toxic brominated substance and the possible transfer into local aquifers.

In recent years, there has been a desire for an effective utilization of resources, and techniques for recycling a variety of materials have been under

development. In the case of material recycling of thermoplastic resins, undesired additives can cause the degradation of the resins and decrease the quality of recycled products.

Solvent extraction has been proposed to remove BFR content from polymeric substrate. For example, the patent U.S. 6,388,050 discloses a method for treating FRs-containing thermoplastic resin with glycol ether based compounds. The resin composition can thus easily be separated into a flame retardant and a thermoplastic resin that retains most of its virgin qualities, and the solvent can be reused by distillation [1]. Although effective, the use of organic solvents should be minimized due to related health and safety issues (toxicity, flammability, risk of distillation). Another drawback of these approaches is that the subsequent distillation and drying processes are energy-intensive and hence costly.

In another example, the patent US 6,429,284 describes a method that can reduce the flame retardancy of resins containing FRs and reuse the resulting resins with supercritical carbon dioxide (ScCO_2) at a pressure comprised between 7.4 and 22.2 MPa, mixed with an auxiliary solvent (1-20 mol%) [2]. This method can substantially reduce the use of organic solvent with the replacement of pressurized CO_2 , which is regarded as a green solvent due to its non-toxic and non-flammable nature. Furthermore, distillation or drying is not required because of the easy gasification of CO_2 by simple decompression. However, the invention with batchwise operation in a pressurized system limits its extraction efficiency. Furthermore, the invention only highlights the recycling of resin parts, while the recovery of the FRs, which can be valuable, is envisaged but not implemented. The use of auxiliary solvents is systematic in all the ScCO_2 extraction of BFRs found in the literature. It allows increasing the solubility of the BFRs in ScCO_2 which is usually lower than that in classical organic solvents.

Some rare publications exist in the academic literature concerning the solubility measurements of BFRs at very high-pressure above 50 MPa in pure ScCO_2 or with the use of a co-solvent, propanol, and limonene. The low solubility in pure ScCO_2 is presented as a problem for the extraction, hence the necessity of using a co-solvent [3-6].

Thus, the inventors have set themselves the aim of proposing an easily industrialised, safe and easy method making it possible to extract BFRs and more generally

additives from resins containing them in order to recover and recycle both the extracted BFRs or additives and the resins free from BFRs or additives.

DESCRIPTION OF THE INVENTION

The present invention makes it possible to resolve the technical problems as defined previously and to attain the aim that the inventors have set themselves.

Indeed, the invention relates to the extraction and separation of additives from polymeric materials or composites using an environmentally friendly solvent, in order to detoxify the starting materials and enable their recycling and also the recycling of additives. The method according to the present invention completely eliminates the negative effect of using organic solvent.

The inventors have found that BFRs can be efficiently extracted from plastic parts, for example from waste electronic and electrical equipment (also known as "WEEE") using a pressurized dense fluid such as supercritical CO₂ (ScCO₂). This leads to two streams, the first one is made of a condensate of BFRs and the second one of purified plastics. Interestingly, what has been observed for BFRs can be generalized not only to any flame retardants but also to any additive present in polymeric materials or composites. In other words, the present invention allows, for the first time, to use a pressurized dense fluid such as ScCO₂ to effectively extract additive BFRs from polymeric parts of WEEE, despite their low solubility and thus goes against all current approaches of ScCO₂ extraction of BFRs that are all looking to increase solubility and therefore using auxiliary solvents.

The invention takes advantage of a combination of (1) tunable solubility in pressurized dense fluid such as ScCO₂ by changing operating conditions; (2) the high diffusivity of a pressurized dense fluid such as ScCO₂; (3) a temperature and/or pressure gradient; (4) flow circulation by natural convection or by pressurization-depressurization cycle; (5) recycle of additives such as BFRs in a form of pure polycrystalline structure; and (6) floatation separation between additives such as BFRs and plastics.

Thanks to this combination, the method according to the present invention makes it possible to easily and efficiently extract additives such as BFRs from

polymeric matrices in order to recover purified additives such as BFRs in the form of polycrystals or precipitates and in order to recover polymeric substrates in a purified form, therefore allowing their recycling. The use of a temperature gradient or pressure gradient and of convection or circulated flow improves the extraction efficiency. In other words, the method of the present invention permits great potential savings both financially and environmentally to be realized from the recovery and recycling of contaminated plastics waste.

More particularly, the present invention concerns a method for extracting an additive from a material containing a polymer matrix and said additive comprising the steps of

a) bringing into contact said material with a pressurized dense fluid in a device at a temperature T and a pressure P at which said pressurized dense fluid is saturated with said additive and

b) creating in said device either a temperature gradient or a pressure gradient whereby said device presents a gradient of solubility of said additive with a zone of minimum solubility in which said additive precipitates or crystallizes and a zone of maximum solubility containing said material depleted in said additive,

step a) and step b) being performed simultaneously or one after the other one.

The expression "method for extracting an additive from a material containing a polymer matrix and said additive" is taken to mean, within the scope of the present invention, forming from a material containing a polymer matrix and said additive, in one hand, a fraction rich in additive and, in the other hand, a fraction depleted in this additive. Once the method of the invention has been implemented, the fraction rich in additive corresponds to the additive in the form of a precipitate or polycrystal and the fraction depleted in the additive corresponds to the material depleted in this additive.

Thus, the method of the present invention can be considered as a method for treating a material containing a polymer matrix and said additive allowing the partial or total reduction (elimination) of the additive load present in the material to be treated. If

the additive is considered as a contaminant, the method of the present invention can also be considered as a decontamination method.

A “material depleted in the additive” means, in the context of the present invention, a material in which the additive load is significantly reduced compared to the material prior to the implementation of the method of this invention. Advantageously, at least 70%, at least 80%, at least 90%, at least 95% and advantageously at least 99% or even all of the additive initially contained in the material is eliminated as a result of the implementation of the invention. In other words, the additive load in the material depleted in the additive is at least 70%, at least 80%, at least 90%, at least 95% lower and advantageously at least 99% lower than the initial load in the material. It should be noted that, if the amount of additive is to be further reduced in the material depleted therein, this material may need to be subjected to additional treatment such as a method according to the present invention.

A “material containing a polymer matrix and an additive” is taken to mean, within the scope of the present invention, a material whose main structural element is a polymer matrix in which additive molecules are embedded or distributed. This embedment or distribution may be uniform. Alternatively, this embedment or distribution may be randomized. It should be noted that the additive molecules are maintained at the surface of or within the polymer matrix thanks to non-covalent bonds with low energy such as hydrogen bonds or Van der Waals bonds. In other words, no bond of higher energy such as a covalent bond exists between the polymer matrix and the additive.

In a particular embodiment of the present invention, the implemented material only contains a polymer matrix and an additive. This material thus consists of a polymer matrix and an additive. This material can also be designated as a plastic with an additive.

In an alternative embodiment of the present invention, the implemented material contains a polymer matrix, an additive and at least one another element. The latter may be, for example, a woven or non-woven fabric or glass or carbon fibers whereby the material is a composite material. During the extraction method according to the present invention, this additional element remains in the material depleted in the additive.

A “polymer matrix” is taken to mean, within the scope of the present invention, a porous or non-porous structure essentially constituted of one (or more) (co)polymer(s). The polymer matrix used in the present invention may be formed of one or more thermoplastic polymer(s), one or more thermosetting polymer(s), one or more glassy polymer(s) or a mixture thereof.

Advantageously, the polymer matrix implemented in the present invention is a matrix whose constituent material is chosen from the group consisting of a polyamide such as nylon, a polyimide, a parylene, a polycarbonate, a polydimethylsiloxane, a polyurethane, a silicon polymer, a polyolefin such as polyethylene (PE) or polypropylene (PP), a polysulfone, polyethersulfone, a polyetheretherketone (PEEK) and its derivatives, a polyvinyl chloride (PVC), a polyvinylidene fluoride (PVDF), a polyvinyl pyrrolidone (PVP), a cellulose acetate (AC), an acrylic resin (or polyacrylate), a polystyrene (PS), a polymethylmethacrylate (PMMA), a polymethacrylate (PMA), polyethylene terephthalate, polybutylene terephthalate, an epoxy resin, a phenol resin, an urea resin, a polyurethane, a polyester, a copolymer of acrylonitrile-butadiene-styrene (ABS), a copolymer of styrene-ethylene-butylene-styrene (SEBS), a copolymer of styrene-isoprene-styrene (SIS), a polyfluorene, a polypyrene, a polynaphthalene, a polypyrrole, a polycarbazole, a polyindole, a polyazepine, a polyaniline, a polythiophene, an ABA type polymer composed of an aromatic unit B such as benzene, thiophene, pyrrole, carbazole, fluorene, optionally functionalised by alkyl, alkoxy, oligoether, thioether chains, or conjugated alkene or alkyne and electropolymerisable A units of the thiophene, alkylthiophene, 3,4-alkylenedioxythiophene type and derivatives thereof or pyrrole, alkylpyrrole, N-alkylpyrrole, 3,4-alkylenedioxy-pyrrole type and a mixture thereof.

The additive present in the material implemented in the invention may be any compound remaining following the polymerisation of the polymer matrix or any compound added to modify the chemical and/or physical properties of said polymer matrix. Advantageously, this additive is selected in the group consisting of plasticizers, flame retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds, thermal stabilizers and mixtures thereof. In a

particular embodiment, this additive is a flame retardant and more particularly an organic flame retardant.

A flame retardant is a compound which, under the effect of heat, chemically reacts by producing most often water and thus cooling the material. The volatile products of this chemical reaction also enable the combustion to be slowed down by decreasing the amount of flammable mixtures. Such a flame retardant is also known as an "endothermic filler". When the flame retardant is a halogenic flame retardant, the latter can act on preventing occurrence of combustion because halogens are effective in capturing free radicals, hence removing the capability of the flame to propagate.

Any flame retardant and in particular any organic flame retardant known to those skilled in the art is usable within the scope of the present invention.

Advantageously, the flame retardant implemented as additive in the present invention may be selected from the group consisting of organic halogen-based flame retardants such as brominated flame retardants and chlorinated flame retardants, organophosphorus flame retardants, melamine-based flame retardants and nitrogen-based flame retardants.

More particularly, the flame retardant implemented as additive in the present invention can be selected from the group consisting of decabromodiphenyl, polybrominated diphenyl ethers (PBDEs) such as decabromodiphenyl ether, decabromodiphenyl oxide, octabromodiphenyl oxide, tetrabromodiphenyl oxide, tetrabromobisphenol A (TBBPA), tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE), tetrabromobisphenol A-bis(2,3-dibromophenyl ether), tetrabromobisphenol A-bis(allyl ether), hexabromocyclododecane, bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB or EHTBB), bis(2-ethylhexyl) tetrabromophthalate (TBPH or BEHTBP), hexabromobenzene (HBB), 2,3,4,5,6-pentabromoethylbenzene (PBEB), 2,3,4,5,6-pentabromotoluene tribromophenol, tetrabromophthalic anhydride, bistetrabromophthalimide, ethylenebistetrabromophthalimide, chlorinated paraffin, chlorinated polyethylene, perchlorocyclopentadecane (dechlorane plus), chlorendic acid, a melamine monophosphate, a melamine pyrophosphate, a melamine polyphosphate, a melamine

cyanurate, an hydromagnesite, a tripolyphosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), bisphenol-A bis(diphenyl phosphate) (BPADP) and mixtures thereof.

In particular, the additive present in the material implemented in the present invention is an organic halogen-based flame retardant.

Moreover, the additive in the material implemented in the present invention may be a mixture of different additives selected from one group or in different groups of additives as above defined. Indeed, the invention takes advantage of the density difference between different additives as well as the fact that density of the pressurized dense fluid such as ScCO_2 is tunable (based on the operating conditions: temperature and pressure). Indeed, the pressurized dense fluid such as ScCO_2 has a certain solvation power on polymeric materials and additives, which could lead to the deposition of a mixture of polymers (oligomers) and of different additives. But, since the pressurized dense fluid such as ScCO_2 can provide different buoyancy effect on substances with different densities, this invention also allows to minimize cross contamination between the different additives extracted by floatation separation. It should however be noted that if the different additives in the mixture do not present a sufficient density difference, the recovered additive will also be a mixture.

In a particular embodiment of the present invention, the material containing a polymer matrix and an additive as previously defined and notably the material containing a polymer matrix and a flame-retardant is a waste electronic and electrical equipment (also known as "WEEE"), a waste furniture, a waste vehicle or one of their mixtures.

Typically the material containing a polymer matrix and an additive implemented in the present invention is in a fragmented form and in particular in a particulate or powder form.

Therefore, before the method according to this invention is implemented and therefore before step (a) of this method, the material containing a polymer matrix and an additive such as previously defined may be submitted to at least one treatment and notably to at least two treatments selected from the group consisting of a sorting treatment, a shredding treatment and a grinding or crushing treatment.

The sorting treatment is advantageously performed by optical means and aims to obtain fragments of the material with uniform size and shape, and also with uniform polymer matrix and thus to obtain a uniform extraction of additives therefrom.

A shredding treatment and/or a grinding or crushing treatment can reduce the material containing the polymer matrix and the additive into smaller fragments, typically smaller than or equal to 10 mm and notably smaller than or equal to 5 mm in order to ensure sufficient contact area with the pressurized dense fluid.

In a particular embodiment, the material containing a polymer matrix and an additive such as previously defined may be submitted to a sorting treatment, followed by a shredding treatment and then a grinding or crushing treatment whereby the material implemented in step a) of the method according to the invention presents a size of less than 1 mm to increase the contact area with the pressurized dense fluid.

The method of the present invention implements a pressurized dense fluid which can be defined as a fluid heated at a temperature higher than the critical temperature thereof (maximum temperature in the liquid phase, whatever the pressure or temperature of the critical point) or subjected to a pressure higher than the critical pressure thereof (critical point pressure).

Thus, the pressurized dense fluid may be in a subcritical gaseous state, in a subcritical liquid state or in the supercritical state. In the supercritical state, the fluid is heated at a temperature higher than the critical temperature thereof and subjected to a pressure higher than the critical pressure thereof, the physical properties of such a supercritical fluid (density, viscosity, diffusivity) being intermediate between those of liquids and those of gases.

Any pressurized dense fluid known to a person skilled in the art and generally used in methods for extracting or solubilising organic materials may be used in the present invention.

Advantageously, the pressurized dense fluid implemented in the present invention may be selected from the group consisting of carbon dioxide, nitric oxide, nitrous oxide, argon, ammonia, Freon-22, Freon-23, and any mixture thereof.

In particular, the pressurized dense fluid implemented in the present invention is carbon dioxide and more particularly supercritical carbon dioxide.

Indeed, CO₂ is abundant, inexpensive and considered an interesting molecule in the field of supercritical fluids because of its advantageous properties. It is chemically neutral, non-flammable, non-corrosive and considered part of a "green chemistry" process. In addition, the supercritical conditions associated with CO₂ (P_c = 7,38 MPa, T_c = 31,1°C) are easily accessible.

As already explained, one advantage of the present invention relative to the prior art methods is the fact that no organic solvent is needed for the extraction of additives such as BFRs. Thus, the pressurized dense fluid implemented in the present invention is free of co-solvent and in particular, of organic solvent such as, for example, glycol ether-based compounds as disclosed in U.S. 6,388,050 [1].

Alternatively, pressurized dense fluid implemented in the present invention may nevertheless contain a co-solvent such as water.

Advantageously, during the extraction method according to the present invention, the density of the pressurized dense fluid ranges from 800 kg/m³ to 1200 kg/m³. During the process, the density of the pressurized dense fluid may be controlled in order to be adjusted in the above range and to further separate precipitated/crystallized additives from the material containing them.

In step a) of the method according to the present invention, the material containing the polymer matrix and the additive is brought into contact with the pressurized dense fluid at a temperature T and a pressure P at which the pressurized dense fluid is saturated with the additive, step a) being carried out in a device which comprises a single vessel (single-vessel device or single-reactor device) or alternatively a plurality of vessels (multi-vessel device or multi-reactor device). The present invention method implements a device with one or more high-pressure vessels.

In a first embodiment, the material containing the polymer matrix and the additive is placed in the single-vessel device or in at least one of the vessels of the multi-vessel device and then the pressurized dense fluid at a temperature T and a pressure P is introduced therein.

In a second embodiment, the material containing the polymer matrix and the additive is placed in the single-vessel device or in at least one of the vessels of the multi-vessel device on or before the pressurized dense fluid at a temperature T_1 lower than the temperature T and a pressure P_1 lower than the pressure P . Then the temperature of the pressurized dense fluid is increased to the temperature T while its pressure is increased to the pressure P . Typically, the temperature T_1 is room temperature (i.e. $23^{\circ}\text{C} \pm 5^{\circ}\text{C}$) and pressure P_1 is atmospheric pressure.

In both embodiments, the temperature T is higher than the critical temperature of the pressurized dense liquid and the pressure P is higher than the critical pressure thereof. The temperature T and the pressure P to be implemented may be determined beforehand by routine experiments. Alternatively, it is possible to measure the additive concentration in the pressurized dense fluid in particular thanks to Fourier Transform Infrared Spectroscopy (FTIR).

The method of the present invention requires both a pressurized dense fluid saturated with the material containing the polymer matrix and the additive and a temperature or pressure gradient. The temperature or pressure gradient induces a gradient of solubility of the additive with a zone of minimum solubility, designated as "crystallization zone", in which the pressurized dense liquid is oversaturated with the additive and the latter precipitates or crystallizes and a zone of maximum solubility, designated as "extraction zone", in which there is the material containing the polymer matrix and the additive and the concentration of the additive solubilized in the pressurized dense liquid is below saturation. In the extraction zone, the additive load of the material decreases over time, until a material depleted in the additive is obtained.

Thanks to the Le Chatelier's principle, which states that "when any system at equilibrium for a long period of time is subjected to change in concentration, temperature, or pressure, (1) the system changes to a new equilibrium and (2) this change partly counteracts the applied change," and the convection within the single-vessel device or within different vessels of the multi-vessel device : since some additives are deposited in one part of the single-vessel device or in one vessel of the multi-vessel device, it allows for more additives to be extracted on the high solubility zone of the single-vessel device or

on the high solubility vessel of the multi-vessel device where the material containing the polymer matrix and the additive is located.

It is therefore a dynamic extraction in which a high solubility of the additive in the pressurized dense fluid is not needed. In fact, low solubility is, in the present invention, an advantage as it allows for more additives to be finally extracted. At the end of the extraction, one retrieves a purified material containing a polymer matrix in the highest solubility zone, and extracted additives in the low solubility area. In some cases, it is possible to crystallize the extracted additives whereby the method of the present invention does not require a purification step of the extracted additives.

More specifically, the solubility of a compound dissolved in a pressurized dense fluid such as ScCO_2 can be described as a function of density and temperature of the fluid such as CO_2 [7]. According to Peng-Robinson equation of state [8], the fluid density such as CO_2 density is decided by operating temperature, pressure and volume. That is to say, the solubility of a compound is tunable based upon varying the operating conditions, which allows for readily achieving oversaturation to grow crystals or to precipitate.

When a temperature gradient is implemented during the method of the invention, this gradient will induce the formation of a pressure gradient. Nevertheless, the pressure in the device is advantageously maintained at a pressure close to the pressure P i.e. the pressure in the device is $P \pm 10\%$ and notably $P \pm 2\%$. Advantageously, the temperature gradient implemented is to set from $50^\circ\text{C}/\text{m}$ to $500^\circ\text{C}/\text{m}$. The temperature will be maximum in the crystallization zone and minimum in the extraction zone when the solubility of the additive to be extracted in the pressurized dense fluid decreases with the temperature. On the contrary, the temperature will be maximum in the extraction zone and minimum in the crystallization zone when the solubility of the additive to be extracted in the pressurized dense fluid increases with the temperature.

When a pressure gradient is implemented during the method of the invention, this gradient will induce the formation of a temperature gradient. Nevertheless, the temperature in the device is advantageously maintained at a temperature close to the temperature T i.e. the temperature in the device is $T \pm 20\%$ and notably $T \pm 10\%$.

Advantageously, the temperature in the extraction zone ranges from 32°C to 200°C, and, in particular, from 60°C to 150°C, whether the method of the present invention implements a temperature gradient or a pressure gradient. This range applies, for example, when the pressurized dense fluid is CO₂.

Advantageously, the pressure in the extraction zone ranges from 7.4 MPa to 100 MPa, and, in particular, from 20 MPa to 50 MPa, whether the method of the present invention implements a temperature gradient or a pressure gradient. This range applies, for example, when the pressurized dense fluid is CO₂.

As already indicated, step a) and step b) of the method according to present invention are performed simultaneously or one after the other one. In a particular embodiment, step a) may be performed before step b).

In the method according to the present invention, the temperature gradient or the pressure gradient ensures solute transport between the extraction zone and the crystallization zone thanks to natural convective flow of the pressurized dense fluid. Nevertheless, the solute transport between the zone of maximum solubility and the zone of minimum solubility may be enhanced thanks to pressurization-depressurization cycles or dynamic flow.

In the method according to the present invention, the extraction of additive from the material containing a polymer matrix and this additive continues until the concentration of additive in the extraction zone is equal to the saturation concentration in the crystallization zone. It is possible to follow the progress of the extraction method according to the invention, in particular, by observing the status of the additive crystals/precipitates in particular with a microscope or by measuring the additive concentration in the pressurized dense fluid in particular thanks to FTIR.

It should be noted that step b) of the method according to the present invention also covers the case in which the temperature or pressure gradient is created over time. In this alternative, the temperature (or the pressure) in the vessel is increased to a predetermined temperature higher than the temperature T (or to a predetermined pressure higher than the pressure P) and then natural cooling (or slow/step decompression) occurs whereby a temperature (or pressure) gradient is obtained over

time. In this case, at a particular time during step b), the temperature (or the pressure) inside the vessel is homogenous. In addition, the two zones i.e. the extraction zone and the crystallization zone are not present in the vessel at the same time but rather one after the other one.

The method according to the present invention comprises a step of recovering the additive crystals/precipitates and the material depleted in this additive. For example, the solute can be transported following convection flow and the crystals/precipitates can grow on the pre-located mesh material in the crystallization zone, so the crystals/precipitates can be simply collected from said mesh. When the additive is in a pure form, it does not require any additional purification step to be reused. The material depleted in additive can also be reused once recovered.

As already explained, the method according to the present invention can be implemented using a single-vessel device or a multi-vessel device.

The present invention also concerns a particular multi-vessel device usable for this extraction method. This multi-vessel device comprises at least two vessels identical or different in series with a pressure gradient existing between the different vessels while, in each vessel, a temperature gradient is also implemented. This particular device makes it possible to optimize the additive extraction by implementing a temperature gradient at different pressures.

In addition, this particular multi-vessel device allows for a continuous process or at least a semi-continuous process. Indeed, the loop connection makes it possible to realize a continuous processing, which significantly fastens the process and avoids stop by batchwise loading/unloading. In addition, the continuous processing can save the pressurized dense fluid consumption to the highest extent.

In this case, when the extraction method according to the present invention starts, the pressure difference between two consecutive vessels of the multi-vessel device should be set according to the number of vessels in the device. The pressure reduction can be averaged by each vessel from maximum pressure to atmospheric pressure.

Thus, the present invention concerns a multi-vessel device comprising:

- at least two high-pressure vessels, identical or different, connected in series, each vessel comprising means for generating a temperature gradient therein and
- transfer circuits for transferring the pressurized dense fluid from a high-pressure vessel to the next one, each transfer circuit fluidly connecting the outlet of a high-pressure vessel to the inlet of the next one and presenting means for generating a negative pressure gradient between both vessels.

In the multi-vessel device according to the present invention, the high-pressure vessels are connected in series thanks to the transfer circuits for transferring the pressurized dense fluid from a high-pressure vessel to the next one, each transfer circuit fluidly connecting the outlet of a high-pressure vessel to the inlet of the next one.

The inlet of the first vessel in the series is fluidly connected to a storage tank in which the fluid implemented during the extraction method is stored. The fluidic connection between the storage tank and the first high-pressure vessel implements a transfer circuit.

The latter comprises a pump for delivering fluid from the storage tank to the first vessel and thus generating a positive pressure gradient. The fluid in the storage tank can be liquid or gaseous. When the fluid in the storage tank is gaseous, the transfer circuit advantageously comprises a cooling unit localized between the storage tank and the delivering pump. This cooling unit is used to condensate the gaseous fluid into a liquid fluid.

The inlet of each vessel after the first one in the series can also be fluidly connected with the storage tank, the transfer circuit implemented for this connection also presenting a delivering pump and a cooling unit as already disclosed. Advantageously, the same delivering pump and the same cooling unit are used when delivering fluid from the storage tank to any vessel in the series.

In addition, the transfer circuit between two consecutive vessels comprise at least one element selected from the group consisting of valves, solenoid valves and three-way valves in order to control the flow of pressurized dense fluid. Advantageously, the transfer circuit between two consecutive vessels comprise at least two three-way valves and at least one element selected from the group consisting of valves and solenoid valves. The transfer circuit between the storage tank and the first vessel in the

series can also comprise at least one valve or solenoid valve to control the flow of pressurized dense fluid, while the transfer circuit between the storage tank and the vessels other than the first one in the series can comprise at least one three-way valve in order to control the flow of pressurized dense fluid.

The transfer circuit between two consecutive vessels is advantageously equipped with a heat exchanger or with heating pipe to counteract decompress cooling due to the Joule-Thompson cooling effect.

Typically, the means for generating a negative pressure gradient between two consecutive vessels are selected from the group consisting of orifices, valves, solenoid valves and back-pressure regulators. In particular, these means comprise at least one back-pressure regulator and at least one element selected from the group consisting of orifices, valves and solenoid valves. In the multi-vessel device according to the present invention, the outlet of each vessel is (i) fluidly connected with the inlet of a next vessel, (ii) directly go to atmosphere to draw off the fluid implemented during the extraction method fluid if there is no toxicity problem and/or (iii) fluidly connected to the storage tank.

At least one three-way valve can be present at the outlet of the last vessel in the series in order to control the flow of pressurized dense fluid.

The outlet of the last vessel in the series is fluidly connected to the storage tank thanks to a transfer circuit. The latter comprises a pump for recycling the fluid from the last vessel to the storage tank and advantageously a cooling unit localized between the last vessel and the recycling pump in order to condensate the gaseous fluid into a liquid fluid prior to pumping.

The outlet of each vessel before the last one in the series can also be fluidly connected with the storage tank, the transfer circuit implemented for this connection also presenting a recycling pump and a cooling unit as already disclosed. Advantageously, the same delivering pump and the same cooling unit are used when recycling fluid from any vessel in the series to the storage tank.

In this configuration, the multi-vessel device according to the present invention, the at least two high-pressure vessels, identical or different, are connected in a loop. The loop connection makes it possible to save the pressurized dense fluid

consumption to the highest extent. In addition, in a loop connection, when one vessel is on the stage of loading or unloading either material or additive crystals, the other vessels can still work for extraction and/or crystallization, thus continuous process techniques are applicable, which avoid stop by batchwise loading/unloading.

In this multi-vessel device implementing a pressure gradient, the latter and the flow of pressurized dense fluid are advantageously controlled by one or more computer(s) with readable memories. This can be used to control the solenoid valve between two vessels.

The multi-vessel device according to the present invention can comprise two high-pressure vessels, identical or different. In this case, if one of the two vessels is stopped and released to load/unload materials, the other one can still work for extraction/deposition with an applied temperature gradient. This configuration makes it possible to implement a semi-batch process with dual vessels.

In a particular embodiment, the multi-vessel device according to the present invention can comprise at least three high-pressure vessels, identical or different, connected in series, each vessel comprising means for generating a temperature gradient therein. Thus the multi-vessel device according to the present invention can comprise three high-pressure vessels, identical or different; four high-pressure vessels, identical or different; five high-pressure vessels, identical or different; six high-pressure vessels, identical or different; seven high-pressure vessels, identical or different; eight high-pressure vessels, identical or different; nine high-pressure vessels, identical or different or even ten high-pressure vessels, identical or different.

Each high-pressure vessel in the multi-vessel device according to the present invention is advantageously designed as a horizontal cylinder, which facilitates convection flow and localized crystallization in a single vessel. Typically, the main body and inner metallic structures of each high-pressure vessel are made of stainless steel or any other alloy which withstands high pressure and temperature. Typically, this horizontal cylinder presents a circular cross-section.

The inner volume of each vessel is divided in two compartments c1 and c2 thanks to a porous thermally insulated plate. Each compartment c1 and c2 is limited by

an arc-shaped part of main body of the device and the porous thermally insulated plate. The latter is advantageously made of inert fibrous materials with low thermal conductivity and presents openings thanks to which the compartment c1 is in fluid connection with the compartment c2. These openings present diameters, identical or different, large enough so as not to clog readily but not too large so as to be effective for heat insulating, advantageously these diameters range from 1 mm to 10 mm.

The porous thermally insulated plate can be of any shape provided that the thermally insulated plates with openings play a role of defining different zones in the vessel and regulating flow trajectory. In a particular embodiment, the thermally insulated plate is in two parts, each part being fixed to the other one and to the internal wall of the single-well device. The angle formed by the two parts of the thermally insulated plate can be adjusted and typically is above or equal to 90° and below 180°.

Each vessel in the multi-vessel device according to the invention presents at least one heater member at level of the arc-shaped part of the compartment c1 (or c2) and at least one chiller member at the level of the arc-shaped part of the compartment c2 (or c1). The heater member may be outside and/or inside the vessel. In a first implementation, heating is performed by a member located outside the vessel i.e. mounted on the walls of the vessel or positioned in the proximity thereof. Such a member may be in the form of a heater belt or a heater cable of the resistive or inductive type or that is heated by passing a fluid heated to a temperature that is adapted to heat part of the pressurized dense fluid contained in the vessel to a desired temperature. In a second implementation, the heater member is inside the vessel and is typically presented in the form of a heater resistor positioned in the inside volume of one of the compartments c1 and c2. The same applies with the chiller member which is advantageously in the form of a cable that is chilled by passing a fluid chilled to a temperature that is adapted to chill part of the pressurized dense fluid contained in the device to a desired temperature. It is further preferable to assemble the at least one heater member in bottom zone of the device and the at least one chiller member in top zone so as to maintain the circulation of the loop fluid due to the buoyancy effect. In heating zone, fluid is heated therefore upward velocity is obtained along the wall whereas it is the reverse in case of the cooling zone.

In one of the compartments c1 and c2, there is the extraction zone, while the crystallization zone is located in the other one. Advantageously, a sample basket container is placed in the extraction zone and a crystal collector is placed in the crystallization zone. In a particular embodiment, the sample basket container is driven by a roller and/or at least one stirrer element is amounted in the vessel in order to accelerate the extraction rate and avoid polymer binding.

The mesh size of sample basket container should be smaller than the particulate size of the material containing a polymer matrix and an additive. In one specific embodiment, the mesh size of the basket container ranges from 0.01 mm to 1 mm.

The crystal collector is advantageously arc-shaped and attached to the bottom wall of the compartment c1 or c2. It can be composed of several mesh layers fixed on a rack close to the heater member or to the chiller member. It should be readily replaceable from the vessel and the crystals on it should be readily stripped away.

Each vessel in the multi-vessel device according to the invention presents an inlet opening and an outlet opening. Typically, the inlet opening is placed near the extraction zone and the outlet opening is placed near the crystallization zone. Advantageously, the device is equipped with a filter such as a sintered filter in both the inlet opening and the outlet opening. In particular, the filter retains entrained solutes in the device as much as possible when drawing off pressurized dense fluid.

Besides, the device is also equipped with at least one window and advantageously with two parallel windows, which allow for measurement of concentration in solution using an FTIR and/or observation of crystal growth using a microscope. Typically, the window(s) is/are made of CaF₂ crystal, diamond or sapphire.

In each vessel implementing a temperature gradient, the latter and the flow of pressurized dense fluid are advantageously controlled by one or more computer(s) with readable memories.

Other features and advantages of the present invention will become apparent from the following detailed description which makes reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 presents the change of molar fraction of TBBPA and temperature versus elapsed time.

Figure 2 presents a SEM (for “Scanning Electron Microscopy”) image of TBBPA crystals obtained from the method of natural cooling.

Figure 3 presents the change of molar fraction of TBBPA and pressure versus elapsed time.

Figure 4 presents a SEM image of TBBPA crystals obtained from the method of step decompression.

Figure 5 presents the change of integrated IR absorbance and pressure versus elapsed time.

Figure 6 presents the solubility of TBBPA as a function of temperature at constant pressure.

Figure 7 presents the images showing the process of density floatation of PMP and TBBPA-BDBPE in ScCO_2 .

Figure 8 presents the mass of TBBPA sample before and after the temperature gradient assisted extraction.

Figure 9 is a schematic representation of the multi-vessel device according to the present invention.

DETAILED DISCUSSION OF PARTICULAR EMBODIMENTS

I. Preliminary experiments.

In order to demonstrate the feasibility of the present invention, the following examples are performed using the simplest configuration of the extraction system, where only one high-pressure vessel was used for both extraction and recrystallization. The vessel is equipped with a filter in the openings of both inlet and outlet. Besides, the vessel is also equipped with two parallel windows, which allow for measurement of concentration in solution using an FTIR and/or observation of crystal growth using a microscope.

Three types of samples, referred herein after as “standard sample”, “customized sample” and “real sample”, respectively were prepared.

Standard sample (designated as “T+ABS”) was a mixture of ABS resin (Br-free), fabricated by Shandong Tianyi Chemical Co., Ltd. (China), and chemical grade TBBPA, from Sigma Aldrich, by homogenizing weighted TBBPA powder with ABS powder, whose particulate size were less than 0.25 mm (checked by sieving). TBBPA content was loaded at 16.7 w%, thus Br content was 9.8 w%.

Customized sample (designated as “T/ABS”) was fabricated by Shandong Tianyi Chemical Co., Ltd. (China) following industrial practices by hot blending ABS resin and industrial grade TBBPA and extruding them to obtain pellets. We then grinded these purchased pellets, at cryogenic temperature using liquid N₂, into powders with particulate size of less than 0.25 mm (checked by sieving). The Br content is 8.6 w%, determined by XRF.

Real sample (designated as “RS”) was collected from the casing of a paper shredder (HP), in which TBBPA was the major BFRs (proved by HPLC and GC-MS results). The sample was cut and grinded, at cryogenic temperature using liquid N₂, into powders with particulate size of less than 0.25 mm in diameter (checked by sieving). The Br content is 9.9 w%, determined by XRF.

I.1. Using standard sample.

In this example, 0.50 g of T+ABS sample (standard sample) was weighted and packaged within Solidweave mesh (Mesh size = 9 μm). The sample package was loaded into the upper part of a high-pressure vessel, which total volume was 75.4 mL. A seed mesh was put on the bottom of the vessel to collect crystals. A magnetic stirring bar was also placed right on the seed mesh to stir the involved fluid.

After sealing the vessel properly, the vessel was heated by a PID-controlled heater, meanwhile liquid CO₂ with purity of 99.9% was delivered into the vessel by a dual piston pump at a flow rate of 10 mL/min. Once the temperature and pressure of the vessel reached 333 K and 25 MPa, the vessel was closed and the stirring started running at a speed of 1000 rpm. The extraction was performed in a static mode for 4 hours until it

reached thermodynamic equilibrium. At this point, the saturated molar fraction (MF) of was 0.030 ± 0.001 mmol/mol of CO₂ molecule.

After reaching the saturation in solution, two methods were implemented to grow crystals.

One of the approaches was to stop heating to slowly cool the vessel naturally down to room temperature over a 2 hours period while keeping a constant amount of CO₂ in the closed vessel (Figure 1). The pressure within the vessel therefore decreases with the decrease of temperature until the temperature reaches room temperature. The difference of MF between total value and dissolved value in solution is the degree of oversaturation, which allows for TBBPA to precipitate as nuclei particles and then more TBBPA molecules are deposited to form polycrystalline structure. After cooling, liquid CO₂ in the vessel was rapidly released, remaining the crystals on seed area at the bottom of the vessel. Compact polyhedral shape of crystal can be seen in the SEM image (Figure 2).

Another approach for growing crystal was to use a slow/step decompression (Figure 3). Once the equilibrium was achieved, a metering valve was used to slowly release CO₂ with a 5 MPa of pressure drop per step while keeping a constant temperature. Similarly, an obvious degree of oversaturation can be detected, allowing for TBBPA to precipitate and form polycrystalline structure. After 6 hours for crystal growth, all the remaining CO₂ was gradually released. The crystals mainly grew on seed area at the upper and middle part of the vessel due to upward flow direction of ScCO₂. The needle-like crystal of TBBPA can be seen in the SEM image (Figure 4).

As for the above two alternatives, TBBPA was extracted at an efficiency of $26.0\% \pm 0.7\%$, and it was separated as a form of polycrystalline substance, which can be directly reused. Meanwhile, ABS oligomer was dissolved in ScCO₂ at a weight percentage of $1.2\text{ w}\% \pm 0.1\text{ w}\%$, thus the negative effect of its contamination on the purity of TBBPA crystal was insignificant. After three batches of the same extraction process, TBBPA removal efficiency was $78.0\% \pm 2.0\%$. If higher pressure is performed, higher solubility of both TBBPA and ABS is expected, then floatation of TBBPA and ABS should be considered to ensure a more desired separation performance.

I.2. Using customized sample.

Customized sample T/ABS was weighted for 0.60 g and packaged within Solidweave mesh (Mesh size = 9 μm). The extraction procedure was as the same as that in the first example. The total mass lost rate was $3.6 \text{ w}\% \pm 0.0 \text{ w}\%$ (determined by gravimetric method) and Br removal efficiency was $31.8 \text{ w}\% \pm 0.8 \text{ w}\%$ (determined by XRF). The infrared signal was monitored through the ScCO_2 solution during extraction and subsequent step decompression (Figure 5), which indicates a similar trend of kinetics compared with that using standard samples. However, white precipitations instead of crystals were found in the vessel probably due to grade difference of BFR involved.

I.3. Using real sample.

In this example, 0.94 g of real sample (RS) containing unknown type of BFR was packed within Solidweave mesh (Mesh size = 9 μm) and loaded into the vessel, and the extraction and subsequent cooling procedure was also performed consistently with the first example. After processing, the total mass lost rate was $8.3 \text{ w}\% \pm 1.3 \text{ w}\%$ (determined by gravimetric method) and Br removal efficiency was $14.5 \text{ w}\% \pm 0.3 \text{ w}\%$ (determined by XRF). Ivory white precipitates were found on seed area at the bottom of the vessel.

In addition to natural cooling and slow decompression, there is a third alternative to generate oversaturation by creating temperature gradient in a vessel. Since the pressure in an enclosed vessel is almost the same everywhere, the density of ScCO_2 only varies with different temperatures in different partitions. Therefore, the solubility of TBBPA also varies in different partitions of the vessel (Figure 6). For example, at pressure of 50 MPa, the solubility of TBBPA increases from 0.07 to 0.35 mmol/mol of CO_2 when temperature rises from 40°C (313 K) to 80°C (373 K). On the contrary, at pressure of 20 MPa, the solubility of TBBPA decreases from 0.04 to 0.02 mmol/mol of CO_2 when temperature rises from 40°C (313 K) to 80°C (373 K).

II. Validation of the feasibility of the method according to the invention.

II.1. Density floatation in ScCO₂.

In order to validate the feasibility of density floatation to separate a polymer from a BFR, the inventors mixed polymethylpentene (PMP, density = 0.84 g/mL) with 2,2-Bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propane (TBBPA-BDBPE, density = 2.17 g/mL) and loaded the mixture into a vessel.

As more and more CO₂ input, its state in the vessel turned from gas to liquid and then to supercritical state at a constant temperature of 40°C. Also, PMP granules started to float at 40°C and 20 MPa (density of CO₂ = 0.84 g/mL), and they all floated up to the top of the vessel as more CO₂ was input until 25 MPa (density of CO₂ = 0.88 g/mL), while TBBPA-BDBPE still remained sinking on the bottom of the vessel (Figure 7).

Therefore, the density floatation allows to minimize cross contamination between the heavier additives and lighter polymers. Besides, the tunable density ranges from 0.8 to 1.2 g/mL.

II.2. Enhanced dissolution and recrystallization by temperature gradient.

In this trial, the inventors checked the feasibility of generating oversaturation by temperature gradient.

An up-scaled vessel with a volume of 1L was used in this example. Two propellers are amounted to allow fast stirring and thus homogenizing the temperature of solution in the vessel. The thermally insulated plate made of PTFE has several openings, segregating the vessel into an extraction zone located in the lower part and a crystallization zone located in the upper part, while the medium is still connected through flows. When stirring is stopped, the cooling and heating are performed on both sides of the thermally insulated plate to generate a significant temperature gradient.

According to the previous solubility measurements, the solubility of TBBPA is 0.405 g/L. Therefore, four TBBPA samples were loaded, each of which contained 0.50 g TBBPA packaged into solid mesh to ensure saturation. Besides, the four samples were evenly located in the vertical space of the vessel, with two in crystallization zone (samples 1 and 2) and the other two in extraction zone (samples 3 and 4). After sealing the vessel, the vessel was heated and CO₂ was delivered to desired $60 \pm 0.1^\circ\text{C}$ and $30 \pm 0.1\text{ MPa}$

to extract/dissolve TBBPA with stirring at 500 rpm for 5h. Then stirring was stopped and temperature gradient was started to generate.

When it became stable, the temperature of the top part inside the vessel ($T_{top,in}$) was 46.2°C, the temperature of the middle part of external vessel wall ($T_{mid,out}$) was 76.3°C, and the temperature of the external vessel bottom ($T_{bottom,out}$) was 169.2°C. The temperature of the cooling liquid contacting with the cooling tube was 8.0°C. The pressure was maintained isobaric at 30 ± 0.1 MPa. This constant temperature gradient was lasted for 10h for recrystallization.

After the process, obvious recrystallization phenomenon of TBBPA was observed in the crystallization zone, while no such phenomenon in the extraction zone. TBBPA crystals looks like ice cubes and can easily be peeled off. For the sample packages, their total dissolved mass is 1.49 g, which is three times higher than that without temperature gradient. It is worth noting that the two samples located in extraction zone (samples 3 and 4) were almost depleted (determined by gravimetric method) (Figure 8), indicating a significant increase of overall solubilisation due to the temperature gradient and the induced convection flow and the generated steady state.

It is reasonable to deduce that the dissolved amount of TBBPA can be increased to one or even two orders of magnitude, if we operate the extraction at 50 MPa with the aid of temperature gradient.

II.3. Enhanced extraction by temperature gradient.

In this example, the inventors used customized sample (T/ABS) with particle size ranging from 0.1-1 mm, and loaded 2.0 g of the sample into the extraction zone of the 1L vessel.

Then the extraction was implemented according to the procedure as mentioned in section II.2. After the one-batch extraction, the Br removal efficiency was improved to $62.3 \text{ w\%} \pm 3.4 \text{ w\%}$ (determined by XRF). Meanwhile, ABS oligomer was dissolved in ScCO_2 at a weight percentage of $2.5 \text{ w\%} \pm 0.1 \text{ w\%}$. In the crystallization zone, TBBPA deposits coated on the cooling tube can also be observed. The color of the plastic samples after extraction were closer to the virgin resin itself.

III. Method according to the present invention.

The present invention relates to recycling both BFRs and polymers from BFRs-containing plastics by extraction, recrystallization, circulation and floatation in ScCO_2 .

The basic procedures comprise:

- Shredding the plastic parts into small pieces,
- Optionally grinding these small pieces of plastic to smaller grain size to enlarge the contact area with the ScCO_2 ,
- Loading the plastic powders into porous sample holder,
- Placing the holder containing plastic powders into an extraction zone of a high-pressure vessel.
- Introducing CO_2 into the vessel by a pump,
- Heating and pressurizing CO_2 to a desired temperature and pressure,
- Forming a solution until the solvation and diffusion reach thermodynamic equilibrium / saturation concentration at a given condition,
- Extracting BFRs from plastic in ScCO_2 by generating temperature and/or pressure gradient to achieve oversaturation in one zone of the vessel or in one vessel and allow another zone of the vessel or another vessel to be below saturation.
- Maintaining flow circulation of ScCO_2 solution by natural convection, dynamic flow or by pressurization-depressurization cycle.
- Optionally, controlling the density of ScCO_2 and flow direction to further separate precipitated/crystallized BFRs from polymer resins,
- Maintaining the growth of BFR crystals on seed area for a given period of time.
- Slowly releasing CO_2 from the vessel to draw off solution. CO_2 can be recovered for further reuse, by recompression.
- Removing the BFR crystals/precipitates from crystallization zone (seed area) of the vessel to reuse the desired BFRs.
- Removing the remaining plastic from the basket container if the concentration of BFRs in the plastic is decreased to a desired concentration.

- Reloading untreated plastic powders into the vessel to start a new loop of extraction.

- Optionally, when performing in a few of vessels connecting in series, the crystals/precipitates can be removed from one of the vessels and untreated plastic powders will be loaded into this vessel while other vessels are still ongoing of extraction or crystallization. In this case, one can realize a continuous processing as well as minimize the loss of CO₂.

IV. Multi-vessel device according to the present invention.

Figure 9 presents a simplified scenario of the multi-vessel device. In this scenario, three identical vessels (A, B, and C) are connected in series/loop, with one's outlet connected with the next one's inlet. Meanwhile, the inlets of the vessels are also connected with the main pump (02), which delivers fresh CO₂ from CO₂ storage tank (01) to the vessels, thus generating a positive pressure gradient. The orifices/valves/solenoid valves (07, 09, 11, and 12) and the back-pressure regulators (BPR, 13-15) located between two vessels are used to generate a negative pressure gradient. Thus, the outlet of each vessel is either connected with the inlet of a next vessel or directly go to atmosphere to draw off CO₂. The valves/solenoid valves (06, 08, and 10) located at the inlet of the vessels and the three-way valves (16-21) are used to regulate the on/off and the flow of CO₂ into the vessel. The cooling units (04 and 05) are used to condensate gaseous CO₂ into liquid CO₂ prior to pumping.

Each vessel (A, B, and C) presents means to generate a gradient temperature therein. Thus, as already explained, the inner volume of each vessel is divided in two compartments and thanks to a porous thermally insulated plate. All what has been previously disclosed for vessels in which a temperature gradient is implemented applies to the vessels A, B and C of the multi-vessel of Figure 9.

In the case of a continuous process, at boot stage, untreated plastic samples are loaded in all vessels A, B and C, and the extraction of vessel A is performed at 50 MPa with the aid of temperature gradient. The BPRs (13 and 14) are set at 30 MPa and 10 MPa, respectively. After a certain period of extraction such as, for example, 5h, in vessel

A, with the replenishment of CO₂ at isobaric condition, ScCO₂ is allowed to transport from vessel A to vessel B, then to vessel C, and the extra CO₂ is either drawn off or recycled in the system through pump (03), until the samples in vessel A are purified to a desired extent. Meanwhile, the extraction in vessel B and C are still ongoing.

At the end of the extraction in vessel A, the remaining CO₂ is either drawn off or recycled in the system through pump (03), and the decontaminated plastics and condensed additives are separately collected from the vessel A. While the vessel A is unloaded and reloaded, vessel B is compressed to 50 MPa, to perform the same extraction process as the role of vessel A just did, but with a shorter time such as, for example, 2h, due to a pre-extraction process at 30 MPa. Then vessel B becomes the major vessel for extraction/crystallization, and vessel C and vessel A are remained at 30 MPa and 10 MPa, respectively.

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CLAIMS

1) Method for extracting an additive from a material containing a polymer matrix and said additive comprising the steps of

a) bringing into contact said material with a pressurized dense fluid in a device at a temperature T and a pressure p at which said pressurized dense fluid is saturated with said additive and

b) creating in said device either a temperature gradient or a pressure gradient whereby said device presents a gradient of solubility of said additive with a zone of minimum solubility in which said additive precipitates or crystallizes and a zone of maximum solubility containing said material depleted in said additive,

step a) and step b) being performed simultaneously or one after the other one.

2) Extraction method according to claim 1, wherein said material is a composite material.

3) Extraction method according to claim 1 or 2, wherein said additive is selected from the group consisting of plasticizers, flame retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds, thermal stabilizers and mixtures thereof.

4) Extraction method according to any one of claims 1 to 3, wherein said additive is an organic halogen-based flame retardant.

5) Extraction method according to any one of claims 1 to 4, wherein said material is a waste electronic and electrical equipment, a waste furniture, a waste vehicle or one of their mixtures.

6) Extraction method according to any one of claims 1 to 5, wherein, before said step (a), said material is submitted to a sorting treatment, followed by a shredding treatment and then a grinding or crushing treatment.

7) Extraction method according to any one of claims 1 to 6, wherein said pressurized dense fluid is selected from the group consisting of carbon dioxide, nitric oxide, nitrous oxide, argon, ammonia, Freon-22, Freon-23, and any mixture thereof.

8) Extraction method according to any one of claims 1 to 7, wherein said pressurized dense fluid is carbon dioxide and more particularly supercritical carbon dioxide.

9) Extraction method according to claims 1 to 8, wherein the temperature in said zone of maximum solubility ranges from 32°C to 200°C, and, in particular, from 60°C to 150°C and/or the pressure in said zone of maximum solubility ranges from 7.4 MPa to 100 MPa, and, in particular, from 20 MPa to 50 MPa.

10) Extraction method according to claims 1 to 9, wherein the solute transport between said zone of maximum solubility and said zone of minimum solubility is enhanced thanks to pressurization-depressurization cycles or dynamic flow.

11) Multi-vessel device implemented during the extraction method as defined in any one of claims 1 to 10, comprising:

- at least two high-pressure vessels, identical or different, connected in series, each vessel comprising means for generating a temperature gradient therein and
- transfer circuits for transferring the pressurized dense fluid from a high-pressure vessel to the next one, each transfer circuit fluidly connecting the outlet of a high-pressure vessel to the inlet of the next one and presenting means for generating a negative pressure gradient between both vessels.

12) Multi-vessel device according to claim 11, comprising at least three high-pressure vessels, identical or different, connected in series, each vessel comprising means for generating a temperature gradient therein

13) Multi-vessel device according to claim 11 or 12, wherein the means for generating a negative pressure gradient between two consecutive vessels comprise at least one back-pressure regulator and at least one element selected from the group consisting of orifices, valves and solenoid valves.

14) Multi-vessel device according to any one of claims 11 to 13, wherein the inner volume of each vessel is divided in two compartments c1 and c2 thanks to a porous thermally insulated plate.