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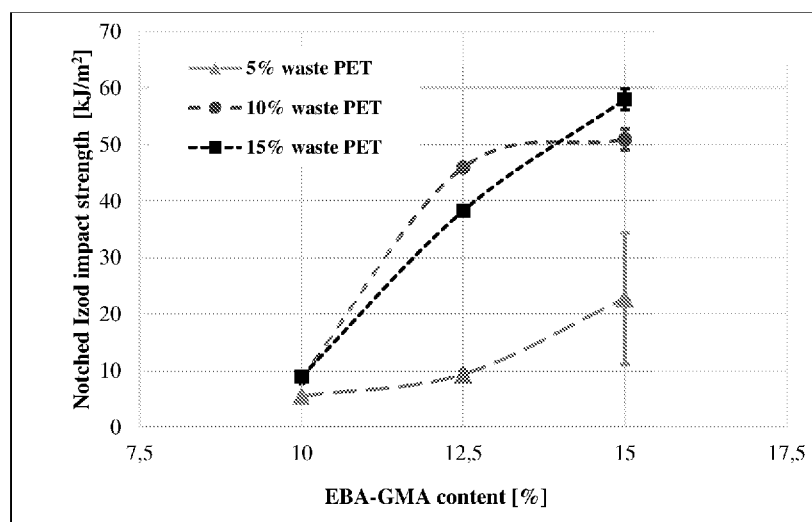


Figure 2.a

(57) Abstract: Thermoplastic polyester that contains original thermoplastic polyester raw material, waste thermoplastic polyester and impact modifier additive, where the original thermoplastic polyester raw material and the waste thermoplastic polyester are of the same type and are selected from the following list : polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polylactic acid (PLA), furthermore where the original thermoplastic polyester raw material and the waste (recycled) thermoplastic polyester are differentiated by that the weight average molecular weight of the waste (recycled) thermoplastic polyester is at least 10% lower than that of original thermoplastic polyester raw material of the same type. The invention also relates to a method for the production of the thermoplastic polyester.



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Thermoplastic polyester and its production

The field of the invention

5 The object of the present invention relates to thermoplastic polyester, which is produced using original thermoplastic polyester raw material, waste thermoplastic polyester, and an impact modifier additive. The object of the invention also relates to a method for the production of such thermoplastic
10 polyester. The thermoplastic polyester according to the invention has high impact strength.

The background of the invention

15

Polymers are the totality of macromolecules, this term includes natural polymers, elastomers, plastics and cross-linked resins, as well.

20 An environmental problem today is the huge amount of plastic produced then the disposal of the residual waste after its use. Due to the growing expectations of environmental protection, waste management and recycling, it is necessary to perform the recycling of plastic wastes at the appropriate
25 level, if possible in a value-increased way. Recycling may be performed chemically, during which lower molecular mass components are produced from the polymer, or mechanically, during which physical steps are mostly performed (chopping, melting, reshaping). One of the main objectives of the
30 development of original and recycled plastics, in harmony with the demands of the market, is the development of materials with high impact strength. Components that improve impact strength may be other polymers mixed with the matrix polymer, most frequently elastomers. The heterogeneous structure formed

in this way makes it possible for the degree of plastic deformation to increase during fracture, thereby increasing the fracture energy absorbed by the plastic.

5 Nowadays, one of the greatest volumes of waste polymer is polyethylene terephthalate (PET), which comes from the polyesters, which is used for the production of large numbers of bottles and thin-walled containers in the packaging industry. Following selective collection and cleaning PET,
10 which becomes waste in a relatively short amount of time with the termination of the packaging function, may be recycled. The secondary PET raw material regained from waste is used mainly in the production of fibres and packaging materials. It is expected that in the future several types of polyester that
15 have not been recycled to date (e.g. polybutylene terephthalate (PBT), polylactic acid (PLA)) will need to be collected and recycled within the framework of waste management.

20 Thermoplastic polyesters are plastics that have good electrical insulation and gas tightness properties; in addition their strength and rigidity are outstanding compared to other mass plastics. Because of their aforementioned properties they have an exceptionally broad spectrum of use,
25 which uses include the packaging and textiles industries producing short lifecycle products. Because of the increasing production of thermoplastic polyesters it is becoming necessary to recycle the large amount of waste formed in this way. The markets for recycled thermoplastic polyester waste
30 may include both the electronics and vehicle industries. However, the rigidity and sensitivity to cracking of thermoplastic polyesters, which are made worse by the unavoidable degradation occurring during recycling and the related reduction in average molecular mass, result in low

notched impact strength. Due to this it is necessary to improve the impact strength of these typically rigid polymers.

5 With consideration to the aforementioned factors, according to literature and patent sources numerous plastics containing thermoplastic polyester with increased impact strength are known.

According to patent application No. WO2019106124A1
10 polyethylene terephthalate (PET) is used without glass fibre reinforcing, according to their observations the impact strength of injection moulded toy building blocks may be influenced by using just a small amount (1-4%) of impact modifier material (ethylene glycidyl methacrylate, e-GMA).
15 Certain embodiments contain recycled PET polyesters, the two types of which are mechanically or chemically recycled PET. In Example 2 the impact modifier additive E-GMA is added separately to original PET and separately to recycled PET, however, they do not investigate what would happen if it were
20 to be added to a mixture of the two.

Patent applications No. WO2013118020A1 and No. WO2013118021A1 disclose a thermoplastic composition produced from rigid renewable raw materials, in which there is a polymeric impact
25 modifier additive dispersed in the polyester. The impact modifier additive used is usually selected so that its solubility is close to that of the renewable thermoplastic polyester. In certain cases the impact modifier additive is reactive, such as, for example, a polyepoxide modifier that
30 contains at least two oxirane rings per molecule. Patent application WO2013118020A1 discloses a thermoplastic polymer composition that contains recycled polyester (PLA), and which may be viewed as a rigid polymer. The known phenomenon of the

impact strength being improved with the addition of an additive may be observed in the examples.

Patent application No. EP2785793A1 discloses thermoplastic polyester compositions that contain polyalkylene terephthalate (such as PET and PBT), functionalised or non-functionalised block copolymer and a reinforcing material (e.g. glass fibre, carbon fibre, metallic fibre, ceramic fibre). The block copolymer contains a partially crystalline polyolefin block, at least one vinyl aromatic polymer block and an elastomer polyolefin block. In the case of a functionalised block copolymer the group performing the function may be an amine or epoxy group.

The biocomposite disclosed in patent application No. WO20014792A1 contains polyamide, engineering polyester and carbon-based reinforcing material from an organic source. These mixtures have a high recycled content. A widespread procedure used in industry is that the properties of polyamides, particularly polyamide 6 (PA6) and polyamide 6,6 (PA66) are influenced by mixing with other thermoplastic plastics and elastomers. Exceptional rigidity may be achieved in combination with reinforcing materials. From the prior art section it turns out that PA6, PBT and PET do not mix well with each other, and so it becomes necessary to use a compatibilizer, the use of which results in a significant improvement in tensile strength.

Patent application No. EP3548540A1 discloses a dynamically crosslinked polymer composition, and the connection between the chains of the polyester is ensured by a linking agent and one or more crosslinking impact modifier additives. On the basis of the one example the linking component used contains at least two epoxy groups, and the chain contains polyester with

one or more reactive end groups; to this is added the one or more crosslinking impact modifier additives, and the reaction is carried out in the presence of a catalyst.

5 Patent application No. US2013298427A1 describes a polymer composition of ski boots and of other products used in cold weather. The polymer components of the above products may be: thermoplastic polymer, thermoplastic elastomer, impact modifier additive, abrasion resistance enhancer additive. The
10 thermoplastic polymer may be PBT, PET or a mixture of the two, and it may contain a reactive modifier, which may be an impact modifier and/or reactive compatibiliser.

Patent application No. WO2008124604A1 relates to a
15 thermoplastic polyester composition that has high impact strength. The composition according to the specification contains thermoplastic polyester (50-95 m/m%), 16-25 m/m% impact modifier additive containing carboxyl and 0-5 m/m% polymer containing fluorine. One embodiment of the invention
20 contains PET and/or PBT, as composition containing thermoplastic polyester, and contains ethylene-, glycidyl methacrylate and methyl acrylate derivatives as impact modifier and polytetrafluoroethylene as the polymer containing fluorine. It is mentioned that in order to produce it a
25 recycled polymer, as well as a mixture of original and recycled polymer may be used.

The improvement of the properties of recycled PET polyester using a chain extension reaction is described in the
30 publication of Tavares et al. (Chain extension of virgin and recycled polyethylene terephthalate, 2016, Polymer Testing 50, 26-32.).

The article written by Geyer et al. deals with the energetic, thermo-mechanical, and chemical recycling of PET, which is of key importance due to the large amount of PET waste throughout the world (Recycling of poly(ethylene terephthalate)- A review focusing on chemical methods, 2016, eXPRESS Polymer Letters, 10(7), 559-586.).

Patent application No. WO9622330A2 discloses at least two-phase melt processed polymer compositions. The first phase is a polylactide-based polymer, and the second is a phase containing elastomer. These compositions are suitable for extruding, injection blow moulding, film casting, film blowing, foam production, thermal shaping, and fibre spinning. The following composition is disclosed as one of the most preferable embodiments: in the first phase it contains a polylactide-based polymer and in the second epoxidized rubber and a reactive compatibilizer agent. The impact strength of the multi-phase composition formed in this way may be maximised.

Montava-Jorda et al. in their publication entitled Mechanical Recycling of partially bio-based and recycled polyethylene terephthalate blends by reactive extrusion with poly(styrene-co-glycidyl methacrylate), *Polymers*, 2020, 12, 174, 1-20. disclose the production of a mixture of PET of biological origin and recycled PET via reactive extrusion with the use of the additive poly(styrene-co-glycidyl methacrylate). From their investigations it turns out that impact strength is lower in the case of the PET of biological origin and higher in the case of the original PET, and the impact strength of the mixture is between the two. In other words in spite of the additive used the impact strength of the mixture did not exceed the values measured in the case of the original PET.

- When examining the mechanical properties of recycled PET bottles Torres et al. (Study of thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding, European Polymer Journal, 2000, 36, 2075-2080.) found that polymer originating from such bottles is more rigid (elongation at rupture value is under 10%) than original PET polyester (elongation at rupture value greater than 200%).
- 10 According to the state of the art, the impact strength of the thermoplastic polyesters or other plastics may only be increased to a certain extent with the addition of a rational amount of impact modifier additive.
- 15 The objective of the present invention is the production of a thermoplastic polyester that has improved impact strength and is free of the problems according to the state of the art. No method is known according to the state of the art in which the impact strength of a mixture of original thermoplastic
- 20 polyester and reactive impact modifier additive may be increased with waste thermoplastic polyester.

It was recognised that if waste thermoplastic polyester with a lower molecular mass is added to original thermoplastic

25 polyester, then a less than expected amount of impact modifier additive is sufficient to achieve the same impact strength. The impact strength of the thermoplastic polyester produced with the method according to the invention may be increased by even as much as ten to fifteen times compared to that of the

30 original thermoplastic raw material. It was also recognised that the effect of the reactive impact modifier additive may be increased with waste thermoplastic polyester that has a low intrinsic viscosity value.

Brief description of the drawings

Figure 1.a shows a scanning electron microscope image of 10
5 m/m% EBA-GMA impact modifier additive dispersed in original
thermoplastic PET polyester raw material.

Figure 1.b shows a scanning electron microscope image of 10
m/m% EBA-GMA impact modifier additive dispersed in waste
thermoplastic PET polyester.

10 Figure 2.a shows the notched Izod impact strength of various
thermoplastic polyesters according to the invention as a
function of the amount of the EBA-GMA impact modifier additive
in the case of waste thermoplastic PET polyester contents of 5
/ 10 / 15 m/m%.

15 Figure 2.b shows graphs illustrating the impact strengths of
original thermoplastic PET polyester raw material and of waste
thermoplastic PET polyester.

Figure 3 shows a bar chart comparison of the notched Izod
impact strengths of thermoplastic polyesters containing 10
20 m/m% EBA-GMA and not containing EBA-GMA, containing 20 m/m%
waste PBT and not containing waste PBT.

Figure 4 shows a bar chart comparison of the notched Izod
impact strengths of thermoplastic polyesters containing 10
m/m% EBA-GMA and not containing EBA-GMA, containing 10 m/m%
25 waste PLA and not containing waste PLA.

Figure 5 shows the change in notched Izod impact strength of
thermoplastic polyesters made from compositions containing 13
m/m% EBA-GMA and 87 m/m% original thermoplastic PET polyester
depending on the moisture content used.

30

Brief description of the invention

The present invention is based on a mixture of original thermoplastic polyester raw material and waste (recycled) thermoplastic polyester with a lower molecular mass produced with given technological parameters in melt state, to which a specific amount of impact modifier additive is added. The impact strength of the thermoplastic polyester according to the present invention produced with this method may be increased by as much as ten to fifteen times compared to that of the original thermoplastic polyester. The method may be implemented, for example, in the scope of continuous operation using extruding technology and may be typically used for the production of two different product ranges: firstly, e.g. extruded panels, ribbons, profiled products, secondly, secondary raw material (regranulate).

In other words the present invention relates to a thermoplastic polyester that contains original thermoplastic polyester raw material, waste thermoplastic polyester and impact modifier additive, where the original thermoplastic polyester raw material and the waste thermoplastic polyester are of the same type and are selected from the following list: polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polylactic acid (PLA), furthermore where the original thermoplastic polyester raw material and the waste thermoplastic polyester are differentiated by that the weight average molecular weight of the waste thermoplastic polyester is at least 10% lower than that of original thermoplastic polyester raw material of the same type.

The invention preferably relates to a thermoplastic polyethylene terephthalate (PET) polyester the impact strength of which is at least 1.5 times, preferably at least 3 times,

most preferably at least 6 times that of thermoplastic PET polyester not containing waste thermoplastic polyester in the case of the use of the same amount of impact modifier additive.

5

The invention also preferably relates to a thermoplastic polybutylene terephthalate (PBT) polyester the impact strength of which is at least 1.25 times that of thermoplastic PBT polyester not containing waste thermoplastic polyester in the case of the use of the same amount of impact modifier additive.

10

The invention preferably relates to a thermoplastic polylactic acid (PLA) polyester the impact strength of which is at least 3 times that of thermoplastic PLA polyester not containing waste thermoplastic polyester in the case of the use of the same amount of impact modifier additive.

15

The present invention also relates to a thermoplastic polyethylene terephthalate (PET) polyester where the intrinsic viscosity of the waste thermoplastic PET polyester is a maximum of 0.74 g/dl.

20

According to another preferable embodiment the thermoplastic polyester according to the invention preferably contains an epoxy functional impact modifier additive, which even more preferably is selected from a group containing the following: ethylene glycidyl methacrylate (E-GMA), ethylene-butyl acrylate-glycidyl methacrylate (EBA-GMA), epoxidized rubber elastomer.

25

30

The invention preferably relates to a thermoplastic polyethylene terephthalate (PET) polyester that contains 15-80 m/m% original thermoplastic polyester raw material, 10-75 m/m%

waste thermoplastic polyester and 2.5-20.0 m/m% impact modifier additive; preferably 65-80 m/m% original thermoplastic polyester raw material, 10.0-35.0 m/m% waste thermoplastic polyester and 10-15 m/m% impact modifier additive; most preferably 77.5 m/m% original thermoplastic polyester raw material, 10.0 m/m% waste thermoplastic polyester and 12.5 m/m% impact modifier additive.

Furthermore, the present invention also relates to a method for the production of thermoplastic polyester, during which method original thermoplastic polyester raw material, waste thermoplastic polyester and impact modifier additive are used, where the original thermoplastic polyester raw material and the waste thermoplastic polyester are differentiated by that the weight average molecular weight of the waste thermoplastic polyester is at least 10% less than that of original thermoplastic polyester raw material of the same type, and the method contains the following steps:

- a) if necessary the original thermoplastic polyester raw material, the waste thermoplastic polyester and the impact modifier additive are processed to have the appropriate particle size and then, optionally, dried;
 - b) the original thermoplastic polyester raw material, the waste thermoplastic polyester and the impact modifier additive are homogenised in the form of a melt, which is preferably performed by extrusion or internal mixer kneading at a high temperature;
 - c) optionally the homogenous granulate obtained in step b) is shaped at the appropriate temperature;
- and where the type of the original thermoplastic polyester raw material and of the waste thermoplastic polyester is selected from among the following: polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polylactic acid (PLA).

According to a preferred implementation of the invention the shaping according to step c) is the extrusion, the compressing or the injection moulding.

- 5 According to an even more preferred implementation of the invention the extrusion according to step b) is performed in a twin-screw extruder.

According to an even more preferred implementation of the
10 invention the temperature applied in step b) is between 190 °C – 290 °C, preferably in the case of PET between 240 °C – 290 °C, in the case of PBT between 225 °C – 260 °C, in the case of PLA between 190 °C – 220 °C; the temperature applied in step
15 c) is between 150 °C – 300 °C, preferably in the case of PET between 235 °C – 270 °C, in the case of PBT between 225 °C – 260 °C and in the case of PLA between 180 °C – 210 °C.

According to a preferred implementation of the invention, where the type of the thermoplastic polyester is PET, in step
20 b) of the method 15-80 m/m% original thermoplastic polyester raw material, 10-75 m/m% waste thermoplastic polyester and 2.5-20 m/m% impact modifier additive; preferably 65-80 m/m% original thermoplastic polyester raw material, 10.0-35.0 m/m% waste thermoplastic polyester and 10-15 m/m% impact modifier
25 additive; most preferably 77.5 m/m% original thermoplastic polyester raw material, 10.0 m/m% waste thermoplastic polyester and 12.5 m/m% impact modifier additive are mixed together.

30 According to a preferred implementation of the invention the appropriate average molecular mass of the original thermoplastic polyester raw material and/or the waste thermoplastic polyester is formed *in situ* at the high temperature used during step b) by omitting the drying step of

a part of or all of the original thermoplastic polyester raw material and/or the waste thermoplastic polyester and/or by increasing its moisture content.

5

Detailed description of the invention

Unless referred to otherwise in the present specification m/m% is understood to mean mass percent (mass%), and in the case of ratios these are understood to mean mass ratios.

In the scope of the present specification if a numerical value is given, this is understood to mean that the last digit of the given number shows the precision of the given value according to the rounding-up rules. In other words, for example, 1.5 m/m% is understood to mean the range 1.45-1.54 m/m%.

In accordance with the present invention thermoplastic polyester (e.g. PET) of the same type is used from two sources. Within the scope of the present invention the one is called "original thermoplastic polyester", with which it is expressed that regarding its nature this component is the same as new, original material, which is newly made from conventional polyester raw material. The other is called "waste thermoplastic polyester", with which it is expressed that this component typically but not essentially originates from waste.

In the scope of the present invention original thermoplastic polyester and waste (otherwise known as recycled) thermoplastic polyester are differentiated in that the weight average molecular weight of the waste (recycled) thermoplastic polyester - typically as a result of the degradation process

occurring during use or recycling - is at least 10% less than that of original thermoplastic polyester of the same type. It should be noted that in the present specification the word "waste" is used for this component, as this component typically originates from waste, however this should not be understood as meaning that this component is exclusively limited to waste sources. For example, today in the case of PBT or PLA this component is less available from waste. Furthermore the degradation process, and via this the molecular mass reduction as compared to the original polyester may be elicited *in situ*, for example by omitting the drying step before processing and/or the moisture content of the original thermoplastic polyester raw material is increased (e.g. in a climate chamber), and so the following high-temperature extrusion or kneading step is performed in the presence of water, which high temperature is typically between 190 °C - 290 °C, preferably in the case of PET between 240 °C - 290 °C, in the case of PBT between 225 °C - 260 °C, and in the case of PLA between 190 °C - 220 °C. In other words if there is no waste thermoplastic polyester available or it is not sufficiently degraded, then, the efficiency of the impact modifier additive may be achieved by merely adding water. Within the scope of the present invention the original thermoplastic polyester raw material and the waste thermoplastic polyester are of the same type and are selected from the following list: PET, PBT and PLA. In the case of PET, PBT and PLA the weight average molecular weightes for the original thermoplastic polyester raw material and the waste thermoplastic polyester are as follows: original thermoplastic PET polyester raw material: at least 26,000 g/mol; waste thermoplastic PET polyester: up to 24,000 g/mol; original thermoplastic PBT polyester raw material: at least 45,000 g/mol; waste thermoplastic PBT polyester: up to 40,000 g/mol; original thermoplastic PLA polyester raw material: at least

80,000 g/mol; waste thermoplastic PLA polyester (oligomeric PLA): 20,000 g/mol; all this being viewed that there is a difference of at least 10% between the weight average molecular weight of the original thermoplastic polyester raw material and of the waste thermoplastic polyester. Those thermoplastic polyesters are viewed as being of the same type that are formed from the same monomer units. For example, the original polylactic acid raw material and the oligomeric lactic acid are of the same type, because the monomer forming them is in both cases lactic acid. The idea behind the present invention is valid for any thermoplastic polyester. Among these the followings are highlighted: polyethylene terephthalate (its abbreviation also frequently used in the present specification: PET), polybutylene terephthalate (its abbreviation also frequently used in the present specification: PBT), and polylactic acid (its abbreviation also frequently used in the present specification: PLA).

Within the scope of the present invention those thermoplastic polyesters are considered to be thermoplastic that melt reversibly at the temperature characteristic of the given type of polyester. There are simple covalent bonds between the monomer molecules of the thermoplastic polyester, and there are weak van der Waals bonds between the polymer chains. The latter bonds are weaker, and so they are easily broken with heat treatment. The processing of thermoplastic polyesters takes place at a high temperature with the exertion of external force. After cooling they solidify and retain the shape given to them during shaping.

Intrinsic viscosity is obtained by extrapolating the reduced viscosity to zero concentration. The Billmeyer formula describes the relationship between intrinsic viscosity and reduced viscosity:

$$\eta = 0.25(\eta_r - 1 + 3\ln\eta_r)C$$

η : intrinsic viscosity (dl/g)

η_r : relative viscosity

C : solution concentration (g/dl)

The following formula is used for calculating relative

5 viscosity:

$$\eta_r = t/t_0$$

t : average efflux time of the solution (s)

t_0 : average efflux time of the solvent (s)

10 Impact strength characterises the resistance of plastics to breakage, during its measurement the magnitude of the impact energy is determined on test specimens that have standard dimensions and a standard notch. Most frequently it is the Charpy and the Izod methods that are used for the

15 determination of the magnitude of impact energy, where the test specimens are subjected to three and two-point bending [Plastics – Determination of Izod impact strength ISO 180); Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test (ISO 179-1)]. The principle of

20 the measurement is the same in both cases. In the case of the Charpy test the impact energy absorbed by the notched test specimen is referred to the cross-sectional surface of the notch of the test specimen. In the case of this test the test specimen is supported at two points, then a hammer is released

25 from a given height to impact the specimen on the side opposite to the notch. The potential energy of the hammer is transformed into kinetic energy while it is falling, a part of which is devoted to fracture, which may be read after the fracture from the angle of over-swing on a calibrated scale.

30 The Izod test is based on a similar principle, but here the fracture is performed with two-point bending. In the case of the Izod test the impact energy absorbed by the notched test specimen is referred to the cross-sectional surface of the notch of the test specimen. The test specimen is impacted with

the hammer from the direction of the notch. The values obtained using standard methods depend on the dimensions of the test specimen and the test conditions; the results are only comparable if the conditions are identical. Nevertheless the aforementioned methods may be used for qualification of raw materials, quality control and for the development of new materials, as the relative impact strength order may be reliably determined using these.

10 Within the scope of the present invention when reference is made to impact strength, this is understood to mean impact strength measured using the notched Izod test and is expressed in kJ/m². In the scope of the present invention the comparison of the impact strengths of two different polyesters is expressed as a percentage value.

Flexible polymers are frequently used for increasing the impact strength of rigid polymers, which may increase impact strength in two different ways: by the creation of microfractures and with shear deformation [Pearson RA., Introduction to the Toughening of Polymers. Toughening of Plastics - Advances in Modeling and Experiments, American Chemical Society; 2000, 1-12.]. The role of the dispersed particles of impact modifier additive is dual: firstly they reduce local stress concentration, as the stress in the surrounding matrix material has to be distributed, secondly they have to make the formation of deformation possible. Certain studies have pointed out that the particle size formed during the processing of the impact modifier additive and the critical distance between the particles are also dependent on the molecular mass of the matrix [Dompas D., Groeninckx G., Isogawa M., Hasegawa T., Kadokura M., Polymer; 1994, 35:4760-4765.]. Furthermore, it was found that in a matrix with a greater molecular mass the broader particle size range of the

impact modifier additive results in an increase of impact strength. Due to their hydroxyl and carboxyl functional groups thermoplastic polyesters are considerably polar, and the elastomer-type impact modifier additives are mostly apolar, so stress is formed on the border between the two when there is a load, due to this it becomes necessary to use a reactive compatibiliser additive. An example of such an additive is E-GMA [Loyens W., Groeninckx G., Polymer; 2002, 43:5679-5691.], in the case of which it was found that following compatibilization it was able to form secondary crosslinks between the hydroxyl / epoxy groups (for example between E-GMA and PET), the structure created by this is more viscous and is less easily deformed. Multiple studies have dealt with the EBA-GMA terpolymer, and with its distribution in thermoplastic polyester. In the case of PET with an intrinsic viscosity of 0.90 dl/g it was found that with an EBA-GMA content of 20 m/m% a 26-times increase in impact strength may be observed. A chemical reaction takes place between the PET chains and the epoxy groups of the EBA-GMA due to the high extrusion processing temperature. Reactive impact modifier additives are a subgroup of impact modifier additives, it should be noted that the efficiency of reactive impact modifier additives only may be increased with waste thermoplastic polyester.

EBA-GMA is also used for increasing the impact strength of glass fibre reinforced PET composites. By systematically increasing the amount of terpolymer between 0-16 m/m%, impact strength increases almost linearly [Cheng H., Tian M., Zhang L. Toughening of recycled poly(ethylene terephthalate)/glass fiber blends with ethylene-butyl acrylate-glycidyl methacrylate copolymer and maleic anhydride grafted polyethylene-octene rubber, Journal of Applied Polymer Science; 2008, 109, 2795-2801.].

In the course of their investigations the inventors of the present invention made the following findings. By separately adding impact modifier additive to the original and to the waste PET fractions then on examining the injection moulded test specimens it may be seen in the scanning electron microscope (SEM) images taken after the selective dissolving of the impact modifier component of the fragment surface of two-component original PET-based mixtures with an EBA-GMA impact modifier content of between 10-20 m/m% that the size of the additive droplets dispersed in the original PET matrix is greater and less regular (fig. 1.a). In the case of the waste PET the droplets formed after the addition of the EBA-GMA impact modifier are smaller (nearly sub-micron) and their shape is more rounded (fig. 1.b). In the case of the original PET the EBA-GMA droplets are irregular in shape due to the cross-linkage taking place in the dispersed phase, the parts secured with cross-links prevent the smaller particle size and the formation of a rounded surface. Contrary to this on the basis of the SEM images it may be seen that even with a 10 m/m% EBA-GMA content the waste PET mixture forms a more finely distributed homogenous dispersion, which results in a small distance between the particles and, due to this, a sharp rise in impact strength.

This is consistent with the findings of Wu et al. [Wu S., Journal of Applied Polymer Science; 1988, 35:549-561.] that by reducing the distance between the dispersed phases to under a critical value the impact energy is absorbed by the extensive shear deformation. In the case of the original PET an EBA-GMA content of 20 m/m% is required in order to achieve a similar increase in impact strength, and significant embrittlement may be observed in the case of EBA-GMA content less than 20 m/m%. The explanation of the phenomenon is that the waste PET has more reactive chain-end functional groups, furthermore due to the increased fluidity resulting from the smaller average

molecular mass they are able to form bonds more quickly and efficiently with the impact modifier additive in the processing conditions, consequentially resulting in the number of stress distribution particles being greatly multiplied and the impact strength of the product being greatly increased compared to an original PET mixture with the same EBA-GMA content. In other words, in the case of the use of waste PET 50% less EBA-GMA (10 m/m% EBA-GMA) impact modifier additive is sufficient to achieve the same impact strength.

10

However, in connection with the increase of the impact strength of thermoplastic polyesters no investigation has been performed to date to determine the relationship between the EBA-GMA and the molecular mass of the matrix material with respect to the efficiency of compatibilisation and the crosslinking reactions.

15

In order to examine the aforementioned relationship two-component thermoplastic polyester mixtures were used containing original or waste fractions, with the other component being the impact modifier additive. The following thermoplastic polyesters were examined in detail: PET, PBT, PLA.

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The increase in the reactive impact strength of two-component (original or waste) thermoplastic PET polyester mixtures was examined with EBA-GMA contents of 0-20 m/m% (increasing the EBA-GMA content by 5 m/m% on each occasion). During the investigations the surprising recognition was made that less than a half of the amount of EBA-GMA impact modifier additive used to date results in a considerable increase in impact strength if the original PET is mixed with waste PET, i.e. PET with a lower molecular mass and containing more reactive chain end groups on average. Usually 20-25 m/m% EBA-GMA impact

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modifier additive is necessary in order to drastically increase the impact strength of rigid original PET.

The difference between original and waste PET observed in
5 impact strength is due to the differences in terms of morphology, boundary surface and deformation properties. During extrusion while the melt is being created at the processing temperature the shorter chain molecules of the waste PET react with the functional groups of the EBA-GMA. In
10 order to create the large specific surface and to successfully increase impact strength it is of key importance to simultaneously compatibilise and fragment the particles of the impact modifier additive. Following this, crosslinking reactions with the unreacted epoxy groups of the impact
15 modifier additive start to occur, thereby stabilising the particle size. However, if the system does not contain a short chain then the crosslinking occurring before the longer and less agile PET chains and the EBA-GMA particles become linked prevents fragmentation of the EBA-GMA particles, and so a
20 greater particle size of the impact modifier additive becomes stabilised. As a consequence to achieve even dispersion of the impact modifier additive, due to the compatibilisation the carboxyl/epoxy group reaction must come before the crosslinking reaction occurring between the hydroxyl/epoxy
25 groups. In other words the increased proportion of carboxyl terminal groups and the lower viscosity of the degraded PET chains contribute to the prevalence of compatibilisation, thereby preventing crosslinking. Therefore, preferably it is recommended that a significantly degraded (with intrinsic
30 viscosity less than 0.74 dl/g) 10 m/m% waste fraction be used in order for the EBA-GMA to successfully increase impact strength.

In the case of PBT, which is very similar to PET in terms of structure and its functional groups, functioning similar to PET may be presumed in the course of the increase of impact strength, as PBT is a thermoplastic polyester, as mentioned previously, that has a very similar structure to PET. Both polyesters are produced through the reaction of terephthalic acid and an alcohol. While in the case of PBT the alcohol is butylene glycol, in the case of PET it is ethylene glycol. However, this apparently small difference between the repeating units still results in that the properties of the two similarly structured polymers are different, and thereby so are their areas of use. Because of the greater distance of the phenyl rings it crystallizes more effectively than PET, under normal processing conditions amorphous PBT products cannot be produced. In contrast with this the shorter ethylene group in the molecular chain of PET makes crystallinity optional. On fast cooling amorphous PET is obtained, but semi-crystalline PET is obtained if cooling is performed slowly. The latter usually has better mechanical properties, including strength, rigidity and heat resistance, than semi-crystalline PBT. However, PET is still mostly used in amorphous form, for example as packaging material, where the transparency characteristic of the amorphous structure is exploited. However, because of its rapid crystallization transparent PBT products cannot be produced. Compared to semi-crystalline PET, PBT, being less rigid and having better impact strength, is used in the plastic components of electronics products. Therefore, when sorting used electronic products, an increasing proportion of which is being collected from year to year, PBT, as recycled secondary polymer raw material, is appearing in increasing quantities.

Within the scope of the present invention the impact strength of PBT was increased, similarly to PET, with the EBA-GMA

impact modifier additive. The effect of the impact modifier additive may be greatly amplified with the use of waste PBT (free of contaminants created during the production of electronic components, with lower molecular mass due to the multiple thermo-mechanical processing, i.e. the number of repeated units is smaller, and so has increased flowability). According to the results of our investigations compared to the effect of mixing 10 m/m% EBA-GMA impact modifier additive to the original PBT raw material, if the same amount of impact modifier additive is used in waste PBT an approximately 4-times increase in impact strength may be achieved (notched Izod impact strength above 20 kJ/m²). Using another approach, exceptional notched Izod impact strength of 25 kJ/m² may be achieved using 5 m/m% less EBA-GMA (10 m/m% instead of 15 m/m%) than in the case of the matrix formed with the original PBT raw material. Our DSC (differential scanning calorimetry) test results show that the EBA-GMA additive is more effective at preventing the crystallization of waste PBT than in the original PBT polymer. This is explained by that due to the greater molecular mobility of the lower molecular mass polymer chains characteristic of waste PBT and due to its more reactive carboxyl groups at chain ends, under the same processing conditions more bonds may be formed more quickly with the epoxy groups of the impact modifier additive. It is these crosslinks that prevent the polymer chains from being arranged in a crystal lattice, thereby resulting in a finer phase structure. The fine and homogenous distribution of the EBA-GMA displayed in waste PBT results in outstanding notched Izod impact strength of above 20 kJ/m² with just 10% additive. Exploiting this phenomenon in the case of specimens containing 10% EBA-GMA a 40% improvement in impact strength may be achieved by using a mixture of 80 m/m% original PBT and 20 m/m% waste PBT as the matrix material instead of 100 m/m% original PBT. It should be noted that the mass ratio of 80%-

20% is not optimised, therefore by using a suitable original PBT and waste PBT ratio an even greater improvement in impact strength may probably be achieved.

5 PLA is also classed as a thermoplastic polyester, however its rigid behaviour prevents its widespread use in numerous areas. In order to make PLA more utilisable it is essential to increase its impact strength while also ensuring biological decomposition. Increasing the impact strength of PLA by
10 copolymerisation is very expensive and has not yet been achieved at the industrial scale. The main method used for increasing impact strength is the admixture of the polymer in its melt state. Admixture is a cheaper method that may also be used on the industrial scale, and its disadvantage is that due
15 to the effect of certain additives that are not biodegradable in the majority of cases the entire mixture loses its biodegradable property. In the literature it is known that if natural rubber grafted with glycidyl methacrylate (hereinafter NR-g-GMA) is added to PLA containing unfilled and natural
20 rubber then already at an NR-g-GMA content of 1 m/m% the elongation at rupture and impact strength values may be significantly improved [Juntuek P., Ruksakulpiwat C., Chumsamrong P., Ruksakulpiwat Y., Effect of Glycidyl Methacrylate-Grafted Natural Rubber on Physical Properties of
25 Polylactic Acid and Natural Rubber Blends, Journal of Applied Polymer Science; 2011, 125(1), 745-755.]. An additional solution for increasing the impact strength of PLA is the admixture with natural rubber (hereinafter NR). In this case the incompatibility of PLA and natural rubber due to their
30 structures is not a factor that may be ignored: the PLA is polar while rubber counts as an apolar compound. The weak boundary surface adhesion formed between the two damages the mechanical properties that are sensitive to this. On the basis of the method disclosed within the scope of the present

invention it was possible to increase the impact strength of PLA with the addition of epoxidized natural rubber (ENR). On the basis of the results of investigations it may be determined that the tensile strength of the specimens drops with the addition of ENR, as does the modulus value of their elasticity, in other words the specimen became more flexible. According to that described above in order to increase impact strength it is essential to increase compatibility between the ENR and the PLA, which was solved with the use of lower molecular weight, oligomeric lactic acid (OLA), the average molecular mass of which is lower than 3000 g/mol. In this case the epoxy groups of the ENR react with the free carboxyl groups of the more agile OLA in greater proportion. There is more than an order of magnitude of difference between the elongation at rupture values in the case of the PLA + 10 m/m% OLA + 10 m/m% ENR specimen and the OLA-free PLA + 10 m/m% ENR specimen, furthermore the Izod impact strength of the specimen also containing OLA is significantly greater (5-times). In spite of the identical ENR content of the two specimens the low molecular mass oligomeric lactic acid (OLA) as additive effectively reduced the particle size characteristic of ENR and improved distribution in the PLA matrix under identical processing conditions, which then resulted in an improvement of the mechanical properties of the product.

25

The most common industrial processing technologies of thermoplastic polymers are extrusion, injection moulding, moulding, foam moulding and compression. The particle size of the components used during the listed thermoplastic polyester processing technologies is an important factor determining the various properties of the finished product. The particle size is selected to correspond with the sizes that the apparatuses (extruder or internal mixing kneading chamber) are able to accommodate. It may be necessary to dry the starting materials

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before certain processes are performed. Among the listed industrial processing technologies, one of the most common types is extrusion, with which panels, strips, profile products, and products produced with further processing may be manufactured by hot shaping.

Essentially any thermoplastic polyester waste may be processed with extruding and subsequent granulation and thereby thermoplastic polyester products may be produced that have increased impact strength in the way according to the present invention. The use of PET waste in this way may give new impetus to the recycling of PET even in the case of unsellable, very degraded fractions.

15

Examples

Example 1: thermoplastic PET polyester

During the extrusion process original PET thermoplastic polyester raw material, waste PET thermoplastic polyester and impact modifier additive are used, where the original PET thermoplastic polyester raw material and the waste PET thermoplastic polyester are differentiated in that the weight average molecular weight of the waste PET thermoplastic polyester is at least 10% lower than that of original PET thermoplastic polyester raw material of the same type. The following steps are performed during the extrusion process:

a) before processing original NePET thermoplastic polyester of the appropriate particle size (Neo Group, PET type; intrinsic viscosity 0.80 ± 0.02 dl/g) and ground waste PET of the appropriate particle size (JP Pack, intrinsic viscosity 0.56 ± 0.03 dl/g) is dried at 160 °C for 4 hours. It is not necessary to dry the impact modifier additive EBA-GMA of the

appropriate particle size (Elvaloy PTW (DuPont, EBA-GMA type, 5.25 m/m% GMA content; melting point: 72 °C) as long as it is stored in factory sealed packaging;

- b) the original PET raw material, the waste PET, and the EBA-GMA are fed into a twin-screw extruder (LTE 26-48, Labtech Scientific) via the hopper and melted and homogenised at 240-290 °C, the screw speed is 40-60 1/min, the mass ratios of the three components are contained in table 1;
- c) the cord product produced during extrusion in step b) is granulated, then from this granules test specimens are produced by injection moulding at a zone temperature of between 260-270 °C for the impact strength tests (during injection moulding the temperature of the tool is 60 °C), the impact strengths measured for the individual ratios of waste thermoplastic PET polyester as a function of the EBA-GMA content are depicted in the graph in Figure 2.

Specimen	Original thermoplastic PET polyester raw material (m/m%)	Waste thermoplastic PET polyester (m/m%)	EBA-GMA impact modifier additive (m/m%)
1.	85.0	5.0	10.0
2.	82.5	5.0	12.5
3.	80.0	5.0	15.0
4.	80.0	10.0	10.0
5.	77.5	10.0	12.5
6.	75.0	10.0	15.0
7.	75.0	15.0	10.0
8.	72.5	15.0	12.5
9.	70.0	15.0	15.0

Table 1

20

It may be seen that in the case of the use of 10 - 15 m/m% waste thermoplastic PET polyester and more than 12.5 m/m% EBA-

GMA impact modifier additive the impact strength of the thermoplastic polyester obtained exceeds 40 kJ/m². In Figure 2.b it may be seen that using the original thermoplastic PET polyester raw material on its own a similar degree of impact strength may only be achieved with the use of a significantly higher ratio of EBA-GMA impact modifier additive.

Example 2: thermoplastic PBT polyester

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During the extrusion process original PBT thermoplastic polyester raw material, waste PBT thermoplastic polyester and impact modifier additive are used, where the original PBT thermoplastic polyester raw material and the waste PBT thermoplastic polyester are differentiated in that the weight average molecular weight of the waste PBT thermoplastic polyester is at least 10% lower than that of original PBT thermoplastic polyester raw material of the same type. The following steps are performed during the extrusion process:

20

a) before processing original Pocan B1305 (Lanxess, PBT type; MFI value (250 °C/2.16 kg): 49.4 g/10 min) thermoplastic polyester and ground waste PBT (injection moulding scrap, MFI value (250 °C/2.16 kg) 54.0 g/10 min) are dried at 120 °C for 4 hours. It is not necessary to dry the impact modifier

25

additive EBA-GMA (Elvaloy PTW (DuPont, EBA-GMA type, 5.25 m/m% GMA content; melting point: 72 °C) as long as it is stored in factory sealed packaging;

30

b) 70 m/m% original PBT raw material, 20 m/m% waste PBT, and 10 m/m% EBA-GMA are fed into a twin-screw extruder (LTE 26-48, Labtech Scientific) via the hopper and melted and homogenised at 225-260 °C, the screw speed is 50-70 1/min;

c) the cord product produced during extrusion in step b) is granulated, then from this granules test specimens are produced by injection moulding at a zone temperature of

between 225-260 °C for the impact strength tests (during injection moulding the temperature of the tool is 60 °C).

In Figure 3 it may be seen that the notched Izod impact strength of the thermoplastic polyester composition according to Example 2 (10 m/m% EBA-GMA, 70 m/m% original PBT raw material, 20 m/m% waste PBT) is 7.38 kJ/m², in other words better than the value of the Izod impact strength of 5.17 kJ/m² of the composition not containing the waste PBT (10 m/m% EBA-GMA, 90 m/m% original PBT raw material) and exceeds the value of compositions not containing the EBA-GMA (100 m/m% original PBT raw material; 20 m/m% waste PBT, 80 m/m% original PBT raw material).

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Example 3: thermoplastic PLA polyester

During the extrusion or kneading chamber mixture formation original PLA thermoplastic polyester raw material, waste thermoplastic polyester (oligomeric PLA) and impact modifier additive of the appropriate particle size are used, where the original PLA thermoplastic polyester raw material and the waste thermoplastic polyester (oligomeric PLA) are differentiated in that the weight average molecular weight of the waste thermoplastic polyester is at least 10% lower than that of original PLA thermoplastic polyester raw material of the same type. The following steps are performed during the compression (shaping) process:

- a) before processing the original PLA (Ingeo™ Biopolymer 2003D, NatureWorks, average molecular mass 100.500 g/mol) is dried at 80 °C for 4 hours;
- b) 80 m/m% original PLA raw material, 10 m/m% oligomeric lactic acid (OLA8-10T, Condensia Glyplast, average molecular mass approximately 2000 g/mol, which value is at least 10% lower

than that of the original PLA) and 10 m/m% ENR (Epoxyprene ENR50) impact modifier additive are homogenised in a Brabender Plastograph internal mixing kneading chamber at 190 °C at a speed of 50 1/min for 10 minutes;

- 5 c) the mixture homogenised in step b) is compressed into 100×100×4 and 160×160×0.5 mm sheets in a Teach-Line Platen Press 200E laboratory press at 190 °C and at a pressure of 50 bar, with additional cooling during compression;
- 10 d) test specimens are made from the flat sheets using a band saw or by punching.

On the column chart in Figure 4 it may be seen that the notched Izod impact strength of the thermoplastic polyester composition according to Example 3 (10 m/m% EBA-GMA, 80 m/m% 15 original PLA raw material, 10 m/m% waste PLA, in this case oligomeric lactic acid) is 3.6 kJ/m², in other words more than five times greater than the notched Izod impact strength value of the composition not containing waste PLA (in this case 20 oligomeric lactic acid) (10 m/m% EBA-GMA, 90 m/m% original PLA raw material) and exceeds the value of compositions not containing the EBA-GMA (100 m/m% original PLA raw material; 10 m/m% waste PLA, in this case oligomeric lactic acid, 90 m/m% original PLA raw material).

25 Example 4: thermoplastic PET polyester

The procedure was as in the case of Example 1 with the difference that instead of the waste thermoplastic PET polyester the same % proportion of PET was used that was 30 produced by setting the moisture content of the original thermoplastic PET raw material in a climate chamber, then due to the effect of the high temperature used in step b) the molecular mass reduction takes place *in situ*. In the present example 13 m/m% EBA-GMA (Elvaloy PTW (DuPont, EBA-GMA type,

5.25 m/m% GMA content; melting point: 72 °C) impact modifier additive was used.

In Figure 5 it may be seen that with an identical amount (13
5 m/m%) of impact modifier additive, compared to the dry (0%
moisture content) original thermoplastic PET polyester
approximately six times greater impact strength may be
achieved with original thermoplastic PET polyester with a
moisture content of 0.2% (due to the effect of the molecular
10 mass reduction caused by hydrolytic degradation occurring in
the high-temperature step b)).

The significant advantage of the solution according to the
15 present invention compared to the thermoplastic polyesters
according to the state of the art is that it enables the
recycling of a significant amount of waste polyester of
varying quality, and that is even significantly degraded. The
latter may be selectively collected household waste,
20 industrial waste, polymer with reduced molecular mass due to
in situ degradation (e.g. moisture content), or even
surface/sea wastes, which represent an increasingly severe
environmental burden today. During recycling polyester usually
becomes significantly more rigid, which limits the
25 possibilities of its use. However, in the case of the method
according to the present invention it is the waste fraction
itself that contributes to the outstanding increase of the
impact strength of the product and to the reduction of the
amount of impact modifier used. Furthermore, the method
30 according to the present invention is suitable for the
production of secondary raw materials and recycled products
that satisfy special demands, with greater added value
compared to conventional recycling, and still in a cost-
effective way.

With the method according to the present invention a large amount of waste with inhomogeneous quality may be reused in a way that adds value during the improvement of the impact strength of a thermoplastic polyester.

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Claims

1. Thermoplastic polyester, **characterised by** that it
5 contains original thermoplastic polyester raw material,
waste thermoplastic polyester and impact modifier
additive, where the original thermoplastic polyester raw
material and the waste thermoplastic polyester are of the
same type and are selected from the following list:
10 polyethylene terephthalate (PET), polybutylene
terephthalate (PBT) and polylactic acid (PLA),
furthermore where the original thermoplastic polyester
raw material and the waste thermoplastic polyester are
differentiated by that the weight average molecular
15 weight of the waste thermoplastic polyester is at least
10% lower than that of original thermoplastic polyester
raw material of the same type.
2. Thermoplastic polyester according to claim 1,
20 **characterised by** that the type of the thermoplastic
polyester is polyethylene terephthalate (PET), the impact
strength of which is at least 1.5 times, preferably at
least 3 times, most preferably at least 6 times that of
thermoplastic PET polyester not containing waste
25 thermoplastic polyester in the case of the use of the
same amount of impact modifier additive.
3. Thermoplastic polyester according to claim 1,
characterised by that the type of the thermoplastic
30 polyester is polybutylene terephthalate (PBT), the impact
strength of which is at least 1.25 times that of
thermoplastic PBT polyester not containing waste
thermoplastic polyester in the case of the use of the
same amount of impact modifier additive.

4. Thermoplastic polyester according to claim 1,
characterised by that the type of the thermoplastic
polyester is polylactic acid (PLA), the impact strength
5 of which is at least 3 times that of thermoplastic PLA
polyester not containing waste thermoplastic polyester in
the case of the use of the same amount of impact modifier
additive.
- 10 5. Thermoplastic polyester according to claim 1 or 2,
characterised by that the type of the thermoplastic
polyester is polyethylene terephthalate (PET), the
intrinsic viscosity of the waste thermoplastic PET
polyester is a maximum of 0.74 g/dl.
- 15 6. Thermoplastic polyester according to any of claims 1
to 5, **characterised by** that it contains an epoxy
functional impact modifier additive, which preferably is
selected from a group containing the following: ethylene
20 glycidyl methacrylate (E-GMA), ethylene-butyl acrylate-
glycidyl methacrylate (EBA-GMA), epoxidized rubber
elastomer.
- 25 7. Thermoplastic polyester according to any of claims 1,
2 and 5 to 6 **characterised by** that the type of the
thermoplastic polyester is polyethylene terephthalate
(PET), the thermoplastic polyester contains 15-80 m/m%
original thermoplastic polyester raw material, 10-75 m/m%
waste thermoplastic polyester and 2.5-20.0 m/m% impact
30 modifier additive; preferably 65-80 m/m% original
thermoplastic polyester raw material, 10.0-35.0 m/m%
waste thermoplastic polyester and 10-15 m/m% impact
modifier additive; most preferably 77.5 m/m% original
thermoplastic polyester raw material, 10.0 m/m% waste

thermoplastic polyester and 12.5 m/m% impact modifier additive.

5 8. Method for the production of thermoplastic polyester, **characterised by** that during the method original thermoplastic polyester raw material, waste thermoplastic polyester and impact modifier additive are used, where the original thermoplastic polyester raw material and the waste thermoplastic polyester are differentiated by that
10 the weight average molecular weight of the waste thermoplastic polyester is at least 10% less than that of original thermoplastic polyester raw material of the same type, and the method contains the following steps:
a) if necessary the original thermoplastic polyester raw material, the waste thermoplastic polyester and the
15 impact modifier additive are processed to have the appropriate particle size and then, optionally, dried;
b) the original thermoplastic polyester raw material, the waste thermoplastic polyester and the impact modifier
20 additive are homogenised in the form of a melt, which is preferably performed by extrusion or internal mixer kneading at a high temperature;
c) optionally the homogenous granulate obtained in step b) is shaped at the appropriate temperature;
25 and where the type of the original thermoplastic polyester raw material and of the waste thermoplastic polyester is selected from among the followings: polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polylactic acid (PLA).

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9. Method for the production of thermoplastic polyester according to claim 8, **characterised by** that the shaping according to step c) is extrusion, compressing or injection moulding.

10. Method for the production of thermoplastic polyester according to claim 8, **characterised by** that the process according to step b) is extrusion, which is performed in a twin-screw extruder.

11. Method for the production of thermoplastic polyester according to any of claims 8 to 10, **characterised by** that the temperature applied in step b) is between 190 °C - 290 °C, preferably in the case of PET between 240 °C - 290 °C, in the case of PBT between 225 °C - 260 °C, in the case of PLA between 190 °C - 220 °C; the temperature applied in step c) is between 150 °C - 300 °C, preferably in the case of PET between 235 °C - 270 °C, in the case of PBT between 225 °C - 260 °C and in the case of PLA between 180 °C - 210 °C.

12. Method for the production of thermoplastic polyester according to any of claims 8 to 11, **characterised by** that the type of the thermoplastic polyester is PET, the thermoplastic polyester contains 15-80 m/m% original thermoplastic polyester raw material, 10-75 m/m% waste thermoplastic polyester and 2.5-20 m/m% impact modifier additive; preferably 65-80 m/m% original thermoplastic polyester raw material, 10.0-35.0 m/m% waste thermoplastic polyester and 10-15 m/m% impact modifier additive; most preferably 77.5 m/m% original thermoplastic polyester raw material, 10.0 m/m% waste thermoplastic polyester and 12.5 m/m% impact modifier additive.

13. Method for the production of thermoplastic polyester according to any of claims 8 to 12, **characterised by** that the appropriate average molecular mass of the original

thermoplastic polyester raw material and/or the waste thermoplastic polyester is formed *in situ* at the high temperature used during step b) by omitting the drying step of a part of or all of the original thermoplastic polyester raw material and/or the waste thermoplastic polyester and/or by increasing its moisture content.

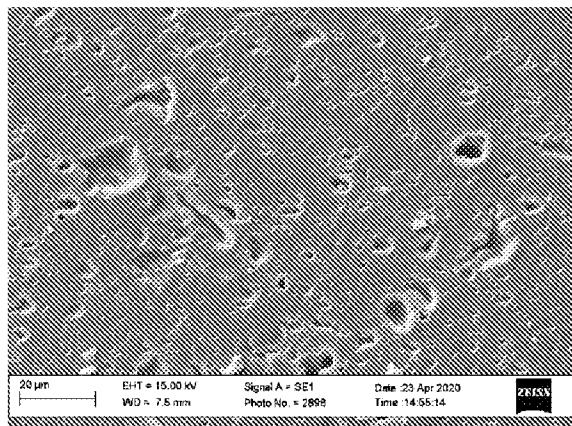


Figure 1.a

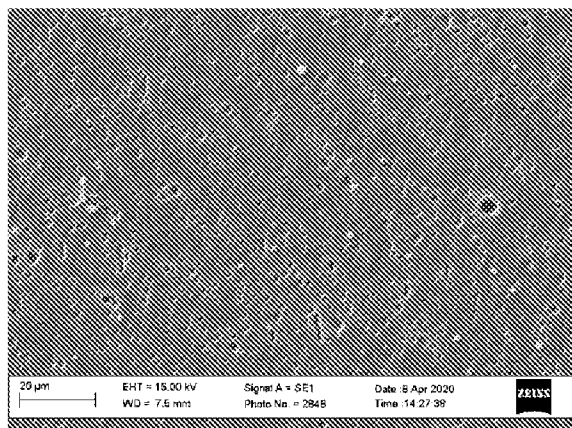


Figure 1.b

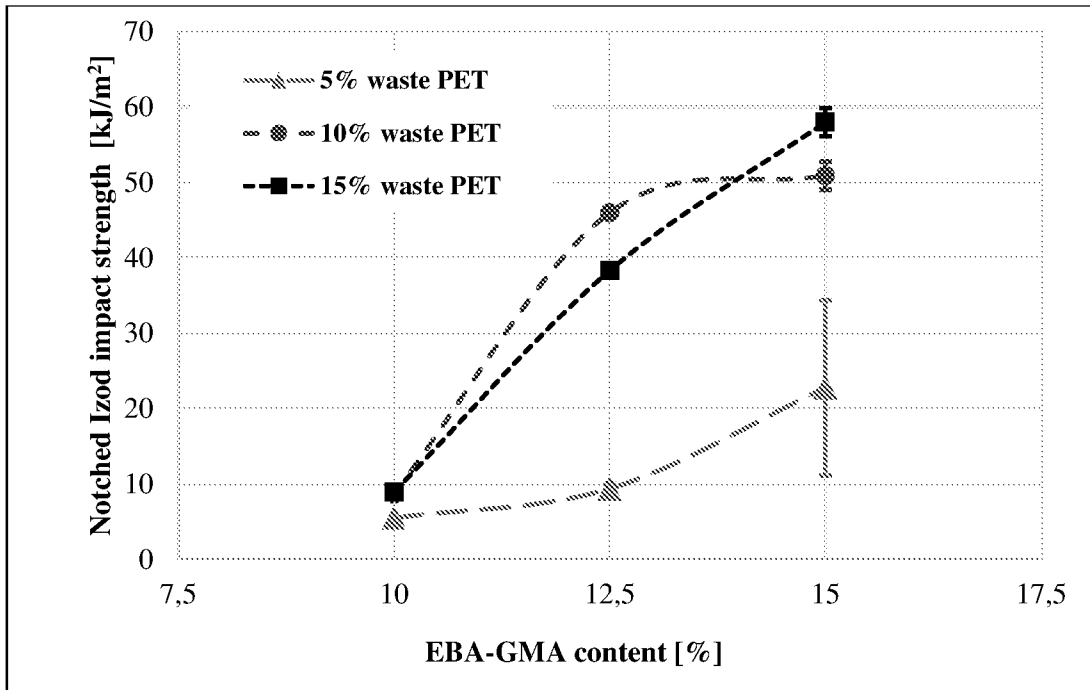


Figure 2.a

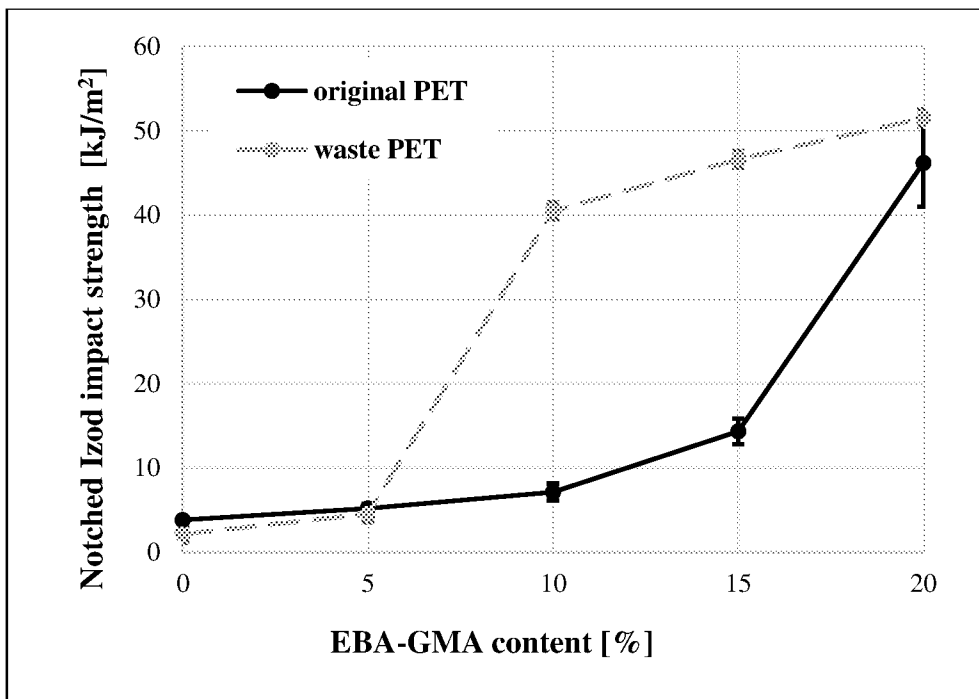


Figure 2.b

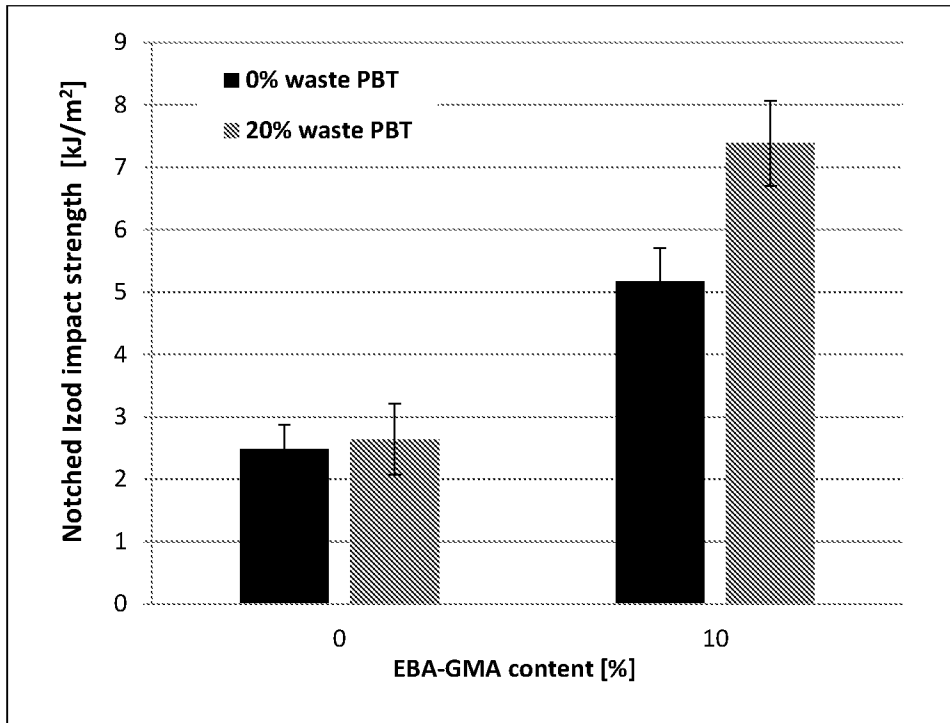


Figure 3

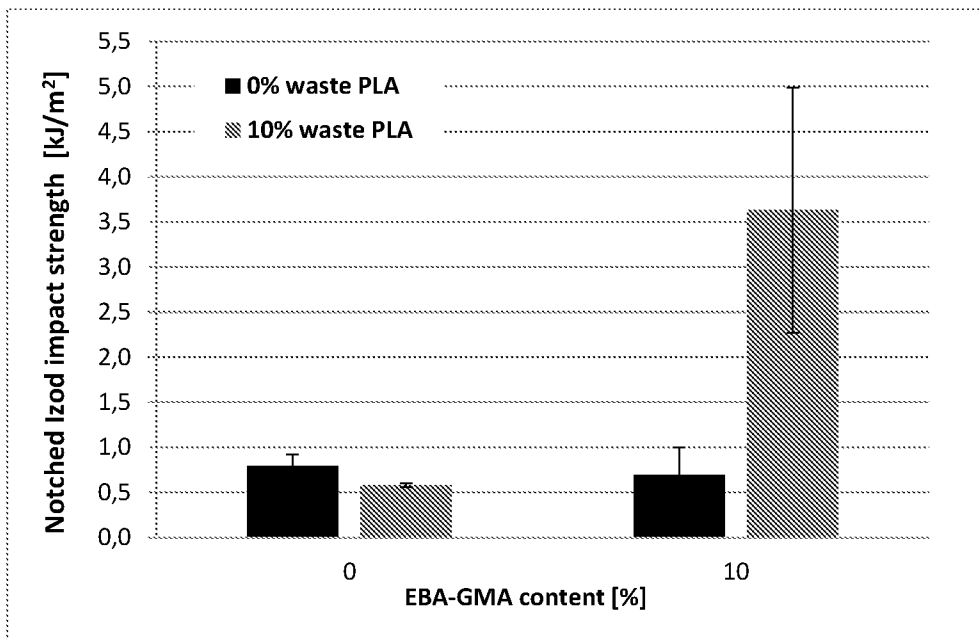


Figure 4

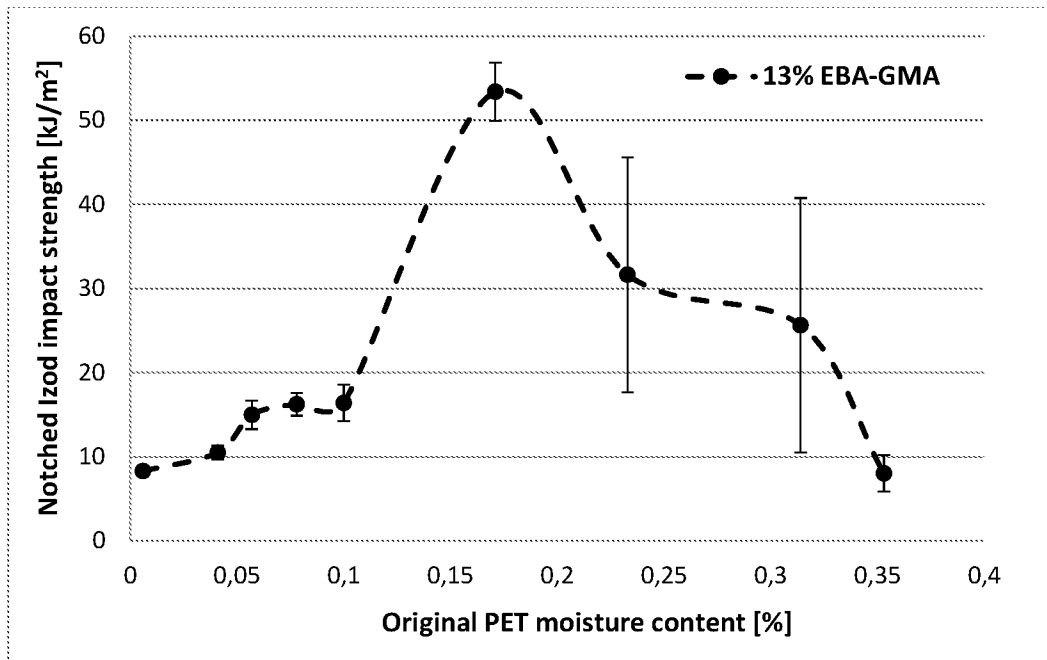


Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/HU2021/050064

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L67/02 C08L67/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/115029 A2 (UNIV GUELPH [CA]) 31 July 2014 (2014-07-31) claims 1, 3, 5, 48-50 page 9, line 25 - page 10, line 5; claims 1,3,5 page 9, lines 11-13 page 12, line 4 - page 13, line 12 -----	1, 4, 6, 9-11, 13
X	WO 2019/217675 A1 (SABIC GLOBAL TECHNOLOGIES BV) 14 November 2019 (2019-11-14) claims 1,2,8 examples paragraphs [0010], [0024] ----- -/--	1-13

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "E" earlier application or patent but published on or after the international filing date
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search
26 April 2022

Date of mailing of the international search report
03/05/2022

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INTERNATIONAL SEARCH REPORT

International application No

PCT/HU2021/050064

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 2019/106124 A1 (LEGO AS [DK]) 6 June 2019 (2019-06-06) cited in the application claims 1,9-13 page 21, lines 5-10 page 14, line 25 - page 15, line 26 -----</p>	1-13
A	<p>MONTAVA-JORDA SERGI ET AL: "Mechanical Recycling of Partially Bio-Based and Recycled Polyethylene Terephthalate Blends by Reactive Extrusion with Poly(styrene-co-glycidyl methacrylate)", POLYMERS, vol. 12, no. 1, 9 January 2020 (2020-01-09), page 174, XP055914590, DOI: 10.3390/polym12010174 cited in the application page 4, paragraph 2.2; table 1 -----</p>	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/HU2021/050064

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014115029 A2	31-07-2014	US 2015361258 A1 WO 2014115029 A2	17-12-2015 31-07-2014

WO 2019217675 A1	14-11-2019	CN 112912440 A EP 3790930 A1 JP 2021523276 A KR 20210008513 A US 2021238410 A1 WO 2019217675 A1	04-06-2021 17-03-2021 02-09-2021 22-01-2021 05-08-2021 14-11-2019

WO 2019106124 A1	06-06-2019	BR 112020010243 A2 CN 111417445 A EP 3717086 A1 JP 2021504064 A KR 20200096559 A US 2020391133 A1 WO 2019106124 A1	10-11-2020 14-07-2020 07-10-2020 15-02-2021 12-08-2020 17-12-2020 06-06-2019
