A composition comprises polyalkylene terephthalate and terpolymer of alkylene diol, isophthalic acid and terephthalic acid, and polyalkylene terephthalate reinforcing fiber. The composition may be used to form an article, alone or with other thermoplastic material, at lower processing temperature, with higher melt fluidity. The article formed is characterized with lower warpage and improved mechanical properties. The article may be useful for automotive, electrical, household, construction, and industrial applications. A method of preparing such thermoplastic polyester is also disclosed.
Composition of reinforced polyalkylene terephthalate, preparation and use thereof

Description

The present invention is directed to a composition of modified reinforced polyalkylene terephthalate, which has superior processability such as lower processing temperature and higher melt flowability, as well as better material performance such as lower warpage when forming a shaped article together with another thermoplastic material, and higher mechanical properties. The present invention is also directed to the preparation and use of said composition.

Thermoplastic polyester, i.e., polyalkylene terephthalate (PAT), such as polybutylene terephthalate (PBT) and polyethylene terephthalate (PET), is commonly reinforced by PAT-reinforcing fiber, such as glass fiber (GF), and is commercially available. PAT is typically formed into an article utilizing melt forming technique such as extrusion, blow molding or injection molding. A lower processing temperature makes PAT easier to process because PAT melt flows faster. As processing temperature is dictated by melting point, the parameter to watch in searching of lower processing temperature is mostly melting point of the PAT. On the other hand, it is apparent that increasing melt flowability will be beneficial if the melt flowability can be increased via modification. Therefore the low processing temperature (or melting point) and/or higher melt flowability also decreases cycle-time for making the articles.

In recent years, GF reinforced PBT has been used to replace steel in extruded polyvinyl chloride (PVC) profile as a reinforced material. In US2010/0319843A1, PBT strip and PVC profile are produced separately and the PBT strip is inserted into PVC profiles to reinforce the PVC profiles as replacement of metal insert. However, with increased GF content, the GF-reinforced PAT suffers from poor processability and performance, such as high warpage, high processing temperature, and low melt flowability. It is essential to improve the low warpage and processability for GF reinforced PAT to be used in many injection molding, blow molding and extrusion applications.

When the GF-reinforced PAT is used to form composite structure with other thermoplastic material, application of GF-reinforced PAT is also limited by the high processing temperature of PAT. For example, in EP243152A2, GF filled PBT is co-extruded with PVC to produce co-extruded PVC profile. However, glass filled PBT's melting point (and thus processing temperature) is too high. The melt PBT material caused color change, degradation, and poor adhesion to the PVC profile with poor overall performances.

Therefore, there is a need to find a way to produce reinforced PAT with high GF content and lower processing temperature, lower warpage, higher flowability, and/or better mechanical properties.
In JP41784725A, terpolymer of ethylene glycol, isophthalic acid and terephthalic acid (PEIT) and PBT is blended to obtain low melting point PBT. However, JP41784725A did not disclose the use of GF to reinforce PAT. In fact, the PEIT modified PBT of the application was targeted to improve thermal bonding of textile layers in fiber industry. There is no need to incorporate glass fiber for such composition or application. In addition, melting point of the PEIT-modified PBT is still too high to be used for, for example, forming composite structure with PVC.

Thus, an objective of the present invention is to provide a composition comprising PAT, more specifically PBT or PET, which is reinforced by PAT-reinforcing fiber, more specifically GF, and is modified by a terpolymer of an alkylene diol, isophthalic acid and terephthalic acid (PAIT), more specifically PEIT, so that the product has superior processing properties such as lower processing temperature, higher flow, better mechanical properties, and lower warpage.

Another objective of the present invention is to provide a process for the production of said composition.

A further objective of the present invention is to provide the use of said composition to form shaped article, either alone or with other thermoplastic materials, by melt forming such as blow molding, injection or co-extrusion.

A final objective of the present invention is to provide a shaped article using said composition. The objects are achieved by a composition comprising i) polyalkylene terephthalate, ii) (polyalkylene isophthalate)-co-(polyalkylene terephthalate), iii) polyalkylene terephthalate-reinforcing fiber, and iv) optionally, one or more additives, wherein the alklenes in component i) is selected from the group consisting of methylene group, ethylene group, propylene group, butylene group and cyclohexene dimethylene group, and the alkylene in component ii) is selected from the group consisting of methylene, ethylene, propylene and butylene and a process for its production, wherein the components i) to iii) and optionally iv), or precursor of any of the components thereof, are compounded under the condition that component i) and ii) can be melt processed, the use of the composition, wherein the composition is melt formed, optionally together with one or more additional thermoplastic material, to form shaped article. The object is furthermore achieved by a process to modify a first thermoplastic material with a second thermoplastic material, wherein the second thermoplastic material is melt formed together with the first thermoplastic material, wherein the melting point of the modified first thermoplastic material is reduced, and by the use of the modified first thermoplastic material produced by the process, wherein the modified first thermoplastic material is melt formed, optionally together with an additional third thermoplastic material.

It was found that by blending PAT, more specifically PBT or PET, with PAIT, more specifically PEIT, and PAT-reinforcing fiber, more specifically GF, the objectives of the present invention can be achieved. The so-produced PAIT-modified fiber-reinforced PAT has superior processability such as higher melt flowability of the melt and lowered melting point (and thus lower pro-
cessing temperature), and has lower warpage of the product when being used to form shaped article together with other thermoplastic material, such as PVC. The PAIT-modified fiber-reinforced PAT can be formed into shaped body alone or in combination with other thermoplastics, such as PVC, by forming composite structure.

Figs. 1 to 3 are DSC of PEIT-modified GF-reinforced PBT in Example III.

Fig. 4 is a photograph showing a profile formed by co-extruding PVC with GF-reinforced PBT.

The composition comprising PAT, PAIT and PAT-reinforcing fiber can be preferably obtained by compounding PAT, PAIT and the PAT-reinforcing fiber.

In an embodiment of the invention, PAT is a thermoplastic copolymer of an alkylene diol and an alkylene terephthalate. Preferably, the PAT is selected from the group consisting of polymethylene terephthalate, polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate and polycyclohexene dimethylene terephthalate. Most preferably, the PAT is selected from PET and PBT. It can be appreciated by those skilled in the art that mixtures of PAT can also be used.

Suitable specification of the PAT, such as molecular weight, and the content of the PAT in the composition, can be determined by those skilled in the art by conventional means in order to achieve desirable mechanical property and processability.

In an embodiment of the invention, PAIT is a thermoplastic terpolymer of an alkylene diol, isophthalic acid and terephthalic acid. Preferably, the PAIT is selected from the group consisting of poly(methylene terephthalate-co-polyethylene isophthalate), polyethylene terephthalate-co-polyethylene isophthalate, polypropylene terephthalate-co-polypropylene isophthalate and polybutylene terephthalate-co-polybutylene isophthalate. The copolymer can be of any architecture, such as that of random, alternating or block copolymer. Most preferably, the PAT is selected from PEIT and PBIT. It can be appreciated by those skilled in the art that mixtures of PAIT can also be used.

Suitable specification of the PAIT, such as molecular weight, molar ratio of terephthalate units and the isophthalate units, and content of the PAIT in the composition, can be determined by those skilled in the art by conventional means in order to achieve desirable mechanical property and processability. It should be noticed that the content of isophthalate unit in PAIT is preferably higher than zero, more preferably 5 to 50%, even more preferably 10 to 40%, most preferably 15 to 25%, by mole based on the total number of isophthalate unit and terephthalate unit in the PAIT.

In an embodiment of the invention, PAT-reinforcing fiber is any fibrous material that can be used to reinforce PAT. Preferably, the PAT-reinforcing fiber is selected from the group consisting of
glass fibers, polyamide fibers, cellulose fibers, and ceramic fibers, however, it is can be appreciated by those skilled in the art that the fiber is not limited to these. Most preferably, the PAT-reinforcing fiber is GF. It can also be appreciated that various combinations and mixtures of the above PAT-reinforcing fibers may be used.

More preferred PAT-reinforcing fibers are those comprising functional structures such as epoxy groups for reacting with the carboxyl groups of the PAT to create ether linkages. The reaction between the functional structures and the PAT or the intermediate compound may also ensure that the fiber has good adhesion thereby improving the physical properties of the article formed therefrom. The functional structures are preferably a polyurethane structure, and, more preferably, a reaction product of bis(cyclohexylisocyanato) methane, 1,6-hexanediol and adipic acid polyester, and bisphenol glycidyl ether.

Suitable specification of the PAT-reinforcing fiber and content of the fiber in the composition can be determined by those skilled in the art by conventional means in order to achieve desirable mechanical property and processability.

It can be appreciated by those skilled in the art that the composition may further comprise other known additives.

For example, in an embodiment of the invention, the composition may further include one or more lubricant. If included, the lubricant is preferably an ester or amide of saturated aliphatic carboxylic acids having from 10 to 40 carbon atoms and saturated aliphatic alcohols or amines having from 2 to 40 carbon atoms. It is believed that when the lubricant includes fatty acid chains that are highly hydrophobic, the lubricant further aids in the hydrolysis resistance of the composition and the thermoplastic polymer. A preferred lubricant is pentaerythritol tetrastearate. If included, the lubricant is preferably present in an amount of about 0.01 to 5% by weight, more preferably of about 0.01 to 3% by weight, and most preferably of about 0.01 to 2% by weight, each based on the total weight of the composition.

In an embodiment of the invention, the composition may include one or more thermal antioxidant. If included, the thermal antioxidant preferably has a sterically hindered phenolic group. Those skilled in the art appreciate that various thermal antioxidants are available to stabilize the composition and the thermoplastic polymer against discoloring and to prevent thermo-oxidative degradation. In one embodiment, the thermal antioxidant is one or more material selected from the group consisting of pentaerythritoltetraakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), tetrakis(methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate) methane, octadecy1-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, 1,3,5-trimethy1 -2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, and 4,4'-(2,2-diphenylpropyl)diphenylamine. It is also to be appreciated by those skilled in the art that various combination and mixtures of the above thermal antioxidants may also be utilized with the present invention. The preferred thermal antioxidant is pentaerythritol tetraakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate). If included, the thermal an-
tioxidant is preferably present in an amount of 0.01 to 5% by weight, more preferably of 0.01 to
3% by weight, and most preferably of 0.01 to 1.5% by weight, each based the total weight of the
composition.

In an embodiment of the invention, the composition may include one or more nucleating agents. If included, the nucleating agent is preferably selected from at least one of, but not limited to, talc, kaolin, mica, sodium carbonate, calcium sulfate, and barium sulfate. It is to be appreciated by those skilled in the art that various combination and mixtures of the above nucleating agents may also be utilized with the present invention. If included, the nucleating agent is preferably present in an amount of about 0.01 to 2% by weight, more preferably of about 0.01 to 1% by weight, and most preferably of about 0.01 to 0.1% by weight, each based on the total weight of the composition.

In an embodiment of the invention, the composition may include one or more pigments. If included, the pigment may include inorganic or organic compounds and may impart a special effect and/or color to the article. The pigment may also be dispersed in a carrier matrix, such as a plastic resin, as understood by those of ordinary skill in the art. In one embodiment, the pigment is carbon black pigment. It is to be appreciated by those skilled in the art that the pigment may be any one of or combination of pigments known in the art. If included, the pigment is present in an amount of about 0.05 to 5% by weight, more preferably of about 0.5 to 3% by weight, and most preferably of about 0.5 to 1.5% by weight, each based on the total weight of the composition. The amount of the pigment includes the amount of the carrier matrix, if any. If the carrier matrix is employed, the pigment is preferably present in an amount of 10 to 50% by weight based on the total weight of the pigment and carrier matrix.

In an embodiment of the invention, PAT, PAIT and PAT-reinforcing fiber and optional additives are compounded in conventional means to form the PAIT-modified fiber-reinforced PAT composition as described above. The method of preparing the composition preferably comprises the steps of providing the PAT, the PAIT, and the PAT-reinforcing fiber, along with other optional components as described above; and the step of compounding of the components, which is usually conducted at a temperature of between about 150 to 350°C. It is to be appreciated by those skilled in the art that these steps may also be conducted at lower or higher temperatures. The method of the present invention may be conducted in an apparatus selected from the group consisting of compounders, single-screw extruders, twin-screw extruders, ring extruders, mixers, and reaction vessels alike. The preferred apparatus is a twin-screw extruder. Those of ordinary skill in the art will be able to appreciate that other apparatuses may be used.

Without wishing to be limited to a certain theory or mechanism, it is believed that transesterification occurred during compounding process to form a copolymer in order to achieve a better performance, such as lower melting point, higher melt flowability, and lower warpage.
The PAIT-modified fiber-reinforced PAT may then be heated and molded into the article, preferably via extrusion processes, blow molding or injection molding processes. It is to be appreciated by those skilled in the art that the present invention is not limited to one particular method of making the article. Alternatively, the composition can also be then used to reinforce other thermoplastic materials, preferably PVC, in conventional means, such as co-extrusion, to form a composite structure.

The present invention will be illustrated with PBT as the thermoplastic PAT, PEIT as PAIT, and GF as PAT-reinforcing fiber, to form a composition with lower melting point, higher melt flowability, and lower warpage of the molded or extruded article when being used to form the article together with other thermoplastic material, such as PVC, compared with GF-reinforced PBT. However, those skilled in the art will be able to appreciate that the present invention is not limited to such materials.

PBT is commercially available material and is used as received without further treatment. Typical melting point of the PBT is about 225°C. Preferably, the PBT is characterized by viscosity number of 80 to 170, more preferably 100 to 150. The content of PBT is preferably 15 to 75%, more preferably 20 to 50% by weight based on the total weight of the composition.

PEIT is commercially available material and is used as received without further treatment. Typical melting point of the PEIT is about 100 to 200°C. Preferably, the PEIT is characterized by melting point of 110 to 180°C. The content of PEIT is preferably 15 to 75%, more preferably 20 to 50%, by weight based on the total weight of the composition. Higher PEIT content will result in lower melting point and thus lower processing point.

GF is commercially available material and is used as received without further treatment. The content of the GF is preferably 5 to 60%, more preferably 10 to 55%, by weight based on the total weight of the composition.

A typical process of preparing the composition includes dry blending the components followed by pelletizing to form pellets. The pellets are then extruded to form the pellets. It is to be appreciated by those skilled in the art that other processes may also be used.

The composition of PEIT-modified GF-reinforced PAT composition can be heated and molded into shaped articles, preferably via extrusion processes, blow molding or injection molding processes. It is to be appreciated by those skilled in the art that the present invention is not limited to one particular method of making the article.

Alternatively, the composition can also be then used to reinforce other thermoplastic materials, preferably PVC, in conventional means, such as co-extrusion to form a composite structure.
Co-extrusion of PVC and PBT is an easy process for the production of PVC/PBT composite structure. However, there is a technical obstacle for PVC/PBT co-extrusion because of significantly different melting points between PVC and PBT, around 200 and 225°C, respectively. Due to this fact, the extrusion is performed at elevated temperature up to 230 to 240°C. In this area of temperature, PVC already started to show severe thermal degradation and it becomes impossible to obtain the desired product. With the present invention, modified reinforced PBT can have a lowered melting point of around 200°C while maintaining other key and ancillary properties. This makes it possible to co-extrude PVC and PBT in conventional manner.

In order to co-extrude PVC and PBT, melting point of PBT is adjusted by controlling the content of PEIT to a specific value within the range of content of PEIT defined above, so that a desirable melting point of modified reinforced PBT can be obtained, in order to avoid color change, deformation, warpage, and degradation of PVC upon co-extrusion. The higher PEIT content is, the lower the melting point of PEIT-modified GF-reinforced PBT will be.

It is apparent for those skilled in the art that PBT can be replaced with PET or other PAT such as polycyclohexane dimethylene terephthalate, and/or PEIT is replaced with terpolymer of propylene glycol, isophthalic acid and terephthalic acid, or terpolymer of butylene glycol, isophthalic acid and terephthalic acid. It is also apparent for those skilled in the art that, in such cases, the present invention can be implemented in a manner that is similar to the process for PBT and PEIT.

By modifying PAT with PAIT and reinforcing PAT with PAT-reinforcing fiber, PAT with superior processability such as lower processing temperature and higher melt flowability, as well as better material performance such as lower warpage of the produced article when being used together with other thermoplastic material and higher mechanical properties can be achieved. With such PAT, it is possible to obtain, by conventional means, alone or together with other thermoplastic material, shaped article with better appearance or mechanical performance.

The present invention will be illustrated by the examples below.

**Example 1. Production of PEIT-modified GF-reinforced PBT**

PEIT-modified GF-reinforced PBT is produced by compounding the composition according to Table I in a conventional twin screw extruder using the standard PBT extrusion conditions, which is listed below in Table II.
Table I.

<table>
<thead>
<tr>
<th>Component</th>
<th>Ex-1</th>
<th>Ex-2</th>
<th>Ex-3</th>
<th>Ex-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultradur B4500 NAT, wt%</td>
<td>PBT</td>
<td>43.40</td>
<td>25.40</td>
<td>21.70</td>
</tr>
<tr>
<td>Loxiol P661/3.5, wt%</td>
<td>Lubricant</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Sodium Carbonate IPH, wt%</td>
<td>Nucleating agent</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Printex 60A, wt%</td>
<td>Carbon black pigment</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Low melt point polyester Chip (Type III), (m.p. 180°C), wt%</td>
<td>PEIT</td>
<td>18.00</td>
<td>21.70</td>
<td></td>
</tr>
<tr>
<td>Low melt point polyester Chip (Type I), (m.p. 130°C), wt%</td>
<td>PEIT</td>
<td></td>
<td></td>
<td>21.70</td>
</tr>
<tr>
<td>NEG T-187H, wt%</td>
<td>GF</td>
<td>55.00</td>
<td>55.00</td>
<td>55.00</td>
</tr>
</tbody>
</table>

Table II.

<table>
<thead>
<tr>
<th>TZ1 (°C)</th>
<th>TZ2 (°C)</th>
<th>TZ3 (°C)</th>
<th>TZ4 (°C)</th>
<th>TZ5 (°C)</th>
<th>TZ6 (°C)</th>
<th>TZ7 (°C)</th>
<th>TZ8 (°C)</th>
<th>TZ9 (°C)</th>
<th>TZ11 (°C)</th>
<th>TZ12 (°C)</th>
<th>TZ13 (°C)</th>
<th>Screw (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>260</td>
<td>260</td>
<td>240</td>
<td>240</td>
<td>240</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>400 to 500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Example II. Mechanical Properties of PEIT-modified GF-reinforced PBT

Mechanical properties are measured by standard processes. MVR is measured according to ISO 1133. Tensile strain at break, tensile strength at break, tensile modulus are measured according to ISO 527. Charpy impact is measured according to ISO 179. Melting point and crystallization point are determined by DSC. The respective result is shown in the Table III.

Table III.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Ex-1</th>
<th>Ex-3</th>
<th>Ex-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVR (275°C/2.16kg)</td>
<td>cm³/10min</td>
<td>1.674</td>
<td>5.32</td>
<td>6.83</td>
</tr>
<tr>
<td>Tensile Strain at break</td>
<td>%</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Tensile Strength at break</td>
<td>MPa</td>
<td>138</td>
<td>152</td>
<td>146.0</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>MPa</td>
<td>18800</td>
<td>21000</td>
<td>21000.0</td>
</tr>
<tr>
<td>Charpy Impact - notched</td>
<td>KJ/m²</td>
<td>8.4</td>
<td>11</td>
<td>11.0</td>
</tr>
<tr>
<td>Charpy Impact - un-notched</td>
<td>KJ/m²</td>
<td>40</td>
<td>43</td>
<td>37.0</td>
</tr>
<tr>
<td>Melting Point</td>
<td>°C</td>
<td>220.1</td>
<td>203</td>
<td>182.5</td>
</tr>
<tr>
<td>Crystallization Point</td>
<td>°C</td>
<td>201.1</td>
<td>183.5</td>
<td>167.3</td>
</tr>
</tbody>
</table>

Clearly, by PEIT-modification (Ex-2 to Ex-4), mechanical properties like tensile strain at break, Tensile modulus, MVR (flowability), Charpy impact strength can be improved as compared with GF-reinforced PBT (Ex-1).
Example III. Melting point of PEIT-modified GF-reinforced PBT

Melting point of PBT is determined with DSC and is shown in Fig. 1 to 3.

Fig. 1 and Fig. 2 shows DSC result of Ex-2 and Ex-3. Determined melting point and crystallization temperature is listed in Table IV.

<table>
<thead>
<tr>
<th>Table IV</th>
<th>Fig.1 (Ex-2)</th>
<th>Fig.2 (Ex-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>210.13</td>
<td>195.13</td>
</tr>
<tr>
<td>Crystallization temperature (°C)</td>
<td>183.37</td>
<td>144.44</td>
</tr>
</tbody>
</table>

It can be seen that with the increase of level of PEIT (18.00 to 21.70% by weight), melting point of PEIT-modified GF-reinforced PBT is reduced from to 210 and 195°C, respectively, from the melting point of PBT (225°C).

Fig. 3 shows the heating curves obtained by DSC for different blend ratios in another series of experiment with Ultradur B2550 used as PBT, replacing Ultradur B4500 NAT in Table I, and PEIT with melting point of 180°C is used in all the experiments. Note that LMP in Fig.3 has the same meaning as PEIT. Contents of PBT and PEIT are shown in Table V together with Tg and Tm. It can be seen that with the increase of level of PEIT, melting point of formed PAT is reduced.

<table>
<thead>
<tr>
<th>Table V</th>
<th>PBT:PEIT* (wt%)</th>
<th>Tg (°C)</th>
<th>Tm(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% : 0%</td>
<td>44.51</td>
<td>223.72</td>
<td></td>
</tr>
<tr>
<td>80% : 20%</td>
<td>47.78</td>
<td>219.99</td>
<td></td>
</tr>
<tr>
<td>60% : 40%</td>
<td>52.59</td>
<td>216.6</td>
<td></td>
</tr>
<tr>
<td>40% : 60%</td>
<td>57.33</td>
<td>208.8</td>
<td></td>
</tr>
<tr>
<td>0% : 100%</td>
<td>68.17</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* m.p. 180°C

Example IV. PVC profiles made of PVC and PEIT-modified GF-reinforced PBT

PVC profile was made by co-extruding a PVC profile as shown in Fig.4 with GF-reinforced PBT in Table II (Ex-1) and PEIT-modified GF-reinforced PBT in Table II (Ex-3) at extrusion temperature specified in Table VI.
Fig. 4 is a photograph showing a profile formed by co-extruding PVC with GF-reinforced PBT, in which PBT almost filled the cavity on the left side, while only filled part of the cavity on the right side.

Warpage of the profile is measured according to GB/T 8814-2004, section 6.4.

To determine PBT’s filling degree and adhesion to PVC, the profile is ripped apart to expose the PBT part. The exposed PBT part is peeled off from the rest of the profile and weighted. Volume of the PBT filled in the profile is determined from the weight of the PBT part peeled off and specific weight of the PBT. Filling degree is calculated as the percentage of the volume of the designed cavity that PBT filled. Adhesion to PVC roughly determined from the force needed to peel off the PBT from PVC.

Performance of the material is listed in Table VI.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Ex-1</th>
<th>Ex-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warpage based on 6-m co-extruded profile</td>
<td>mm/m</td>
<td>4.0 to 5.0 (245°C)</td>
<td>0.3 (205°C)</td>
</tr>
<tr>
<td>Filling degree at extrusion temperature of 205°C</td>
<td>%</td>
<td>0 (can't melt)</td>
<td>100</td>
</tr>
<tr>
<td>Filling degree at extrusion temperature of 215°C</td>
<td>%</td>
<td>0 (can't melt)</td>
<td>100</td>
</tr>
<tr>
<td>Filling degree at extrusion temperature of 245°C</td>
<td>%</td>
<td>30 to 40</td>
<td>100</td>
</tr>
<tr>
<td>Adhesion to PVC (by peeling)</td>
<td>N/A</td>
<td>Poor (245°C)</td>
<td>Good (205°C)</td>
</tr>
</tbody>
</table>

It can be seen that with GF-reinforced PBT, it is not possible to co-extrude with PVC at the temperature of 205 and 215°C as the PBT is not melting. Only at the temperature of 245°C, can the GF-reinforced PBT be successfully processed. On the other hand, With PEIT modification, the PEIT-modified GF-reinforced PBT can be process at the low temperature of 205°C, the lowered process temperature

It can also be seen that, for the produced article, PEIT-modified GF-reinforced PBT such as Ex-3 greatly reduces the warpage of co-extruded PVC profile by 13 to 17 times, filling degree is improved from 30 to 40% to 100% at even lower temperature, and adhesion to PVC is also greatly improved.

It should be appreciated by those skilled in the art that butylene group shall be understood as tetramethylene group.
Claims

1. A composition comprising i) polyalkylene terephthalate, ii) (polyalkylene isophthalate)-co-(polyalkylene terephthalate), iii) polyalkylene terephthalate-reinforcing fiber, and iv) optionally, one or more additives, wherein the alkylenes in component i) is selected from the group consisting of methylene group, ethylene group, propylene group, butylene group and cyclohexene dimethylene group, and the alkylene in component ii) is selected from the group consisting of methylene, ethylene, propylene and butylene.

2. The composition of claim 1 wherein component i) is polybutylene terephthalate and/or polyethylene terephthalate.

3. The composition of claim 1 or 2 wherein component ii) is (polyethylene isophthalate)-co-(polyethylene terephthalate).

4. The composition of any one of claims 1 to 3, wherein component iii) is glass fiber.

5. The composition of any one of claims 1 to 4, wherein the component i) and ii) form a copolymer.

6. The composition of any one of claims 1 or 5, wherein the additives are independently selected from the group consisting of lubricants, thermal antioxidant, nucleating agents, and pigments.

7. The composition of claim 6, wherein, independently, the lubricant, if present, is pentaerythritol tetraesterate; the thermal antioxidant, if present, is selected from the group consisting of pentaerythritol tetrasodium 3,5-di-tert-butyl-4-hydroxybenzoate, tetraakis(methylene-3,5-di-tert-butyl-4'-hydroxyphenyl) propionate), tetrakis(methylene-3,5-di-tert-butyl-4'-hydroxyphenyl) propionate), octadecyl 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, and 4,4'-((2,2-diphenylpropyl)diphenylamine; the nucleating agent, if present, is selected from the group consisting of talc, kaolin, mica, sodium carbonate, calcium sulfate, and barium sulfate; and/or the pigment, if present, is carbon black.

8. A process to produce a composition of any one of claims 1 to 7, wherein the components i) to iii) and optionally iv), or precursor of any of the components thereof, are compounded under the condition that component i) and ii) can be melt processed.

9. The process of claim 8, wherein the components i) and ii) are reacted by transesterification to form a copolymer.

10. The use of the composition of any one of claims 1 to 7, wherein the composition is melt formed, optionally together with one or more additional thermoplastic material, to form
shaped article.

11. The use of claim 10, wherein the melt formation is blow molding, injection molding or extrusion.

12. The use of claim 10 or 11, wherein the additional thermoplastic material is polyvinyl chloride.

13. The use of any one of claims 10 to 12, wherein the shaped article is tubing, window profile, connector, tank or other extruded profile parts.

14. A shaped article comprising the composition of any one of claims 1 to 7.

15. The shaped article of claim 14, further comprising one or more additional thermoplastic material.

16. The shaped article of claim 14 or 15, wherein the additional thermoplastic material is polyvinyl chloride.

17. The shaped article of any one of claims 14 to 16, wherein the shaped article is tubing, window profile, connector, tank or other extruded profile parts.

18. A process to modify a first thermoplastic material with a second thermoplastic material, wherein the second thermoplastic material is melt formed together with the first thermoplastic material, wherein the melting point of the modified first thermoplastic material is reduced.

19. The use of the modified first thermoplastic material produced by the process of claim 18, wherein the modified first thermoplastic material is melt formed, optionally together with an additional third thermoplastic material.
FIG. 1

Perkin Elmer Thermal Analysis

Area = 44.598 mJ
Peak = 210.13°C
Delta A = 7.0790 J/g
Onset = 203.17°C

Onset = 186.76°C
Peak = 183.37°C
Area = -70.631 mJ
Delta A = -11.2113 J/g
FIG. 2

Perkin Elmer Thermal Analysis

Area = 6.640 mJ
Delta H = 1.0215 J/g
Peak = 195.13°C
Onset = 153.13°C

Area = -32.239 mJ
Peak = 144.44°C
Delta H = -19.5752 J/g

Heat Flow Endo Up (mW)

Temperature (°C)

97.41  120  140  160  180  200  220  240  251.1

-30.55  -25  -20  -15  -10  -5  0  5  10  15  20  25  30  33.6
FIG. 3

Heat flow vs. Temperature (°C)

Exothermic

Glass transition temperature

Melting temperature

PBT:PEIT = 0:100

PBT:PEIT = 100:0

PBT:PEIT = 80:20

PBT:PEIT = 60:40

PBT:PEIT = 40:60

Temperature (°C)

30 40 50 60 160 180 200 220 240

68.17

44.51

223.72

47.78

219.99

52.59

216.6

57.33

208.8
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

### INV. C08L67/02

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

## B. FIELDS SEARCHED

**Minimum documentation searched (classification system followed by classification symbols):**

<table>
<thead>
<tr>
<th>Classifications</th>
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<td>C08L</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<tr>
<td>X</td>
<td>DE 102 11 513 AI (T0RAY INDUSTRIES [JP]; DENS0 CORP [JP]) 10 October 2002 (2002-10-10) examples 2,6 paragraphs [0061] - [0062] page 5</td>
<td>1-16, 18, 19</td>
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</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier application or patent but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - "Y" document of particular relevance; the claimed invention cannot be considered novel or 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
  - "Z" document member of the same patent family

Date of the actual completion of the international search: 12 September 2014

Date of mailing of the international search report: 18/09/2014

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Pouilley, Delphine

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
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<th>Relevant to claim No.</th>
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This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

   2. X Claims Nos. 18, Imparti al ly)
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.
Contuatio n of Box 11.2

Claims Nos.: 18, 19 (partially)

Present claims 18 and 19 relate to a process for modifying a first thermoplastic material with a second thermoplastic material, and the use of the modified thermoplastic material. Such as drafted, the claims encompass an extremely large number of possible products, since the first and second thermoplastic materials are not specified. Support and disclosure in the sense of Article 6 and 5 PCT, however, is to be found for only a small proportion of products, since the disclosure on only mentions the modification of a polyalene terephthalate with a (polyalene isophthalate) -co- (polyalene terephthalate).

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 18-19 (PCT Guidelines 9.19 and 9.23).

The search of claims 18 and 19 was restricted to a process to modify a polyalene terephthalate with a (polyalene isophthalate) -co- (polyalene terephthalate), wherein (polyalene isophthalate) -co- (polyalene terephthalate) is melt formed together with the polyalene terephthalate, wherein the melting point of the polyalene terephthalate is reduced, and the use of the modified polyalene terephthalate.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination on (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examination Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter 11 procedure. If the applicant proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination on before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.
<table>
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