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Description

5 Area of the invention

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10 The invention relates to plastic laminates comprising at least two incompatible plastic materials A and B bonded in several layers, in which the layer sequence alternates between A and B, the layers made of plastic material B are interrupted at regular spacings and the gaps in the layers B are filled with plastic material A.

15 Prior art

Plastic laminates are known. Here, the main aim is a good adhesion between the bonded members. In so doing, the reinforcement of the plastic plates with fibres or strips is one of the predominant aspects industrially. Thus, DE-OS 38 35 575 describes, for example, a process for preparing continuous moulded particles made of reinforcing fibre formations which are impregnated into thermoplastic material, the fibre formations being guided through a thermoplastic melt. The impregnation then produces a good adhesion of the reinforced fibres in the thermoplastic matrix material.

DE-OS 38 10 374 discloses thermoplastic, fibre-reinforced composite materials which are obtained by impregnating reinforced fibres into the melt of thermoplastic materials, polyamides, a low-molecular weight acid amide and, optionally, an adhesive agent as well as processes for the preparation and use thereof. This document describes inter alia a process in which a mixture is used which comprises thermoplastic material, polyamide, acid amide and, optionally, an adhesive agent in the form of a previously prepared film or a newly extruded synthetic film, and in which the mixture,



together with reinforced fibres which are present in the form of a mat or of unidirectional filament strands, is guided to a continuous press. Again, in this invention, a good adhesion between fibres and thermoplastic matrix is of significance.

US-Patent 4 058 581 describes a process for the continuous preparation of moulded articles reinforced by graphite fibres, in which initially the individual graphite fibres are guided through a solution of a thermoplastic resin, preferably a polypropylene grafted with acrylic acid, in order to provide the adhesive impregnation.

A process for preparing fibre composite materials comprising a thermoplastic matrix and unidirectional reinforcing fibres, in which the fibres are impregnated into a molten thermoplastic material, is described in EP-A 0 282 199. Here, continuously parallel, mechanically non-connected fibre bundles and a thermoplastic material are guided into a double band press and compressed at high pressure and an elevated temperature over a certain time and then cooled. In this process, the fibres are completely and simultaneously impregnated, making it possible to obtain high fibre contents of more than 50% by volume in the thermoplastic matrix. Again, a good adhesion between fibre and thermoplastic matrix is important.

EP-PS 0 407 852 discloses plates made of acrylic glass, which are suitable as noise-protection members and contain plastic monofilaments or a latticed fabric made of such fibres, embedded in the centre of the plate. Here, polyamide fibres are preferably used. At low temperatures, the polyamide fibres exhibit no notable loss in tear resistance as the adhesion between such fibres and the surrounding acrylic glass is relatively low.



Object and solution

Apart from EP-PS 0 407 852, the prior art patents and published patent applications exclusively describe plastic laminates with adhesive layers. The use of additional adhesive generally requires a great deal of expenditure such as feed devices for the adhesive or special guidance for the melt and/or extrudate in co-extruded plastic composite materials. Furthermore, the adhesion which may be achieved through adhesive layers in the plastic laminate is limited. This means that a process is required which combines non-compatible plastic materials, and especially the mechanical characteristics thereof, and which does not use adhesive. The prior art document EP-PS 0 407 852 only achieves this object to a limited extent in a very complex manner, the discontinuous preparation of the plastic laminates made of acrylic glass and plastic fibres being especially expensive.

Surprisingly, it has been found that multi-layer plastic laminates may be prepared from at least two incompatible plastic materials A and B, and with excellent cohesion between the layers if the layer sequence alternates between A and B and the layer material B is interrupted at regular spacings, with the gaps in the layer being filled with plastic A. In a particular preferred embodiment of the invention, the layers of material B are embedded in the material A as unidirectional strands.

In a further preferred embodiment of the invention, the material B has a greater thermal expansion than material A, material A preferably being amorphous and material B being amorphous, crystalline or partially crystalline. The laminates are preferably prepared by co-extrusion. Here, it is especially preferred if material B is processed with an oscillating mass in the stream which



results in a periodic change of the cross-sections of the segments comprising the layer of material B.

Implementation of the invention

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Thermoplastic materials A and B.

Mixtures of two polymers (plastic materials) are normally incompatible. Incompatible polymer mixtures are known from e.g. mechanical polymer mixtures (cf. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 18, p. 443 to 47, Wiley Interscience, 1982). Therefore, there are few limitations to the choice of plastic materials A and B. The thermoplastic A is amorphous and has a lower coefficient of thermal expansion than that of material B which may be amorphous, partially crystalline or crystalline. Preferably, material B has a higher tear resistance, a higher shear stability and a higher viscosity than the matrix material A.

Amorphous plastic materials A or B include e.g. polyvinylester, polyvinylether, amorphous polyvinylhalides, polystyrenes, polyphenylene oxides, polyphenylene sulphides, polycarbonates, polysulphones, amorphous polyamides, polyether ketones, polyether ether ketones, polyether sulphones, polyimides, polyether imides, polyfluoro alkenes, polyester carbonates, amorphous polyolefins and more especially poly(meth)acrylates. Examples of crystalline or partially crystalline materials B are polymers whose crystallinity is due to a uniform tacticity or a sufficient number of small substituents, so that a crystal lattice may form at least partially. Examples include polyester, crystalline polyolefins, crystalline polyvinyl halides, liquid-crystalline polymers with mesogenic groups in the main and/or side chain or preferably preferred crystalline polyamides. A



description of the preparation and the characterisation of the plastic materials A and B is given in e.g. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Ed. Vol. 18, p. 720 to 755, Wiley Interscience, 1982.

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Plastic laminates

Figure 1 shows the basic structure of a three-layered plastic laminate comprising an amorphous material A and an amorphous, crystalline or partially crystalline material B in the layer sequence A-B-A. The layer B is discontinued at regular spacings, the gaps being filled with material A thereby ensuring a close adhesion between the two layers A. Material B has a greater coefficient of thermal expansion than material A. This means that as the result of the greater thermal retraction of B a pretensioning of the material layers may be achieved, when these layers which are embedded in material A cool down. This produces advantageous mechanical characteristics in the plastic laminate such as higher breaking strength, higher bending strength, greater dimensional stability and splintering upon impact is avoided.

A further advantageous embodiment of the invention is produced by incorporating laminated segments made of plastic material B whose cross-sections are subjected to periodic change, thereby achieving an excellent securement of the layers made of plastic material B to plastic material A (Fig.2). Equally, the pretensioning of the layers B clearly increases upon cooling which contributes to the mechanical advantages of the plastic laminate, as described above.

When a transparent material A and a non-transparent or only partially transparent material B are used a plastic laminate with a shaded effect may be produced which is used, for example, for sunshades or light collectors.



By using materials A and B in different colours, plastic laminates may be produced for illuminated advertising or further applicational possibilities in the field of lighting or decoration.

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Preparing plastic laminates

According to the invention, plastic laminates preferably made of amorphous material A and amorphous, crystalline or partially crystalline material B are preferably prepared by co-extrusion, in one production step which is comparatively simple.

Figure 3 shows the so-called extrusion nozzle which is the centre piece of the device for preparing the above laminate. Material A is fed into the feed points (2) of the nozzle shown and then distributed to the desired product width in the two separate distribution channels (5). Material B is fed to a distribution cross bore (6) at the feed point (3) arranged between the distribution channels (5) for material A. Material B leaves the distribution cross bore through a larger number of bores (7) which corresponds to a number of segments made of B provided in the matrix made of A. At the point where B leaves the bores, the two layers A are also guided together thereby enclosing the strands made of material B.

The cross-sectional shape of segments B in A largely depends on the shape of the bores (7) in the discharge region and the viscosity ratio of materials A and B. If the viscosity of B is greater than that of A, the segments of B and A have a more or less round cross-section and in the opposite case, a more or less flat one. After the laminate has left the nozzle, it may be calibrated by conventional smoothing rollers. As the material B is embedded in material A, it can only cool down relatively slowly. If material B is partially



crystalline or crystalline, considerably higher degrees of crystallinity are achieved than with conventional extrusion of strands B. If a lengthwise intermittent change of the cross-section of segment B is required, it may easily be achieved by intermittently changing the stream of the compound fed in at point (3). Since material B has a higher thermal expansion than material A, a pretensioning of segments B is obtained in combination with the positive connection between the two plastic materials (comparable with reinforced concrete). This makes it possible to further improve the mechanical characteristics of the laminate.

The following Example serves to illustrate the invention:

Example

If a steel ball with a diameter of 100 mm (weight about 4 kg) is allowed to drop from a height of 1.5 m, at an angle of 45°, onto a flat plate of 8 mm thickness made of polymethyl methacrylate (PMMA, Plexiglas® 7H. Fa. Röhm), this plate will break up with the formation of many large splinters. If the same experiment is carried out with the plate, according to the invention, in which material A is PMMA (Plexiglas® 7H, made by Röhm, thermal expansion co-efficient $\alpha_1 = 1.8 \times 10^{-4} \text{ K}^{-1}$ at 120°C) and material B is polyamide 12 (Vestamid® X 1852 made by Hüls AG, thermal expansion coefficient $\alpha_2 = 2.7 \times 10^{-4} \text{ K}^{-1}$ at 120°C), and in which the segments B have a spacing of 30 mm and an oval cross-section with an average diameter of 3 mm, the plate is only chipped and indented to the rear at the point where the ball hits the plate, the ball is retained and no splinters occur.

If the drop height of the ball falling onto the plate, according to the invention, is increased to 2.2 m, the

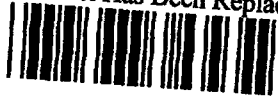


plate is broken by the ball. However, no splinters
break loose. A further improvement of the above
characteristics is achieved by using segments B with a
cross-section which intermittently changes over the
5 length, thereby producing a positive connection between
A and B.

The thermal expansion coefficient α is determined
according to DIN 53752.



Claims

1. Multi-layered plastic laminate comprising at least two incompatible thermoplastic materials A and B,
5 characterised in that the layer sequence alternates between A and B, that the layers of material B are interrupted at regular spacings, and that the gaps in layers B are filled with material A.
- 10 2. A multi-layered plastic laminate, according to claim 1, characterised in that the layers of material B are incorporated in material A as unidirectional strands.
- 15 3. A multi-layered plastic laminate according to claims 1 and 2, characterised in that material B has a larger thermal expansion coefficient than material A.
- 20 4. A multi-layered plastic laminate according to claims 1 to 3, characterised in that material A is amorphous and material B is amorphous, partially crystalline or crystalline.
- 25 5. A multi-layered plastic laminate according to claim 1 to 4, characterised in that the cross-sections of the laminated segments made of material B change intermittently.
- 30 6. A process for preparing multi-layered plastic laminates according to claims 1 to 5, characterised in that the laminated structure is prepared by co-extrusion.

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Fig. 1

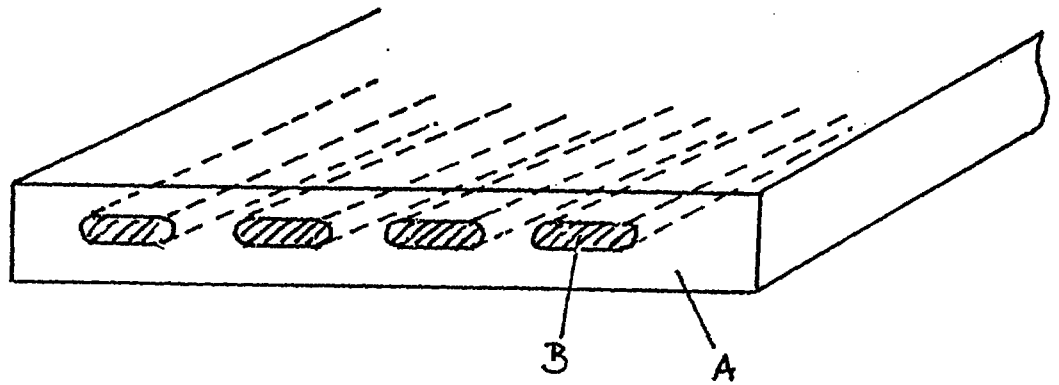
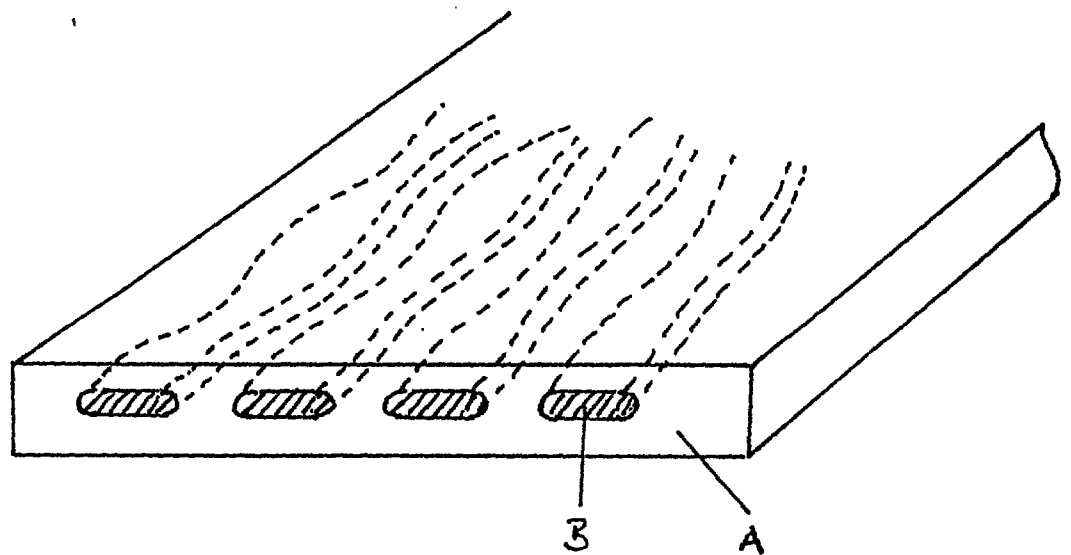


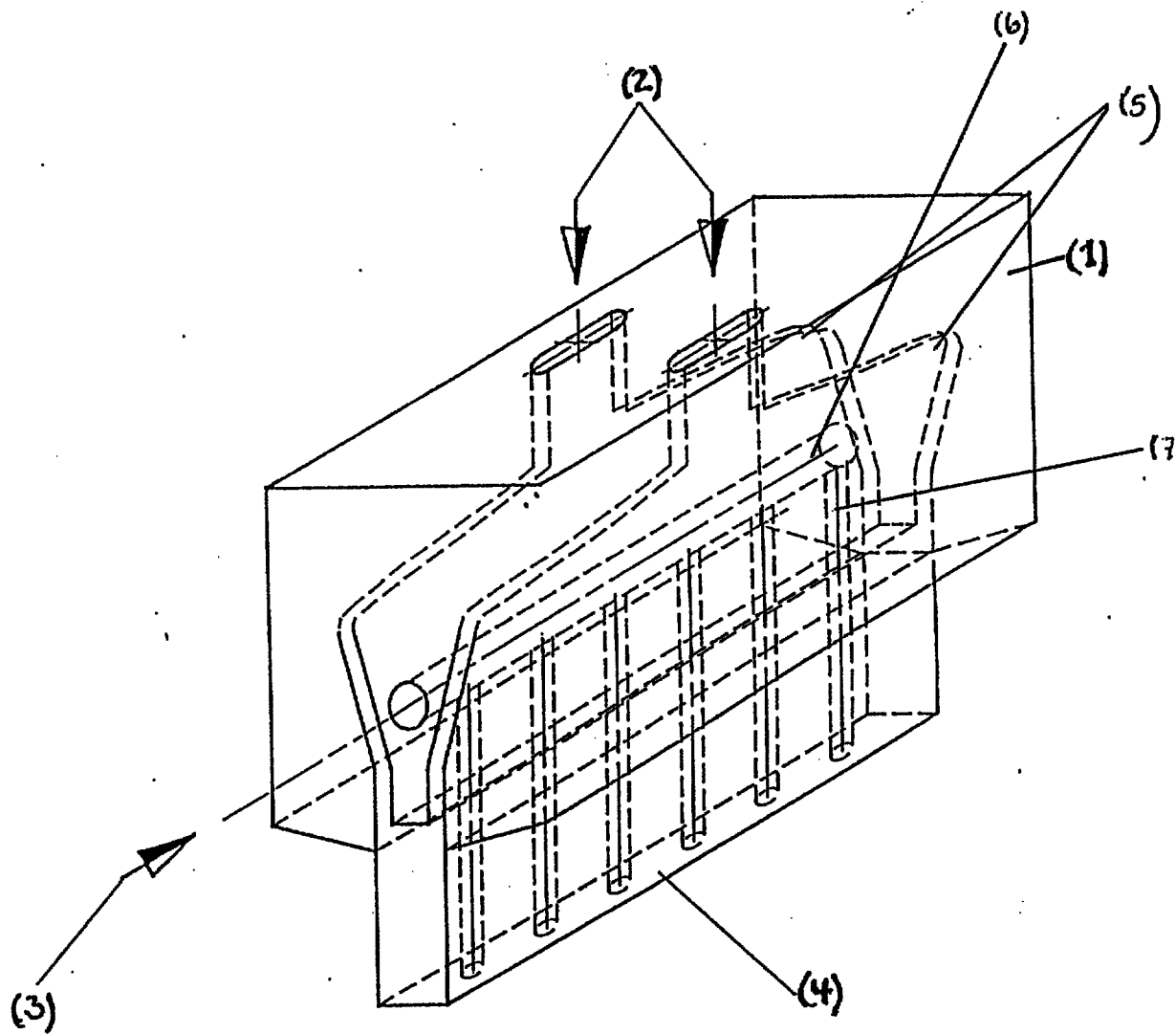
Fig. 2



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Fig. 3



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Abstract

The invention relates to multi-layered plastic laminates and processes for their preparation from at least two incompatible plastic materials A and B with improved
5 adhesion between the layers, wherein the layer sequence alternates between A and B, the layers of material B are interrupted at regular spacings and the gaps in the layers are filled with material A. In preferred
10 embodiments of the invention the amorphous, crystalline or partially crystalline material B has a higher thermal expansion coefficient than the amorphous material A. Preferably, the plastic laminates are prepared by co-extrusion.

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COMPOSITE MADE OF INCOMPATIBLE PLASTICS

Description

Area of the invention

The invention relates to plastic laminates comprising at least two incompatible plastic materials A and B bonded in several layers, in which the layer sequence alternates between A and B, the layers made of plastic material B are interrupted at regular spacings and the gaps in the layers B are filled with plastic material A.

Prior art

Plastic laminates are known. Here, the main aim is a good adhesion between the bonded members. In so doing, the reinforcement of the plastic plates with fibres or strips is one of the predominant aspects industrially. Thus, DE-OS 38 35 575 describes, for example, a process for preparing continuous moulded particles made of reinforcing fibre formations which are impregnated into thermoplastic material, the fibre formations being guided through a thermoplastic melt. The impregnation then produces a good adhesion of the reinforced fibres in the thermoplastic matrix material.

DE-OS 38 10 374 discloses thermoplastic, fibre-reinforced composite materials which are obtained by impregnating reinforced fibres into the melt of thermoplastic materials, polyamides, a low-molecular weight acid amide and, optionally, an adhesive agent as well as processes for the preparation and use thereof. This document describes inter alia a process in which a mixture is used which comprises thermoplastic material, polyamide, acid amide and, optionally, an adhesive agent in the form of a previously prepared film or a newly extruded synthetic film, and in which the mixture,

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together with reinforced fibres which are present in the form of a mat or of unidirectional filament strands, is guided to a continuous press. Again, in this invention, a good adhesion between fibres and thermoplastic matrix is of significance.

US-Patent 4 058 581 describes a process for the continuous preparation of moulded articles reinforced by graphite fibres, in which initially the individual graphite fibres are guided through a solution of a thermoplastic resin, preferably a polypropylene grafted with acrylic acid, in order to provide the adhesive impregnation.

A process for preparing fibre composite materials comprising a thermoplastic matrix and unidirectional reinforcing fibres, in which the fibres are impregnated into a molten thermoplastic material, is described in EP-A 0 282 199. Here, continuously parallel, mechanically non-connected fibre bundles and a thermoplastic material are guided into a double band press and compressed at high pressure and an elevated temperature over a certain time and then cooled. In this process, the fibres are completely and simultaneously impregnated, making it possible to obtain high fibre contents of more than 50% by volume in the thermoplastic matrix. Again, a good adhesion between fibre and thermoplastic matrix is important.

EP-PS 0 407 852 discloses plates made of acrylic glass, which are suitable as noise-protection members and contain plastic monofilaments or a latticed fabric made of such fibres, embedded in the centre of the plate. Here, polyamide fibres are preferably used. At low temperatures, the polyamide fibres exhibit no notable loss in tear resistance as the adhesion between such fibres and the surrounding acrylic glass is relatively low.

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Object and solution

Apart from EP-PS 0 407 852, the prior art patents and published patent applications exclusively describe plastic laminates with adhesive layers. The use of additional adhesive generally requires a great deal of expenditure such as feed devices for the adhesive or special guidance for the melt and/or extrudate in co-extruded plastic composite materials. Furthermore, the adhesion which may be achieved through adhesive layers in the plastic laminate is limited. This means that a process is required which combines non-compatible plastic materials, and especially the mechanical characteristics thereof, and which does not use adhesive. The prior art document EP-PS 0 407 852 only achieves this object to a limited extent in a very complex manner, the discontinuous preparation of the plastic laminates made of acrylic glass and plastic fibres being especially expensive.

Surprisingly, it has been found that multi-layer plastic laminates may be prepared from at least two incompatible plastic materials A and B, and with excellent cohesion between the layers if the layer sequence alternates between A and B and the layer material B is interrupted at regular spacings, with the gaps in the layer being filled with plastic A. In a particular preferred embodiment of the invention, the layers of material B are embedded in the material A as unidirectional strands.

In a further preferred embodiment of the invention, the material B has a greater thermal expansion than material A, material A preferably being amorphous and material B being amorphous, crystalline or partially crystalline. The laminates are preferably prepared by co-extrusion. Here, it is especially preferred if material B is processed with an oscillating mass in the stream which

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results in a periodic change of the cross-sections of the segments comprising the layer of material B.

Implementation of the invention

Thermoplastic materials A and B.

Mixtures of two polymers (plastic materials) are normally incompatible. Incompatible polymer mixtures are known from e.g. mechanical polymer mixtures (cf. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 18, p. 443 to 47, Wiley Interscience, 1982). Therefore, there are few limitations to the choice of plastic materials A and B. The thermoplastic A is amorphous and has a lower coefficient of thermal expansion than that of material B which may be amorphous, partially crystalline or crystalline. Preferably, material B has a higher tear resistance, a higher shear stability and a higher viscosity than the matrix material A.

Amorphous plastic materials A or B include e.g. polyvinylester, polyvinylether, amorphous polyvinylhalides, polystyrenes, polyphenylene oxides, polyphenylene sulphides, polycarbonates, polysulphones, amorphous polyamides, polyether ketones, polyether ether ketones, polyether sulphones, polyimides, polyether imides, polyfluoro alkenes, polyester carbonates, amorphous polyolefins and more especially poly(meth)acrylates. Examples of crystalline or partially crystalline materials B are polymers whose crystallinity is due to a uniform tacticity or a sufficient number of small substituents, so that a crystal lattice may form at least partially. Examples include polyester, crystalline polyolefins, crystalline polyvinyl halides, liquid-crystalline polymers with mesogenic groups in the main and/or side chain or preferably preferred crystalline polyamides. A

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Plastic laminates

Figure 1 shows the basic structure of a three-layered plastic laminate comprising an amorphous material A and an amorphous, crystalline or partially crystalline material B in the layer sequence A-B-A. The layer B is discontinued at regular spacings, the gaps being filled with material A thereby ensuring a close adhesion between the two layers A. Material B has a greater coefficient of thermal expansion than material A. This means that as the result of the greater thermal retraction of B a pretensioning of the material layers may be achieved, when these layers which are embedded in material A cool down. This produces advantageous mechanical characteristics in the plastic laminate such as higher breaking strength, higher bending strength, greater dimensional stability and splintering upon impact is avoided.

A further advantageous embodiment of the invention is produced by incorporating laminated segments made of plastic material B whose cross-sections are subjected to periodic change, thereby achieving an excellent securement of the layers made of plastic material B to plastic material A (Fig.2). Equally, the pretensioning of the layers B clearly increases upon cooling which contributes to the mechanical advantages of the plastic laminate, as described above.

When a transparent material A and a non-transparent or only partially transparent material B are used a plastic laminate with a shaded effect may be produced which is used, for example, for sunshades or light collectors.

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By using materials A and B in different colours, plastic laminates may be produced for illuminated advertising or further applicational possibilities in the field of lighting or decoration.

Preparing plastic laminates

According to the invention, plastic laminates preferably made of amorphous material A and amorphous, crystalline or partially crystalline material B are preferably prepared by co-extrusion, in one production step which is comparatively simple.

Figure 3 shows the so-called extrusion nozzle which is the centre piece of the device for preparing the above laminate. Material A is fed into the feed points (2) of the nozzle shown and then distributed to the desired product width in the two separate distribution channels (5). Material B is fed to a distribution cross bore (6) at the feed point (3) arranged between the distribution channels (5) for material A. Material B leaves the distribution cross bore through a larger number of bores (7) which corresponds to a number of segments made of B provided in the matrix made of A. At the point where B leaves the bores, the two layers A are also guided together thereby enclosing the strands made of material B.

The cross-sectional shape of segments B in A largely depends on the shape of the bores (7) in the discharge region and the viscosity ratio of materials A and B. If the viscosity of B is greater than that of A, the segments of B and A have a more or less round cross-section and in the opposite case, a more or less flat one. After the laminate has left the nozzle, it may be calibrated by conventional smoothing rollers. As the material B is embedded in material A, it can only cool down relatively slowly. If material B is partially

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crystalline or crystalline, considerably higher degrees of crystallinity are achieved than with conventional extrusion of strands B. If a lengthwise intermittent change of the cross-section of segment B is required, it may easily be achieved by intermittently changing the stream of the compound fed in at point (3). Since material B has a higher thermal expansion than material A, a pretensioning of segments B is obtained in combination with the positive connection between the two plastic materials (comparable with reinforced concrete). This makes it possible to further improve the mechanical characteristics of the laminate.

The following Example serves to illustrate the invention:

Example

If a steel ball with a diameter of 100 mm (weight about 4 kg) is allowed to drop from a height of 1.5 m, at an angle of 45°, onto a flat plate of 8 mm thickness made of polymethyl methacrylate (PMMA, Plexiglas® 7H. Fa. Röhm), this plate will break up with the formation of many large splinters. If the same experiment is carried out with the plate, according to the invention, in which material A is PMMA (Plexiglas® 7H, made by Röhm, thermal expansion co-efficient $\alpha_1 = 1.8 \times 10^{-4} \text{ K}^{-1}$ at 120°C) and material B is polyamide 12 (Vestamid® X 1852 made by Hüls AG, thermal expansion coefficient $\alpha_2 = 2.7 \times 10^{-4} \text{ K}^{-1}$ at 120°C), and in which the segments B have a spacing of 30 mm and an oval cross-section with an average diameter of 3 mm, the plate is only chipped and indented to the rear at the point where the ball hits the plate, the ball is retained and no splinters occur.

If the drop height of the ball falling onto the plate, according to the invention, is increased to 2.2 m, the

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plate is broken by the ball. However, no splinters break loose. A further improvement of the above characteristics is achieved by using segments B with a cross-section which intermittently changes over the length, thereby producing a positive connection between A and B.

The thermal expansion coefficient α is determined according to DIN 53752.

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Claims

1. Multi-layered plastic laminate comprising at least two incompatible thermoplastic materials A and B, characterised in that the layer sequence alternates between A and B, that the layers of material B are interrupted at regular spacings, and that the gaps in layers B are filled with material A.
2. A multi-layered plastic laminate, according to claim 1, characterised in that the layers of material B are incorporated in material A as unidirectional strands.
3. A multi-layered plastic laminate according to claims 1 and 2, characterised in that material B has a larger thermal expansion coefficient than material A.
4. A multi-layered plastic laminate according to claims 1 to 3, characterised in that material A is amorphous and material B is amorphous, partially crystalline or crystalline.
5. A multi-layered plastic laminate according to claim 1 to 4, characterised in that the cross-sections of the laminated segments made of material B change intermittently.
6. A process for preparing multi-layered plastic laminates according to claims 1 to 5, characterised in that the laminated structure is prepared by co-extrusion.

COMPOSITE MADE OF INCOMPATIBLE PLASTICS

Abstract

The invention relates to multi-layered plastic laminates and processes for their preparation from at least two incompatible plastic materials A and B with improved adhesion between the layers, wherein the layer sequence alternates between A and B, the layers of material B are interrupted at regular spacings and the gaps in the layers are filled with material A. In preferred embodiments of the invention the amorphous, crystalline or partially crystalline material B has a higher thermal expansion coefficient than the amorphous material A. Preferably, the plastic laminates are prepared by co-extrusion.

FIGURE 1

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Fig. 1

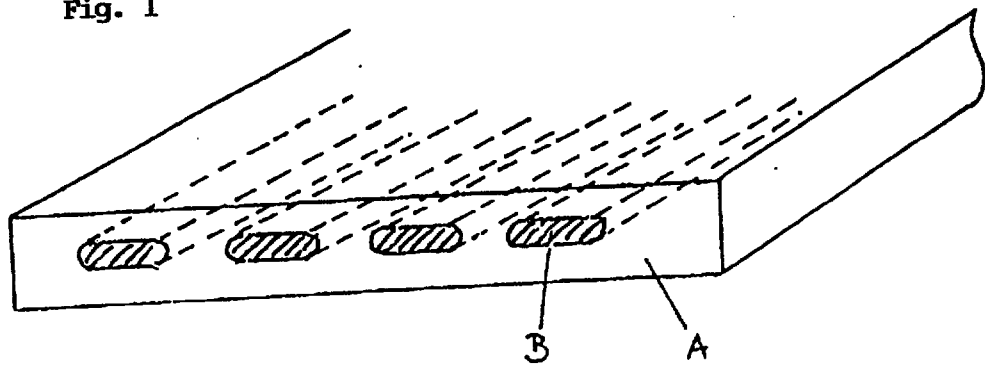
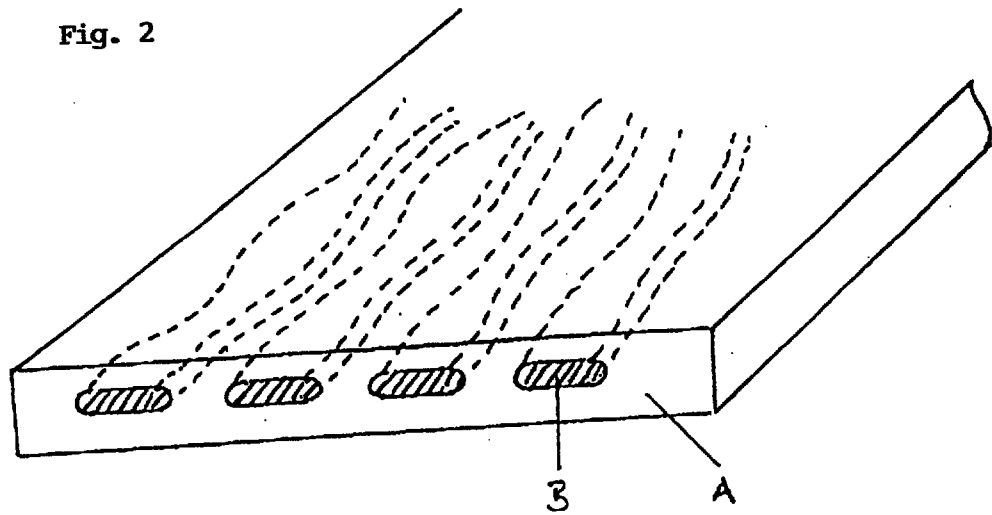


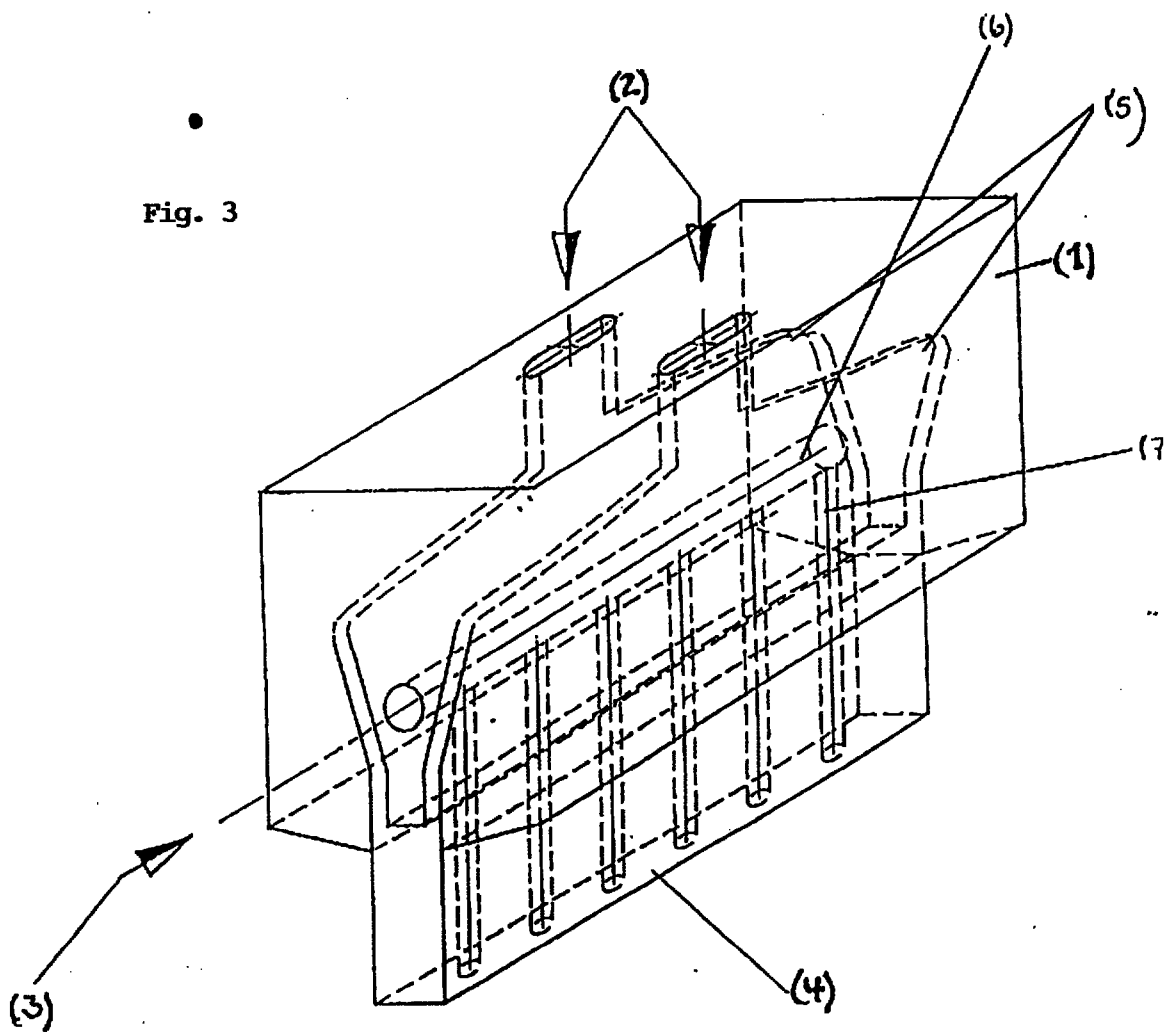
Fig. 2



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Fig. 3



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