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(54) Title: COMPOSITE MATERIAL SHEET AND PROCESS FOR MANUFACTURING THE SAME

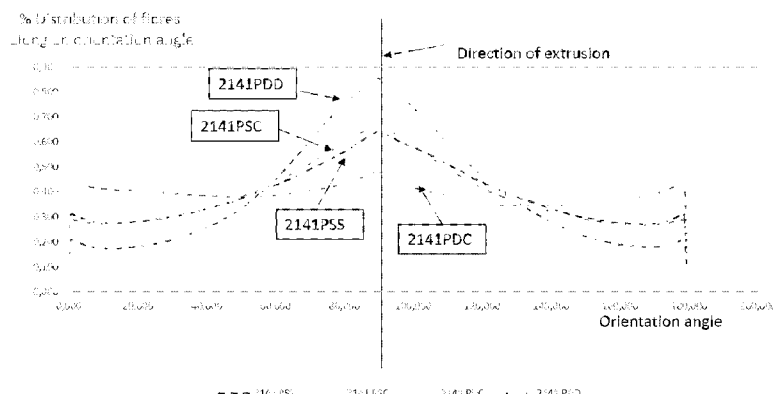


Fig. 1

(57) Abstract: The invention relates to a composite material sheet or panel obtained by extruding a mixture composed of at least one thermoplastic material, particularly of the polyolefin family, and of mineral fibers having predetermined dimensional characteristics (diameter and length). The extrusion process is performed with such parameters to generate in the sheet a three-dimensional structure embedded in the thermoplastic material.

RENOLIT GOR SPA.

- 5 Composite material sheet and process for manufacturing the same.

The invention relates to a composite material sheet and process for manufacturing the same.

- 10 The term "composite" means a material obtained by combining two or more components, called also as phases, combined according to various proportions and shapes, such that the final product has a non-homogeneous structure and has chemical-physical properties different
15 from those of the individual constituents. One of the phases, called as matrix, has a continuous form and it mainly acts for maintaining the cohesion of the reinforcement phase or phases, for guaranteeing a certain shape of the piece, as well as for protecting and
20 uniformly transmitting the load to the other reinforcement phase. This latter on the contrary is composed of a discontinuous constituent, generally made of fibers or particles whose task is to guarantee mechanical strength and stiffness, most of the external
25 load being borne by it.

- In particulate composites the reinforcement is composed of "particles", which (unlike fibers) can be considered equiaxial, namely the diameter to length ratio of each particle is equal about to one (while the fibers
30 are more developed in length direction).

The composite materials with the dispersed phase made of fibers exhibit a strong anisotropy. Such anisotropy is not found (or at least it is very lower) in particulate composites, provided that said particles
5 are equiaxial.

The basic idea of the composites is to optimize the performances of the so called traditional materials, as regards the chemical-physical, mechanical and lightweight properties.

10 By combining a material having a given property (for example a polymer) with another one having different properties (for example carbon fibers), it is possible to obtain a material, composed of such two materials, that enhances the best properties thereof. The composite
15 materials are particularly interesting since they offer particular combinations of different properties that cannot be contemporaneously present in conventional materials such as metal alloys, ceramics and polymers.

In the automotive industry, it is known to use panels
20 made of composite material for manufacturing internal parts of motor vehicles such as headliners, load spaces, rear shelves etc.

Said panels have to exhibit a considerable mechanical strength in combination with a good
25 flexibility level and a weight as low as possible.

The panels made of thermoplastic material filled with vegetable fillers are a good compromise due to their mouldability, for example by thermoforming, their good mechanical strength, their good fracture behavior, in
30 combination with low manufacturing costs. Moreover

vegetable fillers allow very light panels to be produced with obvious advantages as regards handling and fuel consumption for the vehicles bearing them.

The document EP2247653 describes a composite
5 material sheet having a polypropylene matrix and a filler composed of vegetable fibers, in particular cellulose.

An alternative to vegetable fibers is the use of mineral or inorganic fibers, particularly glass fibers. Such type of fibers is more resistant, more rigid, have
10 a high melting point and are completely flame-resistant. On the contrary, except for metal fibers, they are very brittle.

In particular glass fibers have a high bending and impact strength and a low thermal and electrical
15 conductivity together with a relatively low density, which make them particularly useful for being used in the automotive industry.

On the other side, if they are not well embedded in the matrix of the composite, which guarantees the
20 mouldability thereof, they can be spread in the environment and be dangerous for the health, unlike vegetable fibers.

The aim of the present invention is to provide a composite material sheet or plate with a polymer matrix
25 and a filler of inorganic fibers, particularly glass fibers, wherein the matrix is able to perfectly embed the filler, firmly incorporating it therein, thus avoiding the presence of surface fibers that can detach therefrom and be dispersed in the environment, particularly in a
30 vehicle compartment.

The invention achieves the aim by providing a composite material sheet having the characteristic of being obtained by extrusion of a mixture composed of a thermoplastic material, particularly of polyolefin family, such as for example polyethylene, polypropylene, mixtures of polyolefins or the like and of groups of non-vegetable fibers, typically glass fibers, having a predetermined length and wherein the extrusion is performed with such parameters to generate a three-dimensional fiber structure called as fiber "mat", where the fibers are entangled on themselves.

In particular, such mat is composed of the combination of fibers mainly arranged in the extrusion direction, but, at the same time, exhibiting a kind of isotropy in the other two directions of the plane, due to the mechanical action exerted by the extruder opening and aligning the individual fiber bundles.

The invention is based on a unexpected technical effect. As it is known, it is possible to produce composite sheets by impregnating a preformed layer of glass fibers with a polymer matrix, for example polypropylene. The fibers that compose the layer, oriented or not according to a main direction, woven or non-woven, can be dampened by the matrix by coating and compression with a calender or by using softening techniques with cycles at different temperatures. The inventors have found that it is possible to obtain three-dimensional fiber structures completely covered by a polymer matrix by an extrusion process while keeping the dimensions of the fibers under control.

In particular, the invention relates to the use of fibers, with a diameter ranging from 5 to 50 micron and a length ranging from 1 to 20 mm.

In particular, the invention relates to the use of
5 fibers with the characteristics described at the previous point grouped together in bundles of fibers, that are disgregated into individual units and oriented by forming a three-dimensional structure by the mechanical action exerted firstly by the mixer, then by the screw or screws
10 of the extruder and then by the output die of the extruder.

The maximum effect occurs when the groups of fibers have the shape of cylinders having a thickness ranging from 0.5 to 2 mm, preferably about 1 mm, and a length
15 ranging from 2 to 20 mm, preferably in the order of 2-3 mm. Such effect is well clear if a calcination of the composite material is performed by using a muffle furnace. The inorganic component composing the so called mat in the composite material, remains unchanged while
20 organic matter, by being calcinated, is removed from the system. Therefore, it is possible to analyse the amount and the arrangement of the inorganic filler that was embedded in the polymer matrix.

The mechanical action exerted by the extrusion on an
25 heterogeneous mixture composed of granules or powder of a thermoplastic polymer and agglomerates of glass fibers is able to break the fiber groups and to disperse the filaments in the polymer matrix.

Specifically, the process for producing a composite
30 material sheet according to the invention provides to mix

the thermoplastic material in the form of granules or powder with groups of fibers having a predetermined length and to form the sheet by extruding the mixture through an extrusion die. Mixing and extrusion are performed with such parameters to generate a three-dimensional fiber structure called as mat, embedded in the thermoplastic material. It is the mixing step that causes the fiber bundles to be disgregated without considerably changing the dimensional characteristics thereof. In the extrusion step the individual fibers are arranged to form the mat, in turn completely impregnated by the thermoplastic material.

It has to be noted how the sheets according to the invention are completely recyclable. To this end, according to one embodiment, the process provides the step of preliminarily grinding the recycle composite sheets to obtain the thermoplastic material and the fibers to be mixed. In this case a further step is provided such to add in the mixture an amount of the material obtained by grinding the side trims and waste pieces in general (provided that they are consistent with each other as regards the formulation).

If one considers that the thermoplastic material and the fibers are typically present in the sheet substantially under the same proportion, that is 50 and 50 by weight, by feeding the mixer with recycle material and with polymer material in the same amount, the final extrusion will be able to maintain the same proportion of the components if the same amount of fibers is added in a step following the mixing step.

The mixing and extrusion steps advantageously are performed in an extruder, particularly a twin-screw extruder, with an output flat die. The fibers entangle with each other due to the mechanical action exerted by the mixing screws and the extrusion die thus generating a fiber entanglement contemporaneously to the mixing/extrusion step.

The plates or sheets according to the invention are particularly useful for being used in the automotive industry. For example, they can be used for forming rear shelves, load spaces, headliners for motor vehicles, bodywork parts, truck cabs, spoilers, control boards, tool-holding panels, housings for lights and the like.

However also other applications are possible, particularly in those fields requiring small encumbrances and contemporaneously high levels of mechanical strength especially in low cost products and lightweight products.

Examples of the present invention are described hereinafter by means of the following figures in which:

Figure 1 illustrates a graphic representation of the percentage of the distribution of the orientation of the fibers in relation to the extrusion direction which corresponds to an angle of 90° and for different settings of the temperature and of the length of the extrusion die of platform in a direction of extrusion.

Figure 2 illustrates a similar graph as in figure 1 but the measurement is limited to a layer of about 0,5mm depth along each of the two opposite surfaces of the sheet.

Figure 3, is a graph putting in relation the ratio

of the flexural modulus along the direction of extrusion and perpendicular to the direction of extrusion of the sheets according to the examples of the figures 1 and 2 with the peak values of the graphs of figures 1 and 2.

5 In the following some examples will be described with the help of the annexed drawings.

 An extruded sheet comprising a blend of polyolefine resins and of glass fibres according to the present invention has been extruded. The sheet thickness is of
10 2,2mm.

 The length of the die in the direction of extrusion has been varied in four steps between 40 and 100mm.

 The temperature of the material being extruded is between 200 and 220° degress C.

15 Figure 1 shows the curves of distribution of the fibres relatively to their orientation in respect to the direction of extrusion and expressed in percent.

 The measurement of the data has been carried out by evaluating the fibres oriented along a certain angle with
20 respect to the direction of extrusion which coincides with a 90° angle in figure 1.

 Maximum angle of orientation of the fibres is 0° and 180° which corresponds to an orientation of the fibres perpendicular to the direction of extrusion and in the
25 two directions strting from the direction of extrusion.

 Measurement has been carried out by means of an RX tomograph which has been angularlrly displaced each time of 0.5° relatively to a centre of rotation falling on an axis oriented in the direction of extrusion.

30 At each angle of acquisition, the corresponding

percentage of fibres oriented along the said angle has been determined.

The curves have been rescaled in order that their integral from 0° to 180° corresponds to the 100% of the
5 fibers comprised in the sheet.

The different curves relate to different length of the extrusion die starting from 30cm up to 100cm.

The four curves are identified by symbols and by a name 2141PDC, 2141PSS, 2141PSC, 2141PDD.

10 As it appears from the curves by varying the length of the die, the distribution of the fibres becomes more and more non isotropic. The curve defined as 2141PDC is the flattest one. This means that the fibres are isotropically oriented in relation to the direction of
15 extrusion.

This has an effect on the ratio of flexural modulus values in longitudinal and in transverse direction as referred to the direction of extrusion and where this direction is parallel to the longitudinal direction.

20 The ratio of the distributions at the maximum of the curve to the minimum of the curve relating to the example 2141PDC is about 1,2.

By varying the length of the die a higher number of fibres are aligned in the direction parallel to the
25 direction of extrusion. The curve relating to the example 2141PDD shows the higher dynamic in range and indicates a ratio of the distributions at the maximum of the curve to the minimum of the curve of about 5.7:1.

This means that in this case a higher percentage of
30 the fibers are oriented in a direction parallel to the

direction of extrusion than the ones oriented transversally to it. In this case the ratio between longitudinal and transversal flexural modulus as defined above is different and the higher so that the sheet has
5 a higher resistance against flexural stresses in the longitudinal direction.

Figure 2 shows what happens to the distribution of the orientation of the fibres in respect to the direction of extrusion in a thin superficial layer of about 0,5mm
10 depth from a surface of the sheet.

Again the measurements are taken in relation to the direction of extrusion corresponding to the 90° angle in the graph and using the same RX tomograph as for figure 1.

15 Four sheets obtained with four die length has been scanned as explained above. The four sheets and the relative curves are identified as already done above.

In reading the curves it appears that varying the die length has the effect not only of flattening the
20 curve, meaning having a higher degree of isotropy or unisotropy of the fibres orientation distribution, but it varies also the angular width of the possible orientation of the fibres centered along the direction of extrusion (90°). Curve 2141PDC is more flattened and most fibres
25 will be distributed in a isotropic way along directions comprised between about -50° and $+50^\circ$ relatively to the direction of extrusion (90°). Curve 2141PDD shows a more unisotropic distribution of the fibres on the different orientations but the angular width of the possible
30 orientations is reducing to about -30° to $+30^\circ$ relatively

to the direction of extrusion. Examples 2141 Psc and Pss show an intermediate behavior between 2141PDC and 2141PDD.

Although the eabove examples are limited to a
5 variation in the length of the dye, experiemnts has shown also a similar influence on the distribution of the fibres on different angular irentations in respect to the direction of extrusion determined by varying the temperature of the mixture being extruded.

10 Fgiure 3 shows the ratio of the longitudinal flexural modulus to the transverse flexural modulus on sheets according to the present invention showing different distributions of the fibres along different orientations with respect of the direction fo extrusion.

15 As already indicated above the term longitudinal direction means here paralle to the direction fo extrusion, while the term transverse direction means a direction perpendicular to the direction of extrusion.

Two further examples have been added to the one
20 indicated by 2141 and discussed in relation to the four cases of figure 1 and 2.

As it appers from the above description, the invention allows to optimize the mechanical properties of the sheet in relation to two different directions
25 (longitudinal and transverse) paralle and perpendicular to the direction fo extrusion of the sheet. This is achieved without the need of modifying the composition of the sheet material or the thickness of the sheet but only setting different distribution of the fibers onto
30 different orientations in relation to the direction fo

extrusion by varying only some parameters of the extrusion process and particularly length of the extrusion die and/or temperature of the mass of material to be extruded.

5

CLAIMS

1. Process for manufacturing a composite material sheet comprising the following steps:

5 Providing a thermoplastic material, particularly of the polyolefin family in the form of granules or powder;

 providing a non-vegetable fibers, particularly glass fibers, in the form of groups or bundles of fibers having a predetermined length width and thickness;

10 mixing the said thermoplastic material and the said non-vegetable fibres and disgregating the fiber bundles during the mixing;

 feeding the said mixture to an extruder forming a sheet by extruding the mixture through an extrusion die
15 of the extruder, the said sheet comprising a a three-dimensional fiber structure the fibers are entangled on themselves, which structure is embedded in the thermoplastic material;

 the distribution percentage of the orientation of
20 the fibers versus the direction of extrusion being set between a ratio of 1:1 to a ratio of 6:1 between the percentage of the fibers oriented in the direction of exrrusion and the ratio of fibers directed in a direction perpendicular to the direction of extrusion.

25 2. Process according to claim 1 in which the setting of the percentage of the orientation of the fibres relatively to the direction of extrusion is obtained by varying alternatively or in combination the temperatures of the mixture of the said thermoplastic material and the
30 said non-vegetable fibres and the length of the die plate

between 30 to 150 preferably between 40 to 100cm.

3. Process according to claim 1 or 2 in which the distribution percentage of the orientation of the fibres between a direction perpendicular to the direction of
5 extrusion and a direction parallel to the said direction of extrusion varies continuously according to a polynomial function having a degree of two or higher.

4. Process according to one or more of the preceding claims in which the fiber bundles, are composed of groups
10 of individual fibers adherent to each other, the individual fibers having a length between 2 to 20mm preferably in the order of 2-3 mm and the bundles having the shape of bars or cylinders with a thickness ranging from 0.5 to 2 mm, preferably about 1 mm.

15 5. Process according to claim 4 in which the step is provided of generating the fiber bundles from individual bundles.

6. Process according to one or more of the preceding claims, wherein there is provided the step of grinding
20 the composite sheets and to add recycled material to the thermoplastic material and fibers in a quantity to maintain the same starting formulation.

7. Process according to one or more of the preceding claims, wherein the mixing and extrusion steps are
25 performed in an extruder, particularly a twin-screw extruder, with an output flat die, wherein the fibers entangle with each other due to the mechanical action exerted by the mixing screws and the die, thus generating a three-dimensional fiber structure contemporaneously
30 with the mixing/extrusion step.

8. Process according to claim 7, wherein the fiber bundle disgregation is obtained by the mechanical action exerted by the mixing screws and the entangling and fiber orientation distribution is generated by the mechanical action exerted by the extrusion die opening and aligning the individual fiber of the bundles.

9. Extruded composite material sheet or panel characterized in that it comprises a thermoplastic material, particularly of the polyolefin family, embedding non-vegetable fibers having a predetermined length and forming a three-dimensional fiber structure wherein the fibers are entangled on themselves, the non vegetable fibers of the three dimensional distribution showing a distribution percentage of the orientation of the fibers relatively to the direction of extrusion which is between a ratio of 1:1 to a ratio of 6:1 between the percentage of the fibers oriented in the direction of extrusion and the ratio of fibers directed in a direction perpendicular to the direction of extrusion.

10. Extruded composite material sheet according to claim 9, having a thickness and in which the distribution percentage of the orientation of the fibres relatively to the direction of extrusion varies along the thickness of the sheet.

11. Extruded composite material sheet according to claim 10 in which about half the number of the fibres within a layer of the said sheet forming the surfaces of the sheet at the two opposed faces, has an orientation between a direction about $+60^\circ$ and -60° , especially $+45^\circ$ to -45° relatively to the direction of extrusion, the

ratio of the distribution percentage of the orientation of the fibres relatively to the direction of extrusion, between the orientation of the fibres along the directions at $+60^\circ$ or -60° , preferably at $+40^\circ$ to -40° relatively to the direction of extrusion and an orientation fo the fibres parallel to the direction of extrusion being between a ratio of 1:1 to a ratio of 6:1

12. Extruded composite material sheet according to one or more of the preceding claqims 2, wherein said
10 three-dimensional fiber structure is composed of the combination of fibers mainly arranged in the extrusion direction, and for a part, at the same time, exhibiting isotropy in the other two directions of the plane, due to the mechanical action exerted by the extrusion opening
15 and aligning the individual fiber bundles.

13. Extruded composite material sheet according to one or more of the preceding claims 9 to 12, wherein the thermoplastic material belongs to the group comprising polyethylene, polypropylene or mixtures of polyolefins.

20 14. Extruded composite material sheet according to one or more of the preceding claims 9 to 13, wherein the non-vegetable fibers comprise glass fibers.

15. Extruded composite material sheet according to one or more of the preceding claims, wherein the
25 thermoplastic material and the fibers are present substantially in the same proportion.

16. Composite panel, particularly for forming rear shelves, characterized in that it comprises one or more sheets according to one or more of the preceding claims
30 9 to 15.

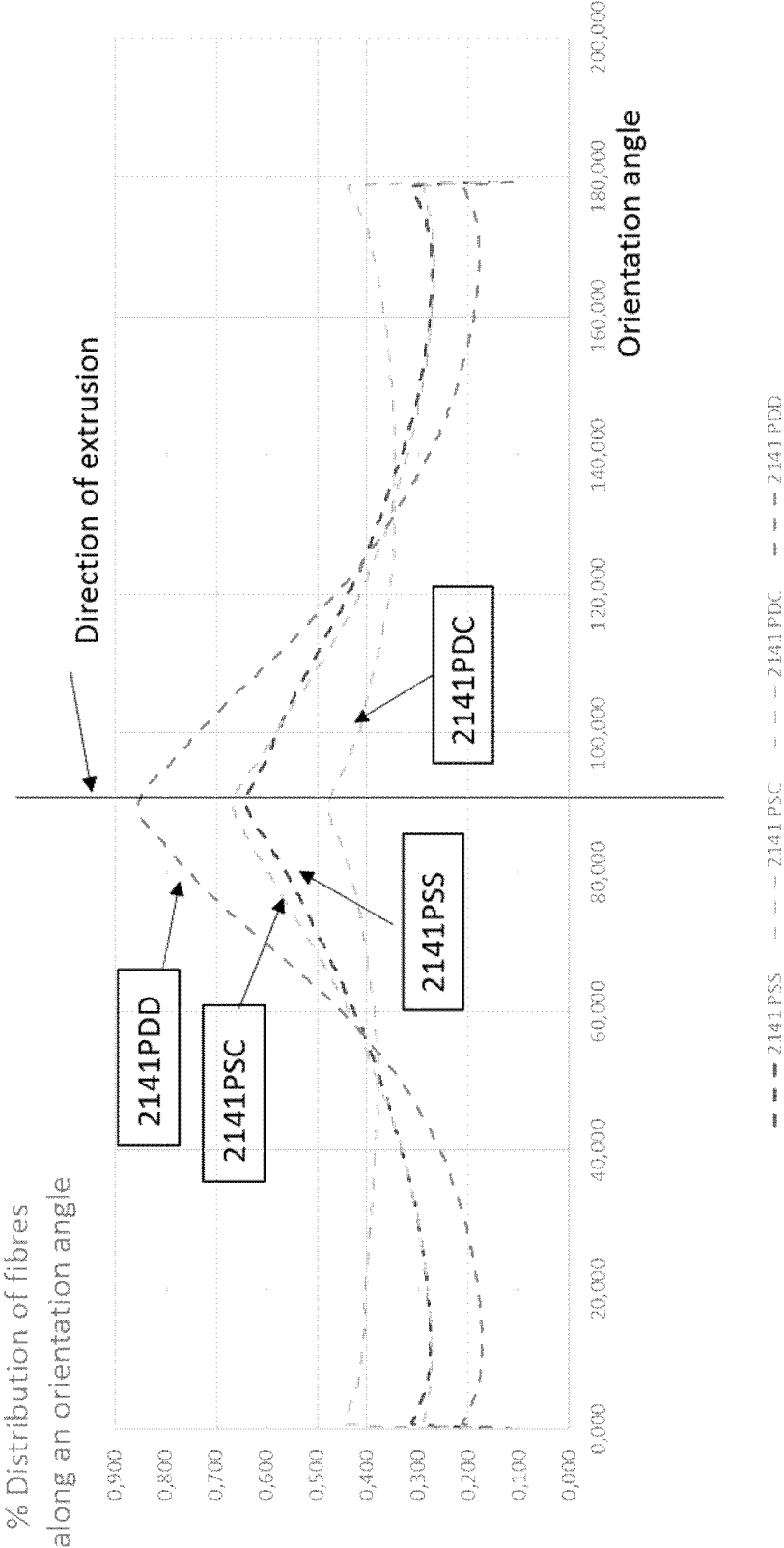


Fig. 1

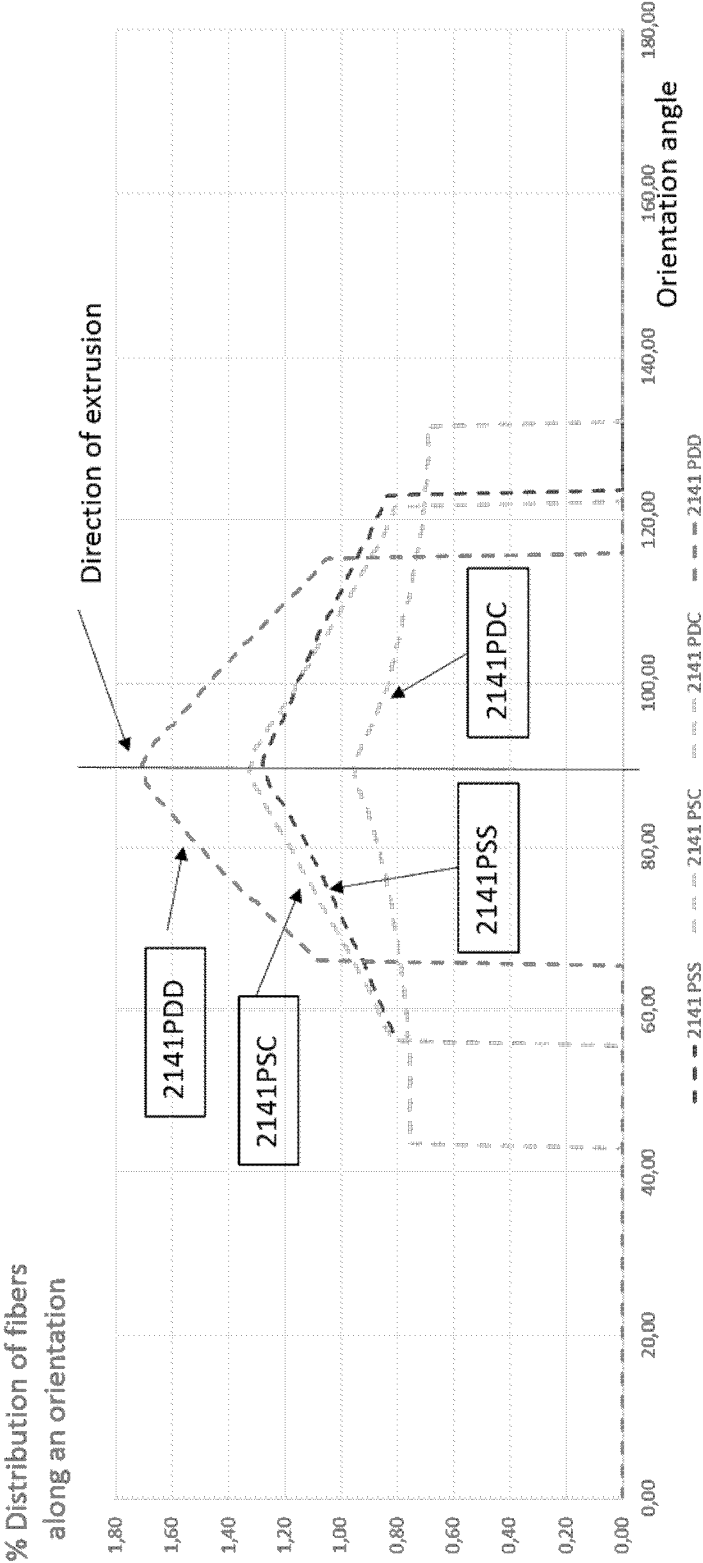


Fig. 2

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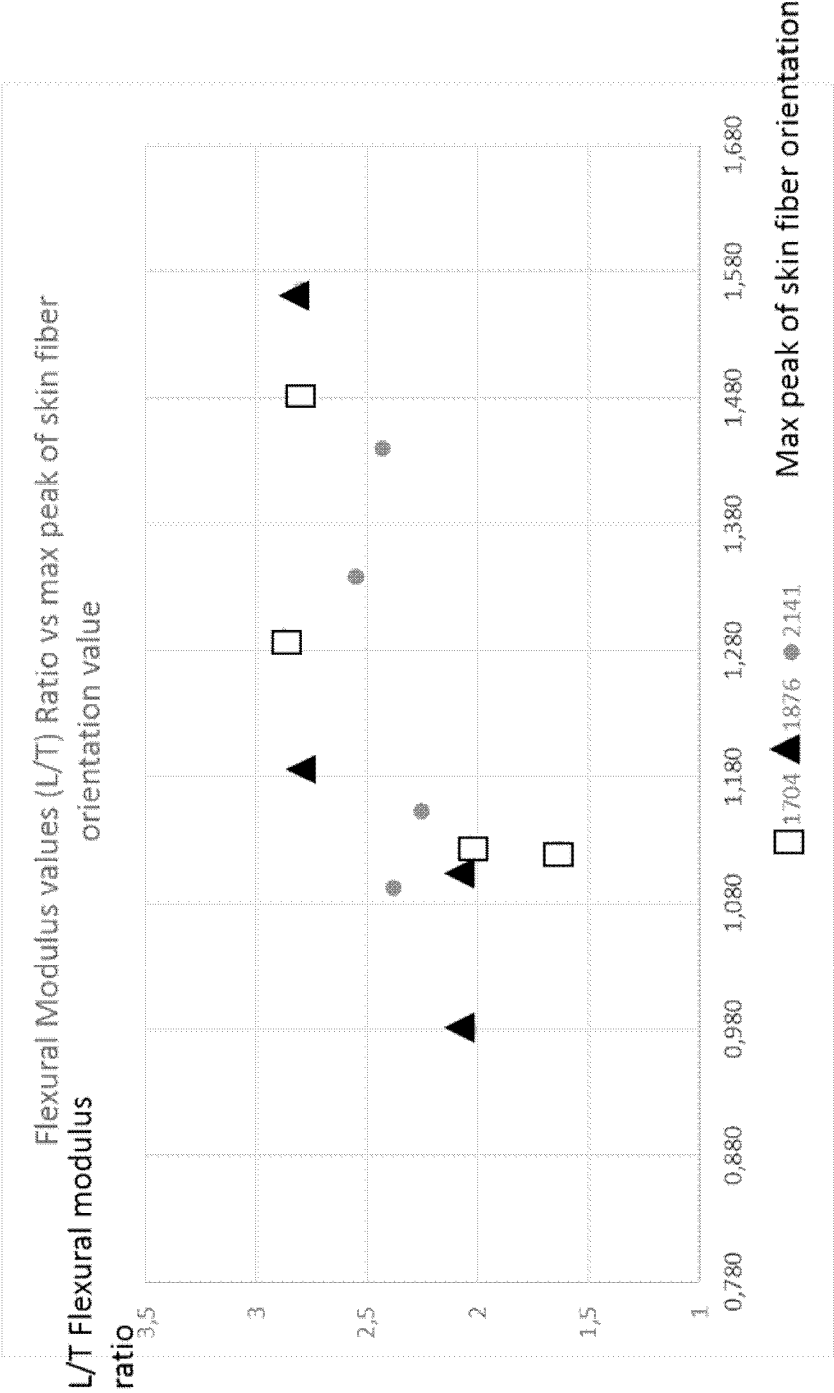


Fig. 3