(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 August 2014 (14.08.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/123478 A1

(51) International Patent Classification:
B29C 47/10 (2006.01) *C08J 5/04* (2006.01)

(21) International Application Number:
PCT/SE2014/050149

(22) International Filing Date:
6 February 2014 (06.02.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1350147-3 7 February 2013 (07.02.2013) SE

(71) Applicant: **SÖDRA SKOGSÄGARNA EKONOMISK FÖRENING** [SE/SE]; Södra Innovation, S-351 89 Växjö (SE).

(72) Inventors: **BOLDIZAR, Antal**; Örnvägen 9, S-511 42 Kinnahult (SE). **ARINO, Ruth**; De Geersgatan 10, S-416 57 Göteborg (SE).

(74) Agent: **VALEA AB**; Anna Lindhs Plats 4, S-211 19 Malmö (SE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: A METHOD FOR PROVIDING A COMPOSITE MATERIAL COMPRISING A THERMOPLASTIC MATRIX AND CELLULOSE FIBERS

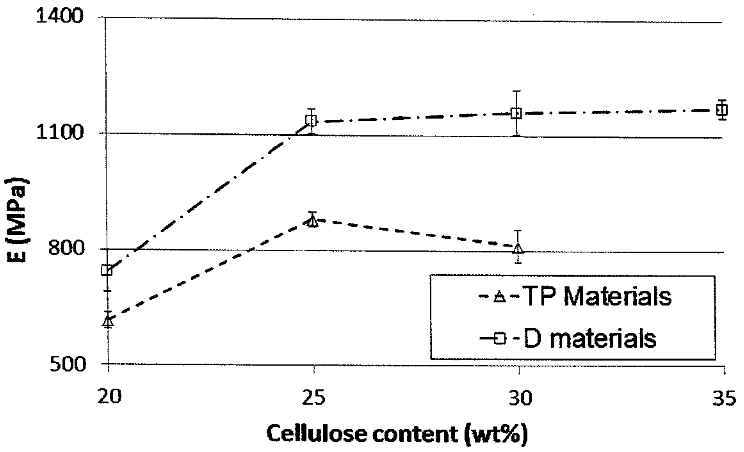

Fig. 4

(57) **Abstract**: The present invention relates to a method for providing composite materials comprising a thermoplastic matrix and cellulose fibers. The method comprises extruding one or more cellulose fiber-based webs in a mixture with a melted thermoplastic matrix material by means of a twin screw thereby forming an extrudate composite material, which may be further transformed into a cellulose fiber-reinforced composite article in which the cellulose fibers are evenly distributed within the thermoplastic matrix. The method provides improved possibilities for large scale manufacturing, by improved feeding of the cellulose part. The cellulose fiber-reinforced composite articles have excellent mechanical properties, the best results being obtained when the cellulose fiber content is between 20 and 30 wt % based on the composite article.

WO 2014/123478 A1

A METHOD FOR PROVIDING A COMPOSITE MATERIAL COMPRISING A THERMOPLASTIC MATRIX AND CELLULOSE FIBERS

TECHNICAL FIELD

The present invention relates to a method for providing composite materials comprising a thermoplastic matrix and cellulose fibers.

BACKGROUND

The ever increasing need for materials combining properties such as low weight, mechanical strength and wear resistance has prompted the development of a large number of fiber-reinforced composite materials. Many of these materials combine fibers and a thermoplastic or thermoset polymer to yield lightweight composite materials with excellent mechanical properties. For instance, glass-fiber reinforced plastic is a fiber reinforced polymer made of a plastic matrix reinforced by fine glass fibers. Examples of glass-fiber reinforced plastics are boat hulls and pipes. However, although the fibers for reinforcement have traditionally been synthetic such as glass fibers more recent research and development has shown excellent results also for reinforcement with natural fibers.

Cellulose fibers are natural fibers that have attracted particular interest in the context of composite materials due to their properties such as renewability, biodegradability, low density, high specific stiffness, low abrasiveness, physiological harmlessness, high availability and low cost.

However, the manufacture of cellulose fiber-reinforced composite materials is associated with challenges since short cellulose fibers such as wood pulp fibers are difficult to feed in a continuous way and disperse evenly in a matrix. Furthermore, the cellulose fibers may be subjected to breaking and thermal degradation during processing.

The low density and high bulkiness of cellulose fibers make them difficult to use in continuous industrial processes. In order to facilitate mixing of cellulose fibers with thermoplastic polymers in continuous processes the cellulose fibers have been converted into granules or pellets. However, such granulating or pelletizing leads to severe fiber breakage resulting in composite materials with poor mechanical performance. Alternatively, the cellulose fibers may be converted into a fiber roving or tow that is fed into the process, but unfortunately this does not work well when the fibers are short such as in the case of wood pulp fibers.

It is desirable that the cellulose fibers are evenly distributed within the matrix of the composite material as individual fibers will form a better reinforcing fibrous network in the composite material than will bundles or clusters of fibers. An even distribution of fibres in the polymeric matrix is also beneficial for the further processability of the composite material into articles having high surface finish and detail definition.

It is known that long fibers are more difficult to disperse than short fibers since they have a greater tendency to agglomerate, i.e. to form bundles, than short fibers. Fiber dispersion may be improved by using compatibilizers improving adhesion between the fibers and the matrix and/or by using appropriate processing conditions. For example, in extrusion the amount of shear forces to which the material undergoing extrusion is subjected will depend on the extruder screw configuration used. The shear forces required to break the fiber bundles will also reduce fiber length thereby negatively influencing the mechanical properties of the resulting material. Therefore, achieving breakage of fiber bundles while minimizing fiber breakage during extrusion in order to produce a composite material with good mechanical performance is a difficult task.

In addition, parameters such as thermal degradation of the polymer matrix and degradation of the cellulose by moisture have to be taken into account during manufacturing of the cellulose fiber-reinforced composite material.

EP 2 511 323 discloses processes such as extrusion mixing for manufacturing cellulose fiber-reinforced ethylene acrylic acid copolymer (EAA). No compatibilizer or coupling agent is required to promote the compatibility between the EAA and the cellulose fibers. Agglomerates, i.e. pellets of cellulosic fibers and EAA, are used for producing the composite materials. This way of extrusion mixing does not allow for complete dispersion of the cellulose fibers into the matrix of EAA.

Accordingly, the manufacturing of cellulose fiber-reinforced composite materials with good mechanical performance is a complex task due to the difficulties associated with handling and feeding of the cellulose fibers as well as the large number of parameters being interrelated in a non-straightforward way and affecting the mechanical properties.

There remains a need for a manufacturing process suitable for industrial production of cellulose fiber-reinforced composite materials having improved mechanical and processability properties.

It is an object of the present invention to overcome or at least mitigate some of the problems associated with manufacturing processes of cellulose fiber-reinforced composite materials and/or the resulting composite materials thereof.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a method for producing a composite material comprising cellulose fibers and a thermoplastic matrix by means of an extruder. The extruder comprises a twin screw,
and the method comprises the steps of:
a) feeding one or more cellulose fiber-based webs into the extruder, and
b) extruding the one or more cellulose fiber-based webs in a mixture with a melted thermoplastic matrix material by means of the twin screw thereby providing a composite material.

In the context of extrusion, such as in step b) in the method described herein, it will be appreciated that co-extrusion is understood to mean extrusion of the one or more cellulose fiber-based webs in a mixture with a melted thermoplastic matrix material.

By using a continuous cellulose fiber-based web as a source for cellulose fibers handling of the fibers in the process is significantly facilitated. For instance, the web may be provided in roll form or in the form of a stack or pile of Z-folded web material so that the desired amount of fibers can be easily fed into the extruder. The cellulose fiber-based web may also be provided as individual sheets. These ways of providing cellulose fibers are beneficial in continuous processes that are desired in industry, since batch-wise processes are more time consuming and less efficient. The use of a cellulose fiber-based web also allows for convenient adjustment of the cellulose fiber content by controlling the speed with which the web is fed into the extruder which is dependent on the extruder screw rotation speed. Additionally, personnel operating the equipment is exposed to less dust when the cellulose fibers are provided in the form of a web instead of pellets or granules. The amount of added fibers is also determined by the basis weight of the fiber-based web, the width of the fiber-based web and by the number of webs or plies that are fed into the extruder. Accordingly, with the same equipment, composite materials having different fiber content may be produced by varying one or more of process speed, basis weight of the web, width of the web and number of webs or plies used in the process.

During the extrusion the web will be broken and mixed with the melted thermoplastic matrix material in an efficient way so that a composite material is formed with the cellulose fibers well dispersed within the thermoplastic matrix. It has been found that introducing the web into a melted thermoplastic matrix material in accordance with the invention helps to minimize fiber length reduction resulting in improved mechanical performance and evenness of the resulting composite material. This is in contrast to the use of fibers which have been pre-processed into solid pellets or granules together with thermoplastic polymer. Pre-processing of the fibers and the matrix polymer into pellets or granules involves mechanical working of the materials resulting in grinding of the fibers and causing the fiber length to diminish. Thus, in addition to the improved handling aspects the use of a cellulose fiber-based web has a positive impact on the properties of the resulting composite material as the web allows for improved fiber dispersion within the thermoplastic matrix with minimal fiber length reduction during processing.

The composite article obtained in step b) may be subsequently formed into a composite material of desired shape such as a sheet shape or a three-dimensional shape and allowed to assume room temperature by cooling. The cooling speed may be increased by using cooled rollers, cooling air, etc. as known in the art.

Thus, the method may further comprise the steps of:
c) forming the composite material into a composite article, and
d) cooling the composite article to ambient temperature.

The composite article may be given its final shape at this stage or may be further processed, e.g. from a sheet or pellet-form by thermoforming methods such as form pressing or molding techniques.

Measurement of properties such as fiber length, aspect ratio, area percentage of cellulose fiber aggregates in the thermoplastic matrix, tensile modulus (E), tensile strength (σ_b) and strain at break (ε_b) were used to characterize the formed composite article. It was found that extrusion generally resulted in shorter fiber length and lower aspect ratio to some minor extent; while fiber dispersion was very good as measured visually or by microscopy analysis. In order to achieve complete or almost complete fiber dispersion the formed composite article may be further subjected to additional melting and extrusion.

Thus, the method may further comprise subjecting the composite article to the steps of:
e) melting and extruding by means of one or more twin screws or one or more single screws to provide a composite material,
f) shaping the composite material into a composite article, and
g) cooling the composite article to ambient temperature.

If desired, further thermoplastic matrix material and/or cellulose fiber-based web material may be added during step e). The additional thermoplastic matrix material and/or the cellulose fiber-based web material may be the same or different as those used for making the composite material resulting from steps a) and b). Preferably, the thermoplastic matrix material is melted prior to extrusion with the one or more cellulose fiber-based webs. If using more than one extruder screw in step e), the screws may be sequentially arranged in the extruder or the composite material may be passed more than once through the same extruder screw arrangement.

It should be understood that although a twin screw is required in process step b) in order to achieve satisfactory fiber dispersion, further processing of the material may be carried out using either a single screw or a twin screw or any combination of two or more extruder screws as set out herein. A barrier screw is an example of a single screw that may be used. As used herein, a twin screw is understood to be two screws placed side by side. The twin screw may be co-rotating or counter-rotating. The twin screw used in step b) is preferably operated in a co-rotating manner. In addition, the configurations of the screws may be varied using forward conveying elements, reverse conveying elements, kneading blocks, and other means for achieving particular mixing characteristics.

By a fiber-based web as used herein is implied a continuous coherent structure having an undefined length, a defined width and a defined thickness. The thickness is small in comparison with the width such that the web is a generally two-dimensional structure. The webs used in the mixing process of the invention may comprise any type of cellulosic fibers such as wood pulp fibers, cotton fibers, viscose fibers, flax, hemp, etc., with wood pulp fibers being preferred. Mixtures of different kinds of cellulosic fibers may also be used.

Various dry-formed or wet-formed cellulose fiber-based webs may be used. For instance, the cellulose fiber-based web may be an air-laid cellulose fiber-based web or a paper web. The paper web may be a creped or non-creped tissue paper web, i.e. a lightweight paper web. It will be appreciated that tissue paper is wet-formed paper while airlaid paper is dry-formed paper.The cellulose fiber-based web may comprise one, two, three, four or more plies. Each individual ply may have a basis weight of from 10 to 50 g/m^2. For instance, tissue paper typically has a basis weight of from 15 to 40 g/m^2.

In addition to cellulose fibers, the fiber-based webs used in the methods of the invention may comprise additives such as pigments and fillers. However, the amount of additives should preferably not exceed 20 % by volume, by that limiting the processing difficulties arising from an increased viscosity.

A further advantage of the method disclosed herein is that the cellulose fiber-based web may comprise softwood fibers, hardwood fibers or mixtures thereof. This is in contrast to, for example, roving and carding techniques where short wood pulp fibers are difficult to use. The method also provides a way of using recycled fibers which due to having been previously subjected to various processing steps generally have a smaller fiber length as compared to corresponding virgin fibers i.e. fibers that are used for the first time. However, due to the generally shorter length of recycled fibers, it may be preferred that not all of the fibers in the fiber-based webs used in the methods of the invention are recycled fibers. It may be preferred that recycled fibers are used in combination with virgin fibers of similar type and/or in combination with other longer cellulosic fibers such as cotton fibers. Accordingly, the method of the invention and the composite materials and/or composite articles produced therefrom offer high versatility as well as increased environmental benefits.

The presence of moisture in the cellulose fiber-based web may affect the formed composite material in a negative way. If too much moisture is present is it difficult to achieve satisfactory fiber dispersion and blisters may form in the resulting composite material. Therefore, ideally no or little moisture should be present in the cellulose fiber-based web. Ideally, the moisture content is from 0 to 10 weight% (wt %), from 0 to 7 wt%, from 6 to 8 wt%, from 5 to 6 wt%, from 2 to 4 wt% or about 3 wt% based on the cellulose fiber-based web.

The amount of cellulose fibers incorporated into the thermoplastic matrix influences the properties of the formed composite material. The best results have been found when the cellulose fiber content is from 20 to 30 wt % or from 25 to 30 wt% based on the weight of the composite material. Thus, the cellulose fiber-based web should provide from 20 to 30 wt % or from 25 to 30 wt% of cellulose fibers to the composite composition. It was found that the tensile modulus and tensile strength decreased or remained relatively constant when the cellulose fiber content was increased from about 25 to 30 wt%. A cellulose fiber content above about 30 wt% did not afford additional benefits to the mechanical properties of the composite material, but an increased level of fiber content was found to lead to more difficulties with the flow properties of the material mixture.

A thermoplastic polymer or a mixture of different thermoplastic polymers may be used as the thermoplastic matrix material. The thermoplastic polymer or polymers may be derived from recycled or non-recycled thermoplastic resources. It is desirable that the thermoplastic polymer has a softening or melting temperature that is less than about 100^{o} C since cellulose fibers may deteriorate above this temperature. The thermoplastic matrix may be prepared according to conventional methods such as grinding, shredding, pelletizing and the like. The thermoplastic polymer or polymers may be independently selected from one or more in the group consisting of: ethylene acrylic acid copolymer, polyethylene, polypropylene, polyimide, polyvinylchloride, acrylonitrile butadiene styrene polymer, aliphatic polyester, aromatic polyester and mixtures thereof.

The thermoplastic polymer may be ethylene acrylic acid copolymer (EAA). Use of EAA as the thermoplastic matrix has the advantages that no compatibilizers are required to promote adhesion between the EAA and the cellulose fibers, and the low melting point of the EAA allows using a low operating temperature. The amount of acrylic acid in the EAA may vary between 3 and 15 weight % (wt%). For instance, the amount of acrylic acid may be 7 wt%.

Compatibilizers are substances that improve the interfacial bond between the cellulose fibers and the thermoplastic matrix. The compatibilizers create a bridge between the fibers and the thermoplaxtic matrix which improves the tensile and flexural properties of the thermoplastic composite under load. However, the use of compatibilizers add to the cost of manufacturing the composite material. Examples of compatibilizers are maleic anhydride grafted polyethylene and maleic anhydride grafted polypropylene. The amount of compatibilizers is usually less than 10 wt% based on the thermoplastic matrix.

There is also provided a method as described herein wherein polyethylene is used as thermoplastic matrix optionally in conjunction with up to 10 wt% of maleic acid anhydride polyethylene.

The extruded fiber-reinforced composite material may be provided with a desired shape by passing the composite material through a die. Alternatively, the composite material may be formed through hot compression molding. Once extracted from the die or mold, the finished composite article may be allowed to assume ambient temperature through cooling with air or water.

A particular benefit of the highly uniform fiber/polymer composite materials of the invention is that they can be shaped into three-dimensional objects having high surface definition. The high degree of individualized fibers in the fiber/polymer mixtures of the invention results in a very even mixture both with regard to homogeneity and with regard to surface properties. As the composites of the invention are practically free from fiber bundles they can be formed into products with very good surface definition and with a minimum of irregularities in the surface. Accordingly, the composites of the invention are highly useful in articles such as screw-on caps and other devices where a high definition is required in small details on the surface of the article. Furthermore, the composites of the invention can be formed into sheets having excellent smoothness and surface finish.

The extrusion of the mixture of thermoplastic matrix material with the one or more cellulose fiber-based webs may take place at a temperature that is equal to or above the melting temperature of the thermoplastic matrix material. The temperature may be the same throughout the extruder, i.e. the temperature is the same within the barrel from the hopper to the die. Alternatively, there may be a temperature profile along the barrel. For instance, the temperature may be increased in a stepwise or continuous way from the hopper to the die.

In accordance with the invention, there is also provided a cellulose-fiber reinforced thermoplastic composite article in which the cellulose fibers are completely dispersed within the thermoplastic matrix, i.e. no or very few bundles of fibers are detectable. The presence of fiber bundles may be detected visually or by microscopy analysis as described in the experimental part of this document. This composite article exhibits excellent mechanical performance when the cellulose fiber content is from 20 to 30 wt% or 25 to30 wt% based on the composite material, and the polymer matrix is ethylene acrylic acid copolymer. Accordingly, there is provided a a cellulose-fiber reinforced thermoplastic composite article in which the cellulose fibers constitute about 25 wt% and are completely dispersed within the thermoplastic matrix consisting of ethylene acrylic acid copolymer

There is also provided a composite material and/or composite article obtainable by the method as disclosed herein. The composite material and/or composite article is characterized in that the cellulose fibers are completely dispersed within the thermoplastic matrix, i.e. no or very few bundles of fibers are detectable. The presence of fiber bundles may be detected visually or by microscopy analysis as described in the experimental part of this document.

The composite article produced in accordance with the method described herein may be used in packaging components such as bottles and screw caps or any other article that may be formed by molding techniques. Furthermore, sheets of the composite materials disclosed herein may be provided with a three-dimensional shape by hot pressing and formed into articles such as containers, ornamental items, furnishing, etc.

DEFINITIONS

Aspect ratio as used herein is refers to the ratio fiber length/ fiber diameter.

The terms “thermoplastic” or “thermoplastic polymer” refer to polymers that become pliable or moldable above a specific temperature, and returns to a solid state upon cooling.

The term “basis weight” stands for the weight divided by the area of a piece of cellulose fiber-based web such as tissue paper. Basis weight is usually expressed in grams per square meter (g/m^2) or gsm.

Rpm is an abbreviation of revolutions per minute and is a measure of rotation frequency.

TP is an abbreviation for tissue paper.

D is an abbreviation for diaper paper.

MPa megapascal

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows composite materials having a cellulose fiber content of 30 wt% and being made from a two-ply tissue paper (TP) and EAA % by means of extrusion in accordance with the method described herein.

Figure 2 shows composite materials having a cellulose fiber content of 30 wt% and being made from four-ply diaper paper (D) and EAA by means of extrusion in accordance with the method described herein.

Figure 3 is a schematic view of an extruder system used in the method for producing cellulose-fiber reinforced composite material as described herein.

Figure 4 is a graph showing the tensile modulus versus the cellulose content for composite articles made from two-ply tissue paper (TP) and EAA, and four-ply diaper paper (D) and EAA, respectively.

DETAILED DESCRIPTION

Figure 1 shows composite articles having a cellulose fiber content of 30 wt% and being made from a two-ply tissue paper (TP) and EAA by means of extrusion in accordance with the method described herein.

In figure 1 the composite article denoted with the letter a results from extrusion of TP with melted EAA using a twin screw. Visual inspection shows aggregates of cellulose fibers as light regions. The area percentage of the light regions as determined by microscopy analysis was determined to be 2.1 %.

In figure 1 the composite article denoted with the letter b results from melting and extrusion of the composite article denoted with the letter a using a barrier screw, i.e. a single screw. Visual inspection shows that that the number of aggregates of cellulose fibers has diminished compared to the material denoted with the letter a. The area percentage of the light regions as determined by microscopy analysis was determined to be 0.2 %.

In figure 1 the composite article denoted with the letter c results from melting and extrusion of the composite article denoted with the letter a using a twin screw. Visual inspection shows that that the number of aggregates of cellulose fibers has diminished compared to the material denoted with the letter a. The area percentage of the light regions as determined by microscopy analysis was determined to be 0 %, i.e. no aggregates of cellulose fibers were detected.

Figure 2 shows composite articles having a cellulose fiber content of 30 wt% and being made from four-ply diaper paper (D) and EAA by means of extrusion in accordance with the method described herein.

In figure 2 the composite article denoted with the letter a results from extrusion of a four-ply diaper paper (D) and EAA using a twin screw. Visual inspection shows the presence of aggregates of cellulose fibers as light regions. The area percentage of the light regions as determined by microscopy analysis was determined to be 13 %.

In figure 2 the composite article denoted with the letter b results from melting and extrusion of the composite article denoted with the letter a using a barrier screw. Visual inspection shows the presence of aggregates of cellulose fibers as light regions. The area percentage of the light regions as determined by microscopy analysis was determined to be 1.1%.

In figure 2 the composite article denoted with the letter c results from melting and extrusion of the composite article denoted with the letter a using a twin screw. Visual inspection shows the presence of aggregates of cellulose fibers as light regions. The area percentage of the light regions as determined by microscopy analysis was determined to be 0.4 %.

Comparison of the results for the TP based composite articles denoted with the letters b and c in figure 1 show that a second run with the twin screw is better for providing a composite article with evenly distributed cellulose fibers than the barrier screw. In the same way, inspection of the results for the D based composite articles denoted with the letters b and c in figure 2 shows that a second run with the twin screw provides better fiber dispersion than the barrier screw.

Figure 3 is a schematic representation of the processing used to compound the cellulose fiber-based web with the thermoplastic matrix, and the extruder screw configuration. Pellets of thermoplastic matrix material are fed into the hopper 1 and melted in temperature zones A and B of the barrel 2 while being fed forward towards the die 6 by the extruder screw 3. A cellulose fiber-based web is dried in a dryer box 4 prior to being fed through a connecting tube 5 to temperature zone C of the barrel where it is extruded in a mixture with the melted thermoplastic matrix material to yield a composite material that is extruded and fed forward through temperature zones D and E towards the die 6. The composite material is passed through the die 6 to form an article of desired shape which is subsequently allowed to assume ambient temperature.

Figure 4 shows the tensile modulus versus the cellulose content for articles made from two-ply tissue paper (TP) and EAA, and articles made from four-ply diaper paper (D). The articles were obtained after two consecutive extrusions with twin extruder. For the article made from TP and EAA the tensile strength had a maximum when the cellulose fiber content was 25 wt%. For the article made from D and EAA the tensile modulus remained relatively constant when the cellulose content was increased from 25 to 30 wt%.

The invention is further illustrated by the following non-limiting examples.

EXAMPLES

Materials

The polymer used as matrix material was EAA Primacor 3540 from Dow Chemical Company. The EAA had a 7% acrylic acid content, average molecular mass of 16100 g/mol, melt flow rate (MFR) (190°C/2.16 kg, ISO 1133) of 8 g/10 min and a density of 0.932 g/cm^3.

The cellulose fibers used in this work were in form of tissue. Two different tissues were used: a two-ply tissue with 100% primary fibers from Metsä Tissue and a four-plytissue DG2490 from Swedish Tissue AB, denoted herein as TP and D respectively. The TP tissue consisted in 75% birch and 25% softwood fibers with no additives and a basis weight of 34 g/m^2. The D material contained 2 wt% wet strength and 0.3 wt% dry strength agents and consisted in 20% birch fibers and the rest softwood fibers. The basis weight was approximately 96 g/m^2. In this case, the cellulose fibers were less loosely bonded than in the TP tissue.

Melt processing

The compounding of the tissue with the polymer was performed with a co-rotating twin screw Werner & Pfleiderer ZSK 30 M9/2 (Stuttgart, Germany) with a screw diameter of 30 mm and 966 mm length and provided with 5 heating zones and the die zone. The temperatures profile used from the hopper to the die was: 100, 130, 140, 140, 150, 150°C. Since the polymer was fed into the extruder in a controlled manner, it was possible to calculate the cellulose content by the dragging speed of the tissue. In this case, the screw speed was fixed for each material and the polymer feeding was adjusted depending on the desired cellulose content. The screw speed used with the TP tissue was 96 rpm while for the four layered tissue a lower speed had to be used, specifically 60 rpm. A schematic representation of the processing and the screw configuration are shown in Fig. 3. The tissue which was in drying chamber was fed into the extruder and then dragged by the screws through an opening in the zone C. In order to have the tissue constantly dried, a tube was used to connect the drying chamber with the entry of the extruder. The tissue was dried for 3 days at 75°C resulting in a water content of 3 wt% before the compounding.

By feeding the cellulose fibers in the zone C, which is located downstream of the hopper (see Figure 3), less fiber degradation and also better impregnation of the fibers with the polymer can be obtained since the polymer is already completely melted. The configuration of the screw was optimized for effective breaking of the tissue and mixing with the polymer just after the tissue feeding.

Fig. 3. is a schematic representation of the processing used to compound the cellulose tissue with the polymer and the screw configuration. The type and number of elements of the screw from the hopper to the die was: 1 pressure element, 9 fast transport elements, 1 slow transport element, 1 mixing element, 4 fast transport elements, 1 slow transport element, 2 pressure elements, 5 mixing (kneading) elements, 1 pressure element with contrary direction to the flow and 5 pressure elements.

The second extrusion performed with the twin screw extruder was done with the same screw speed and the same screw configuration that was used for compounding the tissue with the polymer. In case of the material obtained with TP tissue was 96 rpm and 60 rpm for the four layered tissue.

A second extrusion was also performed with a single screw Brabender compact extruder, Brabender OHG, Duisburg, Germany, with a screw diameter D = 19 mm and a screw length of 25D (i.e. the screw length was 25 times the screw diameter), three individually controlled temperatures zones and a temperature-controlled circular die with a diameter of 3 mm. In this case a Maillefer barrier-flighted screw (Maillefer, 1960, 1967) with a compression ratio 2.5:1 with a Saxton distributive mixer element at the screw end was used. The temperature profile along the barrel from hopper to die was 90, 130, 140 and 140°C and the screw speed was 100 rpm. In this work, the second extrusion performed with the twin screw is denoted TS while in case of the barrier-flighted screw is BS.

The injection molding was performed with an injection molding machine Arburg Allrounder, 221M-250-55, Austria. The temperature profile from the hopper to the die was 90, 130, 140, 150 and 150°C, the injection pressure was 125 MPa, the cycle time 50 s and the mold was at room temperature. The mold used had a single cavity, producing a test bar with a shape according to DIN 53455 with a mass of about 6 g. The flow path from the cylinder nozzle to the cavity was a sprue diverging from diameter 3.5 Millimeters (mm) to diameter 6.5 mm along the sprue length of 54 mm; a first runner of 80 mm length with a cross section of 35 mm^2, a second runner of 35 mm length with a cross section of

25 mm^2 and a rectangular cavity gate with dimensions of 15 x 1 mm and a land length of 1.5 mm.

Measurements

The composite samples and the samples of pure polymer below were taken from the middle section of the test bar with a shape according to DIN 53455 produced as described above.

Fiber content

The fiber content was measured using Soxhlet extraction with xylene. A small sample piece of the composite sample was cut, weighed and placed into a sample container, i.e. a thimble. The thimble was weighed prior to use. The thimble containing the composite sample was placed in a Soxhlet apparatus containing xylene. Heating to reflux during Soxhlet extraction using xylene was performed for approximately 96 h. After this time, the thimble containing the cellulose fibers was dried and weighed. The weight difference between the dried thimble containing cellulose fibers and the weight of the thimble prior to use was calculated to yield the fiber weight. The fiber content was calculated by dividing the fiber weight in the composite sample by the sum of the fiber weight in the composite sample and the weight of the pure polymer in the composite sample.The given values are based on one measurement.

The fiber content was also measured by determining the weight difference between the composite sample and a sample of pure polymer (the matrix polymer EAA). A total of 10 samples were weighed and the average value was calculated. The average value for the composite sample was subtracted with the weight value for the sample of pure polymer to yield the weight of the fibers in the composite sample. The fiber content was calculated by dividing the fiber weight in the composite sample by the sum of the fiber weight in the composite sample and the weight of the pure polymer in the composite sample.

For the above calculations of the fiber content it was assumed that the volume of the composite sample was the same as for the sample of pure polymer, i.e. 1.8 cm^3. This volume was set to be equal to the fiber weight in the composite sample divided by the fiber density plus the unknown weight for the pure polymer divided by the pure polymer density. Thus, the weight of the pure polymer in the composite sample was obtained. The calculations were based on a fiber density of 1,5 g/cm^3 and 0,932 g/cm^3 for the pure polymer, i.e. EAA.

Microscopal image analysis

In order to enable studies of the number and size of cellulose aggregates by microscopal analysis, the middle region of each injection-molded sample was milled from 4 mm to a thickness of 1 mm. The analysis was performed with a stereomicroscope type SteREO discovery.V20 from Carl Zeiss, Germany. The total characterized area was 10 x 20 mm^2. In the images, the number of aggregates and the relative area percentage were assessed with the digital image processing software AxioVision from Carl Zeiss MicroImaging GmbH, Germany.

Fiber length measurements

Fiber length measurements were made with an optical analyzer Kajaani FS300, Metso Automation, Finland, based on light polarization measurements of fibers in water. In this case, the polymer was extracted directly with xylene during approximately 12h. After the extraction, the cellulose fibers were washed and kept in water before performing the measurements. With this method the fiber length distribution and the width distribution obtained were calculated according to the standardized methods TAPPI T271 0–7.60 mm and ISO 16065 0.20–7.00 mm. The mean value of the fiber length and the standard deviation was calculated based on three measurements.

Tensile testing

The tensile mechanical properties were measured with a tensile testing machine equipped with a free-standing clip-on extensometer with adjustable gauge length Zwick 1455, Germany, and according to ISO527-1. A cross-head speed of 6 m/min corresponding to a strain rate of about 1.4×10^{-3} s^{-1} was used and the gauge length of the extensometer was 60 mm. The tensile modulus was calculated from data points between 0.1 and 0.25 % strain. The mean value and the standard deviation of all mechanical properties were calculated based on seven measurements.

Fiber content

The fiber content was measured with two different methods in order to have a better assessment of the actual fiber content in the final composites. Soxhlet extraction, used in previous work, seemed to be a quite accurate method but because of the long time needed to completely extract the polymer together with a high number of samples, it was necessary to use a faster method in parallel. Tables 1 and 2 show the results obtained by both weight difference and Soxhlet methods for materials made with TP and D tissue respectively. It could be observed that similar results were obtained with both methods. It could also be observed that the cellulose fiber content were very close to the desired content being more accurate with the TP materials than for materials made with D tissue. The slightly higher measured cellulose content in this last case could be due to the number of plies that made the feeding more difficult and thus not as continuously homogeneous as with the TP material which contained less plies.

Sample	Cellulose content (wt%)	
	Weight difference	Soxhlet
20% TP	20.8	20.4
20% TP BS	20.1	20.8
20% TP TS	19.8	20.1
25% TP	25.9	24.8
25% TP BS	26.2	25.9
25% TP TS	25.8	25.3
30% TP	30.4	29.1
30% TP BS	27.6	28.8
30% TP TS	27.0	28.4

Table 1. Cellulose content measured with the two different methods of materials obtained with TP tissue.

Sample	Cellulose content (wt%)	
	Weigh difference	Soxhlet
20% D	23.1	22.5
20% D BS	21.8	21.9
20% D TS	23.2	22.9
25% D	29.3	26.0
25% D BS	28.4	26.8
25% D TS	28.7	27.2
30% D	-*	31.2
30% D BS	-*	30.6
30% D TS	31.5	30.8
35% D TS	34.1	34.9

Table 2. Cellulose content measured with the two different methods of materials obtained with D tissue.* No weigh difference was possible to perform in these samples because of the uncomplete filling of the mold.

Visual Characterization

Differences between materials obtained with different tissue materials and also between materials obtained with the same tissue material but processed differently could be clearly seen by the naked eye. The middle part of injection-molded specimens of TP materials containing 30 wt% cellulose fibers are shown in Fig. 1. It could be observed that the specimen having more cellulose aggregates was the one obtained after just compounding the tissue with the polymer, i.e. after only one pass with the twin screw (specimen a, Fig. 1). Almost no cellulose aggregates were observed in specimens obtained after a second extrusion with the barrier-flighted screw (specimen b, Fig. 1) while the specimen obtained after two passes in the twin screw presented no detectable cellulose aggregates (specimen c, Fig. 1). The same trend was observed for materials with lower cellulose content.

As observed in the TP materials, cellulose aggregates in D materials (Fig. 2) diminished with the further processing but in no case disappeared completely. A possible reason for these differences may be the higher difficulty to break the multi-ply tissue and disperse the more bonded fibers.

Fig. 1. TP materials. a) 30% TP b)30% TP BS c) 30% TP TS

Fig. 2. D Materials. a) 30% D b) 30% D BS c) 30% D TS

Microscopy analysis

All injection-molded specimens were studied by microscopy analysis. The number of aggregates and the aggregate area percentage of the total characterized area were measured and the results are shown in Table 3. The results corroborated what it was observed by the naked eye. The specimens with higher aggregate area percentage were those obtained after one pass with the twin screw extruder. After the second extrusion the aggregate area percentage decreased considerably. When comparing specimens obtained after two extrusions, in general those extruded with the barrier screw had a higher aggregate area percentage than those extruded twice with the twin screw for which values close to 0% were obtained.

Sample	Number of regions	Relative fiber aggregate area (%)
20% TP	12	3.1
20% TP BS	19	0.7
20% TP TS	0	0.0
25% TP	14	1.7
25% TP BS	6	0.2
25% TP TS	4	0.1
30% TP	33	2.1
30% TP BS	2	0.2
30% TP TS	0	0.0
20% D	50	17.0
20% D BS	34	2.5
20% D TS	11	0.7
25% D	39	13.6
25% D BS	35	2.1
25% D TS	24	2.0
30% D	56	13.0
30% D BS	18	1.1
30% D TS	9	0.4
35% D TS	14	0.8

Table 3. Number of regions and aggregate area percentage measured by microscopal analysis.

Fiber length

Tables 4 and Table 5 show the measured fiber length of the specimens made with the TP tissue and the D tissue, respectively. As expected, the original fiber length in the D tissue, which contained more softwood fibers, was greater than for the TP tissue. In both cases the fiber length was reduced more than 25% after compounding with the twin screw extruder and even more after a second extrusion. The fiber shortening was more pronounced after a second extrusion with the twin screw than with the barrier screw. As could be expected, the fiber length was also affected by the fiber content, as higher fiber loading increases the melt viscosity and thus the shear forces responsible for the fiber breakage.

The fiber length shortening was about 50 % after two passes of the material through the twin screw extruder, at 25 % cellulose fiber content obtained with both tissue TP and tissue D. With an increased fiber content of 30 - 35 % and still two passes through the twin screw extruder, the fiber length reduction increased to about 65 %, with no significant difference between using tissue TP or tissue D, as can be estimated from tables 4 and 5.

	Sample	L (mm)	L/D
	TP Tissue	1.06 (0.006)	62.4 (1.1)
1 Pass Twin screw	25% TP	0.79 (0.006)	42.8 (0.5)
	30% TP	0.75 (0.012)	38.6 (0.8)
2nd Pass Barrier Screw	25% TP BS	0.60 (0.006)	27.2 (0.2)
	30% TP BS	0.54 (0.010)	28.8 (0.6)
2 Passes Twin Screw	25% TP TS	0.54 (0.006)	24.5 (0.4)
	30% TP TS	0.41 (0.006)	21.9 (0.3)

Table 4. Average values of three fiber length measurements and aspect ratio of specimens made with TP tissue. The standard deviation values are in parentheses.

	Sample	L (mm)	L/D
	D Tissue	1.54 (0.021)	60.9 (4.3)
1 Pass Twin screw	25% D	1.10 (0.074)	45.9 (2.8)
	35% D*	0.99 (0.015)	41.4 (0.3)
2nd Pass Barrier Screw	25% D BS	0.78 (0.006)	33.4 (0.2)
	35% D BS*	0.57 (0.006)	24.7 (0.2)
2 Passes Twin Screw	25% D TS	0.75 (0.006)	29.0 (0.2)
	35% D TS	0.48 (0.006)	19.4 (0.3)

Table 5. Average values of three fiber length measurements and aspect ratio of specimens made with D tissue. The standard deviation values are in parentheses. * Mold not completely filled.

Tensile properties

The tensile mechanical properties of all injection-molded specimens are shown from Table 6 to Table 9. For the specimens made with the TP tissue, it could be observed that both tensile modulus (E) and tensile strength (σ_b) decreased with the number of the extrusions while the opposite trend was observed for the strain at break (ε_b). The lower aspect ratio of the fibers after two consecutive extrusions could explain the lower reinforcing effect of the fibers while the better dispersion achieved by the two consecutive extrusions with the twin screw could explain the higher elongation at break since the interaction fiber–matrix could be improved by a better wettability of the fibers with the polymer. The second extrusion with the barrier screw also had a beneficial effect on the mechanical properties. Higher tensile modulus and tensile strength values compared to the second extrusion with the twin screw were obtained but the elongation at break values were considerably lower. These differences could be explained by the aspect ratio of the fibers as well as the fiber dispersion in the final composite.

Fiber content also influenced the mechanical properties. As expected, the tensile modulus increased with increasing fiber content and the opposite trend was observed for the elongation at break. Only in the case of two consecutive extrusions with the twin screw extruder, shown in Fig. 4 no improvement in stiffness was observed when increasing the fiber content from 25 wt% to 30 wt% which could indicate that in this particular case the maximum packing fraction is 25 wt%. The same trend was observed for the tensile strength where the maximum value was obtained at 25 wt% of cellulose fibers.

For the materials made with the D tissue, i.e. containing more softwood fibers and less loosely bonded than the TP tissue, a different trend was observed. Both tensile modulus and tensile strength improved with the second extrusion. This could be due to the better fiber dispersion obtained after the second extrusion. In this case the breakage of the tissue was more difficult since the fibers were less loosely bonded than in the TP tissue. A better dispersion could be obtained by using a high screw speed which would increase the shear forces capable to break the tissue but due to the high grammage of the tissue, it was not possible to use a higher speed. Less fiber breakage should be expected when using lower screw speed. This was observed for the specimens made with the D tissue which could explain the slightly better mechanical performance compared to the TP tissue specimens. Because of the higher aspect ratio, it was not possible to fill the mold in all cases. Only the materials run twice in the twin screw were possible to fill completely. Fig. 4 shows how in this case, both tensile modulus and tensile strength increased with the content of cellulose but not so significant differences were obtained from 25 wt% to 35 wt%.

	Sample	E (MPa)	σ_b (MPa)	ε_b (%)
	EAA	118 (18)	12.4 (0.1)*	76 (2)*
1 pass twin screw	20% TP	783.0 (28.7)	19.7 (0.4)	9.1 (0.6)
	25% TP	1101.6 (48.4)	24.9 (0.6)	7.6 (0.6)
	30% TP	1362.6 (48.6)	27.3 (0.8)	6.1 (0.3)
2 passes twin screw	20% TP TS	616.4 (21.5)	18.5 (0.2)	19.3 (1.5)
	25% TP TS	878.2 (19.1)	22.4 (0.3)	13.6 (1.9)
	30% TP TS	811.7 (41.6)	21.4 (0.5)	15.0 (0.8)

Table 6. Tensile mechanical properties of TP specimens after one pass with the twin screw and two passes with the twin screw. * These values correspond to difficulties in breaking specimens.

Sample	E (MPa)	σ_b (MPa)	ε_b (%)
20% TP BS	748.5 (24.9)	20 (0.3)	12 (0.5)
25% TP BS	1013.8 (31.0)	21.1 (0.5)	9.7 (0.5)
30% TP BS	1097.0 (43.1)	27.0 (0.7)	9.3 (0.2)

Table 7. Tensile mechanical properties of TP specimens obtained after a second pass with the barrier-flighted screw.

	Sample	E (MPa)	σ_b (MPa)	ε_b (%)
1 pass twin screw	20% D	677.14 (21.1)	16.6 (0.5)	9.7 (1.4)
	25% D	NIM	NIM	NIM
	30% D	NIM	NIM	NIM
2 passes twin screw	20% D TS	743.93 (53.4)	20.4 (0.3)	12.5 (1.4)
	25% D TS	1133.31 (31.8)	24.5 (0.5)	7.4 (0.3)
	30% D TS	1158.66 (56.5)	25.1 (0.6)	8.4 (0.7)
	35% D TS	1170.58 (25.3)	26.0 (0.7)	8.5 (1.1)

Table 8. Tensile mechanical properties of D specimens after one pass with the twin screw and two passes with the twin screw. In the table, NIM stands for no completely filling of the mold.

Sample	E (MPa)	σ_b (MPa)	ε_b (%)
20% D BS	760.05 (19.0)	19.0 (0.3)	10.5 (0.9)
25% D BS	1165.76 (58.1)	24.9 (0.7)	7.8 (0.6)
30% D BS	NIM	NIM	NIM
35% D BS	NIM	NIM	NIM

Table 9. Tensile mechanical properties of D specimens after a second pass with the barrier-flighted screw. In the table, NIM stands for no completely filling of the mold.

It will be appreciated that the invention is not limited by the embodiments described above, and further modifications of the invention within the scope of the claims would be apparent to a skilled person.

CLAIMS

1. A method for producing a composite material comprising cellulose fibers and a thermoplastic matrix by means of an extruder, said extruder comprising a twin screw, wherein the method comprises the steps of:
a) feeding one or more continuous cellulose fiber-based webs into the extruder, and
b) extruding the one or more cellulose fiber-based webs in a mixture with a melted thermoplastic matrix material by means of said twin screw thereby providing a composite material.

2. A method according to claim 1, wherein said extruder comprises at least one further extrusion screw said at least one further extrusion screw being a twin screw or a single screw.

3. A method according to claim 1 or 2, further comprising the steps of:
c) forming the composite material into a composite article, and
d) cooling the composite article to ambient temperature.

4. A method according to claim 3, wherein the composite article in step c) or d) is further subjected to the steps of:
e) melting and extruding by means of one or more extrusion screws selected from twin screws and single screws to provide a composite composition,
f) forming the composite material into a composite article, and
g) cooling the composite article to ambient temperature.

5. A method according to claim 4, further comprising addition of melted thermoplastic matrix material and/or one or more cellulose fiber-based webs during step e).

6. A method according to any one of the previous claims, wherein the screws of said twin screw are co-rotating.

7. A method according to any one of the previous claims, wherein the one or more cellulose fiber-based webs is an air-laid cellulose fiber-based web or a paper web.

8. A method according to claim 7, wherein the paper web is a tissue paper web.

9. A method according to any one of the previous claims, wherein the one or more cellulose fiber-based webs comprise(s) one, two, three, four or more plies.

10. A method according to claim 9, wherein the ply or or plies independently has/have a basis weight from 10 to 50 g/m^2.

11. A method according to any one of the previous claims, wherein the cellulose fiber-based web comprises softwood fibers, hardwood fibers or mixtures thereof.

12. A method according to any one of the previous claims, wherein the cellulose fiber-based web comprises virgin fibers, recycled fibers or mixtures thereof.

13. A method according to any one of the previous claims, wherein the one or more cellulose fiber-based webs has a moisture content from 0 to 10 wt%.

14. A method according to any one of the previous claims, wherein the one or more cellulose fiber-based webs provides from 20 to 30 wt% or from 25 to 30 wt% of cellulose fibers to the composite material and/or to the composite article.

15. A method according to any one of the previous claims, wherein the thermoplastic matrix material is selected from the group consisting of: ethylene acrylic acid copolymer, polyethylene, polypropylene, polyimide, polyvinylchloride, acrylonitrile butadiene styrene polymer, aliphatic polyester, aromatic polyester and mixtures thereof.

16. A method according to any one of the previous claim, wherein the thermoplastic matrix material is ethylene acrylic acid copolymer.

17. A composite material obtainable by claim 1 or 2.

18. A composite article obtainable by any one of claims 3-16.

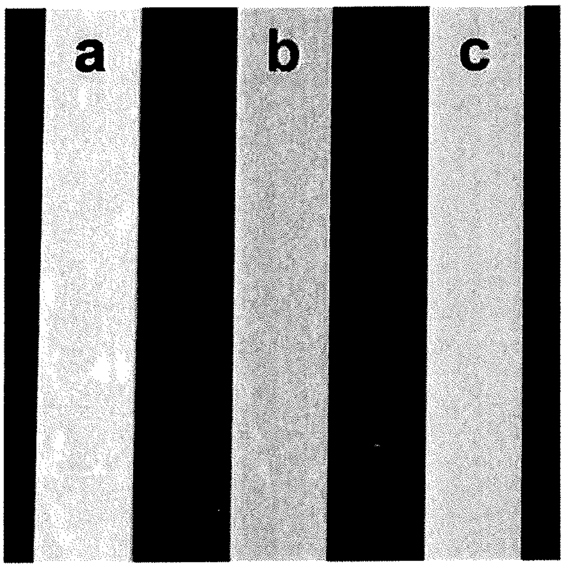

Fig. 1

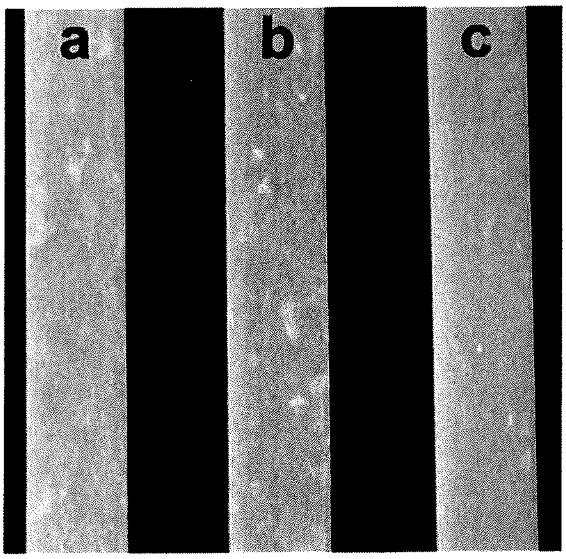

Fig. 2

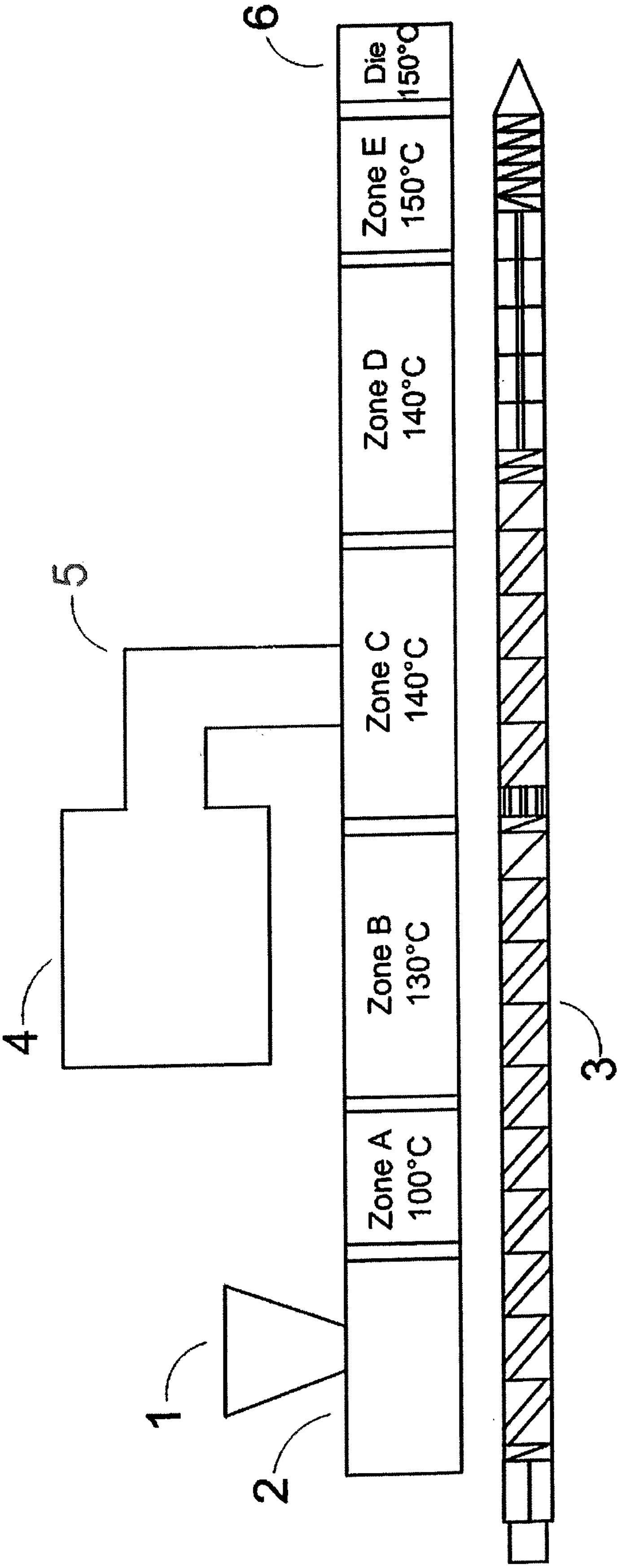
6
Die
150°C
Zone E
150°C
Zone D
140°C
Zone C
140°C
Zone B
130°C
Zone A
100°C
5
4
3
1
2

Fig. 3

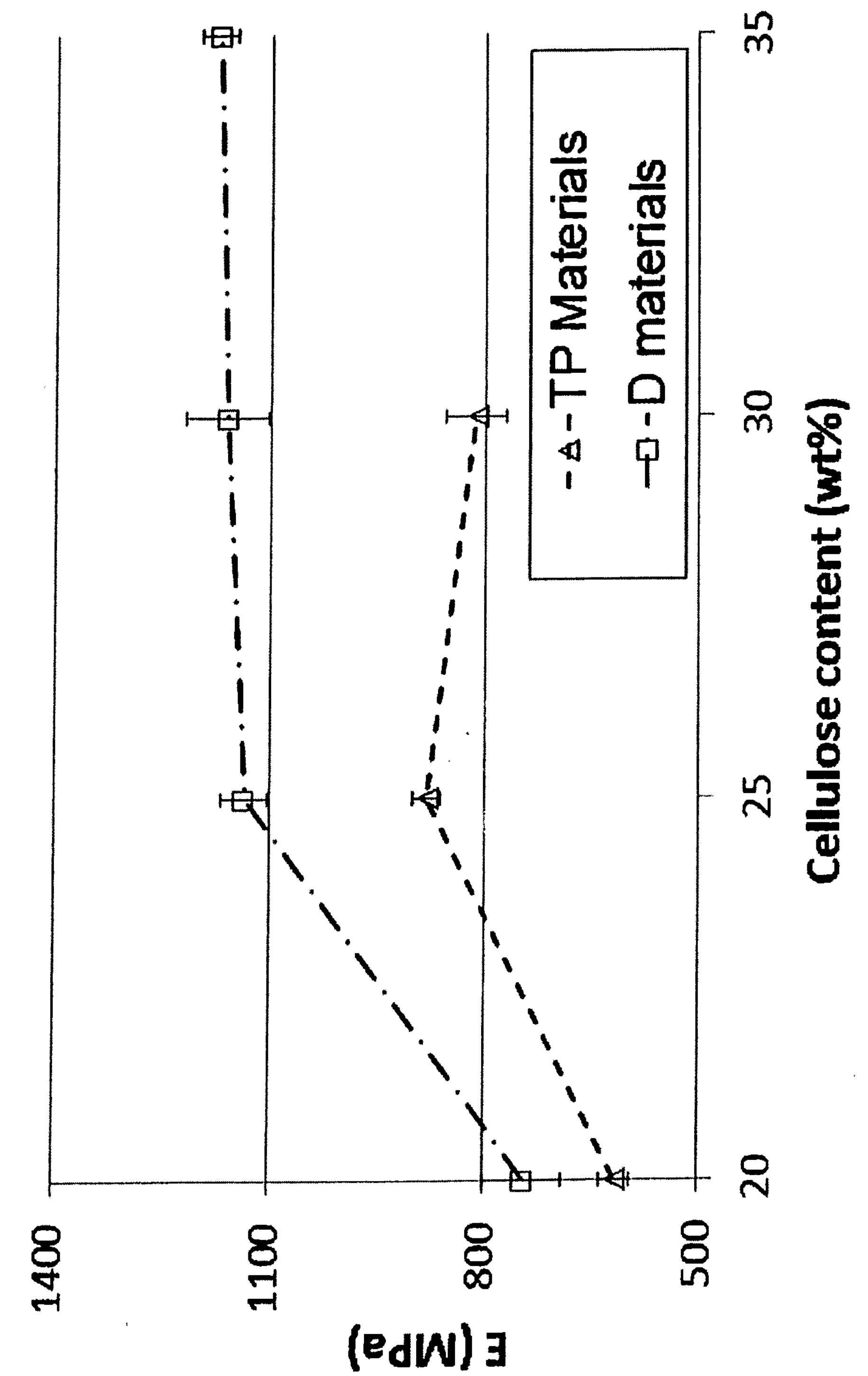
E (MPa)
1400
1100
800
500
20
25
30
35
Cellulose content (wt%)
TP Materials
D materials

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2014/050149

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B29C, C08J

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

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0303015 A1 (SIGNODE SYSTEM GMBH), 15 February 1989 (1989-02-15); whole document --	1-18
A	EP 2511323 A1 (SOEDRA SKOGSAEGARNA EKONOMISKA FOERENING), 17 October 2012 (2012-10-17); whole document --	1-18
A	US 6565348 B1 (SNIJDER MARTINUS HENDRICUS BER ET AL), 20 May 2003 (2003-05-20); whole document --	1-18
A	EP 1070782 A1 (WWJ L L C), 24 January 2001 (2001-01-24); whole document --	1-18

☒ 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 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
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06-05-2014	07-05-2014

Name and mailing address of the ISA/SE
Patent- och registreringsverket
Box 5055
S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer
Erika Stenroos
Telephone No. + 46 8 782 25 00

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20050118410 A1 (LIN ALLEN F -(B2) LIN ALLEN FONG-CHIN [TW]), 2 June 2005 (2005-06-02); whole document --	1-18
A	US 6379605 B1 (LIN ALLEN FONG-CHIN), 30 April 2002 (2002-04-30); whole document --	1-18
A	US 20100320637 A1 (BOLDIZAR ANTAL), 23 December 2010 (2010-12-23); whole document -- --------	1-18

Continuation of: second sheet

International Patent Classification (IPC)

B29C 47/10 (2006.01)
C08J 5/04 (2006.01)

EP	0303015	A1	15/02/1989	AU	613936	B2	15/08/1991
				AU	2035888	A	09/02/1989
				DE	3725965	A1	16/02/1989
				JP	H01118425	A	10/05/1989
				NZ	225668	A	28/11/1989
				US	4894192	A	16/01/1990
EP	2511323	A1	17/10/2012	EP	2697291	A1	19/02/2014
				WO	2012141645	A1	18/10/2012
US	6565348	B1	20/05/2003	AT	251021	T	15/10/2003
				AU	3853599	A	23/11/1999
				CA	2332041	C	17/07/2007
				CN	1304350	A	18/07/2001
				CN	1168591	C	29/09/2004
				DE	69911762	T2	29/04/2004
				DK	1075377	T3	19/01/2004
				ES	2203130	T3	01/04/2004
				JP	2002513692	A	14/05/2002
				JP	4365529	B2	18/11/2009
				WO	9956936	A1	11/11/1999
EP	1070782	A1	24/01/2001	NONE			
US	20050118410	A1	02/06/2005	EP	1537991	B1	25/04/2007
				JP	2005125708	A	19/05/2005
				JP	4259980	B2	30/04/2009
				US	7041243	B2	09/05/2006
US	6379605	B1	30/04/2002	JP	2001232682	A	28/08/2001
US	20100320637	A1	23/12/2010	CN	101918200	A	15/12/2010
				EP	2227374	A2	15/09/2010
				WO	2009082350	A3	27/08/2009