



(22) Date de dépôt/Filing Date: 2005/11/18

(41) Mise à la disp. pub./Open to Public Insp.: 2007/05/18

(45) Date de délivrance/Issue Date: 2014/05/06

(51) Cl.Int./Int.Cl. *B29B 7/92* (2006.01),
B27N 1/00 (2006.01), *B29C 70/12* (2006.01),
B29C 70/40 (2006.01), *B32B 21/08* (2006.01),
D21B 1/34 (2006.01)

(72) Inventeurs/Inventors:
SAIN, MOHINI M., CA;
PANTHAPULAKKAL, SUHARA, CA;
LAW, SHIANG F., CA

(73) Propriétaires/Owners:
SAIN, MOHINI M., CA;
PANTHAPULAKKAL, SUHARA, CA;
LAW, SHIANG F., CA

(74) Agent: GRAHAM, LORELEI G.

(54) Titre : METHODE DE FABRICATION DE MATERIAU COMPOSITE HAUTE PERFORMANCE A BASE DE FIBRES
LIGNOCELLULOSIQUES

(54) Title: MANUFACTURING PROCESS FOR HIGH PERFORMANCE LIGNOCELLULOSIC FIBRE COMPOSITE
MATERIALS

(57) **Abrégé/Abstract:**

A process for the manufacture of composite materials having lignocellulosic fibres dispersed in a thermoplastic matrix, while generally maintaining an average fibre length not below 0.2 mm. The process includes defibrillation of the lignocellulosic fibres using a mixer and at a temperature less than the decomposition temperature of the fibres in order to separate the fibres and generate microfibrils, followed by dispersion of the fibres in the thermoplastic matrix by mechanical mixing to get the moldable thermoplastic composition, followed by injection, compression, extrusion or compression injection molding of said composition. The composite materials of the present invention are well-suited for use in automotive, aerospace, electronic, furniture, sports articles, upholstery and other structural applications.

ABSTRACT

A process for the manufacture of composite materials having lignocellulosic fibres dispersed in a thermoplastic matrix, while generally maintaining an average fibre length not below 0.2 mm. The process includes defibrillation of the lignocellulosic fibres using a mixer and at a temperature less than the decomposition temperature of the fibres in order to separate the fibres and generate microfibrils, followed by dispersion of the fibres in the thermoplastic matrix by mechanical mixing to get the moldable thermoplastic composition, followed by injection, compression, extrusion or compression injection molding of said composition. The composite materials of the present invention are well-suited for use in automotive, aerospace, electronic, furniture, sports articles, upholstery and other structural applications.

MANUFACTURING PROCESS FOR HIGH PERFORMANCE LIGNOCELLULOSIC FIBRE COMPOSITE MATERIALS

FIELD OF THE INVENTION

This invention relates generally to lignocellulosic fibre / thermoplastic composites. This invention relates more particularly to a method of producing a lignocellulosic fibre / thermoplastic composition with improved material characteristics.

BACKGROUND OF THE INVENTION

Lignocellulosic fibre composites are widely used in a broad spectrum of structural as well as non-structural applications including automotive, building and construction, furniture, sporting goods and the like. This is because of the advantages offered by natural fibres compared to conventional inorganic fillers, including:

- plant fibres have relatively low densities compared to inorganic fillers;
- plant fibres result in reduced wear on processing equipment;
- plant fibres have health and environmental related advantages;
- plant fibres are renewable resources and their availability is more or less unlimited;
- composites reinforced by plant fibres are CO₂ neutral;
- plant fibres composites are recyclable and are easy to dispose of; and
- complete biodegradable composite products can be made from plant fibres if used in combination with biopolymers.

There is extensive prior art in the field of lignocellulosic fibre composite materials. Notably, Zehner in United States Patent No. 6,780,359 (2004) describes a method of manufacturing a component mixing cellulosic material with polymer, forming composite granules and molding granules into a component, utilizing a selection of thermoplastic resins, cellulose, additives, and inorganic fillers as feedstock and

specifying a preference of wood flour over wood fibre in order to achieve a sufficient coating of cellulose by the plastic matrix.

Hutchison et al. in United States Patent No. 6,632,863 (2003) teaches manufacturing of a pellet comprising at least 55% cellulosic fibre, blending the pellet with more polymer to form a final composition of at least 35% fibre and molding said pellet into articles.

Snijder et al. in United States Patent No. 6,565,348 (2003) describes a multi-zone process involving melting the polymer, feeding the fibre continuously into the melt and kneading the mixture to produce fibres of the highest aspect ratio, and extruding the mixture and form granules. Sears et al. in United States Patent No. 6,270,883 (2001) describes use of a twin-screw extruder blending of fibre granules or pellets with the polymer and additives

Medoff et al. in United States Patent No. 6,258,876 (2001) teaches a process for manufacturing a composite comprising shearing cellulosic or lignocellulosic fibre to the extent that its internal fibres are substantially exposed to form texturized fibres, and combining them with a resin. Medoff et al. in United States Patent No. 5,973,035 (1999) teaches a similar cellulosic composite.

Mechanical properties of the lignocellulosic fibre-filled polymer composites are mainly determined by: (i) the length of the fibres in the composite; (ii) the dispersion of the fibres in the polymer matrix; (iii) the interfacial interaction between the fibres and the polymer matrix; and (iv) the chemical nature of the fibre. In conventional lignocellulosic fibre composites, fibre agglomeration has been observed, which is a constraint in developing structural materials. The prime challenges allied with the development of a manufacturing process for high performance structural materials from short lignocellulosic filled thermoplastic materials include retention of the fibre length required for the effective stress transfer from the matrix to the fibre, and well dispersion of fibres in the matrix to avoid stress concentrating agglomerates, in addition to a good fibre matrix interfacial adhesion which enhances the stress transfer to the fibre. Lignocellulosic fibres are rich in hydroxyl groups and because of the strong hydrogen

bonds between these hydroxyl groups it is extremely difficult to get a homogeneous dispersion of these fibres in the hydrophobic thermoplastic matrix. The highly hydrophilic cellulosic fibres are incompatible with the hydrophobic thermoplastic matrix and this also leads to poor wetting and dispersion of the fibres. Use of proper interface modifiers can improve the wetting and dispersion to a certain extent and improve the performance of the composites. Extensive research has been conducted to improve dispersion and interfacial adhesion and hence to improve the properties of the lignocellulosic composites.

For example, in United States Patent No. 4,250,064 (1981), Chandler describes the use of plant fibres in combination with fine or coarse inorganic filler such as CaCO_3 to improve the dispersion of fibres in the polymer matrix. Methods such as pretreatment of cellulosic fibres by slurring them in water and hydrolytic pre-treatment of cellulosic fibres with dilute HCl or H_2SO_4 was described by Coran et al. and Kubat et al. in United States Patent Nos. 4,414,267 (1983) and 4,559,376 (1985), respectively. Pretreatment of cellulosic fibres with lubricant to improve dispersion and bonding of the fibres in the polymer matrix was disclosed by Hamed in United States Patent No. 3,943,079 (1976).

Use of functionalized polymers and grafting of cellulosic fibres with silane for improving dispersion and adhesion between fibre and matrix have been disclosed by Woodhams in United States Patent No. 4,442,243 (1984) and Besahay in United States Patent No. 4,717,742 (1988) respectively. Raj et. al in United States Patent No. 5,120,776 (1992) teaches a process for chemical treatment of discontinuous cellulosic fibres with maleic anhydride to improve bonding and dispersability of the fibres in the polymer matrix. Beshay in United States Patent No. 5,153,241 (1992) explained use of titanium coupling agent to improve bonding and dispersion of cellulosic fibres with the polymer.

Horn disclosed, in United States Patent No. 5,288,772 (1994), the use of pre-treated high moisture cellulosic materials for making composites. A hydrolytic treatment of the fibres at a temperature of 160-200 degrees Celsius using water as the softening agent has been claimed by Pott et al. in a Canadian Patent No. 2,235,531 (1997). Sears et al. disclosed a reinforced composite material with improved properties containing

cellulosic pulp fibres dispersed in a high melting thermoplastic matrix, preferably nylon as described in United States Patent No. 6,270,883 (2001) and European Patent No. 1121244 (2001)].

Performance of a discontinuous fibre filled composite is also highly dependent on fibre length. For example, longer discontinuous fibres have the capacity to withstand greater stress and hence have greater tensile properties than shorter fibres of similar nature, as larger fibres can absorb more stress prior to failure than a shorter fibre. Jacobsen disclosed in the United States Patent No. 6,610,232 (2003) the use of long discontinuous lignocellulosic fibres for thermoplastic composites.

Another technique to improve the dispersion of the lignocellulosic fibres is to use high shear during melt blending of the fibres with plastics. Since the fibres are prone to break down, the high shear results in small fibres in the resultant compound where the fibres are not effective to carry the load from the matrix. In other words, due to the high shear, the fibre length is reduced to less than the critical fibre length. This is especially significant where inorganic glass fibres are used in combination with organic fibres. Glass fibres easily breakdown to small length and this adversely prevents the exploitation of the full potential of the composite materials. In order to achieve a high performance material from lignocellulosic thermoplastic composites, it is necessary to well disperse the fibres in the matrix while preserving the critical fibre length.

In an earlier patent application of the present inventors, namely United States Publication No. 20050225009, and Application No. 11/005,520, filed on 12/06/2004 disclose a process to obtain high performing cellulosic and glass fibre filled thermoplastic composites with improved dispersion of the cellulosic fibres.

Although prior art show processing of thermoplastic composites containing different lignocellulosic fillers with different combinations of thermoplastics, coupling agents, and fibre treatments, they are deficient in producing high strength performance cellulosic filled thermoplastic composite materials, which is attained by the present invention. The present invention can achieve high performance structural composite materials where the organic fibres have an effective fibre length and well dispersed and

bonded with the inexpensive thermoplastic matrix materials. Also, there is a need in certain applications for thermoplastic composites containing lignocellulosic fibre without glass fibre. There is a further need for producing such thermoplastic composites that have desirable thermal resistance characteristics.

BRIEF SUMMARY OF THE INVENTION

In one aspect of the present invention, a method of producing high performance recyclable and moldable lignocellulosic fibre filled thermoplastic structural composites is provided. The production method involves defibrillation and dispersion of the lignocellulosic fibres into a thermoplastic matrix using a high intensity thermokinetic mixer.

In a more particular aspect of the present invention, a method is provided by which recyclable and moldable lignocellulosic fibre filled structural polymer composite materials can be produced after being injection, compression or compression injection molded into a structural composite product of the same composition, the following material characteristics are achieved: preferably tensile strength not less than 55 MPa, flexural strength not less than 80 MPa, stiffness not less than 2 GPa, notched impact strength not less than 20 J/m, and un-notched impact strength not less than 100 J/m. The method involves processing steps where the lignocellulosic fibres are defibrillated in a high shear mixer during a time period that is operable to achieve the separation of hydrogen-bonded lignocellulosic fibres and to generate microfibrils on the individual lignocellulosic fibre surface and then dispersed in a thermoplastic by an intensive mechanical mixing, or kneading, at a temperature that is greater than the melt temperature of the thermoplastic and less than the decomposition temperature of the lignocellulosic fibres, during a time period that is operable to achieve the dispersion or blending of the lignocellulosic fibres throughout the thermoplastic. The resulting characteristics of the lignocellulosic fibres, mechanical entanglement of the fibres and interfacial adhesion between the fibres and the thermoplastic yield a composite material with high strength characteristics that is well-suited for structural applications, including in the automotive, aerospace, furniture and other industries.

Preferably the thermoplastic matrix material is a polyolefin, more preferably polypropylene, but other thermoplastic materials are useful as well, e.g., polyethylene, polystyrene, and polyethylene-polypropylene copolymers, poly-vinyl chlorides, polylactides, polyhydroxybutyrates, and polyethyleneterephthalate.

Surface active agents may be used in the composite depending on the chemical properties of the thermoplastic, e.g. maleated polypropylene with propylene used as the matrix material. Other preferable surface active agents can be selected from the group consisting of a maleated polyethylene, maleated polystyrene, maleated polylactides, maleated hydroxybutyrates and maleated terephthalates in combination with polyethylene, polystyrene, polylactides, polyhydroxybutyrates and polyethylene terephthalates respectively.

The lignocellulosic fibres used in the present invention can be obtained from both wood sources, including softwood or hardwood, as well as non-wood fibres, often referred to as agro-pulp. The fibres can be prepared using common chemical, mechanical, or chemi-mechanical pulp processes, as is described in the prior art.

As mentioned earlier, the process and the composite product developed by the present invention will find many structural applications, preferably in automotive, aerospace and furniture industry. In addition to the environmental and economical advantages of such composite products, the said composite products can meet the stringent requirements of the said industries including cost, weight reduction, fuel efficiency, disposal, and recycling.

The key advantage of the technology of the present invention in comparison to known techniques is the ability to maximize the performance properties. The technology is practiced in the laboratory scale, but can scale up to the industry level, in a manner that is known. Another advantage of the composite product of the invention is that they can compete with the existing glass fibre filled composite and use of lignocellulosic fibres reduces the amount of plastics and synthetic fibres used in the composite and results in energy savings due to reduced quantity of polyolefin and glass fibre. These two later components are much more energy intensive compare to that of natural fibre production..

BRIEF DESCRIPTION OF THE DRAWINGS

A detailed description of the preferred embodiment(s) is(are) provided herein below by way of example only and with reference to the following drawings, in which:

Figure 1 illustrates the microfibril development during the course of defibrillation in accordance with the present invention, at 70 times magnification.

Figure 2 illustrates the microfibril development during the course of defibrillation in accordance with the present invention, at 80 times magnification.

Figure 3 illustrates the initial stage of fibre opening during the course of defibrillation in accordance with the present invention, at 500 times magnification.

Figure 4 illustrates the microfibril development during the course of defibrillation in accordance with the present invention, at also at 500 times magnification in another view thereof. Separate microfibrils are visible at the bottom part of the micro-photograph with fibre diameter less than 10 microns.

Figure 5 illustrates the reduction of fibre diameter during the course of defibrillation in accordance with the present invention, at 1000 times magnification.

Figure 6 illustrates the microfibril development on the fibre surface during the course of defibrillation in accordance with the present invention, also at 1000 times magnification in another view thereof.

Figure 7 illustrates the average fibre diameter before defibrillation in accordance with the present invention, at 5000 times magnification

Figure 8 illustrates the microfibril development with diameter less than 10 micron during the course of defibrillation in accordance with the present invention, also at 5000 times magnification in another view thereof.

Figure 9 illustrates creep behaviour of 40% by weight of TMP filled polypropylene composite under flexural load at ambient condition.

In the drawings, preferred embodiments of the invention are illustrated by way of example. It is to be expressly understood that the description and drawings are only for the purpose of illustration and as an aid to understanding, and are not intended as a definition of the limits of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The natural fibre composite products of the present invention have enhanced properties, preferably tensile strength not less than 55 MPa, flexural strength not less than 80 MPa, stiffness not less than 2 GPa, notched impact strength not less than 20 J/m, and un-notched impact strength not less than 100 J/m.

Figure 9 illustrates the properties of the fibre/thermoplastic composite of the present invention. Samples of the composite were tested for creep resistance properties by allowing them to stand a load of 30% of their flexural load as a function of time. The deflection of the samples as a function of time was measured and is shown in Figure 9, as defined by creep. The higher the creep, the lower the load bearing capacity. A very low creep value indicates that the composite has good load bearing qualities.

The present invention provides a method of producing high performing moldable and recyclable lignocellulosic fibre filled thermoplastic compositions and structural composite products consisting of lignocellulosic fibres dispersed in a matrix of thermoplastic material. Preferably the fibre/thermoplastic composite comprise of less than or equal to 60% by weight cellulosic fibres, where lignocellulosic fibres have a moisture content of less than 10% by weight, and preferably less than 2% by weight.

Depending on the chemical composition of the thermoplastic used in developing the composition, a surface active agent may be necessary to improve the interaction between the cellulosic and inorganic fibres with the matrix and to substantially disperse the cellulosic fibres throughout the matrix.

The defibrillation of the lignocellulosic fibres is achieved in a high shear thermo-kinetic mixer for not less than 30 seconds at a temperature of 230 degrees Celsius or less to separate the hydrogen-bonded fibres and, importantly, generate microfibrils on the surface of the individual lignocellulosic fibres. Microfibrils are microfibrils which develop on the surface of the individual lignocellulosic fibre, typically having a relatively small diameter relative to diameter of the fibres prior to defibrillation. These microfibrils once formed either remain attached to the fibre or are separated as a result of the defibrillation, as illustrated in the Figures. The generation of microfibrils increases the surface area of the fibres and causes mechanical entanglement and furthers the eventual interfacial adhesion between the fibres and the thermoplastic matrix and the fibres themselves, resulting in the production of an interpenetrating network structure and thereby causing an overall increase in the strength of the composite. Further, the strength of the fibre is enhanced by the formation of microfibrils because the number of fibre defects decreases as the fibre diameter decreases.

In a particular aspect of the present invention, the defibrillation generates extensive microfibrils on the fibre surface due to a high shear generated during the process in the thermo-kinetic mixer, such microfibrils having a relatively small diameter and an average aspect ratio greater than 10. This microfibril formation is highly dependent on the time and intensity of shear imparted on the fibre surface and also depends on the dynamic temperature profile inside the thermo-kinetic mixer. The defibrillation generally causes the fibril diameter to decrease significantly to achieve the aspect ratio referred to above. The microfibril formation also results in the formation of anchors on the fibre surface, which then penetrate the molten plastic matrix to form a microfibril-enhanced plastics interface during the melt-blending step described below. Again, this improves the mechanical entanglement and provides for an interpenetrating fibre network structure within the matrix, and greatly increases the strength of the

composite due to two specific effects: (i) the increased surface area of the microfibrils improves overall surface area of interaction between the molten plastic and fibres; and (ii) the enhanced strength of the microfibrils compared to that of the fibre helps to improve mechanical performance and other known performance attributes of the composite. The enhanced strength as per (ii) results from less heterogeneous fibre composition, their greater uniformity due to fewer impurities such as residual lignin and/or hemicelluloses. The heterogeneous composition of fibre with larger diameter results from multiple microfibrils being bonded together physically or chemically. These bundles of microfibrils have multiple interfaces. The higher the number of interfaces, the greater the likelihood of defects or structural damage (e.g. due to friction or due to inherent nature of the fibre). The greater the incidence of defects, the weaker the fibres. Defibrillation in accordance with the present invention, reduces the number of interfaces and therefore the number of resultant defects or damage.

Also, microfibril formation results in greater net surface area per unit of weight. This greater net surface area results in improved interfacial adhesion between the fibres and the matrix developed by good dispersion, as discussed below, produce a composite material with superior performance characteristics.

Compositions coming out from the thermo-kinetic mixer in the form of lumps may be used with or without a granulation for the subsequent processing steps. In other words, the lumps coming out from thermo-kinetic mixer could be used for subsequent processing steps without further granulation or pelletization.

Suitable lignocellulosic fibres can be pulp manufactured by mechanical refining, chemical pulping or a combination of both. Known chemical pulp manufacturing processes include high temperature caustic soda treatment, alkaline pulping (kraft cooking process), and sodium sulfite treatment. Suitable fibres include commercially available unbleached thermo-mechanical pulp (TMP), bleached thermo-mechanical pulp, unbleached chemi-thermo-mechanical pulp (CTMP), bleached chemi-thermo-mechanical fibre (BCTMP), kraft pulp and bleached kraft pulp (BKP). The fibres can be selected from any virgin or waste pulp or recycled fibres from hardwood, softwood or agro-pulp. Hardwood pulp is selected from hardwood species, typically aspen, maple, eucalyptus,

birch, beech, oak, poplar or a suitable combination. Softwood pulp is selected from softwood species, typically spruce, fir, pine or a suitable combination. Agro-pulp includes any type of refined bast fibres such as hemp, flax, kenaf, corn, canola, wheat straw, and soy, jute or leaf fibres such as sisal. Alternatively, the fibre pulp selection can include a suitable combination of hardwood and softwood or a combination of wood pulp and agro-pulp.

The initial moisture content of the pulp fibre influences the processing and performance properties of composite. A moisture content of below 10% w/w is recommended. More specifically the pulp moisture content that is below 2% w/w is preferred.

Depending on the nature of wood species, the performance of the composite of the present invention may vary significantly. For example, a hardwood species, such as birch in the brightness range of above 60 can provide improved mechanical performance compared to that of maple, for example. Similarly, agro-pulp, and other fibres that are easy to defibrillate tend to give higher mechanical performance. For example, chemical and mechanical pulps made from hemp and flax provide improved performance compared to that of corn or wheat stalk pulp based composites. These varying characteristics of pulp fibres and their selection for applications dependent on such characteristics are well known to those skilled in the art.

Specific fibre characteristics include the following. The average lengths of the fibres are in the range of 0.2 to 3.5 mm, with the average diameter of natural fibre ranging between 0.010 mm to 0.070 mm. The fibres have a brightness value between 20 and 95% ISO (according to Tappi Standard), and typically between 60 to 85 ISO. Another important characteristic of the fibres is the fibre bulk density. Fibres are fed in the form of loosely held agglomerates having a bulk density of 20 grams per cubic centimetre or more and freeness not below 40 CSF (CSF means Canadian Standard Freeness and is described in the prior art). The fibres have a reciprocal bulk density between 0.6 to 3.8 cubic centimetres per gram, and typically between 0.7 to 3.0 cubic centimetres per gram. The average fibre length as relates to "pulp freeness" needs to be

controlled. The freeness of fibres are in the range of 50 to 600 CSF (Tappi standard), and typically between 100 to 450 CSF. In addition, fibres are not 100% lignin free and they may typically contain 0.01% to 30% (w/w) lignin.

Although brightness of the pulp can be varied depending on the performance requirement, a brightness range above 40 ISO (Tappi Standard) is preferred. A pulp bleached or brightened with oxidizing and/or reducing chemicals could influence the overall mechanical performance, dispersion of the fibres and the microfibril formation. In general, the higher the brightness, the higher the microfibril formation in thermo-kinetic mixer. A brightness range above 60 ISO is particularly suitable for efficient generation of microfibrils.

The matrix material used in the present invention comprises a polymeric thermoplastic material with a melting point preferably 230 degrees Celsius or less. Suitable polymeric materials include polyolefins, preferably polypropylene, polyethylene, copolymers of propylene with other monomers including ethylene, alkyl or aryl anhydride, acrylate and ethylene homo or copolymer or a combination of these and the most preferred general purpose injection mold or extrusion grade polypropylene. Still further materials include polystyrene, polyvinyl chloride, nylon, polylactides, and polyethyleneterphthalate. Polypropylene with a density of 0.90g/cm^3 was used in the present invention.

The surface active agents that may be used in the present invention depending on the chemical composition of the thermoplastic preferably comprise functional polymers, preferably maleic anhydride grafted polyolefins, terpolymers of propylene, ethylene, alkyl or aryl anhydrides and alkyl or aryl acrylates, and more preferably maleated polypropylene, acrylated-maleated polypropylene or maleated polyethylene, their acrylate terpolymers or a suitable combination for use with polypropylene and polyethylene matrix materials. Other useful coupling agents include maleated polystyrene and maleated polylactide in combination with polystyrene and polylactide matrix materials. Preferably, the surface active agent(s) is/are present in an amount

greater than 2% by weight and less than 15% by weight of the entire composition of the composite, and more preferably in an amount less than or equal to 10% by weight.

After *in situ* defibrillation, the fibres are melt blended, or kneaded, with the matrix preferably by intensive mechanical mixing achieved in the same high shear thermokinetic mixer *in situ*. As stated, the improved performance in the present invention is a combined effect of physical and physical/chemical entanglement developed by the microfibrils structure and the interfacial adhesion formed between said structure and the thermoplastic matrix, in the presence of one or more functional additives such as surface active agents as described above.

The degree of agglomeration is a good measure as to the dispersion of fibres, as well as detached microfibrils, within the thermoplastic matrix. In essence, a perfect dispersion means that there are no visible agglomerates of fibres in a thin film formed from the composites. Typically, visible agglomerates in such a composite are in the range of 250 micrometers and above. The degree of agglomeration, as determined by an image analyzer, is the number and the sizes of agglomerates that are present in the final composition per unit surface area of the composite film. A good dispersion within a composite as taught by the present invention yields composite material that contains less than one visible agglomerate of size 250 micrometers and above per square inch of a thin film.

An important factor in the defibrillation and dispersion stages is the residence time. The higher the residence time under high shear, the greater the microfibril formation. Also, higher residence time during the dispersion stage means better dispersion. The present invention involves maximizing residence time during the defibrillation and dispersion stages while ensuring that the temperature over time does not attain the decomposition temperature. While the decomposition temperature provides the upper limit of temperature within mixer, in accordance with the present invention 230 degrees Celsius is defined as an appropriate upper limit as many fibres begin discoloration at this temperature, which generally means that the decomposition temperature is not far behind. Therefore, 230 degrees Celsius, in a particular

embodiment of the present invention is defined as the upper temperature limit for defibrillation.

As well, the sequence of the addition of fibres, thermoplastic and additives into the thermo-kinetic mixer is also significant. Typically, the fibres are added and defibrillated for a minimum residence time to provide adequate microfibril generation and dispersion of fibres. During this time, the temperature in the mixing zone rises. Once an adequate residence time has been achieved, the polymers and additives (if applicable) are added. These parameters are well known to those skilled in the art.

When the defibrillation and dispersion of the individual fibres is formed by a high shear mixing process as described above, the dispersion of these fibres and microfibrils can be further improved by adding an extra step where the so obtained composites mixtures are further dispersed in a low shear thermo-mechanical process, such as a extruder, injection or a compression injection process, whereby the extruders are designed to reduce fibre breakage. Compression and then dispersion of the melt-mix under high pressure injection in a compression-injection process is described in the prior art as a process where the composites formed in the first stage are heat melted and then injected in a cavity under very high pressure.

According to one particular embodiment, discontinuous lignocellulosic pulp fibres were defibrillated for not more than 4 minutes in a high shear mixer and melt blended to disperse the fibres with thermoplastic material in the presence of surface active agents (if applicable) in a high shear thermokinetic mixer.

Another embodiment relates to a method of making injection or compression or compression injection molded composite products from the granulates or pellets of the fibre/thermoplastic composite of the present invention or using them as is without forming any granulates or pellets as they comes out in the forms of lumps from the high speed mixer. Preferably the method comprising injection molding of the pre-dried granulates or pellets by removing moisture by drying to below 5% by weight. In a process of injection compression molding, a minimum pressure of 200 tonnes is recommended. In accordance with the present invention, dispersion of the fibre in the

polymer matrix can be further improved by increasing the injection pressure up to 1200 tonnes without increasing the melt temperature above 230 degrees Celsius.

According to one embodiment of the present invention, the composite comprising thermoplastic filled with bleached pulp has tensile and flexural strengths greater than that of the unfilled thermoplastic matrix material and tensile and flexural moduli greater than that of unfilled thermoplastic matrix material. More preferably, the composite has tensile and flexural strength and moduli greater than that of the thermoplastic matrix material.

According to another preferred embodiment, the composite comprising thermoplastic filled with thermo-mechanical pulp (TMP) has tensile and flexural strengths greater than that of the unfilled thermoplastic matrix material and tensile and flexural moduli greater than that of unfilled thermoplastic matrix material. More preferably, the composite has tensile and flexural strength and moduli greater than that of the thermoplastic matrix material.

According to another preferred embodiment, the composite comprising thermoplastic filled with unbleached kraft fibres has tensile and flexural strength greater than that of the unfilled thermoplastic matrix material and tensile and flexural moduli greater than that of unfilled thermoplastic matrix material. More preferably, composite has tensile and flexural strength and moduli greater than that of the thermoplastic matrix material.

According to another preferred embodiment, the composite comprising thermoplastic filled with chemi-thermo-mechanical wood fibres has tensile and flexural strength greater than different from the unfilled thermoplastic matrix material and tensile and flexural moduli greater than that of unfilled thermoplastic matrix material. More preferably, composite has tensile and flexural strength and moduli greater than that of the thermoplastic matrix material.

According to yet another preferred embodiment, the defibrillation of the lignocellulosic fibres and their dispersion in the molten thermoplastic occurs in a single

stage of a high shear mixing process, with the generation of microfibrils occurring prior to the dispersion in the thermoplastic matrix.

In yet another preferred embodiment, the amount of natural fibre that could be introduced is up to 60% by total weight of the composition. A preferred range of natural fibre content in the composition is between 30 percent by weight of the total composition to about 50 percent by weight of the total composition.

EXAMPLES

The following examples illustrate some of the moldable thermoplastic compositions and composite products comprising lignocellulosic fibres and the methods of making the same within the scope of the present invention. These are illustrative examples only and changes and modifications can be made with respect to the invention by one of ordinary skill in the art without departing from the scope of the invention.

For the purposes of comparison, the performance properties of polypropylene are shown in Table 1.

ASTM Test	Performance property	Sample D
ASTM D638	Tensile strength, MPa	31.6
ASTM D638	Tensile Modulus, GPa	1.21
ASTM D790	Flexural Strength, MPa	50
ASTM D790	Flexural Modulus, GPa	1.41

Table 1. Properties of polyolefin.

Examples of the composition of the moldable thermoplastic composition are given in Table 2. Pulp fibres were defibrillated in a high shear internal mixer for not less than thirty seconds and melt blended with thermoplastic and surface active agents in the same mixer at a temperature not more than 190 degree Celsius. The melt composition from the internal mixer was granulated to prepare the lignocellulosic composite granulates.

Materials (wt%)	Sample D	Sample E
Polypropylene	55	45

Chemi- thermomechanical pulp	40	50
Surface active agent	5	5

Table 2. Composition of the lignocellulosic composites D and E.

Performance properties of the lignocellulosic composites (samples D and E) are summarized in Table 3. The composite samples exhibit a tensile strength of 62 and 72 MPa and a flexural strength of 95 and 116 MPa. Flexural stiffness of the said composites are 3.8 and 5 GPa, respectively. These composite products would be sufficient for applications requiring high strength and stiffness.

ASTM Test	Performance property	Sample	
		D	E
ASTM D638	Tensile strength, MPa	63	72
ASTM D638	Tensile Modulus, GPa	3.4	4.2
ASTM D790	Flexural Strength, MPa	95	116
ASTM D790	Flexural Modulus, GPa	3.8	5.1
ASTM D 256	Notched impact strength, J/m	30	35
ASTM D 256	Un-notched impact strength, J/m	266	244

Table 3. Properties of the lignocellulosic composites D and E.

ASTM Test	Performance property	Sample			
		30% TMP + 5% Additive A + 65%PP	35% TMP + 5% Additive B + 60%PP	40% TMP + 5% Additive A+ 55%PP	50% TMP + 10% Additive B + 40%PP
ASTM D638	Tensile strength, MPa	47.5	50.2	52.5	61.4
ASTM D638	Tensile Modulus, GPa	2.7	2.9	3.2	3.9
ASTM D790	Flexural Strength, MPa	74.8	82	86	105
ASTM D790	Flexural Modulus, GPa	2.7	3.2	3.6	4.8
ASTM D 256	Notched impact strength, J/m	22	20	23	28
ASTM D 256	Un-notched impact strength, J/m	201	177	185	203

Table 4: Properties of TMP composites with two different additive systems

ASTM Test	Performance property	Sample	
		40% TMP + 5% Additive B+ 55%PP	50% TMP + 5% Additive B+ 45%PP
ASTM D638	Tensile strength, MPa	53.1	55.8
ASTM D638	Tensile Modulus, GPa	3.2	3.4
ASTM D790	Flexural Strength, MPa	87.7	91.1

ASTM D790	Flexural Modulus, GPa	3.6	4.5
ASTM D 256	Notched impact strength, J/m	21	23
ASTM D 256	Un-notched impact strength, J/m	164	139

Table 5: Effect of TMP Fibre loading

Additive A contains an interface modifier with acrylate- maleate polypropylene; Additive B contains an interface modifier with maleated polypropylene.

REFERENCES CITED

US PATENT DOCUMENTS:

6,610,232	Aug 26, 2003	Jacobsen; William W.	264/177.2
6,270,883	Aug 7, 2001	Sears; Karl D., Jacobson; Rodney E., Caulfield; Daniel F., Underwood; John	428/292.1
5,288,772	Feb 22, 1994	Hon; David N.-S.	524/35
5,153,241	Oct 06, 1992	Beshay; Alphons D.	524/8
5,120,776	June 9, 1992	Raj; Govinda, Kokta; Bohuslav V.	524/13
4,559,376	Dec 17, 1985	Kubat; Josef, Klason; Tore C. F.	524/13
4,717,742	Jan 5, 1988	Beshay; Alphons D.	523/203
4,442,243	April 10, 1984	Woodhams; Raymond T.	523/212
4,414,267	Nov 08, 1983	Coran; Aubert Y., Goettler; Lloyd A.	428/36
4,250,064	Feb 10, 1981	Chandler; Hermann	524/35

3,943,079

March 09,1976

Hamed;Parviz

524/14

OTHER REFERENCES:

CA 2235531 : April 25,1997. Groeneveld; Hendrik Adrian Cornelis., Zomers;
Franciscus Hillebrand Adriaan., Pott; Gerard Tjarko., Appl. No. 97201249-6

EP 1121244: Aug 08, 2001 Sears Karl D., Jacobson Rodney E. IPC: B32B5/16

CLAIMS

1. A method of producing a lignocellulosic fibre/thermoplastic composite characterized in that the method includes the steps of:
 - (a) defibrillating lignocellulosic fibres in a mixer at a temperature less than the decomposition temperature of the lignocellulosic fibres, during a time period that is operable to achieve:
 - (i) separation of hydrogen-bonds present between the lignocellulosic fibres;
 - (ii) generation of microfibrils on the surface of the lignocellulosic fibres; the microfibrils being formed to either remain attached to the surface of the lignocellulosic fibres; or be partially or fully separated from the lignocellulosic fibres; and
 - (iii) coating the lignocellulosic fibres with a surface agent;
 - (b) dispersing the lignocellulosic fibres obtained in (a) throughout a melted thermoplastic in situ in the mixer;whereby the lignocellulosic fibres and microfibrils dispersed in the thermoplastic.
2. The method of claim 1 wherein the mixer is a thermokinetic high shear mixer.
3. The method of claim 1 wherein the defibrillating is achieved at a temperature of 100 to 140 degrees Celsius.
4. The method of claim 1 wherein the dispersing is achieved by mechanical mixing at a temperature greater than the melt temperature of the thermoplastic.
5. The method of claim 1 wherein the microfibrils are either attached to the surface of the lignocellulosic fibres or detached.
6. The method of claim 5 wherein the detached microfibrils further contribute to the interfacial adhesion with the thermoplastic.

7. The method of claim 1 wherein the lignocellulosic fibres are selected from pulp and is not more than 75 weight percent of the composite.
8. The method of claim 7 wherein the pulp is selected from hardwood pulp, softwood pulp or agro-fibre pulp.
9. The method of claim 7 wherein the wood pulp is manufactured by mechanical refining or chemical pulping, or a combination thereof.
10. The method of claim 7 wherein the lignocellulosic fibres have a moisture content of less than 10 weight percent.
11. The method of claim 1 wherein the lignocellulosic fibres have an average length of about 0.2 mm to 3.5 mm.
12. The method of claim 1 wherein the lignocellulosic fibres have an average diameter of about 0.005 mm to 0.070 mm.
13. The method of claim 1 wherein the lignocellulosic fibres have a bulk of about 0.7 to 3.0 cubic centimeters per gram.
14. The method of claim 1 further comprising the step of applying at least one interface modifier to the lignocellulosic fibres so as to improve dispersion of the lignocellulosic fibres in the thermoplastic.
15. The method of claim 14 wherein the interface modifier is surface active agent and comprises between about 2 and 15 weight percent of the composite.
16. The method of claim 14 wherein the interface modifier is a functional polymer selected from the group consisting of maleated polyethylene, maleated polypropylene, copolymers and terpolymers of polypropylene containing acrylate and maleate, maleic anhydride grafted polystyrene, polylactide, polyhydroxyalkonate, or polyphenylene terephthalate, or any combination thereof.
17. The method of claim 1 wherein the dispersing occurs for no less than 10 seconds.

18. The method of claim 1 wherein the thermoplastic is selected from the group consisting of polyethylene, polypropylene, polystyrene, polyethylene copolymer, polypropylene co-polymer, polyvinyl chloride, polylactic acid, polyphenylene terephthalate, or polyhydroxyalkonate, or any combination thereof.
19. The method of claim 1 further comprising granulating the lignocellulosic fibre/thermoplastic composite.
20. The method of claim 1 wherein the thermoplastic has a melting point of less than 250 degrees Celsius.
21. A method of producing a molded fibre/thermoplastic composite product, characterized in that the method comprises the steps of:
 - (a) defibrillating a mass of lignocellulosic fibres in a mixer to achieve separation of hydrogen-bonds and to generate microfibrils; on the surface of the lignocellulosic fibres, the microfibrils being formed to either remain attached to the surface of the lignocellulosic fibres or be partially or fully separated from the lignocellulosic fibres and coating the lignocellulosic fibres with a surface agent;
 - (b) dispersing the lignocellulosic fibres obtained in (a) throughout a thermoplastic by melt blending to produce a moldable fibre/thermoplastic composite; and
 - (c) injection, compression, extrusion or compression-injection molding the moldable fibre/thermoplastic composite to form a molded fibre/thermoplastic composite product.
22. A fibre/thermoplastic composite comprising:
 - (a) lignocellulosic fibres having a length of at least 0.2 mm and selected from wood pulp comprising hardwood pulp, softwood pulp or agro-pulp, and manufactured by mechanical refining or chemical pulping, or a combination thereof; and

(b) a thermoplastic;

characterized in that the lignocellulosic fibres have been defibrillated in a mixer to separate the hydrogen bonds and to generate microfibrils on the surface of the lignocellulosic fibres, the microfibrils being formed to either remain attached to the surface of the lignocellulosic fibres or be partially or fully separated from the lignocellulosic fibres and coating the lignocellulosic fibres with a surface agent; and

wherein the lignocellulosic fibres are dispersed in the thermoplastic and achieve interfacial adhesion with the thermoplastic.

23. An article of manufacture comprising the fibre/thermoplastic composite claimed in claim 22.
24. An article of manufacture of claim 23, whereby the fibre/thermoplastic composite is used for automotive, aerospace, electronic, furniture and other structural applications.

Application number/numéro de demande: 02527325

Figures: 1-8

Pages: _____

DRW-IP

Unscannable items
received with this application
(Request original documents in File Prep. Section on the 10th Floor)

Documents reçus avec cette demande ne pouvant être balayés
(Commander les documents originaux dans la section de préparation des dossiers au
10ième étage)

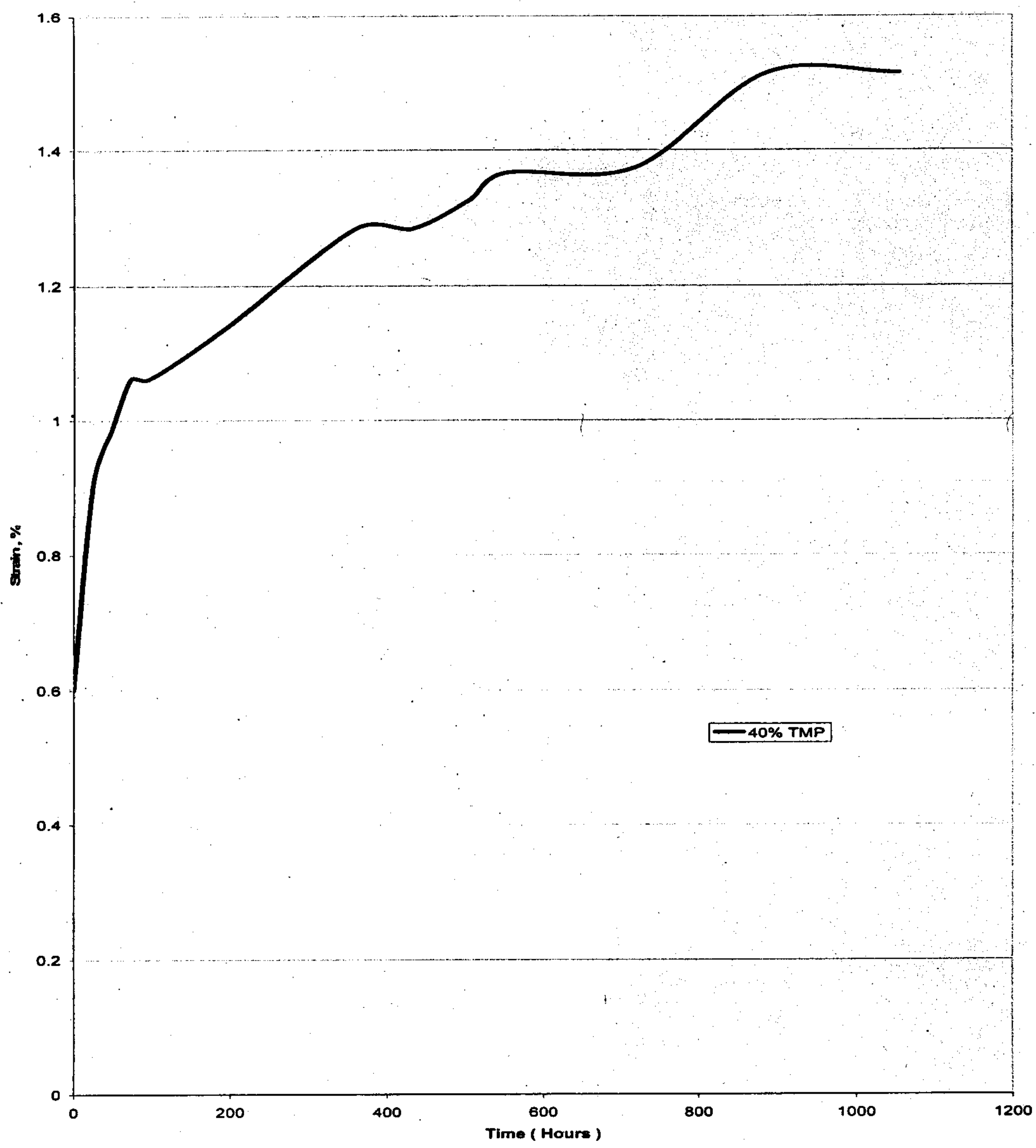


FIG. 9