Abstract: A cellulose fibre - polymer composite material where said material includes; (a) a cellulose fibre and (b) a polymer, characterised in that said composite material further includes at least one coupling agent selected from a zirconate or a titanate.
CELLULOSE FIBRE - POLYMER COMPOSITE MATERIAL

TECHNICAL FIELD

The invention relates to composite materials made from cellulose fibres such as wood fibres, in combination with a polymer. In particular, the invention relates to a cellulose fibre - polymer composite material containing a coupling agent selected from a zirconate or titanate. The composite material has numerous structural applications.

BACKGROUND ART

The following descriptions are provided to assist the reader to understand the relevance of the invention. However the background art is not intended and do not of themselves provide any admission by the applicant that they are published as may be required for an assessment of novelty or obviousness or are common general knowledge according to the laws of and in any particular country in the world.

Composite materials made by combining a cellulose fibre with a polymer have become more popular in recent years, as the interest in recycling plastics and cellulose fibres has improved. Cellulose fibres can be derived from wood sources, card board, reeds, rice husks, palm fibre, coconut, bamboo, sugar cane and many other sources of plant material including keratin from vegetable fibres and bird feathers. The polymer can be a plastic that is commonly recycled.

US patent US7550404 (Fisher et al) discloses a wood polymer composite further including a zeolite. Applicant found that while the composite materials according to this document provided satisfactory rigidity in many situations, there were some instances that the composites did not have sufficient impact, tensile, strength, and flex modulus. For example, when the composites were used in the manufacture of pallets, it was found in
hot temperatures that the composite beams forming the pallets tended to sag and lose their flex. An improved composite material is therefore desirable. The current invention aims to improve flexural strength, flex modulus and impact strength of the cellulose fibre-composite polymer material for the purpose of load bearing duties in material handling applications, by at least including a coupling agent selected from the group including a zirconate or a titanate.

The composite material of the current invention may have applications in a wide variety of fields such as buildings marine, or any other use where certified structural specifications are required. The composite material of the current invention has or can be readily modified to have numerous desirable properties including termite resistance, flame retardancy, light weight due to reduction in density, UV resistance, anti static properties and high temperature tolerance.

SUMMARY OF INVENTION

In one form of this invention although this need not be the only or indeed the broadest of this there is provided a cellulose fibre - polymer composite material where said material includes a cellulose fibre and a polymer characterised in that composite material further includes at least one coupling agent selected from a zirconate or a titanate.

The cellulose fibre may be selected from the group consisting of wood fibres, wood pulp, paper, card board, wheat fibres, rice hulls, kenaf, flax hemp, keratin and mixtures of these.
Preferably the cellulose fibre of the current invention is selected from a wood fibre.
Preferably the wood fibre has a moisture content of less than 3% and can pass through a minimum 400 mesh sieve.

Preferably, the polymer is selected from the group consisting of polymers including at least 50 wt % ethylene repeat units, polymers including at least 50 wt % propylene repeat
units, polymers including at least 50 wt % polystyrene, polymers including at least 50 wt % vinyl chloride repeat units, and mixtures thereof.

Preferably the polymer of the composite material of the current invention is a polymer selected from the group including polyethylene, polypropylene, polystyrene and polyvinyl chloride.

In some embodiments, the polymer may comprise a low- or high-density polyethylene, polypropylene, or polyvinyl chloride homopolymer. One suitable polymer is a high-density polyethylene sold as Equistar ALATHON L5040 by Lyondell Chemical Company of Houston, Tex. Copolymers may also be used, for example when the physical properties of the finished product need modification, such as copolymers of ethylene with hexene or heptene. Or, other copolymers such as polypropylene with approximately 3% ethylene comonomer content (as a fluxing agent) may be used when faster production rates are desired. In the case of polyvinyl chloride polymers, polyvinyl chloride homopolymer resins such as Shintech SE950EG or copolymers of vinyl chloride with 3-10% of vinyl acetate can be used. Mixtures of any of the above-noted polymers may be used, for example mixtures of recycled or virgin polymers.

In a preferred embodiment, the polymers are recycled polymers. The recycled polymers can be repolymerized using any method well known in the art. One example of a suitable repolymerization technique is that disclosed in US patent US4657988.

The amount of polymer in the composition is normally about 20% to 70%, preferably, 40% to 60%, based on the total weight of the composition.

The coupling agent of repolymerization of the current invention is selected from the group including a zirconate or a titanate.
Preferably the zirconate or titanate is in a powder or pellet form and has flame retardant properties when used with a zeolite filler. Liquid zirconate or titanate can be used for same results depending on extruder feed system.

Suitable zirconates or titanates include organo titanates or organo zirconates. Suitable titanates include those that are disclosed in US patent US4600789, and one suitable example neo alkoxy pyrophosphate titanate.

Preferably the amount of the coupling agent in the composite material is about 0.25% to 3% based on the total final Weight of the composite material.

The composite material may further include a compatibilizing agent. Preferably the compatibilizing agent is a maleic anhydride grafted polyolefin.

Preferably the composite material further includes a particulate filler. Preferably the filler is an inorganic particulate filler. Specific examples of fillers are vermiculite, talc, kaolinite, montmorillonite, synthetic mica, clay, zeolite, silica, graphite, carbon black, zinc oxide, magnesium oxide, titanium oxide, calcium sulfide, boron nitride, calcium carbonate, barium sulfate, aluminium oxide, neodymium oxide, and metal salts of phenyl phosphorates.

Preferably, the filler is a zeolite. There are many known varieties of zeolites both natural and synthetic that may be suitable in the composite materials of the invention. The zeolite may be natural mined zeolite such as a natural rock clinoptilolite that is sourced from Australia. Preferably the zeolite has a particle size of less than 10 microns, a surface area of greater than 300m$^2$/g. Preferably the zeolite is present in an amount of about 1% to 70% based on the amount of polymer matrix in the composition and the desired structural result.

Preferably the zeolite is in a particulate form.
Preferably the zeolite is surface activated. More preferably, the activated zeolite surface contains channels that are commensurate with the dimensions of the repolymerized polymer chain.

Preferably the zeolite surface has sorption of the polymer chain.

Preferably the zeolite present improves the fire retardancy properties of the composite material. Preferably the zeolite present improves optiminal mechanical characteristics of the composite.

In a further aspect of the invention there is provided a method of making a composite material, the method including blending together a) cellulose fibre component b) a coupling agent selected from the group of a zirconate and titanate and c) a polymer selected from the group consisting of polyethylene, polypropylene, polystyrene and polyvinyl chloride, or a mixture of any of these, including recycled or virgin polymers.

The composite material of the current invention may further include any of a number of other ingredients. Examples include stabilizers, process aids, impact modifiers (e.g., rubber-based modifiers), lubricants, plasticizers, antioxidants, UV absorbers, and pigments or other colorants. Also useful may be foaming agents, fungicides and/or algaecides, all of which are known in the art.

The composite materials according to the invention may be used in any of a number of end-use applications, in which their superior physical performance properties may be used to advantage. One useful application is in building products, including non-limiting examples, lumber and related structural materials. As used herein, the term "lumber" means planks, sheets, or other pieces resembling typical wood-based materials such as sawn lumber, oriented strand board, particle board, plywood etc. Thus, the composite
materials may be used to make products such as fences, railings, decking for outdoor porches and the like, panels for floors, ceilings, wall, bath or shower stalls, cabinetry, countertops, and other structural items. They may also be used as automotive construction materials, for example in decorative interiors, door panels, headliners, seat interiors, and other uses, as well as in any of a variety of industrial products such as piers and docks, or consumer products such as furniture. In particular the inventors have found that the properties of the composite materials are particularly suitable in the manufacture of pallets. The strength, rigidity in high temperatures, cost of manufacture, fire retardancy properties, capability of being manufactured without potential carcinogenic chemicals, all make the composite material especially attractive in the manufacture of pallets and other load carrying devices.

DETAILED DESCRIPTION OF THE INVENTION

For a better understanding of the invention, further description will now be given, with reference to the examples.

Prior art Example.

Ingredients
46% Recycled polyolefin (50% LDPE, 50% HDPE).
3% Compatabilizing agent. Maleic anhydride grafted polyethylene "Polybond 3039" from Chemtura Corp., Middleberry, USA.
1% High molecular mixed fatty acid ester "Loxiol G70" from Coenis Corp., Cincinatti, USA.
50% Dried wood flower (Pinus radiata) that can pass through a 400 sieve size and has less than 3% moisture. Supplied locally from different mills.

Method
The ingredients were mixed in a ribbon type mixer then conveyed via gravimetric feeding units to an ENTEK co-rotating twin screw extruder and the composite material extruded
there from. The screw speed was set at 75 rpm and the heater zones on the extruder barrel were set at 185, 185, 175 and 175 degrees Celsius to create a melt phase.

Results
The resulting composite material had the following properties when using the ASTM D638 test method:

- Tensile Strength @ Yield: 1598 PSI
- Tensile Strength @ Break: 1664 PSI
- Flex Modulus: 275 KSI
- Displacement® Failure: 25 mm

Invention Example.

Ingredients
46% Recycled polyolefin (50% LDPE/50% HDPE). Supplied by PGS., Kilburn, South Australia.
3% compatibilizing agent, maleic anhydride grafted polyethylene "Polybond 3039" from Chemtura Corp., Middleberry, USA.
0.3% Neoalkoxy titanate, "Capow L38/H" or "Capow KRTTS/H" or "Capow KR38S/H". All powder form. From Kenrich Petro Chemicals Inc., Bayonne USA.
0.7% Carbon Black, from local supplier Carbon Black Australia.
30% Natural clinoptilolite zeolite from Zeolite Australia. P/L.
20% Dried wood flower (Pinus radiata) that can pass through a 400 sieve size and has less than 3% moisture, from local supplier, different mills.

Method
The wood flower and activated zeolite were conveyed via gravimetric feeding units to an ENTEK co-rotating twin screw extruder with the other ingredients during the melt phase, and the composite material extruded through a 90mm x 20mm die then water cooled conveyer. The screw speed was set at 75 rpm and the heater zones on the extruder barrel were set at 185, 185, 175 and 175 degrees Celsius to create a melt phase.
During the process the titanate was thoroughly dispersed throughout the polymer matrix prior to the melt phase.
The active zeolite and wood flower were introduced during the melt phase.

Results
The resulting composite material had the following properties when using the ASTMD790 test method:

- Tensile Strength @ Yield: 2560 PSI
- Tensile Strength @ Break: 3708 PSI
- Flex Modulus: 566 KSI
- Displacement @ Failure: 16.25 mm

Throughout this specification the purpose of the description has been to illustrate the invention and not to limit this.
CLAIMS

1. A cellulose fibre - polymer composite material where said material includes;
   (a) a cellulose fibre, and
   (b) a polymer,
   characterised in that said composite material further includes at least one coupling agent
   selected from a zirconate or a titanate.

2. The composite material of claim 1 where the cellulose fibre is selected from the group
   consisting of wood fibres, wood pulp, wheat fibres, rice hulls, kenaf, flax hemp, keratin
   and mixtures of these.

3. The composite material of claim 2 where the cellulose fibre is selected from a wood
   fibre.

4. The composite material of claim 3 where the wood fibre has a moisture content of
   less than 3% and can pass through a minimum 400 mesh sieve.

5. The composite material of claim 1, where the polymer is selected from the group
   consisting of polymers including at least 50 wt % ethylene repeat units, polymers
   including at least 50 wt % propylene repeat units, polymers including at least 50 wt %
   polystyrene repeat units, 50 wt % vinyl chloride repeat units, and mixtures thereof,
   including virgin and/or recycled polymers.

6. The composite material of claim 5 where the virgin or recycled polymer of the
   composite material is a polymer selected from the group including polyethylene,
   polypropylene, polystyrene and polyvinyl chloride.
7. The composite material of claim 1 where the polymer is a recycled polymer that has been repolymerised.

8. The composite material of claim 1 where the amount of polymer is 20% to 70% based on the total weight of the composition.

9. The composite material of claim 8 where the amount of polymer is 40% to 60%, based on the total weight of the composition.

10. The composite material of claim 1 where the zirconate or titanate is a neo organo titanate or neo organo zirconate.

11. The composite material of claim 1 where the zirconate or titanate is a neo alkoxy organo titanate or neo alkoxy organo zirconate.

12. The composite material of claim 1 where the zirconate or titanate is in powder form.

13. The composite material of claim 1 where the amount of the coupling agent in the composite material is about 0.25% to 3% based on the total final weight of the composite material.

14. The composite material of claim 1 where the composite material further includes a filler.

15. The composite material of claim 14 where the filler is a zeolite.

16. The composite material of claim 15 where the zeolite is in particulate form.

17. The composite material of claim 16 where the zeolite has a particle size of less than 10 microns.
18. The composite material of claim 15 where the zeolite is activated.

19. The composite material of claim 18 where the activated zeolite is surface activated, and the activated surface includes channels that are commensurate with the dimensions of the repolymerized polymer chain.

20. The composite material of claim 1 where the composite material further includes a compatibilizing agent.

21. The composite material of claim 20 where the compatibilizing agent is a maleic anhydride grafted polyolefin.

22. A method of making a composite material, where said method includes blending together a) cellulose fibre component, b) a coupling agent selected from the group of a zirconate and titanate and c) a polymer selected from the group consisting of polyethylene, polypropylene, polystyrene and polyvinyl chloride, or a mixture of any of these including virgin or recycled polymers.

23. The method of making a composite material according to claim 22 where the material is heat extruded to form a melt phase.

24. The method of making a composite material according to claim 23 where the coupling agent is thoroughly dispersed throughout the polymer matrix prior to the melt phase.

25. The method of making a composite material according to claim 23 where zeolite and wood flower are introduced during the melt phase.
26. The method of making a composite material according to claim 25 where the zeolite is activated.

27. A composite material having structural applications according to any one of claims 1 to 21.

28. A method of making composite material having structural applications, where said method includes blending the components according to any one of claims 1 to 21.
A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08L 7/02 (2006.01) C08L 23/04 (2006.01) C08L 27/06 (2006.01)
B29C 47/00 (2006.01) C08L 23/10 (2006.01) C08L 97/02 (2006.01)
C08K 5/00 (2006.01) C08L 25/04 (2006.01)

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)

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

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

WPI, EPDOC, CAPLUS, Keywords: +neo+titan+, +neo+zircon+, +titanate, +zirconate, +cellulos+, +wood+, +fiber+, +fibre+, +polymer+, +composit+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search: 13 May 2011

Date of mailing of the international search report: 23 May 2011

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer
GIUSEPPE ZAGARI

AUSTRALIAN PATENT OFFICE
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### DOCUMENTS CONSIDERED TO BE RELEVANT

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