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(54) **Title:** COUPLING AGENTS FOR NATURAL FIBER-FILLED POLYOLEFINS

(57) **Abstract:** Disclosed herein is a process for preparing a composite material comprising mixing at least one natural fiber, at least one polyolefin resin, and at least one functionalized polyolefin coupling agent to provide said composite material; wherein said ftmctionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_W/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about I mmole of at least one polar monomer per 100 grams of fimctionalized polyolefin coupling agent.

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COUPLING AGENTS FOR NATURAL FIBER-FILLED POLYOLEFINS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Application Number 10/412,981, filed April 14, 2003.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to polyolefin composites comprising natural fibers. More particularly, the present invention relates to natural fiber-filled polyolefin composites having increased strength resulting from the inclusion of a functionalized polyolefin coupling agent having a broad molecular weight distribution and containing more than about 1 mmole of functionalized monomer per 100 grams of polymer.

2. Description of Related Art

It is known in the art to prepare composites comprising thermoplastic resinous matrix materials having dispersed therein organic reinforcing fillers, such as cellulosic or lignocellulosic fibers. It is also known in the art to improve the mechanical properties of such composites by treating such fibers with coupling agents prior to their introduction into the thermoplastic resinous matrix material. The following articles are among many that make reference to known technology:

P. Jacoby, et. al., "Wood Filled High Crystallinity Polypropylene," Wood-Plastic Conference sponsored by Plastics Technology, Baltimore, MD, December 5-6, 2000;

M. Wolcott et al., "Coupling Agent/Lubricant Interactions in Commercial Wood Plastic Formulations," 6th International Conference on Woodfiber-Plastic Composites, Madison, WI, May 15-16, 2001;

M. Chowdhury et al., "Effect of Maleated Polyolefin Copolymer and Lubricant in Wood-Polyolefin Composites," 6th International Conference on Woodfiber-Plastic Composites, Madison, WI, May 15-16, 2001;

W. Sigworth, "The Use of Functionalized Polyolefins in Environmentally Friendly Plastic Composites," GPEC 2002, February 13-14, 2002, Detroit, MI;

J. Wefer and W. Sigworth, "The Use of Functionalized Coupling Agents in Wood-filled Polyolefins," Wood-Plastic Composites, A Sustainable Future Conference, May 14-16, 2002, Vienna, Austria;

R. Heath, "The Use of Additives to Enhance the Properties and Processing of Wood Polymer Composites," Progress in Woodfibre-Plastic Composites Conference 2002, May 23-24, 2002, Toronto, Canada; and

W. Sigworth, "Additives for Wood Fiber Polyolefins: Coupling Agents, Progress in Woodfibre-Plastic Composites Conference 2002, May 23-24, 2002, Toronto, Canada.

Additionally, Kokta, B.V. *et al., Polym.-Plast. Technol. Eng., 28(3)*:247-259 (1989) studied the mechanical properties of polypropylene with wood flour. The wood flour was pretreated with polymethylene polyphenylisocyanate and silane coupling agents before adding it to the polymer.

Raj, R.G. *et al., Polym.-Plast. Technol. Eng., 29(4)*:339-353 (1990) filled high density polyethylene with three different cellulosic fibers that had been pretreated with a silane coupling agent/polyisocyanate to improve the adhesion between the fibers and the polymer matrix.

Matuana, L.M. *et al. ANTEC 3*:3313-3318 (1998) studied the effect of the surface acid-base properties of plasticized PVC and cellulosic fibers on the mechanical properties of

the plastic/cellulosic composite. They modified the surface of the fibers with γ-aminopropyltriethoxysilane, dichlorodiethylsilane, phthalic anhydride, and maleated polypropylene.

U.S. Patent No. 4,717,742 discloses resin composites reinforced with silanes grafted onto organic fillers that are said to have improved durability, even at sub-zero degrees or at high temperatures, improved physical properties and can be prepared by a process, in which the organic filler is grafted with a silane coupling agent in maleated polymer matrix.

U.S. Patent No. 4,820,749 discloses a composite material based on a polymeric or copolymeric substance which may be a thermoplastic or thermosetting material or rubber, and an organic material which is cellulosic or starch. The cellulosic material is grafted with a silylating agent. Processes for preparing this composite are also disclosed.

U.S. Patent No. 6,265,037 discloses an improved composite structural member comprising a complex profile structural member, made of a composite comprising a polypropylene polymer and a wood fiber. The material is said to be useful in conventional construction applications.

U.S. Patent No. 6,300,415 discloses a polypropylene composition for the production of various molded articles which are said to be excellent in moldability, mold shrinkage factor on molding, rigidity, flexibility, impact resistance, in particular low-temperature impact resistance, transparency, gloss, stress-whitening resistance, and the balance thereof; various molded articles having the above properties; a propylene composition which is suitable for a base resin for the polypropylene composition; and a process for the production thereof. The propylene composition comprises a propylene homopolymer and a propylene-ethylene copolymer.

The disclosures of the foregoing are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

It has now been discovered that functionalized polyolefins that are characterized by having a broad molecular weight distribution are more effective in improving the mechanical strength properties, creep resistance, and water absorption resistance of natural fiber-filled polyolefin composites than are more conventional functionalized polyolefins that have narrower molecular weigh distributions.

More particularly, the present invention is directed to a process for preparing a composite material comprising mixing together at least one natural fiber, at least one polyolefin resin, and at least one functionalized polyolefin coupling agent to provide said composite material; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

In another aspect, the present invention is directed to a composite material prepared by a process comprising mixing together at least one natural fiber, at least one polyolefin resin, and at least one functionalized polyolefin coupling agent to provide said composite material; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

In still another aspect, the present invention is directed to a composite material comprising at least one natural fiber, at least one polyolefin resin, at least one functionalized

polyolefin coupling agent, and at least one lubricant selected from the group consisting of fatty acid amides and fatty acid esters; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is often desirable to increase the strength properties of natural fiber-filled polyolefin composites, e.g., wood-polyolefin composites, for construction and automotive applications. It is known to use maleated polyolefins to improve dispersion of the natural fiber in the polyolefin and to increase interfacial adhesion between the fiber and resin. These improvements lead to increased strength properties. The maleated polyolefins used heretofore have narrow molecular weight distributions (M_w/M_n by GPC < 2.5).

It has been discovered that substantial improvements in strength properties can be obtained by using a functionalized polyolefin that possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole, preferably more than about 5 mmoles, more preferably more than about 10 mmoles, of at least one polar monomer per 100 grams of base polyolefin resin.

The present invention permits the use of wood/polyolefin composites in marine decking, deck supports, railing systems, automotive parts, and similar applications where additional structural strength is needed. The invention also provides composites with improved long-term durability by reducing water absorption and increasing creep resistance.

As employed herein, the term "natural fiber" means a fiber obtained, directly or

indirectly, from a source in nature. Included within the term, but not limited thereto, are wood flour, wood fiber, and agricultural fibers such as wheat straw, flax, hemp, kenaf, nut shells, and rice hulls. Preferably, the natural fiber is selected from the group consisting of starch or cellulosic material such as cotton fibers, wood pulps, stem or vegetable fibers, wood flours, starch, waste papers, cartons, or cellulosic cloth. More preferably, the natural fiber is wood flour, wood fiber, hemp, flax, or kenaf. Wood fiber, in terms of abundance and suitability, can be derived from either soft woods or evergreens or from hard woods commonly known as broadleaf deciduous trees. While soft wood and hard wood are preferably the primary sources of fiber for the invention, additional fiber make-up can be derived from a number of secondary or fiber reclaim sources, including hard woods, bamboo, rice, sugar cane, and recycled fibers from newspapers, boxes, computer printouts, and the like. However, the primary source for wood fiber used in the process of this invention comprises the wood fiber by-product of sawing or milling softwoods and hardwoods commonly known as sawdust or milling tailings. Fiber levels in the range of from about 20 to about 85 weight % based on the total formulation weight of the composite can be used. Fiber levels in the range of from about 30 to about 80 weight % are preferred. Fiber levels in the range of from about 40 to about 70 weight % are most preferred.

The polyolefins employed in the practice of the present invention are typically polymerized from ethylene, propylene, and/or other alpha olefins. Where ethylene is used, it can be, for example, high density polyethylene (HDPE), low density polyethylene (LDPE), or linear low density polyethylene (LLDPE). Polypropylene homopolymer, as well as copolymers and terpolymers containing ethylene, propylene, and/or other alpha olefins, and/or non-conjugated dienes can also be advantageously employed, as can blends of these

polymers.

Thus, the polyolefin materials of the invention can, if desired, comprise either a polypropylene copolymer wherein the polymer comprises a major proportion of propylene combined with a minor proportion (typically less than 50 wt %, more commonly between about 0.1 and 10 wt %) of a second monomer that can comprise ethylene or a C_4-C_{16} monomer material. Such copolymers often have improved processability, flexibility, and compatibility.

Preferred ethylene copolymers can comprise a major proportion of ethylene and a minor proportion (typically less than 50 wt %, preferably about 0.1 to about 10 wt %) of a C_3-C_{18} monomer.

Polypropylene homopolymer and HDPE, i.e., high density polyethylene, are most preferred for use in the practice of the present invention.

The functionalized polyolefin, which preferably comprises polyethylene or polypropylene as the base polyolefin resin, is one that contains reactive groups that can react with the functional groups on the surface of the natural fiber. The reactive groups are provided by grafting at least one polar monomer onto the base polyolefin resin. Suitable polar monomers include ethylenically unsaturated carboxylic acids or ethylenically unsaturated carboxylic acid anhydrides. Mixtures of the acids and anhydrides, as well as their derivatives, can also be used. Examples of the acids include maleic acid, fumaric acid, itaconic acid, crotonic acid, acrylic acid, methacrylic acid, maleic anhydride, itaconic anhydride, and substituted maleic anhydrides. Maleic anhydride is preferred. Derivatives that may also be used include salts, amides, imides, and esters. Examples of these include, glycidyl methacrylate, mono- and disodium maleate, and acrylamide. Virtually any

olefinically reactive residue that can provide a reactive functional group on a modified polyolefin polymer can be useful in the invention.

In accordance with the present invention, the coupling agents comprise a functionalized polyolefin, such as a functionalized polyethylene or polypropylene, that has a molecular weight distribution as measured by the ratio of weight average molecular weight to number average molecular weight (M_w/M_n) by gel permeation chromatography (GPC) of greater than 2.5. Preferably, the molecular weight distribution should be greater than 3.0, more preferably 3.5. Generally, such functionalized polyolefins will have a weight average molecular weight (by GPC) that ranges from about 5,000 to about 200,000.

The functionalized polyolefin coupling agent is modified with from about 1 to as much as about 100 mmoles of polar monomer per 100 grams of the functionalized polyolefin coupling agent. Preferred coupling agents comprise either a modified polypropylene or a modified polyethylene modified with maleic anhydride residues. The most preferred coupling agents are maleic anhydride modified polypropylenes and maleic anhydride modified high density polyethylenes. Thus, the preferred materials contain more than about 1, preferably more than about 5, more preferably more than about 10, mmoles of maleic anhydride per 100 grams of functionalized polyolefin.

It is known to prepare functionalized polyolefin coupling agents by a melt-state process called reactive extrusion. This mechanism is well established and has been described by DeRoover et al., in the Journal of Polymer Science, Part A: Polymer Chemistry, vol. 33, pp 829-842 (1995). Polymer, functionalized monomer, and a free radical initiator are added to a twin screw extruder and subjected to elevated temperatures. During this process, a hydrogen atom is abstracted from the polymer chain by the initiator. The polymer undergoes

chain scission leaving the free radical at the end of the shortened chain. The functional monomer then reacts at the site of the free radical resulting in the formation of a functional site at the end of the polymer chain. Since higher molecular weight polymer chains are statistically more likely to react with the free radicals, narrowing of the molecular weight distribution of the polymer is characteristic of reactive extrusion processes.

Although in no way intended to limit the scope of the present invention, functional polyolefin coupling agents of the present invention can be prepared by solution or solid-state processes. Such processes are well known to those skilled in the art, and are described, for example, in U.S. Patent Nos. 3,414,551 and 5,079,302, G. Ruggeri, et.al., European Polymer Journal, 19, 863 (1983) and Y. Minoura, et.al., Journal of Applied Polymer Science, 13, 1625 (1969), the contents of each of which are incorporated by reference herein. These processes favor a reaction of the functional monomer with the free radical site on the polymer before the polymer can undergo chain scission. The end result is then to have functional monomer along the polymer chain instead of just at the ends. In addition, the narrowing of the molecular weight distribution of the polymer noted in reactive extrusion processes does not take place during solution or solid-state functionalization processes.

Functionalized polyolefin levels of about 0.5 to about 10% based on the total formulation weight of the composite can be used with levels of about 1-5 % being preferred.

Depending on their end use requirement, the composites of the present invention can also contain further additives and stabilizers, for example, potassium, sodium, calcium, magnesium, and barium soaps or other tin derivatives, as well as, inter alia, plasticisers, epoxide compounds, metal perchlorates, lubricants, fillers, non-natural fiber reinforcing agents, antioxidants, polyols, dawsonites, hydrotalcites, organic phosphites, 1,3-diketo

compounds, mono-, oligo- or polymeric dihydropyridines, sterically hindered amines (HALS), light stabilisers, UV absorbers, fatty acid esters, paraffins, blowing agents, fluorescent whitening agents, pigments, flame retardants, antistatic agents, aminocrotonates, thiophosphates, gelling assistants, metal deactivators, peroxide scavenging compounds, modifiers and further sequestrants for Lewis acids, and the like, all as described in detail in U.S. Patent No. 6,531,533, the disclosure of which is incorporated herein by reference in its entirety.

The products of this invention can be processed using conventional techniques, including, but not limited to, the following:

1. Adding the products of the invention to the main hopper of an extruder along with resin and other additives followed by addition of the natural fiber downstream via a side feeder;

2. Adding the natural fiber through the main feeder and allowing it to be dried prior to adding the resin, coupling agent, and other additives downstream via a side feeder;

3. Mixing all ingredients together in a heated internal batch mixer, such as the types commonly referred to as Banbury or Brabender mixers; and

4. Proprietary extrusion and batch processing procedures which have been found to be suitable for compounding natural fiber/thermoplastic composites.

The advantages and the important features of the present invention will be more apparent from the following examples.

EXAMPLES

Functionalized polyolefin coupling agents both within and outside the scope of the invention were synthesized. Characterization data for these coupling agents are set forth in

Tables 1-A and 1-B below.

The maleic anhydride content of the coupling agents was determined by dissolving them in boiling xylene and titrating to a Thymol Blue end point using a standardized 0.3N methanolic KOH solution. The KOH titrant was standardized using benzoic acid. The number of milliequivalents of KOH titrant needed to neutralize one hundred grams of coupling agent was determined. The percent maleic anhydride in the coupling agent was then calculated assuming one mole of KOH neutralized one mole of maleic anhydride. This assumption was confirmed by titration of straight maleic anhydride under the same conditions that the coupling agents were tested. The number of millimoles of functionality per 100 gms of coupling agent was calculated by dividing the percent maleic anhydride by the molecular weight of this chemical (98) and multiplying by 1000.

The Melt Flow Ratings of the coupling agents were determined using a Tinius Olsen Extrusion Plastometer Model MP600 following the procedures outlined in ASTM D1238.

Molecular weight analysis was conducted by gel permeation chromatograph using a Waters GPC 150C with Styragel HT 5, 4, 3, 6A columns and refractive index detector. Test temperature was 140°C and o-dichlorobenzene was used as the solvent. Calibration was done using two standards: PP 105 and PP 150 from American Polymer Standards.

The coupling agents were evaluated in wood-filled polypropylene formulations. All of the ingredients were blended together and fed into the main hopper of a 30 mm Coperion twin screw extruder. A strand of the compounded product was cooled in a water bath and pelletized. The pellets were dried overnight at 100° C and injection molded to make the specimens for mechanical property testing.

The following ASTM test procedures were used to generate the mechanical

properties: D638 (tensile strength), D790 (flexural strength), Izod impact (D256), and Charpy (D6110). In the impact testing, the notched Izod bar was placed in the impact tester so that the notch was on the face of the sample which was opposite the side impacted by the swinging pendulum of the tester. In the Charpy test, the bar was not notched. Water absorption was determined by immersing two halves of a tensile bar in tap water for thirty days at room temperature and measuring the weight gain.

Table 1-A

Characterization of Maleic Anhydride Functionalized Polyolefins

Example	1 (Comparative)	2 (Comparative)	3	4	5
Titration – meq KOH/100 gm polymer	9.59	16.32	32.63	30.17	32.04
% Maleic Anhydride	1.0	1.6	3.2	3.0	3.2
Mmoles of MA/100 gm Coupling Agent	10.2	16.3	32.7	30.6	32.7
MFR (230°C, 2.16 kg)	250	1000	2.9	2.7	9.3

M_w by GPC	86,200	59,600	294,800	53,900	65,900
M_n by GPC	35,900	24,400	46,250	19,600	17,600
M_w/M_n by GPC	2.40	2.44	6.4	2.75	3.74

Table 1-B

Characterization of Maleic Anhydride Functionalized Polyolefins

Example	6	7	8
Titration – meq KOH/100 gm polymer	24.06	23.68	16.41
% Maleic Anhydride	2.4	2.4	1.6
Mmoles of MA/100 gm Coupling Agent	24.5	24.5	16.3
MFR (230° C, 2.16 kg)	157	320 @ 190° C	720
M_w by GPC	109,400	78,800	72,600
M_n by GPC	21,200	20,800	23,100
M_w/M_n by GPC	5.16	3.79	3.14

In each of Examples 1 through 8, polypropylene homopolymer was used as the polyolefin.

In the following examples, the product of Example 1 will be referred to as Prodex 1, the product of Example 2 will be referred to as Prodex 2, and so on.

Table 2

Initial Trials

Example	9 Comparative	10 Comparative	11 Comparative	12
Wood Flour	40	40	40	40
Phenol/Phosphite Anti-Oxidant	0.25	0.25	0.25	0.25
Prodex 1		2.5		
Prodex 2			2.5	
Prodex 3				2.5
Polypropylene (4 MFR)	59.75	57.25	57.25	57.25
Tensile Strength, MPa	27.1	32.3	33.4	36.3
Change vs. Example 9 (%)	0	19	23	34
Flexural Strength, MPa	45.7	53.6	51.4	58.5
Change vs. Example 9 (%)	0	17	12	28
Reversed Notch Izod Impact, J/m	55.5	70.5	60.9	77.4
Change vs. Example 9 (%)	0	27	10	39
Unnotched Charpy Impact, J/m	146	139	140	165

Change vs. Example 9 (%)	0	-5	-4	13
Water Absorption (% Wt. increase after 30 days immersion)	7.9	5.0	6.1	2.7

Example 12 containing the coupling agent of the present invention gave higher tensile, flexural, and impact strengths, and lower water absorption than Comparative Examples 10 and 11 containing the coupling agents of Examples 1 and 2.

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Table 3

Comparison of Prodex 1 vs. Prodex 4 and Prodex 5 in 50% Wood-Filled Polypropylene

Example	13 Comparative	14 Comparative	15	16
Wood Flour	50	50	50	50
Phenol/Phosphite Anti-Oxidant	0.125	0.125	0.125	0.125
Prodex 1		2		
Prodex 4			2	
Prodex 5				2
Polypropylene (4 MFR)	49.9	47.9	47.9	47.9
Tensile Strength, MPa	29.4	37.1	52.2	52.6

Change vs. Example 13 (%)	0	26	78	79
Flexural Strength, MPa	47.2	57.4	81.1	82.6
Change vs. Example 13 (%)	0	22	72	75
Reversed Notch Izod Impact, J/m	65.7	63.0	106	108
Change vs. Example 13 (%)	0	-4	61	65
Unnotched Charpy Impact, J/m	138	162	248	249
Change vs. Example 13 (%)	0	18	80	81
Water Absorption (% Wt. increase after 30 days immersion)	8.2	6.6	4.3	4.2

Examples 15 and 16 containing the coupling agents of the present invention had significantly higher strength properties and lower water absorption compared with Comparative Example 14, containing the coupling agent of Example 1.

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Table 4

Comparison of Prodex 1 vs. Prodex 4

in 60% Wood-Filled Polypropylene Containing a Lubricant

Example	17 Comparative	18 Comparative	19 Comparative	20
Wood Flour	60	60	60	60

Phenol/Phosphite Anti-Oxidant	0.1	0.1	0.1	0.1
Prodex 1		2	2	
Prodex 4				2
Lubricant - Fatty Acid Ester			3	3
Polypropylene (4 MFR)	39.9	37.9	34.9	34.9
Tensile Strength, MPa	25.3	33.4	30.1	44.4
Change vs. Example 17 (%)	0	32	19	75
Flexural Strength, MPa	40.9	51.8	45.7	73.4
Change vs. Example 17 (%)	0	27	12	79
Reversed Notch Izod Impact, J/m	49.7	60.9	52.9	91.3
Change vs. Example 17 (%)	0	23	6	84
Unnotched Charpy Impact, J/m	90	106	90	186
Change vs. Example 17 (%)	0	17	0	107
Water Absorption (% Wt. increase after 30 days immersion)	1.2	8.2	6.1	3.2

Lubricants are known to negate the positive effects that maleated coupling agents have on strength properties. These Examples show that even when a lubricant is used, coupling agent Prodex 4 in Example 20 provides superior properties to Prodex 1 in

Comparative Example 18 without lubricant and Comparative Example 19 with lubricant.

Table 5

Effect of Lubricants

Example	21 Comp.	22 Comp.	23 Comp.	24 Comp.	25	26	27	28
Wood Flour	50	50	50	50	50	50	50	50
Phenol/Phosphite Antioxidant	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125
Prodex 1		2	2	2				
Prodex 4					2	2	2	2
Lubricant - Fatty Acid Ester			3	0.75		3	0.75	
Lubricant - Fatty Acid Amide				2.25			2.25	3
Polypropylene (4 MFR)	49.875	47.875	44.875	44.875	47.875	44.875	44.875	44.875
Tensile Strength , MPa	29.3	37.6	33.3	31.0	44.9	45.3	44.8	42.6

Change vs. Example 21	0 %	28 %	14 %	6 %	53 %	55 %	53 %	45 %
Flexural Strength, MPa	47.0	59.5	53.3	45.0	74.3	66.9	66.5	64.6
Change vs. Example 21	0 %	26 %	13 %	-4 %	58 %	42 %	41 %	37 %
Reversed Notched Izod Impact, J/m	59.3	70.0	70.0	65.1	123	74.8	100	100

Table 5, cont.

Effect of Lubricants

Example	21 Comp.	22 Comp.	23 Comp.	24 Comp.	25	26	27	28
Change vs. Example 21	0 %	18 %	18 %	10 %	107 %	26 %	69 %	69 %
Unnotched Charpy Impact, J/m	134	139	138	113	231	179	210	178
Change vs. Example 21	0 %	3 %	3 %	-16 %	72 %	33 %	57 %	32 %

Water Absorption (% Increase after 30 Days Immersion	7.0	5.8	3.4	4.0	2.7	2.8	2.7	3.8

Comp. = Comparative

MA-PP = Maleic Anhydride-Polypropylene

Table 5 provides additional proof that the functionalized coupling agents of the present invention are less susceptible to interference from lubricants than are previously known coupling agents. Adding either a fatty acid ester or a blend of fatty acid esters and amides to formulations containing to such previously known coupling agents resulted in a significant reduction in mechanical properties (see Comparative Examples 22-24). When a functionalized polyolefin coupling agent of the present invention was combined with the same two lubricants, reductions in mechanical properties were much smaller (see Examples 25-28).

Table 6

Evaluation of Lower Molecular Weight Samples

Example	29 Comp.	30 Comp.	31	32	33
Wood Flour	50	50	50	50	50
Phenol/Phosphite Antioxidant	0.125	0.125	0.125	0.125	0.125
Prodex 1		2			
Prodex 6			2		
Prodex 7				2	
Prodex 8					2
Polypropylene (4 MFR)	49.875	47.875	47.875	47.875	47.875

Tensile Strength , MPa	28.9	37.6	50.9	50.0	49.9
Change vs. Example 29	0 %	30 %	76 %	73 %	73 %
Flexural Strength, MPa	47.2	59.1	79.6	80.0	79.4
Change vs. Example 29	0 %	25 %	69 %	70 %	68 %
Reversed Notched Izod Impact, J/m	55.5	65.1	107	106	104
Change vs. Example 29	0 %	17 %	93 %	90 %	88 %
Unnotched Charpy Impact, J/m	130	158	268	224	239
Change vs. Example 29	0 %	21 %	107 %	73 %	84 %
Water Absorption (% Increase after 30 Days Immersion	6.4	4.4	2.5	3.1	3.4

It can readily be seen that functionalized polyolefin coupling agents of the present invention provide superior mechanical properties compared to previously known coupling agents with similar Melt Flow Rates.

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.

CLAIMS

What is claimed is:

1. A process for preparing a composite material comprising mixing at least one natural fiber, at least one polyolefin resin, and at least one functionalized polyolefin coupling agent to provide said composite material; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

2. The process of claim 1 wherein the natural fiber is selected from the group consisting of wood flour, wood fiber, and agricultural fiber.

3. The process of claim 1 wherein the natural fiber is selected from the group consisting of wood flour, wood fiber, hemp, flax, and kenaf.

4. The process of claim 1 wherein the natural fiber is employed at a level in the range of from about 20 to about 85 weight % based on the total formulation weight of the composite material.

5. The process of claim 1 wherein the base polyolefin resin is grafted with a total of more than about 5 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

6. The process of claim 1 wherein the base polyolefin resin is grafted with a total of more than about 10 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

7. The process of claim 1 wherein the polyolefin resin is a polypropylene copolymer comprising a major proportion of propylene combined with a minor proportion of a second monomer selected from the group consisting of ethylene and C_4-C_{16} monomer materials.

8. The process of claim 1 wherein the polyolefin resin is an ethylene copolymer comprising a major proportion of ethylene and a minor proportion of at least one C_3-C_{18} monomer.

9. The process of claim 1 wherein the polyolefin resin is polypropylene homopolymer.

10. The process of claim 1 wherein the polyolefin resin is high density polyethylene.

11. The process of claim 1 wherein the polar monomer is selected from the group consisting of ethylenically unsaturated carboxylic acids, ethylenically unsaturated carboxylic acid anhydrides, and derivatives of the foregoing.

12. The process of claim 11 wherein the polar monomer is selected from the group consisting of maleic acid, fumaric acid, itaconic acid, crotonic acid, acrylic acid, methacrylic acid, maleic anhydride, itaconic anhydride, substituted maleic anhydrides, and derivatives of the foregoing.

13. The process of claim 1 wherein the polar monomer is maleic anhydride.

14. A composite material prepared by a process comprising mixing at least one natural fiber, at least one polyolefin resin, and at least one functionalized polyolefin coupling agent to provide said composite material; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

15. A composite material comprising at least one natural fiber, at least one polyolefin

resin, at least one functionalized polyolefin coupling agent, and at least one lubricant selected from the group consisting of fatty acid amides and fatty acid esters; wherein said functionalized polyolefin coupling agent possesses a molecular weight distribution of greater than 2.5 (M_w/M_n by GPC) and comprises a base polyolefin resin that is grafted with a total of more than about 1 mmole of at least one polar monomer per 100 grams of functionalized polyolefin coupling agent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/011974

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L97/02 C08L51/00 B32B27/00

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 7 C08L B32B

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/161072 A1 (CROSTIC WILLIAM H ET AL) 31 October 2002 (2002-10-31) paragraphs '0016!, '0024!	1-15
X	US 6 265 037 B1 (GODAVARTI SHANKAR ET AL) 24 July 2001 (2001-07-24) column 17, lines 6-45	1-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document but published on or after the international filing date

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'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
26 August 2004	06/09/2004

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INTERNATIONAL SEARCH REPORT

[redacted]Information on patent family members

International Application No
[redacted]/US2004/011974

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