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 (54) Title: FILLED THERMOPLASTIC COMPOSITION

(57) **Abrégé/Abstract:**

A filled thermoplastic composition having improved combinations of processability, stiffness and toughness which demonstrates improved scuff resistance in extruded or molded articles is prepared by admixing a thermoplastic polymer, an uncalcined filler and a calcined filler.

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(57) Abstract: A filled thermoplastic composition having improved combinations of processability, stiffness and toughness which demonstrates improved scuff resistance in extruded or molded articles is prepared by admixing a thermoplastic polymer, an uncalcined filler and a calcined filler.

FILLED THERMOPLASTIC COMPOSITION

This invention relates to filled thermoplastic compositions and fabricated articles thereof.

Molded or extruded articles comprising thermoplastic polymers find wide use in a large variety of applications, for example in automobiles, boats, snow mobiles, personal water crafts, all terrain vehicles, home appliances, electronic housings, furniture, floor coverings, wall coverings, footwear such as shoes, boots, ski boots and skates.

Physical property requirements for such articles are varied and application dependent. It is well known to this art that thermoplastic polymers can contain non-polymeric materials as fillers, in order to alter certain of their properties. Thus, various mineral or inorganic fillers can be used in order to change one or more mechanical property of a thermoplastic polymer, such as coefficient of linear thermal expansion; modulus; impact, especially low temperature impact; tensile strength; flexural strength and resilience. For instance, see US-A-4,528,303 which discloses a polymer matrix comprising a filler prepared by the calcination of clay and, for optimal property performance, the use of a coupling agent.

One important property, especially for the surface of the article, is the resistance to scuffing, sometimes referred to as scratch and mar resistance. "Scuffing" is a surface deformation caused by sliding contacts between two surfaces resulting in a surface or "scuff" mark. For example, when a thermoplastic material used in a vacuum cleaner housing, an automotive bumper fascia, a floor covering or ski boots has a low resistance to scuffing, scuff marks become visible when the vacuum cleaner or bumper occasionally bumps into other objects or when people walk on the floor or when the right ski boot contacts the left ski boot. Such scuff marks are highly undesirable.

Accordingly, a major object of the present invention is the provision of a filled thermoplastic composition having a balance of mechanical properties, such as processability, stiffness, toughness and scuff resistance, in extruded or molded articles previously unknown to this art.

The filled thermoplastic composition of the present invention comprises (a) a thermoplastic polymer, (b) an uncalcined filler, (c) a calcined filler having an average particle size less than 2.5 microns and a maximum particle size equal to or less than 13 microns, optionally (d) an impact modifier and optionally (e) a slip agent.

In another aspect, the present invention involves a method of fabricating (for example, extruding or molding) articles from a filled thermoplastic composition described hereinabove.

In a further aspect, the invention involves fabricated (for example, extruded or molded) articles of a filled thermoplastic composition described hereinabove.

The filled thermoplastic compositions of the present invention are especially useful in the preparation of molded objects notably articles having large surfaces prepared by injection molding techniques requiring a good balance of strength and toughness and good scratch and mar resistance. Such properties are particularly desired for fabricated articles in automotive applications such as trims, bumper beams, bumper fascia, pillars, and instrument panels; in snow mobile, personal water craft and all terrain vehicle applications such as cowlings, fenders, panels, and body covers; in boats; in electrical and electrical equipment device housing and covers; as well as other household and personal articles, including, for example, appliance housings such as vacuum cleaner housings, housewares, freezer containers, and crates; lawn and garden furniture; building and construction sheet, including floor coverings and wall coverings; footwear such as shoes, boots and outer shells for ski boots, roller skates and ice skates.

Component (a) in the filled thermoplastic composition of the present invention is a thermoplastic polymer. The thermoplastic polymer can be a homopolymer or a copolymer. Preferably, the thermoplastic polymer is a polyolefin (PO), a polycarbonate (PC), a polystyrene (PS), a polyphenylene oxide (PPO), a styrene and acrylonitrile copolymer (SAN), an acrylonitrile, butadiene and styrene copolymer (ABS), a polyester, a polyamide (for example, Nylon), a thermoplastic polyurethane (TPU, for example, PELLATHANETM or ISOPLASTTM made by The Dow Chemical Company), or blends thereof (for example, PC/ABS, PC/polyester, PPO/PS, Nylon/PPO, Nylon/PO, and PO/PS). Generally the polyolefin polymers which are most frequently used are polyethylene (PE) and polypropylene (PP) made by conventional Ziegler-Natta or metallocene catalysts. Polypropylene is most preferred.

The polypropylene suitable for use in this invention is well known in the literature and can be prepared by known techniques. In general, the polypropylene is in the isotactic form, although other forms can also be used (for example, syndiotactic or atactic). The polypropylene used for the present invention is preferably a homopolymer of polypropylene or a copolymer, for example, a random or block copolymer, of propylene and an alpha-

olefin, preferably a C₂, or C₄ to C₂₀ alpha-olefin. The alpha-olefin is present in the polypropylene of the present invention in an amount of not more than 20 percent by mole, preferably not more than 15 percent, even more preferably not more than 10 percent and most preferably not more than 5 percent by mole.

5 Examples of the C₂, and C₄ to C₂₀ alpha-olefins for constituting the propylene and alpha-olefin copolymer include ethylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-hexadecene, 4-methyl-1-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, diethyl-1-butene, trimethyl-1-butene, 3-methyl-1-pentene, ethyl-1-pentene, propyl-1-pentene, dimethyl-1-pentene, methylethyl-1-pentene,
10 diethyl-1-hexene, trimethyl-1-pentene, 3-methyl-1-hexene, dimethyl-1-hexene, 3,5,5-trimethyl-1-hexene, methylethyl-1-heptene, trimethyl-1-heptene, dimethyloctene, ethyl-1-octene, methyl-1-nonene, vinylcyclopentene, vinylcyclohexene and vinylbornene, where alkyl branching position is not specified it is generally on position 3 or higher of the alkene.

 Preferably the polypropylene of the present invention is an isotactic polypropylene
15 having a high degree of crystallinity. A preferable method of determining the degree of crystallinity in polypropylene is by differential scanning calorimetry (DSC). A small sample (milligram size) of the polypropylene is sealed into an aluminum DSC pan. The sample is placed into a DSC cell with a 25 centimeter per minute nitrogen purge and cooled to -100°C. A standard thermal history is established for the sample by heating at 10°C per
20 minute to 225°C. The sample is then cooled to -100°C and reheated at 10°C per minute to 225°C. The observed heat of fusion ($\Delta H_{\text{observed}}$) for the second scan is recorded. The observed heat of fusion is related to the degree of crystallinity in weight percent based on the weight of the polypropylene sample by the following equation:

$$25 \quad \text{Crystallinity, percent} = \frac{\Delta H_{\text{observed}}}{\Delta H_{\text{isotactic PP}}} \times 100$$

where the heat of fusion for isotactic polypropylene ($\Delta H_{\text{isotactic PP}}$), as reported in B.

Wunderlich, Macromolecular Physics, Volume 3, Crystal Melting, Academic Press, New Your, 1980, p 48, is 165 Joules per gram (J/g) of polymer.

30 As defined herein, a high degree of crystallinity, as determined by DSC, is at least 62 weight percent, more preferably at least 64 weight percent, even more preferably at least 66 weight percent, even more preferably at least 68 weight percent and most preferably at least 70 weight percent based on the weight of the polypropylene. The degree of

crystallinity for the polypropylene as determined by DSC is less than or equal to 100 weight percent, preferably less than or equal to 90 weight percent, more preferably less than or equal to 80 weight percent, and most preferably less than or equal to 70 weight percent based on the weight of the polypropylene.

5 The melt flow rate (MFR) of the polypropylene useful in the present invention is generally equal to or greater than 1 gram/10 minutes (g/10 min.), preferably equal to or greater than 5 g/10 min., more preferably equal to or greater than 10 g/10 min., even more preferably equal to or greater than 15 g/10 min., and most preferably equal to or greater than 20 g/10 min. The melt flow rate for polypropylene useful herein is generally equal to or
10 less than 100 g/10 min., preferably equal to or less than 75 g/10 min., more preferably equal to or less than 65 g/10 min., even more preferably equal to or less than 50 g/10 min., and most preferably equal to or less than 35 g/10 min. Unless otherwise stated, melt flow rate is determined according to ASTM D 1238 at 230°C and an applied load of 2.16 kilogram (kg).

If more than one polypropylene component is used it is preferable to have a first
15 polypropylene component with a MFR from 1 to 20 g/10 min., and a second polypropylene component with a MFR from 20 to 100 g/10 min., wherein the resulting polypropylene has a MFR in the range of 15 to 75 and preferably 20 to 65 g/10 min.

Part or all of the polypropylene of the present invention may be graft modified. A preferred graft modification of the polypropylene is achieved with any unsaturated organic
20 compound containing, in addition to at least one ethylenic unsaturation (for example, at least one double bond), at least one carbonyl group (-C=O) and that will graft to a polypropylene as described above. Representative of unsaturated organic compounds that contain at least one carbonyl group are the carboxylic acids, anhydrides, esters and their salts, both metallic and nonmetallic. Preferably, the organic compound contains ethylenic
25 unsaturation conjugated with a carbonyl group. Representative compounds include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, -methyl crotonic, and cinnamic acid and their anhydride, ester and salt derivatives, if any. Maleic anhydride is the preferred unsaturated organic compound containing at least one ethylenic unsaturation and at least one carbonyl group.

30 The unsaturated organic compound containing at least one carbonyl group can be grafted to the polypropylene by any known technique, such as those taught in US-A-3,236,917; US-A-5,194,509 and US-A-4,905,541.

The unsaturated organic compound content of the grafted polypropylene is at least 0.01 weight percent, preferably at least 0.1 weight percent and most preferably at least 0.5 weight percent based on the combined weight of the polypropylene and organic compound. The maximum amount of unsaturated organic compound content can vary to convenience, but typically it does not exceed 10 weight percent, preferably it does not exceed 5 weight percent and most preferably it does not exceed 2 weight percent based on the combined weight of the polypropylene and the organic compound.

In general, (a) the thermoplastic polymer is employed in an amount of at least 40 parts by weight, preferably at least 45 parts by weight, more preferably at least 50 parts by weight, most preferably at least 55 parts by weight based on the weight of the total composition. In general, the thermoplastic polymer is used in amounts less than or equal to 95 parts by weight, preferably less than or equal to 90 parts by weight, more preferably less than or equal to 80 parts by weight, even more preferably less than or equal to 70 parts by weight, and most preferably less than or equal to 65 parts by weight based on the weight of the total composition.

Component (b) in the present invention is one or more uncalcined filler, such as calcium carbonate, talc, kaolin, mica, wollastonite, hollow glass beads, titanium oxide, silica, carbon black, glass fiber, potassium titanate or single layers of a cation exchanging layered silicate material, such as montmorillonite, bidelite, saponite and hectorite. Preferred uncalcined fillers are calcium carbonate, talc, kaolin, mica, wollastonite, or combinations thereof. See for example US-A-5,091,461; US-A-3,424,703; EP 639,613 A1 and EP 391,413, where these materials and their suitability as an uncalcined filler for polymeric resins are generally described. A preferred uncalcined filler is talc.

Preferred uncalcined talcs have very low free metal oxide content. The mineral talcs best suited are hydrated magnesium silicates as generally represented by the theoretical formula:



Compositions of talcs may vary somewhat with locality in which they are mined.

The suitability of uncalcined fillers in maintaining the preferred properties, for example toughness and stiffness, of molded articles prepared from the resin has been found to be a function of the average length to thickness ratio (L/T) of the filler particles together with obtaining a uniformly small particle-sized filler. Preferred uncalcined fillers have an

average L/T preferably from 1 to 30. Highly preferred are those compositions incorporating fillers having an average L/T as measured according to the below-described technique of at least 1, preferably at least 1.5, more preferably at least 2, even more preferably at least 3, and most preferably at least 4. With regard to the maximum level for the L/T, it has been
5 found desirable to have a value up to and including 30, preferably up to and including 25, more preferably up to and including 20, even more preferably up to and including 15, and most preferably up to and including 12.

For determining the L/T ratio, the length of the fillers (or longest dimension, such as the diameter of a plate-shaped particle) as well as their thickness (shortest dimension of the
10 two dimensions measurable) can be measured by preparing a filler modified polymeric resin sample and measuring the particle dimensions of the dispersed particles from digitized images produced by back scattered electron imaging using a scanning electron microscope and analyzing the digitized images in an image analyzer. Preferably, the size of the image is at least 10X the size of the maximum particle size.

15 The filled thermoplastic compositions included within the scope of this invention generally utilize uncalcined fillers with a number average particle size, as measured by a sedimentation process which measures the gravity-induced settling rates of different size particles in a liquid with known properties, of less than or equal to 10 microns (μm) preferably less than or equal to 3 μm , more preferably less than or equal to 2 μm , more
20 preferably less than or equal to 1.5 μm and most preferably less than or equal to 1.0 μm . In general, smaller average particle sizes equal to or greater than 0.001 μm , preferably equal to or greater than 0.01 μm , more preferably equal to or greater than 0.1 μm , or most preferably equal to or greater than 0.5 μm , if available, could very suitably be employed. The filled thermoplastic compositions included within the scope of this invention generally utilize
25 uncalcined fillers with a largest particle size, sometimes referred to as maximum particle size, of less than or equal to 13 μm , preferably less than or equal to 12 μm , more preferably less than or equal to 10 μm and most preferably less than or equal to 8 μm .

Preferably, particle size determinations are performed on a SEDIGRAPHTM 5100 (using a WINDOWSTM-based software program) available from Micromeritics. Test
30 samples are prepared by suspending three grams of talc in 25 ml of a 0.1 percent Daxad 30 solution followed by addition of 2 ml of isopropyl alcohol. The mixture is stirred. An additional 25 ml of 0.1 percent Daxad 30 solution is added and the sample is sonicated then

analyzed. The following report options are selected: Cumulative Fraction Table, Cumulative Graph and Frequency Graph.

The uncalcined fillers in the filled thermoplastic compositions according to the present invention are present in an amount of at least 1 part by weight, preferably at least 2 parts by weight, more preferably at least 3 parts by weight, even more preferably at least 4 parts by weight, and most preferably at least 6 parts by weight based on the total weight of the composition. Usually it has been found sufficient to employ an amount of uncalcined filler up to and including 30 parts by weight, preferably up to and including 25 parts by weight, more preferably up to and including 20 parts by weight and most preferably up to and including 15 parts by weight based on the total weight of the composition.

Component (c) in the present invention is one or more calcined filler, preferably talc, kaolin or combinations thereof. See for example US-A-4,528,303 where these materials and their suitability as a calcined filler for polymeric resins are generally described. Calcined talc is a preferred calcined filler.

Calcination treatment consists of heating the selected mineral to a temperature of at least 800°C, the process being carried out in the atmosphere, under a nitrogen atmosphere or under a moist air atmosphere; it is possible to carry out the process in a static or dynamic furnace. This calcination causes, on the one hand, a dehydroxylation reaction of the mineral, which will evolve its structural water above 800°C, and on the other hand, a conversion reaction of its initial crystallographic structure, which will give rise to an intimate in-situ mixture of enstatite and silica. The admixture is essentially enstatite and silica but, can also contain small amounts of mineral impurities associated with the nature of the deposit, which do not constitute a problem. The heating time is not critical and can vary over wide limits, for example, ranging from a few seconds (in the case of flash calcination) to ten hours (in the case of calcination in a batch rotary furnace). Of course, this time must in all cases be sufficient to perform the crystallographic conversion referred to above.

The calcined talc which is preferably used according to the present invention consists of heating in a static or rotary furnace at a temperature from 900°C to 1300°C for a period of time ranging from 30 minutes to five hours.

Percent calcination of the talc can be determined by the following formula:

$$\text{Percent Calcination} = 100 \times [1.0 - (\text{adjusted LOI} / \text{total theoretical weight loss})]$$

Where loss on ignition (LOI) is determined by weighing a sample, preferably a 1.5 to 2.0 gram sample, of talc into a pre-fired, pre-weighed (W1) platinum crucible. It is transferred to an oven, dried at 200°C for 10 minutes and cooled in a desiccator. The cooled sample and crucible is weighed (W2), transferred to a muffle furnace, calcined at 1000°C for 30 minutes, and cooled in a desiccator. The cooled sample and crucible is weighed (W3) and the weight loss (LOI) is calculated as follows:

$$\text{Percent Weight Loss} = [(W2-W3)/(W2-W1)]*100$$

10

The LOI is adjusted to account for any residue or artifact included in the LOI measurement (adjusted LOI). The adjusted LOI is compared to the total theoretical weight loss for 100 percent calcination of the talc, which is typically 4.4 percent. For example, a 1 gram sample of talc with an adjusted LOI of 0.0022 gram would have a 95 percent calcination of:

15

$$95 \text{ Percent Calcination} = 100 \times [1.0 - (0.0022 \text{ gram}/0.044 \text{ gram})]$$

Preferably the calcined talc of the present invention has a percent calcination equal to or greater than 80, more preferably equal to or greater than 85 and most preferably equal to or greater than 90 as measured by LOI.

20

Preferably the calcined talc of the present invention has a Hunter L* dry brightness value equal to or greater than 60, more preferably equal to or greater than 65 and most preferably equal to or greater than 70 as measured by test method ASTM E 1347.

The filled thermoplastic compositions included within the scope of this invention generally utilize calcined fillers with a number average particle size as measured by a sedimentation method discussed hereinabove of less than 2.5 μm preferably less than or equal to 2.4 μm, more preferably less than or equal to 2.2 μm, more preferably less than or equal to 2 μm and most preferably less than or equal to 1.5 μm. In general, smaller average particle sizes equal to or greater than 0.1 μm, preferably equal to or greater than 0.3 μm, more preferably equal to or greater than 0.5 μm, or most preferably equal to or greater than 0.6 μm, if available, could very suitably be employed. The filled thermoplastic compositions included within the scope of this invention generally utilize calcined fillers with a maximum particle size, of less than or equal to 13 μm, preferably less than or equal

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to 12 μm , more preferably less than or equal to 10 μm , even more preferably less than or equal to 8 μm , even more preferably less than or equal to 6 μm and most preferably less than or equal to 4 μm .

The calcined fillers in the filled thermoplastic compositions according to the present invention are present in an amount of at least 1 part by weight, preferably at least 2 parts by weight, more preferably at least 3 parts by weight, even more preferably at least 4 parts by weight, and most preferably at least 6 parts by weight based on the total weight of the composition. Usually it has been found sufficient to employ an amount of calcined filler up to and including 30 parts by weight, preferably up to and including 25 parts by weight, more preferably up to and including 20 parts by weight and most preferably up to and including 15 parts by weight based on the total weight of the composition.

The filled thermoplastic compositions of the present invention may further comprise component (d) an impact modifier. Preferable impact modifiers are elastomeric or rubbery materials having a T_g equal to or less than 0°C , preferably equal to or less than -10°C , more preferably equal to or less than -20°C , and most preferably equal to or less than -30°C . T_g is the temperature or temperature range at which a polymeric material shows an abrupt change in its physical properties, including, for example, mechanical strength. T_g can be determined by differential scanning calorimetry.

Suitable impact modifiers include polymers such as acrylate rubbers, particularly homopolymers and copolymers of alkyl acrylates having from four to six carbons in the alkyl group. Suitable impact modifiers can also be grafted homopolymers or copolymers of butadiene that are grafted with a polymer of styrene and methyl methacrylate. Some of the preferred rubber-containing materials of this type are the known methyl methacrylate, butadiene, and styrene-type (MBS-type) core/shell grafted copolymers having a T_g equal to or less than 0°C and a rubber content greater than 40 percent, typically greater than 50 percent. They are generally obtained by graft polymerizing styrene and methyl methacrylate and/or equivalent monomers in the presence of a conjugated diene polymer rubber core, preferably a butadiene homo- or co-polymer. The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and, when added in sequence, layers, shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other.

Polyolefin elastomers comprising one or more C_2 to C_{20} alpha-olefins in polymerized form are preferred impact modifiers. Examples of the types of polymers from

which the present polyolefin elastomers are selected include copolymers of alpha-olefins, such as ethylene and propylene, ethylene and 1-butene, ethylene and 1-hexene or ethylene and 1-octene copolymers, and terpolymers of ethylene, propylene and a diene comonomer such as hexadiene or ethylidene norbornene.

5 A preferable polyolefin elastomer is a substantially linear ethylene polymer or a linear ethylene polymer (S/LEP), or a mixture of one or more of each. Both substantially linear ethylene polymers and linear ethylene polymers are known. Substantially linear ethylene polymers and their method of preparation are fully described in US-A-5,272,236 and US-A-5,278,272. Linear ethylene polymers and their method of preparation are fully
10 disclosed in US-A-3,645,992; US-A-4,937,299; US-A-4,701,432; US-A-4,937,301; US-A-4,935,397; US-A-5,055,438; EP 129,368; EP 260,999; and WO 90/07526.

As used here, "a linear ethylene polymer" means a homopolymer of ethylene or a copolymer of ethylene and one or more alpha-olefin comonomers having a linear backbone (that is no cross linking), no long-chain branching, a narrow molecular weight distribution
15 and, for alpha-olefin copolymers, a narrow composition distribution. Further, as used here, "a substantially linear ethylene polymer" means a homopolymer of ethylene or a copolymer of ethylene and of one or more alpha-olefin comonomers having a linear backbone, a specific and limited amount of long-chain branching, a narrow molecular weight distribution and, for alpha-olefin copolymers, a narrow composition distribution.

20 Short-chain branches in a linear copolymer arise from the pendent alkyl group resulting upon polymerization of intentionally added C₃ to C₂₀ alpha-olefin comonomers. Narrow composition distribution is also sometimes referred to as homogeneous short-chain branching. Narrow composition distribution and homogeneous short-chain branching refer to the fact that the alpha-olefin comonomer is randomly distributed within a given
25 copolymer of ethylene and an alpha-olefin comonomer and virtually all of the copolymer molecules have the same ethylene to comonomer ratio. The narrowness of the composition distribution is indicated by the value of the Composition Distribution Branch Index (CDBI) or sometimes referred to as Short Chain Branch Distribution Index. CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of
30 the median molar comonomer content. The CDBI is readily calculated, for example, by employing temperature rising elution fractionation, as described in Wild, Journal of Polymer Science, Polymer Physics Edition, Volume 20, page 441 (1982), or US-A-4,798,081. The CDBI for the substantially linear ethylene copolymers and the linear

ethylene copolymers in the present invention is greater than 30 percent, preferably greater than 50 percent, and more preferably greater than 90 percent.

Long-chain branches in substantially linear ethylene polymers are polymer branches other than short chain branches. Typically, long chain branches are formed by insitu
5 generation of an oligomeric alpha-olefin via beta-hydride elimination in a growing polymer chain. The resulting species is a relatively high molecular weight vinyl terminated hydrocarbon which upon polymerization yields a large pendent alkyl group. Long-chain branching may be further defined as hydrocarbon branches to a polymer backbone having a chain length greater than n minus 2 (“ $n-2$ ”) carbons, where n is the number of carbons of the
10 largest alpha-olefin comonomer intentionally added to the reactor. Preferred long-chain branches in homopolymers of ethylene or copolymers of ethylene and one or more C_3 to C_{20} alpha-olefin comonomers have at least from 20 carbons up to more preferably the number of carbons in the polymer backbone from which the branch is pendant. Long-chain branching may be distinguished using ^{13}C nuclear magnetic resonance spectroscopy alone,
15 or with gel permeation chromatography-laser light scattering (GPC-LALS) or a similar analytical technique. Substantially linear ethylene polymers contain at least 0.01 long-chain branches/1000 carbons and preferably 0.05 long-chain branches/1000 carbons. In general, substantially linear ethylene polymers contain less than or equal to 3 long-chain branches/1000 carbons and preferably less than or equal to 1 long-chain branch/1000
20 carbons.

Preferred substantially linear ethylene polymers are prepared by using metallocene based catalysts capable of readily polymerizing high molecular weight alpha-olefin copolymers under the process conditions. As used here, copolymer means a polymer of two or more intentionally added comonomers, for example, such as might be prepared by
25 polymerizing ethylene with at least one other C_3 to C_{20} comonomer. Preferred linear ethylene polymers may be prepared in a similar manner using, for instance, metallocene or vanadium based catalyst under conditions that do not permit polymerization of monomers other than those intentionally added to the reactor. Other basic characteristics of substantially linear ethylene polymers or linear ethylene polymers include a low residuals
30 content (that is a low concentration therein of the catalyst used to prepare the polymer, unreacted comonomers and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability

even though the molecular weight distribution is narrow relative to conventional olefin polymers.

While the substantially linear ethylene polymers or the linear ethylene polymers used in the practice of this invention include substantially linear ethylene homopolymers or linear ethylene homopolymers, preferably the substantially linear ethylene polymers or the linear ethylene polymers comprise between 50 to 95 weight percent ethylene and 5 to 50, and preferably 10 to 25 weight percent of at least one alpha-olefin comonomer. The comonomer content in the substantially linear ethylene polymers or the linear ethylene polymers is generally calculated based on the amount added to the reactor and as can be measured using infrared spectroscopy according to ASTM D-2238, Method B. Typically, the substantially linear ethylene polymers or the linear ethylene polymers are copolymers of ethylene and one or more C₃ to C₂₀ alpha-olefins, preferably copolymers of ethylene and one or more C₃ to C₁₀, alpha-olefin comonomers and more preferably copolymers of ethylene and one or more comonomers selected from the group consisting of propylene, 1-butene, 1-hexene, 4-methyl-1-pentane, and 1-octene. Most preferably the copolymers are ethylene and 1-octene copolymers.

The density of these substantially linear ethylene polymers or linear ethylene polymers is equal to or greater than 0.850 grams per cubic centimeter (g/cm³), preferably equal to or greater than 0.855 g/cm³, more preferably equal to or greater than 0.857 g/cm³ and most preferably equal to or greater than 0.858 g/cm³. Generally, the density of these substantially linear ethylene polymers or linear ethylene polymers is less than or equal to 0.935 g/cm³, preferably less than or equal to 0.900 g/cm³, more preferably less than or equal to 0.872 g/cm³, even more preferably less than or equal to 0.868 g/cm³ and most preferably less than or equal to 0.863 g/cm³.

If more than one substantially linear ethylene polymer component or linear ethylene polymer component is used, it is preferable to have a first substantially linear ethylene polymer component or linear ethylene polymer component with a density from 0.855 to 0.864 g/cm³ and a second substantially linear ethylene polymer component or linear ethylene polymer component with a density from 0.865 to 0.872 g/cm³, wherein the resulting substantially linear ethylene polymer, linear ethylene polymer or combination thereof has a density from 0.857 to 0.870 g/cm³ and most preferably from 0.858 to 0.868 g/cm³.

The melt flow ratio for substantially linear ethylene polymers, measured as I_{10}/I_2 , is greater than or equal to 5.63, is preferably from 6.5 to 15, and is more preferably from 7 to 10. I_2 is measured according to ASTM Designation D 1238 using conditions of 190°C and 2.16 kilogram (“kg”) mass. I_{10} is measured according to ASTM Designation D 1238 using
5 conditions of 190°C and 10.0 kg mass.

The molecular weight distribution (M_w/M_n) for substantially linear ethylene polymers is the weight average molecular weight (M_w) divided by number average molecular weight (M_n). M_w and M_n are measured by gel permeation chromatography (GPC). For substantially linear ethylene polymers, the I_{10}/I_2 ratio indicates the degree of
10 long-chain branching, that is the larger the I_{10}/I_2 ratio, the more long-chain branching exists in the polymer. In preferred substantially linear ethylene polymers M_w/M_n is related to I_{10}/I_2 by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$. Generally, M_w/M_n for substantially linear ethylene polymers is at least 1.5 and preferably at least 2.0 and is less than or equal to 3.5, more preferably less than or equal to 3.0. In a most preferred embodiment, substantially linear
15 ethylene polymers are also characterized by a single differential scanning calorimetry (DSC) melting peak.

The preferred I_2 melt index for these substantially linear ethylene polymers or linear ethylene polymers is from 0.1 g/10 min. to 100 g/10 min., more preferably 0.5 g/10 min. to 20 g/10 min. and most preferably 0.5 g/10 min. to 10 g/10 min.

20 If more than one substantially linear ethylene polymer component or linear ethylene polymer component is used, it is preferable to have a first substantially linear ethylene polymer component or linear ethylene polymer component with a I_2 melt index from 0.4 to 0.9 g/10 min. and a second substantially linear ethylene polymer component or linear ethylene polymer component with a I_2 melt index from 1 to 10 g/10 min.

25 The impact modifier is employed in the filled thermoplastic composition of the present invention in amounts sufficient to provide the desired balance of processability and impact resistance. In general, the impact modifier is employed in amounts of at least 1 part by weight, preferably at least 5 parts by weight, more preferably at least 10 parts by weight and most preferably at least 15 parts by weight based on the weight of the total composition.
30 In general, the impact modifier is used in amounts less than or equal to 40 parts by weight, preferably less than or equal to 35 parts by weight, more preferably less than or equal to 30 parts by weight, even more preferably less than or equal to 25 parts by weight and most

preferably less than or equal to 20 parts by weight based on the weight of the total composition.

The filled thermoplastic composition of the present invention optionally contains component (e) a slip agent. Preferably the slip agent is ionic more preferably the slip agent is non-ionic. Exemplary of ionic slip agents are salt derivatives of aromatic or aliphatic hydrocarbon oils, such as magnesium stearate, calcium stearate or zinc stearate.

Useful non-ionic slip agents include, but are not limited to, for example, aromatic or aliphatic hydrocarbon oils, as well as esters, amides, alcohols and acids of such oils, for example, mineral oils, naphthenic oils, paraffinic oils, glycerol monostearate, pentaerythritol monooleate, stearamides, saturated fatty acid amides or ethylenebis(amides), unsaturated fatty acid amides or ethylenebis(amides), adipic acid, sebacic acid, styrene-alpha-methyl styrene, natural oils such as castor, corn, cottonseed, olive, rapeseed, soybean, sunflower, other vegetable and animal oils, as well as esters, alcohols, and acids of the oils, polyether polyols or waxes, such as polyethylene waxes.

Preferred non-ionic slip agents are glycols or fluoro-containing polymers. Even more preferred non-ionic slip agents are silicone polymers, preferably silicone oils. Most preferred non-ionic slip agents are unsaturated fatty acid amides for example, oleamide, erucamide, linoleamide, and mixtures thereof.

Generally preferred concentrations of the slip agent is in the range of from 0 parts to 0.5 parts by weight, preferably of from 0.1 parts to 0.4 parts by weight and most preferably of from 0.2 parts to 0.3 parts by weight based on the weight of the total composition.

Further, the claimed filled thermoplastic compositions may also optionally contain one or more additives that are commonly used in thermoplastic compositions of this type. Preferred additives of this type include, but are not limited to: ignition resistant additives, stabilizers, colorants, antioxidants, antistats, flow enhancers, nucleating agents, including clarifying agents, etc. Preferred examples of additives are ignition resistance additives, such as, but not limited to halogenated hydrocarbons, halogenated carbonate oligomers, halogenated diglycidyl ethers, organophosphorous compounds, fluorinated olefins, antimony oxide and metal salts of aromatic sulfur, or a mixture thereof may be used.

Further, compounds which stabilize thermoplastic compositions against degradation caused by, but not limited to heat, light, and oxygen, or a mixture thereof may be used.

Depending on the additive and the desired effect, such additives may be present in an amount from at least 0.01 parts, preferably at least 0.1 parts, more preferably at least 1

part, more preferably at least 2 parts and most preferably at least 5 parts by weight based on the total weight of the composition. Generally, the additive is present in an amount less than or equal to 25 parts, preferably less than or equal to 20 parts, more preferably less than or equal to 15 parts, more preferably less than or equal to 12 parts, and most preferably less than or equal to 10 parts by weight based on the total weight of composition.

Preparation of the filled thermoplastic compositions of this invention can be accomplished by any suitable mixing means known in the art, including dry blending the individual components and subsequently melt mixing, either directly in an extruder used to make the finished article (for example, the automotive part), or pre-mixing in a separate extruder (for example, a Banbury mixer). Dry blends of the compositions can also be directly injection molded without pre-melt mixing.

When softened or melted by the application of heat, the filled thermoplastic compositions of this invention can be fabricated into articles using conventional techniques such as compression molding, injection molding, gas assisted injection molding, calendaring, vacuum forming, thermoforming, extrusion and/or blow molding, alone or in combination. The filled thermoplastic compositions can also be formed, spun, or drawn into films, fibers, multi-layer laminates or extruded sheets, or can be compounded with one or more organic or inorganic substances, on any machine suitable for such purpose. The filled thermoplastic compositions of the present invention are preferably injection molded.

To illustrate the practice of this invention, examples of the preferred embodiments are set forth below. However, these examples do not in any manner restrict the scope of this invention.

EXAMPLES

The compositions of Example 1 and Comparative Examples A and B are compounded on a Werner and Pfleiderer ZSK-30, 30 millimeter (mm) twin screw extruder. An intimate mixture of the components, polymers and fillers, is added via a single vibratory feeder. The extruder output is 44 pounds per hour (lb/h.). The following are the compounding conditions on the ZSK-30 extruder: Barrel temperature profile: 169°C, 181°C, 192°C and 208°C; Die temperature: 217°C; Melt temperature: 225°C; Screw speed: 250 revolutions per minute (rpm); Pressure: 32 pounds per square inch (psi) and Torque: 21 ft-lb. The extrudate is cooled in the form of strands and comminuted as pellets. The pellets are used to prepare test specimens on a 90 ton Toyo injection molding machine,

having the following molding conditions: Melt temperature: 200°C; Mold temperature: 43°C; Back pressure: 500 psi and Cycle time: 41 seconds (s.).

The formulation content of Example 1 to 3 and Comparative Examples A to C are given in Table 1 below in parts by weight of the total composition. In Table 1:

5 “PP-1” is an isotactic polypropylene copolymer comprising 3.4 percent by weight ethylene having a density of 0.903 g/cm³, a melt flow rate of 65 at 230°C and an applied load of 2.16 kg;

“PP-2” is an isotactic polypropylene/ethylene copolymer available as C712-50RNSA Dow propylene from Dow Chemical having a density of 0.90 g/cm³ and a melt flow rate of 10 50 at 230°C and an applied load of 2.16 kg;

“PP-3” is an isotactic polypropylene homopolymer available as AMOCO 9934 from Amoco having a molecular weight distribution of 14.8, density of 0.91 g/cm³, a melt flow rate of 35 at 230°C and an applied load of 2.16 kg;

“PP-4” is an isotactic polypropylene homopolymer available as AMOCO 9433 from 15 Amoco having a molecular weight distribution of 19.8, density of 0.91 g/cm³, a melt flow rate of 12 at 230°C and an applied load of 2.16 kg;

“PP-5” is a maleic anhydride grafted polypropylene available as EPOLENETM E43P from Eastman Chemical;

“S/LEP-1” is a substantially linear ethylene/octene copolymer available as 20 AFFINITYTM EG 8200 from The Dow Chemical Company having a density of approximately 0.87 g/cm³, a melt flow rate of 5 g/10 min. determined at 190°C and an applied load of 2.16 kg, a molecular weight distribution of 2.1 and a CBDI of greater than 50;

“S/LEP-2” is a substantially linear ethylene/octene copolymer available as 25 AFFINITY EG 8180 from The Dow Chemical Company having a density of approximately 0.863 g/cm³, a melt flow rate of 0.5 g/10 min. determined at 190°C and an applied load of 2.16 kg, and a CBDI of greater than 50;

“TALC 1” is a calcined mineral talc having a median particle size of 1.2 μm and a maximum particle size of 7 μm;

30 “TALC 2” is a calcined mineral talc having a median particle size of 1.8 μm and a maximum particle size of 13 μm;

“TALC 3” is a calcined mineral talc commercially available as STEAPLAST™ 9502 from Luzenac having a median particle size of 2.5 μm and a maximum particle size of 12 μm;

“TALC 4” is a commercially available uncalcined mineral talc available as JETFIL™ 700C from Luzenac having a median particle size of 1.5 μm and a maximum particle size of 10 to 12 μm;

“Erucamide” is an unsaturated fatty amide with the formula C₂₁H₄₁CONH₂ available as KEMAMIDE™ from Witco; and

“IRGANOX™ B 225 FF” is a 1:1 mixture of IRGANOX 1010 and tris(2,4-di-tert-butylphenyl phosphite antioxidant available from Ciba Geigy in the form of a flake.

Table 1

Example Comparative Example	1	A	B	2	3	C
COMPOSITION						
PP-1	57.5	57.5				
PP-2			10.5			
PP-3			40.2	24.5	24.5	24.5
PP-4				24.5	24.5	24.5
PP-5				1.5	1.5	1.5
SLEP-1	9	9				
SLEP-2	9	9	24	25	25	25
Talc-1	12	24			12	
Talc-2				12		
Talc-3						12
Talc-4	12		25	12	12	12
Erucamide	0.3	0.3		0.3	0.3	0.3
IRGANOX B 225	0.2	0.2	0.2	0.2	0.2	0.2

The following tests are run on Example 1 to 3 and Comparative Examples A to C and the results of these tests are shown in Table 2:

“MFR” melt flow rate is determined according to ISO 1133 on a Kayness apparatus operating at 230°C and an applied load of 2.16 kg;

“Flexural Tangent Modulus” is determined in accordance with ISO 178. Testing is performed using a United mechanical tester;

“Notched Izod” is determined according to ISO 180/1A at 23°C;

“Ash” is determined using a Microwave Muffle Furnace MAS-7000;

“Density” is measured according to ISO 1183;

“Tensile Strength” is done in accordance with ISO R527. Testing is performed using a United mechanical tester;

“HDT” heat distortion under load is determined on a Ceast HDT 300 Vicat machine in accordance to ISO 75 where test specimens are unannealed and tested under an applied pressure of 0.45 MPa;

“Dart” instrumented impact is determined according to ASTM D 3763 using a MTS 810 instrumented impact tester at 15 miles per hour (MPH) impact. Test results were determined at 0°C. Specimens were inspected and judged as brittle or ductile fractures, test results are reported as number of specimens with ductile failure;

“Hardness” Shore D hardness is measured according to ISO 868; and

“Scratch Resistance” levels are determined according to the Ford Lab Test Method (FLTM BN108-13). The apparatus consists of a moveable platform connected to five beams (250mm long). A scratch pin is attached to one end of each beam. On the tip on each pin is a highly polished hardened steel ball (1.0 +/- 0.1mm diameter). Each pin is loaded with a weight that exerts a force on the surface of a test plaque. Four force levels were selected for this study: 15 Newton (N), 10N, and 7N and 3N. Driven by compressed air, the beams draw the pins across the surface of the plaque, which generates scratches. A sliding velocity of approximately 100 mm/s is maintained. All tests are performed at room temperature on test plaques conditioned at 25°C for more than 24 h prior to testing. The highest force value that doesn’t produce scratches is reported.

Table II

Example Comparative Example	1	A	B	2	3	C
PROPERTIES						
MFR @ 230°C/ kg, g/10 min.	23	24	14	8.5	8	7.9
Flexural Tangent Modulus, MPa	1900	1600	2200	2020	2020	1950
Notch Izod, ft-lb/in	36.1	36.9	35	43.2	42.6	37.9
Ash, percent (%)	24.1	24.2	24.4	23.4	23.6	23.4
Density, g/cm ³	1.079	1.08	1.077	1.069	1.067	1.065
Tensile Yield, psi	20.2	19.8	21	22.8	22.1	22.9
HDT @ 0.45 MPa, °C	111.6	104.2	119	108	112.9	108
Dart, ductile breaks out of 5 @ 0°C	5	5	5	5	5	3
Hardness (Shore D)	68.3	67.8	68.2	42.1	41.7	41
Scratch Resistance, N	15	15	7	10	10	10

The improvement in retention of impact properties, flexural modulus and scratch
5 resistance when using a filled thermoplastic composition of the present invention is
apparent from comparison with the controls.

CLAIMS:

1. A filled thermoplastic composition comprising:
 - (a) a polypropylene,
 - (b) an uncalcined filler5 and
 - (c) a calcined filler having an average particle size less than 2.5 microns and a maximum particle size equal to or less than 13 microns.
2. The filled thermoplastic composition of Claim 1 wherein (b) the uncalcined filler is calcium carbonate, talc, kaolin, mica, wollastonite, hollow glass beads, titanium oxide, silica, carbon black, glass fiber, potassium titanate or single layers of a cation 10 exchanging layered silicate material.
3. The filled thermoplastic composition of Claim 1 wherein (b) the uncalcined filler is talc.
4. The filled thermoplastic composition of Claim 1 wherein (c) the calcined filler is 15 talc, kaolin or combinations thereof.
5. The filled thermoplastic composition of Claim 1 wherein (c) the calcined filler is talc.
6. The filled thermoplastic composition of Claim 1 further comprising an impact modifier.
7. The filled thermoplastic composition of Claim 6 wherein the impact modifier is 20 a substantially linear ethylene polymer, a linear ethylene polymer or combinations thereof, wherein the substantially linear ethylene polymer and linear ethylene polymer are characterized as having:
 - (i) a density of less than 0.93 g/cm^3 ,
 - (ii) a molecular weight distribution, M_w/M_n , of less than 3.0 and
 - (iii) a Composition Distribution Branch Index of greater than 30 percent.
8. A filled thermoplastic composition comprising:
 - (a) from 40 to 95 parts by weight an isotactic polypropylene having a crystalline phase determined by differential scanning calorimetry equal to or 30 greater than 62 weight percent based on the weight of the isotactic polypropylene;
 - (b) from 1 to 30 parts by weight of an uncalcined talc;

(c) from 1 to 30 parts by weight of a calcined talc having an average particle size less than 2.5 microns and a maximum particle size equal to or less than 13 microns,

and

5 (d) from 1 to 40 parts by weight of a substantially linear ethylene polymer, a linear ethylene polymer or combinations thereof, wherein the substantially linear ethylene polymer and linear ethylene polymer are characterized as having:

(i) a density of less than 0.93 g/cm^3 ,

(ii) a molecular weight distribution, M_w/M_n , of less than 3.0 and

10 (iii) a Composition Distribution Branch Index of greater than 30 percent;

wherein parts by weight are based on the weight of the total filled thermoplastic composition.

9. A process of extruding or molding the filled thermoplastic composition of Claim 1 or 8 into a fabricated article.

15 10. The process of Claim 9 wherein the fabricated article is an automotive trim, bumper beam, bumper fascia, pillar, or instrument panel; a snow mobile cowling or body cover; a personal water craft cowling or body cover; an all terrain vehicle cowling, fender, panel or body cover; an electrical equipment device housing; an appliance housing; a freezer container; lawn and garden furniture; building and construction sheet; a shoe; a boot;
20 an outer ski boot shell; or an outer skate shell.

11. The filled thermoplastic composition of Claim 1 or 8 in the form of a fabricated article.

25 12. The filled thermoplastic composition of Claim 11 wherein the fabricated article is an automotive trim, bumper beam, bumper fascia, pillar, or instrument panel; a snow mobile cowling or body cover; a personal water craft cowling or body cover; an all terrain vehicle cowling, fender, panel or body cover; an electrical equipment device housing; an appliance housing; a freezer container; lawn and garden furniture; building and construction sheet; a shoe; a boot; an outer ski boot shell; or an outer skate shell.