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<b>(54) Title:</b> COMPOSITION OF POLYKETONE AND POLYOLEFIN  <b>(57) Abstract</b>  The present invention relates to a process comprising reacting an aminated polyolefin with a polyketone polymer. Preferably, the aminated polyolefin has been obtained by reacting a polyolefin containing carboxylic acid groups, e.g. a polyolefin which has been modified with carboxylic acid containing compounds, with a compound containing at least 2 amine groups. Further, the invention relates to a composition obtainable by such process, to a composition based on an aminated polyolefin and a polyketone polymer, to an aminated polyolefin and to laminates and blends comprising such composition.		

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## COMPOSITION OF POLYKETONE AND POLYOLEFIN

This invention relates to compositions comprising a polyketone polymer and an aminated polyolefin, and to processes for preparing such compositions.

Combinations of polymers are of great commercial interest because of the potential to combine the valuable attributes of a number of materials into one system. Composite laminates of two or more polymers are widely used in barrier packaging applications where the barrier characteristics of one material are combined with the low cost and mechanical properties of another. In polymer blends, combinations of barrier/cost, chemical resistance/-dimensional stability, toughness/strength are achieved with a number of commercial materials.

In combinations of polymers, the compatibilization of the polymer/polymer interface is of critical importance. Weak bonding between the polymers results in delamination and poor mechanical properties. However, strong interfacial bonds are desired to attain the ultimate characteristics of the composite or blend.

It is well known that most polymer combinations are immiscible and do not have strong enough interactions to generate strong interfacial bonds during coextrusion or melt blending. However, several compatibilization strategies have emerged to resolve the expected poor adhesion between polymers. Compatibility and adhesion can be improved by 1) incorporation of a third mutually compatible "tie-layer" between phases, 2) addition of a suitable block or graft copolymer or mutually miscible polymer which bridges the interface, or 3) promotion of in-situ grafting reactions via appropriate functionalization of one or both of the polymers.

Polyketone polymers have excellent mechanical and chemical resistance properties which make them particularly attractive for the production of compositions.

It is an object of this invention to provide a process for preparing a composition comprising polyolefins that are grafted to

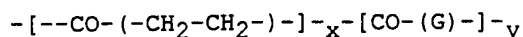
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polyketone polymer. The present invention relates to a process comprising reacting an aminated polyolefin with a polyketone polymer, to a composition obtainable by such process, to an aminated polyolefin and to a composition based on an aminated polyolefin and a polyketone polymer.

The polyketone polymer useful for the present invention preferably is a linear alternating polymer of carbon monoxide and at least one olefinically unsaturated hydrocarbon. The polyketone polymer can further contain additives such as fillers, extenders, lubricants, pigments, plasticizers, and other polymeric materials to improve or otherwise alter its properties.

The polyketone polymers which are employed as a component of the oxidatively stabilized polymer composition of the invention are preferably of a substantially linear alternating structure and preferably contain substantially one molecule of carbon monoxide for each molecule of olefinically unsaturated hydrocarbon. The more preferred polyketone polymers are copolymers of carbon monoxide and ethylene or terpolymers of carbon monoxide, ethylene and a second ethylenically unsaturated hydrocarbon of at least 3 carbon atoms, particularly an  $\alpha$ -olefin such as propylene.

When the preferred polyketone terpolymers are employed as the major polymeric component of the blends of the invention, there will be within the terpolymer at least 2 units incorporating a moiety of ethylene for each unit incorporating a moiety of the second hydrocarbon. Preferably, there will be from 10 units to 100 units incorporating a moiety of the second hydrocarbon. The polymer chain of the preferred polyketone polymers is therefore represented by the repeating formula



where G is the moiety of ethylenically unsaturated hydrocarbon of at least 3 carbon atoms polymerized through the ethylenic unsaturation and the ratio of  $y:x$  is no more than 0.5. When copolymers of carbon monoxide and ethylene are employed in the compositions of the invention, there will be no second hydrocarbon present and the copolymers are represented by the above formula wherein  $y$  is zero. When  $y$  is other than zero, i.e. terpolymers are employed, the

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-CO-(-CH<sub>2</sub>-H<sub>2</sub>-)- units and the -CO-(-G-)- units are found randomly throughout the polymer chain, and preferred ratios of y:x are from 0.01 to 0.1. The precise nature of the end groups does not appear to influence the properties of the polymer to any considerable extent so that the polymers are fairly represented by the formula for the polymer chains as depicted above.

Of particular interest are the polyketone polymers of number average molecular weight from 1000 to 200,000, particularly those of number average molecular weight from 20,000 to 90,000 as determined by gel permeation chromatography. The physical properties of the polymer will depend in part upon the molecular weight, whether the polymer is a copolymer or a terpolymer, and in the case of terpolymers the nature of the proportion of the second hydrocarbon present. Typical melting points for the polymers are from 175°C to 300°C, more typically from 210°C to 270°C. The polymers have a limiting viscosity number (LVN), measured in m-cresol at 60°C in a standard capillary viscosity measuring device, from 0.5 dl/g to 10 dl/g, more frequently from 0.8 dl/g to 4 dl/g.

A preferred method for the production of the polyketone polymers has been described in US-A-4,843,144, EP-A-314,309 and EP-A-391,579.

Any aminated polyolefin is suitable in the practice of the invention. Such aminated polyolefins include those which have been obtained by reacting a polyolefin containing carboxylic acid groups with a compound containing at least 2 amine groups. The polyolefin containing carboxylic acid groups preferably is a polyolefin modified with carboxylic acid containing compounds, preferably a polyolefin grafted with acrylic acid, maleic acid, maleic anhydride and/or azido sulfonyl benzoic acid. The maleic anhydride grafted polyolefins are preferred. The preferred polyolefin is polypropylene. Particularly preferred is maleic anhydride modified polypropylene containing from 0.1 to 2.5 %wt of maleic anhydride. Such polyolefins are commercially available from BP Chemicals under the trademark of Polybond. Polybond 3001, 3002, and 3005 are reported to have 0.25, 0.5, and 1.0 wt% maleic anhydride incorporated either at the end or as a pendent along the backbone of

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the polymer chain. Further, a blend of polyolefin and aminated polyolefin can be used in the present invention. By diluting or blending the aminated polyolefin with homopolymer, it is possible to adjust and optimize the desired level of adhesion for a particular blend, coextrusion, or coating application. The blends also provide a mechanism to easily control rheological properties in addition to reducing cost.

The useful functionalizing agents are typically compounds containing at least 2 amine groups. Examples of such amines include polymethylene diamine, aromatic diamine, diethyltriamine (DETA), triethylenetetramine (TETA), isophorene diamine, and polyether diamines. Diamines with an alkyl containing at least 2 primary amines, preferably at least 2 unhindered primary amines, are preferred.

The method of compatibilizing the polyketone and polyolefin polymers, suitably comprises a two step process. The first step involves the formation of an aminated polyolefin. In the second step, the aminated polyolefin is reacted with a polyketone polymer.

The formation of aminated polyolefins can be achieved by the melt reaction of an amine with maleated polyolefin. The reaction of maleated polyolefins and compounds containing primary amine groups in the melt state is thought to lead to the conversion of maleic anhydride moieties to imides. The reaction of a compound containing at least 2 amine groups with grafted maleic anhydride moieties is thought to leave a free primary amine which in turn can be employed in other grafting reactions. The melt mixing and reaction of the amine with the maleated polyolefin can be performed during conventional melt processing of the polyolefin. The reaction will readily proceed at temperatures above the melting point of both the polyolefin and the amine. The molar ratio of amine groups to maleic anhydride moieties in the melt reaction is preferably above 1, more preferably within the range of 2 to 5.

The second step involves reacting the aminated polyolefin with the polyketone. The reaction of amine with the polyketone backbone is typically performed at temperatures above the melting point of the polyolefin (e.g., polyethylene approximately = 140°C and

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polypropylene approximately = 160°C). Temperatures above the melting point of the polyketone polymer are not required to produce the grafting reaction. The reaction between the polyolefin and the polyketone can be achieved with the polyketone being a solid substrate or in the melt state. Thus, co-extrusion, blending, and coating applications are suitable. The reaction of the polyolefin with the substrate generally increases with increasing bonding temperature, bonding pressure, and/or duration of bonding time. When both materials are in the melt states, the extent of reaction will increase with higher melt temperatures, longer residence time in the melt, and/or more intensive mixing. The reaction of the aminated polyolefin with the polyketone can occur inter alia during a hot coating application, co-extrusion or blending processes.

The inventive method can be used in many applications such as laminates and blends. More specifically, it can be used in 1) tie-layer systems, 2) polymer/polymer blends, and 3) coatings. Tie-layer systems are used to compatibilize the various components of composite structures such as the layers in coextruded multi-layer films used in packaging applications. Tie-layer systems are also employed in the construction of coextruded tubes and pipes, multi-layer plastic bottles, retortable plastic containers, composite food boxes, and composite cans. Compatibilization mechanisms such as that described in this invention are often employed to achieve the desired balance of properties of barrier/cost, chemical resistance/dimensional stability, and toughness/strength in immiscible polymer/polymer blends. Both tie-layer systems and polymer/polymer blends involve the bonding of two polymers from the melt state where materials are combined during conventional melt processing techniques such as coextrusion and melt blending.

The present invention can be used to bond polyolefin coatings to a polyketone substrate. Examples include the application of polyolefin coatings for improved barrier properties, UV protection, and/or decorative purposes.

The invention is further illustrated by the following examples.

EXAMPLESExample 1

The preparation of aminated polypropylene was carried out in a Brabender mixing head. The modified polymer was introduced to the mixing head at 190°C and mixed for 3 minutes. At that time, the diamine powder was added to the melt and mixed for an additional three minutes. The diamine was added so that 4 moles of amine groups were present for each mole of maleic anhydride. The excess amine was added to limit the amount of crosslinking while providing an ample number of free amine groups to react across the polyketone/polypropylene interface. The amount of 1,12-diaminododecane ranged from 1 to 4 wt% depending on the level of maleic anhydride modification in the polypropylene. Controls were run with a polypropylene homopolymer (PP 5384 from Shell). After mixing, the compounded material was removed and dried. The aminated polypropylenes exhibited an amber colour after the reactive processing step.

Films of the aminated and as received maleated polypropylene materials were prepared by compression moulding. T-peel test samples were prepared by compression moulding and modified polypropylene films between two  $5 \times 10^{-4}$  m (20 mil) extruded sheets of polyketone polymer. Using a mould temperature of 200°C, the bonding protocol was one minute at 0 tons pressure and one minute at 2 tons pressure. Half of the T-peel specimens were subsequently subject to a steam retort process cycle at 127 °C (260 °F) for 30 minutes in the Barnstead benchtop apparatus. Adhesion was measured on the T-peel specimens using a method based on the D-1876 ASTM method.



Table 1. Polypropylene Materials Used

Sample	Maleic Anhydride Level (wt%)	Melt Flow (ASTM D1238) (g/10 min.)
Shell PP 5384	0.00	2
PolyBond 3001 (PB3001) <sup>a</sup>	0.25	3 - 6
PolyBond 3002 (PB3002) <sup>b</sup>	0.50	5 - 8
PolyBond 3005 (PB3005) <sup>c</sup>	1.00	40 - 65

<sup>a</sup>polypropylene having 0.25 %wt of maleic anhydride incorporated  
(Polybond is a trademark)

<sup>b</sup>polypropylene having 0.5 %wt of maleic anhydride incorporated  
(Polybond is a trademark)

<sup>c</sup>polypropylene having 1.0 %wt of maleic anhydride incorporated  
(Polybond is a trademark)

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Table 2. T-Peel Test<sup>1</sup> results showing maximum load observed with the various modified polypropylenes both before and after retort.

Sample	Before Retort Max Load	After Retort Max Load
PP 5384	No Adhesion	-
PP 5384 " 1 wt% 1,12DA <sup>(a)</sup>	No Adhesion	-
PB 3001	No Adhesion	-
PB 3001 + 1 wt% 1,12DA <sup>(b)</sup>	175 kg/m (9.8 lbs/in)	168 kg/m (9.4 lbs/in)
PB 3002	No Adhesion	-
PB 3002 + 2 wt% 1,12DA	163 kg/m (9.1 lbs/in)	189 kg/m (10.6 lbs/in)
PB 3005	No Adhesion	-
PB 3005 + 4 wt% 1,12DA	152 kg/m (8.5 lbs/in)	91 kg/m (5.1 lbs/in)

(a) 1,12DA = 1,12 diaminododecane (98% pure grade available from Aldrich Chemical Company)

(b) Diamine was compounded with the maleic anhydride modified polypropylene at 2 moles diamine per mole maleic anhydride.

<sup>1</sup>ASTM D1876 describes the T-peel test method. In our method, samples were prepared by compression moulding the adhesive polypropylene between two polyketone polymer sheets. The free ends of the polyketone polymer sheet were then clamped into the Insertion and pulled with a crosshead speed of 5 in/min. The output is lbs. force versus time. The maximum load and average load per inch width are reported.

The peel test results are listed in Table 2. No adhesion was observed between polyketone polymer and the as-received maleated polypropylenes. However, upon reaction with the amine, the materials exhibited maximum load, peel strengths in the order of 142 to 179 kg/m (8 to 10 lbs/in). The strength of the bond appeared to be almost independent of the level of maleic anhydride in the

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system. The bond strength was maintained throughout the retort process.

As was expected, the polypropylene homopolymer did not adhere to the polyketone polymer sheet. No adhesion was observed in the polypropylene homopolymer modified with 1 wt% diamine; although, pyrrole formation was apparent from the yellowing of the polyketone polymer sheet.

It is evident that the invention method produces an effective bond at the polypropylene/polyketone polymer interface. The strength of the bond is maintained after the retort sterilization process.

#### Example 2

In this example, the interfacial compatibilization mechanism is demonstrated by diluting the amine modified polypropylene in blends of polypropylene homopolymer.

The materials used in these experiments were Polybond 3001 (Polybond is a trademark), 1,12 diaminododecane and polypropylene homopolymer (WRD-1074 obtainable from Shell) with a 35 melt flow which was used to dilute the functionalized polypropylene systems.

The amine modified polypropylene materials were prepared by reactive extrusion in a Berstroff 25 mm twin screw extruder. Pellets of the maleated polypropylene and polypropylene homopolymer were dry blended with the diamine powder so that 4 moles of amine end groups were present for each mole of maleic anhydride. The zone temperatures along the barrel were set from 220 to 190°C. The melt temperature was 205°C.

The different compositions of amine modified polypropylene materials are listed in Table 3. The 25/75 amine modified polypropylene/polypropylene material was prepared by blending the polypropylene homopolymer and 100/0 amine modified polypropylene materials in a second extrusion step.

T-peel specimens were prepared and tested in the same manner as described previously in Example 1. The results are shown in Table 3.

Table 3. Amine modified polypropylene (AMPP) polypropylene (PP) homopolymer blends.

Sample	Blend Composition	Avg. Max. Load
AMPP/PP 0/100	100 wt% WRD-1074	0
AMPP/PP 100/0	100 wt% AMPP	146 kg/m (8.2 lbs/in)
AMPP/PP 75/25	75 wt% AMPP + 25 wt% WRD-1074	134 kg/m (7.5 lbs/in)
AMPP/PP 50/50	50 wt% AMPP + 50 wt% WRD-1074	113 kg/m (6.3 lbs/in)
AMPP/PP 25/75	25 wt% AMPP/PP 100/0 + 75 wt% WRD-1074 PP	57 kg/m (3.2 lbs/in)

In Table 3, the average maximum load for the T-Peel tests are given as a function of polypropylene homopolymer composition in the AMPP materials. The adhesive strength of the AMPP materials decreases as the functionalized material is diluted with polypropylene homopolymer. However, the level of adhesion even in the most dilute blends is significantly higher than that achieved with the homopolymer and sufficient for use in many applications including tie-layer systems, blends, and coextrusion.

#### Example 3

Coextruded products such as tubings, pipes, and films manufactured from polyolefins and polyketone combine the desirable attributes of both materials. However, the combination of these polymers to form useful products is limited by the poor interfacial adhesion between the polymer layers. In this example, it is shown that compatibilization can be used to improve the adhesion between the polyolefin and polyketone layers of coextruded tubings.

The materials used in this example are polyketone polymer, polypropylene homopolymer, and the aminated polypropylene/polypropylene 50/50 material described in Example 2. Coextruded tubing was manufactured using the polyketone as the inner layer and the

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polyolefin materials as the outer layer. A manifold die was used with the standard melt processing conditions for polyolefins and polyketone being employed. The outer diameter of the tubing was roughly 6.3 cm (¼-inch).

5           The adhesion was tested by observing the failure of the interface from a "kink test". In this test, the nominal ¼" coextruded tube was bent until the tubing kinked. The interface in this high strain region was then examined for delamination between the polyolefin and polyketone layers of the tubing. Tubes which  
10           showed interfacial delamination in the kinked area were labelled failures. Coextruded tubing which maintained its integrity without delaminating passed. The results are shown in Table 4.

Table 4. Result for co-extruded composite systems.

Coextruded Tube Construction (polyketone/polyolefin)	Kink Test Result
Polyketone/Polypropylene homopolymer	Fail
Polyketone/ (AMPP/PP 50/50)	Pass

15           The coextruded tubing constructed of polypropylene homopolymer and polyketone layers displayed a significant amount of delamination both before and after the bend test. Tubing processed with the amine modified polyolefin passed the "kink test". The adhesion of the polyketone and modified polyolefin interface was sufficient to endure the high strain levels at the bond of the kink.

20           While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

C L A I M S

1. Process comprising reacting an aminated polyolefin with a polyketone polymer.
2. Process according to claim 1, in which the aminated polymer has been obtained by reacting a polyolefin containing carboxylic acid groups with a compound containing at least 2 amine groups.
3. Process according to claim 2, in which the polyolefin containing carboxylic acid groups is a polyolefin modified with carboxylic acid containing compounds.
4. Process according to claim 3, in which the polyolefin containing carboxylic acid containing compounds is an acrylic acid, maleic acid, maleic anhydride, and/or azido sulfonyl benzoic acid grafted polyolefin.
5. Process according to any one of claims 1-4, in which the polyketone polymer is a linear alternating polyketone polymer of carbon monoxide and at least one olefinically unsaturated hydrocarbon.
6. Process according to any one of claims 1-5, in which the polyolefin is polypropylene.
7. Process according to any one of claims 1-6, in which the compound containing at least 2 amine groups is polymethylene diamine, aromatic diamine, diethyltriamine, triethylenetetramine, isophorene diamine, polyether diamine and/or an alkyl containing at least 2 primary amines.
8. Process according to claim 7, in which the compound containing at least 2 amine groups is an alkyl containing at least 2 primary amines.
9. Process according to any one of claims 1-8, in which a blend is used of polyolefin and aminated polyolefin modified with carboxylic acid containing compounds.
10. Composition obtainable by a process as described in any one of claims 1-9.

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11. Aminated polyolefin obtainable by reacting a polyolefin modified with carboxylic acid containing compounds, with a compound containing at least 2 amine groups.
12. Composition based on an aminated polyolefin and a polyketone polymer.
13. Composition according to claim 12, in which composition the aminated polyolefin is an aminated polyolefin which contained carboxylic acid containing compounds.
14. Laminate comprising a composition according to any one of claims 10, 12 or 13.
15. Blend comprising a composition according to any one of claims 10, 12 or 13.