## (12) UK Patent Application (19) GB (11) 2 339 201 (13) A

(43) Date of A Publication 19.01.2000

(21) Application No 9912834.0

(22) Date of Filing 02.06.1999

(30) Priority Data

(31) 9812035

(32) 04.06.1998

(33) **GB** 

(71) Applicant(s)

BP Chemicals Limited (Incorporated in the United Kingdom) Britannic House, 1 Finsbury Circus, LONDON, EC2M 7BA, United Kingdom

(72) Inventor(s)

Alan Gray

(74) Agent and/or Address for Service

Frances Mary Collins
BP International Limited, Group Patents &
Agreements, Chertsey Road,
SUNBURY-ON-THAMES, Middlesex, TW16 7LN,
United Kingdom

(51) INT CL7

C08L 23/06 23/08 23/16 23/28

(52) UKCL (Edition R)

**C3M** MXC MX1A MX1C MX1X M119 M139 M139C

(56) Documents Cited

EP 0293059 A2

US 4698392 A

US 4677163 A

(58) Field of Search

UK CL (Edition Q.) C3M MXC

INT CL<sup>6</sup> C08L

(54) Abstract Title

A blend of a polyketone, a polyolefin and a chlorinated polyolefin

(57) A polymer composition comprising a polymer blend and optionally conventional additives suitable for forming items such as containers, films and sheets, particularly by extrusion, blow-moulding and thermoforming. The polymer blend consists of one or more linear polyketones having an alternating structure of units derived from carbon monoxide and units derived from one or more olefinically unsaturated compounds, one or more polyolefins and one or more chlorinated polyolefins, where both the polyolefin(s) and the chlorinated polyolefin(s) may be homopolymers or copolymers. In the examples given, specific polymers used include: polyethylene, polypropylene, chlorinated polyethylene, chlorinated polypropylene, ethylene/propylene/carbon monoxide copolymer and ethylene/butylene/carbon monoxide copolymer.

# A BLEND OF A POLYKETONE, A POLYOLEFIN AND A CHLORINATED POLYOLEFIN

The present invention relates to a polymer blend composition comprising a polyketone, a polyolefin and a chlorinated polyolefin, in particular, to a polymer blend composition comprising a polyketone, a polyethylene and a chlorinated polyethylene.

For the purposes of this patent, polyketones are defined as linear polymers having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds.

Such polyketones have the formula:

5

20

$$\begin{matrix} \text{O} \\ \text{II} \\ [(\text{CR}_2\text{-CR}_2)\text{C}]_m \end{matrix}$$

where the R groups are independently hydrogen or hydrocarbyl groups, and m is a large integer; they are disclosed in several patents e.g. US 3694412. Processes for preparing the polyketones are disclosed in US 3694412 and also in EP 181014 and EP 121965. Although for the purposes of this patent polyketones correspond to this idealised structure, it is envisaged that materials corresponding to this structure in the main but containing small regimes (i.e. up to 10 wt %) of the corresponding homopolymer or copolymer derived from the olefinically unsaturated compound, also fall within the definition.

According to "Encyclopaedia of Polymer Science and Engineering" Second Edition, Volume 6, page 505, little true dissolution takes place between chlorinated polyethylene and other polymers. It is said that the miscibility with polycaprolactones, ethylene-acrylic rubbers, and a few other polymers appears to be strongly influenced by chlorine content and distribution.

Surprisingly, it has now been found that when a chlorinated polyolefin is blended with a mixture of a polyketone and a polyolefin that the chlorinated polyolefin acts as a compatibiliser for the polyketone and polyolefin components of the blend.

Thus, according to the present invention there is provided a polymer composition comprising a polymer blend and optionally conventional additives, the polymer blend consisting of:

- (A) a linear polyketone having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds;
- 10 (B) a polyolefin; and

5

15

20

25

30

(C) a chlorinated polyolefin.

Without wishing to be bound by any theory it is believed that the chlorinated polyolefin acts as a compatabiliser allowing improved mixing and interfacial adhesion of the polyketone and polyolefin components of the polymer blend.

Further advantages of the polymer composition of the present invention include improved mechanical properties (for example, impact strength), paintability, chemical resistance, barrier properties and flame retardancy when compared with polyketone/polyolefin blends.

As noted above, for the purposes of this patent, polyketones are defined as linear polymers having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds. Suitable olefinic units are those derived from  $C_2$  to  $C_{12}$  alpha-olefins or substituted derivatives thereof or styrene or alkyl substituted derivatives of styrene. It is preferred that such olefin or olefins are selected from  $C_2$  to  $C_6$  normal alpha-olefins and it is particularly preferred that the olefin units are either derived from ethylene or most preferred of all from a mixture of ethylene and one or more  $C_3$ - $C_6$  normal alpha-olefin(s) especially propylene or butylene. In these most preferable materials it is further preferred that the molar ratio of ethylene derived units to  $C_3$ - $C_6$  normal alpha-olefin derived units is greater than or equal to 1 most preferably between 2 and 30. Typically, the polyketone will be a copolymer of ethylene/propylene/CO or ethylene/butylene/CO where the units derived from propylene or butylene are in the range 0.5-10 mole % e.g. 6 mole % of the polymer. Blends of two or more polyketones may be used.

The polyketone will suitably have a number average molecular weight of between 10,000 and 500,000 preferably between 15,000 and 300,000, more preferably between 20,000 and 200,000, for example, 25,000 to 250,000.

5

10

15

20

25

30

The polyolefin may be a homopolymer or copolymer of an olefin e.g. ethylene or propylene, in particular high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) or very low density polyethylene (VLDPE), preferably LLDPE. Where the polyolefin is a copolymer of ethylene the comonomer is typically one or more C<sub>3</sub> to C<sub>10</sub> alpha-olefins such as propylene, butene-1, hexene-1, 4 methylpentene-1 and octene-1. Such homopolymers and copolymers are known and any such polymer can be used. The polyolefin may also be a copolymer of an olefin with a diene e.g. ethylene with propylene and a diene. Blends of two or more polyolefins can be used. Preferably, the polyolefin is a polypropylene or polyethylene. Where the polyolefin is polypropylene this can be atatic, syndiotactic or isotactic polypropylene.

The weight ratio of polyketone to polyolefin in the polymer blend is suitably in the range 1:20 to 20:1, preferably 1:10 to 10:1, more preferably 1:3 to 3:1, most preferably 1:1.5 to 1.5:1, for example 1:1. However, where the physical properties (e.g. toughness, impact strength and melt processability) of the polyketone are to be improved, then it is preferred to use 1 to 20% by weight of polyolefin, more preferably 5 to 15%, for example 10% by weight of polyolefin based upon the total weight of the polymer blend. On the other hand, if other properties such as thermal characteristics (e.g. Vicat softening point and heat distortion temperature) and gaseous or liquid barrier properties (e.g. oxygen, water and hydrocarbon) of the polyketone are to be improved, then it is preferred to use 1 to 25% by weight of polyketone, more preferably 1 to 20%, most preferably 2 to 10%, for example, 5% by weight of polyketone, based upon the total weight of the polymer blend.

The chlorinated polyolefin can be a chlorinated homopolymer of an olefin or a chlorinated copolymer of an olefin. Suitable polyolefins which can be chlorinated include those described above. Blends of two or more chlorinated polyolefins can be used.

Methods for preparing chlorinated polyolefins are well known and any suitable method can be used to prepare the chlorinated polyolefin. One such suitable method comprises treating the polyolefin, for example a polyethylene, with chlorine. The

chlorination reaction proceeds via a free-radical mechanism, usually catalysed by ultraviolet light or initiators. Thus, a chlorine radical abstracts a hydrogen atom from the polymer chain leaving a carbon radical which reacts with a molecule of chlorine to attach one chlorine atom to the polymer chain and liberate the other to continue the chain reaction.

The chlorinated polyolefin may contain 5 to 50% by weight chlorine, preferably 20 to 50%, more preferably 23 to 48%, most preferably 25 to 40% by weight chlorine.

5

10

15

20

25

30

Suitably, the chlorinated polyolefin comprises 1 to 25, preferably 1 to 15, more preferably 2 to 10 %, most preferably 3 to 7, for example 5 % by weight of the polymer blend.

Other polymers may be blended with the polymer composition of the present invention; the nature and amount of such a polymer will depend upon what modifications of the polymer properties are required. Furthermore, the polymer compositions of the present invention may contain conventional polymer additives such as anti-oxidants, stabilisers, and mould release agents.

It is to be understood that when in the specification and claims herein, the amounts of the individual components of the polymer blend are expressed in terms of percent by weight, it is meant, unless otherwise indicated, percent by weight based on the total weight of the polymer blend, excluding further components.

The polymer composition of the present invention can be prepared using conventional techniques and equipment for batch or continuous blending such as a two-roll mill, a Banbury mixer, or a single/twin screw compounding extruder.

The scope of the present invention extends to articles (for example, mouldings, containers, pipes and tubes), films, sheets, coatings, liners, fibres and monofilaments comprising the polymer compositions as defined hereinbefore.

According to a further aspect of the present invention there is provided a polymer-based container wherein the polymer comprises a polymer composition as defined above.

Such a container may be made at least in part from a monolayer of the composition of the present invention. Alternatively it could be of a multi-layer construction at least one layer of which is a composition according to the present invention.

Methods of fabricating the compositions into either containers, films or other

applications are standard in the art, for example extrusion, coextrusion, injection moulding, blow-moulding and thermoforming. Preferred methods of fabricating the compositions are those where orientation of the polymer is likely e.g. extrusion (film extrusion), blow-moulding and thermoforming.

The invention will now be illustrated by the following Examples.

### **Materials**

5

10

15

20

25

30

The materials in the blending experiments were:

Polyethylenes (PE): Lupolen 6031M supplied by BASF which is used for injection moulding; Rigidex HD5502 XA supplied by BP Chemicals Limited which is used for blow moulding; and Rigidex PC002-40 supplied by BP Chemical Limited which is used for pipe applications.

Chlorinated polyethylene (CPE): Tyrin BH9000 supplied by Du Pont Dow Elastomers.

Polyketone (PK): an ethylene/propylene/CO copolymer having a melting point of 195°C and a melt flow rate (MFR) of 20 g/10 minutes (at 250°C, 2.16kg load) compounded with 0.1 % w/w of Irganox 1010 and 1 % w/w of pseudoboehmite.

The polyethylene (PE), chlorinated polyethylene (CPE) and polyketone (PK) were separately pre-compounded to pellet form.

### Melt Flow Rate

The melt flow rate of the polyketone was determined using a Davenport Melt Indexer fitted with a 2.095 mm diameter die. The test temperature was 250°C and a loads of 2.16 kgs was used.

### Blend Preparation

Blends of the pellets were prepared using a Prism 16mm co-rotating twin screw extruder. The feed, barrel and die sections of the extruder were set to the following temperatures: 185, 195, and 205°C respectively. A screw speed of 200 rpm and a torque of 30-50% were used throughout production runs.

### Blend Characterisation

Scanning electron microscopy (SEM) was used to examine the phase structure of the blends and hence the degree of compatibilisation. Samples were prepared by cryo polishing a surface on a pellet of material.

### Examples

Polyethylene/polyketone/chlorinated polyethylene blends containing 85% w/w polyethylene, 10% w/w polyketone and 5% w/w chlorinated polyethylene were prepared using a Prism 16mm co-rotating twin screw extruder as described above. In addition, a sample of the polyethylene and a polyethylene/polyketone blend (90% w/w polyethylene, 10% w/w polyketone) were also processed under the above conditions.

SEM showed that the blends according to the present invention had very small phase sizes, a property associated with good compatibility. Where the blends contain high amounts of polyethylene, the polyketone was found to be distributed in a polyethylene matrix.

Tensile properties were determined in accordance with ISO 527-1966 (ASTM D 638M-93) using compression moulded sheets. The test conditions were as follows:

23°C

50% RH (relative humidity); and

50 mm/min (cross head speed).

Measurements were carried out using an Instron Series IX Automated Materials testing system 1.16 machine.

The polymer blends according to the present invention had a high tensile elongation to break, a further property associated with good compatibility. The polymer blends according to the present invention showed a slight decrease in yield stress compared with the non-compatabilised blend which is believed to arise from the rubbery nature of the CPE compatibiliser.

The results of the tensile tests are given in Table 1.

25

20

5

10

30

# TABLE 1 - TENSILE TESTS

		Materi	terial Composition (wt%)	ı (wt%)	-	Tensile F	Tensile Properties
Experiment	PK	Lupolen	HD5502XA	PC002-40	CPE	Yield Stress	Elongation at break
•		·				(MPa)	(%)
Comparative Ex A		100	ı	ı	1	26.6	1719
Comparative Ex B	•	•	100	ı	1	23.5	912
Comparative Ex C	1	ı	ī	100	,	16.7	930
Comparative Ex D	10	•	1	06	1	14.3	17
Example 1	10	85	1	1	5	22.8	301
Example 2	10	ı	85	,	5	20.5	828
Example 3	10	1	t	85	5	15.3	847

### Claim

- 1. A polymer composition comprising a polymer blend and optionally conventional additives, the polymer blend consisting of:
- (A) a linear polyketone having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds;
- 5 (B) a polyolefin; and
  - (C) a chlorinated polyolefin.

10

15

20





INVESTOR IN PEOPLE

**Application No:** 

GB 9912834.0

Claims searched:

**Examiner:** Date of search:

Annabel Ovens 1 November 1999

Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C3M (MXC)

Int Cl (Ed.6): C08L

Other:

Online: PAJ, EPODOC, WPI

### Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	EP 0293059 A2	(E.I. DU PONT DE NEMOURS AND COMPANY)	
A	US 4698392	(CHOU)	
A	US 4677163	(SEIICHI TADA AND YASUHISA HOSOAI)	

- Document indicating lack of novelty or inventive step
- Document indicating lack of inventive step if combined P with one or more other documents of same category.
- Member of the same patent family

- A Document indicating technological background and/or state of the art. Document published on or after the declared priority date but before the filing date of this invention.
- Patent document published on or after, but with priority date earlier than, the filing date of this application.