

CROSS-LINKABLE COMPOSITIONS FOR EXTRUSION

This invention relates to polymer compositions based on ethylene polymers that can be crosslinked after extrusion and has important applications in compositions for use as the dielectric (insulation) and/or sheath (jacket) of electric cables.

Crosslinking of the polymeric parts of wires and cables is desirable, and sometimes essential, to impart good mechanical toughness and resistance to solvents and thermal deformation. Radiation crosslinking necessitates the installation of plant at very high capital cost, and also gives problems in obtaining a uniform dose (and therefore crosslink density) over the cross-section of the cable. Conventional chemical crosslinking with peroxides and/or sulphur requires pressurised curing chambers at high temperatures. The high temperatures required for cure severely limit line speeds, and have high energy costs plus high scrap rates at start-up due to inability to observe the product until it has emerged from the long curing chamber.

There has therefore been considerable interest in the past decade and a half in a low capital cost chemical crosslinking technique that does not require a pressurised and heated chamber and hence enables the extrusion quality to be observed as easily and quickly as that of a thermoplastic product; it is based on a two-step chemical reaction in which a hydrolysable unsaturated silane is first grafted to a base polymer (usually a homopolymer or copolymer of ethylene) and subsequently crosslinking is brought about by catalysed condensation reaction between pairs of silane groups. This 'Sioplas' process was first introduced by Dow Corning Limited (formerly Midland Silicones Limited) as a 2-stage process using separate machines for the grafting and extrusion steps (U.K. Patent No. 1286460) but was subsequently improved by the applicants in conjunction with Étabs. Maillefer S A (U.K. Patent No. 1526398) to operate as a single-stage process with

grafting in the extruder. This one-stage process has been used on a significant scale, but its application has been restricted, hitherto, by the inability of experts in the art to provide halogen-free compositions crosslinkable by this process having commercially acceptable flame retardant characteristics.

Experiments with alumina trihydrate, or other flame-retardant fillers that evolve water on heating, in conventional compositions for one-stage Sioplas crosslinking based on ethylene polymers (copolymers with ethyl acetate, ethyl acrylate, propylene etc. and some homopolymers) have failed, partially through unacceptable premature crosslinking (as might have been expected because of the risk of the filler evolving water at grafting temperature) and partially through the production of a porous product that was wholly unacceptable for electrical applications; and experts have drawn the conclusion that water-evolving fillers are incompatible with one-stage Sioplas chemistry (see, e.g. Mod. Plastics Int., December 1984 pp 38-40).

We have now discovered that this conclusion of the prior art is unjustified and that satisfactory results can be obtained simply by making an unconventional choice of initiator for the crosslinking reaction.

In accordance with the invention, a halogen-free crosslinkable polymer composition for extrusion comprises:

at least one flame-retardant filler of the class that evolve substantial amounts of bound water on heating at temperatures above a value T_d which value lies in the range 120-250°C;

a compatible ethylene polymer base in which the filler is dispersed;

the ratio of filler to polymer being in the range from 3:1 to 1:2 by weight;

a hydrolysable unsaturated silane;

and a free-radical grafting initiator having a half-life of less than 10 minutes at a temperature 25°C

below T_d as determined by Differential Thermal Analysis using chlorobenzene as solvent; see for instance "Noury Initiators", Delivery Programme of the Thermoplastics Industry, a current publication of Akzo Chemie U.K. Limited.

A silanol condensation catalyst will also be required to obtain crosslinking in an acceptably short time.

The most readily available fillers of the class defined are gypsum ($T_d=128^\circ\text{C}$), alumina trihydrate (minimum $T_d=170^\circ\text{C}$), and magnesium hydroxide (minimum $T_d=250^\circ\text{C}$.) Gypsum is the least satisfactory of the three as there are practical difficulties with most polymers if T_d is below 150°C , and magnesium hydroxide is much preferred as its higher T_d value not only gives a much wider choice of initiators but also allows a higher extrusion rate because of the higher permissible processing temperature. Fillers coated to enhance compatibility with the polymer are preferred, suitable coating materials including oleates and other fatty acid soaps, silanes, titanates, siloxanes, and carboxylated butadiene polymers (for example those described in British Patent No. 1603300) and other low-molecular weight polymers and oligomers containing carboxyl groups. Particularly suitable magnesium hydroxide fillers are commercially available from Kyowa Chemical Industry Company Limited (Japan) under the trade mark 'Kisuma'. If more than one water-evolving filler is present, the relevant T_d will, of course, be the lower or lowest.

The polymer may be any of the well-known types that is capable of accepting the quantity of filler needed to meet flame retardance requirements without unacceptable loss of physical and/or electrical properties; ethylene-vinyl acetate copolymers (EVA) (containing from about 5 to about 70 mole % of vinyl acetate) are most preferred, but ethylene/ethyl acrylate, ethylene/methyl acrylate, ethylene butyl acrylate and rubbery and non-rubbery ethylene/propylene

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copolymers (and terpolymers) are also suitable), as are some ethylene homopolymers, such as the one of low molecular weight sold by Union Carbide Group, under the Trade Mark UCAR as UCAR FLX, and butyl grafted

- 5 polyethylenes such as that sold by ASEA Kabel AB under the designation ET Polymer. Mixtures of polymers can be used.

Filler to polymer ratios are subject to limits of compatibility and optimum values will depend upon the
10 balance of flame retardance to physical and electrical properties required.

The most usual silane is vinyl trimethoxy silane (VTMOS), but any of the silanes used in conventional Sioplas processes can be used. A list is included in
15 the specification of U.K. Patent No. 1286460. Amounts required are broadly as for the conventional process, based upon the active polymer content of the mixture.

The grafting initiator will normally be peroxide, examples of suitable commercially available peroxides
20 being as follows:

(a) for gypsum, alumina trihydrate and magnesium hydroxide

Tertiary butyl per pivalate

Tertiary amyl per pivalate

- 25 Di(3,5,5 trimethyl hexanoyl) peroxide

Bis (2 methyl benzoyl) peroxide

Di normal octanoyl peroxide

Di - decanoyl peroxide

Dilauroyl peroxide

- 30 (b) for both alumina trihydrate and magnesium hydroxide (but not for gypsum):

Tertiary butyl per 2-ethyl hexanoate (TBPEH).

Tertiary butyl per isobutyrate

Tertiary butyl peroxy diethyl acetate

- 35 Dibenzoyl peroxide

1,1 Di-tertiary butyl peroxy - 3,3,5-trimethyl cyclohexane

Tertiary butyl peroxy 3,5,5, trimethyl hexanoate

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Tertiary butyl peroxy isopropyl carbonate

Tertiary butyl peracetate

Tertiary butyl perbenzoate

1,1 Bis (tertiary butyl peroxy) cyclohexane

5 2,2 Bis (tertiary butyl peroxy) butane.

Normal butyl 4,4 bis (tertiary butyl peroxy) valerate
and (c) for magnesium hydroxide (but not for alumina
trihydrate or gypsum):

Dicumyl peroxide

10 2,5-Dimethyl 2,5-di (tertiary butylperoxy) hexane

1,4-Di (tertiary butylperoxy iso propyl) benzene

Tertiary butyl cumyl peroxide

Di-tertiary butyl peroxide

15 Quantities of grafting initiator can be
determined by trial in the usual way.

Dibutyl tin dilaurate (DBTDL) (at a level of the
order of 0.01%) is the only silanol condensation
catalyst in regular use for Sioplas crosslinking and is
preferred; many alternatives are listed in the
20 specification of U.K. Patent No. 1286460.

The compositions may also include conventional
Sioplas-compatible antioxidants and other stabilisers,
processing aids, lubricants, pigments and usually minor
amounts of other fillers such as magnesium carbonate,
25 calcium carbonate, double carbonates of magnesium and
calcium (such as dolomite), antimony trioxide, antimony
pentoxide and zinc borate.

Preferably the polymer and filler are
pre-blended and dried prior to the addition of the other
30 ingredients.

In the following examples, all parts are by
weight unless otherwise indicated.

Example 1

35 49.7 Parts of the ethylene-vinyl acetate
copolymer (28 weight % vinyl acetate) sold under the
trademark Evatane and the grade designation 28-05 was
melted and homogenised on a two roll mill at 80-90°C and
blended on the mill with 49.8 parts of the magnesium

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hydroxide filler sold under the trademark Kisuma and the grade designation 5B (believed to be oleate coated and of the kind described and claimed in U.K. Patent No.1514081) and 0.5 parts of the antioxidant sold under the trademark Flectol as Flectol pastilles.

The blend was dried for at least 16 hours at 55°C using a dehumidified hot air dryer (sold under the designation Drymaster). To this dried base mix were added 0.9 parts VT MOS, 0.45 parts TBPEH and 0.01 parts DBTDL and the mixture was extruded in a 38mm 20D laboratory extruder with a screw of nominal compression ratio 2:1 operating at a uniform temperature of 130°C to give an insulating covering free of porosity with a radial thickness of 0.75mm on a round copper wire 1.2mm in diameter at a line speed of 1.8m/min. Curing was in water at 70°C for 24 hours.

The insulation had a tensile strength of 12.7 MPa, elongation at break of 172% and in a hot set test at 2 bar and 200°C showed an elongation of 15% and a set of -5%. Its volume resistivity (at 75°C and 600 V d.c.) was higher than $10^{10} \Omega m$ after 30 weeks immersion in water at that temperature. (Two samples were tested; one had unchanged volume resistivity after 62 weeks; the other had fallen to $8 \times 10^9 \Omega m$).

Example 2

Substantially the same procedure was followed as in Example 1 but using:

- (a) as the base mix 37 parts of Evatane 28-05, 5 parts of another EVA sold by Allied Chemical Company under the designation AC400A (to improve extrusion characteristics) and 57.5 parts of Kisuma 5A (similar to Kisuma 5B but believed to be stearate coated) and 0.5 parts of Flectol pastilles; and
- (b) as curative system 0.65 parts VT MOS, 0.25 parts TBPEH, and 0.01 parts DBTDL.
- The line speed in this case was 2.6 mm/min.

The insulation had a tensile strength of 11.9 MPa, elongation at break of 145% and in the hot set test

showed an elongation of about 40% and sets of -2.5 and 0 on two samples. Its volume resistivity after 37 weeks under the same conditions as in Example 1 was better than $10^{10} \Omega m$.

5 Example 3

Substantially the same procedure was followed as in Example 1 but using as the base mix 40.5 parts Evatane 28-05, 5 parts of AC400A and 54 parts of the hydrated alumina sole under the trademark Hydral and the
10 grade number 710. The line speed was 2m/min.

The insulation had a tensile strength of 14.2 MPa, elongation at break of 199% and in the hot set test showed an elongation of about 20% and a set of -3%. Its volume resistivity (at 75°C and 600 V d.c.) was
15 higher than $5 \times 10^8 \Omega m$ after 45 weeks immersion in water at that temperature.

Examples 4-36

The procedure of example 3 was followed with a variety of base mixes (all including approximately 0.5
20 parts Flectol pastilles, not listed in the tables) with the results indicated below. (Line speed and radial thickness varied somewhat). Ingredients used in these examples and not previously referred to are as follows:

25	Fillers: Marinco H:	Uncoated magnesium hydroxide from Merck & Co. Inc. U.S.A. (Marinco is a trademark).
	Kisuma 5E:	Another coated magnesium hydroxide from Kyowa Chemical Industry Co. Ltd. Japan.
30	DC:	Magnesium hydroxide, received uncoated from Morton Thiokol Inc. U.S.A. and coated with 1.6% Y9774.
35	(RTM) Lycal/96HSE and PDM/PH10/200	Uncoated magnesium hydroxides respectively from Steetley Magnesia Division U.K. and Pennine Darlington Magnesia Limited, U.K.

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(RTM)

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Ultracarb/U5:

A mixed filler of magnesium hydroxy carbonate and calcium magnesium carbonate from Microfine Minerals Limited, U.K.

5

Ultracarb M5:

a version of Ultracarb U5 with a polymeric coating (The T_d 's of Ultracarb fillers have not yet been accurately measured)

10

Ethylene

polymers: DPDM 6182

Ethylene/ethyl acrylate copolymer from BP Chemicals Limited, U.K.

15

DEFD1225

A polyethylene of very low density from Union Carbide Corp., U.S.A.

Other

ingredients:

AC6A: Polyethylene, from Allied Chemicals, U.S.A.

20

Omya EXH1: Calcium carbonate from Croxton and Garry Limited, U.K.

A174: Gamma methacryloxypropyl trimethoxy silane from Union Carbide Corporation, U.S.A.

25

DC1107: Methyl hydrogen polysiloxane from Dow Corning Limited, U.K.

Y9774: A proprietary silane from Union Carbide Group, U.S.A.

30

Surlyn 9450: An ionomeric polymer from Du Pont, U.S.A. (Surlyn is a trademark)

In the case of precoated fillers, the quantity shown in the tables includes the weight of the coating, the percentage of which, relative to the total weight of that coated filler, is given immediately below.

35

All compositions of the Examples showed low values in the hot set test, indicative of a sufficient degree of crosslinking for typical wire and cable applications and all passed the Horizontal Specimen
5 Flame Test defined in paragraph 102 of UL 62 Standard for Flexible Cord and Fixture Wire.
The compositions of Examples 2 and 24 also passed the IEC 332 Part 1 vertical burning test, which is a very stringent test for the small wire size of these
10 samples.

All the Examples except Examples 7-12 and Example 36 met the electrical property requirements required of conventional PVC-based materials by the applicable British Standard (BS 6746:1984).

TABLE 1

Example	4	5	6	7
Base Composition				
<u>Fillers</u>				
Kisuma 5B	55	55		
Kisuma 5E			49.5	
Marinco# H				49.8
Lycal 96 HSE				
(Coating A174(%))				
(Coating Other (%))				
Hydral 710				
<u>Copolymer</u>				
Evatane 28-05	44.5	39.5	50	49.7
Evatane 18-02				
Nordel# 2722				
DPDM 6182				
<u>Additives</u>				
AC 400A		5.0		
AC6A				
Surlyn# 9450				
Tensile Strength MPa	13.1	11.5	15.6	13.6
Elongation %	121	142	152	189
Hot-Set Extension %	15	15-20	20	25-30
Set %	-3to0	-3to0	-3to0	0
Remarks	B	C	C	

Trademark

TABLE 2

Example	8	9	10	11
Base Composition: <u>Fillers</u> Kisuma 5B Kisuma 5E Marinco H Lycal 96 HSE Coating A174(%) Coating Other (%) Hydral 710 <u>Copolymer</u> Evatane 28-05 Evatane 18-02 Nordel 2722 DPDM 6182 <u>Additives</u> AC400A AC6A Surlyn 9450	50	50	50	50
Tensile Strength MPa Elongation % Hot Set-Extension % Set %	43.5 6.0	45.5 4.0	49.5 -3to0	49.5 -2.5
Remarks				

TABLE 3

Example	12	13	14	15
Base Composition:				
<u>Fillers</u>				
Kisuma 5B				
Kisuma 5E				
Marinco H				
Lycal 96 HSE	50	51	51.5	52
Coating A174(%)		(2)	(3)	(4)
Coating Other (%)				
Hydral 710				
<u>Copolymer</u>				
Evatane 28-05	37.1	48.5	48.0	47.5
Evatane 18-02				
Nordel 2722				
DPDM 6182				
<u>Additives</u>				
AC400A				
AC6A				
Surlyn 9450	12.4			
Tensile Strength MPa	10.5	13.9	14.0	13.2
Elongation %	116	148	150	144
Hot Set-Extension %	25-30	15-20	15	20
Set %	7.5	-2%to0	-5	0
Remarks				

TABLE 4

Example	16	17	18	19
Base Composition:				
<u>Fillers</u>				
Kisuma 5B				
Kisuma 5E				
Marinco H				
Lycal 96 HSE	52.5	53.5	50.2	40.8
Coating A174(%)	(5)	(7)	(2)	(2)
Coating Other (%)				
Hydral 710				
<u>Copolymer</u>				
Evatane 28-05	47.0	46.0		58.6
Evatane 18-02				
Nordel 2722			49.3	
DPDM 6182				
<u>Additives</u>				
AC400A				
AC6A				
Surlyn 9450				
Tensile Strength MPa	13.6	12.8	5.7	11.4
Elongation %	144	117	100	125
Hot Set-Extension %	10-15	15	35	20-25
Set %	-2.5	0	-3	-3to0
Remarks			D	

TABLE 5

Example	20	21	22
Base Composition:			
<u>Fillers</u>			
Kisuma 5B			
Kisuma 5E			
Marinco H			
Lycal 96 HSE	50.2	51.0	51.5
Coating A174(%)	(2)	(2)F	(3)F
Coating Other (%)			
Hydral 710			
<u>Copolymer</u>			
Evatane 28-05		49.5	48.0
Evatane 18-02			
Nordel 2722			
DPDM 6182	49.3		
<u>Additives</u>			
AC400A			
AC6A			
Surlyn 9450			
Tensile Strength MPa	13.1	13.3	13.7
Elongation %	66	132	146
Hot Set-Extension %	30	10-15	10-15
Set %	-7.5 to 10	-2.5 to 5	-2.5 to 5
Remarks		F	F

TABLE 6

Example	23	24	25	26
Base Composition:				
<u>Fillers</u>				
Kisuma 5B				
Kisuma 5E				
Marinco H				
Lycal 96 HSE	52	52.5	52.0	50.75
Coating A174(%)				
Coating Other (%)	(4)F	(4)F	(4)H	(1.5)J
Hydral 710				
<u>Copolymer</u>				
Evatane 28-05	47.5	47.0	47.5	48.75
Evatane 18-02				
Nordel 2722				
DPDM 6182				
<u>Additives</u>				
AC400A				
AC6A				
Surlyn 9450				
Tensile Strength MPa	13.7	13.3	14.4	12.3
Elongation %	140	146	124	87
Hot Set-Extension %	15±20	15	15	15-20
Set %	-2.5to -5	±2.5to ±5	±2.5to ±5	±5 to 0
Remarks	F	F,G	H	J

TABLE 7

Example	27	28	29	30
Base Composition:				
<u>Fillers</u>				
Kisuma 5B				57.5
Kisuma 5E				
Marinco H				
Lycal 96 HSE		30.0	20.0	
Coating A174(%)		(2)	(2)	
Coating Other (%)				
Hydral 710	54.0	25.0	40.0	
<u>Polymer</u>				
Evatane 28-05	40.5	39.5	34.5	32.8
Evatane 18-02				
Nordel 2722				
DPDM 6182				
DEFD 1225				4.2
<u>Additives</u>				
AC400A	5.0	5.0	5.0	5.0
AC6A				
Surlyn 9450				
Tensile Strength MPa	13.3	11.7	12.3	10.4
Elongation %	196	119	442	173
Hot Set-Extension %	25-30	10	65-70	65
Set %	±3	0	±5	±2.5
Remarks				K

TABLE 8

Example	31	32	33
Base Composition:			
<u>Fillers</u>			
Kisuma 5B		28.3	28.2
DC	54.4		
Ultracarb M5		28.3	28.2
<u>Polymer</u>			
Evatane 28-05	40.1	37.9	38.1
DEFD 1225			
<u>Additives</u>			
AC400A	5.0	5.0	5.0
Tensile Strength MPa	8.2	9.4	10.4
Elongation %	386	224	193
Hot Set+Extension % Set %	25+30 0	30 +2.5	10+15 +2.5/7.5
Remarks	K	K	K

TABLE 9

Example	34	35	36
Base Composition: <u>Fillers</u> Kisuma 5B DC PDM/PH10/200 Ultracarb M5 <u>Polymer</u> Evatane 28-05 DEFD 1225 <u>Additives</u> AC400A	57.5	56	53.8
Tensile Strength MPa Elongation % Hot Set-Extension % Set %	32.0 10 30 -10/-12.5	38.5 60 2.5	40.7 50-55 2.5
Remarks	K	K	K

REMARKS TO TABLES

- B VT MOS and TOPEH reduced to 0.7 parts and 0.35 parts respectively.
- C VT MOS and TOPEH reduced to 0.8 parts and 0.4 parts respectively.
- 5 D Peroxide content increased to 0.75 parts.
- F Coating is silane Y9774.
- G Passed vertical burning test.
- H Coating is DC 1107.
- J Coating is magnesium stearate
- 10 K The curative systems used in these Examples were as follows (in weight %)

	Example	VT MOS	TBPEH	DBTDL
	30	0.65	0.20	0.01
15	31	0.72	0.33	0.01
	32	0.75	0.35	0.01
	33	0.75	0.35	0.01
	34	0.65	0.175	0.01
	35	0.80	0.40	0.01
20	36	0.77	0.36	0.01

Example 37

In a trial on a commercial extruder, a composition comprising 37 parts Evatane 28-05, 57.5 parts Kisuma 5B, 5 parts AC400A, 0.05 parts Flectol pastilles, 0.65 parts VT MOS, 0.30 parts TBPEH and 0.01 parts DBTDL was successfully extruded at line speeds up to 550 m/min and at temperatures up to 190°C. Samples extruded at 130°C had a tensile strength of 10.7 MPa, Elongation at break of 182% and in the Hot Set test recorded Extensions of 25 to 30% and Sets of -2.5% to 0. These samples also passed the IEC 332 vertical burning test.



CLAIMS

1. A halogen-free cross-linkable polymer composition for extrusion comprising:
at least one filler;
5 a compatible ethylene polymer base in which the filler is dispersed;
a hydrolysable unsaturated silane;
and a free-radical grafting initiator;
characterised in that the filler is a flame-retardant
10 filler of the class that evolve substantial amounts of bound water on heating at temperatures above a value T_d which value lies in the range 120-250°C; the ratio of filler to polymer is in the range from 3:1 to 1:2 by weight; and the initiator has a half-life of less than
15 10 minutes at a temperature 25°C below T_d as determined by Differential Thermal Analysis using chlorobenzene as solvent.
2. A composition as claimed in Claim 1 wherein the flame-retardant filler is magnesium hydroxide.
- 20 3. A composition as claimed in Claim 1 or Claim 2 in which the initiator is tertiary butyl per 2-ethyl hexanoate.
4. A composition as claimed in Claim 1 or Claim 2 in which the said filler is gypsum, alumina trihydrate
25 or magnesium hydroxide and the grafting initiator is selected from:
Tertiary butyl per pivalate
Tertiary amyl per pivalate
Di(3,5,5 trimethyl hexanoyl) peroxide
30 Bis (2 methyl benzoyl) peroxide
Di normal octanoyl peroxide
Di - decanoyl peroxide
Dilauroyl peroxide
5. A composition as claimed in Claim 1 or Claim 2
35 in which the said filler is alumina trihydrate or magnesium hydroxide and the grafting initiator is selected from
Tertiary butyl per 2-ethyl hexanoate (TBPEH).



Tertiary butyl per isobutyrate

Tertiary butyl peroxy diethyl acetate

Dibenzoyl peroxide

5 1,1 Di-tertiary butyl peroxy - 3,3,5-trimethyl
cyclohexane

Tertiary butyl peroxy 3,5,5, trimethyl hexanoate

Tertiary butyl peroxy isopropyl carbonate

Tertiary butyl peracetate

Tertiary butyl perbenzoate.

10 1,1 Bis (tertiary butyl peroxy) cyclohexane

Normal butyl 4,4 bis (tertiary butyl peroxy) valerate

2,2 Bis (tertiary butyl peroxy) butane.

6. A composition as claimed in Claim 1 or Claim 2
in which the said filler is magnesium hydroxide and the
15 grafting initiator is selected from:

Dicumyl peroxide

2,5-Dimethyl 2,5-di (tertiary butylperoxy) hexane

1,4-Di (tertiary butylperoxy iso propyl) benzene

Tertiary butyl cumyl peroxide

20 Di-tertiary butyl peroxide.

7. A composition as claimed in any of the preceding
claims including also a silanol condensation catalyst.

8. A halogen-free crosslinkable polymer composition
for extrusion substantially as described with reference
25 to any one of the numbered examples.

9. An electric cable having dielectric and/or
sheath made of a composition claimed in any one of the
preceding claims in its crosslinked form.