



(43) International Publication Date
26 July 2012 (26.07.2012)

(10) International Publication Number
WO 2012/099478 A1

(51) International Patent Classification:

C09K 21/14 (2006.01) *C08K 13/02* (2006.01)
C08J 3/22 (2006.01) *C08L 23/12* (2006.01)
C08K 3/32 (2006.01) *C09K 21/04* (2006.01)
C08K 5/13 (2006.01)

(21) International Application Number:

PCT/NZ2012/000002

(22) International Filing Date:

16 January 2012 (16.01.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

590534 17 January 2011 (17.01.2011) NZ

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FIRE RETARDANT POLYPROPYLENE

(57) Abstract: A fire retardant material comprising preferably at least 60% polypropylene having a flexural modulus of 2.8 GPa or above and a fire retardancy rating of UL-94 V-1 or better. The fire retardant material is preferably halogen and glass-fibre free. It may contain a fire retardant agent (e.g. a polymeric APP -crystal phase II type fire retardant) and a filler. Also methods for producing such a fire retardant material.



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FIRE RETARDANT POLYPROPYLENE

TECHNICAL FIELD

The invention relates to polymers, and in particular polypropylene polymers which have both high fire resistance and a high degree of mechanical strength.

BACKGROUND ART

Polymeric materials are well known and widely used because of their high versatility. Polypropylene is a particularly desirable polymer because of its low cost compared to engineered plastics and because it is highly amenable to recycling. One particular drawback of polymers is that because they are hydrocarbon-based, they are generally not fire resistant.

It is known to make polymeric materials more fire resistant or fire retardant by the use of additives. However, the use of additives can compromise other qualities of the polymer, such as for example the mechanical strength.

Some additives provide an appropriate balance between fire resistance and mechanical strength, however many of these additives are undesirable from point of view of cost or chemical toxicity. For instance, the most efficient flame retardant additives currently available are brominated materials, such as the decabromodiphenyl ethers (DecaBDEs). DecaBDEs have been used as flame retardants in electronics, wire and cable insulation, textiles, automobiles and aircraft, amongst others. Although DecaBDEs are very good at minimising the spread of flame, they are not recyclable and in addition have highly toxic and carcinogenic degradation products. DecaBDEs have been banned in many places including Europe and the US, where it is expected that they will be phased out completely by the end of 2013.

Other additives used to combat the spread of fire in polymeric materials include metal hydroxides such as alumina trihydrate (ATH) and $\text{Mg}(\text{OH})_2$ or materials such as halloysite nanotubes (HNT). These have been used to impart fire retardancy properties to polymeric materials, however they require a very high dose, usually greater than 50% w/w, in order to achieve a high (UL-94 V-0) fire rating. They have a low level of compatibility with the polymer matrix and the resultant material typically has a very poor appearance as well as low gloss and scratch resistance.

It is an object of the present invention to provide a fire retardant material including polypropylene which has both high fire retardancy rating and a good level of flexural and tensile modulus.

According to a first aspect the invention provides a fire retardant material comprising polypropylene having a flexural modulus of 2.8 GPa or above and a fire retardancy rating of UL-94 V-1 or better.

Alternatively, the fire retardant material may have a flexural modulus of 3 GPa or above and a fire retardancy rating of UL-94 V-1 or better.

Alternatively, the fire retardant material may have a flexural modulus of 2.8 GPa or above and a fire retardancy rating of UL-94 V-0.

- 5 Preferably the fire retardant material has a flexural modulus of 3 GPa or above and a fire retardancy rating of UL-94 V-0.

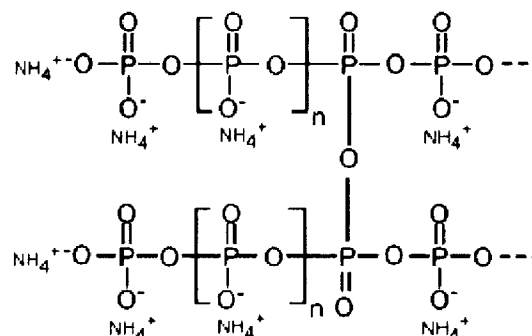
The fire retardant material is preferably halogen-free and/or free from glass-fibres.

Preferably, the fire retardant material comprises at least 60% polypropylene, more preferably 60-80% polypropylene and most preferably at least about 70% polypropylene.

- 10 In the present invention, any form of polypropylene can be used. Isotactic or syndiotactic polypropylene or any mixture thereof, or of any degree of crystallinity can be used. The polypropylene may be initially in pelletised form, or it may be all or partially in powdered form. The fire retardant material further includes a fire retardant, preferably in an amount of 10-35%, more preferably in an amount of 15-25% and most preferably in an amount of about 20%.

- 15 Preferably the fire retardant is an ammonium polyphosphate (APP), more preferably a polymeric APP-crystal phase II type fire retardant.

The preferred fire retardant of the present invention is a polymeric APP-crystal phase II type fire retardant. APP fire retardants are based around ammonium polyphosphates of the following structure.



20

The APP II structure is cross-linked or branched, with "n" being typically higher than 1000. Polymeric APP-crystal phase II type fire retardants have high stability and low water solubility.

- Most preferably the fire retardant agent is Budit[®]3167. Budit[®]3167 is a commercially available fire retardant. Budit[®]3167 is of low extractability in water compared to other traditional fire retardants and is thus considered to be an environmentally friendly halogen-free alternative. Budit[®]3167 contains all active components necessary for intumescence: catalyst, carbonific and spumescent agent. Budit[®]3167 is also regarded as a highly desirable smoke retardant from the point of view of its low smoke density and low smoke toxicity upon burning.
- 30 Budit[®]3167 satisfies the stringent requirements for use in aircraft interiors, with the limits of

hydrogen cyanide, carbon monoxide, nitrous gases, sulphur dioxide, hydrogen fluoride and hydrogen chloride all falling well below the limits specified by the ABD (Airbus Directive) 0031 test.

The fire retardant material further includes a filler, preferably talc. The talc is preferably
5 present in an amount of 5-20 % wt/wt, more preferably 8-12 % wt/wt and most preferably in an amount of about 10% wt/wt to impart higher stiffness to the fire retardant material.

Talc is a hydrated magnesium silicate whose chemical formula is $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ with flattened tabular crystals with a hexagonal cross-section. Talc is present as a chemically inert filler, a reinforcing agent, a heat sink and a nucleating agent to provide improvements in the
10 crystallisation temperature (i.e. raising of the freezing point of the polypropylene) as measured by differential scanning calorimetry (DSC). An improved crystallisation temperature with a consequently lower heat flow translates into a high heat deflection temperature, greater control of warpage, shrinking and other dimensional elements and may further provide improvements in injection moulding cycle times to enable parts to be removed more quickly from the mould.

15 It is known that talc consists of a layer or sheet of brucite ($\text{Mg}(\text{OH})_2$) sandwiched between two sheets of silica (SiO_2). The layers of $\text{Mg}(\text{OH})_2$ are bonded by weak van der Waals' forces and hence talc can readily undergo exfoliation and cleavage to form high aspect ratio particles, which can significantly improve the stiffness of polymers. Milling is a useful way to achieve high aspect ratio particles.

20 The fire retardant may further include an antioxidant, for example, Irganox[®] 1010. The antioxidant may be present in an amount up to 3% wt/wt, more preferably in an amount up to 1% wt/wt.

According to a second aspect the invention provides a fire retardant material comprising:
polypropylene 60-80%;
25 fire retardant 10-30%; and
talc 5-20%

According to a third aspect the invention provides a fire retardant material comprising:
polypropylene 60-70%;
fire retardant 20%; and
30 talc 5-20%

According to a fourth aspect the invention provides a fire retardant material comprising:
polypropylene 60-80%;
a polymeric APP-crystal phase II type fire retardant 10-30%; and
talc 5-20%

35 According to a fifth aspect the invention provides a fire retardant material comprising:
polypropylene 60-70%;

a polymeric APP-crystal phase II type fire retardant 20%; and
talc 5-20%

The present applicants have surprisingly found that a polypropylene having a specific combination of fire retardants and prepared in a specific manner displays suitable levels of
5 mechanical strength and fire retardancy.

According to a sixth aspect the invention provides a method of forming a fire retardant material comprising:

forming a first blend of polypropylene and filler;
forming a second blend of polypropylene and fire retardant
10 combining the first and second blends; and optionally adding polypropylene

According to a seventh aspect the invention provides a method of forming a fire retardant material comprising:

forming a first blend of polypropylene and filler;
combining the first blend with a fire retardant ; and optionally adding polypropylene
15 Preferably, total polypropylene is 60-80%, more preferably at least 60% and most preferably at least 70%.

Preferably total fire retardant is 10-35%, more preferably 15-25% and most preferably 20%

Preferably, the fire retardant is an ammonium polyphosphate, more preferably a polymeric
20 APP-crystal phase II type fire retardant, most preferably the fire retardant agent is Budit[®]3167.

Preferably the filler is talc, which is preferably present in an amount of 5-20% wt/wt, more preferably 8-12 % wt/wt and most preferably about 10 % wt/wt.

The method may also further include the step of adding an antioxidant, such as Irganox[®]1010. The antioxidant may be present in an amount up to 3% wt/wt, or more preferably
25 in an amount up to 1% wt/wt.

The method of combining the chemical species in the present invention is of considerable significance. The method of mixing requires that the talc is added in a "masterbatch" form. That means the talc is pre-mixed with the polypropylene prior to the addition of the fire retardant, or a pre-prepared commercial blend of polypropylene and talc is used. Without wishing to be bound
30 by theory, it is believed mixing in this order minimises interference between the talc and the fire retardant. It is believed fire retardants such as Budit[®]3167 can become trapped or bonded to the magnesium hydroxide in between the silica plates in talc. By preparing the masterbatch of the polypropylene with the talc, this subsequent deactivation of the fire retardant is avoided.

Figure 1 shows the X-ray powder diffraction pattern of talc and talc in a number of PP
35 blends with Budit 3167 of the present invention, illustrating exfoliation of talc in the PP Budit 3167 blends.

Scanning electron microscopy (SEM) studies indicate the commercially available heat stabilized crystal phase II APP fire retardant additives disappear from the PP matrix in the presence of traditional fire retardant additives like $\text{Mg}(\text{OH})_2$ indicating a possible reaction with APP and diminishing the effectiveness of the fire retardant additive. Similar effects were observed in the presence of nanotubes such as halloysite. However the presence of an inert filler like talc resulted in no interference to the effectiveness of the fire retardant additive. Figure 2 shows a series of SEM images which illustrate the dispersion of the fire retardant in the polypropylene matrix, the exfoliation of talc and, in some cases, the disappearance of the fire retardant in the presence of unsuitable fillers.

DESCRIPTION OF THE FIGURES

Figure 1 shows the X-ray powder diffraction pattern of talc and talc in a number of PP blends with Budit 3167 of the present invention, illustrating exfoliation of talc in the PP Budit 3167 blends.

Figure 2 shows a series of SEM images which illustrate the dispersion of the fire retardant in the polypropylene matrix, the exfoliation of talc and, in some cases, the disappearance of the fire retardant in the presence of unsuitable fillers.

Figures 2a - 2j show FRB-B reacting with $\text{Mg}(\text{OH})_2$ and disappearing from the surface. Specifically:-

2a FR 79-30%FR-B additive - 5000 magnification.

2b FR 91-12:20:12 HNT:FR-B: $\text{Mg}(\text{OH})_2$ -5000 magnification.

2c FR 79 - 30% FR- B additive - 10000 magnification.

2d FR 91-12:20: 12 HNT:FR-B: $\text{Mg}(\text{OH})_2$ -10000 magnification.

2e FRPP 91-HNT:FR-B: $\text{Mg}(\text{OH})_2$ 12:20:12 50,000 magnification.

2f FRPP 79 - FR-B 30 25000 magnification.

2g FRPP X(s)-HNT: $\text{Mg}(\text{OH})_2$ 20:20 5000 magnification.

2h FRPP 71 (s)–HNT:FR-B:Mg(OH)₂4:12:4 5000 magnification.

2i FRPP X(s)–HNT:MgH 20:20 10000 magnification .

5

2j FRPP 71(s) –HNT:FR-B: Mg(OH)₂ 4:12:4 10000 magnification.

Figures 2k - 2m show NHT disperses well in the PP matrix. Specifically:-

10 2k NN – 30% HNT 5,000 magnification.

2l NN 30% HNT mag 10,000.

2m NN – 30% HNT 25,000 magnification.

15

Figures 2n - 2w show FR 104-1 – 20% FR-B + 10% Talc – Show the distribution of platy talc and FR-B – Pass UL-94-V-0 test.

Figures 2x - 2y show FR 86 – 20% FR-B + 10% Mg(OH)₂ FR-B disappears due to a reaction
20 with Mg(OH)₂ Fails the UL-94-V-0 FR test.

Figures 2z - 2cc show FR 87 – 20% FR-B + 10% HNT –Fails the UL-94-V-0 FR test.

Figure 3 shows Variation of Flexural Modulus with % FR additive and comparison with two
25 commercial grades of FRPP.

Figure 4 shows Variation of Tensile Strength with % FR additive and comparison with two commercial grades FRPP. Note- FR sample are based on Tensile tests done with flexural bars for comparison .

30

Figure 5 shows Variation of flexural modulus in FR-B:Talc blends.

Figures 6 and 7 show injection speed, fill time, pressure and viscosity relationships for the fire retardant polypropylene of the present invention and a reinforced polypropylene of similar
35 mechanical strength, respectively.

PREPARATION AND PRODUCT EXAMPLE 1

The most preferred blend of the present invention involves the initial formation of a first master batch of 59% polypropylene (HA 5009), 40% fire retardant (Budit[®] 3167), and 1% Irganox[®] 1010 as antioxidant (known as 40% FR-B Masterbatch FR 113).

40% FR-B Masterbatch (FR 113)	
Component	% wt/wt
HA 5009 (Polypropylene)	59
Budit [®] 3167 (FR B)	40
Irganox [®] 1010 (Antioxidant)	1

A second masterbatch of 60% talc-filled polypropylene is also prepared.

Second Masterbatch	
Component	% wt/wt
BI 750 (Polypropylene)	40
Plustalc N625 (Talc)	60

Alternatively, a 60% talc filled polypropylene masterbatch available from a commercial source can be used as the second masterbatch. This has the following composition:

60% talc filled masterbatch	
Material	%wt/wt
Polypropylene BI 750	28
Talc (Plustalc N625)	60
TiO ₂	6
Carbon fibre	0.5
Process aid	4.0
Calcium stearate	0.5
Anti-static agent	0.4
Ultra marine blue	0.1
Irganox [®] 1010	0.5
	100

The first masterbatch and second masterbatch are combined, and extra polypropylene
 5 (HA5009) is subsequently added to adjust the fire retardant level to about 20% and the talc level to about 10%.

FR 113-1		
Batch and Amount	Material	%wt/wt
40% FR-B Masterbatch (FR 113) at 49.9% of total	HA 5009 (Polypropylene)	29.44%
	Budit [®] 3167 (FR B)	19.96%
	Irganox [®] 1010 (Antioxidant)	0.5%
Second Masterbatch at 16.22% of total	BI 750 (Polypropylene)	6.49%
	Plustalc N625 (Talc)	9.73%
	Irganox [®] 1010	0.19%
Polypropylene at 33.68% of total	HA 5009 (Polypropylene)	33.68%
		99.99%

Or, combining ultimate amounts:

FR 113-1	
Material	%wt/wt
HA 5009 + BI 750 (Polypropylene)	69.61%
Budit [®] 3167 (FR B)	19.96%
Irganox [®] 1010 (Antioxidant)	0.69%
Plustalc N625 (Talc)	9.73%
	99.99%

PREPARATION AND PRODUCT EXAMPLE 2

- Alternative fire retardant polypropylenes were prepared as follows. These were FR104-1, 5 FR104-2 and FR104-3. A first masterbatch was prepared that contained polypropylene, fire retardant and Irganox 1010[®]:

40% FR-B Masterbatch based on BI 452 (FR 100)	
Material	%wt/wt
PP BI 452	59
Budit [®] 3167	40
Irganox [®] 1010	1

A second Masterbatch containing polypropylene and talc was also prepared.

Second Masterbatch	
Component	% wt/wt
BI 750 (Polypropylene)	40
Plustalc N625 (Talc)	60

The first masterbatch and second masterbatch are combined in varying amounts to control the total amounts of talc and fire retardant. Extra polypropylene (BI452) is added as required to adjust the fire retardant level to about 20% and the talc level to about 10%.

Comparative Examples				
Batch and Amount	Material	FR 104-1 %wt/wt	FR 104-1 EX %wt/wt	FR 104-2 %wt/wt
40% FR-B Masterbatch (FR 100) At 50%	Polypropylene BI 452 59%	29.5	29.5	29.5
	Budit [®] 3167 (FR B) 40%	20	20	20
	Irganox [®] 1010 (Antioxidant) 1%	0.5	0.5	0.5
Second Masterbatch at 16.25 or 33.25%	BI 750 (polypropylene) 40%	6.5	6.5	13.3
	Plustalc N625 (Talc) 60%	9.75	9.75	19.95
Polypropylene BI 452 at 33.275% or 16.75%		33.75	33.75	16.75
		100	100	100

Or, combining ultimate amounts:

	FR 104-1	FR 104-1 EX	FR 104-2
Material	%wt/wt	%wt/wt	%wt/wt
BI 750+ BI 452 (Polypropylene)	69.75	69.75	59.55
Budit [®] 3167 (FR B)	20	20	20
Irganox [®] 1010 (Antioxidant)	0.5	0.5	0.5
Plustalc N625 (Talc)	9.75	9.75	19.95
	100.00	100.00	100.00

- 5 It will be appreciated that different masterbatches can be used to achieve the same final polypropylene, fire retardant, talc and antioxidant ratios in the final product. The important step required is to ensure that the talc is blended with the polypropylene prior to the fire retardant to ensure no deleterious interactions between the talc and the fire retardant.

PHYSICAL TESTS

A number of tests were then run to determine the physical and fire retardancy properties of the polypropylenes of the present invention. These were compared against non fire retardant polypropylenes and also against some comparative examples prepared by simple mixing rather than the “masterbatch” process of the present invention, as well as against formulations prepared solely for strength or fire retardancy, but not both. The following comparative examples are referred to throughout the text:

Comparative examples			
Material	FR 93 %wt/wt	FR 98 %wt/wt	FR 103 %wt/wt
Polypropylene BI 452	79.5	72.37	
Budit [®] 3167	19.5	17.72	20
Irganox [®] 1010	1.0		
Talc (Plustalc N625)		5.4	30
Polypropylene		3.6	50

The properties of the preferred composition of the present invention are shown in the table below. The flexural modulus is a simple three point test, with an elongate section of the test material held at either end and pressed downwardly in the middle, whilst observing the force required to cause a specified deviation.

	Poly-propylenes		Preferred fire retardant polypropylenes of the present invention		Comparative fire retardant polypropylenes					
Property	HA 5009	PP BI 452	FR 113-1	FR 104-2	FR 100	FR 104-1	FR104 -1EX	FR93	FR 98	FR 103
Flexural modulus GPa	2.15	1.93	3.00	2.83	2.37	2.56	2.44	2.07	2.08	3.31
Tensile modulus GPa	2.20	2.08	2.98	3.03	2.87	2.66	2.64	2.37	2.32	3.47
Tensile strength MPa	33.8	27.2	21.5	18.6	17.5	19.2	20.6	22.7	11.53	66.83
Impact strength J m ⁻¹	26.8	100	29.5	25.08	23.1	24.79		26.49	24.54	27.15

PHYSICAL AND FIRE RETARDANCY TESTS

Fire retardancy is determined according to the UL 94 (Underwriters Laboratory) test standard for flammability, summarised in the table below ([http://www.boedeker.com/bpi-](http://www.boedeker.com/bpi-ul94.htm)

5 [ul94.htm](http://www.boedeker.com/bpi-ul94.htm))

5VA Surface Burn	Burning stops within 60 seconds after five applications of five seconds each of a flame (larger than that used in Vertical Burn testing) to a test bar. Test specimens MAY NOT have a burn-through (no hole). This is the highest (most flame retardant) UL94 rating.
5VB Surface Burn	Burning stops within 60 seconds after five applications of five seconds each of a flame (larger than that used in Vertical Burn testing) to a test bar. Test specimens MAY HAVE a burn-through (a hole).
V-0 Vertical Burn	Burning stops within 10 seconds after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.
V-1 Vertical Burn	Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.
V-2 Vertical Burn	Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. Flaming drips ARE allowed.
H-B Horizontal Burn	Slow horizontal burning on a 3mm thick specimen with a burning rate is less than 3"/min or stops burning before the 5" mark. H-B rated materials are considered "self-extinguishing". This is the lowest (least flame retardant) UL94 rating.

Table 1 shows some commercially available fire retardant polypropylene materials which are UL 94 rated as V-0 and compares their physical properties. A number of general conclusions can be drawn from the data. All halogen-free commercial fire retardant polypropylenes have a lower FM (flexural modulus) than the samples of the present invention. The main drawback of halogen-free fire retardant polypropylenes is the lack of stiffness, which is <2GPa in all cases. Some halogenated products have acceptable physical properties, but of course these suffer from the drawback of producing dangerous fumes on ignition. Halogenated products could be strengthened to very high FM's, as can be seen for the glass fibre products, however, these materials were of low processability.

TABLE 1									
Product	Supplier	Halogen ated	UL-94 rating	TS /YS MPa	FM GPa	TM GPa	Density kg/m3	HDT – 1.8 MPa	Notched Impact St
Polyflam RIPP 490 *	A Schulman (Gmbh)	NO	V-0	22.0	-	1.9	1.04	58	3 kJ/m ²
Polyflam RIPP 3625 CS1–FRPP brominated	A Schulman (Gmbh)	YES	V-0	17.0	3.5	2.2	1.39	54	7.5 kJ/m ²
8010F – halogenated	Asia Enterprise (HK)	YES	V-0	17.2	1.8	2.2	1.01	81	50 J/m
FB63FNH	Samsung Total min.5T	NO	V-0	27.4	2.02		1.02	120	3.8 kgcm/cm (Izod)
FB50NHD1	Samsung Total (min.5T)	NO	V-0	28.4	2.10		1.02	128	4.0 kgcm/cm (Izod)
FB55G (20% Glass Fiber filled)	Samsung Total (min.5T)	YES	V-0	71.0	5.30		1.63	163	12.0 kgcm/cm (Izod)

IGNITION TESTS

In addition to the UL94 tests, the IEC Glow Wire Ignition (GWI) & IEC Glow Wire
5 Temperature (GWT) values are helpful in assessing the usefulness of the produces to raw
material manufacturers and end users respectively. The fire retardant polypropylenes of the
present invention passed the GWFI test and have a GWIT value of $>950^{\circ}\text{C}$.

Table 2 and Figures 3 to 5 show consolidated results for a variety of compositions,
including some comparative fire retardant polypropylenes. The labelled "FR" are the fire
10 retardant polypropylenes of the present invention. The % of fire retardant and talc presented in
all Tables are the % in the end composition.

Samples PPSCo452 (polypropylene without any added fire retardant additives), FR93 and
FR98 were not fire rated. Samples 113-1, 104-1 are the two preferred embodiments of the
present invention with a V-0 fire rating plus high stiffness.

15 Sample 103 has high stiffness but not quite V-0 fire rating. Sample 104-2 was also not
quite V-0 fire rated. Both were approximately V-1

The present inventors have found that polymer crystallinity can be improved by the
addition of an inert filler such as talc that acts as a nucleating agent for the polypropylene. This
leads to improvements in the crystallization temperature with lower heat flow that could
20 eventually result in a higher heat deflection temperature, better warpage, shrinkage and
dimensional control and improvement in injection molding cycle times, where parts can be
removed more quickly from the mold providing productivity optimization. High stiffness also
allows a reduction in wall thickness of molded products. The flexural modulus and impact
strength also improved primarily due to increase in the crystallization of the polypropylene.

TABLE 2									
Properties	Test Method	Condition	Unit	FR 13	FR 84	FR 70	FR104-1*	FR 113-1	FR 103
Physical Properties									
Melt Index * - (reads 2 units less)	ASTM D1238	2.16kg/230°C	g/10min	5.8 base MFI-12	4.9	10 base MFI-12	5.4 base MFI-8	10.8 base MFI-18	
Specific Gravity	ASTM D 792	-	g/cm ³	1.10	1.25	1.02	1.11	1.11	1.33
Mechanical & Thermal Properties									
Tensile Strength (Yield)–Flex bars	ASTM (D638)	5mm/m in	MPa	31.21	29.5	25.6	20.6	21.5	18.4
Tensile modulus	ASTM D790	5mm/m in	GPa	3.15	3.19	2.40	2.66	2.98	3.47
Flexural modulus	ASTM D790	5mm/m in		2.97	3.25	2.26	2.56	3.00	3.31
Notched Charpy impact strength	ASTM D6110	0.5J hammer	J/m	24.33	25.70	23.28	24.79	25.00	27.15
Recognition									
Flammability	UL-94/ ASTM D3801	-	-	No UL-V rating	No UL-V rating	V-0	V-0	V-0	No UL-V-rating
	IEC695-2-12-GWFI -775C	-	-	Pass	Pass	Pass	Pass	Pass	
	IEC695-2-13-GWIT-	Highest –no drip	°C			950°C	950°C	950°C	
% Total powders	-	-	%	26%	30%	20%	30%	30%	50%(20%B+30%talc)
Raw material cost –	-	-	NZ \$	\$ 3.38	\$ 6.48	\$ 6.38	\$ 5.75	\$ 5.75	\$ 5.71

The differential scanning calorimetry (DSC) data below show how the crystalline temperature and the heat flow varies with different additives.

Furthermore, these data show that the incorporation of fillers acts as a diluent or a heat sink and reduces the heat flow which could result in reduction of concentration of decomposition gases. However, too much or too little filler can diminish the action of the fire retardant in the final material.

FRPP 113-1 grade shows higher peak crystallization temperature of 129.3°C giving processing advantages such as improvements in cycle times and hence the processing productivity, low warpage, better aesthetics (haze and gloss) and high stiffness.

FR 104-1 EX is FR 104-1 that has been extruded with 40% FR-B and 60% talc masterbatches after blending. That sample did not pass the UL-94-V-0 test (it had a V-1 rating). It is believed that the further shear applied by the extruder could damage the talc structure and mask the fire retardant.

DSC information		
Sample	Peak crystallization temperature °C	Exothermic crystallization heat flow J/g
8010 – brominated from Asia	116.4 (broad peak)	54.6
RIPP-3625 brominated from A Schulman	118.5 (broad peak)	29.8 (XRF shows presence of Br + Sb ₂ O ₃ +Mg(OH) ₂)
BI 452 – high crystallinity polypropylene	126.4 (narrow peak)	105.9
BI 750 – high crystallinity polypropylene talc base	129.3	76.9
FR104-1	124.7 (narrow peak)	59.0
FR104-2-	124.9 (narrow peak)	48.8
HA 5009 – high crystallinity polypropylene	126.5	100.4
FR 113	125.8 (narrow peak)	55.8
FR113-1	129.3 (narrow peak)	72.9

WORKABILITY DATA

The workability of fire retardant materials is an important consideration. The workability was tested as follows:

Processing data –

- 5 Processing was carried out in a twin screw extruder. For example, a masterbatch of 40% Budit®3167 in polypropylene was prepared using the method below as follows: The masterbatch mixture (i.e. polypropylene pellets + fire retardant additive Budit®3167 + Antioxidant Irganox® 1010) was pre-mixed in a sealed polyethylene bag, fed into the hopper and extruded using the twin-screw feeder. The temperature profile was 185°C, 185°C, 195°C, 195°C, 200°C, 200°C, 10 220°C, 220°C and 220°C respectively, from the feeding zone to the heating zones. The die temperature was approximately 220°C. Extruded strands were pelletized.

Injection molding parameters –

- The 40% Budit®3167 based masterbatch was mixed (with 60% talc based masterbatch in 15 some formulations – FR 98, FR 104-1, 104-2, 113-1, 103) and blended with polypropylene so that the final formulation had approximately 20% Budit®3167, the optimized level of fire retardant additive tested. All formulations contain approximately 1% antioxidant to protect the possible thermal degradation of polypropylene. These blends were injection molded using the temperature profile 195-220°C, pressure 80-100 bar, mold temperature 29-30°C, injection speed 20 50 mm/s, pack pressure 40 bar, pack time 3 s, back pressure 15 bar, screw speed for plasticizer 80 rpm.

Extrusion tests

- The fire retardant polypropylene of the present invention has proven to be relatively 25 highly processable for a material having such good fire resistant properties and mechanical strength. In particular, the preferred fire retardant polypropylene of the present invention was tested for extrudability in comparison with a reinforced polypropylene of similar strength.

- Extrusion trials were conducted on the preferred fire retardant polypropylene of the present invention (FR113-1) and GC20282H, which is a glass fibre reinforced polypropylene of 30 comparable mechanical strength to FR113-1.

A rheology test was used to establish the pressures involved for a given injection speed. While this test is not comprehensive, it does provide some guidance as to how processable the material is likely to be.

RHEOLOGY DATA		
	GC20282H	FR113-1
Peak Injection Pressure (kgf)	45	33
Fill Time (s)	0.35	0.31
Peak Hold Pressure (kgf)	30	25
Back Pressure (kgf)	5	5
Injection Speed Set-point (%)	50	50
50%=72 mm/s injection speed		

Figures 6 and 7 show injection speed, fill time, pressure and viscosity relationships for the fire retardant polypropylene of the present invention and a reinforced polypropylene of similar mechanical strength, respectively. It can be seen that the fire retardant polypropylene of the present invention was processable at a much lower hydraulic pressure and was of lower viscosity, resulting in much less wear and damage to the processing equipment.

Overall the fire retardant material of the present invention was found to be fairly 'robust' in regards to processing.

CLAIMS

1. A fire retardant material comprising polypropylene having a flexural modulus of 2.8 GPa or above and a fire retardancy rating of UL-94 V-1 or better.
- 5 2. A fire retardant material comprising polypropylene having a flexural modulus of 3 GPa or above and a fire retardancy rating of UL-94 V-0.
3. A fire retardant material according to claim 1 or 2 which is halogen-free.
- 10 4. A fire retardant material according to any one of the preceding claims which is free from glass-fibres
5. A fire retardant material according to any one of the preceding claims comprising at least
15 60% polypropylene
6. A fire retardant material according to any one of the preceding claims comprising at least 70% polypropylene
- 20 7. A fire retardant material according to any one of the preceding claims comprising at least 60-80% polypropylene
8. A fire retardant material according to any one of the preceding claims including a fire
retardant.
- 25 9. A fire retardant material according to any one of the preceding claims including a fire retardant in an amount of 10-35%
10. A fire retardant material according to any one of the preceding claims including a fire
30 retardant in an amount of 15-25%
11. A fire retardant material according to any one of the preceding claims including a fire retardant in an amount of 20%
- 35 12. A fire retardant material according to any one of the preceding claims wherein the fire retardant is an ammonium polyphosphate.

13. A fire retardant material according to any one of the preceding claims wherein the fire retardant is a polymeric APP-crystal phase II type fire retardant.
- 5 14. A fire retardant material according to any one of the preceding claims wherein the fire retardant is Budit[®] 3167.
15. A fire retardant material according to any one of the preceding claims further including a filler.
- 10 16. A fire retardant material according to any one of the preceding claims wherein the filler is talc.
17. A fire retardant according to any one of the preceding claims wherein the filler is talc
15 present in an amount of 5-20% wt/wt.
18. A fire retardant material according to any one of the preceding claims wherein the filler is talc present in an amount of 5-20% wt/wt.
- 20 19. A fire retardant material according to any one of the preceding claims wherein the filler is talc present in an amount of 10% wt/wt.
20. A fire retardant material according to any one of the preceding claims further including an antioxidant.
- 25 21. A fire retardant material according to any one of the preceding claims wherein the antioxidant is Irganox[®] 1010.
22. A fire retardant material according to any one of the preceding claims wherein the
30 antioxidant is Irganox[®] 1010 present in an amount up to 3% wt/wt.
23. A fire retardant material according to any one of the preceding claims wherein the antioxidant is Irganox[®] 1010 present in an amount up to 1% wt/wt.
- 35 24. A fire retardant material comprising:
polypropylene 60-80%;

fire retardant agent 10-30%; and
talc 5-20%

25. A fire retardant material comprising:
5 polypropylene 60-70%;
fire retardant agent 20%; and
talc 5-20%
26. A fire retardant material comprising:
10 polypropylene 60-80%;
a polymeric APP-crystal phase II type fire retardant fire retardant agent 10-30%; and
talc 5-20%
27. A fire retardant material comprising:
15 polypropylene 60-70%;
a polymeric APP-crystal phase II type fire retardant fire retardant agent 20%; and
talc 5-20 %
28. A method of forming a fire retardant material comprising:
20 forming a first blend of polypropylene and filler;
forming a second blend of polypropylene and fire retardant
combining the first and second blends; and optionally adding polypropylene
29. A method of forming a fire retardant material comprising:
25 forming a first blend of polypropylene and filler;
combining the first blend with a fire retardant ; and optionally adding polypropylene
30. A method according to claim 28 or 29 wherein total polypropylene is at least 60%.
- 30 31. A method according to any one of claims 28 to 30 wherein total polypropylene is at least 70%.
32. A method according to any one of claims 28 to 31 wherein total polypropylene is 60-80%.
- 35 33. A method according to any one of claims 28 to 32 wherein total fire retardant is 10-35%

34. A method according to any one of claims 28 to 33 wherein total fire retardant is 15-25%
35. A method according to any one of claims 28 to 34 wherein total fire retardant is 20%
- 5 36. A method according to any one of claims 28 to 35 wherein the fire retardant agent is an ammonium polyphosphate.
37. A method according to any one of claims 28 to 36 wherein the fire retardant agent is a
- 10 polymeric APP-crystal phase II type fire retardant.
38. A method according to any one of claims 28 to 37 wherein the fire retardant agent is Budit[®] 3167.
- 15 39. A method according to any one of claims 28 to 38 wherein the filler is talc.
40. A method according to any one of claims 28 to 39 wherein the filler is talc present in an amount of 5-20% wt/wt.
- 20 41. A method according to any one of claims 28 to 40 wherein the filler is talc present in an amount of 5-20% wt/wt.
42. A method according to any one of claims 28 to 41 wherein the filler is talc present in an amount of 10% wt/wt.
- 25 43. A method according to any one of claims 28 to 42 further including the step of adding an antioxidant.
44. A method according to claim 43 wherein the antioxidant is Irganox[®] 1010
- 30 45. A method according to claim 43 or 44 wherein the antioxidant is present in an amount up to 3% wt/wt.
46. A method according to any one of claims 43 to 45 wherein the antioxidant is present in an
- 35 amount up to 1% wt/wt.

FIGURE 1

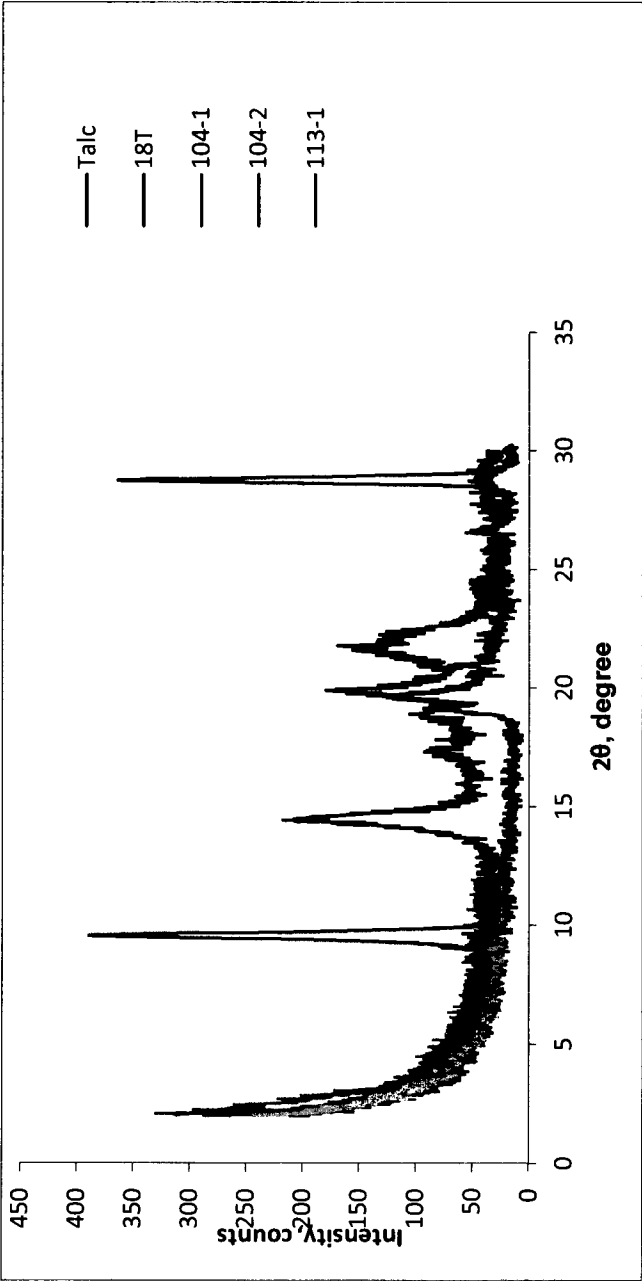
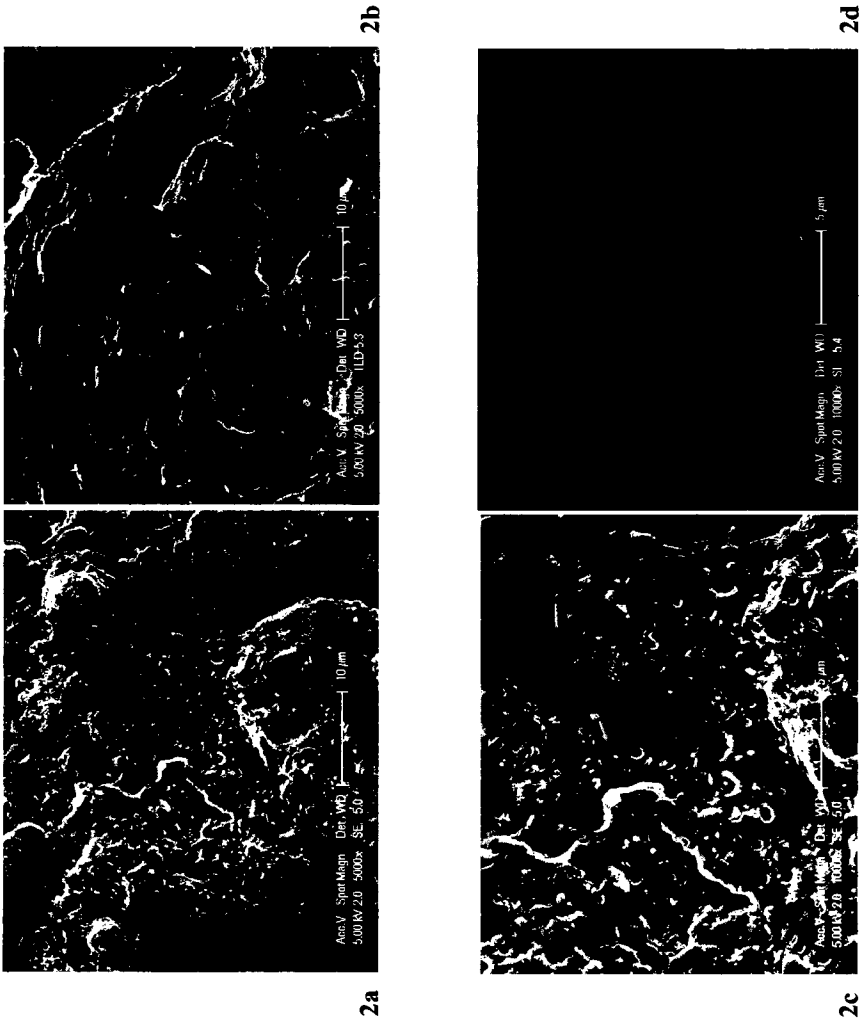
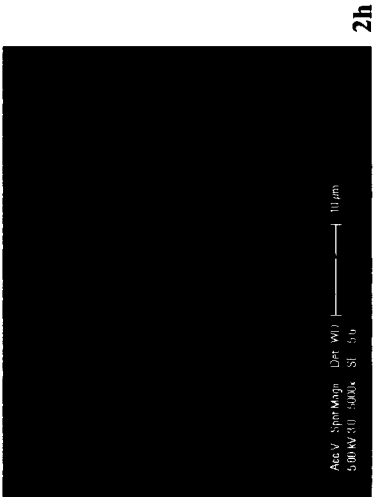
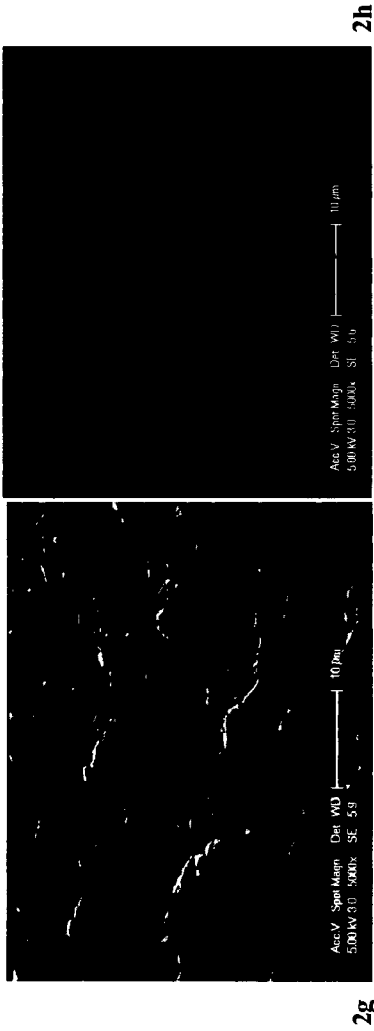
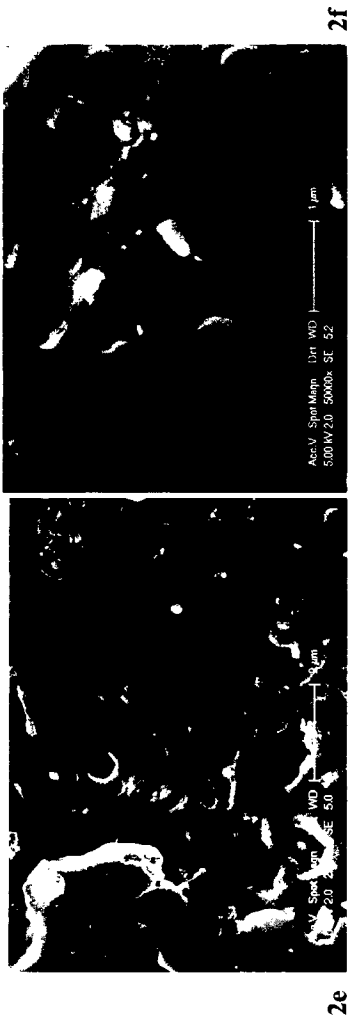
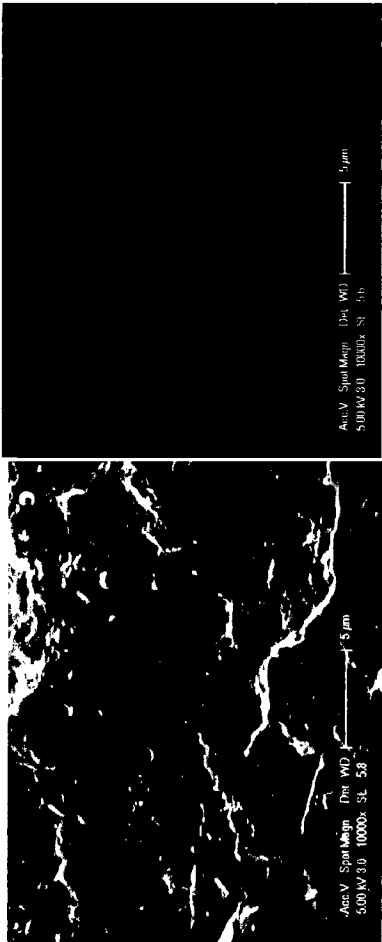


FIGURE 2

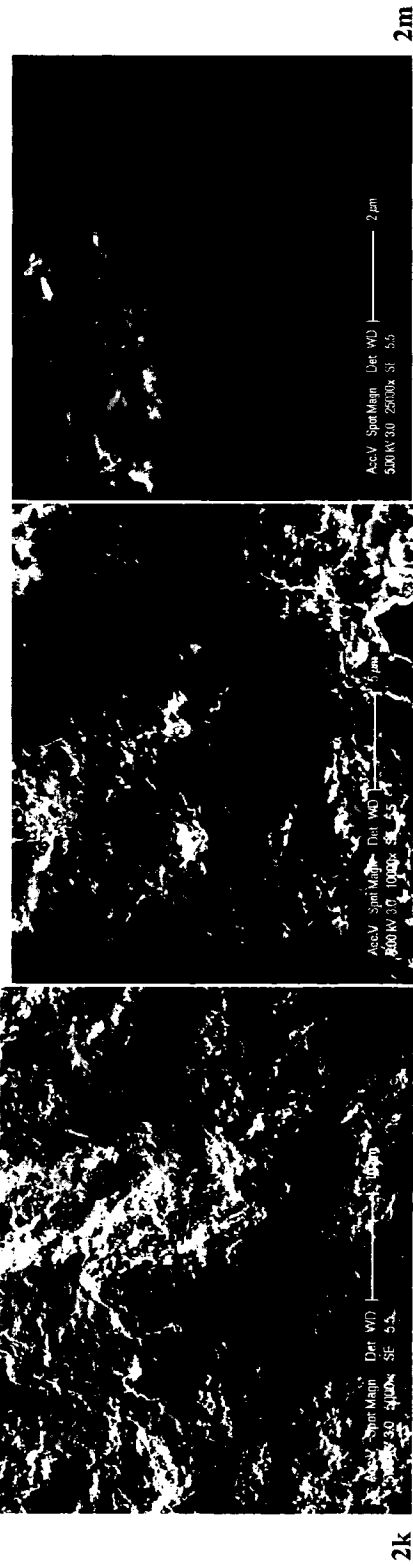






2i

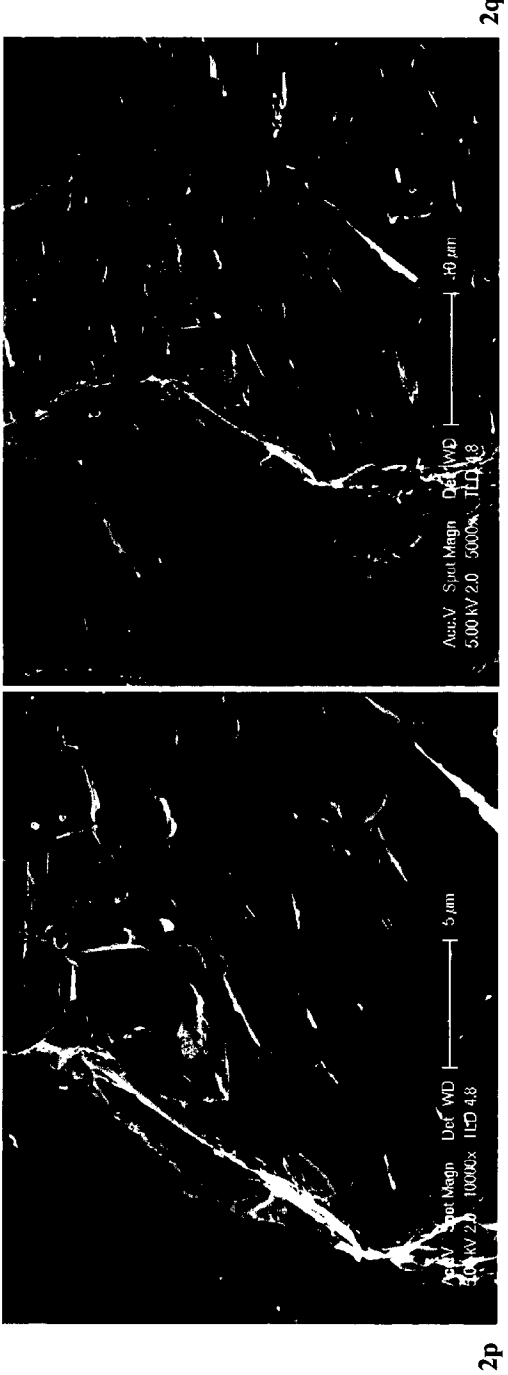
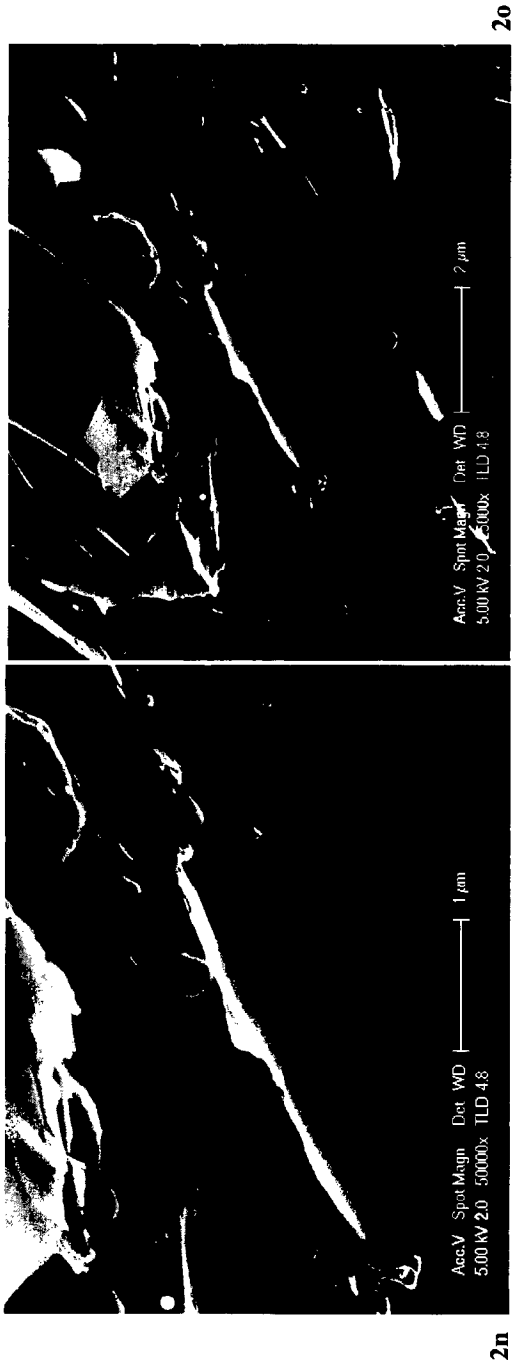
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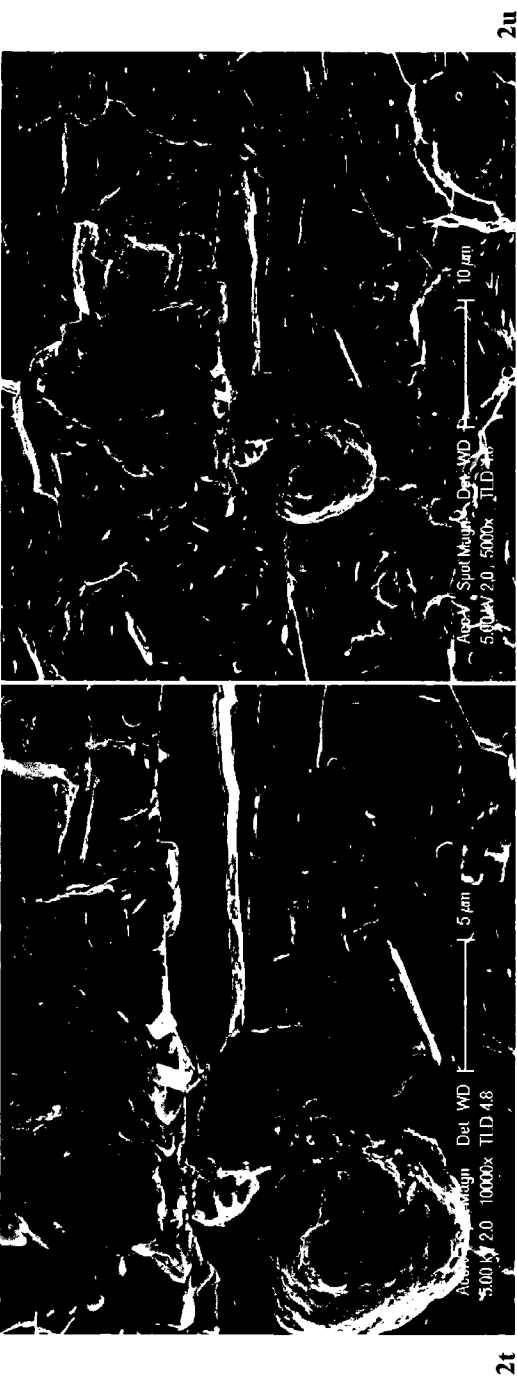
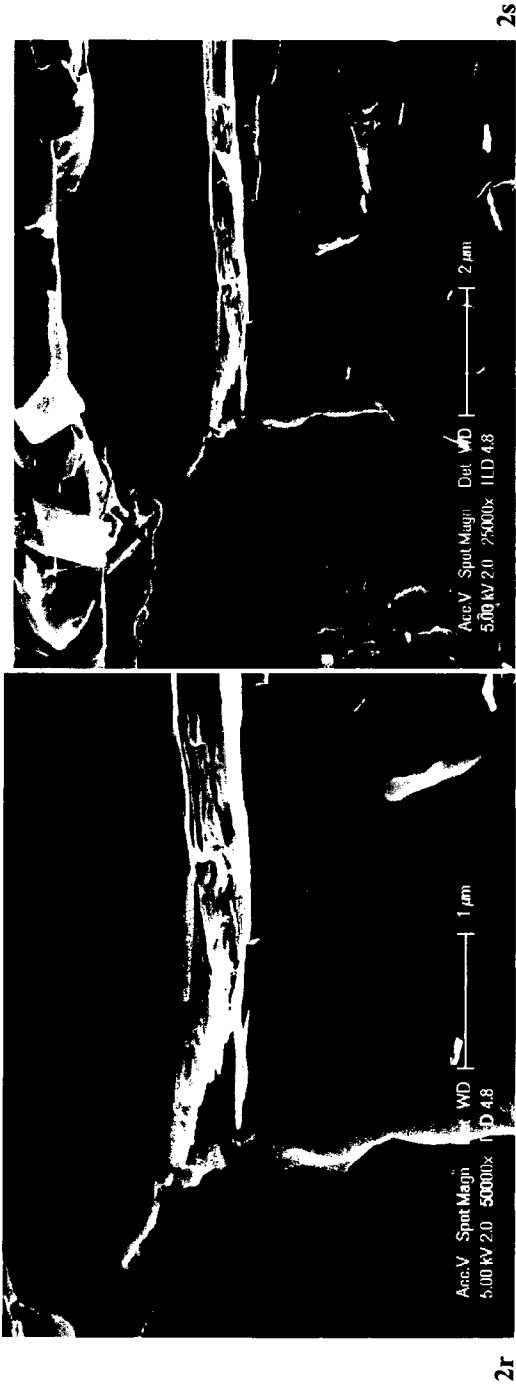


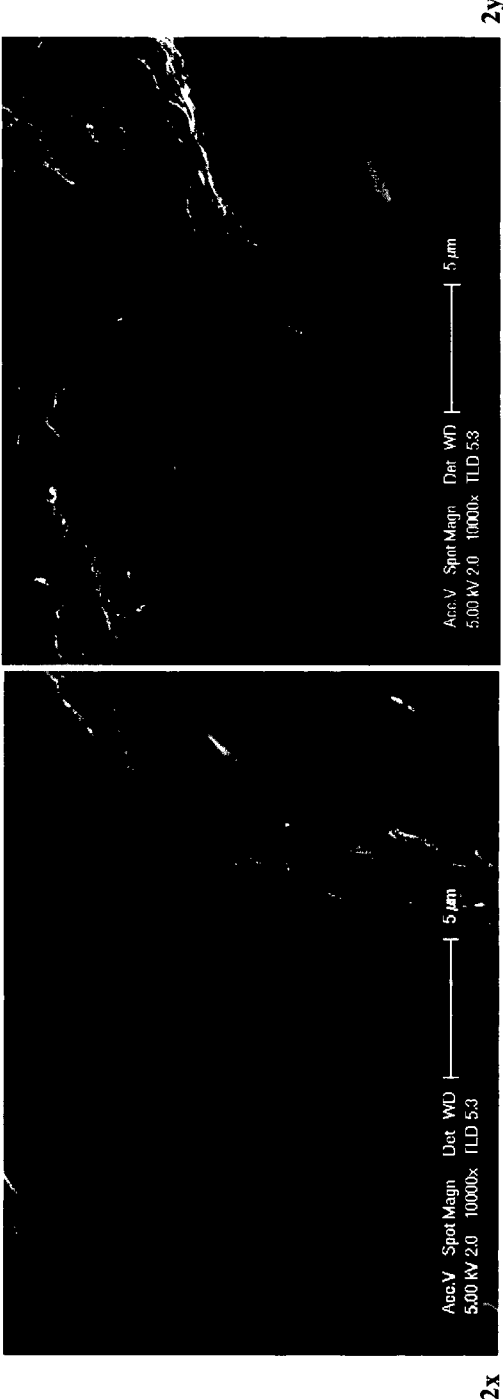
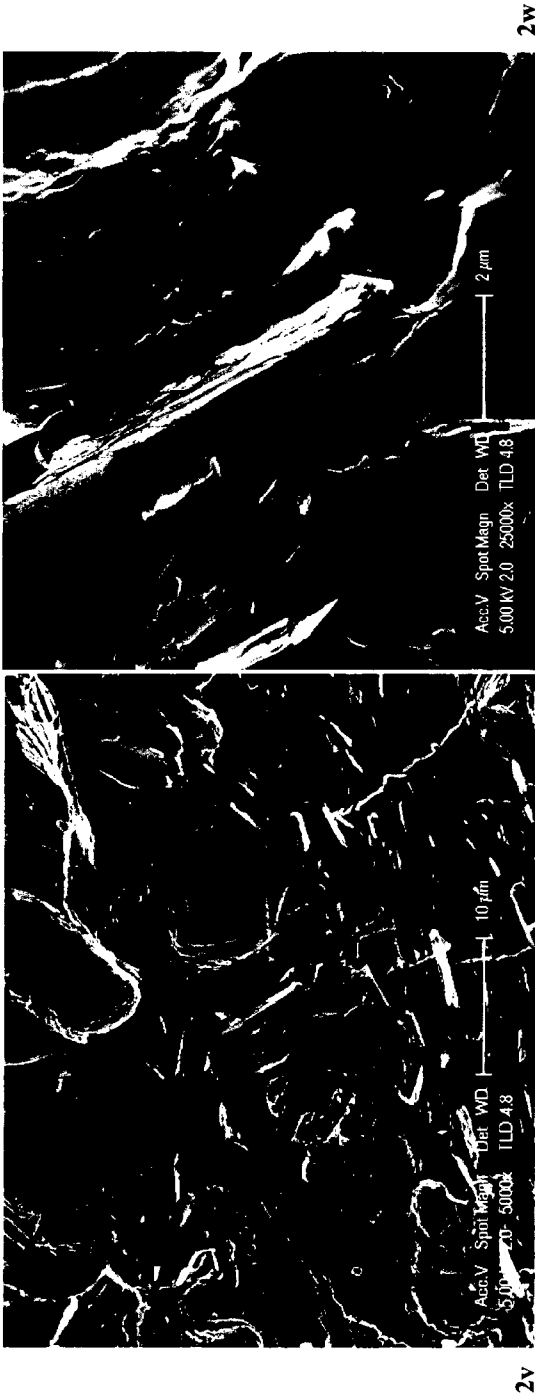
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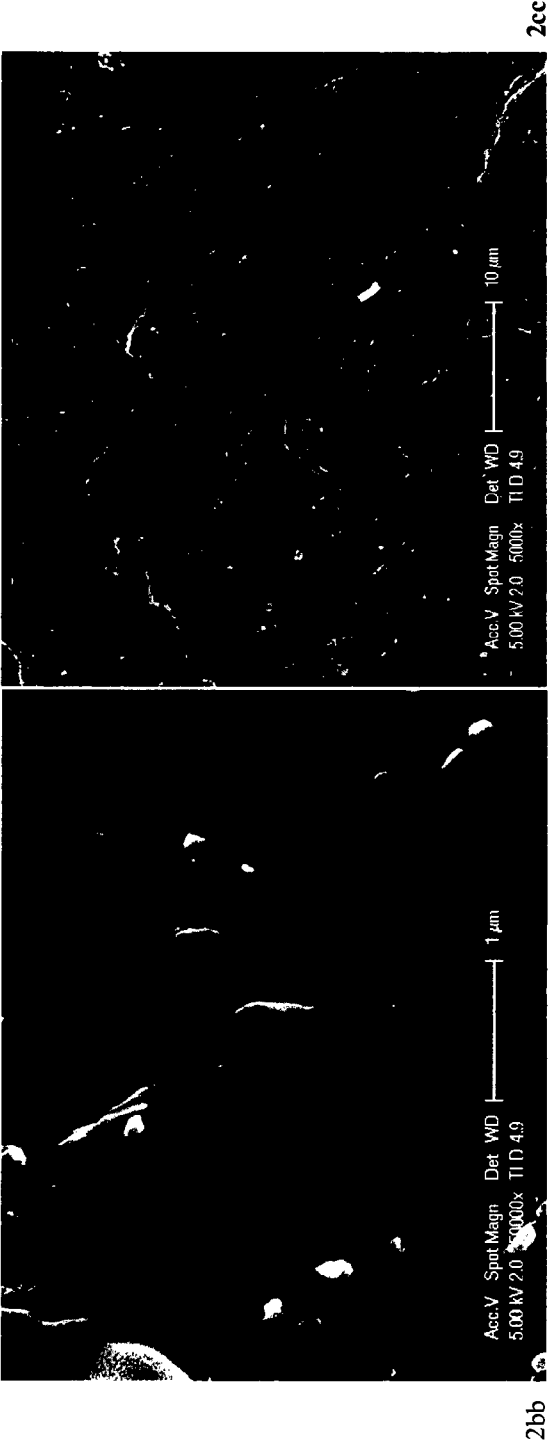
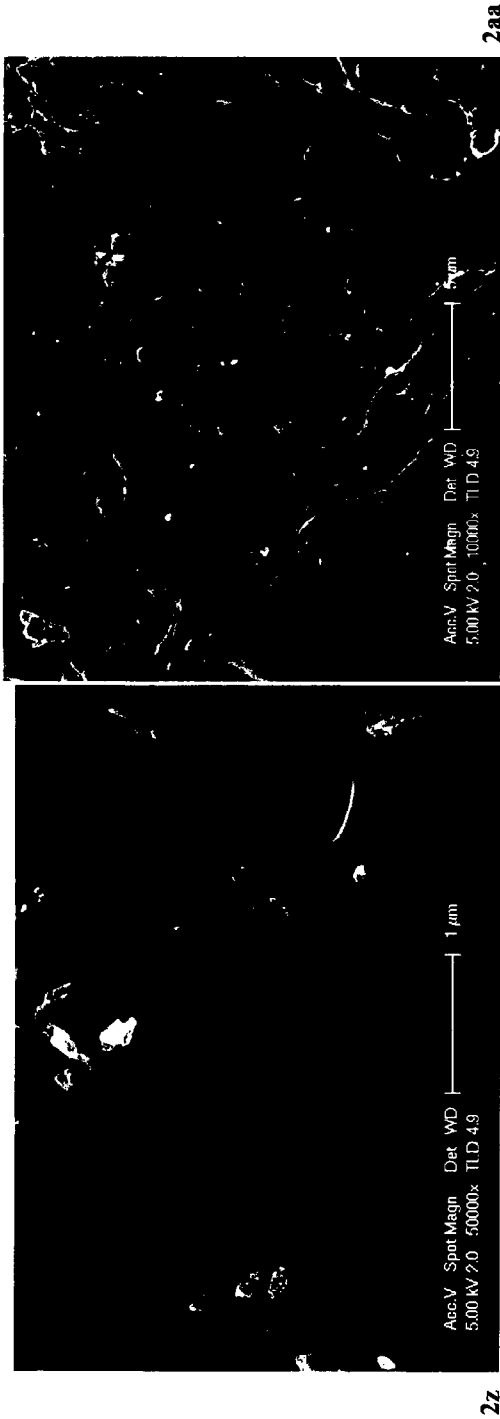


FIGURE 4

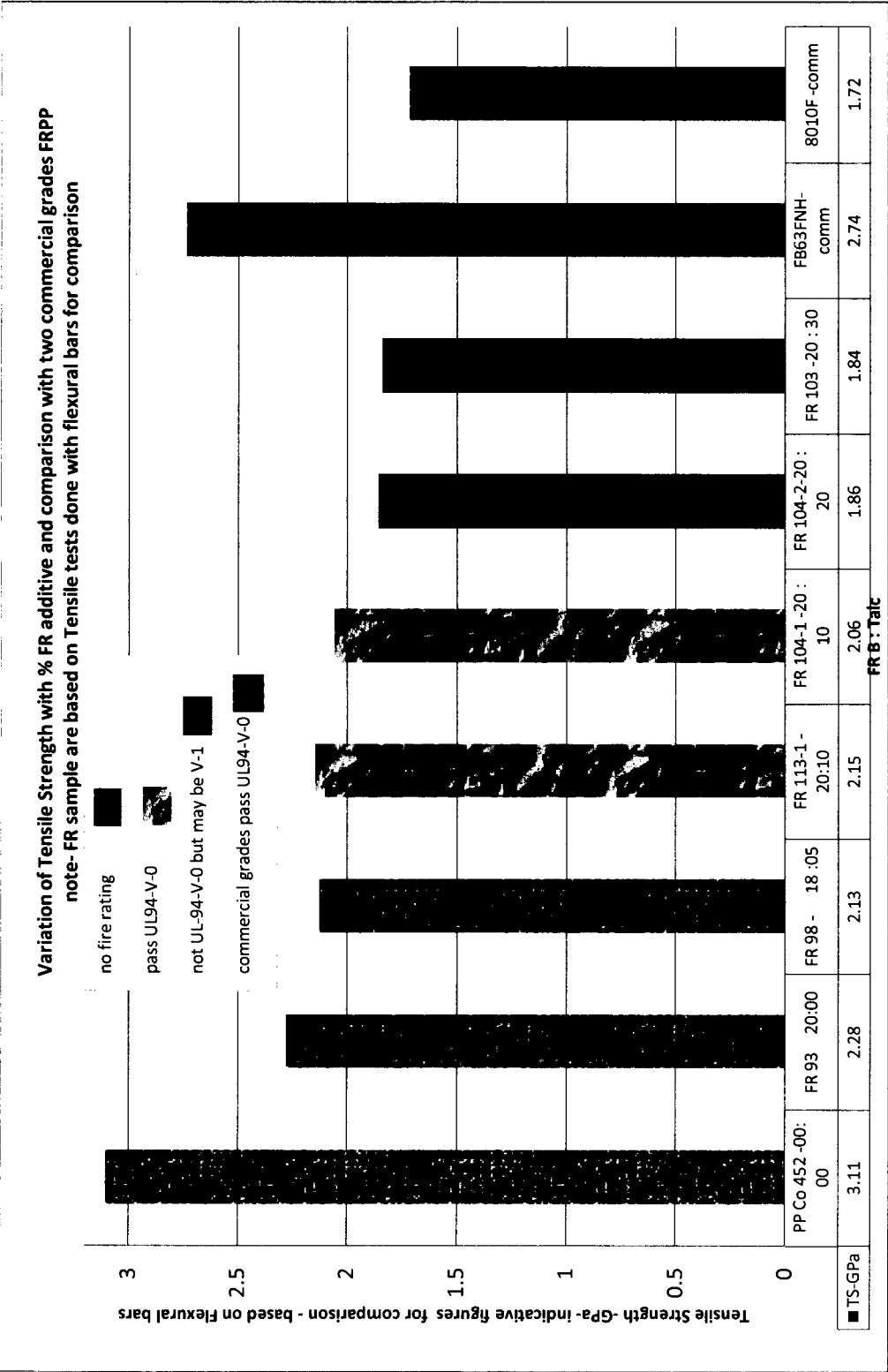


FIGURE 5

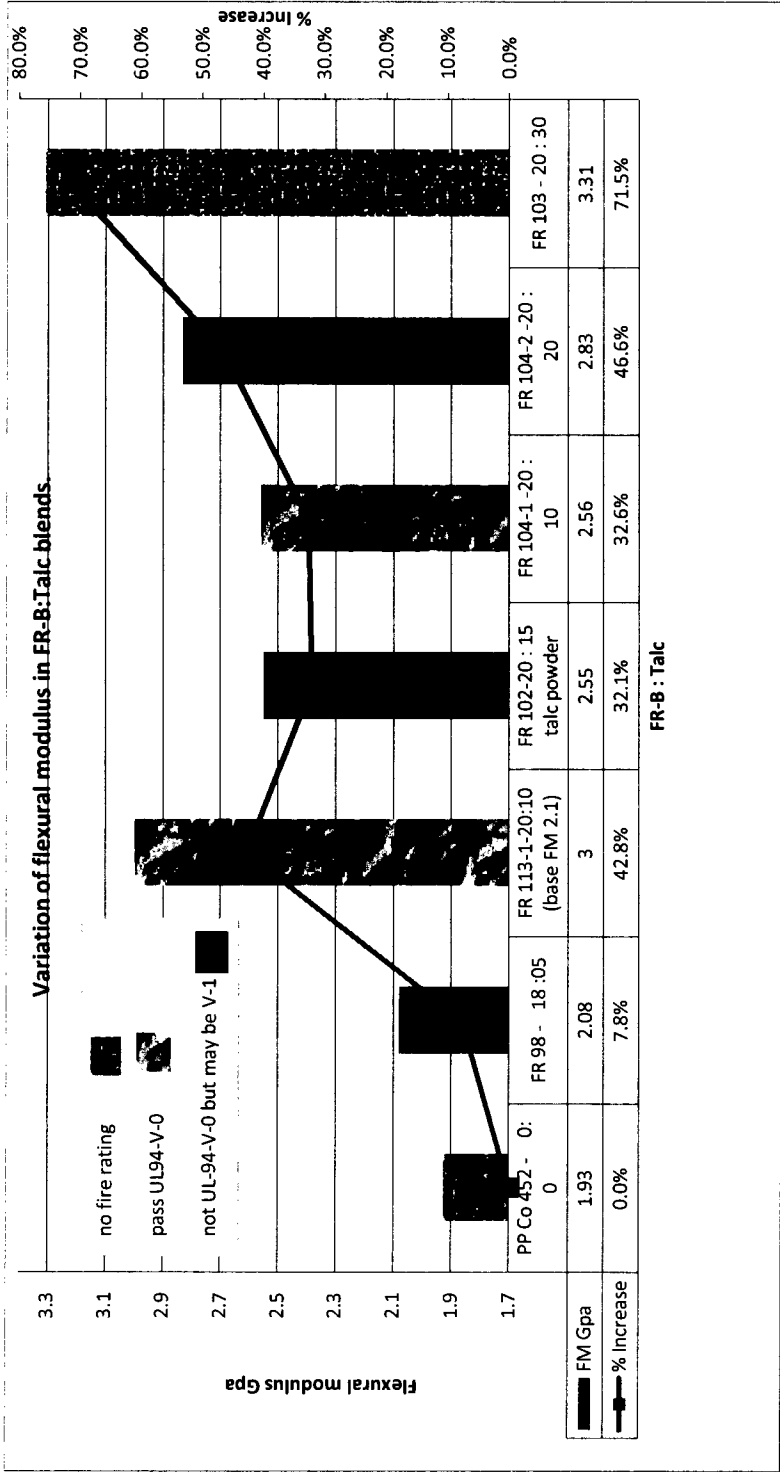


FIGURE 6

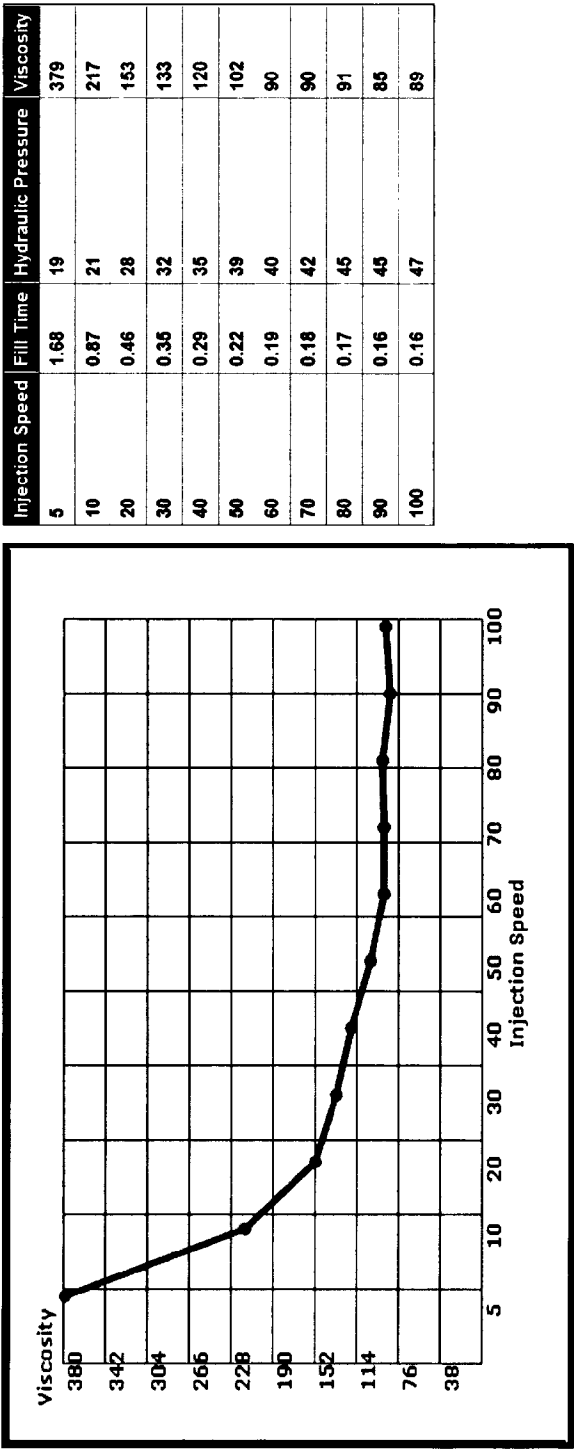
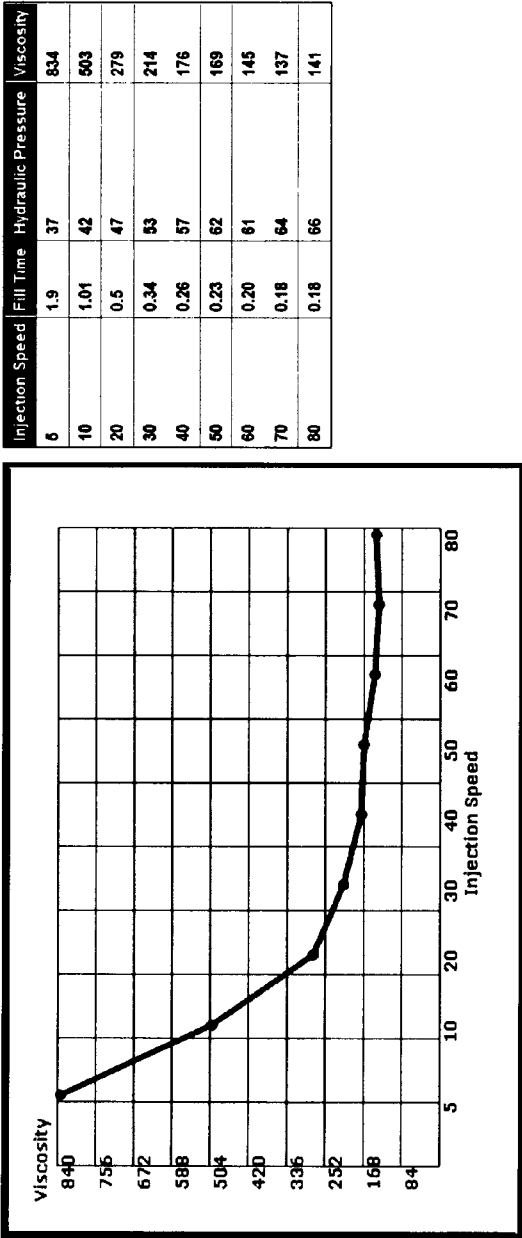


FIGURE 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2012/000002

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C09K 21/14 (2006.01)

C08K 5/13 (2006.01)

C09K 21/04 (2006.01)

C08J 3/22 (2006.01)

C08K 13/02 (2006.01)

C08K 3/32 (2006.01)

C08L 23/12 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

WPI, EPODOC; IPC C08L23; C09K21& Keywords: (FIRE RETARDANT; FIRE RESISTANT; INTUMESCENT; PROPYLENE; FLEXURAL MODULUS; UL-94; TALC; FILLER; AMMONIUM POLYPHOSPHATE; and associated terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LONGEREY, M et al. "Talc and brominated trimethylphenyl indane/Sb ₂ O ₃ blend in a PP-PE copolymer" Polymer Degradation and Stability (1999), vol 64, pages 489-496 See page 491, paragraph 3; page 492, paragraph 1; page 494, Tables 4 & 5, compositions with talc type C, D or E and FR)	1-2, 4, 8-11, 15-18, 28, 33-35 & 39-41
X	ALMERAS, X et al. "Effect of fillers on the fire retardancy of intumescent polypropylene compounds" Polymer Degradation and Stability (2003), vol 82, pp. 325-331 See paragraph 2.1; Table 1; paragraph 2.2	29, 33-34 & 36-41
X	DUQUESNE, S et al. "Influence of talc on the fire retardant properties of highly filled intumescent polypropylene composites" Polymers for Advanced Technologies (2008), vol 19, pp. 620-627 See page 620, paragraph 2; page 622, Table 3, Formulation PP/Intu/Talc-25/10	1-5, 7-10, 12-19, 24 & 26



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"E" earlier application or patent but published on or after the international filing date

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"O" document referring to an oral disclosure, use, exhibition or other means

"&" document member of the same patent family

"P" document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

26 April 2012

Date of mailing of the international search report

27 April 2012

Name and mailing address of the ISA/AU

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2012/000002

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

[---Please see Supplemental Box---]

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2012/000002

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/0155348 A1 (GITTO) 24 October 2002 See Example 14	24
X	WO 2009/081381 A1 (SABIC INNOVATIVE PLASTICS IP B.V.) 02 July 2009 See Abstract; paragraphs 9, 19, 20, 26, 30, 34, 35, 36 & 59; Table 1, Formulations 1-4; Table 2, Formulations 1-4	1, 3-18, 20-41 & 43-46
X	WO 2008/079998 A1 (DOW GLOBAL TECHNOLOGIES INC.) 03 July 2008 See page 3, lines 6-15; page 15, Table 3; page 28, lines 14-17; page 29, lines 1-4 & 18-20; page 30, lines 17-18; page 43, Table 10 & lines 18-23	29-46

Supplemental Box

(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No: III

Please note that the following abbreviations have been used throughout this report:

Fire retardant material – FRM; Fire retardant agent - FRA; Fire retardancy rating - FRR; Flexural modulus – FM

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-23: A FRM comprising PP, having a flexural modulus (FM) of at least 2.8 GPa and a FRR of at least UL-94 V-1 is specific to this group of claims;
- Claims 24-46: A FRM comprising PP, a fire retardant agent (FRA) and talc is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions is a FRM comprising PP. However this feature does not make a contribution over the prior art because it is well known in the art, as disclosed in each of the following citations:

- D1: LONGEREY, M et al. "Talc and brominated trimethylphenyl indane/Sb₂O₃ blend in a PP-PE copolymer" Polymer Degradation and Stability (1999), vol 64, pages 489-496;
- D2: ALMERAS, X et al, "Effect of fillers on the fire retardancy of intumescent polypropylene compounds" Polymer Degradation and Stability (2003), vol 82, pp. 325-331;
- D3: DUQUESNE, S et al. "Influence of talc on the fire retardant properties of highly filled intumescent polypropylene composites" Polymers for Advanced Technologies (2008), vol 19, pp. 620-627;
- D4: US 2002/0155348 A1 (GITTO) 24 October 2002;
- D5: WO 2009/081381 A1 (SABIC INNOVATIVE PLASTICS IP B.V.) 02 July 2009; and,
- D6: WO 2008/079998 A1 (DOW GLOBAL TECHNOLOGIES INC.) 03 July 2008.

The disclosures of these documents are further discussed under novelty in Box V.

Therefore this common feature cannot be a special technical feature. Hence there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/NZ2012/000002

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	2002/0155348	CA	2255554	EP	0906639	JP	2000511343
		WO	97/045884				
WO	2009/081381	CN	101945937	EP	2222777	KR	20100094528
		US	2010/0087573				
WO	2008/079998	CN	101611088	EP	2125948	JP	2010514857
		KR	20090092333	TW	200844169	US	2010/0016482
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							